American Mineralogist, Volume 72, pages 273–279, 1987

Quartz: Heat capacities from 340 to 1000 K and revised values for the thermodynamic properties

BRUCE S. HEMINGWAY
U.S. Geological Survey, Reston, Virginia, U.S.A.

ABSTRACT

New heat-capacity data for quartz have been measured over the temperature interval of 340 to 1000 K by differential scanning calorimetry. The data were combined with recent heat-content and heat-capacity data to provide a significantly revised set of thermodynamic properties for α-quartz and to resolve the problem of disparate heat-content and heat-capacity data for α- and β-quartz. The results of this study show that the values of heat capacity and/or heat content and of the properties derived from these values that are listed in *all* recent tabulations of the thermodynamic properties of α-quartz are significantly low between about 600 and 800 K. The revised thermodynamic properties for α-quartz will most strongly affect calculations involving mineral reactions at moderate temperatures and higher pressures, such as those describing the evolution of materials in subducted plates, particularly where the data for α-quartz must be extrapolated to temperatures above 844 K for calculations involving higher pressures.

INTRODUCTION

The high-temperature thermodynamic properties of quartz have been extensively studied; however, results from both recent and older experimental studies differ significantly. Early compilations of the thermodynamic properties of quartz (e.g., Sosman, 1927) were based primarily upon the heat-content results reported by White (1919) and Wietzel (1921). Moser (1936) reported directly measured heat capacities that suggested that the earlier results of White (1919) and Wietzel (1921) were significantly high. Subsequent measurements by Sinelnikov (1953), O'Neill and Fyans (1971), and Ghiorso et al. (1979) tended to support the results reported by Moser (1936). More recent tabulations of the thermodynamic properties of quartz (e.g., Kelley, 1960; JANAF tables, Stull and Prophet, 1971; Barin and Knacke, 1973; Robie et al., 1979; Haas et al., 1981; and Hemingway et al., 1982) have given greater weight to the more recent experimental data. Richet et al. (1982) have reported heat-content results for the temperature interval 1000 to 1800 K. These modern experimental values strongly support a higher heat content as suggested in the results of White (1919) and Wietzel (1921). Consequently, both modern and older experimental data display a range of some 900 J/mol in the heat content (also called relative enthalpy or enthalpy) calculated at 1000 K (see Table 1), a range that is about four times the estimated precision of the experimental data sets.

Because the results reported by Richet et al. (1982) and Ghiorso et al. (1979) should have roughly equivalent precision and accuracy, and because both data sets were collected utilizing modern experimental equipment, it is important to identify the source of the discrepancy so that the thermodynamic properties of quartz may be unambiguously defined.

The disparate data are in the temperature interval of 400 to 1000 K, within the range of the laboratory differential scanning calorimeter (DSC). DSC data were collected over this interval to aid in the evaluation of the published data sets.

CODATA (Committee on Data for Science and Technology, International Council of Scientific Unions) has organized a Task Group on Geothermodynamic Data whose task shall be the evaluation and recommendation of key values and formats for tabulations of the thermodynamic properties of geologic materials. The subcommittee on the Thermodynamic Properties of Minerals has selected as key values the thermodynamic properties of quartz. This report provides a review of the experimental high-temperature heat-capacity and heat-content data and preliminary recommendations of the thermodynamic properties of quartz at 1 bar and at higher temperatures. CODATA committees (CODATA, 1976) have provided recommended values at 298.15 K for the entropy [41.46 ± 0.20 J/(mol·K)], heat content ($H_{298.15} - H_0 = 6.916 \pm 0.020$ kJ/mol), and enthalpy of formation from the elements (−910.7 ± 1.0 kJ/mol) of quartz that are based, in part, upon unpublished low-temperature heat-capacity data of E. F. Westrum, Jr. (e.g., Stull and Prophet, 1971), and confirmed by Gurevich and Khlyustov (1979). The CODATA recommended values are accepted and used as reference values in this report.

APPARATUS AND MATERIALS

The calorimeter and measurement procedures have been described elsewhere (Hemingway et al., 1981).

0003–004X/87/0304–0273$02.00

TABLE 1. Relative enthalpies calculated at 1000 K from experimental and tabulated data for quartz

Reference	Enthalpy* ($H_{1000} - H_{298}$) kJ/mol
Experimental	
White (1919)	45.551
Wietzel (1921)	45.861
Roth and Bertram (1929)	44.727
Moser (1936)	44.968
Sinelnikov (1953)	45.250
Holm et al. (1967)	45.680
Ghiorso et al. (1979)	44.705
Richet et al. (1982)	45.579
This study	45.520
Tabulations	
Mosesman and Pitzer (1941)	45.702
Kelley (1960)	45.689
Barin and Knacke (1973)	45.689**
Stull and Prophet (1971, JANAF)	45.355
Robie et al. (1979)	44.967
Haas et al. (1981) and Hemingway et al. (1982)	45.352
Pankratz (1982)	45.848
Ghiorso et al. (as corrected)	45.465†

* The enthalpy for intervals not reported in the original studies are calculated from the data given in this report.

** The authors used the tabulation from Kelley (1960).

† See discussion in text.

The quartz sample was a 27.918-mg portion of Standard Reference Material 1654, α-quartz (U.S. National Bureau of Standards, NBS). The source of the quartz was listed by NBS as Brazil. The sample was provided as a powder with a size range from 100− to 400+ mesh. The DSC sample was compacted and enclosed in a loosely crimped gold pan.

EXPERIMENTAL RESULTS

The heat capacities determined in this study are listed in Table 2. The observed heat capacities for α- and β-quartz have been fit with an equation of the form suggested by Haas and Fisher (1976). The data for α-quartz were constrained to fit the heat capacity of quartz at 298.15 K given by Westrum (pers. comm.; also see Gurevich and Khlyustov, 1979). The data for β-quartz were constrained to fit the smoothed values reported by Richet et al. (1982). The equations are listed in Table 3.

The usual polynomial form of the equations provides an excellent fit to the observed heat capacities except in the region of the α–β transition, from about 810 to 850 K. However, because the contribution of the heat capacity to the entropy varies as C_P/T and because the heat content is a fairly large value in comparison to the true heat capacity in this region, values of the entropy and heat content derived from integration of heat-capacity equations (Table 3) combined with an enthalpy of transition at 844 K of 625 J/mol will only differ significantly from the best values in a rather restricted temperature interval (about 840 to 850 K). Because the transition temperature is not well known (a point that will be discussed below) and because the change in the transition temperature is about 1 K for each 36 bars, the use of equations with functional forms designed to exactly fit λ-shaped heat-capacity curves is not, in general, warranted.

TABLE 2. Experimental DSC heat capacities for quartz

T K	C_P J/(mol·K)	T K	C_P J/(mol·K)	T K	C_P J/(mol·K)
Series 1		Series 5		Series 11	
340.3	48.78	587.7	64.74	816.1	77.32
350.1	49.48	597.6	65.19	821.1	77.41
359.9	50.24	607.6	65.45	826.1	78.73
369.6	50.93	617.5	66.00	831.0	80.46
379.4	51.68	627.5	66.28	836.0	82.62
389.2	52.41	637.4	66.74	838.5	85.98
399.0	53.06	647.4	67.14	840.9	88.33
408.8	53.76	657.4	67.54	841.9	90.52
418.6	54.44	667.3	68.19	842.9	92.93
428.4	55.10	677.3	68.60	843.9	99.91
438.3	55.72	687.2	69.12	844.9	186.3
448.3	56.30	696.2	69.61	845.9	282.0
458.3	56.86			846.9	116.7
468.2	57.56	Series 6		847.9	76.61
478.2	58.28			848.9	71.61
488.1	58.88	587.7	64.93	850.9	70.50
498.1	59.54	597.6	65.37	855.5	69.36
508.0	60.18	607.6	65.56	860.1	68.48
518.0	60.93	617.5	66.08	865.1	68.56
527.9	61.76	627.5	66.43	873.7	68.44
537.9	62.26	637.4	66.84		
546.9	62.93	647.4	67.06	Series 12	
		657.4	67.60		
Series 2		667.3	68.22	864.7	68.96
		677.3	68.82	874.4	68.08
528.5	61.83	687.2	69.32	884.0	68.96
538.4	62.00	696.2	69.55	892.7	69.25
548.4	62.17				
558.3	62.68	Series 7		Series 13	
568.3	63.46				
578.2	63.94	687.2	69.64	865.2	68.40
588.1	64.44	697.2	69.79	874.9	68.62
597.1	64.88	707.1	69.95		
				Series 14	
Series 3		Series 8			
				796.7	73.97
537.9	62.03	717.1	70.27	806.7	74.81
547.8	62.50	727.0	70.83	816.6	76.87
557.8	62.94	737.0	71.43	826.6	79.31
567.8	63.51	745.7	71.57		
577.7	63.96			Series 15	
587.7	64.52	Series 9			
596.6	65.08			913.5	68.29
		746.9	71.58	932.8	68.31
Series 4		756.9	71.81	941.5	68.64
		766.9	72.64		
797.7	74.36	776.8	72.63	Series 16	
807.7	75.14	786.8	73.40		
817.6	77.14			913.5	68.41
827.6	79.51	Series 10		923.1	68.67
837.5	85.14			932.8	68.23
845.4	236.0	796.7	73.98	941.5	69.02
		806.7	74.82		
		816.6	76.90	Series 17	
		826.6	79.32		
				989.6	69.25

Richet et al. (1982) have suggested that a polynomial of the form suggested by Haas and Fisher (1976) and used here will not adequately fit the data for α-quartz above 700 K. This perception arose as a consequence of the weighting scheme used by Richet et al. (1982), in which the data of Moser (1936) were preferentially selected. This problem will be discussed later in this paper.

The data of Ghiorso et al. (1979) were not used directly in calculating the thermodynamic properties of quartz for two reasons. First, the experimental data were not given.

TABLE 3. Thermodynamic properties for quartz from 298.15 to 1800 K

Note: The table is presented in a preliminary format for comment and discussion. The first line of references is reserved for the properties at 298.15 K. References on following lines are for the properties at higher temperatures. Reference 101 is Stull and Prophet (1971), 102 is CODATA, and 103 is this study. The molar volume of quartz and melting point for Si are from Robie et al. (1979).

QUARTZ Formula weight 60.085

SiO_2: Alpha quartz 298.15 to 844 K. Beta quartz 844 to 1700 K. Beta quartz is metastable above 1140 K. Melting point estimated to be 1700 K.

Temp.	Heat capacity	Entropy	Enthalpy function	Gibbs energy function	Formation from elements Enthalpy	Gibbs free energy
T	C_p°	S_T°	$(H_T^\circ - H_{298}^\circ)/T$	$-(G_T^\circ - H_{298}^\circ)/T$		
K	J/(mol·K)				kJ/mol	
298.15	44.59	41.460	0.000	41.460	-910.700	-856.288
	±0.09	±0.200			±1.000	
300	44.78	41.736	0.276	41.461	-910.708	-855.950
350	49.39	48.997	6.974	42.024	-910.857	-846.810
400	53.27	55.853	12.525	43.328	-910.868	-837.658
450	56.65	62.326	17.243	45.083	-910.746	-828.512
500	59.68	68.454	21.338	47.116	-910.559	-819.383
550	62.46	74.274	24.951	49.323	-910.261	-810.279
600	65.04	79.820	28.185	51.635	-909.877	-801.206
650	67.49	85.124	31.115	54.008	-909.410	-792.168
700	69.82	90.211	33.798	56.414	-908.860	-783.170
750	72.07	95.106	36.275	58.831	-908.233	-774.214
800	74.25	99.827	38.580	61.247	-907.527	-765.301
844	76.13	103.853	40.489	63.363	-906.840	-757.497
844	68.41	104.594	41.230	63.363	-906.215	-757.497
850	68.43	105.079	41.421	63.657	-906.164	-756.441
900	68.62	108.995	42.927	66.068	-905.746	-747.645
950	68.86	112.711	44.285	68.426	-905.343	-738.874
1000	69.12	116.250	45.520	70.730	-904.949	-730.123
1100	69.74	122.866	47.693	75.173	-904.183	-712.677
1200	70.43	128.963	49.559	79.405	-903.426	-695.301
1300	71.17	134.630	51.193	83.437	-902.663	-677.987
1400	71.96	139.933	52.648	87.285	-901.884	-660.733
1500	72.77	144.925	53.962	90.963	-901.078	-643.537
1600	73.60	149.648	55.163	94.485	-900.238	-626.396
1700	74.45	154.136	56.273	97.863	-949.865	-608.853
1700	81.37	159.662	61.799	97.863	-940.470	-608.853
1800	81.37	164.313	62.887	101.426	-938.605	-589.398
References	101 103	102			102	

$H_{298}^\circ - H_0^\circ$ 6.916 ±0.020 kJ

Molar volume 2.2688 ±0.0001 J/bar

Transitions in phase

Alpha - beta 844 K
Enthalpy 0.625 kJ

Melting point 1700 K
Enthalpy 9.395 kJ

Transitions in reference state elements

Silicon M.P. 1685 K

Equations

$$C_p^\circ = 81.1447 + 0.0182834T + 5.4058\times10^{-6}T^2 - 698.458T^{-0.5} - 180986T^{-2}$$

(Valid range: 298.15 to 1000K; Average absolute percent deviation: 0.30)

$$C_p^\circ = 57.9588 + 9.33019\times10^{-3}T + 1834713T^{-2}$$

(Valid range: 844 to 1700 K; Average absolute percent deviation: 0.36)

Compiled 86/04/25

Second, a review of the heat capacities calculated from the equation given by Ghiorso et al. (1979) shows two nearly linear sections, 400 to 450 K and 450 to 750 K. Such linear segments are typical of underfitting and overfitting of heat-capacity data. If the experimental heat capacities were underfit from about 450 to 750 K, as seems probable, then the equation would tend to overfit the experimental results from 750 to about 800 K. Even though the curvature of the equation may locally deviate from the curvature of the experimental heat capacities, integration of the equation over the interval represented by the data should provide a reasonably accurate value for the relative enthalpy because of the least-squares procedure employed by Ghiorso et al. (1979).

Smoothed values of the thermodynamic properties for quartz are listed in Table 3. The enthalpy of fusion and the heat capacity of the melt are taken from Richet et al. (1982). The heat capacities reported here are in excellent

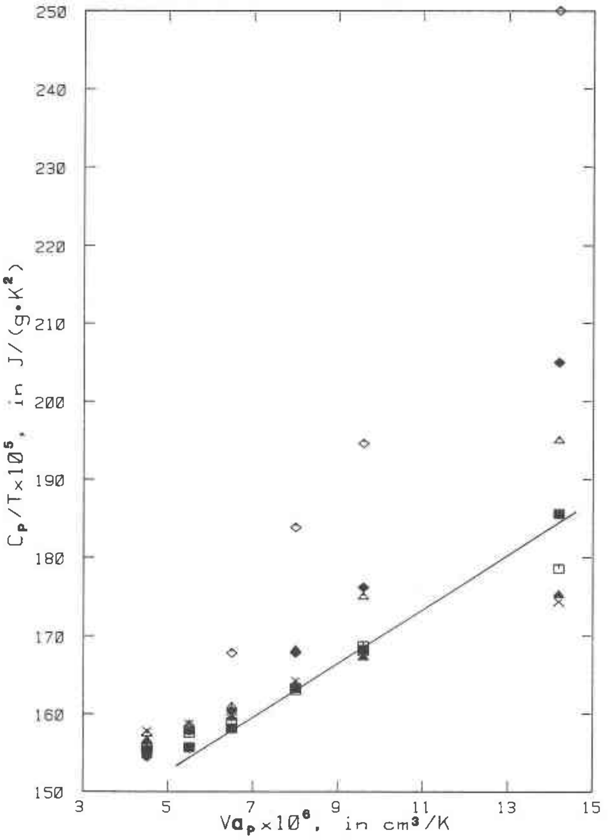

Fig. 1. C_P/T vs. $V\alpha_P$ utilizing Pippard's (1957) relationship as described by Equation 4. The values of $V\alpha_P$ are taken from Hughes and Lawson (1962). The filled squares (■) are based on the heat capacities reported in this study. The slope of the line through these data is 0.029 K/bar. The remaining data are ◇, Hosieni et al. (1985); ▲, Richet et al. (1982); ×, Ghiorso et al. (1979); △, O'Neill and Fyans (1971); ◆, Sinelnikov (1953); and □, Moser (1936).

agreement with the heat-capacity equations given by Ghiorso et al. (1979). The enthalpy calculated for quartz at 1000 K from the heat capacities reported in this study also is in excellent agreement with the value determined independently by Richet et al. (1982). These apparently contradictory results will be discussed in a later section.

SELECTION OF HEAT CAPACITIES FOR α-QUARTZ

Pippard (1957) has suggested a cylindrical approximation to the form of the entropy (S) and volume (V) surfaces in the region of the critical temperature that can be used to test the heat-capacity data reported here as well as the older results. The entropy at the critical temperature will be a smoothly varying function of pressure if the heat capacity tends to rise to infinity at the critical temperature, and the surface will have a regular fold along the transition line (Pippard, 1957). The cylindrical surface is defined over a short range of pressure (P) in the region of a critical temperature by Equation 1,

$$S = S_\lambda(P) + f(P - aT), \qquad (1)$$

where a is the slope (dP/dT) of the critical-temperature line. A similar argument was provided for the volume (Pippard, 1957). Following Hughes and Lawson (1962), in the region of the critical temperature, the heat capacity is given by Equation 2,

$$C_P/T = (dP/dT)_\lambda V\alpha_P + h(P), \qquad (2)$$

where h is a constant for data obtained at constant pressure, α_P is the isobaric coefficient of thermal expansion, and C_P is the specific heat and where a plot of C_P/T vs. $V\alpha_P$ should be a straight line with the slope $(dP/dT)_\lambda$.

Pippard's theory (1957) was tested on the α–β transition in quartz by Hughes and Lawson (1962) and later applied by Garland (1964), Klement and Cohen (1968), and Hosieni et al. (1985). In each study the data of Moser (1936) were examined and found to be less accurate than data for the volumetric or elastic properties of quartz (data from, e.g., Mayer and Lecomte, 1960, and Ackerman and Sorrell, 1974), on the basis of a comparison of the slope $(dP/dT)_\lambda$ calculated for the phase transition in these studies with the slope established by Yoder (1950) of 0.0287 K/bar.

Heat capacities from several experimental and evaluated data sets for α-quartz have been examined using Pippard's theory and following the procedures of Hughes and Lawson (1962). The results are shown in Figure 1. Slopes calculated from these data sets range from 0.0092 K/bar (Hosieni et al., 1985) to 0.039 K/bar (Moser, 1936). The heat-capacity results presented in this study yield a slope of 0.029 K/bar, in good agreement with the results of Yoder (1950) and with calculated values given by Hughes and Lawson (1962) of 0.028 K/bar, by Garland (1964) of 0.026 K/bar, and by Klement and Cohen (1968) of 0.026 K/bar.

Because the calculated value of dP/dT strongly depends on the data closest to the critical temperature, slight errors in the practical temperature scales between laboratories as well as systematic errors in heat capacity will produce significant differences in results calculated from the Pippard theory. In this case, shifting the temperature of the heat capacities for the α–β transition from this study by −1.5 K with respect to those given (Hughes and Lawson, 1962) for the volumetric properties (effectively increasing the width of the transition region) would produce agreement between the recalculated slope and that reported by Hosieni et al. (1985); similarly, a shift of +1.5 K would yield agreement with the slope calculated from the data of Richet et al. (1982).

Application of the Pippard theory to λ-transitions is, in general, restricted to the temperature interval below (or above) the critical temperature unless the heat-capacity curve is symmetrical (Pippard, 1957). The reason for this limitation follows from the shape of the entropy surface above the critical-temperature line. The entropy curve as a function of temperature reaches a point of inflexion at the critical temperature, and, for symmetrical λ-transitions, the curve continues without a discontinuity. For asymmetrical λ-transitions, of which the α–β transition in quartz is an example, the entropy curve has a discontinuity, and the cylindrical approximation is no longer valid across the transition line. Consequently, use of properties of the β-phase to define the α-phase (e.g., Hosieni et al., 1985) is incorrect (also see the discussion by Bachheimer, 1980). Evidence of the asymmetrical shape of the α–β transition in the heat capacity of quartz and evidence of an incommensurate phase between the α and β phases have been presented by Dolino and Bachheimer (1983) using DSC and by Hatta et al. (1985) and Matsuura et al. (1985) using ac-calorimetry, in the thermal expansion and elastic constants by Bachheimer (1980), and in the X-ray diffraction data of Gouhara and Kato (1984). Results similar to those shown by Dolino and Bachheimer (1983) were found in this study.

The excellent agreement between the value of $(dP/dT)_\lambda$ calculated from the heat capacities and the value reported by Yoder (1950) may be fortuitous. However, the added agreement between the enthalpy calculated at 1000 K from the heat capacities reported in this study and the enthalpy independently determined by Richet et al. (1982), as well as the excellent agreement between these heat-capacity data and the heat-capacity equation reported by Ghiorso et al. (1979), strongly supports the selection of the new heat-capacity measurements in preference to those in earlier studies.

DISCUSSION

Comparison of recent studies

The heat-capacity results reported in this study are in excellent agreement, within the limits discussed below, with two recent but discordant experimental data sets for quartz, Ghiorso et al. (1979) and Richet et al. (1982). This result suggests that one of these two discordant data sets contains a systematic error that can be identified by comparison with the new heat-capacity data set. Richet et al. (1982) measured the heat content of β-quartz at 1000 K and obtained a value that is supported by integration of the heat capacities reported in this study. The individual heat capacities reported in this study are in good agreement with the heat-capacity equation provided by Ghiorso et al. (1979). These observations suggest that the systematic error is in the work presented by Ghiorso et al. (1979).

Ghiorso et al. (1979) reported a value for the relative enthalpy of quartz of 32 950 J/mol for the temperature interval of 400 to 900 K. Integration of their heat-capacity equation yields a value of 33 176 J/mol for the same temperature interval, but only if one assumes a constant heat capacity of 70 J/(mol·K) through the anomalous heat-capacity region. Clearly, Ghiorso et al. (1979) did not account for the full value of the anomalous heat capacities associated with the phase transition in quartz in their calculation, as these values rise to greater than 250 J/mol in the region of the anomaly. Using the heat capacities from this study, the enthalpy error can be estimated to be about 760 J/mol, which, when added to the enthalpy reported by Ghiorso et al. (1979), yields an enthalpy for β-quartz in excellent agreement with the data set reported by Richet et al. (1982) and resolves the discrepancy in these data sets. J. Stebbins (pers. comm.) has noted that the value of the correction is equal to the integral of the baseline heat capacity from 842 to 851 K and probably represents the source of the computational error.

Evaluation of the results of Moser (1936)

The heat-capacity values reported by Moser (1936) are in good agreement with the heat capacities reported here for the temperature interval of 300 to 500 K. At temperatures above 500 K, Moser's (1936) results deviate strongly from those reported in this study, reaching a difference of −1.9% at 700 K. Moser (1936) also reported heat capacities for Ag and Ni in the same report. Hultgren et al. (1973) have critically reviewed heat-capacity and heat-content data for Ag and Ni and have concluded that the data for those phases reported by Moser (1936) were significantly low (−1.5 to −2%) at 700 K (also see Klement and Cohen, 1968).

Most modern compilations of the thermodynamic data for α-quartz are strongly influenced by the heat-capacity data reported by Moser (1936) (e.g., Kelley, 1960; JANAF, Stull and Prophet, 1971; Barin and Knacke, 1973; Helgeson et al., 1978; Robie et al., 1979; Haas et al., 1981; Hemingway et al., 1982; Pankratz, 1982; Richet et al., 1982; and Hosieni et al., 1985). The enthalpies of α-quartz at 800 K listed in each of the references cited above agree to better than 0.1%, with the single exception of the results reported by Hosieni et al. (1985). However, these values are about 0.6% (0.9% in the case of Hosieni et al., 1985) lower than the value found in this study or the value that may be deduced from the data of Ghiorso et al. (1979). The systematically low values of Moser (1936) depressed the calculated heat-capacity curves.

Richet et al. (1982) were unable to fit their selected data set for α-quartz using the form of polynomial equation suggested by Haas and Fisher (1976). The systematic deviation of the heat capacities of Moser (1936) that helped constrain the polynomial equations derived by Richet et al. (1982) followed by the onset of higher heat capacities associated with the phase transition resulted in a change in curvature that could not be adequately fit by the standard form of the polynomial. The fault lies in the systematically low data that produce an abnormal flattening of the heat-capacity curve between 600 and 750 K, not in the form of the equation.

Temperature and enthalpy of transition

The transition temperature chosen in this study is the extrapolated onset temperature given by the U.S. National Bureau of Standards (McAdie et al., 1972). The value of 844 K is established from an evaluation of the results reported by an international group of 34 investigators who all worked on portions of the same sample. The estimated uncertainty of this value is ±5 K. The range of values is about ±10 K. This work represents the best efforts of these investigators and thus provides an excellent estimate of the order of magnitude of systematic errors for historic temperature measurements. The values of 846 K (Keith and Tuttle, 1952), 847 K (Moser, 1936), and 848 K (Kelley, 1960) are within the uncertainty interval, but are rejected in favor of the value determined by international consent.

More recently, ASTM (ASTM E967-83, 1985) has published standard practices for the calibration of temperature for differential scanning calorimeters and differential thermal analyzers. Results reported in that paper for an interlaboratory comparison of the transition temperature (melting point) of Pb based on a two-point calibration and using four types of instruments located in 14 laboratories showed an average deviation of 0.52 K and a confidence interval of about 1.5 K. These results should be applicable to the intercomparison of heat-capacity data from modern DSC and thermal-analysis systems. As an example, let us examine the 4-K difference in the α–β transition temperature for quartz as given here and by Ghiorso et al. (1979), both DSC studies. Ghiorso et al. (1979) have reported a transition temperature of about 848 K for quartz samples from six different source materials. Their temperatures are based on a two-point calibration using K_2SO_4 and Pb as temperature standards and using the extrapolated onset calculation method (as used in this study). Their fixed points were 858.2 and 600.62 K, respectively, for K_2SO_4 and Pb. The values chosen by Ghiorso et al. (1979) represent equilibrium temperatures rather than extrapolated onset temperatures. For simplicity, we can assume that errors in the temperature assigned to Pb are insignificant because of the proximity of the transition temperatures for quartz and K_2SO_4. The extrapolated onset temperature for K_2SO_4 used in this study is 855 K or some 3 K lower than the value used by Ghiorso et al. (1979). The equilibrium temperature for the transition in K_2SO_4 is 1 K higher than the extrapolated onset temperature (McAdie et al., 1972). Therefore, we can expect the transition temperatures reported by Ghiorso et al. (1979) to be about 4 K higher than similar values reported from this study. These differences are the consequence of the use of different practical temperature scales in each laboratory and are not a consequence of differences in sample chemistry.

The study by McAdie et al. (1972) has shown that even though individual investigators can attain a high degree of precision [e.g., ±0.2 K for the extrapolated onset temperature reported in this study and similar results reported by Ghiorso et al. (1979) for several samples of quartz from different locations], the standard deviation of mean values for transition temperatures is, in general, 5 to 8 K with a spread of 20 to 50 K depending upon the material studied. Therefore, temperature, as well as heat capacity and heat content, must be appraised when thermodynamic properties are simultaneously evaluated.

Although most modern tabulations of the thermodynamic properties of quartz are in good agreement at 800 K, large deviations exist at 1000 K. These differences are directly attributable to the process by which the enthalpy of the α–β transition is determined. The evaluations by Stull and Prophet (JANAF, 1971), Robie et al. (1979), and Haas et al. (1981) involved evaluation of the transition enthalpies separately and selection of a best estimate for the enthalpy of transition with respect to the equations selected for α- and β-quartz. Richet et al. (1982), Pankratz (1982), and Kelley (1960) evaluated data sets that combined the results from several studies within the region of rapidly increasing heat capacities and obtained values that are significantly larger (by 350 J/mol or more) than those found by Stull and Prophet (1971), Robie et al. (1979), or Haas et al. (1981). The use of the combined data set ignores the potential errors in relative temperature scales and, in general, leads to a broadening of the anomalous heat-capacity region and the calculation of an enthalpy that is too large.

Hosieni et al. (1985) used the Pippard theory (1957) and the properties of β-quartz to calculate heat capacities for α-quartz and to calculate the enthalpy of the phase transition. Pippard (1957) clearly indicated that, for transitions with the form shown by the α–β transition in quartz, the properties of the high-temperature form cannot be used to estimate the properties of the low-temperature form. Therefore, it is not surprising that the value estimated by Hosieni et al. (1985) is significantly larger than the average value calculated from experimental heat-capacity and heat-content data.

CONCLUSIONS

Resolution of the disparate heat-content and heat-capacity data for α- and β-quartz has been possible. Recent experimental data (heat-content, Richet et al., 1982; and heat-capacity, Ghiorso et al., 1979, and this study) combined with an evaluation of older experimental and tabulated data strongly suggest that the results reported by Moser (1936) are systematically in error by about −1.8% at 700 K. As a consequence of the reliance on this data by most authors of recent tabulations of the thermodynamic properties of quartz, the properties of α-quartz listed in all recent tabulations are incorrect for temperatures above 500 to 600 K. Furthermore, differences in processing heat-content and heat-capacity data in the region of the phase transition have led to a wide scatter in the properties reported for quartz at 1000 K in comparison to good agreement in those same tables for temperatures below the transition.

The major consequence of the revision of the thermodynamic properties of α-quartz will be seen in calculations of mineral reactions involving moderate temperatures and higher pressures such as one would expect for reactions occurring in subducted plates and regional metamorphism. This is particularly true where the properties of α-quartz must be extrapolated to temperatures above the 1-bar α–β quartz transition temperature for calculations involving higher pressures.

ACKNOWLEDGMENTS

I thank J. L. Haas, Jr., G. R. Robinson, Jr., J. F. Stebbins, and P. Richet for their informed and constructive comments on this paper.

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MANUSCRIPT RECEIVED JULY 22, 1986
MANUSCRIPT ACCEPTED DECEMBER 1, 1986