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# Low Temperature Thermal Data on Eight $C_8H_{16}$ Alkylcyclohexanes

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In continuation of the program of the Bureau of Mines,[2] to investigate the thermodynamic properties of petroleum hydrocarbons and related substances, low-temperature thermal studies have been made on eight $C_8H_{16}$ alkylcyclohexanes over the temperature range 12 to 300°K. This investigation of a group of isomers represents one of the most comprehensive studies of isomers yet made in the field of low temperature calorimetry. A number of interesting and unusual phenomena were observed which will be discussed. Insofar as the authors are aware this is the first published work on the low temperature heat capacity of these substances.

## Experimental

**The Materials.**—The materials used in this investigation were API–NBS "best" samples prepared by the A.P.I. Research Project 6 at the National Bureau of Standards[3] and certified by them in regard to their purity.

**The Apparatus.**—The measurements were made in the apparatus described by Ruehrwein and Huffman.[4] Very briefly, the method is as follows: About 0.4 mole of the material under investigation was contained in a sealed copper calorimeter, which was mounted in the adiabatic calorimetric system. A measured amount of electrical energy was supplied to the calorimeter, and at all times the temperature of the environment was maintained at that of the calorimeter to prevent heat interchange. The initial and final temperatures of the calorimeter were measured by means of a platinum resistance thermometer. The electrical measurements required for determining the resistance of the thermometer and for the electrical energy were made on a "White" double potentiometer in conjunction with a high-sensitivity galvanometer and accurately calibrated resistances. The potential was in terms of a bank of six saturated cadmium cells, which had been certified by the National Bureau of Standards. Time measurements were made with an electric stopclock driven by alternating current, the frequency of which was controlled with an accuracy of 0.001%. The precision of the measurements was, in general, better than 0.1%; and above 30°K., it is believed that the accuracy uncertainty, unless otherwise stated, 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.

Melting-point studies were made on all of these compounds as a part of the routine measurements and the results are summarized in Table I. It should be borne in mind that the equilibrium temperatures given correspond to triple points since the material in all cases was sealed in the calorimeter under its own vapor pressure. Three of these

TABLE I

$C_8H_{16}$ ALKYLCYCLOHEXANE MELTING POINT SUMMARY

| % liq. | $T_{obs.}$ | $T_{calcd.}$ |
|---|---|---|
| **Ethylcyclohexane** | | |
| 16.86 | 161.8315 | 161.8279 |
| 41.37 | .8354[a] | .8354 |
| 71.32 | .8375 | .8376 |
| 90.37 | .8382[a] | .8382 |
| 100.0 | | .8385 |
| Pure | | 161.8406 |
| $N_x = 0.0382\,\Delta T$ | | |
| Impurity = 0.008 ± 0.004 mole % | | |
| **1,1-Dimethylcyclohexane** | | |
| 24.3 | 239.393 | 239.158 |
| 40.0 | .491 | .414 |
| 53.7 | .540 | .515 |
| 76.4 | .603[a] | .603 |
| 79.2 | .604 | .611 |
| 92.0 | .638[a] | .638 |
| 100.0 | | .652 |
| Pure | | 239.811 |
| $N_x = 0.00423\,\Delta T$ | | |
| Impurity = 0.07 ± 0.03 mole % | | |
| ***cis*-1,2-Dimethylcyclohexane** | | |
| 8.3 | 223.2257 | 223.1420 |
| 37.9 | .2483[a] | .2483 |
| 70.6 | .2618 | .2621 |
| 88.5 | .2654[a] | .2654 |
| 100.0 | .2668 | |
| Pure | | 223.278 |
| $N_x = 0.00397\,\Delta T$ | | |
| Impurity = 0.0045 ± 0.002 mole % | | |

(1) Present address: Carbide and Carbon Chemical Corporation, Oak Ridge, Tennessee.

(2) Knowlton and Huffman, THIS JOURNAL, **66**, 1492 (1944).

(3) These 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 on the "Collection, analysis, and calculation of data on the properties of hydrocarbons." The samples were purified at the National Bureau of Standards by the A. P. I. Research Project 6 on the "Analysis, purification and properties of hydrocarbons," under the supervision of Frederick D. Rossini, from material supplied by the following laboratories:

*Ethylcyclohexane*, *cis-1,3-dimethylcyclohexane*, *trans-1,3-dimethylcyclohexane*, *1,1-dimethylcyclohexane*, *cis-1,2-dimethylcyclohexane* and *trans-1,2-dimethylcyclohexane*, 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 supervision of Cecil E. Boord.

*cis-1,4-Dimethylcyclohexane* and *trans-1,4-dimethylcyclohexane*, by the Standard Oil Development Co., Elizabeth, N. J. through the courtesy of W. J. Sweeney.

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

TABLE I (*Continued*)

| % liq. | $T_{obs.}$ | $T_{calcd.}$ |
|---|---|---|
| | *trans*-1,2-Dimethylcyclohexane (I) | |
| 17.8 | 184.9546 | 184.9470 |
| 47.6 | .9762[a] | .9762 |
| 71.5 | .9817[a] | .9820 |
| 91.4 | .9848 | .9845 |
| 100.0 | | .9853 |
| Pure | | 184.994 |
| $N_x = 0.0368\Delta T$ | | |
| Impurity = 0.030 ± 0.005 mole % | | |
| | II | |
| 16.6 | 184.9515 | 184.9423 |
| 45.6 | .9713[a] | .9707 |
| 68.8 | .9767 | .9769 |
| 88.1 | .9793[a] | .9793 |
| 100.0 | | .9804 |
| Pure | | 184.988 |
| Impurity = 0.028 ± 0.005 mole % | | |
| | *trans*-1,3-Dimethylcyclohexane | |
| 18.2 | 182.929 | 182.920 |
| 39.2 | .997[a] | .997 |
| 66.6 | 183.023 | 183.024 |
| 85.5 | .033[a] | .033 |
| 100.0 | | .037 |
| Pure | | 183.063 |
| $N_x = 0.0354\Delta T$ | | |
| Impurity = 0.090 ± 0.010 mole % | | |
| | *cis*-1,3-Dimethylcyclohexane | |
| 16.78 | 197.5565[a] | 197.5565 |
| 38.99 | .5778 | .5774 |
| 68.63 | .5845 | .5842 |
| 90.85 | .5864[a] | .5864 |
| 100.0 | | .5870 |
| Pure | | 197.593 |
| $N_x = 0.0333\Delta T$ | | |
| Impurity = 0.021 ± 0.005 mole % | | |
| | *cis*-1,4-Dimethylcyclohexane | |
| 19.08 | 185.6916 | 185.6871 |
| 45.50 | .7138[a] | .7138 |
| 69.72 | .7205 | .7204 |
| 91.73 | .7235[a] | .7235 |
| 100.0 | | .7243 |
| Pure | | 185.733 |
| $N_x = 0.0324\Delta T$ | | |
| Impurity = 0.028 ± 0.005 mole % | | |
| | *trans*-1,4-Dimethylcyclohexane | |
| 2.79 | 236.126[a] | 236.126 |
| 12.28 | .197 | .196 |
| 37.53 | .209 | .210 |
| 66.47 | .212 | .213 |
| 88.70 | .214[a] | .214 |
| 100.00 | | .215 |
| Pure | | 236.217 |
| $N_x = 0.026\Delta T$ | | |
| Impurity = 0.007 ± 0.005 mole % | | |

[a] Calculations based on these experimental points.

compounds have small cryoscopic constants, and consequently the triple points may be expected to differ significantly from the melting points which are observed when the liquid materials are saturated with air at atmospheric pressure.

In the case of ethylcyclohexane, which has a low cryoscopic constant, the melting point study was repeated several times to test the precision of the measurements. The results of this study are shown in Fig. 1 which is a plot of $T$ against $1/F$, where $T$ is the absolute temperature and $F$ is the fraction melted. The extreme experimental difference is seen to be slightly greater than 0.002° but in any single series of measurements the precision of measurement is much better than this. In addition to the melting point measurements a single freezing-point[5] measurement was made. This point was approximately 0.015° below the melting-point curves. These data tend to confirm the hypotheses that equilibrium temperatures may be a resultant of the way the material is treated and not necessarily a true equilibrium.

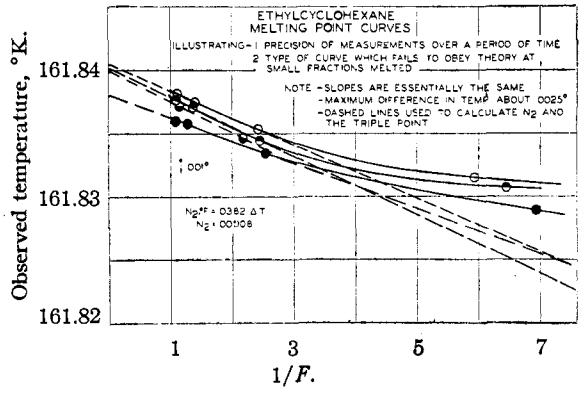


Fig. 1.—Melting point curves for ethylcyclohexane.

In the case of *trans*-1,2-, *trans*-1,3- and *trans*-1,4-dimethylcyclohexane there is some uncertainty in the melting points for pure material and for the mole fraction of impurity in the sample because in none of these materials was it possible to obtain an unambiguous value for the heat of fusion. The uncertainty due to this factor will not be very great in the absolute sense.

## Results

The experimentally determined heat capacities are given in Table II. In Table III are listed specific heat data at integral temperatures as selected from a smooth curve drawn through all of the data. The specific heat data for crystalline *trans*-1,3-dimethylcyclohexane may be less accurate than that of the other compounds for reasons which will be discussed later.

The molal heats of fusion of these compounds are given in Table IV. The uncertainties given are in all cases precision uncertain-

(5) Freezing point means the equilibrium was approached after crystallizing a portion of the material rather than melting.

TABLE II

THE MOLAL HEAT CAPACITY OF THE $C_8H_{16}$ ALKYLCYCLOHEXANES

0°C. = 273.16°K., mol. wt. = 112.208

| $T$, °K. | $\Delta T$ | $C_p$ cal. deg.$^{-1}$ | $T$, °K. | $\Delta T$ | $C_p$ cal. deg.$^{-1}$ |
|---|---|---|---|---|---|
| **Ethylcyclohexane** | | | | | |
| 12.00 | 1.512 | 1.116 | 123.73 | 8.568 | 21.599 |
| 12.61 | 1.989 | 1.270 | 131.86 | 8.930 | 22.670 |
| 13.79 | 2.153 | 1.559 | 132.55 | 9.066 | 22.739 |
| 15.11 | 3.057 | 1.915 | 140.59 | 8.535 | 23.807 |
| 18.34 | 3.468 | 2.819 | 141.41 | 8.661 | 23.854 |
| 19.73 | 2.995 | 3.233 | 148.15 | 6.577 | 24.808 |
| 21.72 | 3.317 | 3.828 | 149.91 | 8.328 | 24.936 |
| 23.09 | 3.724 | 4.221 | 154.63 | 6.380 | 25.693 |
| 25.56 | 4.357 | 4.955 | Liquid | | |
| 26.95 | 3.993 | 5.353 | 167.35 | 6.223 | 39.125 |
| 30.38 | 5.288 | 6.280 | 171.66 | 6.278 | 39.409 |
| 31.01 | 4.110 | 6.450 | 174.55 | 8.188 | 39.542 |
| 35.90 | 5.756 | 7.688 | 179.95 | 10.309 | 39.922 |
| 41.76 | 5.953 | 9.025 | 183.18 | 9.073 | 40.090 |
| 47.74 | 6.021 | 10.281 | 192.68 | 9.910 | 40.740 |
| 53.80 | 6.081 | 11.461 | 193.07 | 9.877 | 40.724 |
| 55.24 | 5.142 | 11.721 | 202.86 | 9.699 | 41.434 |
| 59.92 | 6.158 | 12.558 | 212.95 | 10.486 | 42.199 |
| 60.90 | 6.172 | 12.696 | 223.34 | 10.286 | 43.052 |
| 67.45 | 6.930 | 13.767 | 233.53 | 10.095 | 43.934 |
| 74.84 | 7.848 | 14.872 | 243.98 | 10.797 | 44.885 |
| 82.78 | 8.025 | 16.078 | 254.66 | 10.578 | 45.929 |
| 90.90 | 8.219 | 17.255 | 265.13 | 10.360 | 46.986 |
| 98.86 | 7.702 | 18.313 | 270.92 | 6.847 | 47.566 |
| 103.87 | 6.261 | 18.985 | 275.38 | 10.161 | 48.073 |
| 106.88 | 8.341 | 19.370 | 279.40 | 10.098 | 48.490 |
| 110.00 | 5.990 | 19.790 | 285.46 | 9.975 | 49.176 |
| 115.00 | 7.900 | 20.417 | 289.39 | 9.887 | 49.611 |
| 115.44 | 8.007 | 20.486 | 295.34 | 9.773 | 50.302 |
| 123.17 | 8.442 | 21.530 | 299.19 | 9.715 | 50.746 |
| **1,1-Dimethylcyclohexane** | | | | | |
| Crystals I | | | 121.45 | 9.470 | 20.878 |
| 12.31 | 1.533 | 1.051 | 131.04 | 9.723 | 22.281 |
| 14.10 | 2.110 | 1.512 | 141.61 | 11.410 | 23.909 |
| 15.15 | 3.484 | 1.812 | Crystals II | | |
| 16.25 | 2.229 | 2.128 | 154.15 | 7.027 | 33.286 |
| 18.94 | 3.164 | 2.949 | 165.61 | 11.175 | 34.350 |
| 18.98 | 4.204 | 2.957 | 176.64 | 10.876 | 35.258 |
| 22.73 | 4.423 | 4.129 | 187.37 | 10.591 | 36.167 |
| 23.98 | 5.838 | 4.479 | 190.04 | 64.737 | 36.462 |
| 27.13 | 4.374 | 5.375 | 197.84 | 10.350 | 37.091 |
| 29.97 | 6.139 | 6.115 | 208.07 | 10.098 | 38.084 |
| 31.32 | 4.866 | 6.449 | 216.88 | 29.411 | 38.953 |
| 31.67 | 4.701 | 6.528 | 218.05 | 9.860 | 39.090 |
| 36.55 | 7.009 | 7.637 | 226.07 | 7.328 | 39.988 |
| 36.88 | 6.229 | 7.695 | 227.79 | 9.672 | 40.123 |
| 42.88 | 5.778 | 8.856 | 228.35 | 6.529 | 40.230 |
| 43.46 | 6.802 | 8.964 | 230.80 | 10.132 | 40.473 |
| 48.76 | 5.970 | 9.894 | 232.62 | 5.767 | 40.733 |
| 50.66 | 7.611 | 10.199 | Liquid | | |
| 55.21 | 6.944 | 10.936 | 242.74 | 5.279 | 44.094 |
| 58.16 | 7.362 | 11.405 | 246.71 | 5.359 | 44.483 |
| 61.76 | 6.163 | 11.974 | 249.32 | 5.273 | 44.712 |
| 65.52 | 9.038 | 12.548 | 250.57 | 10.393 | 44.823 |
| 67.66 | 5.617 | 12.890 | 260.69 | 10.141 | 45.868 |
| 75.69 | 11.298 | 14.057 | 260.86 | 10.172 | 45.908 |
| 86.97 | 5.229 | 15.821 | 270.72 | 9.926 | 46.914 |
| 87.49 | 12.303 | 15.866 | 270.92 | 9.951 | 46.982 |
| 94.27 | 9.365 | 16.885 | 279.75 | 8.128 | 47.902 |
| 101.05 | 14.815 | 17.852 | 280.78 | 9.767 | 48.028 |
| 103.28 | 8.663 | 18.186 | 287.81 | 7.989 | 48.828 |
| 112.16 | 9.100 | 19.508 | 295.73 | 7.859 | 49.708 |
| 118.81 | 20.714 | 20.475 | 303.53 | 7.732 | 50.664 |
| ***cis*-1,2-Dimethylcyclohexane** | | | | | |
| | | | 136.27 | 15.200 | 23.082 |
| Crystals I | | | 140.69 | 10.638 | 23.654 |
| 11.92 | 1.740 | 0.873 | 141.66 | 4.672 | 23.686 |
| 13.63 | 1.768 | 1.283 | 142.62 | 9.236 | 23.884 |
| 13.69 | 1.733 | 1.308 | 147.02 | 6.037 | 24.378 |
| 15.55 | 2.115 | 1.777 | 151.07 | 10.115 | 24.944 |
| 16.68 | 4.253 | 2.088 | 151.67 | 8.844 | 25.007 |
| 18.33 | 3.457 | 2.560 | 151.93 | 16.116 | 25.007 |
| 20.60 | 3.589 | 3.241 | 153.72 | 7.400 | 25.284 |
| 21.68 | 3.252 | 3.560 | 160.93 | 7.036 | 26.331 |
| 24.88 | 3.152 | 4.487 | 167.87 | 6.860 | 27.449 |
| 25.11 | 5.438 | 4.552 | Crystals II | | |
| 28.24 | 3.569 | 5.409 | 175.48 | 8.811 | 37.185 |
| 30.33 | 4.993 | 5.968 | 182.98 | 10.396 | 37.514 |
| 32.12 | 4.174 | 6.407 | 183.70 | 9.678 | 37.533 |
| 35.23 | 4.804 | 7.164 | 184.23 | 8.699 | 37.569 |
| 40.60 | 5.929 | 8.334 | 185.69 | 5.727 | 37.700 |
| 46.57 | 5.994 | 9.512 | 187.30 | 18.926 | 37.797 |
| 52.18 | 5.241 | 10.549 | 193.28 | 9.489 | 38.241 |
| 54.89 | 4.131 | 11.021 | 194.42 | 12.017 | 38.314 |
| 57.91 | 6.217 | 11.552 | 202.68 | 9.309 | 38.977 |
| 59.96 | 5.997 | 11.894 | 205.84 | 10.832 | 39.223 |
| 65.06 | 6.863 | 12.742 | 211.90 | 9.134 | 39.727 |
| 65.68 | 5.438 | 12.863 | 215.69 | 8.856 | 40.030 |
| 71.52 | 6.245 | 13.777 | Liquid | | |
| 71.60 | 6.228 | 13.795 | 228.30 | 4.960 | 43.480 |
| 77.59 | 5.752 | 14.767 | 233.46 | 8.379 | 43.934 |
| 77.66 | 6.147 | 14.769 | 234.86 | 8.157 | 44.065 |
| 82.94 | 4.940 | 15.597 | 241.59 | 9.896 | 44.704 |
| 84.04 | 6.513 | 15.777 | 243.75 | 9.639 | 44.767 |
| 88.51 | 6.199 | 16.469 | 252.40 | 9.713 | 45.569 |
| 90.72 | 6.841 | 16.783 | 254.08 | 11.022 | 45.736 |
| 95.25 | 7.279 | 17.446 | 262.02 | 9.534 | 46.514 |
| 97.71 | 7.141 | 17.786 | 264.98 | 10.777 | 46.802 |
| 102.98 | 8.188 | 18.551 | 271.46 | 9.352 | 47.423 |
| 105.31 | 8.052 | 18.875 | 275.66 | 10.597 | 47.849 |
| 113.88 | 9.099 | 20.058 | 280.74 | 9.201 | 48.361 |
| 123.55 | 10.242 | 21.403 | 286.50 | 11.098 | 48.982 |
| 124.63 | 5.116 | 21.497 | 289.86 | 9.043 | 49.317 |
| 131.28 | 8.185 | 22.442 | 297.48 | 10.865 | 50.168 |
| 133.97 | 8.066 | 22.735 | 298.82 | 8.879 | 50.333 |
| **Unstable crystals II** | | | | | |
| 12.19 | 1.029 | 1.496 | 77.58 | 8.450 | 15.480 |
| 13.32 | 1.259 | 1.828 | 81.03 | 5.242 | 16.313 |
| 13.73 | 1.163 | 1.973 | 83.97 | 7.670 | 16.830 |
| 14.91 | 1.976 | 2.308 | 85.12 | 5.041 | 17.216 |
| 15.77 | 2.919 | 2.588 | 85.85 | 6.129 | 17.425 |
| 17.36 | 2.933 | 3.063 | 86.38 | 3.903 | 17.525 |
| 18.90 | 3.333 | 3.549 | 90.39 | 3.550 | 18.825 |
| 20.61 | 3.585 | 4.090 | 91.81 | 5.791 | 20.376 |
| 22.96 | 4.803 | 4.795 | 92.78 | 1.239 | 21.693 |

TABLE II (*Continued*)

| T, °K. | ΔT | $C_p$ cal. deg.$^{-1}$ | T, °K. | ΔT | $C_p$ cal. deg.$^{-1}$ |
|---|---|---|---|---|---|
| 24.33 | 3.855 | 5.179 | 92.88 | 2.426 | 23.584 |
| 27.85 | 4.962 | 6.143 | 93.97 | 1.136 | 26.911 |
| 28.05 | 3.579 | 6.200 | 94.57 | 0.946 | 33.884 |
| 32.09 | 4.482 | 7.187 | 95.56 | 1.033 | 33.302 |
| 33.09 | 5.518 | 7.420 | 97.41 | 5.411 | 32.787 |
| 38.76 | 5.818 | 8.647 | 100.30 | 3.790 | 33.247 |
| 44.63 | 5.927 | 9.770 | 102.77 | 5.297 | 33.226 |
| 50.60 | 6.012 | 10.841 | 107.29 | 10.208 | 33.404 |
| 55.22 | 4.710 | 11.666 | 108.90 | 6.960 | 33.401 |
| 56.64 | 6.080 | 11.888 | 116.64 | 8.540 | 33.680 |
| 57.42 | 8.179 | 12.027 | 117.79 | 10.777 | 33.790 |
| 60.43 | 5.705 | 12.554 | 125.10 | 8.369 | 34.059 |
| 60.63 | 5.665 | 12.570 | 128.49 | 10.622 | 34.242 |
| 62.25 | 7.308 | 12.847 | 133.39 | 8.211 | 34.480 |
| 65.58 | 8.140 | 13.408 | 139.49 | 11.390 | 34.817 |
| 65.89 | 5.215 | 13.479 | 141.53 | 8.065 | 34.890 |
| 67.49 | 7.715 | 13.761 | 149.72 | 8.316 | 35.276 |
| 69.63 | 7.455 | 14.090 | 150.76 | 11.140 | 35.344 |
| 70.91 | 4.839 | 14.330 | 157.96 | 8.177 | 35.733 |
| 73.70 | 8.113 | 14.827 | 161.77 | 10.882 | 36.002 |
| 74.83 | 6.957 | 15.022 | 166.56 | 9.018 | 36.352 |
| 75.87 | 5.073 | 15.242 | 172.49 | 10.571 | 37.063 |
| 76.21 | 7.651 | 15.292 | | | |

*trans*-1,2-Dimethylcyclohexane

| | | | | | |
|---|---|---|---|---|---|
| 11.99 | 1.928 | 0.827 | 140.66 | 9.016 | 23.807 |
| 14.07 | 3.686 | 1.288 | 143.79 | 7.817 | 24.117 |
| 14.14 | 2.417 | 1.299 | 145.10 | 9.715 | 24.412 |
| 16.56 | 2.466 | 1.909 | 149.23 | 9.802 | 24.913 |
| 18.43 | 5.097 | 2.426 | 149.89 | 9.458 | 25.047 |
| 19.49 | 3.400 | 2.721 | 151.46 | 7.520 | 25.178 |
| 23.49 | 4.619 | 3.907 | 154.60 | 9.281 | 25.676 |
| 28.04 | 4.480 | 5.185 | 155.74 | 7.494 | 25.770 |
| 30.50 | 6.425 | 5.835 | 159.15 | 9.050 | 26.300 |
| 32.69 | 4.798 | 6.402 | 159.32 | 10.383 | 26.254 |
| 37.24 | 7.070 | 7.503 | 161.46 | 8.950 | 26.471 |
| 44.16 | 6.765 | 8.983 | 163.70 | 8.909 | 26.865 |
| 51.30 | 7.507 | 10.354 | 172.45 | 8.587 | 28.011 |
| 54.95 | 6.865 | 10.986 | | Liquid | |
| 58.68 | 7.260 | 11.661 | 183.68 | 7.812 | 39.603 |
| 59.04 | 7.201 | 11.706 | 188.64 | 5.820 | 39.924 |
| 62.13 | 7.484 | 12.229 | 192.39 | 9.612 | 40.170 |
| 65.87 | 7.122 | 12.866 | 194.50 | 7.722 | 40.275 |
| 66.18 | 7.082 | 12.922 | 196.34 | 9.568 | 40.427 |
| 69.94 | 8.140 | 13.498 | 202.85 | 11.320 | 40.901 |
| 73.69 | 7.941 | 14.098 | 203.12 | 9.500 | 40.909 |
| 76.47 | 7.426 | 14.537 | 206.29 | 10.342 | 41.129 |
| 82.56 | 9.796 | 15.469 | 214.06 | 11.094 | 41.721 |
| 84.41 | 8.456 | 15.771 | 216.54 | 10.153 | 41.908 |
| 92.09 | 9.278 | 16.960 | 225.05 | 10.875 | 42.596 |
| 92.54 | 7.792 | 16.998 | 227.05 | 10.863 | 42.757 |
| 94.33 | 7.947 | 17.223 | 235.81 | 10.655 | 43.515 |
| 100.62 | 8.381 | 18.157 | 237.80 | 10.645 | 43.678 |
| 101.05 | 8.553 | 18.202 | 246.36 | 10.435 | 44.487 |
| 102.03 | 7.440 | 18.347 | 248.33 | 10.425 | 44.639 |
| 102.05 | 10.654 | 18.377 | 256.68 | 10.221 | 45.504 |
| 110.76 | 10.021 | 19.592 | 258.65 | 10.215 | 45.678 |
| 111.52 | 9.868 | 19.737 | 266.80 | 10.021 | 46.519 |
| 113.25 | 11.735 | 20.037 | 268.76 | 10.003 | 46.749 |
| 120.46 | 9.376 | 20.972 | 275.91 | 8.188 | 47.521 |
| 121.07 | 9.244 | 21.108 | 278.67 | 9.802 | 47.818 |
| 124.56 | 10.893 | 21.587 | 284.83 | 9.657 | 48.488 |
| 129.58 | 8.867 | 22.222 | 288.37 | 9.611 | 48.892 |
| 130.92 | 10.451 | 22.418 | 293.61 | 7.899 | 49.497 |
| 135.13 | 10.241 | 23.044 | 297.89 | 9.421 | 50.019 |
| 139.17 | 10.317 | 23.550 | 301.44 | 7.770 | 50.453 |

*cis*-1,3-Dimethylcyclohexane

| | | | | | |
|---|---|---|---|---|---|
| 11.75 | 1.741 | 0.879 | 109.54 | 8.616 | 19.645 |
| 13.18 | 1.840 | 1.247 | 118.34 | 9.001 | 20.910 |
| 13.71 | 2.200 | 1.384 | 127.11 | 8.524 | 22.165 |
| 15.51 | 2.800 | 1.899 | 135.83 | 8.924 | 23.313 |
| 15.94 | 2.254 | 2.013 | 144.52 | 8.455 | 24.482 |
| 18.63 | 3.137 | 2.831 | 151.85 | 6.024 | 25.411 |
| 18.93 | 4.038 | 2.922 | 153.30 | 9.113 | 25.640 |
| 22.06 | 3.714 | 3.902 | 158.81 | 7.898 | 26.540 |
| 23.29 | 4.699 | 4.279 | 162.68 | 9.683 | 27.127 |
| 25.88 | 3.927 | 5.026 | 166.56 | 7.603 | 27.669 |
| 28.35 | 5.416 | 5.720 | 171.21 | 7.427 | 28.294 |
| 29.86 | 4.027 | 6.112 | 174.49 | 8.428 | 28.827 |
| 33.97 | 5.817 | 7.132 | 182.14 | 7.060 | 30.178 |
| 39.86 | 5.966 | 8.427 | | Liquid | |
| 45.87 | 6.039 | 9.582 | 204.19 | 5.433 | 41.042 |
| 51.93 | 6.095 | 10.690 | 206.28 | 7.229 | 41.212 |
| 54.44 | 6.603 | 11.122 | 211.37 | 8.930 | 41.562 |
| 55.68 | 5.640 | 11.344 | 214.36 | 8.916 | 41.738 |
| 58.06 | 6.157 | 11.752 | 220.67 | 9.655 | 42.277 |
| 61.37 | 7.246 | 12.305 | 230.66 | 10.331 | 43.076 |
| 61.73 | 6.477 | 12.396 | 240.88 | 10.120 | 44.076 |
| 68.22 | 6.491 | 13.442 | 250.91 | 9.925 | 45.003 |
| 68.85 | 7.720 | 13.536 | 260.73 | 9.719 | 46.025 |
| 75.01 | 7.102 | 14.499 | 263.29 | 9.646 | 46.295 |
| 76.35 | 7.281 | 14.715 | 270.35 | 9.525 | 46.972 |
| 82.38 | 7.624 | 15.674 | 272.84 | 9.464 | 47.213 |
| 84.14 | 8.291 | 15.954 | 279.79 | 9.363 | 47.992 |
| 90.09 | 7.805 | 16.853 | 282.22 | 9.295 | 48.240 |
| 92.67 | 8.780 | 17.243 | 289.14 | 9.326 | 49.054 |
| 98.18 | 8.374 | 18.028 | 290.93 | 8.122 | 49.268 |
| 101.14 | 8.165 | 18.463 | 298.31 | 9.015 | 50.029 |
| 106.45 | 8.157 | 19.221 | 299.48 | 8.982 | 50.157 |

*trans*-1,3-Dimethylcyclohexane

| | | | | | |
|---|---|---|---|---|---|
| 12.41 | 1.442 | 1.107 | 150.60 | 9.268 | 25.250 |
| 13.57 | 0.700 | 1.403 | 152.62 | 8.342 | 25.603 |
| 14.14 | 2.040 | 1.558 | 153.98 | 8.459 | 25.742 |
| 15.93 | 3.090 | 2.037 | 155.90 | 8.173 | 26.030 |
| 16.27 | 2.208 | 2.132 | 159.69 | 8.896 | 26.411 |
| 18.96 | 3.163 | 2.904 | 160.80 | 8.019 | 26.748 |
| 19.46 | 3.992 | 3.059 | 162.23 | 8.048 | 26.906 |
| 22.43 | 3.780 | 3.973 | 162.48 | 4.988 | 26.958 |
| 23.83 | 4.768 | 4.362 | 162.50 | 5.022 | 26.890 |
| 26.36 | 4.027 | 5.101 | 164.04 | 7.794 | 27.197 |
| 28.98 | 5.538 | 5.764 | 166.48 | 7.849 | 27.327 |
| 30.44 | 4.133 | 6.124 | 167.04 | 5.839 | 27.528 |
| 34.72 | 5.941 | 7.181 | 167.22 | 4.827 | 27.817 |
| 40.73 | 6.080 | 8.503 | 169.61 | 6.709 | 28.545 |
| 46.84 | 6.172 | 9.645 | 171.93 | 4.579 | 29.957 |
| 53.04 | 6.210 | 10.819 | | Liquid | |
| 55.47 | 5.015 | 11.268 | 187.65 | 5.666 | 41.064 |
| 59.28 | 6.274 | 11.896 | 188.87 | 9.326 | 41.184 |
| 61.01 | 6.058 | 12.217 | 190.27 | 7.499 | 41.285 |
| 61.09 | 7.088 | 12.236 | 190.44 | 5.625 | 41.312 |

TABLE II (*Continued*)

| T, °K. | ΔT | $C_p$ cal. deg.$^{-1}$ | T, °K. | ΔT | $C_p$ cal. deg.$^{-1}$ |
|---|---|---|---|---|---|
| 67.45 | 6.836 | 13.299 | 190.76 | 9.281 | 41.260 |
| 68.32 | 7.373 | 13.422 | 190.79 | 9.276 | 41.271 |
| 74.72 | 7.690 | 14.447 | 194.52 | 7.462 | 41.518 |
| 75.81 | 7.607 | 14.596 | 196.97 | 7.434 | 41.695 |
| 81.95 | 6.783 | 15.602 | 198.64 | 9.244 | 41.774 |
| 83.52 | 7.800 | 15.836 | 202.86 | 9.203 | 42.098 |
| 88.98 | 9.325 | 16.682 | 208.72 | 10.904 | 42.525 |
| 89.43 | 8.164 | 16.763 | 211.61 | 8.310 | 42.734 |
| 91.41 | 7.992 | 17.044 | 219.52 | 10.700 | 43.327 |
| 97.30 | 7.588 | 17.906 | 220.23 | 8.930 | 43.397 |
| 97.94 | 8.603 | 17.971 | 229.96 | 10.529 | 44.142 |
| 99.51 | 8.191 | 18.199 | 230.65 | 10.494 | 44.189 |
| 105.36 | 8.527 | 19.069 | 240.40 | 10.338 | 45.034 |
| 106.75 | 9.016 | 19.246 | 241.04 | 10.289 | 45.091 |
| 107.63 | 8.057 | 19.352 | 250.64 | 10.145 | 45.928 |
| 113.48 | 7.708 | 20.214 | 250.69 | 9.011 | 45.926 |
| 115.50 | 8.472 | 20.470 | 260.17 | 9.940 | 46.824 |
| 115.92 | 8.539 | 20.535 | 260.69 | 9.953 | 46.905 |
| 121.45 | 8.230 | 21.345 | 270.01 | 9.744 | 47.860 |
| 124.18 | 8.895 | 21.693 | 270.54 | 9.762 | 47.887 |
| 124.69 | 8.977 | 21.726 | 279.67 | 9.573 | 48.792 |
| 129.49 | 7.852 | 22.425 | 280.22 | 9.583 | 48.860 |
| 132.86 | 8.456 | 22.884 | 289.16 | 9.398 | 49.831 |
| 137.59 | 8.348 | 23.534 | 289.71 | 9.413 | 49.929 |
| 141.53 | 8.885 | 24.040 | 298.47 | 9.223 | 50.910 |
| 144.10 | 8.703 | 24.418 | 299.04 | 9.243 | 50.973 |
| 145.75 | 7.989 | 24.654 | | | |

*cis*-1,4-Dimethylcyclohexane

| | | | | | |
|---|---|---|---|---|---|
| 12.29 | 1.655 | 0.942 | 119.37 | 8.294 | 20.960 |
| 13.22 | 2.012 | 1.158 | 127.47 | 7.912 | 22.024 |
| 14.21 | 2.206 | 1.406 | 135.62 | 8.389 | 23.127 |
| 15.70 | 2.972 | 1.813 | 144.62 | 9.602 | 24.323 |
| 16.44 | 2.291 | 2.016 | 154.01 | 9.159 | 25.526 |
| 18.84 | 3.320 | 2.723 | 162.72 | 8.044 | 26.520 |
| 19.17 | 3.178 | 2.836 | 167.92 | 5.775 | 27.331 |
| 22.73 | 4.482 | 3.942 | 173.61 | 5.611 | 28.188 |
| 27.31 | 4.312 | 5.288 | | Liquid | |
| 27.38 | 4.810 | 5.312 | 189.49 | 5.527 | 41.663 |
| 32.11 | 4.663 | 6.588 | 193.18 | 5.509 | 41.853 |
| 37.10 | 5.321 | 7.789 | 194.50 | 7.285 | 41.938 |
| 42.59 | 5.646 | 8.945 | 196.80 | 9.088 | 42.059 |
| 48.32 | 5.814 | 10.064 | 199.58 | 7.284 | 42.207 |
| 53.79 | 5.133 | 11.066 | 206.15 | 8.926 | 42.582 |
| 55.51 | 4.954 | 11.362 | 206.71 | 10.761 | 42.645 |
| 59.43 | 6.147 | 12.029 | 214.66 | 8.096 | 43.138 |
| 60.99 | 5.992 | 12.293 | 217.38 | 10.568 | 43.336 |
| 67.16 | 6.362 | 13.298 | 223.92 | 10.438 | 43.782 |
| 73.45 | 6.218 | 14.280 | 227.87 | 10.400 | 44.072 |
| 79.23 | 5.386 | 15.212 | 234.28 | 10.277 | 44.518 |
| 80.14 | 7.152 | 15.320 | 238.17 | 10.213 | 44.877 |
| 85.28 | 6.711 | 16.132 | 248.30 | 10.039 | 45.700 |
| 87.43 | 7.421 | 16.468 | 258.24 | 9.846 | 46.614 |
| 92.54 | 7.818 | 17.214 | 268.39 | 10.453 | 47.624 |
| 94.98 | 7.682 | 17.557 | 277.25 | 7.267 | 48.479 |
| 100.66 | 8.414 | 18.341 | 278.44 | 9.474 | 48.556 |
| 102.96 | 8.293 | 18.679 | 285.57 | 9.366 | 49.313 |
| 108.97 | 8.398 | 19.510 | 287.52 | 8.695 | 49.532 |
| 111.17 | 8.113 | 19.832 | 294.85 | 9.201 | 50.302 |
| 117.73 | 9.300 | 20.700 | 303.22 | 7.536 | 51.273 |

*trans*-1,4-Dimethylcyclohexane

| | | | | | |
|---|---|---|---|---|---|
| 12.27 | 1.889 | 0.881 | 150.82 | 8.207 | 25.536 |
| 13.96 | 1.937 | 1.286 | 159.26 | 8.659 | 26.765 |
| 14.41 | 2.411 | 1.378 | 167.70 | 8.225 | 28.043 |
| 16.61 | 3.364 | 1.954 | 175.77 | 7.919 | 29.319 |
| 16.83 | 2.454 | 2.010 | 184.00 | 8.544 | 30.848 |
| 19.75 | 3.389 | 2.835 | 192.36 | 8.178 | 32.515 |
| 20.39 | 4.209 | 3.028 | 200.77 | 8.649 | 34.567 |
| 23.44 | 3.987 | 3.923 | 205.67 | 6.727 | 35.917 |
| 24.97 | 4.956 | 4.373 | 211.11 | 8.058 | 37.835 |
| 27.52 | 4.180 | 5.080 | 213.00 | 7.929 | 38.713 |
| 30.30 | 5.709 | 5.795 | 217.92 | 5.851 | 41.201 |
| 31.96 | 4.687 | 6.223 | 218.86 | 7.440 | 41.825 |
| 36.21 | 6.106 | 7.241 | 220.61 | 7.282 | 43.056 |
| 42.39 | 6.251 | 8.583 | 222.47 | 4.972 | 44.500 |
| 48.67 | 6.310 | 9.800 | 227.43 | 6.358 | 50.913 |
| 55.01 | 6.371 | 10.957 | 227.47 | 5.053 | 50.896 |
| 55.03 | 5.491 | 10.966 | 230.31 | 2.956 | 57.296 |
| 61.04 | 6.525 | 12.001 | 232.80 | 2.026 | 68.360 |
| 67.94 | 7.272 | 13.171 | 234.38 | 1.125 | 80.632 |
| 75.49 | 7.840 | 14.397 | 235.41 | 0.935 | 99.52 |
| 83.12 | 7.422 | 15.664 | 236.00 | 0.2504 | 300.5 |
| 90.68 | 7.695 | 16.873 | | Liquid | |
| 98.52 | 7.970 | 18.036 | 242.16 | 5.494 | 44.787 |
| 102.99 | 7.609 | 18.662 | 244.77 | 7.224 | 44.961 |
| 105.54 | 6.064 | 19.071 | 248.52 | 7.238 | 45.358 |
| 106.24 | 7.482 | 19.173 | 252.83 | 8.901 | 45.656 |
| 110.38 | 7.185 | 19.764 | 262.09 | 9.619 | 46.501 |
| 112.14 | 7.163 | 20.103 | 271.63 | 9.453 | 47.448 |
| 119.63 | 7.824 | 21.139 | 281.00 | 9.289 | 48.395 |
| 127.73 | 8.372 | 22.282 | 290.21 | 9.127 | 49.370 |
| 135.03 | 6.242 | 23.311 | 299.25 | 8.965 | 50.391 |
| 142.44 | 8.563 | 24.358 | | | |

ties. The accuracy uncertainty may be considerably greater because of premelting and other effects.

Two of these compounds, 1,1-dimethylcyclohexane and *cis*-1,2-dimethylcyclohexane, had isothermal transitions of considerable magnitude. The transition temperature was studied in the usual way by observing the equilibrium temperatures corresponding to various fractions transposed. The transition temperatures are 153.15 ± 0.05°K. and 172.5 ± 0.1°K., respectively. Duplicate measurements were made of the heats of transition and these values are given in Table V.

The thermal data obtained over the temperature range 12 to 298.16°K. were used to calculate the entropies of these compounds in the liquid state. The results of these calculations are summarized in Table VI.

In order to compare the experimental values with those obtained from theoretical considerations it is necessary to convert the experimental values to the hypothetical gaseous standard state of one atmosphere and 298.16°K. This has been done using the data from the A.P.I. Research Project 44 tables[6] and the results are given in

(6) Selected Values of Properties of Hydrocarbons, Circular of the National Bureau of Standards C461, p. 172.

TABLE III

SMOOTHED HEAT CAPACITIES OF $C_8H_{16}$ ALKYLCYCLOHEXANES, CAL./DEG./MOLE

| T, °K. | Ethylcyclohexane | 1,1-dmch. | *cis*-1,2-dmch. | *trans*-1,2-dmch. | *cis*-1,3-dmch. | *trans*-1,3-dmch. | *cis*-1,4-dmch. | *trans*-1,4-dmch. |
|---|---|---|---|---|---|---|---|---|
| 12 | 1.12 | 0.98 | 0.89 | 0.83 | 0.94 | 1.01 | 0.89 | 0.82 |
| 13 | 1.36 | 1.22 | 1.14 | 1.04 | 1.19 | 1.26 | 1.11 | 1.04 |
| 14 | 1.62 | 1.48 | 1.38 | 1.27 | 1.46 | 1.52 | 1.36 | 1.28 |
| 15 | 1.88 | 1.76 | 1.63 | 1.51 | 1.75 | 1.78 | 1.62 | 1.54 |
| 20 | 3.31 | 3.27 | 3.06 | 2.87 | 3.27 | 3.22 | 3.10 | 2.91 |
| 25 | 4.79 | 4.78 | 4.52 | 4.34 | 4.78 | 4.72 | 4.63 | 4.38 |
| 30 | 6.18 | 6.12 | 5.87 | 5.71 | 6.15 | 6.02 | 6.03 | 5.72 |
| 35 | 7.47 | 7.30 | 7.11 | 6.97 | 7.37 | 7.24 | 7.30 | 6.96 |
| 40 | 8.64 | 8.32 | 8.20 | 8.11 | 8.46 | 8.36 | 8.42 | 8.08 |
| 45 | 9.72 | 9.24 | 9.21 | 9.15 | 9.42 | 9.30 | 9.43 | 9.10 |
| 50 | 10.74 | 10.09 | 10.15 | 10.11 | 10.34 | 10.26 | 10.38 | 10.04 |
| 55 | 11.68 | 10.90 | 11.06 | 11.01 | 11.22 | 11.18 | 11.28 | 10.96 |
| 60 | 12.56 | 11.68 | 11.91 | 11.87 | 12.08 | 12.05 | 12.14 | 11.82 |
| 65 | 13.38 | 12.47 | 12.74 | 12.72 | 12.92 | 12.88 | 12.95 | 12.68 |
| 70 | 14.16 | 13.24 | 13.54 | 13.52 | 13.72 | 13.70 | 13.74 | 13.50 |
| 75 | 14.92 | 14.01 | 14.34 | 14.30 | 14.50 | 14.49 | 14.53 | 14.32 |
| 80 | 15.68 | 14.76 | 15.15 | 15.08 | 15.30 | 15.28 | 15.30 | 15.14 |
| 85 | 16.41 | 15.51 | 15.92 | 15.84 | 16.08 | 16.07 | 16.10 | 15.96 |
| 90 | 17.12 | 16.25 | 16.68 | 16.58 | 16.84 | 16.84 | 16.85 | 16.76 |
| 95 | 17.80 | 16.98 | 17.41 | 17.32 | 17.57 | 17.57 | 17.57 | 17.52 |
| 100 | 18.46 | 17.70 | 18.13 | 18.06 | 18.30 | 18.28 | 18.27 | 18.26 |
| 110 | 19.79 | 19.18 | 19.52 | 19.48 | 19.72 | 19.71 | 19.67 | 19.72 |
| 120 | 21.10 | 20.66 | 20.91 | 20.91 | 21.16 | 21.12 | 21.03 | 21.19 |
| 130 | 22.42 | 22.14 | 22.26 | 22.28 | 22.55 | 22.50 | 22.38 | 22.60 |
| 140 | 23.73 | 23.66 | 23.55 | 23.66 | 23.88 | 23.86 | 23.72 | 24.01 |
| 150 | 25.04 | 25.21 | 24.81 | 25.00 | 25.26 | 25.23 | 25.02 | 25.42 |
| 160 | 26.36 | 33.89 | 26.06 | 26.32 | 26.72 | 26.60 | 26.32 | 26.89 |
| 170 | 39.30 | 34.71 | 27.29 | 27.62 | 28.17 | 27.97 | 27.61 | 28.40 |
| 180 | 39.90 | 35.54 | 37.27 | 28.89 | 29.66 | 29.33 | 28.90 | 30.08 |
| 190 | 40.54 | 36.39 | 37.99 | 40.00 | 31.14 | 41.25 | 41.69 | 32.02 |
| 200 | 41.22 | 37.29 | 38.76 | 40.68 | 40.76 | 41.91 | 42.24 | 34.36 |
| 210 | 41.97 | 38.27 | 39.56 | 41.40 | 41.46 | 42.62 | 42.84 | 37.40 |
| 220 | 42.77 | 39.29 | 40.38 | 42.18 | 42.21 | 43.37 | 43.51 | 42.64 |
| 230 | 43.62 | 40.40 | 43.64 | 43.00 | 43.05 | 44.15 | 44.25 | 56.44 |
| 240 | 44.52 | 43.83 | 44.48 | 43.87 | 43.97 | 45.00 | 45.00 | 44.60 |
| 250 | 45.48 | 44.79 | 45.38 | 44.82 | 44.92 | 45.88 | 45.86 | 45.44 |
| 260 | 46.46 | 45.80 | 46.32 | 45.82 | 45.92 | 46.84 | 46.78 | 46.32 |
| 270 | 47.49 | 46.85 | 47.28 | 46.88 | 46.96 | 47.82 | 47.75 | 47.28 |
| 280 | 48.56 | 47.94 | 48.29 | 47.96 | 48.02 | 48.85 | 48.75 | 48.29 |
| 290 | 49.68 | 49.05 | 49.35 | 49.08 | 49.14 | 49.95 | 49.79 | 49.35 |
| 298.16 | 50.62 | 50.01 | 50.24 | 50.05 | 50.04 | 50 87 | 50.69 | 50.25 |
| 300 | 50.84 | 50.23 | 50.44 | 50.27 | 50.24 | 51.09 | 50.90 | 50.46 |
| 310 | 52.02 | | | | | | | |

Table VII. The entropies calculated by Pitzer, *et al.*,[7] have been included for comparison.

## Discussion

A number of interesting phenomena were noted in studying these compounds and will be discussed in the following section. As mentioned previously, *cis*-1,2-dimethylcyclohexane undergoes an isothermal transition at 172.5°K. The rate of transition from the high temperature form (crystals II) of *cis*-1,2-dimethylcyclohexane to the low temperature form (crystals I) was extremely slow. The maximum rate of transition occurred at a temperature 10 to 15° below the transition temperature. Even at this temperature, approximately one week was required to complete the transformation. Because of the slowness of the transition it was readily possible to supercool crystals II without any significant formation of crystals I. Consequently, heat capacity measurements were made on both crystalline forms from liquid hydrogen temperature up to the transition temperature, 172.5°K.

A plot of the molal heat capacity of both crystalline forms is shown in Fig. 2. The most interesting part of the plot is the rapid rise in the heat capacity of crystals II at about 95°K. This rapid change in the heat capacity over a short tempera-

(7) C. W. Becket, K. S. Pitzer and R. W. Spitzer, THIS JOURNAL, 69, 2488 (1948).

TABLE IV

$C_8H_{16}$ ALKYLCYCLOHEXANES: MOLAL HEATS OF FUSION, CAL./MOLE

| Compound | Expt. I | Expt. II | Expt. III | Mean[a] |
|---|---|---|---|---|
| Ethylcyclohexane | 1992.0 | 1991.5 | | 1991.7 ± 0.3 |
| 1,1-Dimethylcyclohexane | 482.6 | 484.1 | 483.6[c] | 483.4 ± 0.8 |
| *cis*-1,2-Dimethylcyclohexane | 393.5 | 392.9 | 392.9 | 393.2 ± 0.3 |
| *trans*-1,2-Dimethylcyclohexane | 2507.4 | 2507.9 | | 2507.6[a] ± 0.3 |
| *cis*-1,3-Dimethylcyclohexane | 2587.2 | 2585.0 | | 2586.1 ± 1.1 |
| *trans*-1,3-Dimethylcyclohexane | .... | .... | | 2358[b] |
| *cis*-1,4-Dimethylcyclohexane | 2224.6 | 2225.9[c] | 2222.7 | 2224.4 ± 1.7 |
| *trans*-1,4-Dimethylcyclohexane | .... | .... | | 2947.2[d] |

[a] In addition to this value three other expts. gave a value of 2490.8 ± 2.0 cal./mole. See text for discussion. [b] See text for discussion of erratic values of heat of fusion. [c] From melting point measurement. [d] The rapid rise in heat capacity before the triple point precludes an accurate value for the heat of fusion, see text. [e] These values are precision uncertainty.

TABLE V

MOLAL HEATS OF TRANSITION, CAL./MOLE

| Compound | I | II | Mean |
|---|---|---|---|
| 1,1-Dimethylcyclohexane | 1430.7 | 1430.0 | 1430.3 ± 0.4 |
| *cis*-1,2-Dimethylcyclohexane | 1971.1 | 1975.7 | 1973.4 ± 2.3 |

TABLE VI

ENTROPY SUMMARY: $C_8H_{16}$ ALKYLCYCLOHEXANES, CAL./DEG./MOLE

| | | |
|---|---|---|
| **Ethylcyclohexane** | | |
| $S_{12}$ (Debye, 4°, $\theta$ = 95.25) | 0.398 | |
| $\Delta S_{12-161.84}$ (graphical) | 27.909 | |
| $\Delta S_{161.84}$ (1991.7/161.84) | 12.306 | |
| $\Delta S_{161.84-298.16}$ (graphical) | 26.522 | |
| $S_{298.16}$ (liquid) | 67.135 | |
| **1,1-Dimethylcyclohexane** | | |
| $S_{12}$ (Debye, 6°, $\theta$ = 117.5) | 0.327 | |
| $\Delta S_{12-153.15}$ (graphical) | 25.509 | |
| $\Delta S_{153.15}$ (1430.3/153.15) | 9.339 | |
| $\Delta S_{153.15-239.81}$ (graphical) | 16.515 | |
| $\Delta S_{239.81}$ (483.4/239.81) | 2.016 | |
| $\Delta S_{239.81-298.16}$ (graphical) | 10.167 | |
| $S_{298.16}$ (liquid) | 63.873 | |
| ***cis*-1,2-Dimethylcyclohexane** | | |
| Crystals II (Unstable Modification) | | |
| $S_{12}$ (Debye, 4.5°, $\theta$ = 90.4) | 0.519 | |
| $\Delta S_{12-172.50}$ (graphical) | 37.852 | |
| $S_{172.50}$ | 38.371 | 38.371 |
| Residual entropy at 0°K. | | 2.053 |
| Crystals I, (stable modification) | | |
| $S_{12}$ (Debye, 6°, $\theta$ = 120.6) | 0.303 | |
| $\Delta S_{12-172.50}$ (graphical) | 28.681 | |
| $\Delta S_{172.50}$ (1973.4/172.50) | 11.440 | 40.424 |
| $\Delta S_{172.50-223.28}$ (graphical) | 9.947 | |
| $\Delta S_{223.28}$ (393.2/223.28) | 1.761 | |
| $\Delta S_{223.28-298.16}$ (graphical) | 13.391 | |
| $S_{298.16}$ (liquid) | 65.523 | |
| ***trans*-1,2-Dimethylcyclohexane** | | |
| $S_{12}$ (Debye, 5°, $\theta$ = 115.5) | 0.286 | |
| $\Delta S_{12-184.99}$ (graphical) | 30.502 | |
| $\Delta S_{184.99}$ (2507.6/184.99) | 13.555 | |
| $\Delta S_{184.99-298.16}$ (graphical) | 20.959 | |
| $S_{298.16}$ (liquid) | 65.302 | |
| ***cis*-1,3-Dimethylcyclohexane** | | |
| $S_{12}$ (Debye, 6°, $\theta$ = 117.9) | 0.323 | |
| $\Delta S_{12-197.59}$ (graphical) | 33.410 | |
| $\Delta S_{197.59}$ (2586.1/197.59) | 13.088 | |
| $\Delta S_{197.59-298.16}$ (graphical) | 18.342 | |
| $S_{298.16}$ (liquid) | 65.163 | |
| ***trans*-1,3-Dimethylcyclohexane** | | |
| $S_{12}$ (Debye, 5°, $\theta$ = 107.90) | 0.349 | |
| $\Delta S_{12-183.06}$ (graphical) | 30.89 | |
| $\Delta S_{183.06}$ (235.8/183.06) | 12.88 | |
| $\Delta S_{183.06-298.16}$ (graphical) | 21.91 | |
| $S_{298.16}$ (liquid) | 66.03 | |
| ***cis*-1,4-Dimethylcyclohexane** | | |
| $S_{12}$ (Debye, 6°, $\theta$ = 121.15) | 0.299 | |
| $\Delta S_{12-185.73}$ (graphical) | 31.169 | |
| $\Delta S_{185.73}$ (2224.4/185.73) | 11.977 | |
| $\Delta S_{185.73-298.16}$ (graphical) | 21.359 | |
| $S_{298.16}$ (liquid) | 64.804 | |
| ***trans*-1,4-Dimethylcyclohexane** | | |
| $S_{12}$ (Debye, 5°, $\theta$ = 114.67 | 0.292 | |
| $\Delta S_{12-236.22}$ (graphical) | 40.350 | |
| $\Delta S_{236.22}$ (2947.2/236.22) | 12.476 | |
| $\Delta S_{236.22-298.16}$ (graphical) | 10.944 | |
| $S_{298.16}$ (liquid) | 64.062 | |

TABLE VII

MOLAL ENTROPY AT 298.16°K., CAL. DEGREE$^{-1}$ MOLE$^{-1}$

| Substance | Experimental Lig. | Experimental Vap. | Calcd.[7] Vap. |
|---|---|---|---|
| Ethylcyclohexane | 67.14 | 91.46 | 91.44 |
| 1,1-Dimethylcyclohexane | 63.87 | 87.22 | 87.24 |
| *cis*-1,2-Dimethylcyclohexane | 65.52 | 89.47 | 89.51 |
| *trans*-1,2-Dimethylcyclohexane | 65.30 | 88.75 | 88.65 |
| *cis*-1,3-Dimethylcyclohexane | 65.16 | 88.72 | 88.54 |
| *trans*-1,3-Dimethylcyclohexane | 66.03 | 89.96 | 89.92 |
| *cis*-1,4-Dimethylcyclohexane | 64.80 | 88.64 | 88.54 |
| *trans*-1,4-Dimethylcyclohexane | 64.06 | 87.45 | 87.19 |

ture interval is very similar to that behavior which is characteristic of organic glasses. A similar case was observed by Kelly[8] in his investigation of cyclohexanol, *i. e.*, the unstable crystals II could be easily supercooled to liquid hydrogen temperature and showed the glassy bump.

Since crystals II have a low heat of fusion, 393 cal. per mole, and a high heat capacity, about 6% less than that of the liquid at the melting point, it seems reasonable to postulate that the molecules are free to rotate in the lattice. However, as the material is cooled it is possible that the restrictions to rotation become greater and a major part of the rotation is frozen in a short temperature interval, thereby causing the rapid change in the

(8) K. K. Kelley, THIS JOURNAL, 51, 1400 (1929).

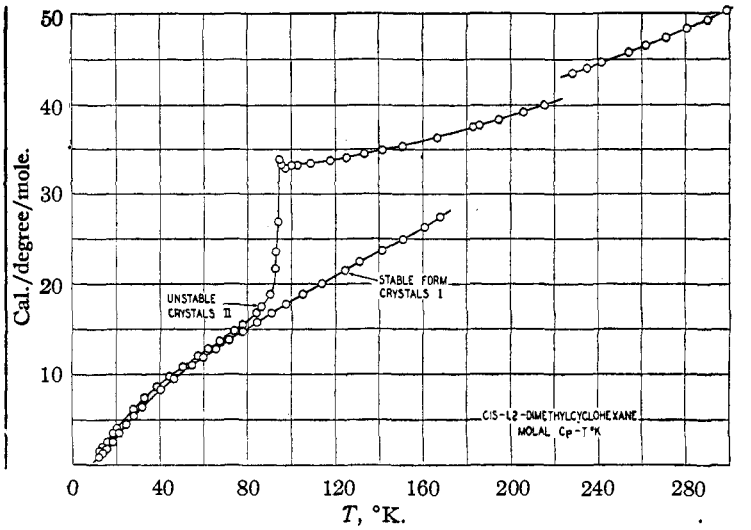


Fig. 2.—Heat capacity curves for the two different forms of *cis*-1,2-dimethylcyclohexane.

heat capacity. When crystals II were rapidly cooled and maintained under adiabatic conditions for a long period of time at a temperature about 10° below that of the rapid rise in heat-capacity curve, heat was evolved. This liberation of energy could be associated with the decrease in the energy of the crystals as the molecules reorient themselves toward equilibrium positions in the crystal lattice.

Since heat-capacity measurements were made on both crystalline forms from liquid-hydrogen temperature, the entropy of crystals II was calculated graphically at 172.5°K. over two different paths. These calculations showed the super-cooled crystals II to have a residual entropy of 2.06 E.U. at 0°K. Since *cis*-1,2-dimethylcyclohexane is a mixture of *d* and *l* forms, a part of this residual entropy can be explained if it is assumed that crystals II is a solid solution of the *d* and *l* forms that persist to 0°K. Thus the value for the entropy of mixing, 50-50 mixture, which is $R$ ln 2 would account for 1.38 E.U. of the observed residual entropy. This leaves approximately 0.6 E.U. unaccounted for and it is possible that imperfect orientation of the molecules is responsible for this difference. However, since there is no positive evidence that a solid solution is formed, it is possible that all of the residual entropy is due to the randomness or disorder of the rapidly cooled crystals.

The *trans*-1,4-dimethylcyclohexane heat-capacity curve, as shown in Fig. 3, has an unusually rapid rise in the temperature region below the melting point. The highest experimental heat-capacity point has an approximate value of 300 cal./mole at 236.0°K. It was first thought that this rapid rise in the curve was due to premelting. However, from the melting point studies, the amount of impurity was calculated to be 0.007 mole per cent. on the assumption that the system obeys Raoult's law. The premelting effect due to this amount of impurity would change the molal heat capacity only 0.1 or 0.2 cal./deg. at 236.0°K., which is insignificant as compared to the magnitude of the experimental value observed. Hence, the unusually steep slope of the curve cannot be due to premelting.

It appears unlikely that the observed behavior is associated with an impurity and hence it is believed that it is characteristic of the material and may be explained as follows. Since the shape of the curve is similar to the low temperature side of a *lambda* point we can assume that a second order transition started but melting took place before the transition was completed.

Egan and Kemp[9] observed a similar effect in the heat-capacity curve of ethylene and explained it in a like manner.

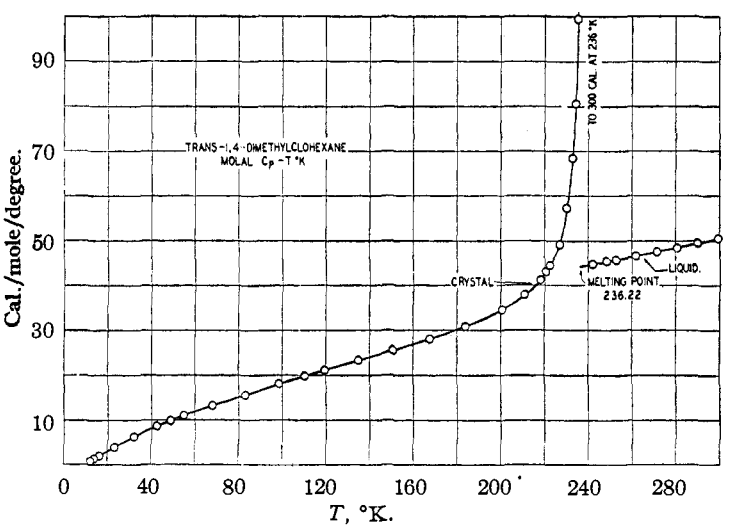


Fig. 3.—Heat capacity curve for *trans*-1,4-dimethylcyclohexane showing high heat capacity of crystals below the melting temperature.

Because of this rapid rise, it was impossible to extrapolate the heat-capacity curve to the melting point with any great reliability. Consequently, it was impossible to calculate an accurate value for the heat of fusion by the usual methods. This uncertainty will be reflected to some extent in the accuracy of the calculated melting point and the amount of impurity; but fortunately, the amount of impurity is probably small so that the accuracy

(9) C. J. Egan and J. D. Kemp, THIS JOURNAL, 59 1264 (1937).

will not be greatly affected in the absolute sense and the reliability of the results will depend principally on how closely the system obeys Raoult's law.

In the study of *trans*-1,2-dimethylcyclohexane four measurements of the heat of fusion and two melting-point determinations were made. The heats of fusion fell into two internally consistent groups which appeared to be related to the manner in which crystallization was initiated. If the liquid material was cooled rapidly to about 85°K. and crystallization was initiated by slowly heating the undercooled liquid, crystals were obtained which gave the high heat of fusion. However, if crystallization was initiated by allowing the liquid to cool slowly across the vacuum and crystallization to take place spontaneously, crystals were obtained which gave the lower value for the heat of fusion. Melting-point studies were made on crystals obtained by both of these methods. These data gave melting points (for pure material) which differed by only 0.006° which is not a very large difference but greater than the expected error of the measurements. The higher melting point was associated with the material having the lower heat of fusion. If it is assumed that there are two crystalline forms of this material, the above data show that the high melting form, although the stable form at its melting point, will have to become the unstable modification at some lower temperature. Furthermore, if both forms obey the third law, the high-melting form, with the low heat of fusion, will have to have a higher heat capacity in some portion of the temperature range or will have to undergo a transition in order to gain the necessary entropy. Our measurements show that above 90°K. the high melting form does have the higher heat capacity by a small but significant amount. In the temperature range 50 to 90° the heat capacity of the two forms are identical within the experimental error. Assuming the postulate of two crystalline forms is correct, the entropy was calculated over the two paths and found to differ by only 0.04 cal./degree which is within the experimental error.

This explanation is substantiated further by an unpublished investigation made in this Laboratory on ethylcyclopentane in which were found, very definitely, two crystalline forms with melting points differing by 0.7°, the stable high-melting form having the lower heat of fusion by approximately 170 cal./mole. The high-temperature form has the higher heat capacity over the entire temperature range from 12° to the m. p. and the entropies over the two paths are identical.

In the case of *trans*-1,3-dimethylcyclohexane it was found impossible to obtain a satisfactorily reproducible value for the heat of fusion. A great many experiments were tried in which the method of crystallizing was varied as widely as was experimentally convenient. At this time it is not possible to explain the reason for the observed behavior of this material. However, the authors are inclined to believe that it is probably due to a very slow rate of crystallization as the crystallization approaches completion. Because of the above effect, the thermal data on this compound are much less reliable than is characteristic of data from this Laboratory. The value for the heat of fusion given in Table IV is the highest value observed but not necessarily the correct value. The value of the entropy calculated from these data will also be less reliable than usual.

Table VII shows that the experimental and calculated values[6] of the entropies are in excellent agreement when the old labels on *cis* and *trans*-1,3-dimethylcyclohexane are interchanged as proposed by Pitzer and Beckett.[10]

## Summary

The heat capacities of eight $C_8H_{16}$ alkyl cyclohexanes have been given over the temperature range 12 to 300°K.

Melting points, transition temperatures, heats of fusion, and heats of transition for these compounds have been given.

Entropy values have been calculated for the liquid and gaseous state at 298.16°K.

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(10) K. S. Pitzer and C. W. Beckett, THIS JOURNAL, **69**, 977 (1947); F. D. Rossini and K. S. Pitzer, *Science*, **105**, 647 (1947).