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# Enthalpy Increment Measurements from 4.5 to 350 K and the Thermodynamic Properties of Titanium Disilicide(cr) to 1700 K[†]

**Donald G. Archer***

Chemical Kinetics and Thermodynamic Division, National Institute of Standards and Technology,
Gaithersburg, Maryland 20899

**Mel S. Sabella, Stacey E. Stillman, and Eric J. Cotts***

Physics Department, Binghamton University, Binghamton, New York 13902-6016

Enthalpy increments for titanium disilicide were measured from 4.5 to 350 K with an adiabatic calorimeter. The enthalpy increments were combined with previous differential scanning calorimetry values to 500 K, Kopp's rule estimates for 500−800 K, and previous enthalpy increment measurements for temperatures to 1700 K in order to give the thermodynamic properties of titanium disilicide to 1700 K. Values of the Debye temperature, $\theta_D$, and the coefficient for the heat capacity of the conduction electrons, $\gamma_{el}$, were determined from the model. Thermodynamic properties for formation from the elements at 298.15 K were also given.

## Introduction

Titanium disilicide is a low resistivity material of high thermal stability. It is used for interconnects in microcircuits as layers deposited on silicon substrates. The thermodynamic properties of the deposited silicides are essential to generation of predictive models of the chemical-vapor deposition processes used to form these electronic interconnects. Because there exist at least five stoichiometrically different stable (in the kinetic sense) solid phases, the deposited phases might be susceptible to small differences in the thermodynamic properties of the different stoichiometries.

The present work provides the thermodynamic properties to 1700 K of titanium disilicide, the titanium silicide presently of most importance for microelectronic usage. The thermal functions are based upon new measurements of enthalpy increments from 4.5 to 350 K obtained with an adiabatic calorimeter, previous heat capacities obtained with a differential scanning calorimeter for temperatures from 350 to 500 K, a Kopp's rule estimate of the heat capacity from 500 to 800 K, and previous measurements of the difference in enthalpy between 298.15 K and upper temperatures ranging from 1200 to 1700 K.

## Experimental Section

Ingots of titanium disilicide were produced by means of arc melting in a titanium-gettered argon atmosphere (Feder et al., 1993; Grosman and Cotts, 1993). The titanium and silicon used in sample preparation were of high purity, <0.01 and <0.005 mol % impurities, respectively. Ingots were turned on their side and remelted at least once. Pieces of each ingot were finely powdered in an acetone medium. Glass slides were coated with a thin layer of Vaseline petroleum jelly, and the powder was sprinkled onto the slide (pouring resulted in preferential orientations of the grains). X-ray diffraction analysis was performed in a standard $\theta$-$2\theta$ theta geometry using Cu K$\alpha$ radiation. X-ray diffraction profiles revealed only peaks indexed to the titanium disilicide phase. The observed lattice parameters ($a = 0.8274 \pm 0.0005$ nm, $b = 0.4795 \pm 0.0002$ nm, $c = 0.8544 \pm 0.0005$ nm) were consistent with previous observations (Sylla et al., 1994; Laves and Walbaum, 1939; Jeitschko, 1977; Dietrich et al., 1978). Selected relatively large pieces of some ingots were cut and polished for optical microscope analysis. After a light etch with Kroll's reagent, optical micrographs revealed grain sizes between 500 and 1000 $\mu$m, primarily of single phase. The level of contamination by secondary phases observed by optical microscopy was estimated to be less than 0.1%. Chemical analysis performed by the LECO Corp. on selected samples indicated that the ingots contained <100 ppm oxygen, <100 ppm carbon, <2 ppm hydrogen, and <30 ppm nitrogen. These impurity levels were typical of the titanium silicides produced in our laboratory except for oxygen, for which more typical values were at the 500 ppm level.

The titanium disilicide ingots were lightly crushed and separated by particle size by means of a 20 mesh sieve. Pieces of the ingots larger than 20 mesh were used to load the calorimeter.

The calorimetric apparatus has been described previously (Archer, 1995). The loaded calorimeter was evacuated, and then approximately 8 kPa (300 K) of helium was sealed in the calorimeter. The mass of titanium disilicide used for the measurements was 11.9037 g and corresponded to approximately 50% of the internal volume of the calorimeter. The density of titanium disilicide was calculated from the X-ray data to be 4.08 g·cm$^{-3}$. The molecular mass was taken to be 104.072 g·mol$^{-1}$. The measured enthalpy increments of the filled calorimeter were converted into enthalpy increments for titanium disilicide by subtraction of the enthalpy increment for the empty calorimeter and for the small differences in the amounts of helium and vacuum grease between the empty and filled calorimeters. The enthalpy increments were corrected for the small systematic biases in the calorimetric system using the equations

$$\epsilon\Delta H_m = -[\{(T_2 + T_1)/2\} - 100\,\mathrm{K}](0.00001\ \mathrm{K}^{-1})\Delta H_m \quad (T_1 > 100\ \mathrm{K}) \qquad (1)$$

$$\epsilon\Delta H_m = -0.0025\Delta H_m \quad (T_2 < 13.8\ \mathrm{K}) \qquad (2)$$

where $T_2$ and $T_1$ are the larger and the smaller of the two

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* To whom correspondence should be addressed.

[†] Certain commercial materials and suppliers are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by either the U.S. Government or the National Institute of Standards and Technology, nor does it imply that the equipment or materials identified are necessarily the best available for the purpose.

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**Table 1. Enthalpy Increment Measurements for Titanium Disilicide**

| $T_1$/K | $T_2$/K | $\Delta H_m(T_1 \rightarrow T_2)$/ ($J \cdot mol^{-1}$) | $\sigma^a$ | $\delta^b$ | $T_1$/K | $T_2$/K | $\Delta H_m(T_1 \rightarrow T_2)$/ ($J \cdot mol^{-1}$) | $\sigma^a$ | $\delta^b$ |
|---|---|---|---|---|---|---|---|---|---|
| 15.5490 | 17.1905 | 0.2245 | U | 4.57 | 202.9065 | 207.8160 | 275.832 | 0.1 | −0.01 |
| 17.1841 | 19.6095 | 0.4207 | 2.5 | −1.27 | 207.7099 | 212.7001 | 284.257 | 0.1 | 0.02 |
| 19.5963 | 21.9613 | 0.5717 | 2.5 | −1.87 | 212.6846 | 217.5796 | 282.345 | 0.1 | −0.02 |
| 21.9582 | 24.3942 | 0.8334 | 2.5 | 0.30 | 217.5627 | 222.4458 | 285.075 | 0.1 | −0.01 |
| 24.4081 | 26.8672 | 1.1600 | 0.6 | 0.47 | 222.4276 | 227.3204 | 288.972 | 0.1 | 0.01 |
| 26.8742 | 29.4220 | 1.6366 | 0.6 | 0.10 | 227.3012 | 232.1854 | 291.631 | 0.1 | 0.03 |
| 29.4234 | 32.0267 | 2.265 | 0.5 | −0.17 | 232.1645 | 237.0579 | 295.045 | 0.1 | −0.01 |
| 32.0244 | 34.6950 | 3.125 | 0.5 | −0.04 | 237.0354 | 241.9228 | 297.575 | 0.1 | 0.00 |
| 34.6937 | 37.8222 | 4.951 | 0.25 | −0.05 | 241.8983 | 246.7837 | 300.133 | 0.1 | −0.01 |
| 37.8179 | 41.0168 | 6.845 | 0.25 | 0.02 | 246.7548 | 251.6510 | 303.507 | 0.1 | 0.02 |
| 4.5403 | 5.9766 | 0.0315 | 6 | 2.33 | 247.9672 | 253.3971 | 337.241 | 0.1 | −0.04 |
| 5.9378 | 7.7684 | 0.0548 | 4 | −0.32 | 253.3683 | 257.7146 | 272.325 | 0.1 | 0.03 |
| 7.7815 | 9.6536 | 0.0769 | 4 | −2.33 | 257.6847 | 262.0331 | 274.233 | 0.1 | −0.01 |
| 9.6255 | 11.6720 | 0.1189 | 4 | 1.27 | 262.0007 | 266.3551 | 276.373 | 0.1 | −0.03 |
| 11.6684 | 13.8014 | 0.1674 | 5 | 0.49 | 266.3209 | 270.6695 | 277.853 | 0.1 | 0.01 |
| 13.8362 | 15.9748 | 0.2307 | 3 | 1.46 | 270.6326 | 274.9919 | 280.004 | 0.1 | −0.07 |
| 15.9874 | 18.2688 | 0.3322 | 2.5 | −0.40 | 274.9527 | 279.3001 | 281.193 | 0.1 | 0.05 |
| 18.2750 | 20.4419 | 0.4411 | 2.5 | 1.03 | 279.2594 | 283.6173 | 283.290 | 0.1 | 0.00 |
| 20.4414 | 22.8674 | 0.6772 | 2.5 | 0.41 | 283.5734 | 287.9239 | 284.334 | 0.1 | 0.00 |
| 22.9104 | 25.3268 | 0.9323 | 0.6 | −0.04 | 287.8772 | 292.2264 | 285.686 | 0.1 | 0.00 |
| 25.3438 | 27.8374 | 1.316 | 0.6 | −0.27 | 292.1776 | 296.5373 | 287.771 | 0.1 | −0.01 |
| 27.8471 | 30.4118 | 1.854 | 0.5 | 0.04 | 296.4856 | 300.8389 | 288.776 | 0.1 | 0.01 |
| 30.4163 | 33.0610 | 2.582 | 0.5 | −0.23 | 300.7844 | 305.1352 | 290.071 | 0.1 | 0.06 |
| 33.0616 | 35.7453 | 3.511 | 0.5 | −0.02 | 81.3527 | 86.7804 | 103.141 | 0.1 | 0.00 |
| 35.7436 | 38.5034 | 4.766 | 0.3 | 0.20 | 86.7801 | 91.9400 | 110.550 | 0.1 | −0.05 |
| 38.4997 | 41.3261 | 6.315 | 0.3 | −0.07 | 91.9386 | 97.1472 | 123.839 | 0.1 | −0.01 |
| 41.3208 | 44.1634 | 8.100 | 0.2 | 0.10 | 97.1447 | 102.3850 | 136.708 | 0.1 | 0.00 |
| 44.1580 | 47.0594 | 10.328 | 0.2 | 0.04 | 102.3813 | 107.6578 | 149.600 | 0.1 | 0.01 |
| 47.0540 | 49.9900 | 12.841 | 0.2 | 0.02 | 107.6537 | 112.9614 | 162.186 | 0.1 | 0.02 |
| 49.9842 | 52.9512 | 15.687 | 0.1 | 0.05 | 112.9566 | 118.2776 | 173.865 | 0.1 | 0.00 |
| 52.9451 | 55.9581 | 18.961 | 0.1 | 0.00 | 118.2724 | 123.6189 | 185.663 | 0.1 | 0.03 |
| 55.9516 | 58.9921 | 22.476 | 0.1 | −0.01 | 123.6133 | 128.9607 | 196.088 | 0.1 | 0.01 |
| 58.9854 | 62.0640 | 26.404 | 0.1 | 0.00 | 128.9543 | 134.3204 | 206.785 | 0.1 | 0.01 |
| 62.0573 | 65.1537 | 30.446 | 0.1 | 0.00 | 134.3132 | 139.6883 | 216.783 | 0.1 | 0.06 |
| 65.1471 | 68.2583 | 34.678 | 0.1 | 0.01 | 139.6809 | 145.0811 | 226.811 | 0.1 | 0.00 |
| 68.2516 | 71.3835 | 39.180 | 0.1 | 0.04 | 145.0736 | 150.4692 | 235.244 | 0.1 | −0.02 |
| 71.3769 | 74.5368 | 43.947 | 0.1 | 0.01 | 150.4611 | 155.8727 | 244.279 | 0.1 | 0.02 |
| 77.6998 | 80.8821 | 53.469 | 0.1 | 0.03 | 155.8639 | 161.2754 | 251.854 | 0.1 | −0.06 |
| 80.8753 | 84.0769 | 58.495 | 0.1 | 0.01 | 161.2657 | 166.6777 | 259.566 | 0.1 | 0.07 |
| 84.0700 | 87.2789 | 63.364 | 0.1 | 0.01 | 166.6664 | 172.0848 | 266.633 | 0.1 | −0.01 |
| 44.5803 | 47.5607 | 10.964 | 0.1 | −0.04 | 172.0736 | 177.5081 | 274.099 | 0.1 | 0.01 |
| 47.5586 | 50.5043 | 13.337 | 0.1 | 0.08 | 177.4948 | 182.9306 | 280.498 | 0.1 | 0.04 |
| 50.5022 | 53.4853 | 16.250 | 0.1 | −0.17 | 182.9168 | 188.3434 | 285.881 | 0.1 | 0.02 |
| 53.4830 | 56.4875 | 19.481 | 0.1 | 0.03 | 188.3230 | 193.7540 | 291.742 | 0.1 | 0.02 |
| 56.4851 | 59.5189 | 23.037 | 0.1 | −0.01 | 193.7413 | 199.1526 | 295.916 | 0.1 | 0.00 |
| 59.5161 | 62.5830 | 26.952 | 0.1 | 0.01 | 199.1390 | 204.5688 | 301.987 | 0.1 | 0.01 |
| 62.5800 | 65.6742 | 31.097 | 0.1 | −0.01 | 204.5537 | 209.9781 | 306.404 | 0.1 | −0.01 |
| 65.6710 | 68.7743 | 35.288 | 0.1 | 0.01 | 209.9618 | 215.3951 | 311.303 | 0.1 | −0.05 |
| 68.7711 | 71.8971 | 39.817 | 0.1 | 0.03 | 215.3776 | 220.8055 | 315.325 | 0.1 | −0.04 |
| 71.8936 | 75.0328 | 44.328 | 0.1 | −0.10 | 220.7868 | 226.2110 | 319.225 | 0.1 | −0.03 |
| 75.0291 | 78.1874 | 49.209 | 0.1 | 0.10 | 226.1912 | 231.6149 | 323.192 | 0.1 | 0.01 |
| 78.1836 | 81.3557 | 53.976 | 0.1 | −0.02 | 231.5935 | 237.0219 | 327.080 | 0.1 | −0.02 |
| 81.3515 | 84.5378 | 58.888 | 0.1 | −0.01 | 236.9988 | 242.4302 | 330.810 | 0.1 | −0.01 |
| 84.5337 | 87.7294 | 63.757 | 0.1 | −0.02 | 242.4050 | 247.8277 | 333.989 | 0.1 | 0.01 |
| 87.7252 | 90.9360 | 68.756 | 0.1 | −0.04 | 247.7984 | 253.2276 | 337.255 | 0.1 | 0.00 |
| 90.9314 | 94.1463 | 73.518 | 0.1 | −0.05 | 253.1893 | 258.6302 | 341.349 | 0.1 | 0.09 |
| 94.1413 | 97.3647 | 78.400 | 0.1 | 0.01 | 258.6012 | 264.0202 | 342.599 | 0.1 | 0.01 |
| 92.0950 | 97.3381 | 125.080 | 0.1 | 0.00 | 263.9867 | 269.4031 | 345.237 | 0.1 | 0.03 |
| 97.3365 | 101.5479 | 109.286 | 0.1 | 0.01 | 269.3665 | 274.7977 | 348.641 | 0.1 | −0.03 |
| 101.5458 | 105.7956 | 118.039 | 0.1 | 0.00 | 274.7583 | 280.1752 | 350.438 | 0.1 | 0.03 |
| 105.7930 | 110.0545 | 126.041 | 0.1 | 0.03 | 280.1328 | 285.5648 | 353.706 | 0.1 | −0.01 |
| 110.0514 | 114.3364 | 134.182 | 0.1 | −0.01 | 285.5192 | 290.9383 | 355.101 | 0.1 | −0.03 |
| 114.3330 | 118.6202 | 141.550 | 0.1 | 0.02 | 290.8889 | 296.3114 | 357.689 | 0.1 | 0.01 |
| 118.6166 | 122.9275 | 149.348 | 0.1 | −0.02 | 296.2588 | 301.6854 | 359.985 | 0.1 | −0.02 |
| 122.9234 | 127.2312 | 156.130 | 0.1 | 0.03 | 301.6288 | 307.0302 | 360.356 | 0.1 | −0.02 |
| 127.2268 | 131.5381 | 162.803 | 0.1 | 0.01 | 306.9694 | 312.3439 | 360.477 | 0.1 | −0.02 |
| 131.5333 | 135.8558 | 169.569 | 0.1 | 0.01 | 311.7298 | 317.0756 | 360.371 | 0.1 | 0.03 |
| 135.8508 | 140.1705 | 175.443 | 0.1 | −0.05 | 317.0051 | 322.3190 | 359.885 | 0.1 | 0.00 |
| 140.1652 | 144.4928 | 181.712 | 0.1 | 0.00 | 322.2437 | 327.3360 | 346.471 | 0.1 | 0.00 |
| 144.4871 | 149.3367 | 210.138 | 0.1 | −0.07 | 327.2570 | 332.3416 | 347.357 | 0.1 | −0.02 |
| 149.3306 | 154.1969 | 217.664 | 0.1 | −0.03 | 332.1361 | 337.3439 | 357.429 | 0.1 | 0.04 |
| 154.1900 | 159.0495 | 223.817 | 0.1 | −0.01 | 337.2548 | 342.3305 | 349.643 | 0.1 | 0.00 |
| 159.0423 | 163.9128 | 230.265 | 0.1 | −0.07 | 342.2371 | 346.5575 | 298.717 | 0.1 | 0.02 |
| 163.9050 | 168.7777 | 236.498 | 0.1 | 0.07 | 346.4607 | 349.7080 | 225.091 | 0.1 | −0.01 |
| 168.7694 | 173.6502 | 242.077 | 0.1 | −0.07 | 301.0654 | 308.1362 | 471.867 | 0.1 | −0.02 |
| 173.6413 | 178.5308 | 247.941 | 0.1 | −0.01 | 308.1298 | 315.1734 | 473.372 | 0.1 | −0.02 |
| 178.5212 | 183.4102 | 252.872 | 0.1 | −0.03 | 315.1591 | 322.2102 | 477.091 | 0.1 | 0.00 |
| 183.4000 | 188.2920 | 257.956 | 0.1 | 0.03 | 322.1880 | 329.2336 | 479.761 | 0.1 | 0.01 |
| 188.2800 | 193.1729 | 262.616 | 0.1 | 0.05 | 329.1933 | 336.2506 | 483.233 | 0.1 | −0.03 |
| 193.1597 | 198.0468 | 266.670 | 0.1 | 0.06 | 336.2114 | 343.2606 | 485.716 | 0.1 | 0.03 |
| 198.0343 | 202.9349 | 271.343 | 0.1 | −0.02 | 343.2135 | 349.8677 | 460.552 | 0.1 | −0.04 |

[a] $\sigma$ is the percentage uncertainty assigned to the observation for the purposes of the least-squares calculation. A U indicates that the observation was not included in the least-squares calculation. [b] $\delta$ is the percentage difference of the calculated enthalpy increment from that observed.

**Table 2. Least-Squares Estimated Knot Positions and $\gamma_{el}$[a]**

| $T_i$/K | $d_i$ | $T_i$/K | $d_i$ | $T_i$/K | $d_i$ |
|---|---|---|---|---|---|
| 0 | 37.4736 | 40 | 21.2103 | 230 | 1.61511 |
| 10 | 37.4736 | 55 | 16.0524 | 280 | 0.04373 |
| 15 | 36.1256 | 75 | 11.9647 | 330 | −1.31053 |
| 20 | 32.8220 | 100 | 8.82794 | 380 | −2.55723 |
| 25 | 29.5381 | 130 | 6.33731 | 1850 | −36.91127 |
| 32 | 25.2729 | 180 | 3.57256 | | |

[a] $\gamma_{el}/C_p^\circ = 0.003\ 605\ 87\ \mathrm{K}^{-1}$.

temperatures for the enthalpy increment, respectively, and $\epsilon\Delta H_m$ is the correction added to the substance's enthalpy increment, $\Delta H_m$. The origin of these corrections has been described previously (Archer, 1995).

## Results and Discussion

The measured enthalpy increments for titanium disilicide are given in Table 1. Above 50 K, the measurements are expected to be uncertain by no more than 0.05−0.1%, dependent upon the particular temperature. These uncertainty values were based on the previous measurements of enthalpy increments for calorimetric reference materials (Archer, 1995), the present reproducibility, and the percentage of the total measured enthalpy increment that was due to the titanium disilicide sample. Below 50 K, the results must be considered less accurate, partly due to limits in the accuracy of platinum resistance thermometer temperature scales below 50 K and partly due to an unfavorable percentage of the total measured enthalpy being due to the titanium disilicide sample. The contribution of the titanium disilicide to the total measured enthalpy increment was a minimum of 8% near 20 K and increased in percentage with both increasing and decreasing temperatures from 20 K. The sample contributed 24% of the total enthalpy increment for the lowest temperature measurement. The increasing contribution of titanium disilicide to the total enthalpy increment at temperatures of less than 20 K was a result of titanium disilicide possessing a much larger contribution to the molar enthalpy from the conduction electrons than does copper, which comprised the bulk of the calorimeter.

Thermodynamic properties for titanium disilicide were calculated from a least-squares representation using a cubic-spline method described previously (Archer, 1992). That method was altered in the present case to allow incorporation of an additional variable value representing the limiting value of the heat capacity of the conduction electrons.

Briefly, a function $f(T)$ was used, where:

$$f(T) = [T\{(C_{p,m} - \gamma_{el}T)/C_p^\circ\}^{-1/3} - bT]/T^\circ \qquad (3)$$

and where $T$ is temperature, $T^\circ$ is 1 K, $C_{p,m}$ is the molar heat capacity, $C_p^\circ$ is 1.0 J·K$^{-1}$·mol$^{-1}$, $\gamma_{el}$ is the coefficient for the contribution to the heat capacity of the conduction electrons, and $b$ is arbitrarily chosen to be 0.25 for the present case. The function $f(T)$ of eq 3 was fitted with a cubic spline using polynomials of the form

$$f(T) = a_i(T - T_i)^3 + b_i(T - T_i)^2 + c_i(T - T_i) + d_i \qquad (4)$$

where the subscript $i$ refers to the polynomial that contained the specified value of $T$ and spanned the temperature range $T_i$ to $T_{i+1}$. A particular ($T_i$, $d_i$) pair is referred to as a "knot." "Natural spline" end conditions (*i.e.*, second derivative equal to 0) were imposed at the two end knots. (For the purpose of calculation $T_{i+1} > T > T_i$). The calculated heat capacity is thus

$$C_{p,m}/C_p^\circ = \left(\frac{T}{T^\circ f(T) + bT}\right)^3 + \gamma_{el}T/C_p^\circ \qquad (5)$$

Equation 5 was integrated numerically to obtain the enthalpy. The model was determined by fitting to the selected values with a nonlinear least-squares program. The vector of residuals was calculated using eq 5 for the heat capacity or the numerical integration of eq 5 to obtain enthalpy increments. The estimated square root of the variance for the least-squares procedure was calculated from twice the irreproducibility for a full calorimeter determination and the percentage of the observed enthalpy due to the titanium disilicide sample. These values, given in Table 1, approximately corresponded to a 95% confidence interval rather than the square root of the variance. However, the calculations will be correct if the relative weighting of all results was correct, which was the case here. In the current work, the first two knot positions were set to have identical values which were determined from the nonlinear least-squares procedure. Representation of the experimental results, over the full range of temperature, required 16 variable values for the knot positions and the variable $\gamma_{el}$. This procedure yielded an estimate of the Debye temperature of approximately (675 ± 50) K and a value of $\gamma_{el}/C_p^\circ$ of $36 \times 10^{-4}$ K$^{-1}$ ± ~10%. The value of the Debye temperature for $TiSi_2$ obtained here was very similar to that obtained by Gottlieb et al. (1993) for the adjacent first-row transition metal disilicide $VSi_2$. Gottlieb et al. (1993) measured the heat capacity of $VSi_2$ from 0.1 to 7.5 K and obtained a value of the Debye temperature of (665 ± 10) K. The value of $\gamma_{el}/C_p^\circ$ obtained here, $36 \times 10^{-4}$ K$^{-1}$, was similar to the value for titanium metal, $35.6 \times 10^{-4}$ K$^{-1}$ (Hultgren et al., 1963). This was different from $VSi_2$ where $\gamma_{el}/C_p^\circ$ was found by Gottlieb et al. to be $60.8 \times 10^{-4}$ K$^{-1}$ compared to the value for vanadium metal of $90.8 \times 10^{-4}$ K$^{-1}$ (Hultgren et al., 1963). Determination of the parameters for vanadium were complicated by a superconducting transition at 5 K.

The final knot positions and the value of $\gamma_{el}$ are given in Table 2. The number of digits given in Table 2 should be sufficient for calculation of thermodynamic properties and were not meant to be representative of any statistical assessment. Calculated thermodynamic properties of titanium disilicide are given in Table 3. One of the present measurements was excluded from the least-squares representation as it disagreed with the other measurements; no reason for the divergence of this point was known.

The values used for determination of the model consisted of the enthalpy increments from Table 1, heat capacities calculated from the equation of Sylla et al. (1994) for 350−500 K, heat capacities estimated by means of Kopp's rule, and the reference heat capacity values for titanium and silicon (Chase et al., 1985) for temperatures from 500 to 800 K. Also included were values of $\Delta H_m(T_1 \rightarrow 298.15\ \mathrm{K})$ calculated from the equation given by Bondarenko (1976) for values of $T_1$ from 1200 to 1700 K (Bondarenko gave only the fitted equation). The equation given by Sylla et al. is a representation of their differential scanning calorimetry measurements that spanned the temperature range of 110−500 K. Differential scanning calorimetry is inherently less accurate than the calorimetry used for the measurements presented here. Because of this large difference in accuracy, the scanning calorimetry results that were included in the least-squares representation were only those for temperatures greater than the largest temperature for the present measurements. The heat capacities from Sylla et al. and from the Kopp's rule estimate were weighted as possessing 95% confidence intervals of 2% and

**Table 3. Thermodynamic Properties of Titanium Disilicide Calculated from Eqs 4 and 5**

| $T$/K | $C_{p,m}$/ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$) | $(T) - H_m(0\ K))$/ ($kJ{\cdot}mol^{-1}$) | $(S_m$/ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$) | $T$/K | $C_{p,m}$/ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$) | $(T) - H_m(0\ K))$/ ($kJ{\cdot}mol^{-1}$) | $(S_m$/ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$) |
|---|---|---|---|---|---|---|---|
| 10 | 0.0517 | 0.000 | 0.041 | 460 | 73.8 | 22.577 | 94.612 |
| 20 | 0.220 | 0.001 | 0.116 | 480 | 74.4 | 24.060 | 97.768 |
| 40 | 2.249 | 0.020 | 0.696 | 500 | 75.0 | 25.555 | 100.819 |
| 60 | 8.366 | 0.120 | 2.633 | 520 | 75.6 | 27.061 | 103.77 |
| 80 | 17.124 | 0.373 | 6.208 | 540 | 76.1 | 28.578 | 106.64 |
| 100 | 26.193 | 0.807 | 11.013 | 560 | 76.6 | 30.10 | 109.41 |
| 120 | 34.363 | 1.414 | 16.529 | 580 | 77.0 | 31.64 | 112.11 |
| 140 | 41.267 | 2.173 | 22.361 | 600 | 77.5 | 33.19 | 114.73 |
| 160 | 46.94 | 3.057 | 28.255 | 620 | 77.9 | 34.74 | 117.27 |
| 180 | 51.54 | 4.043 | 34.058 | 640 | 78.3 | 36.30 | 119.75 |
| 200 | 55.30 | 5.113 | 39.690 | 660 | 78.6 | 37.87 | 122.17 |
| 220 | 58.39 | 6.251 | 45.110 | 680 | 79.0 | 39.45 | 124.51 |
| 240 | 60.95 | 7.445 | 50.304 | 700 | 79.3 | 41.03 | 126.81 |
| 260 | 63.08 | 8.686 | 55.269 | 720 | 79.7 | 42.62 | 129.05 |
| 280 | 64.89 | 9.966 | 60.012 | 740 | 80.0 | 44.22 | 131.24 |
| 298.15 | 66.29 | 11.157 | 64.132 | 760 | 80.3 | 45.82 | 133.38 |
| 300 | 66.42 | 11.279 | 64.543 | 780 | 80.6 | 47.43 | 135.47 |
| 320 | 67.75 | 12.621 | 68.873 | 800 | 80.8 | 49.04 | 137.51 |
| 340 | 68.90 | 13.988 | 73.015 | 900 | 82.1 | 57.19 | 147.10 |
| 360 | 69.91 | 15.376 | 76.983 | 1000 | 83.1 | 65.45 | 155.81 |
| 380 | 70.8 | 16.784 | 80.788 | 1200 | 84.9 | 82.26 | 171.13 |
| 400 | 71.7 | 18.209 | 84.442 | 1400 | 86.3 | 99.38 | 184.32 |
| 420 | 72.4 | 19.650 | 87.958 | 1600 | 87.5 | 116.77 | 195.93 |
| 440 | 73.1 | 21.107 | 91.345 | 1700 | 88.0 | 125.54 | 201.25 |

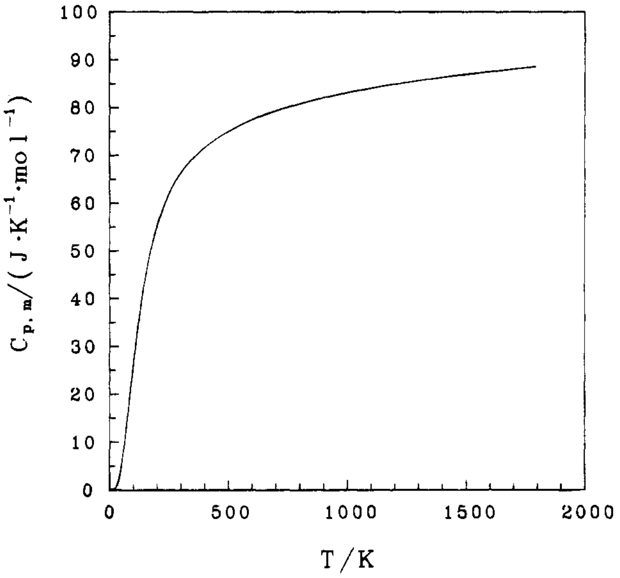

**Figure 1.** Heat capacity of titanium disilicide calculated from the least-squares representation.

3%, respectively. The enthalpy increments from Bondarenko were weighted as possessing 95% confidence intervals of 2% for values of $T_1$ less than 1550 K and were given no weight for values of $T_1$ greater than 1550 K for reasons discussed below. Only a single knot was used beyond 380 K. This was because the accuracy of the fitted results for temperatures greater than 350 K did not justify any tighter of a representation. The enthalpy increment measurements from Golutvin (1959) were found to disagree with the fitted equation with a root-mean-square (rms) difference of 1.3 $kJ{\cdot}mol^{-1}$ for upper temperatures from 108.6 to 774.2 K. This difference was more or less independent of temperature.

Calculated values of the heat capacity are shown in Figure 1. The differences of the present measured values, Sylla et al.'s (1994) equation from 110 to 500 K, the Kopp's rule estimate to 800 K, and the high-temperature enthalpy increments from the model are shown in Figure 2. The rms difference of the present measurements from the fitted model was approximately 0.035% for temperatures greater than 50 K. The fitted equation agreed well with the high-temperature enthalpy increments from 1200 to 1500 K (rms

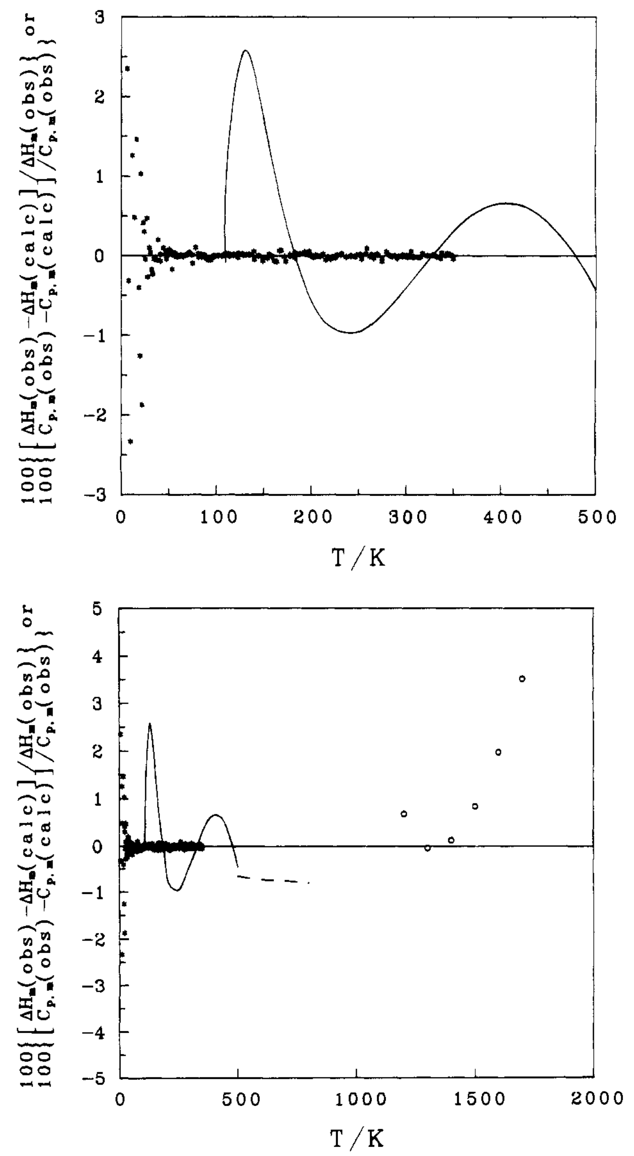

**Figure 2.** Differences from the fitted model, in percent, for the present results, *; the heat capacity equation of Sylla et al. (1994), —; the estimated heat capacity from Kopp's rule, - - -; and enthalpy increments from Bondarenko (1976), ○.

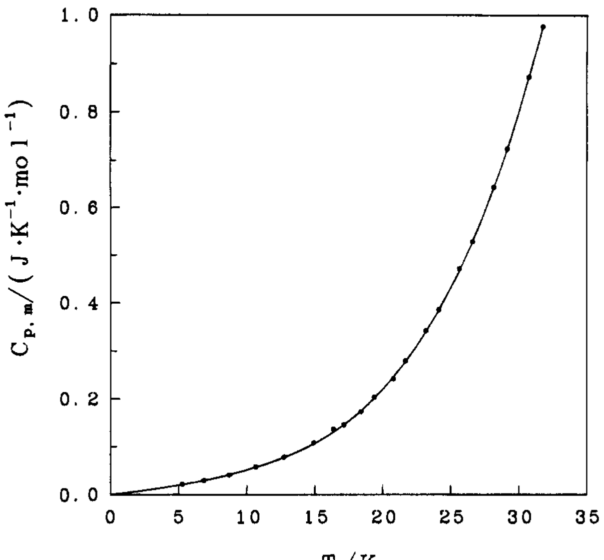

**Figure 3.** Values of the heat capacity at low temperatures. The line is calculated from the least-squares estimated model. The symbols are values approximated from the experimental values as $\Delta H_m(T_1 \rightarrow T_2)/(T_2 - T_1)$.

difference of 0.5%); however, the differences became larger for 1600 and 1700 K (1.9 % and 3.5%, respectively; the rms difference for the total range of 1200−1700 K was 1.7%). The increased differences above 1500 K could have resulted from at least three different possibilities: (1) A significant variation of electrical resistivity above 1470 K had been reported previously for titanium disilicide (Glaser and Moskowitz, 1953). This increased resistivity may be an indicator for the existence of an allotropic transformation of titanium disilicide in the vicinity of 1470 K. This possible transformation may have been the cause of the divergence of the observed enthalpy from the model for temperatures greater than 1550 K. (2) Increased experimental uncertainty for temperatures greater than 1500 K was certainly possible. (3) There is sometimes an observed increase in enthalpy and heat capacity in the temperature region just prior to the melting temperature. This effect may account for the differences. The fitted function should not follow the additional increase in enthalpy for the first two cases, but should follow it for the third case. Some refractory materials, such as aluminum oxide, do not show the decidedly nonlinear behavior seen in nonrefractory materials, *e.g.*, bismuth and sodium chloride. On the basis of the above considerations, the decision was made not to have the fitted function more tightly represent the enthalpy increments at 1600 and 1700 K.

Figure 3 shows a comparison of calculated values of the heat capacity and values of $\Delta H_m(T_1 \rightarrow T_2)/(T_2 - T_1)$ from Table 1. The linear dependence, with respect to $T$, of the calculated heat capacity resulting from the conduction electrons is visible at the lowest temperatures.

Combination of the present 298.15 K entropy with the reference values of the entropies of titanium and silicon (Chase et al., 1985) gives an entropy of formation of −4.27 $J\cdot mol^{-1}\cdot K^{-1}$ for 298.15 K. Schlesinger (1990) recommended a value of the 298.15 K enthalpy of formation, (−170.9 ± 8.3) $kJ\cdot mol^{-1}$, given by Topor and Kleppa (1986). Combination of these two values gives a 298.15 K Gibbs energy of formation of (−169.6 ± 8.3) $kJ\cdot mol^{-1}$. The thermodynamic properties for formation at other temperatures may be calculated from the model given here and the material given by Chase et al. (1985).

A comparison may also be made with the value of the molar entropy for $TiSi_2$, (61.1 ± 9.2) $J\cdot mol^{-1}\cdot K^{-1}$, given by Kubaschewski et al. (1993). The Kubaschewski et al. value appeared to be "estimated" from a purely empirical additivity scheme. As such, it does not have the same standing as a value determined from measured thermal properties. The difference between the Kubaschewski et al. value and the present value, about 5%, is quite significant in thermodynamic calculations. For example, the various phase equilibria occur between 1600 and 2400 K in the phase diagram for the Ti + Si system. The error in the change of the Gibbs energy from 300 to 1700 K for $TiSi_2$ that arises from an error in the 300 K entropy of −3 $J\cdot mol^{-1}\cdot K^{-1}$ is a bit larger than 4 $kJ\cdot mol^{-1}$. This error is of the same magnitude as the error that would arise from a systematic error of −5% in the molar heat capacity over the entire 300−1700 K temperature interval (~6 $kJ\cdot mol^{-1}$). (The uncertainty of the heat capacity values given in Table 3 is probably less than 5%.) The uncertainty Kubaschewski et al. assigned to their entropy value, ±9.2 $J\cdot mol^{-1}\cdot K^{-1}$, would contribute 13 $kJ\cdot mol^{-1}$ to the uncertainty in the change of the Gibbs energy from 300 to 1700 K. These values of the error and uncertainty introduced into Gibbs energy calculations from use of estimated 298.15 K entropies demonstrate the importance of actually determining the 298.15 K molar entropies.

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