

Heat capacity and thermodynamic properties for coesite and jadeite, reexamination of the quartz-coesite equilibrium boundary

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ABSTRACT

The heat capacities of synthetic coesite and jadeite were measured between about 15 and 850 K by adiabatic and differential scanning calorimetry. The experimental data were smoothed and estimates were made of heat capacities to 1800 K. The following equations represent our estimate of the heat capacities of coesite and jadeite between 298.15 and 1800 K:

$$C_p^{\circ}(\text{coesite}) = 141.35 - 0.01514T + 987190.7T^{-2} - 1780.5T^{-1/2} + 1.029 \times 10^{-6}T^2$$

$$C_p^{\circ}(\text{jadeite}) = 259.08 + 0.038032T - 2518908T^{-2} - 1332.57T^{-1/2} - 8.8 \times 10^{-6}T^2.$$

Tables of thermodynamic values for coesite and jadeite to 1800 K are presented. The entropies of coesite and jadeite are 40.38 ± 0.12 and 136.5 ± 0.32 J/(mol·K), respectively, at 298.15 K. The entropy for coesite derived here confirms the value published earlier by Holm et al. (1967).

We have derived an equation to describe the quartz-coesite boundary over the temperature range of 600 to 1500 K, $P(\text{GPa}) = 1.76 + 0.001T(\text{K})$. Our results are in agreement with the enthalpy of transition reported by Akaogi and Navrotsky (1984) and yield -907.6 ± 1.4 kJ/mol for the enthalpy of formation of coesite from the elements at 298.15 K and 1 bar, in agreement with the value recommended by CODATA (Khodakovskiy et al. 1995). Several sources of uncertainty remain unacceptably high, including: the heat capacities of coesite at temperatures above about 1000 K; the heat capacities and volumetric properties of α quartz at higher pressures and at temperatures above 844 K; the pressure corrections for the piston cylinder apparatus used to determine the quartz-coesite equilibrium boundary.

INTRODUCTION

Recently, questions were raised (Kuskov et al. 1991; cf. Akaogi and Navrotsky 1984; Weaver et al. 1973, 1979) regarding the quality of the coesite sample upon which the presently accepted entropies and heat capacities are based (Holm et al. 1967; Robie et al. 1978). The coesite sample was separated from Coconino sandstone taken from the Meteor Crater near Winslow, Arizona. Coesite is thought to have been produced as a result of meteorite impact (Chao 1967). The sample was largely composed of particles less than 0.5 μm in size. Concern arises from the fact that samples composed of very small particles may exhibit excess heat capacity, especially at temperatures below 150 K (e.g., Barron et al. 1959; Richet et al. 1986) as a consequence of high surface energy on the

small grains (e.g., Weaver et al. 1979; Akaogi and Navrotsky 1984). Similar concerns were raised regarding the value reported by Holm et al. (1967) for the enthalpy of the β quartz-coesite transition at 973 K, again because high surface energy characteristics of fine grained materials can cause an increase in the enthalpy of solution compared to that obtained on coarser material (Hemingway and Nitkiewicz 1995).

Questions also were raised about the quality of the jadeite sample upon which currently accepted thermodynamic data are based (Yoder 1950; Robertson et al. 1957). The jadeite is a natural sample from Burma, and it appears to have significant substitution of impurities for both Na and Al (Kelley et al. 1953; Yoder 1950).

This study provides new measurements of the heat capacity of well-crystallized and well-characterized samples of coesite and jadeite, values for the entropies at 298.15

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K, and functions for the heat capacities to 1800 K. We also examine data for the quartz-coesite transition and recommend an equation for the phase boundary.

Several recent reviews have been published on the enthalpy of formation of coesite and jadeite. The CODATA Task Group on Geothermodynamic Data (Khodakovskiy et al. 1995) recommends -907.8 ± 1.2 kJ/mol for the enthalpy of formation of coesite at 298.15 K, based on the difference in the enthalpy of solution of β quartz and coesite in lead borate melt at about 975 K (Akaogi and Navrotsky 1984; Zhidikova et al. 1988; Kuskov et al. 1991). The enthalpy of formation of coesite derived in this study is consistent with the value recommended by the CODATA Task Group. Hemingway and Haselton (1994) have evaluated the aqueous HF and molten salt calorimetric data for jadeite and recommend -3029.3 ± 3.6 kJ/mol for the enthalpy of formation of jadeite at 298.15 K, and that value is adopted here.

SAMPLES

Coesite and jadeite were prepared in approximately one gram batches in a piston-cylinder apparatus using furnaces and pistons 2.54 cm in diameter. The furnace assemblies were similar to the low-temperature NaCl assemblies described by Bohlen (1984), except modifications had been made to allow for use of very large diameter capsules (0.952 cm OD). Temperature was measured using Pt₁₀₀-Pt₉₀Rh₁₀ thermocouples, and no correction was made for the effects of pressure and temperature gradients on emf.

Coesite was synthesized from water-clear natural quartz crystals from Jessieville, Arkansas, ground in alcohol to an average grain size of 20 μm . The quartz powder was loaded into a gold capsule (0.952 cm in diameter and 1.27 cm in length with a wall thickness of 0.02 cm) with approximately 1 wt% H₂O, and the capsules were sealed by arc welding. The samples were held at 32 kbar (nominal pressure) and 800 °C for approximately 48 h.

After synthesis, the samples were inspected carefully using optical and X-ray techniques. The syntheses yielded essentially 100% coesite crystals ranging in size from 30–150 μm with an average grain size estimated to be approximately 80 μm . Detailed optical examination indicated the presence of traces of quenched vapor ($\ll 0.1\%$). Coesite crystals synthesized in the same manner were studied using STEM techniques for a previous study (Bohlen and Boettcher 1982). The results of that investigation revealed that the coesite was extremely well crystallized with remarkably few defects. The coesite sample masses were 12.3622 g and 34.432 mg, respectively, for the adiabatic calorimeter and the differential scanning calorimeter (DSC).

Jadeite was synthesized from natural quartz from Jessieville, Arkansas, and Fisher reagent grade Al₂O₃ and Na₂SiO₃·5H₂O mixed in stoichiometric proportions appropriate for jadeite and ground together for about 15 min. The starting materials were loaded into capsules identical to those used in the synthesis of coesite, and the capsules

were sealed by arc welding. No H₂O was added, and no precautions were taken to keep the starting materials especially dry. The samples were held at 22 kbar (nominal pressure) and 700 °C for approximately 72 h.

After synthesis, as with coesite, the samples were inspected carefully using optical and X-ray techniques. The syntheses yielded essentially 100% jadeite crystals that were surprisingly large, ranging in size from 25–60 μm in the small dimension to 50–250 μm in the large dimension. Traces ($\ll 0.1\%$) of vapor quench were also observed in the optical mounts. Electron microprobe analyses of the crystals indicated that they were stoichiometric jadeite. The jadeite sample masses were 12.0605 g and 37.744 mg, respectively, for the adiabatic calorimeter and the DSC.

APPARATUS AND TECHNIQUES

The adiabatic calorimetric system and procedures used in this study have been described elsewhere with the exception of the small calorimeter. The cryostat used for the low-temperature heat-capacity measurements has been described by Robie and Hemingway (1972). The procedures for sample loading, measurement, calibration, and data reduction have been described by Robie and Hemingway (1972) and Robie et al. (1976). The calorimeter is a smaller version of that described by Robie et al. (1976) with a modified closure and with the thermocouple post located on the bottom instead of the side wall. The thermometer is a strain-free miniature platinum-resistance thermometer of the same design and calibrated against the same thermometer described by Robie et al. (1976). The calorimeter has an internal volume of 10.0 cm³. The DSC and the procedures for measuring heat capacity have been discussed elsewhere (Hemingway et al. 1984; Krupka et al. 1979).

EXPERIMENTAL RESULTS

Heat capacities of coesite and jadeite were measured with the DSC before the low-temperature measurements were made. These values are given in Hemingway et al. (1995). The measurements were terminated at about 850 K because there was not a significant deviation of the new experimental results from the values given in Robie et al. (1978). Values of the heat capacity of coesite between 1000 and 1800 K were estimated from the heat capacities of cristobalite and silica glass. For jadeite, heat capacities were calculated to 1800 K from the enthalpy increment data provided by Kelley et al. (1953). The sets of experimental and, for coesite, estimated heat capacities were fit to an equation of the form suggested by Haas and Fisher (1976). The equations are in units of J/(mol·K):

$$C_p^0(\text{coesite}) = 141.35 - 0.01514T + 987190.7T^{-2} \\ - 1780.5T^{-1/2} + 1.029 \times 10^{-6}T^2$$

$$C_p^0(\text{jadeite}) = 259.08 + 0.038032T - 2518908T^{-2} \\ - 1332.57T^{-1/2} - 8.8 \times 10^{-6}T^2.$$

TABLE 1. Thermodynamic properties of coesite from 298.15 to 1800 K

T (K)	Heat capacity	Entropy J/(mol·K)	Enthalpy function	Gibbs function	Formation from the elements		
					Enthalpy (kJ/mol)	Gibbs energy (kJ/mol)	Log K(f)
298.15	44.91	40.38	0.00	40.38	-907.6	-852.9	149.42
300	45.07	40.66	0.28	40.38	-907.6	-852.5	148.43
400	52.60	54.70	12.45	42.24	-907.8	-834.1	108.92
500	58.36	67.09	21.09	46.00	-907.6	-815.7	85.22
600	62.69	78.13	27.68	50.45	-907.0	-797.4	69.42
700	65.97	88.05	32.92	55.12	-906.3	-779.2	58.14
800	68.49	97.03	37.22	59.81	-905.4	-761.1	49.69
900	70.43	105.21	40.81	64.41	-904.5	-743.1	43.13
1000	71.92	112.71	43.85	68.87	-903.4	-725.2	37.88
1100	73.07	119.63	46.45	73.17	-902.3	-707.5	33.59
1200	73.95	126.02	48.71	77.31	-901.2	-689.8	30.03
1300	74.61	131.97	50.68	81.29	-900.1	-672.2	27.01
1400	75.09	137.52	52.40	85.11	-899.0	-654.7	24.43
1500	75.42	142.71	53.93	88.78	-898.0	-637.3	22.19
1600	75.63	147.58	55.28	92.31	-896.9	-620.0	20.24
1700	75.74	152.17	56.48	95.69	-896.2	-602.2	18.50
1800	75.77	156.50	57.55	98.95	-895.0	-582.0	16.89

Note: Formula wt. = 60.084.

The equations fit the selected experimental values to $\pm 0.3\%$ (including the DSC and low-temperature adiabatic calorimetric data for temperatures above 290 K that are discussed below). Smoothed values of the thermodynamic properties of coesite and jadeite estimated to 1800 K are given in Tables 1 and 2, respectively, in the format adopted by Robie and Hemingway (1995).

There is a suggestion that a small transition occurs in jadeite near 325 K, similar to that seen by Kelley et al. (1953) in nepheline at about 467 K. Differences between the thermal resistance of the standard corundum sample and the jadeite sample made measurements of the jadeite heat capacity with the DSC difficult between 320 and about 400 K. The heat capacity values obtained in this temperature range were nearly linear, atypical for this temperature region. Because of these problems and the possible but unproved heat capacity anomaly, these mea-

surements were not included in the data set fitted to the equation given above. If there is a transition in jadeite near 325 K, the enthalpy effect is small and likely to be within the error of the DSC measurements.

Further support for the hypothesis that a small transition occurs in jadeite comes from the work of Kelley et al. (1953). These authors report both low-temperature heat-capacity and high-temperature enthalpy increment (heat content) data for jadeite, albite, and nepheline. In their discussion of the data for these phases, they note that jadeite is intermediate in composition between albite and nepheline, but the heat capacities at the lower temperatures deviate from the mean of the values for albite and nepheline whereas at higher temperatures, the heat content of jadeite is nearly equivalent to those of the mean of albite and nepheline. Projection of the difference curves to a point of intersection is complicated by the

TABLE 2. Thermodynamic properties of jadeite from 298.15 to 1800 K

T (K)	Heat capacity	Entropy J/(mol·K)	Enthalpy function	Gibbs function	Formation from the elements		
					Enthalpy (kJ/mol)	Gibbs energy (kJ/mol)	Log K(f)
298.15	164.13	136.50	0.00	136.50	-3029.3	-2851.5	499.56
300	164.77	137.52	1.01	136.50	-3029.3	-2850.4	496.29
400	190.51	188.81	45.49	143.32	-3032.7	-2790.4	364.38
500	206.23	233.12	76.17	156.96	-3032.3	-2729.9	285.18
600	217.33	271.76	98.82	172.94	-3031.1	-2669.5	232.39
700	225.88	305.93	116.38	189.54	-3029.4	-2609.3	194.71
800	232.82	336.56	130.52	206.04	-3027.3	-2549.5	166.46
900	238.65	364.32	142.22	222.11	-3025.1	-2489.9	144.50
1000	243.65	389.73	152.12	237.62	-3033.4	-2429.8	126.92
1100	248.01	413.17	160.64	252.53	-3030.7	-2369.5	112.52
1200	251.83	434.91	168.08	266.83	-3124.7	-2307.1	100.42
1300	255.20	455.20	174.66	280.55	-3120.8	-2239.1	89.97
1400	258.18	474.23	180.52	293.71	-3116.8	-2171.5	81.02
1500	260.80	492.13	185.79	306.35	-3112.7	-2104.1	73.27
1600	263.11	509.04	190.55	318.49	-3108.5	-2037.0	66.50
1700	265.11	525.05	194.88	330.18	-3204.6	-1969.2	60.51
1800	266.84	540.26	198.83	341.43	-3199.9	-1896.7	55.04

Note: Formula wt. = 202.139.

small transition in nepheline, but one can infer that the change in behavior should take place between 300 and 400 K, consistent with the region of anomalous heat capacities discussed above. Kelley et al. (1953) note the difference in coordination of aluminum in jadeite as compared to albite and nepheline. This difference has a greater effect on the heat capacities of jadeite at temperatures below ambient. A structural analysis of jadeite between 250 and 380 K would be of great help in resolving questions of how to evaluate the heat-capacity data in this temperature interval.

The heat capacities of coesite have been measured by DSC by Akaogi et al. (1995), but the data were not used in this study. Although their measurements covered the temperature range of 183 to 703 K, those authors included only a graph of their experimental data and an equation for their smoothed data. The values reported by Akaogi et al. (1995) for the temperature range of 298 to 700 K are about 2% lower than those reported by Hemingway et al. (1995) and used in this study. Akaogi et al. (1995) also measured the heat capacities of stishovite in the same temperature range. The values measured below 298 K may be compared to those reported by Holm et al. (1967). Here also, the values reported by Akaogi et al. (1995) are about 2% lower than the values of Holm et al. (1967) for stishovite. Akaogi et al. (1995) report values of 41.81 and 41.94 ± 0.47 kJ/mol, respectively, for the enthalpy change, $H_{983} - H_{298}$, as determined from their heat-capacity measurements and from enthalpy increment (heat content) measurements made with a molten-salt calorimeter. These values are lower by about 2% than the values obtained by Hemingway et al. (1995) and by Holm et al. (1967). Finally, Akaogi et al. (1995) used two containers for the sample, one each for the lower and higher temperatures covered in their DSC study. Where the measurements overlap, the measurements made at the higher temperatures appear to be lower than an extrapolation of the lower temperature measurements to equivalent temperatures.

Low-temperature adiabatic calorimetric measurements of coesite were completed over the temperature interval of 14 to 365 K. The experimental values are listed in chronological order of measurement in Table 3. The values were smoothed using cubic spline fitting routines. Values of the heat capacity were estimated for temperatures below 15 K from a plot of the smoothed and experimental data as C_p/T vs. T^2 . Smoothed values of the thermodynamic properties of coesite are given in Table 4. The entropy and enthalpy functions at 298.15 K are 40.38 ± 0.12 and 23.13 ± 0.05 J/(mol·K), respectively.

Our measurements do not support the theory that the heat capacities and consequently the calculated entropy reported by Holm et al. (1967) for coesite are affected by significant surface energy contributions. Our smoothed value for the heat capacity of coesite at 298.15 K is lower by about 1% than the measured value reported by Holm et al. (1967). A comparison of the smoothed heat capacities reported by Holm et al. (1967) and those given in

TABLE 3. Experimental heat capacities of synthetic coesite corrected for curvature

T (K)	Heat capacity J/(mol·K)	T (K)	Heat capacity J/(mol·K)	T (K)	Heat capacity J/(mol·K)
Series 1					
305.85	45.59	33.29	1.806	169.31	28.24
310.96	46.18	35.80	2.170	174.07	29.01
316.33	46.60	38.98	2.855	178.74	29.76
321.33	47.12	41.99	3.173	183.34	30.51
326.59	47.64	45.11	3.771	187.87	31.20
331.79	48.17	47.86	4.354	192.34	31.88
336.95	48.62	50.34	4.865	196.74	32.54
342.34	49.08	52.61	5.236	201.08	33.17
347.96	49.58	55.16	5.872	205.37	33.78
353.53	50.02	57.87	6.344	209.61	34.39
359.03	50.53	60.57	6.932	213.79	34.94
364.48	51.01	65.95	8.069	217.93	35.51
		71.11	9.135	222.03	36.06
		75.78	10.10	226.08	36.60
		80.09	11.01	230.09	37.10
301.42	45.23	84.75	12.02	234.06	37.61
Series 2					
		89.75	13.10	237.99	38.12
Series 3					
320.50	47.02	94.87	14.16	241.88	38.60
325.75	47.54	100.11	15.28	245.74	39.08
		105.09	16.30	249.56	39.55
Series 4					
15.91	0.2527	109.84	17.29	253.35	40.00
17.82	0.2790	114.41	18.23	257.34	40.38
18.95	0.3161	119.36	19.21	261.53	40.85
20.02	0.4247	124.68	20.26	265.69	41.37
21.07	0.5540	129.82	21.26	269.80	41.88
22.23	0.6825	134.80	22.21	273.89	42.34
23.92	0.8212	139.95	23.10	277.93	42.72
26.34	1.096	144.37	23.98	281.93	43.20
28.47	1.294	149.31	24.90	285.90	43.62
30.16	1.521	154.47	25.75	289.84	44.07
31.70	1.611	159.52	26.61	293.74	44.54
		164.46	27.42	297.60	44.88

Note: Values are listed for a molar mass of 60.084 g.

Table 4 shows systematic differences between two data sets that cross and recross for data reported for the temperature interval 5 to 300 K. The data reported by Holm et al. (1967) are higher in the temperature intervals of 20 to 70 K and 220 to 300 K and lower in the temperature interval in between. The observed differences are larger than what can be expected for data evaluated on different temperature scales (Holm et al. 1967 on IPTS48 and this study on IPTS68; e.g., Robie and Hemingway 1972), or between the calorimeter used by Holm et al. (1967) and that used in this study (e.g., Anovitz et al. 1987). However, even with differences as large as 1.8% at 120 K, the entropies calculated from each data set are identical, 40.38 J/(mol·K). The observed differences in heat capacities could arise from differences in the coesite samples used in the two studies, but this is impossible to verify.

Low-temperature adiabatic calorimetric measurements of jadeite were completed over the temperature interval of 5 to 370 K. The experimental values are listed in chronological order of measurement in Table 5. The values were smoothed using cubic spline fitting routines. Values of the heat capacity were estimated for temperatures below 15 K from a plot of the smoothed and experimental data as C_p/T vs. T^2 . Smoothed values of the thermodynamic properties of jadeite are given in Table 6. The en-

TABLE 4. Thermodynamic properties for synthetic coesite

T (K)	Heat capacity J/(mol·K)	Entropy J/(mol·K)	Enthalpy function J/(mol·K)	Gibbs energy function J/(mol·K)
5	0.007	0.002	0.002	0.001
10	0.057	0.019	0.014	0.005
15	0.191	0.064	0.048	0.016
20	0.453	0.151	0.113	0.038
25	0.944	0.301	0.227	0.074
30	1.471	0.520	0.390	0.129
35	2.058	0.786	0.582	0.204
40	2.932	1.118	0.822	0.296
45	3.760	1.509	1.100	0.409
50	4.766	1.957	1.416	0.541
60	6.812	3.006	2.144	0.862
70	8.902	4.213	2.960	1.253
80	11.00	5.538	3.833	1.705
90	13.14	6.957	4.749	2.209
100	15.25	8.451	5.693	2.758
110	17.32	10.00	6.657	3.345
120	19.34	11.60	7.630	3.966
130	21.29	13.22	8.606	4.615
140	23.18	14.87	9.580	5.289
150	24.99	16.53	10.55	5.983
160	26.70	18.20	11.50	6.694
170	28.35	19.87	12.45	7.420
180	29.97	21.53	13.38	8.158
190	31.53	23.20	14.29	8.906
200	33.01	24.85	15.19	9.661
210	34.43	26.50	16.07	10.42
220	35.79	28.13	16.94	11.19
230	37.10	29.75	17.79	11.96
240	38.37	31.36	18.62	12.74
250	39.58	32.95	19.43	13.51
260	40.73	34.52	20.23	14.29
270	41.87	36.08	21.01	15.07
280	42.99	37.62	21.77	15.85
290	44.08	39.15	22.52	16.63
300	45.09	40.66	23.26	17.40
273.15	42.23	36.57	21.25	15.32
298.15	44.91	40.38	23.13	17.25
	±0.12	±0.12	±0.05	±0.04

Note: Molar mass = 60.084 g.

tropy and enthalpy function at 298.15 K are 136.5 ± 0.32 and 81.68 ± 0.10 J/(mol·K), respectively.

Two vacuum leaks caused problems at temperatures below 50 K. During the Series 5 measurements, a leak developed in the He tank causing the liquid He to vaporize rapidly and the system to warm quickly. The area of the leak closed as the system warmed so that tests at room temperature designed to locate the leak were inconclusive. The likely area was resoldered and the system was cooled to test the repair and to try to complete the measurements. On cooling, a leak appeared at about 20 K. The calorimeter was quickly heated to about 25 K and measurements were begun as the vacuum recovered. The first two measurements of Series 6 were made under conditions of poor vacuum and they show a significant deviation from the remainder of the data set. These values were not used in the data set fitted with the cubic spline smoothing function.

The measurements presented here deviate significantly from those reported by Kelley et al. (1953), being about 2.5% larger except below 100 K. Between 50 and 100 K, the data sets cross with the value reported by Kelley et

al. (1953) at 50 K being about 2% larger than that observed here. This difference is reflected in the entropies, which are about 2% different. The sample studied by Kelley et al. (1953) contained about 4.5% impurities, which probably explains the observed differences in measured values for the heat capacities.

DISCUSSION

We have used the third-law method (Robie 1965) to evaluate the experimental and estimated data for the quartz-coesite transition and to calculate the enthalpy of the transition at 298.15 K. We can calculate the enthalpy of transition from each selected P - T point along a chosen phase boundary using the relation $-\Delta_r H_{298}^0 = T\Delta[(G_T^0 - H_{298}^0)/T] + \int_1^P \Delta V_T^0 dP$. We provide our estimated values for the thermodynamic properties defining the quartz-coesite phase boundary in Table 7. In Figure 1, we show our selected phase boundary [$P(\text{GPa}) = 1.76 + 0.001 T/\text{K}$, for the temperature range 600 to 1500 K] with some of the experimentally determined boundaries for this reaction. Our value for the enthalpy of transition at 298.15 K is 3.09 ± 1 kJ/mol, in agreement with the value obtained by Akaogi and Navrotsky (1984) using molten salt calorimetry and with the estimate made by Kuskov et al. (1991). The uncertainty assigned to this value is large, reflecting the fact that significantly large (but undetermined) uncertainties exist in all portions of the data set. This value represents the average of the values listed in Table 7, excluding the value for 600 K. Combining the enthalpy of transition with the enthalpy of formation of quartz yields a value for the enthalpy of formation of coesite of -907.6 ± 1.4 kJ/mol.

The general third-law procedures are as follows (also see Robie 1965). First, the ancillary data required by the calculations are selected. These are the heat capacity and volumetric functions that are discussed below. Next, one assembles the phase equilibrium data and approximates the best slope for the data set. The boundary of Bohlen and Boettcher (1982) was chosen initially. Using this information, the enthalpy of transition is calculated for a series of P - T points that represent the selected reaction boundary. If the enthalpies of transition calculated from the data set display a drift (increasing or decreasing with increasing P and T), then the data are not internally consistent. In this case, the selected phase boundary was rotated and translated to minimize the drift. When the calculated enthalpies of transition cluster, values with larger deviations can be minimized through adjustments to the ancillary data within the limits of the uncertainty of that data.

As noted above, the calorimetric data provided by Holm et al. (1967) were questioned by several investigators (e.g., Weaver 1973a, 1979; Akaogi and Navrotsky 1984; Kuskov et al. 1991). These questions arise from attempts by the investigators to reconcile calorimetric and phase equilibrium data for the reaction quartz = coesite. The two pieces of data provided by Holm et al. (1967) used in calculating the equilibrium phase boundary be-

TABLE 5. Experimental heat capacities of synthetic jadeite corrected for curvature

<i>T</i> (K)	Heat capacity J/(mol·K)	<i>T</i> (K)	Heat capacity J/(mol·K)	<i>T</i> (K)	Heat capacity J/(mol·K)
Series 1		116.10	62.03	Series 4	
294.50	162.6	120.85	65.88	320.99	171.7
299.58	164.6	125.44	69.47	322.50	172.5
304.90	166.5	130.39	73.38	324.28	173.3
310.16	168.2	135.72	77.52	326.05	173.8
315.37	170.0	140.88	81.41	327.81	174.5
320.53	171.9	145.89	84.98	Series 5	
325.49	195.7	150.76	88.59	5.75	0.019
330.76	181.4	155.51	91.74	6.50	0.030
335.72	177.1	160.16	94.96	7.41	0.040
340.98	178.4	164.71	98.03	8.31	0.059
346.45	180.0	169.17	101.0	9.20	0.110
351.87	181.3	173.56	103.8	10.25	0.136
357.23	182.7	177.86	106.5	11.39	0.190
362.53	184.3	182.10	109.1	12.06	0.260
367.78	184.8	186.27	111.7	13.90	0.356
Series 2		194.43	116.5	15.36	0.521
321.61	171.6	198.43	118.9	16.90	0.670
322.79	172.5	201.93	120.9	18.60	0.881
324.12	173.1	207.00	123.7	20.22	1.110
325.59	173.8	212.00	126.4	21.99	1.350
327.06	174.1	216.92	128.9	24.60	1.752
328.53	174.7	221.78	131.5	27.50	2.335
329.99	175.2	225.58	133.9	29.82	2.783
331.45	175.6	231.31	136.4	32.99	3.411
332.99	176.1	235.99	138.7	36.40	4.150
334.61	176.6	240.61	140.8	Series 6	
Series 3		245.18	142.8	26.25	2.672
54.64	13.83	249.70	144.8	29.07	3.080
58.12	16.11	254.16	146.7	31.52	3.318
61.90	18.68	258.87	148.5	34.44	3.583
66.33	21.89	263.80	150.6	37.86	4.668
71.36	25.69	269.48	153.0	41.02	5.681
75.88	29.22	274.31	155.3	44.43	7.377
80.05	32.54	279.10	157.0	47.74	9.338
84.54	36.21	283.99	158.8	50.61	11.16
89.76	40.54	288.97	160.7	53.18	12.78
95.06	44.88	293.90	162.8	56.04	14.66
100.44	49.30	298.79	164.5	59.19	16.76
105.93	53.82	303.62	166.1	62.05	18.72
111.14	58.03	308.41	167.8	66.09	21.61

Note: Values are listed for a molar mass of 202.139 g.

TABLE 6. Thermodynamic properties for synthetic jadeite

<i>T</i> (K)	Heat capacity J/(mol·K)	Entropy J/(mol·K)	Enthalpy function J/(mol·K)	Gibbs energy function J/(mol·K)
5	0.006	0.002	0.002	0.001
10	0.125	0.033	0.026	0.007
15	0.469	0.139	0.109	0.031
20	1.092	0.356	0.273	0.083
25	1.882	0.681	0.513	0.168
30	2.808	1.105	0.817	0.288
35	3.832	1.613	1.173	0.440
40	5.286	2.204	1.582	0.622
45	7.697	2.958	2.120	0.838
50	10.70	3.921	2.824	1.097
60	17.36	6.452	4.684	1.768
70	24.63	9.665	7.006	2.659
80	32.50	13.46	9.696	3.767
90	40.66	17.76	12.68	5.079
100	48.91	22.47	15.89	6.579
110	57.11	27.52	19.27	8.251
120	65.18	32.84	22.76	10.08
130	73.05	38.36	26.33	12.04
140	80.64	44.06	29.94	14.12
150	87.92	49.87	33.56	16.31
160	94.87	55.77	37.18	18.59
170	101.5	61.72	40.77	20.95
180	107.9	67.71	44.32	23.38
190	114.0	73.70	47.83	25.88
200	119.8	79.70	51.28	28.42
210	125.3	85.67	54.67	31.00
220	130.6	91.63	58.01	33.62
230	135.6	97.54	61.27	36.27
240	140.4	103.4	64.47	38.95
250	144.9	109.2	67.59	41.64
260	149.2	115.0	70.65	44.35
270	153.3	120.7	73.64	47.08
280	157.3	126.4	76.55	49.81
290	161.1	131.9	79.40	52.54
300	164.8	137.5	82.19	55.28
273.15	154.6	122.5	74.56	47.94
298.15	164.1	136.5	81.68	54.78
	±0.35	±0.32	±0.10	±0.09

Note: Molar mass = 202.139 g.

tween coesite and quartz are the enthalpy of transition and the entropy at 298.15 K of coesite. Both of these values have been considered suspect. Each of these values must be examined separately.

Several values for the enthalpy of transformation of β quartz to coesite near 970 K have been measured with molten salt calorimeters: Holm et al. (1967) reported 2.93 ± 0.63 kJ/mol at 970 K; Akaogi and Navrotsky (1984) reported 1.35 ± 0.29 kJ/mol at 975 K; Akaogi et al. (1995) reported 1.27 ± 0.39 kJ/mol at 983 K; and Zhdikova et al. (1988) and Kuskov et al. (1991) reported 1.65 ± 0.42 kJ/mol at 973.15 K. Using these enthalpies of transition and the enthalpies of coesite (Table 1) and quartz (Hemingway 1987), we calculated 4.67 ± 0.8 , 3.08 ± 0.6 , 2.98 ± 0.7 , and 3.38 ± 0.6 kJ/mol, respectively, for the enthalpies of transition at 298.15 K. The latter three values are in agreement, but the value of Holm et al. (1967) is significantly different.

We concur with previous studies in recommending that the value for the enthalpy of transition of quartz to coesite given in Holm et al. (1967) be regarded as flawed. Enthalpy of solution measurements are generally more sensitive to errors arising from sample grain size than are heat-capacity measurements. Hemingway and Nitkiewicz (1995) have shown that the enthalpy of solution of finer grained ($<1 \mu\text{m}$) quartz can be as much as three kJ/mol larger than that for coarser grained (10 μm or greater) quartz. Because Holm et al. (1967) reported that the average grain size of their sample was 0.5 μm or less, it is likely that a significant surface energy effect was measured by Holm et al. (1967) in their enthalpy of solution experiments.

As noted above, this study confirms the entropy reported by Holm et al. (1967). Differences between the heat capacities reported here and those of Holm et al. (1967) were noted in several temperature ranges, but these had little effect on the entropy calculated at 298.15 K from those data.

If the entropy of coesite at 298.15 K reported by Holm et al. (1967) is correct, another value used in the analyses

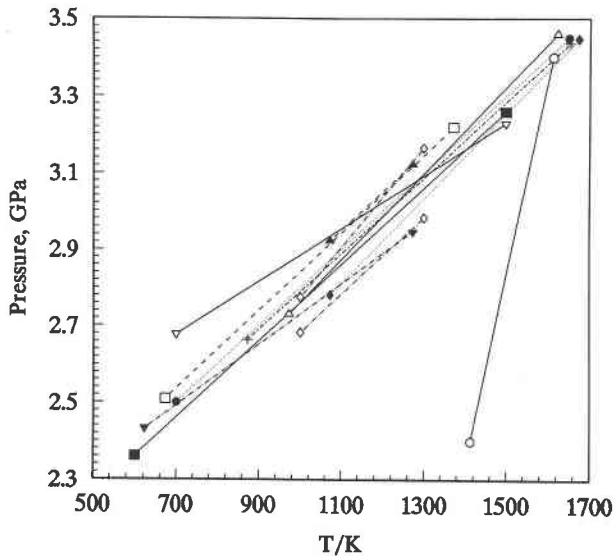


FIGURE 1. Comparison of the phase boundary for the quartz-coesite transition derived in this study with phase boundaries calculated from published experimental data. α quartz is stable at lower temperatures and pressures, coesite is stable at higher pressures, and β quartz is stable at higher temperatures. The curve calculated in this study is terminated by filled squares, and that calculated by Kuskov et al. (1991) is terminated by filled circles. The following symbols terminate curves representing experimental studies: Open diamonds = Mosenfelder et al. (1996); inverted open triangle = Bose and Ganguly (1995); filled diamonds = Kosyakov and Ishbulatov (1984); inverted filled triangles = Bohlen and Boettcher (1982) plus Mirwald and Massonne (1980); filled triangles = Akella (1979); open squares = Kitahara and Kennedy (1964); and open triangles = Boyd and England (1960). The line terminated with the open circles represents the α - β phase boundary for quartz derived by Cohen and Klement (1967).

of the phase equilibrium data sets must be in error. Some of these values are examined below.

The entropy and enthalpy increment (heat content) as a function of temperature are required to calculate the quartz = coesite equilibrium boundary. Commonly, these values are calculated from measured and estimated values

for the heat capacity. Watanabe (1982) measured the heat capacity of coesite and quartz between 350 and about 700 K. Hemingway (1987) and Grønvdal et al. (1989) reported heat-capacity measurements for quartz from 300 to 1000 K, values that are in agreement.

Akaogi and Navrotsky (1984) used the equations of Watanabe (1982) in their analysis of the quartz-coesite-stishovite transformations. Watanabe (1982) provided only an equation representing the experimental data. A comparison of values calculated from the Watanabe (1982) equations and the smoothed data given in Table 1 shows a rapid divergence of these values from the values selected here for coesite (see graph in Hemingway et al. 1995) and from values given by Richet et al. (1982) for silica glass and cristobalite. Extrapolation of these equations to 1500 K, as done by Akaogi and Navrotsky (1984), will result in significant overestimation of the heat capacity of coesite at higher temperatures as noted by Richet (1990) and Bose and Ganguly (1995).

Kuskov et al. (1991) used the equation provided by Watanabe (1982) and the heat capacity and enthalpy increment (heat content) values of Holm et al. (1967) to help derive an equation for the heat capacity of coesite that they used to 1100 K. Values calculated from this equation are in agreement with those adopted here, except at temperatures above about 1000 K.

Other investigations (Berman 1988; Holland and Powell 1990; Fei et al. 1990; Bose and Ganguly 1995) have selected values for the heat capacity of coesite and quartz given by Robie et al. (1978) and Hemingway (1987), respectively. The values given here for coesite are in agreement with those of Robie et al. (1978). However, the estimated heat-capacity values are higher by 1.4 J/(mol·K) at temperatures above about 1000 K. The uncertainty in the estimated heat capacities of coesite contributes to the large uncertainty in the calculated enthalpy of transition of the quartz = coesite reaction.

Values for the heat capacities of α quartz above the temperature of the α - β transition are required but they are problematic. Pre-transition heat effects can be seen in the heat-capacity measurements at temperatures well below the accepted transition temperature. Extrapolation of the

TABLE 7. Calculation of $\Delta_r H_{298.15}^{\circ}$ for the reaction quartz = coesite

$\Delta_r H_{298.15}^{\circ}$ (kJ/mol)	T (K)	P (kbar)	$(P-1) dV$ (J)	$T\Delta\Phi$ (J)	V_{coes}^* (J)	V_{qtz}^{\dagger} (J)	$\Phi_{\text{coes}}^{\ddagger}$ (J/mol)	Φ_{qtz} (J/mol)
2.94	600	23.6	-3653.6	714	2.024	2.179	-50.45	-51.64
3.04	700	24.6	-3941.1	903	2.024	2.184	-55.12	-56.41
3.09	800	25.6	-4244.9	1152	2.025	2.191	-59.81	-61.25
3.07	900	26.6	-4565.7	1494	2.025	2.197	-64.41	-66.07
3.04	1000	27.6	-4903.9	1860	2.026	2.204	-68.87	-70.73
3.05	1100	28.6	-5260.2	2211	2.028	2.212	-73.17	-75.18
3.13	1200	29.6	-5635.1	2508	2.029	2.219	-77.31	-79.40
3.17	1300	30.6	-6029.3	2860	2.030	2.227	-81.29	-83.49
3.10	1400	31.6	-6443.2	3346	2.032	2.236	-85.11	-87.50
3.10	1500	32.6	-6877.4	3780	2.034	2.245	-88.78	-91.30

Note: * $K = 960$ kb, $K' = 8.4$ (Levien and Prewitt 1981); and $\alpha_0 = 7.44 \times 10^{-6}$, $\alpha_1 = 4.44 \times 10^{-9}$ (Skinner 1966).

$\dagger K = 365$ kb, $K' = 5.9$ (d'Amour et al. 1979); and $\alpha_0 = 4.48 \times 10^{-5}$, $\alpha_1 = 6.3 \times 10^{-9}$ (see text).

$\ddagger \Phi = (G_T^{\circ} - H_{298}^{\circ})/T$.

heat-capacity data to higher temperatures requires removal of the effects of the transition at temperatures above about 500–600 K and addition of these effects as the P - T conditions approach the α - β phase boundary at higher pressures. It is not known whether pre-transition effects are important at the higher P - T conditions. Therefore, the values selected for the thermodynamic properties of α quartz at temperatures above the α - β transition temperature represent an educated guess and one of the four major sources of uncertainty in the evaluation of the quartz-coesite phase boundary.

The molar volumes of coesite and quartz as functions of pressure and temperature also are needed to calculate the quartz = coesite equilibrium boundary. Most studies use the thermal expansion data of Skinner (1966), the compressibility data of Levien and Prewitt (1981), and a form of the Murnaghan equation (Murnaghan 1949) to estimate the change of volume of coesite with pressure and temperature. This procedure seems to be satisfactory for coesite, but less so for quartz because of the α - β transition. Data for the compressibility of quartz are available from McSkimin et al. (1965), Jorgensen (1978), d'Amour et al. (1979), and Levien et al. (1980); and for thermal expansion from Kôzu and Takané (1929), Jay (1933), Rosenholtz and Smith (1941), Coenen (1963), Klement (1968), and Ackermann and Sorrell (1974). However, the thermal expansion data are affected by pre-transition effects that can give rise to overestimation of the thermal expansion. As is the case for the heat capacity, the volumetric properties of quartz likely reflect pre-transition effects as the boundary is approached from the α quartz stability field. Hosieni et al. (1985) have taken this approach and have estimated the volumetric properties of quartz at higher P - T conditions, including the pre-transition effects. We have estimated the volume without pre-transition effects at temperature and pressure using the form of the Murnaghan equation used by Akaogi and Navrotsky (1984): $V_T = V_{298}[1 + \alpha(T - 298)]/(PK'/K + 1)^{-1/K}$, where $\alpha = \alpha_0 + \alpha_1(T - 298)$ and represents the temperature dependent thermal expansion, V_{298} is the volume at 298.15 K and 1 bar, P is the pressure in kbar, and K and K' are the bulk modulus and its pressure derivative.

Differences in selection of data can have a large effect on the volume calculated at higher P - T conditions and subsequently on thermodynamic values derived from the data. For example, using the equation and parameters given by Akaogi and Navrotsky (1984), one estimates the volume of quartz to be 2.222 J/bar at 1000 K and 27.4 kbar and, at the same conditions, one estimates 2.188 J/bar from the data of Hosieni et al. (1985). The difference in volume estimates leads to a difference of about 1 kJ/mol in the estimated enthalpy of transition at 298.15 K. The differences are larger at higher temperatures and pressures. The volumetric properties of α quartz at higher P - T conditions are the third major source of uncertainty in the calculations.

We have selected an equation that provides a slope of dV/dT and curvature that is smaller than that used by

Akaogi and Navrotsky (1984) and a slightly larger slope and curvature than that used by Hosieni et al. (1985) in the temperature range 600 to 1200 K and at the pressures given in Table 7. In addition, the volumes calculated from this equation lie between those of the two studies cited. Because we have not applied a correction for pre-transition effects to the heat-capacity data, we do not attempt to estimate such effects for the volume of α quartz. The parameters for the Murnaghan equation that we used are listed in Table 7. They were derived from the thermal expansion and compressibility data listed above.

The fourth source of uncertainty in this analysis is that caused by the uncertainty in the phase equilibrium measurements. Numerous studies of the α quartz-coesite phase boundary have been reported, some of which are shown in Figure 1. Each reaction boundary is described by reversal data, but the set of boundaries define significantly different P - T slopes and initial P - T values. Mosenfelder et al. (1996) have shown significant differences based upon measurements using the same starting material and three different experimental apparatus. Their conclusion is that small differences in the design of a piston-cylinder can exert a significant effect on pressure calibration, thus the pressure uncertainty of many phase equilibrium studies may be significantly larger than reported in those studies. That is piston-cylinder apparatus calibrated at one set of P - T conditions will not necessarily remain in calibration with each other for other P - T conditions.

The procedure that we have taken has been one of attempting to minimize differences between calculated and experimental values by making small adjustments to the more uncertain data to provide a fit to the total data set (for example, the adjustment to the estimated heat capacities of coesite). Through an iterative procedure of calculations, we derived a calculated slope ($dP/dT = 0.001$ GPa/K) for the quartz = coesite phase boundary and an enthalpy of formation for coesite that is nearly the same as that derived by Kuskov et al. (1991). With our heat-capacity values, our value of $\Delta_{\text{trs}}H(298.15)$ for the quartz-coesite transition of 3.09 ± 1 kJ/mol (calculated from our analysis of the phase equilibrium experiments) is compatible with the measured value for the enthalpy of the transition at 975 K determined by Akaogi and Navrotsky (1984) and with the entropy of coesite given by Holm et al. (1967).

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