Heat capacity and thermodynamic functions of tellurium dioxide in the range 5 to 300 K

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(Received 19 December 1983; in revised form 25 June 1984)

1. Introduction

The heat capacity of tellurium dioxide has been studied by Mezaki and Margrave⁽¹⁾ in the range 446 to 1146 K and by Preschner and Schreder⁽²⁾ in the range 352 to 1064 K. Low-temperature heat capacities for TeO₂ are not available. This results in the lack of reliable information on thermodynamic properties of TeO₂ at 298.15 K.

Tentative standard values vary over a wide range. $S^{\circ}(298.15 \text{ K}, \text{s}) = (58.6 \pm 8.4) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ (calculated from the heat-capacity extrapolating equation) is suggested in reference 1, and $S^{\circ}(298.15 \text{ K}, \text{s}) = (79.5 \pm 4.2) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ and $S^{\circ}(298.15 \text{ K}, \text{s}) = (70.29 \pm 4.2) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ are given in reference books.^(3,4)

2. Experimental

Tellurium dioxide of 99.97 moles per cent purity was prepared from metallic tellurium by dissolving it in a mixture of chemically pure hydrochloric and nitric acids followed by neutralization with ammonia.⁽⁵⁾ The precipitate was filtered, washed with water, and dried at 383 K to constant mass. Chemical analysis showed 80.0 mass per cent (theoretical: 79.95 mass per cent) of tellurium in the sample prepared. Tellurium was quantitatively determined by oxidimetric titration.⁽⁶⁾ As for the content of other metals, emission-spectral analysis showed mass percentages: Cr, $< 5 \times 10^{-4}$; Fe, 4×10^{-4} ; Cu, $< 5 \times 10^{-4}$; Al, Ca, Ti, Co, Ni, Se, Ag, Sn, each $\leq 1 \times 10^{-3}$. X-ray analysis was by powder pattern, the sample having a tetragonal lattice. Tetragonal tellurium dioxide is a stable crystalline form up to its melting temperature.⁽⁷⁾ A pure melt of this compound does not form a glass on cooling.⁽⁸⁾

The heat-capacity measurements were performed in a vacuum adiabatic calorimeter. Two shields with constantan heaters maintained adiabatic conditions. The temperature differences between the ampoule and the inner shield as well as between the shields were controlled by batteries of differential Cu-to-(Au + 0.01 mass per cent of Fe) thermocouples capable of recording temperature differences of 10^{-4} K. An automatic control system was used to maintain adiabatic conditions. The platinum calorimeter of 11.5 cm³ volume used in this study had two axially located entrant wells for germanium and platinum resistance thermometers. On the exterior surface of the calorimeter there was a non-inductively wound constantan heater. The potential drop and electric current in the calorimeter heater as well as the resistance of the thermometers were potentiometrically measured. The measuring thermometers (the germanium thermometer over the range 4 to 12 K, and the platinum one above 12 K) were calibrated. The duration of current transmission through the calorimeter heater was measured with a printing chronograph.

The energy equivalent of the calorimeter was determined by measuring the heat capacity of the calorimetric ampoule filled with helium under a pressure of about 8 kPa. To verify the absence of systematic errors the heat capacity of standard benzoic acid was measured. The results obtained coincide with literature data⁽⁹⁾ below 10 K within 1.5 per cent, between 10 and 30 K within 0.5 per cent, and above 30 K within about 0.2 per cent.

A diagram of the calorimeter, and details of the apparatus and experimental techniques employed in this investigation, have already been presented.^(10,11)

Before measurements air was pumped out of the ampoule, and helium (via a copper connecting pipe soldered with Wood's metal) was added to a pressure of about 10 kPa. The amount of Wood's metal as well as of copper and helium was the same in determinations of the calorimeter energy equivalent as in measurements of the sample heat capacity. The heat capacity of a 26.5672 g sample of tellurium dioxide made up 53 to 80 per cent (depending on the temperature) of the total loaded-calorimeter heat capacity.

3. Results

The experimental heat capacities of tellurium dioxide are presented in table 1. Temperature increments for individual runs may be estimated from the differences of adjacent temperatures. To ensure temperature equilibration, the measurements of heat capacity were taken at 45 min intervals.

The deviations of the experimental heat capacities from smooth curves were less than 2 per cent below 10 K, 0.5 per cent between 10 and 30 K, and 0.2 per cent above 25 K. The heat capacities of TeO_2 were taken from a smooth curve obtained by a least-squares programme of approximation with polynomials of the second degree from experimental points. In the calculations the heat capacities were corrected for curvature in the temperature-increment range of a single run.

Preliminary extrapolation of the so-obtained curve of heat capacity above 300 K complies with the results of Mesaki and Margrave⁽¹⁾ reasonably well, but differs from those of Prescher and Schreder.⁽²⁾ The approximation of our results between 250 and 300 K and the results of Mesaki and Margrave⁽¹⁾ between 400 and 450 K gave equations for the heat capacity of TeO₂ between 250 and 450 K (table 2).

| T | <i>C</i> _{<i>p</i>, m} | Т | $C_{p,m}$ | Т | <i>C</i> _{<i>p</i>, m} | Т | <i>C</i> _{<i>p</i>, m} | Т | <i>C</i> _{<i>p</i>, m} |
|------------|--|----------|---------------------------------|----------|---------------------------------|-------|--|--------|--|
| ĸ | $\overline{J \cdot K^{-1} \cdot mol^{-1}}$ | ĸ | $J \cdot K^{-1} \cdot mol^{-1}$ | ĸ | $J \cdot K^{-1} \cdot mol^{-1}$ | ĸ | $\overline{J \cdot K^{-1} \cdot mol^{-1}}$ | ĸ | $\overline{J \cdot K^{-1} \cdot mol^{-1}}$ |
| Series 1 " | | Series 3 | | Series 4 | | | Series 8 | 50.28 | 12.57 |
| 80.30 | 22.88 | 159.74 | 43.22 | 253.38 | 57.17 | 5.43 | 0.0482 | 51.73 | 13.00 |
| 83.13 | 24.14 | 163.56 | 43.99 | 256.39 | 57.47 | 6.10 | 0.0652 | | Series 10 |
| 85.88 | 24.61 | 167.29 | 44.91 | 259.58 | 57.72 | 6.69 | 0.0846 | 230.81 | 54.67 |
| 88.35 | 25.46 | 171.09 | 45.61 | 268.39 | 58.55 | 10.13 | 0.3209 | 233.76 | 54.89 |
| 92.33 | 26.63 | 174.99 | 46.30 | | Series 5 | 11.38 | 0.4351 | 236.68 | 55.45 |
| 94.82 | 27.41 | 178.87 | 47.06 | 260.20 | 58 51 | 13.13 | 0.6736 | 239.58 | 55.74 |
| 97.50 | 28.21 | 182.74 | 47.73 | 209.20 | 58.68 | 14.76 | 0.9531 | | Contra 11 |
| 103.34 | 29.06 | 186.59 | 48.26 | 272.00 | 59.00 | 16.91 | 0.404 | | Series 11 |
| 103.12 | 29.87 | 190.48 | 48.94 | 277.60 | 59.31 | 18.57 | 1.809 | 262.61 | 57.21 |
| 106.08 | 30.64 | 194.39 | 49.61 | 277.00 | 50.58 | 20.16 | 2.228 | 265.54 | 58.39 |
| 109.00 | 31.53 | 196.12 | 49.76 | 280.71 | 59.00 | 22.22 | 2.838 | 271.03 | 58.87 |
| 111.75 | 32.33 | 199.71 | 50.44 | 205.55 | 5,5,7 | 24.43 | 3.565 | 274.02 | . 58.96 |
| | Series 2 | 203.24 | 50.81 | | Series 6 | 28.45 | 4.887 | 276.99 | 59.38 |
| 115.01 | 33 44 | 206.69 | 51.48 | 280.55 | 59.77 | 30.20 | 5.468 | 279.83 | 59.58 |
| 119.28 | 34.49 | 210.13 | 51.84 | 283.75 | 59.92 | 31.81 | 6.058 | | Series 12 |
| 122.92 | 35 38 | 213.00 | 52.54 | 285.71 | 60.22 | 33.21 | 0.531 | 262.20 | 57.86 |
| 126.50 | 36 19 | 217.05 | 52.99 | 288.26 | 60.56 | 34.48 | 7.000 | 266.25 | 5837 |
| 130.01 | 36.58 | 223.84 | 53.85 | 290.73 | 60.61 | 35.67 | 1.370 | 200.2 | 59.73 |
| 133.27 | 37.84 | 227.43 | 54.24 | 293.50 | 60.92 | | Series 9 | 285.82 | 60.05 |
| 136.36 | 38.49 | 230.92 | 55.17 | 296.12 | 61.18 | 39.02 | 8.544 | 205.02 | . 00.05 |
| 140.07 | 39.36 | 234.34 | 55.22 | 299.01 | 61.45 | 40.73 | 9.163 | | Series 13 |
| 144.50 | 40.27 | 237.90 | 55.03 | | Series 7 | 42.54 | 9.828 | 253.78 | 57.15 |
| 148.28 | 41.02 | 241.37 | 56 37 | 67 77 | 16.00 | 43.44 | 10.11 | 256.46 | 5 57.47 |
| 152.78 | 42.01 | 244.00 | 50.52 | 64 21 | 10.99 | 46.38 | 11.12 | 259.08 | 57.69 |
| | | | | 66 12 | 1818 | 48.38 | 11.87 | 261.68 | 57.97 |
| | | | | 00.12 | 10.10 | | | | |

TABLE 1. Experimental molar heat capacities of TeO₂

" The sequence of the series is that of the measurements.

From 5.5 to 17 K experimental heat capacities of TeO₂ follow the Debye T^3 law to within 1 per cent. Therefore the curve $C_{p,m} = f(T)$ from 5 K to 0 was extrapolated using the equation $C_{p,m} = AT^3$, where $A = 29.2 \times 10^{-5} \text{ J} \cdot \text{K}^{-4} \cdot \text{mol}^{-1}$. Functions $\{H_m^\circ(T) - H_m^\circ(0)\}$ and $S_m^\circ(T)$ for TeO₂ were obtained by numerical

TABLE 2. Equations for the molar heat capacity of TeO₂

| Temperature range | | Equation 1 | | | | |
|----------------------|--------------------------------|---|--------------------------|--|--|--|
| | 30 to 80 K | $C_{p, m}/(J \cdot K^{-1} \cdot mol^{-1}) = 0.3685(T/K) - 1.658 \times 10^{-4}(T/K)^2 - 5.543$ | ±0.4 | | | |
| | 80 to 170 K | $C_{p, m}/(J \cdot K^{-1} \cdot mol^{-1}) = 0.4531(T/K) - 8.158 \times 10^{-4}(T/K)^2 - 8.156$ | ±0.29 | | | |
| | 160 to 250 K 250 to 450 K | $C_{p,m}/(1 \cdot K^{-1} \cdot mol^{-1}) = 0.3734(T/K) - 5.499 \times 10^{-4}(T/K)^2 - 2.272$ $C_{p,m}/(1 \cdot K^{-1} \cdot mol^{-1}) = 0.2161(T/K) - 2.18 \times 10^{-4}(T/K)^2 + 16.23$ $C_{p,m}/(1 \cdot K^{-1} \cdot mol^{-1}) = 0.2161(T/K) - 2.18 \times 10^{-4}(T/K)^2 + 16.23$ | ± 0.12 ± 0.17 | | | |
| | 450 to 1006(s) I | $C_{p,m}/(J \cdot K^{-1} \cdot mol^{-1}) = 14.36 \times 10^{-6} (T/K) - 5.021 \times 10^{-6} (T/K)^{-1} + 65.19$ | ± 1.8 | | | |
| | 1006(l) to 1146 K ^a | $C_{p,m}/(J \cdot K^{-1} \cdot mol^{-1}) = 112.63 + 0.002176(T/K)$ | ± 0.2 | | | |

^a From reference 1.

| Т | <i>C</i> _{<i>p</i>, m} | $H^{\circ}_{\mathrm{m}}(T) - H^{\circ}_{\mathrm{m}}(0)$ | $S_{\mathbf{m}}^{\circ}(T)$ | $G^{\circ}_{\mathrm{m}}(T) - H^{\circ}_{\mathrm{m}}(0)$ | |
|---------|---------------------------------|---|---|---|--|
| ĸ | $J \cdot K^{-1} \cdot mol^{-1}$ | J·mol ⁻¹ | $\overline{\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1}}$ | $J \cdot mol^{-1}$ | |
| 5 | 0.03556 | 0.08891 | 0.03201 | 0.07115 | |
| 10 | 0.3033 | 0.6963 | 0.1060 | 0.3638 | |
| 15 | 1.017 | 3.787 | 0.3468 | 1.415 | |
| 20 | 2.201 | 11.66 | 0.7913 | 4.169 | |
| 25 | 3.703 | 26.36 | 1.441 | 9.679 | |
| 30 | 5.418 | 49.15 | 2.267 | 18.87 | |
| 40 | 8.912 | 120.7 | 4.300 | 51.35 | |
| 50 | 12.46 | 227.5 | 6.669 | 106.0 | |
| 70 | 19.49 | 547.8 | 11.99 | 291.6 | |
| 100 | 28.94 | 1277 | 20.57 | 779.4 | |
| 150 | 41.39 | 3056 | 34.82 | 2167 | |
| 200 | 50.42 | 5363 | 48.03 | 4243 | |
| 250 | 56.74 | 8053 | 60.01 | 6949 | |
| 298.15 | 61.38 | 10898 | 70.40 | 10090 | |
| 350 | 65.15 | 14180 | 80.53 | 14010 | |
| 400 | 67.77 | 17500 | 89.41 | 18260 | |
| 450 | 69.31 | 20940 | 97.49 | 22940 | |
| 500 | 70.46 | 24430 | 104.9 | 28000 | |
| 600 | 72.53 | 31580 | 117.9 | 31950 | |
| 700 | 74.35 | 38930 | 129.2 | 51520 | |
| 800 | 76.05 | 46450 | 139.3 | 64950 | |
| 900 | 77.67 | 54130 | 148.3 | 79330 | |
| 1006(s) | 79.34 | 62460 | 157.0 | 95500 | |
| 1006(1) | 114.82 | 91520 | 185.9 | 95500 | |
| 1100 | 115.03 | 102300 | 196.2 | 113500 | |
| 1200 | 115.24 | 113800 | 206.2 | 133600 | |

TABLE 3. Thermodynamic functions of TeO₂

integration of $C_{p,m} = f(T)$ and $C_{p,m}/T = f'(T)$ in the range 0 to 1145 K,[†] using an electronic computer. $\{G_m^{\circ}(T) - H_m^{\circ}(0)\}$ was determined by the Gibbs-Helmholtz equation. Results of these calculations and smoothed heat capacities at selected temperatures are presented in table 3.

The standard molar entropy of formation $\Delta_f S^{\circ}_{m}(\text{TeO}_2, \text{ s}, 298.15 \text{ K}) = -(184.43 \pm 0.81) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ was calculated from the value of $S^{\circ}_{m}(\text{TeO}_2, \text{ s}, 298.15 \text{ K})$ and the standard molar entropies: $S^{\circ}_{m}(\text{Te}, \text{ s}, 298.15 \text{ K}) = (49.50 \pm 0.21) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ and $S^{\circ}_{m}(\text{O}_2, \text{ g}, 298.15 \text{ K}) = (205.04 \pm 0.25) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Assuming $\Delta_f H^{\circ}_m(\text{TeO}_2, \text{ s}, 298.15 \text{ K}) = -(321.75 \pm 5.02) \text{ kJ} \cdot \text{mol}^{-1}, (12)$ we obtained $\Delta_f G^{\circ}_m(\text{TeO}_2, \text{ s}, 298.15 \text{ K}) = -(266.76 \pm 5.83) \text{ kJ} \cdot \text{mol}^{-1}$.

† Due to rough extrapolation of the experimental heat capacity from 450 to 298 K the values of $C_{p,m}(298.15 \text{ K})$, $\{H_m^{\circ}(T) - H_m^{\circ}(298.15 \text{ K})\}$, $\{S_m^{\circ}(T) - S_m^{\circ}(298.15 \text{ K})\}$, and $\{G_m^{\circ}(T) - H_m^{\circ}(298.15 \text{ K})\}$ given in reference 1 might be considered inaccurate.

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