

## Heat capacities and entropies at 298.15 K of MgTiO<sub>3</sub> (geikielite), ZnO (zincite), and ZnCO<sub>3</sub> (smithsonite)

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Heat capacities of synthetic MgTiO<sub>3</sub> (geikielite), ZnO (zincite), and natural crystals of smithsonite (ZnCO<sub>3</sub>) were measured between 9 and 366 K using an automatic adiabatically shielded calorimeter. At 298.15 K the standard molar entropies  $S_m^\circ$  of MgTiO<sub>3</sub>, ZnO, and ZnCO<sub>3</sub> are  $(74.64 \pm 0.15)$ ,  $(43.16 \pm 0.09)$ , and  $(81.19 \pm 0.16)$  J · K<sup>-1</sup> · mol<sup>-1</sup>, respectively. Debye temperatures for MgTiO<sub>3</sub> and ZnO calculated from our  $C_{p,m}^\circ$  values below 20 K are  $(900 \pm 20)$  K and  $(440 \pm 25)$  K respectively. Heat capacities for MgTiO<sub>3</sub> and ZnO were combined with enthalpy increments from the literature to derive heat-capacity equations for these phases from 260 to about 1800 K. The heat capacities of MgTiO<sub>3</sub> between 260 and 1720 K were fitted with an average deviation of 0.3 per cent by the equation:

$$C_{p,m}^\circ / (\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 222.5 - 0.05274(T/\text{K}) - 6.092 \times 10^5 (T/\text{K})^{-2} \\ - 1874.6(T/\text{K})^{-1/2} + 1.878 \times 10^{-5} (T/\text{K})^2,$$

and for ZnO the equation:

$$C_{p,m}^\circ / (\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 53.999 + 7.851 \times 10^{-4} (T/\text{K}) - 5.868 \times 10^5 (T/\text{K})^{-2} \\ - 127.50(T/\text{K})^{-1/2} + 1.9376 \times 10^{-6} (T/\text{K})^2,$$

fits the heat capacities in the temperature interval of 250 to 1800 K with an average deviation of 0.7 per cent.

### 1. Introduction

Haselton *et al.*<sup>(1)</sup> and Haselton and Goldsmith<sup>(2)</sup> have determined the  $p(\text{CO}_2)$  against  $T$  equilibrium curves for a number of mineral reactions involving CO<sub>2</sub> at pressures up to 4.0 GPa and 1773 K. One objective of these studies was to obtain values for the fugacities of CO<sub>2</sub> at pressures and temperatures much greater than those that had been measured directly or that could be estimated accurately from equation-of-state predictions. The maximum pressure and temperature for which volumetric measurements for CO<sub>2</sub> have been made are 0.8 GPa and 1000 K by Shmonov and Shmulovich.<sup>(3)</sup> From a knowledge of the phase-equilibrium curve, the standard molar Gibbs free energies of the individual phases, and the molar volumes of the condensed phases it was possible for Haselton *et al.*<sup>(1)</sup> to calculate CO<sub>2</sub> fugacities at temperatures and pressures corresponding to conditions in the upper mantle of the earth.

The standard molar Gibbs free energies of the mineral phases involved in the calculations of Haselton *et al.*<sup>(1)</sup> depended significantly upon the values of the standard molar heat capacities  $C_{p,m}^\circ$  and entropies  $S_m^\circ$  used. Because the entropy values for several of these phases were quite old and were based upon  $C_{p,m}^\circ$ 's extending downwards in temperature only to 52 K (geikielite and smithsonite), and only to 88 K for ZnO, we felt that new heat-capacity measurements on these phases would be desirable so as to reduce the uncertainties in the calculated fugacities of  $\text{CO}_2$  at these extremes of  $p$  and  $T$ .

Shomate<sup>(4)</sup> has previously measured the heat capacity of synthetic  $\text{MgTiO}_3$  between 52.6 and 296.2 K. His sample was prepared by sintering a 74  $\mu\text{m}$  oxide mixture at 1573 to 1623 K for 11 h. Naylor and Cook<sup>(5)</sup> determined the enthalpy increment of this same material between 402 and 1720 K.

The heat capacity of smithsonite ( $\text{ZnCO}_3$ ) has been studied previously by Anderson<sup>(6)</sup> between 58.7 and 298.8 K on natural crystals from Marion County, AR. Haselton and Goldsmith<sup>(2)</sup> measured  $C_{p,m}^\circ$  of a portion of our smithsonite sample (Tsumeb, Namibia) by d.s.c. between 340 and 497 K.

The heat capacity of ZnO has previously been measured by Maier *et al.*<sup>(7)</sup> between 88.1 and 294.8 K, by Millar<sup>(8)</sup> between 89.7 and 297.9 K, and also by Clusius and Hartek<sup>(9)</sup> from 30 to 200 K. Maier and Ralston<sup>(10)</sup> reported four values for the mean heat capacity  $\{H_m^\circ(T) - H_m^\circ(298.15 \text{ K})\}/(T - 298.15 \text{ K})$  for  $T = 973, 1173, 1373$ , and 1573 K, and Mills<sup>(11)</sup> has measured  $C_{p,m}^\circ$  of ZnO by combined d.s.c. and enthalpy-increment studies between 298.15 K and 1800 K.

## 2. Experimental

Synthetic geikielite ( $\text{MgTiO}_3$ ) was prepared as follows: reagent grade MgO (Baker catalog #2476) and  $\text{TiO}_2$  (Baker 4162) were separately heated in platinum crucibles at 1623 K for 120 h in an electric furnace. They were removed from the furnace and stored in a desiccator over fresh Drierite while still hot. The fired oxides were then weighed, blended together, placed in a platinum crucible, and fired in the furnace at 1623 K for 96 h. The sample was removed from the furnace, X-rayed, ground under acetone in an alumina (Diamonite) mortar, and replaced in the furnace for an additional 41 h at 1673 K.

The unit-cell parameters of our  $\text{MgTiO}_3$  were obtained using  $\alpha\text{-Al}_2\text{O}_3$  (corundum) ( $a = 0.4758$ ,  $c = 1.2991$  nm, Swanson *et al.*<sup>(12)</sup>) as an internal standard and copper  $K_\alpha$  radiation ( $\lambda = 0.1540598$  nm). For  $\text{MgTiO}_3$  the cell parameters are  $a = (0.50537 \pm 0.00003)$  and  $c = (1.3892 \pm 0.0001)$  nm. These results, when combined with Cohen and Taylor's<sup>(13)</sup> value for Avogadro's constant:  $(6.0221367 \pm 0.0000036) \times 10^{23} \text{ mol}^{-1}$ , yield a molar volume of  $(30.840 \pm 0.031) \text{ cm}^3 \cdot \text{mol}^{-1}$ . Swanson *et al.*<sup>(14)</sup> obtained  $a = 0.5054$  and  $c = 1.3898$  nm at 299 K. The mass of the  $\text{MgTiO}_3$  sample used for our measurements was 36.734 g.

The calorimetric sample of zinc oxide (zincite) was reagent-grade ZnO (Fisher Z-52). It was heated in a platinum crucible at approximately 1390 K for 65 h, removed from the furnace, crushed to a coarse consistency, and then heated to 1390 K for 3 h. It was then cooled and stored in a desiccator over Drierite prior to

loading in the calorimeter. Unit-cell parameters measured using NBS Standard Reference Material 640 silicon ( $a = 0.543088$  nm at 299.15 K, Hubbard *et al.*<sup>(15)</sup>) as an internal standard and Cu K $\alpha$  were  $a = (0.32497 \pm 0.00003)$  and  $c = (0.52054 \pm 0.00007)$  nm. McMurdie *et al.*<sup>(16)</sup> give  $a = (0.324982 \pm 0.000009)$  and  $c = (0.520661 \pm 0.000015)$  nm for the reference pattern in the JCPDS powder diffraction file. The sample mass was 63.785 g.

The sample of smithsonite (ZnCO<sub>3</sub>) was from Tsumeb, Namibia (U.S.N.M. 108721) and was obtained through the courtesy of John S. White of the U.S. National Museum. The polycrystalline mass had a pale bluish-green color. It was coarsely crushed in an Al<sub>2</sub>O<sub>3</sub> mortar and the 1.68 to 0.84 mm sized material was hand-picked free of any impurity phases under a binocular microscope. Quantitative spectroscopic analysis of this material showed 0.35 mass per cent of Cu leading to a formula of (Zn<sub>0.993</sub>Cu<sub>0.007</sub>)CO<sub>3</sub>. The calorimeter was filled with 59.999 g of sample.

Our heat-capacity measurements were made using the intermittent-heating method under quasi-adiabatic conditions. The cryostat, calorimeter, and the automatic data-acquisition system used for these measurements have been described previously.<sup>(17-19)</sup> Based upon our earlier measurements of the heat capacity of the Calorimetry Conference samples of benzoic acid and copper,<sup>(17,18)</sup> we believe our  $C_{p,m}^\circ$ s are accurate to  $\pm 0.2$  per cent at temperatures above 25 K. Below 25 K the accuracy of our measurements decreases to approximately  $\pm 5$  per cent at 10 K. With respect to the accuracy of our copper measurements, the discussion by Martin<sup>(20)</sup> is particularly relevant. The heat capacities of all three phases lie on smooth sigmoidal curves and show no indication of possible transitions. The average absolute deviation of the measurements from the smoothed curves was 0.12, 0.094, and 0.11 per cent for MgTiO<sub>3</sub>, ZnCO<sub>3</sub>, and ZnO respectively.

TABLE 1. Measured molar heat capacity of MgTiO<sub>3</sub> (geikielite) ( $R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ )

$T/\text{K}$	$C_{p,m}^\circ/R$	$T/\text{K}$	$C_{p,m}^\circ/R$	$T/\text{K}$	$C_{p,m}^\circ/R$	$T/\text{K}$	$C_{p,m}^\circ/R$	$T/\text{K}$	$C_{p,m}^\circ/R$
Series I		11.39	0.00216	Series III		160.97	6.478	242.32	9.711
302.95	11.296	12.65	0.00275	72.98	1.568	165.38	6.691	246.75	9.838
307.25	11.384	14.15	0.00444	78.12	1.831	169.75	6.902	251.21	9.974
311.90	11.490	15.70	0.00742	82.99	2.088	174.09	7.113	255.70	10.106
316.61	11.585	17.43	0.01127	88.10	2.377	178.40	7.309	260.22	10.230
321.13	11.657	19.36	0.01785	93.52	2.690	182.69	7.502	264.80	10.358
325.64	11.767	21.50	0.02702	98.81	3.000	186.97	7.683	269.42	10.478
330.14	11.858	23.89	0.04045	104.03	3.304	191.22	7.871	274.02	10.602
334.62	11.950	26.55	0.06160	109.15	3.605	195.47	8.051	278.62	10.727
339.09	12.013	29.51	0.09422	114.19	3.899	199.71	8.221	283.20	10.851
343.59	12.099	32.84	0.1438	119.14	4.191	203.92	8.388	287.77	10.957
348.12	12.171	36.57	0.2149	124.03	4.477	208.14	8.545	292.32	11.079
352.64	12.244	40.78	0.2961	128.85	4.747	212.35	8.698	296.85	11.179
357.15	12.316	45.46	0.4350	133.61	5.014	216.56	8.854	301.37	11.253
361.66	12.412	50.66	0.5957	138.32	5.286	220.78	9.005	305.87	11.361
366.17	12.496	56.47	0.8079	142.97	5.548	225.02	9.151	310.35	11.457
Series II		62.57	1.062	147.56	5.779	229.29	9.291	314.81	11.544
8.90	0.00065	68.66	1.345	152.07	6.027	233.59	9.438		
10.38	0.00128	74.69	1.645	156.54	6.260	237.93	9.582		

### 3. Thermodynamic properties

Our experimental results, after correction for the empty calorimeter, helium exchange gas, and curvature, shown in tables 1, 2, and 3, were graphically extrapolated to  $T \rightarrow 0$  using a plot of  $C_{p,m}^\circ/T$  against  $T^2$ . For  $\text{MgTiO}_3$ , this

TABLE 2. Measured molar heat capacity of  $\text{ZnCO}_3$  (smithsonite) ( $R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ )

$T/\text{K}$	$C_{p,m}^\circ/R$	$T/\text{K}$	$C_{p,m}^\circ/R$	$T/\text{K}$	$C_{p,m}^\circ/R$	$T/\text{K}$	$C_{p,m}^\circ/R$	$T/\text{K}$	$C_{p,m}^\circ/R$
Series I		67.64	2.295	162.65	6.625	244.61	8.694	13.42	0.0160
300.43	9.708	73.35	2.639	167.18	6.759	249.49	8.781	14.98	0.0253
304.55	9.784	78.86	2.964	171.69	6.899	254.41	8.888	17.01	0.0396
309.33	9.869	84.29	3.281	176.20	7.030	259.34	8.986	18.97	0.0593
314.19	9.951	89.71	3.588	180.69	7.159	264.27	9.090	21.16	0.0884
319.04	10.056	95.10	3.876	185.18	7.275	269.21	9.174	23.57	0.1298
323.89	10.118	100.37	4.148	189.65	7.399	274.12	9.254	26.22	0.1886
328.72	10.203	105.52	4.410	194.12	7.530	279.02	9.342	29.19	0.2714
333.54	10.272	110.59	4.651	198.60	7.646	283.90	9.442	32.52	0.3862
338.35	10.346	115.58	4.875	203.08	7.756	288.76	9.529	36.25	0.5383
343.15	10.431	120.49	5.090	207.56	7.865	293.60	9.613	40.45	0.7220
347.94	10.504	125.34	5.292	212.05	7.976	298.43	9.714	45.15	0.9724
352.71	10.578	130.15	5.493	216.56	8.075	303.29	9.754	50.36	1.258
357.48	10.653	134.90	5.679	Series III		308.15	9.841	56.18	1.597
362.25	10.719	139.61	5.858	220.88	8.174	313.00	9.920	62.29	1.964
367.01	10.790	144.28	6.027	225.42	8.283	317.83	10.017		
371.76	10.873	148.92	6.182	230.13	8.382	Series IV			
Series II		153.52	6.332	235.01	8.485	8.82	0.0038		
62.71	1.996	158.09	6.479	239.78	8.603	11.41	0.0095		

TABLE 3. Measured molar heat capacity of  $\text{ZnO}$  (zincite) ( $R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ )

$T/\text{K}$	$C_{p,m}^\circ/R$	$T/\text{K}$	$C_{p,m}^\circ/R$	$T/\text{K}$	$C_{p,m}^\circ/R$	$T/\text{K}$	$C_{p,m}^\circ/R$	$T/\text{K}$	$C_{p,m}^\circ/R$
Series I		136.20	2.852	35.23	0.4252	Series V		Series VI, VII	
43.89	0.6906	141.12	2.944	39.35	0.5490	225.47	4.202	319.84	5.007
47.15	0.7907	146.00	3.032	43.97	0.6940	230.30	4.259	324.79	5.047
50.87	0.9041	150.85	3.120	49.11	0.8491	235.17	4.314	329.74	5.074
55.29	1.034	155.68	3.203	54.81	1.019	240.11	4.365	334.66	5.101
60.97	1.193	160.49	3.287	60.83	1.191	245.09	4.419	339.56	5.132
66.73	1.346	165.29	3.368	Series IV		250.11	4.460	344.47	5.157
72.58	1.494	170.07	3.448	167.35	3.404	255.16	4.509	349.40	5.193
78.33	1.633	Series III		172.10	3.477	260.21	4.557	354.31	5.209
83.91	1.764	8.62	0.0030	176.91	3.553	265.29	4.602	359.17	5.237
89.44	1.887	9.93	0.0052	181.76	3.631	270.40	4.641	364.06	5.255
94.94	2.010	10.89	0.0077	186.42	3.700	275.50	4.686	368.91	5.284
100.32	2.126	12.07	0.0110	191.07	3.761	280.58	4.724	Series VIII	
105.61	2.237	13.49	0.0172	195.68	3.872	285.65	4.770	191.37	3.769
Series II		14.98	0.0256	200.36	3.897	290.71	4.818	192.74	3.796
102.60	2.173	16.65	0.0378	205.07	3.964	295.76	4.864	194.01	3.813
106.18	2.249	18.50	0.0559	209.79	4.025	Series VI, VII		195.40	3.832
111.17	2.355	20.55	0.0816	214.51	4.077	300.43	4.867	196.76	3.843
116.20	2.460	22.84	0.1184	219.27	4.137	305.08	4.897	198.11	3.860
121.25	2.559	25.42	0.1683	224.08	4.194	309.96	4.938	199.47	3.884
126.28	2.659	28.31	0.2339	228.96	4.243	314.88	4.967	200.82	3.893
131.26	2.758	31.57	0.3192						

extrapolation below 8 K corresponded to a Debye temperature  $\Theta_D$  of 900 K. For ZnO, our extrapolation below 8.6 K corresponded to a Debye temperature of 440 K. This value for  $\Theta_D$  is in fair agreement with  $\Theta_D = 416$  K calculated by Robie and Edwards<sup>(21)</sup> from the elastic-constant results of Bateman.<sup>(22)</sup>

Smoothed values for the thermodynamic properties  $C_{p,m}^\circ/R$ ,  $\Delta_0^T S_m^\circ/R$ ,  $\Delta_0^T H_m^\circ/(R \cdot K)$ , and  $\Phi_m^\circ/R$  with  $R = (8.31451 \pm 0.00007) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  are listed in tables 4, 5, and 6 for MgTiO<sub>3</sub> (geikielite), ZnO (zincite), and ZnCO<sub>3</sub> (smithsonite), respectively. At 298.15 K the molar entropies are  $(74.64 \pm 0.15)$ ,  $(43.16 \pm 0.09)$ , and  $(81.19 \pm 0.16) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  for MgTiO<sub>3</sub>, ZnO, and ZnCO<sub>3</sub> respectively. Our value for  $S_m^\circ(\text{MgTiO}_3, 298.15 \text{ K})$  is in good agreement with the previous value determined by Shomate<sup>(4)</sup> but has a much smaller uncertainty as a consequence of the near negligible contribution ( $0.001 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ) of the extrapolated part of the entropy below 8.6 K.

We have combined our smoothed heat-capacity values for MgTiO<sub>3</sub> between 250 and 350 K with the enthalpy-increment measurements, between 402 and 1720 K, of Naylor and Cook<sup>(5)</sup> after converting both sets of results into values of the mean heat capacity. The combined sets were fitted by least squares to yield a heat-capacity equation for high temperatures:

$$C_{p,m}^\circ/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 222.5 - 0.05274(T/\text{K}) - 6.092 \times 10^{-5}(T/\text{K})^{-2} - 1874.6(T/\text{K})^{-1/2} + 1.878 \times 10^{-5}(T/\text{K})^2. \quad (1)$$

This equation fits the combined results between 260 and 1720 K with an average deviation of 0.3 per cent.

TABLE 4. Thermodynamic properties of MgTiO<sub>3</sub> (geikielite) ( $R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ,  $p^\circ = 0.1 \text{ MPa}$ )

$T$ K	$C_{p,m}^\circ/R$	$\Delta_0^T S_m^\circ/R$	$\Delta_0^T H_m^\circ/R \cdot K$	$\Phi_m^\circ/R$	$T$ K	$C_{p,m}^\circ/R$	$\Delta_0^T S_m^\circ/R$	$\Delta_0^T H_m^\circ/R \cdot K$	$\Phi_m^\circ/R$
5	0.00007	0.00002	0.00001	0.00001	170	6.916	3.854	2.627	1.227
10	0.0012	0.0003	0.00023	0.00007	180	7.380	4.262	2.878	1.384
15	0.0064	0.0016	0.0012	0.0004	190	7.816	4.672	3.127	1.545
20	0.0208	0.0051	0.0041	0.0010	200	8.228	5.084	3.371	1.713
25	0.0499	0.0124	0.0100	0.0024	210	8.614	5.495	3.612	1.883
30	0.1009	0.0254	0.0203	0.0051	220	8.977	5.904	3.847	2.057
35	0.1822	0.0468	0.0374	0.0094	230	9.319	6.311	4.078	2.233
40	0.2837	0.0775	0.0616	0.0159	240	9.640	6.715	4.303	2.412
45	0.4161	0.1182	0.0933	0.0249	250	9.943	7.114	4.523	2.591
50	0.5738	0.1701	0.1333	0.0368	260	10.23	7.510	4.738	2.772
60	0.9530	0.3068	0.2372	0.0696	270	10.50	7.901	4.946	2.955
70	1.412	0.4873	0.3713	0.1160	280	10.76	8.288	5.149	3.139
80	1.929	0.7090	0.5332	0.1758	290	11.00	8.669	5.346	3.323
90	2.485	0.9681	0.7189	0.2492	300	11.23	9.047	5.539	3.508
100	3.065	1.259	0.9243	0.335	310	11.45	9.418	5.726	3.692
110	3.653	1.579	1.146	0.433	320	11.65	9.785	5.908	3.877
120	4.238	1.922	1.378	0.544	330	11.84	10.146	6.073	4.073
130	4.813	2.284	1.621	0.663	340	12.03	10.503	6.258	4.245
140	5.374	2.662	1.869	0.793	350	12.21	10.854	6.425	4.429
150	5.913	3.051	2.120	0.931	360	12.39	11.201	6.588	4.613
160	6.427	3.449	2.374	1.075	298.15	11.19	8.977	5.504	3.473

For ZnO, our heat capacities are in reasonable agreement with the values of Maier *et al.*,<sup>(7)</sup> less so with those of Millar,<sup>(8)</sup> and are very different from those of Clusius and Hartek.<sup>(9)</sup> Our  $C_{p,m}^\circ$ s are systematically less than those of Clusius and Hartek.<sup>(9)</sup> At 50 K, our value for  $C_{p,m}^\circ$  is 13.7 per cent smaller and at 200 K it is 4.7 per cent smaller than the values given by Clusius and Hartek.<sup>(9)</sup> Our value for the entropy of ZnO at 298.15 K is 0.8 per cent smaller than the value calculated by Kelley and King.<sup>(23)</sup> ( $43.64 \pm 0.4$ ) J · K<sup>-1</sup> · mol<sup>-1</sup>, based upon the measurements of Maier *et al.*,<sup>(7)</sup> Clusius and Hartek,<sup>(9)</sup> and Millar,<sup>(8)</sup> and as adopted by the CODATA Task Group.<sup>(24)</sup> We have combined our heat capacities for ZnO between 250 and 350 K with the high-temperature results of Mills<sup>(11)</sup> to generate an equation which represents  $C_{p,m}^\circ$  to within  $\pm 0.7$  per cent between 300 and 1800 K:

$$C_{p,m}^\circ(\text{ZnO}, T)/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 53.999 + 7.851 \times 10^{-4}(T/\text{K}) - 5.868 \times 10^5(T/\text{K})^{-2} - 127.50(T/\text{K})^{-1/2} + 1.9376 \times 10^{-6}(T/\text{K})^2. \quad (2)$$

For smithsonite, our value for  $S_m^\circ$  at 298.15 K is 1.2 J · K<sup>-1</sup> · mol<sup>-1</sup> smaller than that obtained by Anderson.<sup>(6)</sup> We have not attempted to correct our  $C_p^\circ$ s for smithsonite for the small amount of Cu<sup>2+</sup> replacing Zn<sup>2+</sup> in the crystals. This is because there are no values available for  $C_{p,m}^\circ$  of CuCO<sub>3</sub> (and it is questionable whether the calcite-structure form even exists). The relative atomic mass of Cu is only 2.9 per cent less than that of zinc, and since Cu<sup>2+</sup> has  $s = \frac{1}{2}$  there is no zero-field splitting and thus no Schottky contribution to the  $C_{p,m}^\circ$  at very low temperatures. Haselton and Goldsmith<sup>(2)</sup> have combined our low-temperature heat capacities and entropy at 298.15 K with their d.s.c. results for smithsonite to provide a table of

TABLE 5. Thermodynamic properties of ZnCO<sub>3</sub> (smithsonite) ( $R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ,  $p^\circ = 0.1 \text{ MPa}$ )

$T$ K	$C_{p,m}^\circ$ R	$\Delta_0^\circ S_m^\circ$ R	$\Delta_0^\circ H_m^\circ$ R · K	$\Phi_m^\circ$ R	$T$ K	$C_{p,m}^\circ$ R	$\Delta_0^\circ S_m^\circ$ R	$\Delta_0^\circ H_m^\circ$ R · K	$\Phi_m^\circ$ R
5	0.001	0.000	0.000	0.000	180	7.139	5.518	3.419	2.099
10	0.006	0.002	0.002	0.000	190	7.414	5.911	3.622	2.289
15	0.026	0.008	0.006	0.002	200	7.676	6.298	3.818	2.480
20	0.073	0.021	0.016	0.005	210	7.924	6.679	4.008	2.671
25	0.160	0.045	0.035	0.010	220	8.158	7.053	4.191	2.862
30	0.298	0.086	0.067	0.019	230	8.382	7.420	4.368	3.052
35	0.483	0.145	0.112	0.033	240	8.597	7.782	4.540	3.242
40	0.706	0.224	0.172	0.052	250	8.801	8.137	4.707	3.430
45	0.960	0.321	0.245	0.076	260	8.998	8.486	4.868	3.618
50	1.236	0.437	0.331	0.106	270	9.186	8.829	5.024	3.805
60	1.826	0.714	0.530	0.184	280	9.368	9.166	5.176	3.990
70	2.434	1.041	0.759	0.282	290	9.544	9.498	5.324	4.174
80	3.029	1.405	1.005	0.400	300	9.715	9.825	5.467	4.358
90	3.598	1.795	1.262	0.533	310	9.884	10.15	5.607	4.539
100	4.129	2.202	1.523	0.679	320	10.05	10.46	5.743	4.717
110	4.619	2.618	1.782	0.836	330	10.22	10.77	5.876	4.898
120	5.070	3.040	2.038	1.002	340	10.38	11.08	6.006	5.075
130	5.486	3.462	2.287	1.175	350	10.53	11.38	6.133	5.251
140	5.867	3.883	2.529	1.354	360	10.69	11.68	6.258	5.426
150	6.218	4.300	2.764	1.536	370	10.84	11.98	6.380	5.600
160	6.544	4.712	2.990	1.722	298.15	9.684	9.765	5.441	4.324
170	6.850	5.118	3.208	1.910					

TABLE 6. Thermodynamic properties of ZnO (zincite) ( $R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ,  $p^\circ = 0.1 \text{ MPa}$ )

$T$ K	$\frac{C_{p,m}}{R}$	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_0^T H_m^\circ}{R \cdot K}$	$\frac{\Phi_m^\circ}{R}$	$T$ K	$\frac{C_{p,m}}{R}$	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_0^T H_m^\circ}{R \cdot K}$	$\frac{\Phi_m^\circ}{R}$
5	0.000	0.000	0.000	0.000	170	3.446	2.839	1.688	1.151
10	0.006	0.002	0.001	0.001	180	3.604	3.040	1.791	1.249
15	0.026	0.007	0.005	0.002	190	3.753	3.239	1.890	1.349
20	0.075	0.020	0.016	0.004	200	3.893	3.435	1.987	1.448
25	0.160	0.045	0.035	0.010	210	4.023	3.628	2.081	1.547
30	0.277	0.084	0.065	0.019	220	4.144	3.818	2.172	1.646
35	0.417	0.137	0.105	0.032	230	4.257	4.005	2.260	1.745
40	0.568	0.203	0.154	0.049	240	4.363	4.189	2.345	1.844
45	0.723	0.279	0.208	0.071	250	4.462	4.369	2.428	1.941
50	0.876	0.363	0.268	0.095	260	4.555	4.546	2.508	2.038
60	1.165	0.548	0.393	0.155	270	4.642	4.719	2.586	2.133
70	1.430	0.748	0.523	0.225	280	4.724	4.889	2.660	2.229
80	1.673	0.955	0.652	0.303	290	4.802	5.057	2.733	2.324
90	1.902	1.166	0.778	0.388	300	4.874	5.221	2.803	2.418
100	2.120	1.377	0.901	0.476	310	4.943	5.382	2.871	2.511
110	2.331	1.589	1.022	0.567	320	5.009	5.539	2.937	2.602
120	2.535	1.801	1.139	0.662	330	5.072	5.695	3.001	2.694
130	2.732	2.012	1.254	0.758	340	5.131	5.847	3.062	2.785
140	2.922	2.221	1.367	0.854	350	5.188	5.996	3.122	2.874
150	3.105	2.429	1.477	0.952	360	5.241	6.143	3.180	2.963
160	3.279	2.635	1.584	1.051	298.15	4.861	5.191	2.790	2.401

smoothed thermodynamic properties of smithsonite to 1200 K and an equation for  $C_{p,m}$ .

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