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Heat Capacities of Titanium Disulfide from 5.87 to 300.7 K

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The heat capacity of TiS_2 was determined from 5.87 to 300.7 K by adiabatic calorimetry. The values at 298.15 K for $C_p°$, $S°(T) - S°(0)$, $-[G°(T) - H(0)]/T$, and $H°(T) - H°(0)$ are 67.34, 78.21, 36.69 J mol^{-1} K^{-1}, and 12.38 kJ mol^{-1}, respectively.

Introduction

One of the goals of the U.S. Bureau of Mines is to provide thermodynamic data on minerals and related inorganic compounds. As part of this effort, the heat capacity of TiS_2 was measured from 5.87 to 300.72 K by adiabatic calorimetry, thereby extending the range of existing measurements to below 53 K. The heat capacity of TiS_2 has been measured previously by Todd and Coughlin (*1*) from 53 to 297 K by isoperibol calorimetry, and by Mraw and Naas (*2*) from 100 to 700 K using a differential scanning calorimeter.

Experimental Section

Sample Preparation. The sample of titanium disulfide was provided by A. H. Thompson of Exxon Research and Engineering Co. Details of the preparation and analysis of the TiS_2 sample have been reported previously (*3*). Optical emission spectrographic analysis detected the following impurities, in parts per million by mass of metal: Al, 100, Ca, 40; Cr, 30; Cu, 400; Fe, 50; Mg, 8. X-ray powder diffraction analysis showed only TiS_2. Ignition in air at 1475 K showed the sample to have the theoretically correct amounts of titanium and sulfur to within ±0.05 mass %.

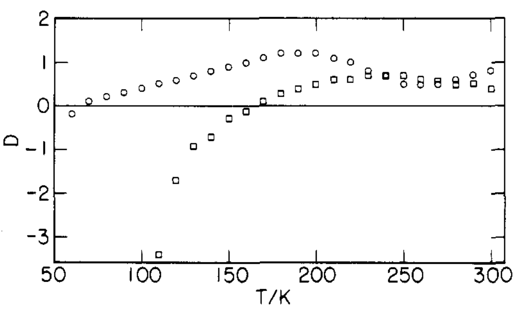

Figure 1. Heat capacity deviation: $D = 100\{[C_p \text{(ref } 1 \text{ or } 2)/C_p \text{(this work)}] - 1\}$; open circles, Todd and Coughlin (*1*); open squares, Mraw and Naas (*2*).

Table I. Experimental Heat Capacities of TiS_2

T/K	$C_p°$/(J mol^{-1} K^{-1})	T/K	$C_p°$/(J mol^{-1} K^{-1})	T/K	$C_p°$/(J mol^{-1} K^{-1})	T/K	$C_p°$/(J mol^{-1} K^{-1})
	Series I				Series II		
48.48	11.333	188.65	56.678	19.04	1.436	34.49	6.133
47.71	11.039	196.80	57.924	20.77	1.841	37.43	7.178
52.47	12.998	204.81	59.031	22.30	2.248	40.64	8.347
57.10	14.934	212.69	60.069	23.59	2.630	44.15	9.657
62.23	17.153	220.48	60.989	25.10	3.043	47.98	11.152
67.85	19.638	228.17	61.809	27.07	3.644	52.15	12.869
74.04	22.365	235.79	62.592	29.34	4.366	56.72	14.773
80.86	25.378	243.33	63.306	31.79	5.195	61.74	16.940
88.38	28.624	250.79	63.974		Series III		
96.68	32.059	235.03	62.484	250.24	63.929	279.93	66.212
105.81	35.623	242.54	63.221	257.74	64.530	287.25	66.673
115.42	39.082	249.98	63.972	265.18	65.096	294.53	67.112
125.15	42.283	257.36	64.569	272.57	65.724		
134.99	45.201	264.69	65.167				
144.70	47.805	271.96	65.708		Series IV		
154.03	50.056	279.21	66.121	5.87	0.034	10.96	0.248
163.05	52.038	286.41	66.602	6.90	0.055	12.05	0.335
171.79	53.775	293.57	67.108	7.52	0.075	13.25	0.454
180.32	55.332	300.72	67.507	8.26	0.102	14.55	0.616
				9.07	0.139	15.99	0.837
				9.97	0.185	17.57	1.134

Table II. Thermodynamic Properties of TiS_2

T/K	$C_p°$/ (J mol^{-1} K^{-1})	{S°(T) − S°(0)}/ (J mol^{-1} K^{-1})	{−[G°(T) − H°(0)]/T}/ (J mol^{-1} K^{-1})	{H°(T) − H°(0)}/ (kJ mol^{-1})
5	0.090	0.007	0.002	0.000
10	0.180	0.073	0.021	0.001
15	0.682	0.227	0.060	0.003
20	1.662	0.547	0.138	0.008
25	3.017	1.058	0.268	0.020
30	4.601	1.745	0.454	0.039
35	6.331	2.582	0.697	0.066
40	8.106	3.541	0.991	0.102
45	9.987	4.603	1.333	0.147
50	11.969	5.757	1.717	0.202
60	16.181	8.309	2.599	0.343
70	20.584	11.132	3.613	0.526
80	25.018	14.170	4.741	0.754
90	29.319	17.367	5.965	1.026
100	33.388	20.669	7.270	1.340
110	37.165	24.031	8.640	1.693
120	40.624	27.416	10.064	2.082
130	43.762	30.793	11.529	2.504
140	46.589	34.142	13.024	2.956
150	49.127	37.444	14.543	3.435
160	51.400	40.689	16.076	3.938
170	53.437	43.867	17.617	4.462
180	55.263	46.794	19.162	5.006
190	56.903	50.007	20.706	5.567
200	58.380	52.964	22.245	6.144
210	59.713	55.845	23.777	6.734
220	60.918	58.651	25.299	7.337
230	62.012	61.383	26.809	7.952
240	63.006	64.044	28.305	8.577
250	63.915	66.635	29.786	9.212
260	64.747	69.158	31.252	9.855
270	65.513	71.616	32.702	10.507
273.15	65.742	72.377	33.155	10.713
280	66.219	74.011	34.135	11.165
290	66.865	76.347	35.550	11.831
298.15	67.343	78.206	36.691	12.378
300	67.444	78.623	36.948	12.503

Calorimetric Technique. The automated adiabatic calorimeter used to measure the heat capacities has been described previously by Beyer (*4*). A sample of 144.2116 g of TiS_2 was loaded into the calorimeter along with 1.8 x 10^{-3} mol of He for series I–III. The amount of He for series IV was reduced to 1.1 x 10^{-4} mol to minimize the effects of possible He absorption on the sample. A molecular weight of 112.028 and a density of 3.24 x 10^{-6} g m^{-3} were used.

Results

The experimental heat capacities are listed chronologically in Table I. The temperature increment for each measurement can be calculated from the preceding and following measurement. The overall uncertainties of the measurements were estimated to be ±2% from 5 to 15 K, ±1% from 15 to 50 K, ±0.2% from 50 to 200 K, and ±0.1% from 200 to 300 K. The heat capacity data were smoothed by a least-squares curve fit and the calculated values of $C_p°$, $S°(T) - S°(0)$, $-[G°(T) - H°(0)]/T$, and $H°(T) - H°(0)$ are listed in Table II. The heat capacities were extrapolated from 5 to 0 K graphically.

The heat capacity curve showed a normal sigmoid shape over the range of measurements. The heat capacity results differ slightly from others as can be seen in the deviation plot in Figure 1.

Acknowledgment

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Registry No. TiS_2, 12039-13-3.

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