# Thorium Dicarbide—Low Temperature Thermodynamic Properties

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**The heat capacity of thorium dicarbide has been measured by adiabatic calorimetry from 5° to 350° K. and was found to be of normal sigmoid shape without transitions or thermal anomalies. At 298.15° K., the measured heat capacity at constant pressure ($C_p$), the practical entropy ($S°$), and the Gibbs function $[-(G° - H_0°)/T]$ are 13.59, 16.42, and 8.18 cal. (g.f.m. ° K.)$^{-1}$.**

HIGH-TEMPERATURE thermodynamic properties of thorium dicarbide ($ThC_2$) have been reported by several authors (*1, 4, 5, 8, 9*), but because of the lack of accurate values for entropy and heat capacity, the over-all chemical thermodynamic properties remain uncertain. The present investigation was made to provide values for the entropy and low temperature chemical thermodynamic properties.

## EXPERIMENTAL

**Cryostat and Calorimeter.** Measurements were made by the adiabatic technique in the Mark II vacuum cryostat (*2, 10*). The gold-plated copper calorimeter (laboratory designation W-30) has a capacity of 18.9 cc., an offset thermometer well which projects through the bottom of the calorimeter for approximately 2.8 cm., but no thermal conduction vanes. The heat capacity of the empty calorimeter was determined in a separate series of measurements using the same amounts of indium-tin solder for sealing the calorimeter and Apiezon-T grease for thermal contact with the heater-thermometer assembly as were used in the loaded calorimeter. The heat capacity of the calorimeter-heater-thermometer assembly was 60 to 70% of the total heat capacity. Buoyancy corrections were made using a density of 8.96 grams cc.$^{-1}$ for thorium dicarbide. A pressure of 118 torr of helium at 300° K. was used to facilitate thermal conduction in the sample space.

Temperatures were determined with a capsule-type, strain-free, platinum-resistance thermometer (laboratory designation A-5) contained within an entrant well in the calorimeter. Temperatures are considered in accord with the thermodynamic temperature scale to within 0.03° from 10° to 90° K. and within 0.04° from 90 to 350° K. Temperature increments may be determined with more precision and are probably correct to a few tenths of a millidegree after correction for quasi-adiabatic drift. All measurements of mass, resistance, potential, temperature, and time are referred to calibrations made by the National Bureau of Standards.

**Preparation and Characterization of the Sample.** The 26.239-gram (in vacuo) sample of thorium dicarbide was a composite of seven separately prepared samples, each of which was made by heating a pellet of thorium powder mixed with "spectroscopically pure" graphite in the molal ratio of 1 to 2. The thorium powder, obtained from K and K Laboratories, Inc., was reported to have a purity of 99.1%. The mixture was pressed at 700 kg. cm.$^{-2}$ into 0.8-cm. diameter pellets which were heated for 30 minutes under vacuum at 2100° C. The pellets were crushed and ground, heated for 5 hours at 2000° C., then reground and reheated for 5 additional hours above 2000° C. to homogenize the sample. X-ray powder diffraction analysis indicated the sample thus prepared to be $ThC_2$, and chemical analysis for the components indicated the composition to be $ThC_{1.98 \pm 0.03}$. The sample was handled only in the argon or nitrogen atmospheres of dry boxes.

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Table I. Heat Capacity of Thorium Dicarbide[a]

| $T$, ° K. | $C_p$ | $T$, ° K. | $C_p$ | $T$, ° K. | $C_p$ |
|---|---|---|---|---|---|
| Series I | | 14.84 | 0.238 | Series V | |
| | | 16.34 | 0.323 | | |
| 75.30 | 5.128 | 17.94 | 0.425 | 134.25 | 8.388 |
| 81.73 | 5.532 | 19.60 | 0.553 | 143.16 | 8.851 |
| | | 21.42 | 0.724 | 152.77 | 9.301 |
| Series II | | 23.52 | 0.937 | 162.86 | 9.768 |
| | | 25.94 | 1.198 | 166.97 | 9.976 |
| 83.21 | 5.628 | 28.64 | 1.508 | 176.77 | 10.355 |
| 90.97 | 6.088 | 31.81 | 1.873 | 186.89 | 10.745 |
| 99.82 | 6.535 | 35.70 | 2.286 | 197.06 | 11.101 |
| 109.60 | 7.066 | 40.18 | 2.715 | 207.30 | 11.453 |
| 119.31 | 7.598 | 45.34 | 3.147 | 217.76 | 11.762 |
| 128.96 | 8.112 | | | 228.44 | 12.067 |
| | | Series IV | | 239.29 | 12.360 |
| Series III | | | | 250.09 | 12.614 |
| | | 40.63 | 2.770 | 260.59 | 12.831 |
| 5.98 | 0.019 | 45.40 | 3.157 | 270.79 | 13.053 |
| 6.87 | 0.025 | 50.27 | 3.523 | 279.87 | 13.229 |
| 7.99 | 0.031 | 55.91 | 3.910 | 289.65 | 13.447 |
| 8.96 | 0.046 | 62.42 | 4.358 | 299.21 | 13.617 |
| 9.92 | 0.075 | 69.70 | 4.797 | 308.55 | 13.760 |
| 10.96 | 0.094 | 77.63 | 5.263 | 317.82 | 13.896 |
| 12.21 | 0.117 | | | 327.01 | 14.033 |
| 13.51 | 0.175 | | | 336.12 | 14.232 |
| | | | | 345.16 | 14.373 |

[a] $ThC_2$: g.f.m. = 256.060. Units: cal. (g.f.m. ° K.)$^{-1}$

Table II. Thermodynamic Properties of Thorium Dicarbide[a]

| $T$, ° K. | $C_p$ | $S°$ | $H° - H_0°$ | $-(G° - H_0°)/T$ |
|---|---|---|---|---|
| 10 | 0.068 | 0.025 | 0.18 | 0.007 |
| 25 | 1.094 | 0.378 | 7.08 | 0.095 |
| 50 | 3.512 | 1.947 | 67.17 | 0.603 |
| 100 | 6.533 | 5.355 | 321.6 | 2.139 |
| 150 | 9.179 | 8.517 | 716.0 | 3.743 |
| 200 | 11.210 | 11.453 | 1228.8 | 5.309 |
| 250 | 12.603 | 14.113 | 1826.2 | 6.809 |
| 300 | 13.623 | 16.506 | 2483.0 | 8.229 |
| 350 | 14.478 | 18.669 | 3185.1 | 9.568 |
| 273.15 | 13.11 | 15.25 | 2124 | 7.476 |
| 298.15 | 13.59 | 16.42 | 2458 | 8.178 |

[a] $ThC_2$: g.f.m. = 256.060. Units: cal., g.f.m., ° K.

The major impurity in the calorimetric sample was 0.79 wt. % of free carbon. The apparent heat capacities were adjusted for this contaminant using the heat capacity data for graphite (3). This adjustment was only 0.5 to 2.5% of the apparent heat capacity of the sample over the range of the measurement even though the molal composition of sample corresponds to 85.49% thorium dicarbide and 14.51% free carbon.

## RESULTS AND DISCUSSION

**Heat Capacities and Thermal Properties.** The experimental heat capacities are presented in chronological order at the mean temperatures of the determinations in Table I. These data are based upon a defined thermochemical calorie equal to 4.1840 j., an ice point of 273.15° K., and a gram formula mass (g.f.m.) of 256.060 for thorium dicarbide. These data have been corrected for curvature—i.e., for the difference between $\Delta H/\Delta T$ and the corresponding derivative. The approximate values of $\Delta T$ used in the heat capacity determinations can usually be estimated from the increments between adjacent mean temperatures given in Table I. These heat capacity values are considered to have a probable error decreasing from about 10% at 5° K. to 1% at 10° K. and to less than 0.1% above 30° K.

The heat capacities and thermodynamic functions at selected temperatures, presented in Table II, are obtained from the heat capacity data by integration of a least squares-fitted curve (carefully compared with a large-scale plot of the data). Both the fitting and quadrature are performed by high-speed digital computers using programs previously described (6, 7). The thermodynamic functions are considered to have a precision corresponding to a probable error of less than 0.1% above 100° K. Additional digits beyond those significant are given in Table II for internal consistency and to permit interpolation and differentiation. The entropies and Gibbs energies have not been adjusted for nuclear spin and isotope mixing contributions and hence are practical values for use in chemical thermodynamic calculations. The present values of $C_p$ and $S$ may be compared with estimates by Krikorian (8), $10.25 \pm 1.44$ and $15.1 \pm 3$ cal. (g.f.m. ° K.)$^{-1}$, respectively, at 298.15° K.


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# Saturated Liquid Density of Carbon Tetrafluoride from 90° to 150° K.


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**The saturated liquid density of carbon tetrafluoride has been measured at 16 temperatures between 90° and 150° K. The data can be represented by the equation**

$$d(\text{grams/cm.}^3) = 2.254 - 3.64 \times 10^{-3} T - 5.40 \times 10^{-6} T^2$$

**with a standard deviation of $7.1 \times 10^{-4}$ grams/cm.$^3$**


MEASUREMENTS of the saturated liquid density of carbon tetrafluoride (Freon-14) have been reported by Chari (2), whose work apparently forms the basis of the table of smoothed values obtainable from Du Pont (5). In a study of the optical properties of liquid $CF_4$, the authors observed seemingly anomalous behavior which could be attributed to inaccuracies in these density values. Moreover, a survey of the literature brought to light isolated measurements of the density and of the coefficient of thermal expansion (3, 7) which were more consistent with the optical results. The present measurements were performed to resolve this discrepancy.

## EXPERIMENTAL

The pycnometer, a cylindrical copper vessel with a volume at 20° C. of 22.45 cm.$^3$, is essentially a low-temperature adiabatic calorimeter. It is equipped with a 25-ohm platinum thermometer mounted in a tapered copper plug which fits snugly into a re-entrant well. The thermometer has been calibrated at the National Bureau of Standards. Within the vessel four 0.005-inch sheet copper fins extend radially outward from the thermometer well at the center

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