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Low-temperature heat capacity of tin dioxide: new standard data on thermodynamic functions

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Abstract

The heat capacity of tin dioxide was measured at low temperatures by the adiabatic calorimeter technique. The measurements were conducted for two samples of tin dioxide. The discrepancy between two sets of the measurements does not exceed experimental error. However, a large disagreement (more than 5%) was observed between this study and data previously used for thermodynamic calculations. Using non-linear least-square method (LSM), the equation approximating and smoothing experimental data was derived. Thermodynamic functions at 298.15 K (heat capacity, entropy and enthalpy increment) values calculated from experimental data are as follows:

$$C^0_{p,\mathrm{m}} = 55.24 \pm 0.03\,\mathrm{J\,mol^{-1}\,K^{-1}},$$

$$\Delta_0^{298} S^0_\mathrm{m} = 51.82 \pm 0.07\,\mathrm{J\,mol^{-1}\,K^{-1}},$$

$$\Delta_0^{298} H^0_\mathrm{m} = 8.806 \pm 0.005\,\mathrm{kJ\,mol^{-1}}.$$

These values of the thermodynamic functions are about 5% larger than those used in reference books elsewhere.

Keywords: Adiabatic calorimetry; Heat capacity; Entropy; Tin dioxide

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Thermal properties of tin dioxide SnO_2 play a key role in the thermodynamics of tin compounds. SnO_2 natural occurring form, cassiterite, is the main tin ore. This is why the accurate measurement of the thermal properties of tin dioxide is an important task attracting interest of investigators for a long time. The first systematic attempts to measure low-temperature heat capacities of tin dioxide over a wide temperature range were conducted in 1929 by Millar [1] and Huttig et al. [2] (Fig. 1).

At the present time, the thermodynamic reference constants of tin dioxide are based on low-temperature measurements of SnO_2 heat capacity carried out by Zhogin et al. [3] (see for example, [4]). In this paper, we present new data on measurements of the low-temperature heat capacity of tin dioxide and new standard data computed on the basis of the these measurements.

We conducted low-temperature measurements on the heat capacity of tin dioxide at low temperatures using two samples. The first one was produced in Russia (hereafter, RP sample), satisfies the Russian “pure for analyses” qualification, represents a fine-grained powder, average grain-size of about 15–20 μm, and contains 99.906 wt.% of SnO_2. Inductively coupled plasma (ICP) analysis of metal-based impurities (Table 1) confirmed the quality warranted by the producer. This sample was heated at 1073 K for 7 days. Thermogravimetric analysis did not reveal any weight loss

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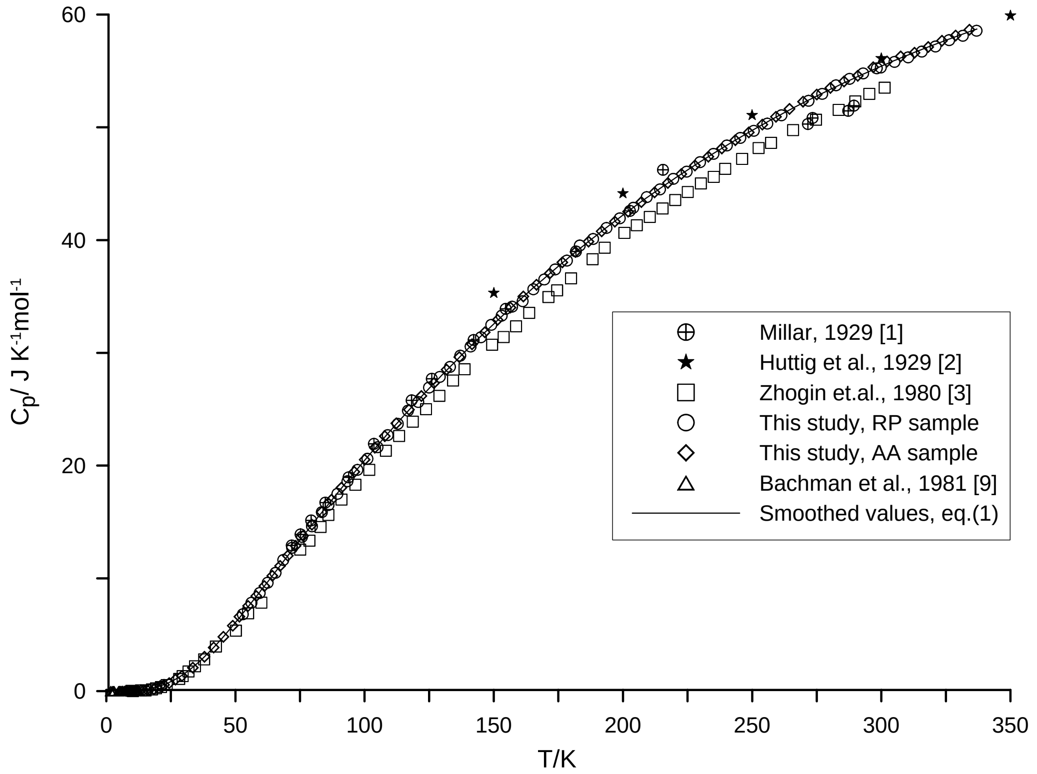

Fig. 1. Heat capacity of tin dioxide. A comparison with previous studies.

in the range from 300 to 1273 K. The second sample is a commercial tin (IV) oxide product of “Alfa Aesar” (hereafter, AA sample). The content of tin dioxide is 99.996 wt.% (metal basis) according to the certificate ICP analysis (Table 2). Microscopic investigations showed the presence of a loose amorphous component (β-stannic acid supposedly) along with needle-shaped crystals of cassiterite. The AA sample was heated at 1273 K for 73 h, and underwent a weight loss (dehydration) of 3.84 wt.% of the sample mass. Tin dioxide remains stable at 1273 K as well as at 1073 K according to the Sn–O phase diagram [5]. After the heating, the TG/DTG and DTA analyses did not reveal any mass change or thermal effects in the range of 298–1373 K. Further X-ray and microscopic studies showed that the AA sample as well as the RP sample represent cassiterite. The average size of grains of the AA sample is about 10–15 μm. The molecular mass of SnO_2 used for calculation of molar heat capacity is 150.7088 g mol^{-1} [6].

Table 1
Trace-element content (metal bases) in the RP sample of tin dioxide according to ICP analysis

Chemical element	Content (ppm)	Chemical element	Content (ppm)
Al	9.84	Mn	1.14
Bi	43.74	Na	357.9
Ca	145.20	Ni	6.0
Cr	7.32	Pb	117.6
Cu	6.30	Si	13.0
Fe	47.4	Sr	1.2
K	35.58	Zn	0.9
Mg	145.6		

We measured the heat capacity of SnO_2 using an adiabatic calorimeter designed and assembled in the Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences [7]. Prior to measurements, the calorimeter was calibrated using the reference substance, benzoic acid, and appropriate systematic corrections in comparison with reference data [8] were made for the heat capacity of the empty device. All experiments were carried out in step-wise heating regime with the step from 2 to 5 K depending on the temperature range. A 50-Ω platinum resistance thermometer was used as the temperature probe. Temperature was measured using the R-363-1 potentiometer (precision 0.1 μV). Input energy was measured applying R-3003 comparator (precision 1 μV). The Cu(Fe)–Cu thermopiles (the first between calorimeter itself and inner adiabatic shield, and the second between inner and outer shields) were applied to support the adiabatic conditions with the accuracy no less than 10^{-4} K. Heat capacity of empty calorimeter was precisely studied in the range 5–340 K and smoothed by procedure, described in [8]. To check the obtained heat capacity values, measurements of standard substance benzoic acid were carried out in the studied temperature region [9]. Above 50 K, the systematic deviations (1.2% at 60 K, 0.3% at 100 K and 0.25% at 300 K) were

Table 2
Trace-element content (metal bases) in the AA sample of tin dioxide according to the producer certificate

Chemical element	Content (ppm)	Chemical element	Content (ppm)	Chemical element	Content (ppm)	Chemical element	Content (ppm)
Ag	<1	Al	<1	As	<5	Au	<1
C	nd[a]	Ca	<1	Cd	<1	Ce	<1
Dy	<1	Er	<1	Eu	<1	Fe	<1
Hg	<5	Ho	<1	In	<1	Ir	<5
Mg	<1	Mn	<1	Mo	<1	Na	<5
P	<5	Pb	<1	Pd	<1	Pr	<1
Ru	<1	S	nd[a]	Sb	<5	Sc	<1
Sr	<1	Ta	<1	Tb	<1	Te	<5
U	<5	V	<1	W	<5	Y	<1
B	<1	Ba	<1	Be	<1	Bi	<1
Co	<1	Cr	<1	Cs	<1	Cu	<1
Ga	<1	Gd	<1	Ge	<1	Hf	<1
K	<5	La	<1	Li	<1	Lu	<1
Nb	<1	Nd	<1	Ni	<1	Os	<5
Pt	<5	Rb	<5	Re	<1	Rh	<1
Se	<1	Si	<1	Sm	<1	Tm	<1
Th	<5	Ti	<1	Tl	<1		
Yb	<1	Zn	<1	Zr	<1		

[a] Not detected.

Table 3
Heat capacity of tin dioxide (in $\mathrm{J\,K^{-1}\,mol^{-1}}$)

T (K)	$C^0_{p,\mathrm{m}}$	T (K)	$C^0_{p,\mathrm{m}}$	T (K)	$C^0_{p,\mathrm{m}}$	T (K)	$C^0_{p,\mathrm{m}}$
RP sample: weight 3.4983 g							
52.85	6.815	108.94	22.70	178.31	38.18	261.36	51.07
56.19	7.841	112.85	23.70	183.29	39.52	271.83	52.35
59.39	8.706	116.77	24.87	188.45	40.10	277.13	52.96
62.48	9.617	120.78	25.64	193.62	41.07	282.46	53.73
65.52	10.49	124.93	26.92	198.78	41.93	287.72	54.30
68.51	11.63	129.10	27.86	204.01	42.86	292.98	54.78
71.92	12.71	133.05	28.75	209.21	43.81	298.26	55.23
75.77	13.68	137.03	29.75	214.34	44.50	299.81	55.30
79.63	14.61	141.02	30.56	219.49	45.43	305.11	55.80
83.45	15.88	145.03	31.38	224.66	46.07	310.40	56.20
86.03	16.51	149.03	32.48	229.84	46.91	315.69	56.71
89.47	17.50	153.06	33.29	235.03	47.64	320.98	57.17
93.96	18.62	157.09	34.09	240.22	48.39	326.27	57.73
97.22	19.62	165.31	35.64	245.44	49.06	331.57	58.12
101.10	20.61	169.55	36.51	250.65	49.69	336.88	58.56
105.00	21.63	173.76	37.40	255.88	50.33		
AA sample: weight 4.2955 g							
13.40	0.0726	61.19	9.317	141.56	30.76	243.50	48.46
14.50	0.0672	64.25	10.22	146.51	31.82	248.73	49.55
15.70	0.131	67.27	11.11	151.47	32.93	253.97	50.24
16.76	0.147	70.27	12.01	156.45	34.02	259.21	50.94
18.45	0.180	73.26	12.89	161.45	35.00	264.47	51.63
19.51	0.368	76.20	13.77	166.53	36.04	269.73	52.58
20.88	0.453	79.58	14.76	171.64	37.03	275.01	52.91
21.59	0.391	83.39	15.88	176.55	38.03	280.30	53.50
22.37	0.562	87.20	16.98	181.60	38.94	285.60	54.07
24.37	0.711	91.01	18.04	186.67	39.86	290.91	54.57
26.78	1.027	96.02	19.44	191.76	40.78	296.90	55.33
29.25	1.338	100.00	20.53	196.87	41.64	302.33	55.84
33.50	2.084	103.96	21.58	201.99	42.52	307.52	56.29
38.03	3.046	107.82	22.61	207.12	43.37	312.86	56.61
41.58	3.866	112.27	23.75	212.24	44.24	318.18	57.12
45.33	4.817	117.15	24.98	217.38	45.07	323.48	57.67
48.95	5.802	121.99	26.17	222.59	45.85	328.80	58.14
51.53	6.607	126.85	27.32	227.83	46.62	334.11	58.65
54.90	7.554	131.72	28.51	233.06	47.40		
58.06	8.432	136.62	29.62	238.27	48.12		

Table 4
Parameters in Eq. (1) for calculating heat capacity of tin dioxide in the range of 0–336 K

Parameter	Value (K)	Parameter	Value
θ_1	314	a_1	0.6670
θ_2	1124	a_2	0.6927
θ_3	1200	a_3	0.7403
θ_E	449	a_4	0.0830
θ_L	135	a_5	0.2500
θ_U	682		

Table 6
Comparison of thermodynamic properties of tin dioxide at 298.15 K

Thermodynamic function	This work	Reference data [3][a]
$C^0_{p,\mathrm{m}}$ (J mol^{-1} K^{-1})	55.24 ± 0.03	53.22
$\Delta_0^{298} S^0_\mathrm{m}$ (J mol^{-1} K^{-1})	51.82 ± 0.07	49.01
$\Delta_0^{298} H^0_\mathrm{m}$ (kJ mol^{-1})	8.806 ± 0.005	8.384

[a] See also the CODATA site: http://www.codata.org/codata/databases/key1.html.

detected. Based on the results obtained the correction of empty calorimeter specific heat was made. Comparison of later studied heat capacities of α-Fe_2O_3, Sb_2S_3 with literature values [10,11] confirms the high accuracy of heat capacity results obtained using the described setup.

Results of our measurements are presented in Table 3. A comparison of our measurements with previous literature data in the range of 0–340 K is shown in Fig. 1. One can see from Table 3 and Fig. 1 that the results of our measurements for both samples are practically identical and the difference lies within experimental error of the single measurement, ±0.25 J K^{-1} mol^{-1}. Nevertheless, appreciable difference (∼5%) is observed between our data and those of Zhogin et al. [3] usually used in thermodynamic calculations. In the range of 1–12 K, reliable heat capacity data were obtained by Bachman et al. [12]. Our values at 13 K as well as data of Zhogin et al. [3] are lower than those expected from [12]. This is not surprising, because this temperature range is very close to low-temperature limit of the adiabatic calorimeters used in [3] and this study.

We used the DEK equation suggested in [13] (also see [14,15] for details) to approximate and smooth our experimental data on heat capacity:

$$C_p^0(T) = n\left[a_1 D\left(\frac{\theta_1}{T}\right) + a_2 D\left(\frac{\theta_2}{T}\right) + a_3 D\left(\frac{\theta_3}{T}\right) + a_4 E\left(\frac{\theta_E}{T}\right) + a_5 K\left(\frac{\theta_L}{T}, \frac{\theta_U}{T}\right)\right] \quad (1)$$

where C_p^0 is the heat capacity at $p = 1$ bar, n the number of atoms in the formula unit ($n = 3$ in the case of tin dioxide), D, E and K are the Debye, Einstein and Kiffer function, respectively, θ_1, θ_2, θ_3, θ_E, θ_L and θ_U are the characteristic temperatures, $a_1, \ldots, a_5$ are the linear coefficients. D, E and K functions are defined as:

Table 5
Thermodynamic functions of tin dioxide in the range of 0–336 K

T (K)	$C^0_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	$\Delta_0^T S^0_\mathrm{m}$ (J K^{-1} mol^{-1})	$\Delta_0^T H^0_\mathrm{m}$ (J mol^{-1})
4	0.00279	0.00093	0.00279
6	0.00943	0.00316	0.0144
8	0.0224	0.00748	0.0452
10	0.0438	0.0146	0.110
12	0.0763	0.0253	0.229
14	0.124	0.0404	0.426
16	0.190	0.0610	0.737
18	0.281	0.0884	1.205
20	0.398	0.124	1.881
25	0.842	0.256	4.893
30	1.517	0.466	10.70
35	2.415	0.765	20.44
40	3.505	1.156	35.17
45	4.743	1.639	55.74
50	6.089	2.208	82.79
55	7.506	2.854	116.7
60	8.963	3.570	157.9
65	10.44	4.345	206.4
70	11.93	5.173	262.3
75	13.40	6.05	325.7
80	14.86	6.958	396.3
85	16.30	7.902	474.2
90	17.72	8.874	559.3
95	19.11	9.869	651.3
100	20.47	10.88	750.3
110	23.10	12.96	968.2
120	25.63	15.08	1212
130	28.04	17.23	1480
140	30.36	19.39	1772
150	32.57	21.56	2087
160	34.68	23.73	2423
170	36.70	25.89	2781
180	38.63	28.05	3157
190	40.47	30.18	3553
200	42.22	32.31	3966
210	43.88	34.41	4397
220	45.46	36.48	4844
230	46.96	38.54	5306
240	48.38	40.57	5783
250	49.72	42.57	6273
260	50.99	44.54	6777
270	52.20	46.49	7293
280	53.33	48.41	7820
290	54.41	50.30	8359
300	55.42	52.16	8908
310	56.38	54.00	9467
320	57.29	55.80	10036
330	58.14	57.58	10613
336	58.63	58.63	10963

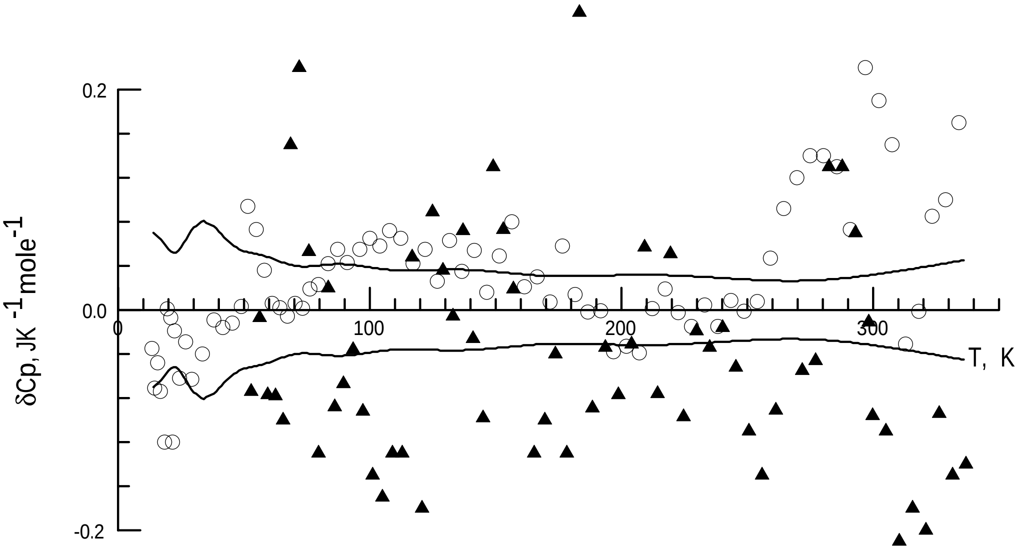

Fig. 2. Absolute values of the deviations from the smoothed. Filled triangles and open circles designate deviations of RP and AA samples, the solid curve designates the 2σ range for the smoothed curve.

$$D\left(\frac{\theta}{T}\right) \equiv 3R\left(\frac{\theta}{T}\right)^{-3}\int_0^{\theta/T}\xi^4\frac{\exp(\xi)}{(\exp(\xi)-1)^2}\,\mathrm{d}\xi, \qquad (2)$$

$$E\left(\frac{\theta_E}{T}\right) \equiv 3R\frac{(\theta_E/T)^2\exp(\theta_E/T)}{(\exp(\theta_E/T)-1)^2}, \qquad (3)$$

$$K\left(\frac{\theta_L}{T},\frac{\theta_U}{T}\right) \equiv \frac{3R}{\theta_U/T-\theta_L/T}\int_{\theta_L/T}^{\Theta_u/T}\frac{\xi^2\exp(\xi)}{(\exp(\xi)-1)^2}\mathrm{d}\xi, \qquad (4)$$

where ξ is the integration variable.

Linear coefficients and characteristic temperatures were found using non-linear least-square method (LSM) and are listed in Table 4.[1] The calculation technique is detailed in [14,15].

The standard heat capacity, entropy and enthalpy change in the range of 0–340 K were calculated on the basis of Eq. (1) using formulas usually used in thermodynamic calculations.

Results of the calculations are given in Table 5. Our recommended data on thermodynamic properties at 298.15 K (25 °C) are listed in Table 6.

Uncertainties in the derived values of the thermodynamic functions (Fig. 2) and, in particular, uncertainties in values at 298.15 K given above, are estimated using the technique described in detail elsewhere [16,17]. As already noted, the measurements of Zhogin et al. [3] have provided the basis for thermodynamic calculations of tin dioxide and other tin compounds up to now. For comparison, the reference thermodynamic values at 298.15 K are also listed in the Table 6.

One can see a significant difference (~5%) in the thermodynamic functions calculated in the present study and those published in [3]. Millar's estimated entropy at 298.15 as $\Delta_0^{298}S_\mathrm{m}^0 = 52.3\,\mathrm{J\,K^{-1}\,mol^{-1}}$ is close to our value [1]. In fact, Millar's data [1] are in good agreement with this study except for a relatively narrow range near room temperature (Fig. 1). It should be noted that heat capacity measurements made at the beginning of the last century are often lower than values from modern measurements. This might result from constructional features of calorimeters used at that time.

The sample preparation and measurement procedures used in present study and that described in [3] were approximately the same. However, practically identical results for AA and RP samples and the preliminary calibration of the calorimeter device using the reference substance (benzoic acid) can be considered as arguments in favour of the reliability of our data.

Summarising, we conclude:

- Measurements of the heat capacity of tin dioxide were conducted in the range from 13 to 336 K.
- Values of the heat capacity of tin dioxide are significantly (about 5%) larger then those measured by Zhogin et al., which have usually been used in thermodynamic calculations.
- The equations for calculating thermodynamic functions of tin dioxide in the range of 0–336 K are established.

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[1] Values of linear coefficients and characteristic temperatures listed in Table 4 provide the value of dispersion $\sigma^2 = 0.008\,\mathrm{J^2\,K^{-2}\,mol^{-2}}$. According to the LSM procedure, fitting parameters are found by minimization of the dispersion $\sigma^2 = [\sum_{j=1}^{k}(\Delta C_{pi})^2]/k$. ΔC_{pi} is the difference between i-th experimental value and smoothing curve giving by Eq. (1).

accomplishing the heating procedures of cassiterite samples. Dr. A. Bychkov is thanked for conducting X-ray investigations. Financial support for this research was partly provided by the Russian Foundation of Basic Researches (grants #01-05-64897 and #98-05-64930). A significant part on the present study was made during the staying of the third author in the Enrico Fermi Institute as a research scholar supported by US National Science Foundation grant EAR 98-15338.

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