# Heat capacity and thermodynamic properties of diamantane from 5 to 540 K [a]

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The heat capacity of diamantane, $C_{14}H_{20}$, has been measured by adiabatic calorimetry from 5 to 350 K. The heat capacity is generally sigmate except for a gradual thermal anomaly with a maximum at 35.7 K and an apparent entropy increment of only 0.8 $cal_{th}$ $K^{-1}$ $mol^{-1}$. No explanation of the mechanism of the anomaly is provided. The values of $C_p$, $S°$, and $\{G°(T)-G°(0)\}/T$ at 298.15 K are 53.35, 47.84, and $-23.60$ $cal_{th}$ $K^{-1}$ $mol^{-1}$. Thermodynamic properties to 540 K are included. $\Delta G_f°(c, 298.15 K)$ is 26.71 $kcal_{th}$ $mol^{-1}$.

## 1. Introduction

Diamantane, $C_{14}H_{20}$, pentacyclo[7.3.1.1$^{4,12}$.0$^{2,7}$.0$^{6,11}$]tetradecane (figure 1) as has already been noted is a molecule possessing at least two thermodynamically interesting aspects.[1–4] To enable the provision of complete thermodynamic tables, the heat capacity was studied over the usual cryogenic range.

## 2. Experimental

SAMPLE PROVENANCE

The preparation and characterization of the sample have been described in the accompanying paper.[1] The sample, transferred from the calorimeter as a liquid in a

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helium atmosphere after the intermediate-temperature measurements, was subjected to three additional sublimations under vacuum at 310 K to an ice-cooled receiver.

## CALORIMETRIC TECHNIQUE

The heat capacity of the sample was determined in the Mark II calorimetric cryostat; major features of the cryostat and adjuvant measuring circuitry have been described elsewhere.[5] The sample was contained in a gold-plated copper calorimeter (laboratory designation W-52) with a capsule-type platinum resistance thermometer (A-5) calibrated by the National Bureau of Standards against IPTS-48. An entrant axially symmetrical well contained the removable bifilarly wound heater assembly surrounding the thermometer. The calorimeter had an internal volume of 59.11 cm$^3$, a mass 13.1 g, excluding the thermometer-heater assembly, and was provided with a knife-edged gold-gasketed screw closure fitting previously described.[5] The heat capacity of the empty calorimeter was determined in a separate series of measurements. The heat capacity of the sample was 90 per cent of the total measured heat capacity below 20 K. It decreased to 60 per cent at 140 K and rose to 80 per cent at 350 K. Buoyancy correction was made on the basis of a crystallographic density of 1.21 g cm$^{-3}$ for $C_{14}H_{20}$.[6] Adjustments were made for small differences in gold, copper, Apiezon-T grease, and helium between measurements on the full and empty calorimeter and contributed less than 0.02 per cent uncertainty even in the 10 K region. To facilitate thermal equilibration, 44.0 kPa of helium gas was added to the evacuated calorimeter prior to sealing of the sample space in the calorimeter.

## 3. Results and discussion

### HEAT CAPACITIES

The experimental molar heat capacities are compiled in table 1 in chronological sequence so that the approximate temperature increments may usually be deduced from differences between adjacent (mean) temperatures. The results are stated in terms of the IUPAC-1973 molar mass of diamantane as 188.314 g mol$^{-1}$. Adjustments for the finite temperature increments used in the measurements ("curvature corrections") were applied to all values in table 1 by the first term in the series derived by Justice *et al.*[5] The estimated standard deviation of the heat capacities is 8 per cent at 5 K, 1 per cent at 15 K, and 0.07 per cent above 25 K. The curve is sigmate with only a small anomaly near 35.7 K.

### THE 35.7 K THERMAL ANOMALY

As may be seen in figure 1, a gradually increasing excess heat capacity with a maximum at 35.7 K is observed. The associated enthalpy and entropy increments are summarized in table 2 assuming that the lattice heat capacity—interpolated with a Debye function—shown in figure 2 obtains. These transitional increments seem too small to be accounted for on the basis of molecular disorder of individual molecules although concerted motions are not excluded. The transition is reminiscent—though about ten times smaller—of that observed in paracyclophane and there tentatively attributed to a weakly cooperative disordering phenomenon.[7]

TABLE 1. Experimental values for the heat capacity of diamantane.
(cal$_{th}$ = 4.184 J)

| $\dfrac{T}{K}$ | $\dfrac{C_p}{\text{cal}_{th}\ K^{-1}\ mol^{-1}}$ | $\dfrac{T}{K}$ | $\dfrac{C_p}{\text{cal}_{th}\ K^{-1}\ mol^{-1}}$ | $\dfrac{T}{K}$ | $\dfrac{C_p}{\text{cal}_{th}\ K^{-1}\ mol^{-1}}$ | $\dfrac{T}{K}$ | $\dfrac{C_p}{\text{cal}_{th}\ K^{-1}\ mol^{-1}}$ |
|---|---|---|---|---|---|---|---|
| | | | Low-temperature adiabatic cryostat (Ann Arbor) | | | | |
| Series I | | 223.65 | 36.03 | 6.32 | 0.209 | Series VI | |
| 49.84 | 9.577 | 233.57 | 38.15 | 7.10 | 0.290 | 32.51 | 7.464 |
| 52.67 | 9.851 | 243.54 | 40.35 | 8.03 | 0.434 | 33.45 | 7.749 |
| 58.03 | 10.380 | | | 9.18 | 0.675 | 34.47 | 7.952 |
| 63.88 | 10.972 | Series III | | 10.30 | 0.963 | 35.51 | 8.091 |
| 70.37 | 11.590 | 245.46 | 40.79 | 11.46 | 1.203 | 36.56 | 7.982 |
| 77.57 | 12.352 | 257.24 | 43.50 | 12.80 | 1.563 | 37.57 | 8.074 |
| 85.47 | 13.277 | 267.03 | 45.82 | 14.22 | 1.991 | 38.55 | 8.174 |
| 93.97 | 14.283 | 277.11 | 48.21 | 15.77 | 2.506 | | |
| 103.20 | 15.44 | 287.23 | 50.69 | 17.45 | 3.056 | Series VII | |
| 112.97 | 16.78 | 297.47 | 53.27 | 19.29 | 3.667 | 30.27 | 6.935 |
| 122.81 | 18.19 | 307.73 | 55.87 | 21.29 | 4.330 | 33.61 | 7.777 |
| 132.61 | 19.66 | 318.03 | 58.52 | 23.59 | 5.058 | 35.17 | 8.070 |
| | | 328.17 | 61.13 | 26.09 | 5.810 | 35.46 | 8.130 |
| Series II | | 338.17 | 63.76 | 28.82 | 6.551 | 35.69 | 8.039 |
| 132.80 | 19.68 | 347.09 | 66.20 | 31.76 | 7.323 | 35.92 | 7.970 |
| 143.11 | 21.31 | | | 35.09 | 7.965 | 36.10 | 7.959 |
| 153.77 | 23.00 | Series IV | | 39.10 | 8.285 | 36.24 | 7.962 |
| 164.25 | 24.75 | 131.36 | 19.47 | 42.56 | 8.706 | 36.38 | 7.959 |
| 174.44 | 26.51 | 143.26 | 21.31 | 46.42 | 9.180 | 36.59 | 8.007 |
| 184.41 | 28.30 | | | 51.28 | 9.713 | 36.86 | 8.024 |
| 194.20 | 30.11 | Series V | | 55.77 | 10.140 | | |
| 203.95 | 32.00 | 4.82 | 0.109 | | | | |
| 213.78 | 33.97 | 5.41 | 0.119 | | | | |

TABLE 2. Enthalpy in the transition region of diamantane
(cal$_{th}$ = 4.184 J)

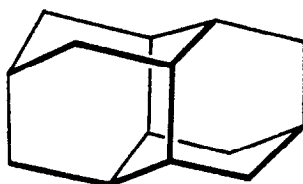| Designation (number of detn's) | $\dfrac{T_1}{K}$ | $\dfrac{T_t}{K}$ | $\dfrac{H°(T_t)-H°(T_1)}{\text{cal}_{th}\ mol^{-1}}$ | $\dfrac{H°(40\ K)-H°(24\ K)}{\text{cal}_{th}\ mol^{-1}}$ |
|---|---|---|---|---|
| Series V (5) | 24.83 | 41.25 | 101.08 | 114.50 |
| Series VII (7) | 28.32 | 39.04 | 82.68 | 114.44 |
| Series VI (7) | 32.72 | 36.99 | 30.02 | 114.56 |
| | | | Mean value | 114.50±0.04 |
| | | Lattice enthalpy $\{H_L°(40\ K)-H_L°(24\ K)\}$: | | 112.0 |
| | | | $\Delta H_t°$: | 2.5 |

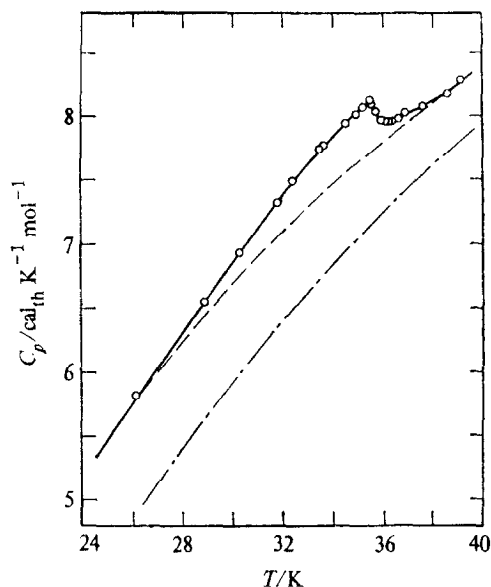$\Delta S_t°/\text{cal}_{th}\ K^{-1}\ mol^{-1} = 0.08$



FIGURE 1. Diamantane molecule.

FIGURE 2. O, Experimental heat capacities in the region of the thermal anomaly. — — —, Lattice heat capacity interpolated from Debye characteristic temperature. — · — · —, Heat capacity of adamantane included for comparison.

While handling the sample in glass we noted that fine crystals were unusually susceptible to the attraction of electrostatic fields (such as that generated by rubbing the outside of the glass).

## THERMAL FUNCTIONS

The experimental heat capacities below 410 K from this paper were combined with those of the related endeavor,[1] and fitted to two overlapping polynomials in temperature by least squares. Values of the thermal functions given in table 3 were obtained by appropriate integrations over the polynomials. Below 5 K, the heat capacity was linearly extrapolated to $T = 0$ on a $C_p/T$ against $T^2$ plot. Appropriate integrations over the several transitions were incorporated into the table. No adjustment was made in the extrapolation process for contributions due to nuclear spin or isotopic mixing; hence, the values are practicable thermal functions for use in ordinary thermochemical calculations. Standard deviations of heat-capacity values selected from the smoothed curve are 0.4 per cent from 10 to 30 K and 0.08 per cent above this temperature; that of the thermal functions is about 0.08 per cent above 100 K.

## THERMOCHEMICAL PROPERTIES

The standard entropy of formation at 298.15 K can be calculated from the results of this research together with $S°(C, c, 298.15 K) = (1.372 \pm 0.029)$ cal$_{th}$ K$^{-1}$ mol$^{-1}$,[8]

TABLE 3. Thermodynamic functions of diamantane
($cal_{th} = 4.184$ J)

| $\dfrac{T}{K}$ | $C_p$<br>$cal_{th}\ K^{-1}\ mol^{-1}$ | $S°(T) - S°(0)$<br>$cal_{th}\ K^{-1}\ mol^{-1}$ | $H°(T) - H°(0)$<br>$cal_{th}\ mol^{-1}$ | $-\{G°(T) - H°(0)\}/T$<br>$cal_{th}\ K^{-1}\ mol^{-1}$ |
|---|---|---|---|---|
| | | Crystal III | | |
| 5 | 0.098 | 0.036 | 0.122 | 0.012 |
| 10 | 0.835 | 0.280 | 2.088 | 0.071 |
| 15 | 2.247 | 0.870 | 9.603 | 0.230 |
| 20 | 3.909 | 1.742 | 24.965 | 0.494 |
| 25 | 5.482 | 2.788 | 48.528 | 0.847 |
| 30 | 6.886 | 3.913 | 79.494 | 1.263 |
| 35 | 8.044 | 5.067 | 117.014 | 1.724 |
| 40 | 8.377 | 6.154 | 157.50 | 2.212 |
| 45 | 9.004 | 7.178 | 201.18 | 2.707 |
| 50 | 9.570 | 8.156 | 247.64 | 3.203 |
| 60 | 10.580 | 9.992 | 348.51 | 4.184 |
| 70 | 11.539 | 11.695 | 459.08 | 5.137 |
| 80 | 12.624 | 13.306 | 579.8 | 6.058 |
| 90 | 13.806 | 14.860 | 711.9 | 6.950 |
| 100 | 15.07 | 16.38 | 856.2 | 7.817 |
| 110 | 16.40 | 17.88 | 1013.5 | 8.664 |
| 120 | 17.80 | 19.36 | 1184.5 | 9.494 |
| 130 | 19.26 | 20.85 | 1369.7 | 10.310 |
| 140 | 20.78 | 22.33 | 1569.9 | 11.115 |
| 150 | 22.37 | 23.82 | 1785.6 | 11.913 |
| 160 | 24.01 | 25.31 | 2017.5 | 12.703 |
| 170 | 25.72 | 26.82 | 2266.1 | 13.489 |
| 180 | 27.49 | 28.34 | 2532.0 | 14.272 |
| 190 | 29.33 | 29.87 | 2816.1 | 15.05 |
| 200 | 31.24 | 31.43 | 3118.9 | 15.83 |
| 210 | 33.22 | 33.00 | 3441.2 | 16.61 |
| 220 | 35.27 | 34.59 | 3783.6 | 17.39 |
| 230 | 37.39 | 36.21 | 3135.8 | 18.18 |
| 240 | 39.58 | 37.84 | 4531.6 | 18.96 |
| 250 | 41.83 | 39.50 | 4938.6 | 19.75 |
| 260 | 44.14 | 41.19 | 5367.9 | 20.54 |
| 270 | 46.49 | 42.90 | 5821.0 | 21.34 |
| 280 | 48.89 | 44.63 | 6297.9 | 22.14 |
| 290 | 51.33 | 46.39 | 6799.0 | 22.94 |
| 300 | 53.81 | 48.17 | 7324.7 | 23.75 |
| 273.15 | 47.24 | 43.44 | 5821.04 | 21.34 |
| 298.15 | 53.35 | 47.84 | 7226.53 | 23.60 |
| 310 | 56.34 | 49.98 | 7875.4 | 24.57 |
| 320 | 58.90 | 51.80 | 8451.6 | 25.39 |
| 330 | 61.49 | 53.66 | 9053.5 | 26.22 |
| 340 | 64.10 | 55.53 | 9681.4 | 27.06 |
| 350 | 66.73 | 57.43 | 10335.6 | 27.90 |

TABLE 3—*continued*

| $\dfrac{T}{K}$ | $\dfrac{C_p}{\text{cal}_{\text{th}}\,K^{-1}\,\text{mol}^{-1}}$ | $\dfrac{S^\circ(T)-S^\circ(0)}{\text{cal}_{\text{th}}\,K^{-1}\,\text{mol}^{-1}}$ | $\dfrac{H^\circ(T)-H^\circ(0)}{\text{cal}_{\text{th}}\,\text{mol}^{-1}}$ | $\dfrac{-\{G^\circ(T)-H^\circ(0)\}/T}{\text{cal}_{\text{th}}\,K^{-1}\,\text{mol}^{-1}}$ |
|---|---|---|---|---|
| | | Crystal III—continued | | |
| 360 | 69.38 | 59.34 | 11016.2 | 28.74 |
| 370 | 72.06 | 61.28 | 11723.3 | 29.60 |
| 380 | 74.79 | 63.24 | 12457.5 | 30.46 |
| 390 | 77.61 | 65.22 | 13219.5 | 31.32 |
| 400 | 80.54 | 67.22 | 14010.1 | 32.19 |
| 407.22 [a] | (82.4090) [b] | 68.66 | 14598.3 | 32.81 |
| | | Crystal II [c] | | |
| 407.22 [a] | (82.94) [b] | 71.25 | 15653.5 | 32.81 |
| 420.00 | 85.55 | 73.87 | 16737 | 34.02 |
| 440.43 [a] | (89.79) [b] | 78.04 | 18529 | 35.97 |
| | | Crystal I [d] | | |
| 440.43 [a] | 92.26 [b] | 82.90 | 20669 | 35.97 |
| 450 | 93.81 | 84.90 | 21560 | 36.99 |
| 460 | 95.33 | 86.98 | 22506 | 38.05 |
| 470 | 96.87 | 89.04 | 23467 | 39.11 |
| 480 | 98.43 | 91.10 | 24444 | 40.18 |
| 490 | 99.99 | 93.14 | 25436 | 41.24 |
| 500 | 101.56 | 95.18 | 26444 | 42.29 |
| 517.92 [a] | (103.85) [b] | 98.80 | 28284 | 44.19 |
| | | Liquid [e] | | |
| 517.92 [a] | (104.79) [b] | 102.81 | 30360 | 44.19 |
| 520 | 105.17 | 103.23 | 30569 | 44.44 |
| 530 | 106.98 | 105.25 | 31630 | 45.57 |
| 540 | 108.61 | 107.26 | 32708 | 46.69 |

[a] Assuming transition to be truly isothermal.
[b] Slightly extrapolated to $T_t$.
[c] Maximum $C_p > 7 \times 10^2\,\text{cal}_{\text{th}}\,K^{-1}\,\text{mol}^{-1}$; $\Delta S_t^\circ(\text{III} = \text{II}) = (10.8_4 \pm 0.06)\,\text{cal}_{\text{th}}\,K^{-1}\,\text{mol}^{-1}$.
[d] Maximum $C_p > 5 \times 10^3\,\text{cal}_{\text{th}}\,K^{-1}\,\text{mol}^{-1}$; $\Delta S_t^\circ(\text{II} = \text{I}) = (20.3_5 \pm 0.3)\,\text{cal}_{\text{th}}\,K^{-1}\,\text{mol}^{-1}$.
[e] Maximum $C_p > 5 \times 10^3\,\text{cal}_{\text{th}}\,K^{-1}\,\text{mol}^{-1}$; $\Delta S(\text{I} = \text{l}) = (16.7_9 \pm 0.15)\,\text{cal}_{\text{th}}\,K^{-1}\,\text{mol}^{-1}$.
(as elsewhere in this paper, the uncertainty indices are standard deviations).

and $S^\circ(H_2, \text{g}, 298.15\ K) = (31.207 \pm 0.008)\,\text{cal}_{\text{th}}\,K^{-1}\,\text{mol}^{-1}$.[8]† The result is

$$\Delta S_f^\circ(C_{14}H_{20}, \text{c}, 298.15\ K) = (-283.44 \pm 0.42)\,\text{cal}_{\text{th}}\,K^{-1}\,\text{mol}^{-1}. \qquad (1)$$

The enthalpy of formation has been determined by oxygen bomb calorimetry in several laboratories.[4,9,10] The $\Delta H_f^\circ(C_{14}H_{20}, \text{c}, 298.15\ K)$ value of Carson *et al.*[9] is $(-67.55 \pm 0.42)\,\text{kcal}_{\text{th}}\,\text{mol}^{-1}$, that of Clark *et al.*[4] is $(-55.5_3 \pm 0.58)\,\text{kcal}_{\text{th}}$ $\text{mol}^{-1}$, and that of Clark and McKervey[10] is $(-57.80 \pm 0.61)\,\text{kcal}_{\text{th}}\,\text{mol}^{-1}$. We select the value of Clark and McKervey as the most reliable. Hence,

$$\Delta H_f^\circ(C_{14}H_{20}, \text{c}, 298.15\ K) = (-57.80 \pm 0.61)\text{kcal}_{\text{th}}\,\text{mol}^{-1}. \qquad (2)$$

† Throughout this paper $\text{cal}_{\text{th}} = 4.184\ J$.

This value may be combined with the $\Delta S_f^{\circ}$ to yield the standard Gibbs energy of formation:

$$\Delta G_f^{\circ}(C_{14}H_{20}, c, 298.15 \text{ K}) = (26.71 \pm 0.63) \text{ kcal}_{th} \text{ mol}^{-1}. \qquad (3)$$

For the gaseous phase, the chemistry of formation is somewhat less secure and the data on which published values are based cannot yet be critically evaluated.

## OBSERVATIONS

Although marked anisotropy in the molecular motions in diamantane below 300 K has been noted by neutron-diffraction techniques,[11] neither this nor the potential-energy calculations[12] shed explanatory insights on the phenomena observed in this study.

In a communication received subsequent to the submission of this paper Jenkins *et al.*[13] report on the basis of Raman spectroscopy that a soft librational mode goes to zero at 35 K and interpret this in terms of collective motions of the diamantane molecules about the principal symmetry axis.

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