

Thermophysical properties of the garnet, grossular: $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ^a

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(Received 15 July 1977; in revised form 21 June 1978)

The heat capacity of a gem-quality mineralogical sample of grossular: $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ has been determined by equilibrium adiabatic-shield calorimetry from 5 through 600 K and adjusted to the stoichiometric terminal-component grossular by a new entropy-adjustment scheme delineated in the paper. At 298.15 K the observed values of C_p , S° , $\{H^\circ(T) - H^\circ(0)\}/T$, and $-\{G^\circ(T) - H^\circ(0)\}/T$ are 79.00, 61.61, 37.92, and 23.69 cal_{th} K⁻¹ mol⁻¹. The entropy adjusted to terminal component grossular is 60.88 cal_{th} K⁻¹ mol⁻¹. The results are combined with higher-temperature differential-scanning calorimetric values of Perkins *et al.* and of Robie *et al.* to provide thermodynamic values over greatly extended ranges of temperature.

1. Introduction

Grossular: $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, an important representative of the garnet-structure group, not only occurs in calcareous rocks formed over a wide variety of pressure and temperature but also is found in a variety of synthetic systems. Surprisingly, in view of importance of both natural and synthetic garnets, particularly YIG (yttrium iron garnet) and YAG (yttrium aluminum garnet), measured heat capacities are not available over adequate temperature ranges to permit evaluation of practical thermodynamic functions. Thermodynamic calculations of phase equilibria involving garnets are limited by this lack of reliable data. The only available values⁽¹⁾ were calculated from phase equilibria approximately determined at pressures of 1 to 2 GPa and 1300 to 1700 K.^(2,3) Large uncertainties in such values are occasioned by extrapolation to 300 K. This lack of reliability is further enhanced by significant uncertainties in the location of the experimental equilibria in these sluggish systems. Because of the expected errors in such widely used thermochemical data for grossular, we measured the low- and intermediate-temperature heat capacity of mineralogical grossular to provide reliable thermodynamic results for phase- and reaction-equilibrium calculations.

^a This research was supported in part by the Chemical Thermodynamics Program of the Chemistry Section of the National Science Foundation under Contract No. GP-42525X.

Because even the best mineralogical samples are far from stoichiometrically pure, we developed a scheme for adjusting the thermodynamic results to correspond to that of the pure substance. We consider this method to be widely applicable and more reliable than conventional methods.

2. Experimental

SAMPLE PROVENANCE

Since an attempted synthesis of grossular initially results in a product of low-purity even on a micro-scale,⁽⁴⁾ we sought well characterized pure natural grossular as close as possible to the end-member composition, $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$.

We obtained some unusually pure gem-quality grossular which occurs as veins in a serpentine at Thetford, Quebec, from Professor A. L. Boettcher of the Department of Geosciences, Pennsylvania State University. The gem quality of the individual crystals, of 1 to 9 mm typical dimensions, allowed rapid hand picking of some 40 g of pure garnet free from visible inclusions. This material was ideal for calorimetric studies because of rapid thermal equilibration of the large crystals. Obtaining an equivalent synthetic $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ would have required prohibitively difficult experiments at high pressures. Microprobe analysis of the major and minor elements revealed no zoning or inhomogeneities down to the 5 μm scale. Wet-chemical analysis of the garnet⁽⁵⁾ yielded the values in table 1 and, in terms of atomic composition, in table 2. The proximate selection of end-member components in table 3 indicates that the garnet is approximately 91 mass per cent pure grossular with several other garnet components in solid solution. This analysis has been confirmed by electron-microprobe analysis. Such solutions are comparable to those of natural samples used for heat-capacity measurements by King, Kelley, and co-workers⁽⁸⁻¹³⁾ and are acceptable when adequate adjustment is made for deviation from ideal stoichiometry.

TABLE 1. Analysis of Thetford garnet sample in terms of mass fractions w of constituent oxides

Oxide	10^2w	Oxide	10^2w	Oxide	10^2w
SiO_2	39.20	FeO	1.81	MgO	0.24
CaO	35.50	MnO	0.65	H_2O	0.19 ^a
Al_2O_3	21.80	TiO_2	0.25	Fe_2O_3	0.00

^a See discussion in text.

TABLE 2. Atomic composition of grossular (Thetford garnet) sample normalized to 12 oxygen atoms

Elements	Si	Al	Ti	Mg	Mg	Fe	Mn	Ca	OH
Atoms	2.98 ₅	1.95 ₇	0.01 ₄	0.01 ₄	0.02 ₇	0.11 ₅	0.04 ₁	2.89 ₇	0.09 ₆
Total atoms	2.98 ₅	1.98 ₅		0.02 ₇		3.08 ₀		0.09 ₆	

TABLE 3. Analysis of grossular sample in terms of end-member components and entropy increments thereof at 298.15 K
($\text{cal}_{\text{th}} = 4.184 \text{ J}$)

Composition	Name	Code	x_i^a	$\frac{\Delta S_i}{\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}}^b$
$\text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_8(\text{OH})_4$	hydrogrossular	hg	0.024	-22.29 ^{c, d}
$\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	pyrope	pp	0.004	9.07 ^c
$\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	spessartine	sp	0.014	-15.3 ^c
$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	almandine	al	0.038	-9.98 ^c
$\text{Ca}_3\text{MgTiSi}_3\text{O}_{12}$	Mg-melanite	mm	0.014	-6.3 ^d
$\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$	andradite	an	0.000	—
$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	grossular	gr	0.906	—

^a Mole fraction of *i*th end-member in sample. Mineralogical end members were selected to express the composition of the Thetford garnet. We have determined the values of the mole fractions of non-grossular components directly from table 2 and have chosen the grossular mole fraction so that the sum of all mole fractions is unity.

^b The entropy increment of the *i*th end-member relative to grossular (see text).

^c Reference 6.

^d Reference 7.

CALORIMETRIC TECHNIQUES

Adiabatic intermittent-heating equilibrium heat-capacity measurements from 5 to 350 K were made in calorimeter W-22 (93.4 cm³; gold-plated copper; platinum resistance thermometer A-3) in the Mark-II cryostat,⁽¹⁴⁾ while those in the 300 to 500 K range were made in the Mark-IV thermostat⁽¹⁵⁾ using calorimeter W-22P (84 cm³; silver; platinum resistance thermometer A-5). Pressures of 1.3 and 7.8 kPa of purified helium gas were used within the calorimeters to facilitate thermal equilibration. All determinations of mass, potential, current, time, and temperature were based ultimately upon calibrations by the National Bureau of Standards.

3. Results and discussion

HEAT CAPACITY OF SAMPLE

The heat-capacity measurements in both ranges are listed in table 4 in chronological sequence so that temperature increments used in these determinations can usually be inferred from adjacent mean temperatures. These results have been adjusted for curvature, *i.e.* for the correction between $\Delta H/\Delta T$ for the finite increments employed and the limit (C_p) of this quantity as ΔT approaches zero. The values in this table represent those on the sample as run; no adjustment has been made to the composition of pure grossular. However, they have been adjusted to a molar mass of 450.454 g mol⁻¹, which is that of pure grossular rather than to a molar mass corresponding to the solution composition. The heat capacities of the empty calorimeters represent from 65 per cent of the total at 15 K to 47 per cent at 100 K and remain at about 35 per cent above 150 K. The curve of heat capacity against temperature is of sigmoid shape without anomalies.

TABLE 4. Heat capacity of grossular
(cal_{th} = 4.184 J)

$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th} K^{-1} \text{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th} K^{-1} \text{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th} K^{-1} \text{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th} K^{-1} \text{mol}^{-1}}$
Low-temperature data—Mark II cryostat							
Series I		Series II		325.23	83.59	16.83	0.138
54.09	4.861	200.11	56.32	335.16	84.82	18.49	0.181
61.80	7.008	212.10	59.71	345.58	86.01	20.56	0.250
70.27	9.629	223.61	62.83			23.19	0.385
79.48	12.82	234.71	65.67	Series IV		25.81	0.512
89.61	16.63	245.47	68.32	5.28	0.002	27.83	0.633
99.84	20.49	255.95	70.70	7.91	0.007	29.82	0.782
110.39	24.64	266.17	72.84			32.29	1.007
121.31	29.01	276.41	74.95	Series V		35.39	1.345
132.06	33.22	286.69	76.89	5.01	0.003	37.71	1.634
142.21	37.11	297.01	78.97	6.11	0.006	39.78	1.912
151.85	40.68	307.40	80.71	7.47	0.006	42.99	2.451
161.40	44.08	317.59	82.41	8.66	0.021	46.88	3.199
171.42	47.48	327.64	84.02	9.77	0.025	51.82	4.285
182.47	51.04	337.54	85.38	11.07	0.042	57.61	5.772
194.57	54.70			12.65	0.051		
206.92	58.28	Series III		14.14	0.079		
218.73	61.55	315.17	81.84	15.43	0.107		
Intermediate-temperature data—Mark IV thermostat							
Series I		Series II		456.54	98.34	532.92	103.67
302.11	71.62	380.75	90.70	466.62	99.20	542.78	104.39
312.04	81.33	391.03	91.87	476.63	100.03	552.59	104.99
321.83	82.89	401.21	93.13	486.57	100.78		
330.15	84.15	411.30	94.10	496.44	101.48	Series V	
340.15	85.61	421.30	95.16			546.44	104.30
350.03	87.02	431.21	96.12	Series IV		556.25	104.68
359.80	88.22	441.05	97.09	487.57	100.52	565.99	105.39
369.87	89.57	450.82	97.89	494.54	101.14	574.90	105.83
380.25	90.75			503.37	101.76	584.31	107.55
390.53	91.95	Series III		513.03	102.42	595.06	107.80
		446.39	97.41	523.01	103.01		

Apart from questions of chemical composition, the heat-capacity values of table 4 are considered to be characterized by standard deviations of 0.08 per cent above 25 K; below this temperature the uncertainty gradually increases to 0.3 per cent at 10 K, and to 10 per cent at 5 K due to the decreasing sensitivity of the platinum resistance thermometer.

THERMODYNAMIC FUNCTIONS OF (IMPURE) GROSSULAR

Values of the heat capacity of grossular as measured at selected temperatures have been presented in table 5 on the basis of a smoothed curve fitted by digital computer using the least-squares method. The thermodynamic functions integrated from the smoothed curve are also presented in the same table. Above 100 K the values of all the functions are considered to be reliable to 0.06 per cent for the composition measured. It is again emphasized that table 5 (like table 4) is based upon the molar mass of pure grossular.

TABLE 5. Thermodynamic functions of grossular^a
(cal_{th} = 4.184 J)

T K	C_p cal _{th} K ⁻¹ mol ⁻¹	$S^\circ(T) - S^\circ(0)$ cal _{th} K ⁻¹ mol ⁻¹	$H^\circ(T) - H^\circ(0)$ cal _{th} mol ⁻¹	$-\{G^\circ(T) - H^\circ(0)\}/T$ cal _{th} K ⁻¹ mol ⁻¹
5	0.019	0.003	0.0141	0.0003
10	0.070	0.034	0.255	0.0090
15	0.118	0.071	0.713	0.0235
20	0.222	0.117	1.527	0.0408
25	0.432	0.187	3.110	0.0626
30	0.780	0.294	6.076	0.0916
35	1.291	0.451	11.18	0.1311
40	1.976	0.666	19.28	0.1838
45	2.839	0.947	31.24	0.2523
50	3.878	1.298	47.96	0.3387
60	6.441	2.222	99.05	0.5715
70	9.543	3.442	178.6	0.8910
80	13.029	4.941	291.2	1.3008
90	16.75	6.688	439.9	1.8001
100	20.55	8.623	626.4	2.360
110	24.55	10.770	851.9	3.025
120	28.51	13.076	1117.3	3.766
130	32.42	15.51	1422.0	4.575
140	36.22	18.06	1765.3	5.446
150	39.92	20.68	2146.1	6.374
160	43.49	23.37	2563.3	7.352
170	46.93	26.11	3015.5	8.375
180	50.22	28.89	3501.3	9.437
190	53.37	31.69	4019.4	10.535
200	56.37	34.50	4568.2	11.663
210	59.24	37.32	5146.4	12.818
220	61.96	40.14	5752.5	13.996
230	64.55	42.96	6385.2	15.19
240	67.01	45.75	7043.1	16.41
250	69.34	48.54	7724.9	17.64
260	71.56	51.30	8429.5	18.88
270	73.66	54.04	9155.6	20.13
280	75.65	56.76	9902.2	21.39
290	77.54	59.44	10668.2	22.66
300	79.33	62.10	11452.7	23.93
273.15	74.29	54.90	9389	20.53
298.15	79.00	61.61	11306	23.69
310	81.03	64.73	12254.5	25.20
320	82.64	67.33	13073.0	26.48
330	84.17	69.90	13907.1	27.75
340	85.63	72.43	14756.2	29.03
350	87.01	74.93	15619	30.31
400	93.00	86.96	20126	36.64
450	97.76	98.20	24899	42.87
500	101.59	108.70	29886	48.93
550	104.59	118.53	35044	54.82
600	107.32	127.74	40340	60.51

^a The table is based upon the molar mass of pure grossular: $M(\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}) = 450.454 \text{ g mol}^{-1}$.

COMPARISON WITH OTHER DATA

Kiseleva *et al.*⁽⁴⁾ used the inverse-temperature drop-calorimetry method of Holm *et al.*⁽¹⁶⁾ with a Tian-Calvet microcalorimeter as receiver over the range 700 to 1400 K. The enthalpy increment between 298 K and the receiver temperature may then readily be determined on even a few milligrams of sample with a standard deviation of 2 per cent and an accuracy several times larger. We have shown the deviations of their data (after adjustment from the approximate 91 per cent "end member" proximate purity by our scheme discussed later) in figure 1.

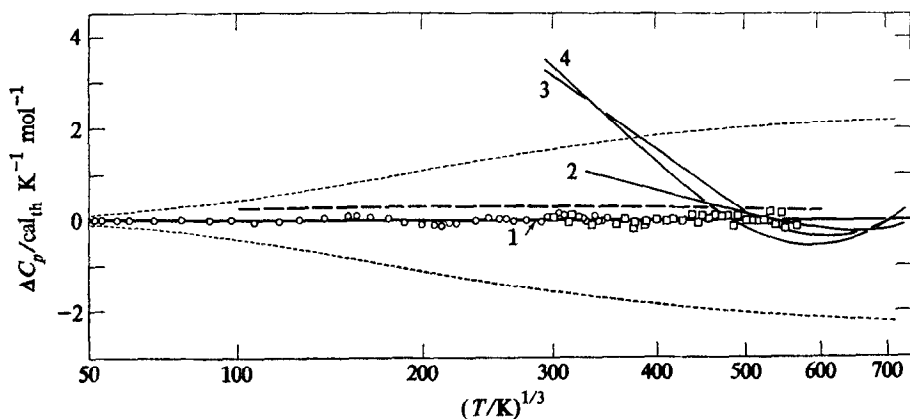


FIGURE 1. Deviations from the adjusted smoothed heat-capacity curve of this research (curve 1) taken from table 6 of \circ , low-temperature and \square , superambient-temperature points of this research. The dashed line represents the deviations of the apparent smoothed heat-capacity curve of this research taken from table 5. Curve 2 is the deviation of the d.s.c. data of Robie and Krupka.⁽¹⁷⁾ Curve 3 is the deviation of the Tian-Calvet microcalorimetric data of Kiseleva *et al.*⁽⁴⁾ Curve 4 shows the d.s.c. data of Kiseleva *et al.*⁽⁴⁾ adjusted by the technique of this research. The dotted lines represent deviations from the adjusted smoothed curve of ± 2 per cent.

Differential-scanning calorimetric values of Robie *et al.*⁽¹⁷⁾ over a more limited range on both a synthetic and a natural sample are also shown in figure 1. These data accord well with those previously reported by the authors on the same apparatus using a portion of the sample from this research.⁽¹⁸⁾ They agree within the combined estimated uncertainty.

ADJUSTMENT OF ENTROPY FOR IMPURITIES

To calculate the effects of dissolved garnet-phase impurities on the thermophysical properties, we assumed that the observed entropy of our sample was equal to the sum of the entropies of the end-member garnets. The analysis of the calorimetric garnet sample given in table 1 is represented in table 2 in terms of the end-member components also shown in table 2.

Rather than adjust entropy values by deduction of the entropies of the oxides which contribute to the non-stoichiometry, as is frequently done,^(8,19) we prefer to use a summation technique for this adjustment since the impurities are certainly

present in solid solution rather than as pure binary oxide phases. Hence, we account for the observed entropy S_{obs} (*i.e.* the molar entropy calculated for the molar mass of the end-member—grossular in this instance—to which the thermodynamic functions are to be adjusted) at any temperature by the expression:

$$S_{\text{obs}} = W \sum_{i=1}^{i=n} x_i S_i, \quad (1)$$

in terms of the product of the mole fractions and the molar-entropy contributions of all the end-member components summed over all the n end-member compositions involved. The factor W involves the molar mass M_i of the end-member compositions, and adjusts the observed molar entropy for the apparent molar mass of the sample to that M_y of the end-member for which molar values are to be sought. Hence:

$$W = M_y \left/ \sum_{i=1}^{i=n} x_i M_i \right. \quad (2)$$

Separating out the pure composition y for which molar values are sought and rearranging:

$$S_y = S_{\text{obs}}/W - \sum_{i=1}^{i=n-1} x_i (S_i - S_y) = S_{\text{obs}}/W - \sum_{i=1}^{i=n-1} x_i \Delta S_i, \quad (3)$$

in which $\Delta S_i = (S_i - S_y)$, and each is referred to its own molar mass. For grossular we may then write (on the basis of and with the notation of table 2):

$$S_{\text{gr}} = S_{\text{obs}}/W - 0.024\Delta S(\text{hg}) - 0.004\Delta S(\text{pp}) - 0.014\Delta S(\text{sp}) \\ - 0.038\Delta S(\text{al}) - 0.014\Delta S(\text{mm}). \quad (4)$$

Since entropies have not been experimentally determined for any of the end-member garnets, the $\Delta S(\text{mm})$ -term was approximated, only for Mg-melanite, by using entropy values for constituent binary oxides:

$$\Delta S(\text{mm}) = S(\text{MgO}) + S(\text{TiO}_2) - S(\text{Al}_2\text{O}_3), \quad (5)$$

in which $\Delta S(\text{mm})$ is the entropy contribution for the substitution of MgTi for 2Al ions.

A more accurate method of approximation involves adjustment in terms of measured entropies of isostructural phases for cations with similar coordination numbers by differencing the entropies of appropriate end-member phases. Thus:

$$\Delta S(\text{al}) = \frac{2}{3}\{S(\text{fa}) - S(\text{Ca-ol})\}, \quad \Delta S(\text{pp}) = \frac{2}{3}\{S(\text{fo}) - S(\text{Ca-ol})\}, \\ \text{and } \Delta S(\text{sp}) = \frac{2}{3}\{S(\text{te}) - S(\text{Ca-ol})\}, \quad (6)$$

in which fa represents fayalite (Fe_2SiO_4), fo represents forsterite (Mg_2SiO_4), te represents tephroite (Mn_2SiO_4), and Ca-ol represents Ca-olivine (Ca_2SiO_4). Moreover,

$$\Delta S(\text{hg}) = 2\{S(\text{br}) - \frac{1}{2}S(\text{fo})\}, \quad (7)$$

in which br represents brucite $\text{Mg}(\text{OH})_2$. Examples of the ΔS_i values are given in table 2. Data for these were taken from references 1 and 16.

The oxidation state of the iron may represent an error in chemical analysis as the charge balance would be better if some of the iron were Fe(III). However, two

independent chemical analyses found only Fe(II) present. If the iron were present entirely as Fe(III) the entropy correction term would be larger from that calculated above by $0.12 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$ (0.3 per cent) at 298.15 K.†

Another potential problem with our adjustment terms involves the presence, and if present the nature, of water (hydroxyl ion) in our sample. There are at least five possibilities and the relevant entropy correction term for its presence would be: (1) the analysis is correct and the garnet includes some hydrogrossular: $\Delta S(298.15 \text{ K}) = -0.73_4 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$; (2) the analysis is correct and the garnet has fluid inclusions of water: $\Delta S(298.15 \text{ K}) = -1.04 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$; (3) the analysis is correct and the garnet includes serpentine (serpentine was a second phase in the original impure materials): $\Delta S(298.15 \text{ K}) = -0.49_9 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$; (4) the analysis is correct and the sample contained serpentine eliminated by our hand picking it before we measured the heat capacity: $\Delta S(298.15 \text{ K}) = -0.57_4 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$; (5) the analysis is incorrect and there is no water present: $\Delta S(298.15 \text{ K}) = -0.64_5 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$.

We ignore possibility (2) since we found no discontinuity in the entropy curve at the $\text{H}_2\text{O}(s) = \text{H}_2\text{O}(l)$ equilibrium temperature. We have assumed that the small amount of OH^- is present as hydrogrossular. Regardless of the specific corrections, the revised entropy values for pure grossular are within $0.3 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$ (0.5 per cent) of the entropy at standard conditions insofar as the water (hydroxyl) adjustment is involved.

STANDARD ENTROPY OF GLOSSULAR

The adjustment of the apparent standard entropy for the grossular composition measured to that for pure grossular using the adjustment equation in the immediately preceding section together with the ΔS_i values from table 2 indicates

$$\Delta S_{gr}^{\circ} / \text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1} = S_{\text{obs}}^{\circ} / W - \sum x_i \Delta S_i = 60.87, \quad (8)$$

as the adjusted value.

Adjustment of the enthalpy by the same method (with similar approximations and estimates) leads to a value of $\{H^{\circ}(298.15 \text{ K}) - H^{\circ}(0)\}$ of $11.250 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$, and the corresponding value of $-\{G^{\circ}(298.15 \text{ K}) - H^{\circ}(0)\}/T$ is $-23.14 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$. A similar procedure serves for the heat capacities.

Adjustments at other temperatures were accomplished by a similar procedure at each temperature. Below about 100 K the scheme is not reliable. A summary of values of thermodynamic properties adjusted to the composition of grossular is presented in table 6.

The standard deviations of our adjusted $S^{\circ}(T)$, $C_p^{\circ}(T)$, and $\{G^{\circ}(T) - H^{\circ}(0)\}/T$ values are presumed to be within $\pm 0.2 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$ for terminal members, but further determinations will be useful in providing a more accurate assessment of this uncertainty.

† Throughout this paper $\text{cal}_{\text{th}} = 4.184 \text{ J}$.

TABLE 6. Smoothed thermodynamic functions adjusted to pure ideal grossular ^a
(cal_{th} = 4.184 J)

T K	Apparent	C_p cal _{th} K ⁻¹ mol ⁻¹	Adjusted	$H^\circ(T) - H^\circ(0)$ kcal _{th} mol ⁻¹	$-\{G^\circ(T) - H^\circ(0)\}/T$ cal _{th} K ⁻¹ mol ⁻¹
	C_p cal _{th} K ⁻¹ mol ⁻¹		$S^\circ(T) - S^\circ(0)$ cal _{th} K ⁻¹ mol ⁻¹		
100	20.55	20.33	8.16	0.613	2.033
200	56.37	56.12	33.87	4.533	11.21
298.15	79.00	78.73	60.88	11.243	23.17
300	79.33	79.06	61.37	11.391	23.40
400	93.00	92.73	86.15	20.04	36.06
500	101.6	101.3	107.8	29.77	48.29
600	107.3	107.1	126.8	40.20	59.84
700	—	110.9	143.6	51.08	70.63
800	—	113.7	158.5	62.30	80.62
900	—	115.9	172.1	73.72	90.19
1000	—	117.6	184.3	85.44	98.86

^a See text.^b Sample as run (table 5), no adjustment for composition.

The authors appreciate the continuing financial support for these thermodynamic studies by the National Science Foundation. We also thank Professor A. L. Boettcher of Pennsylvania State University for sample provenance and acknowledge the cooperation of Drs James J. Bartel, Silverio Henriquez, and Harmas L. Kiwia in assisting in making these determinations.

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