

Thermodynamics of the lambda transition and the equation of state of quartz

KOROSS R. HOSIENI, REED A. HOWALD, AND MATTHEW W. SCANLON

Chemistry Department
Montana State University
Bozeman, Montana 59715

Abstract

The published data on the alpha–beta transition in quartz are reanalyzed using Pippard's theory and modern computer techniques. Volume data confirm the difficulties in reaching equilibrium in alpha quartz near the transition, explaining the low and irreproducible heat capacity measurements in this region. The pressure dependence of the transition temperature and the best X-ray volume measurements are used to evaluate entropy and enthalpy changes in the transition region. At 1000 K the entropy and enthalpy of beta quartz are 116.215 ± 0.1 J mol⁻¹ K⁻¹ and -865256 ± 70 J mol⁻¹ relative to the CODATA selections for alpha quartz at 298.15K. These values are in excellent agreement with the completely independent selections of Richet et al., but not with USGS Bulletin 1452. Full equation of state data for quartz up to 1900 K and 4000 MPa are given graphically and by equations valid for designated portions of the *P*–*T* plane. The SiO₂ phase diagram has been calculated including cristobalite, coesite, and liquid regions. The existence of an intermediate incommensurate phase between alpha and beta quartz is discussed, but not included explicitly in the calculations.

Historical

Quartz is a common and widely studied mineral. Its lambda transition near 846 K was reported by Le Chatelier in 1889 (Le Chatelier, 1889), making it the earliest known example of such behavior. This interesting feature led to an exceptionally large number of experimental studies of quartz.

Thus it would seem reasonable to assume that the thermodynamic properties of quartz are all well established, and that the standard compilations (Stull and Prophet, 1971; Robie et al., 1978) agree. However the heat changes on melting and in many other transformations of SiO₂ are small and discrepancies of 200 J mol⁻¹ are significant in phase equilibria calculations. Thus we were very surprised to find a 380 J mol⁻¹ discrepancy between the JANAF (Stull and Prophet, 1971) and the Bulletin 1452 (Robie et al. 1978) values for beta quartz. Richet et al. (1982) fully document the discrepancy between heat capacity, d.t.a., and drop calorimetry values for quartz. These discrepancies are the cause of the wide range in values for $H_{1000} - H_{298}$ cited in the literature, some of which are shown in Table 1.

One of the main purposes of this paper is to provide accurate and useable thermodynamic data for both alpha and beta quartz. A second result is the demonstration that the alpha–beta transition in quartz can be accurately treated as a lambda transition using the Pippard theory. (Pippard, 1956).

The quartz transition

There are, however, a number of reasons for thinking that a first order transition may be present in quartz in the

region of the alpha–beta transition. Some of these will be examined briefly here, before considering methods of treating second order or lambda type transitions quantitatively.

Alpha quartz and beta quartz do have different crystal structures. However, the crystal structures are related, and in practice the transition occurs without recrystallization. The six-fold screw axis of beta quartz is converted to a three-fold screw axis in alpha quartz, with alignment of kinks in the Si–O–Si chains. Good discussions of the motions involved, and the domains formed, can be found in Liebau and Bohm (1982) or Grimm and Dorner (1975). This alignment is clearly a cooperative phenomenon characteristic of lambda type transitions.

The distinction between first order transitions and lambda type transitions is fairly subtle, because kinetic considerations can spread a first order transition over a range of temperatures, making it appear somewhat like a lambda transition. Thus high heat capacities alone do not signal the presence of a lambda transition. The lambda point, at which a very high heat capacity drops over a very narrow temperature range is diagnostic. There is no doubt that quartz shows a lambda point near 846 K at low pressures, and also along a line of increasing temperature with increasing pressure. The lambda point even appears, without the lambda shape, in differential scanning calorimetry. Thus the accuracy and reproducibility of measurements of the lambda point are surprisingly good, better than that for the temperatures of many first order transitions.

Why then is the concept of a first order part in the alpha–beta quartz transition so persistent in the literature? It is partly a matter of politeness. More importantly, in-

Table 1. Values reported for the enthalpy change between alpha quartz at 298.15 K and Beta Quartz at 1000 K

$H_{1000,\beta} - H_{298,\alpha}$	Type	Reference
45689.3	Compilation	Robie et al. 1968
45689.3	Compilation	Kelley (1960)
45617.	Exp. d.c.	Richet et al. 1982
45579.	Compilation	Richet et al. 1982
45452.	Calculation	*
45444.3	Compilation	This work
45358.7	Compilation	Barin and Knacke, 1973
45354.6	Compilation	Stull et al. 1971
45056.2	Exp. Cp	Moser, 1936
44967.	Compilation	Robie et al. 1978
44826.9	Exp. dta	Ghiorso et al. 1979

* calculation using values for SiO_2 glass and data of (Kracek et al., 1953), (Richet et al., 1982) and (Navrotsky et al., 1980)

cluding a first order transition at the lambda temperature is a convenient simple way to model lambda transitions. For example the curves in Figure 1 can be approximated by straight lines, with a jump from one line to the other at $846 - T = 0$. Thus it is convenient to model the last 20% or so of the transition as first order.

Finally, the assertion that there is a superimposed first order transition associated with a lambda transition cannot be disproved. A first order transition could occur very close to a lambda point. Keeping the temperatures close at high pressures is stretching the coincidence. The thermodynamic analysis presented here, omitting any first order part, demonstrates that the simpler assumption, that this is purely a lambda type transition, is adequate.

This paper is concerned with thermodynamic equilibria and with obtaining accurate values for the two most important quartz phases. Our agreement with Richet et al. (1982) demonstrates that you can get equivalent values of enthalpy by either including or omitting a first order part for the transition.

Of course, non-equilibrium forms of quartz can be prepared, and in fact are usually prepared in practice. The careful study of materials at temperatures near lambda points is providing much important new material including the recognition of incommensurate phases (Shirane (1984); Aslanyan and Levanyuk (1978, 1979, 1984)). The recent work of Bachheimer and his co-workers (Bachheimer, 1980; Bachheimer et al., 1982; Dolino et al., 1983, 1983, 1984) on quartz is an outstanding example.

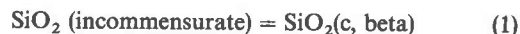
However, in interpreting these papers it must be recognized that the structure of the beta phase must exist in the boundaries between dauphiné domains, so that the equilibrium coexistence of two phases does not necessarily indicate a first order transition between them.

It is possible that one or more other phases are thermodynamically stable near the lambda point in quartz. In this case the direct alpha to beta transition considered here would be metastable.

Bachheimer, Dolino and their co-workers (Bachheimer, 1980; Bachheimer et al., 1982; Dolino et al., 1983, 1983, 1984) have exhaustively studied a transition occurring 1.3 K above the lambda point. It is highly reproducible with

negligible hysteresis, and so probably represents the formation of a stable phase. Probably this is an incommensurate phase as originally suggested by Aslanyan and Levanyuk (1979). As such it represents a small amount of ordering of the twists of SiO_4 tetrahedra with a loss of strict periodicity. The structure can also be described in terms of short range order, or fluctuating small dauphiné domains.

The incommensurate phase will be identical to the beta phase at some temperature near 847 K. It has a higher heat capacity and coefficient of thermal expansion than beta quartz, so by 846 K the reaction



should have $\Delta H = 60 \pm 40 \text{ J mol}^{-1}$, $\Delta S = 0.07 \pm 0.05 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta G = +0.035 \pm 0.02 \text{ J mol}^{-1}$. These quantities are small compared to the overall uncertainties so there is no point in building a separate thermodynamic model for the incommensurate phase.

The enthalpy of beta quartz

The drop calorimetric clearly establish a value for $H_{1000,\beta} - H_{298,\alpha}$ of $45500 \pm 200 \text{ J mol}^{-1}$. Moser's value (Moser, 1936) is clearly outside this range, and two recent tabulations (Robie et al., 1978) (Ghiorso et al., 1979) give even smaller values.

If the transition were a reversible first order transition we could get accurate enthalpies for beta quartz from the volume change and the pressure dependence of the alpha-beta equilibrium. The pressure dependence has been care-

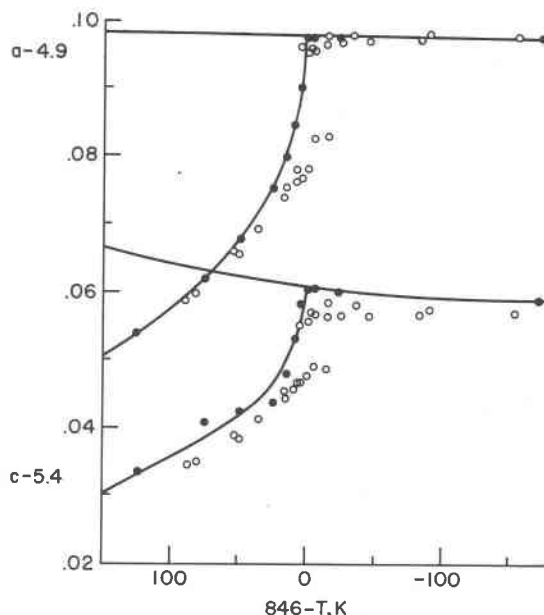


Fig. 1. Cell dimensions for alpha and beta quartz versus temperature. Our calculated fits to the values of Ackerman and Sorrell (Ackermann and Sorrell, 1974, filled circles) are shown as solid lines. Older experimental values (Jay, 1933; Berger et al., 1966) are included as open circles.

fully studied. The initial slope is approximately 0.265 (Cohen et al., 1974) and above 1500 MPa the line is essentially straight with a slope of $0.2272 \text{ K MPa}^{-1}$ (Mirwald and Massone, 1980). However, careful volume measurements near the transition temperature have shown that ΔV for the metastable alpha to beta transition is very small, and may be zero.

In a true lambda transition the heat capacity of the lower temperature phase increases rapidly as the transition temperature is approached, probably approaching infinity, and both ΔH and ΔV are zero. Thus the expression

$$dT/dP = \frac{T \Delta V}{\Delta H} = \Delta V/\Delta S \quad (2)$$

is indeterminate. The equations obtained for the indeterminate expression by taking separate derivatives of the numerator and denominator are easily derived and are quite well known

$$dT/dP = \Delta\alpha VT/\Delta C_p = -\Delta\beta/\Delta\alpha \quad (3)$$

but do not provide much help. The heat capacity, coefficient of thermal expansion, and compressibility for alpha quartz near the lambda point are all large and difficult to measure. In fact it appears that ΔC_p , $\Delta\alpha$ and $-\Delta\beta$ all approach infinity. If the coefficient of thermal expansion of alpha quartz is extremely large at temperatures just below the lambda point, it is not surprising that small temperature fluctuations can introduce significant strain and that reproducible measurements are difficult.

Fortunately, the Pippard theory (Pippard, 1956) provides an accurate way to analyze thermodynamic data in the vicinity of a lambda point. The original equations proposed by Pippard were of the form:

$$V(T, P) = V_0 + aT + f(T/r - P) \quad (4)$$

$$S(T, P) = S_0 + aT + f'(T/r - P) \quad (5)$$

where r stands for the equilibrium slope, $(dT/dP)_\lambda$. We can write the equivalent expressions

$$V_{\text{alpha}} = V_{\text{beta}} - (r/r_0)f(\theta) \quad (6)$$

$$S_{\text{alpha}} = S_{\text{beta}} - (1/r_0)f(\theta) \quad (7)$$

where θ is $T_\lambda(P) - T$, the amount the temperature is below the lambda temperature at any pressure, and where V_{beta} and S_{beta} are the volume and entropy of the beta phase (disordered quartz) as functions of temperature and pressure.

Equations of this kind have been applied to the alpha-beta transition in quartz (Hughes and Lawson, 1962; Klement, 1968; Klement and Cohen, 1968) with moderate success. The Pippard relations are used by Bachheimer and Dolino (Bachheimer et al., 1982; Dolino et al. 1983, 1983) even while they call the transition first order. The principal problems with this approach appear to have been with the experimental data used. The relations are satisfied if all the measurements are on the same sample, or if the same equilibration time is allowed. The Sinelnikov (Sinelnikov, 1953)

heat capacity data are a distinct improvement over Moser's (Moser, 1936), but fundamentally one cannot expect to find good heat capacity data for small temperature intervals in a region where long time periods, 20 minutes or more, are required for equilibration at each temperature. Fortunately, volume measurements are simpler and require only one equilibration per data point. We have evaluated the function $f(\theta)$ from the careful X-ray data of Ackerman and Sorrell (Ackerman and Sorrell, 1974).

Alpha quartz is trigonal and beta quartz is hexagonal. Both crystals can be referenced to hexagonal axes, and two edges of the unit cell, a and c , are needed. For beta quartz the unit cell edges in angstroms from the X-ray measurements can be fitted as quadratics in $\theta = 846 - T$ as:

$$a = 4.9978 + 0.30765 \times 10^{-6} \theta \quad (8)$$

$$c = 5.4608129 + 0.264750 \times 10^{-4} \theta + 0.822328 \times 10^{-7} \theta^2 \quad (9)$$

Both cell dimensions are decreasing slightly with increasing temperature, but the temperature dependence is small enough that an extrapolation to $\theta = 200$, down to 646 K, appears to be justified.

On the other hand the unit cell dimensions for alpha quartz vary drastically with temperature when θ is small. A simple power series using integral exponents is obviously unsatisfactory. Much good work on alpha quartz and similar materials has considered the leading power as a variable. For example the term $[CT(1 - T/847)^{-0.08731} - 1]$ has been used for the heat capacity (Richet et al., 1982). In this situation one can consider a log-log plot and equations like

$$\log(a - a_\alpha) = -2.362348 + 0.49759 \log \theta \quad (10)$$

Such plots are roughly linear with slopes between 0.4 and 0.7, however, adding higher powers in $\log \theta$ even up to a quartic still does not give an accurate representation of the measured values.

A better alternative is using a power series with a leading term in $\theta^{1-\alpha}$ where the power $1 - \alpha$ lies between zero and one. There are sufficient theories for lambda transitions from Bragg-Williams (Bragg and Williams, 1934) through a series of developments (Ross and Ter Haar, 1959; Landau and Lifshitz, 1958) up to renormalization group theory (Kandanoff et al., 1967; Levy et al., 1980) to justify almost any choice of power from 0.20 through 0.875 (Levy et al., 1980) even up to 0.95, but the simplest and easiest is 0.5. In this case $(a - a_\beta)^2$ and $(c - c_\alpha)^2$ will be simple power series in θ with no constant term. We can divide by θ and use standard least squares programs. In this way we obtained the equations:

$$(a_\beta - a_\alpha)^2 = 0.0226806 \times 10^{-3} \theta - 0.867408 \times 10^{-7} \theta^2 + 0.259547 \times 10^{-9} \theta^3 - 0.242458 \times 10^{-10} \theta^4 \quad (11)$$

$$(c_\beta - c_\alpha)^2 = 0.0105995 \times 10^{-3} \theta - 0.573545 \times 10^{-7} \theta^2 + 0.373483 \times 10^{-9} \theta^3 - 0.449171 \times 10^{-12} \theta^4 \quad (12)$$

Figure 1 shows how these calculated cell dimensions compare to measurements between 700 and 900 K. The scatter in the c_z values looks bad, but the largest deviations from the plotted smooth curve are about 0.0025 Å, corresponding to an error in c or in the volume of 0.046%.

We should note parenthetically that it is also possible to represent $a_\beta - a_\alpha$ with a leading term in $\theta^{+0.875} = \theta^{+1-\alpha}$ suggested by more recent estimates (Kandanoff, 1967; Levy et al., 1982) for Landau's critical exponents. However, this is more difficult mathematically and gives a fit which is considerably poorer if the same number of terms are used.

The least square values of the unit cell dimensions were used to calculate the molar volumes of alpha quartz. The values of $f(\theta)$ were then calculated at one degree intervals from the equation:

$$V_\beta(T, 0.1) - V_\alpha(T, 0.1) = f(\theta) \quad (13)$$

giving the values shown in Table 2. The volume increase due to disorder in quartz is somewhat larger than 0.60 cm³ mol⁻¹ since even 150 degrees below the lambda point there is still substantial disorder in equilibrium alpha quartz. The ΔV values of 0.11 to 0.205 cm³ mol⁻¹ reported (Ghiorso et al., 1979; Filatov et al., 1982) for a first order alpha to beta transition result from omitting the very steep and highly curved portions of the last 5 to 15 degrees below the lambda point.

The values in Table 2 are calculated from $a^2c \sin 120$ using expressions for a and c including terms in θ^2 . Thus $f(\theta)$ logically includes terms from $\theta^{1/2}$ through θ^6 , however, a reasonable fit to the values in Table 2 is given by

$$f(\theta) = [0.00351508 \theta - 0.158514 \times 10^{-4} \theta^2 E \\ + 0.733660 \times 10^{-7} \theta^3 - 0.116609 \times 10^{-9} \theta^4]^{1/2} \quad (14)$$

Judging from Figure 1 any errors in the extrapolation of a and c for beta quartz or in the alpha quartz values should be less than 0.005 Å and the values of $f(\theta)$ should be within ± 0.022 cm³ mol even out to $\theta = 150$ K.

Once the function $f(\theta)$ is known we can calculate entropy values for alpha quartz from

$$S_\alpha = S_\beta - (1/r_0)f(\theta) \quad (15)$$

where r_0 is the initial slope of the λ point vs. pressure, 0.265 ± 0.005 K MPa⁻¹ (Cohen et al., 1974). Calculating S_α for temperatures down to 150 K below the lambda point requires an extrapolation of heat capacity values for beta quartz. This extrapolation should be reasonably reliable since this heat capacity contains essentially no contribution from changing the amount of disorder. It was done with the equation

$$C_p = 69.0388 + 0.930215 \times 10^{-2}(T - 1000) - 0.819168 \\ \times 10^{-5}(T - 1000)^2 + 0.547378 \times 10^{-7}(T - 1000)^3 \\ - .587077 \times 10^{10}(T - 1000)^4 \quad (16)$$

which fits the experimental data for beta quartz and extrapolates reasonably to 700 and 1900 K.

Table 2. The Function $f(\theta)$ representing the difference in volume of alpha quartz from a fully disordered beta quartz at the same temperature

$\theta = T_\lambda - T$	K	0	1	2	3	
$f(\theta)$	cm ³ mol ⁻¹	0	.059155	.083456	.10197	
θ		4	5	10	15	20
$f(\theta)$.11748	.13105	.18333	.22219	.25398
θ		25	30	40	50	60
$f(\theta)$.28118	.30510	.34597	.38034	.41022
θ		80	100	150		
$f(\theta)$.46102	.50446	.59937		

We have taken the entropy values for alpha quartz calculated from the S_β and $f(\theta)$ values and used them to calculate C_p values over intervals of 1 to 10 K. This gives the smooth heat capacity curve for alpha quartz shown in Figure 2. The errors in C_p for beta quartz and in $f(\theta)$ could lead to errors as large as 3 J mol⁻¹ K⁻¹ in these values. However, the discrepancies from the experimental values plotted (Moser, 1936; Sinelnikov, 1953) are clearly over 10 J mol⁻¹ K⁻¹ near 830 to 840 K. Table 3 gives our ΔS and ΔH values for intervals of 25 K or less and comparable values using the Moser data (Moser, 1936) and two compilations which give mathematical expressions for C_p which can be integrated over the same regions.

Our values for ΔH and ΔS in Table 3 can be combined with well known heat capacity values below 750 and above 846 K to give $H_{1000} - H_{298,\alpha} = 45444.3 \pm 70$ mol⁻¹ with most of the uncertainty due to possible errors in the heat capacity in the 750 to 846 K range. We also obtain an entropy of beta quartz at 1000 K of 116.215 ± 0.1 J mol⁻¹

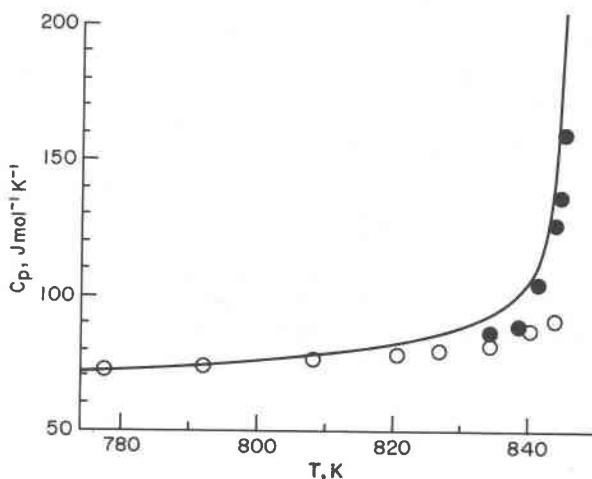


Fig. 2. Heat capacity, C_p , for alpha quartz near the lambda temperature. The solid line represents our calculated values. The experimental points of Moser (Moser, 1936) and Sinelnikov (Sinelnikov, 1953) are shown as open and filled circles respectively.

Table 3. Entropy and enthalpy changes for alpha quartz near the lambda point

Temp. Interval	this work		Literature ΔH values		
	ΔS	ΔH	*	**	+
825-846 K	2.6642	2230	1743	1569.0	2443.5 ⁺⁺
800-825 K	2.454	1994	1925	1844.0	1925.3
775-800 K	2.369	1866	1846	1818.0	1850.7
750-775 K	2.360	1800	1800	1791.7	1802.0
TOTAL	9.847	7890	7314	7022.7	8021.5

* - exp C_p of Moser, 1936

** - Roble et al., 1978

+ - Richet et al., 1980 compilation dependent on new drop calorimetric experiments

++ - The interval used is 826 to 847K to allow for the use of $T_\lambda = 847$. A correction of 655 J mol⁻¹, treated as a first order transition has been added as in the published paper.

K⁻¹ referenced to the CODATA (CODATA, 1976) value of 41.46 for $S_{298.15}^\circ$ for alpha quartz.

A very useful check of these values is provided by the data for the quartz to SiO₂ glass transformation. The two best reported experimental values are 9121 ± 250 J mol⁻¹ at 298.15 K (Kracek et al., 1953) and 7001 ± 200 J mol⁻¹ at 985 K (Navrotsky et al., 1980). Using the heat capacity values of Richet et al. (1982) we can calculate $H_{1000} - H_{298}$ using terms for the transformation to glass at 298, heating the glass to 985, conversion to beta quartz at 985, and then heating the last 15 degrees. Adding these four terms gives the value 45452 ± 300 J mol⁻¹, remarkably close to our value of 45444 ± 70 J mol⁻¹.

Equation of state for beta quartz

Figures 1 and 3 show that beta quartz at low pressures and temperatures from 846 to 1000 K has a negative coefficient of thermal expansion. We expect that, as in the corresponding case of liquid H₂O below 277 K, there will be positive values at higher pressures. In any case we cannot expect the simple behavior of α vs. P and K vs. T of the Murnaghan-Hildebrand equation of state (Howald et al., 1985). We must find experimental values for the bulk modulus as a function of temperature.

Fortunately bulk modulus values for beta quartz are available at least from 863 to 1073 K (Kammer et al., 1948). If we accept the values $V^\circ = 23.70$ cm³ mol⁻¹, $K_0 = 73046$ MPa (Kammer et al., 1948), and N estimated as 6 for 1073 K we can calculate $V = 23.42$ cm³ mol⁻¹ at the lambda point, 1073 K, 897 MPa, from the Murnaghan logarithmic equation of state (Anderson, 1966; Murnaghan, 1944; Howald et al., 1983)

$$V = V_0(1 + NP/K_0)^{-1/N} \quad (17)$$

For the region below 1200 MPa we are using the cubic

$$T = 846 + 0.265 P - 0.11303229 \times 10^{-4} P^2 - 2.4632558 \times 10^{-9} P^3 \quad (18)$$

to relate T and P at the lambda point.

Figure 3 shows $V_{\beta,0.1}$ and V_λ versus temperature up to 1073 K. For a full equation of state it is necessary to ex-

trapolate both of these curves to considerably higher temperatures. The V_λ vs. T plot shows some curvature between 846 and 1073 K, but we have assumed that it is linear,

$$V_\lambda = 24.54953 - 0.00105 T \quad (19)$$

to extrapolate to 1700 K. In extrapolating $V_{0.1}$ we have assumed that V goes through a minimum, and that we get positive alpha values of up to 1.3×10^{-6} as T approaches 1600 K. The fourth degree polynomial

$$V_{0.1} = 23.7013 - 0.105873 \times 10^{-5}(T - 100) + 0.854633 \times 10^{-8}(T - 1000)^2 - 0.18860 \times 10^{-10}(T - 1000)^3 + 0.144073 \times 10^{-13}(T - 1000)^4 \quad (20)$$

extrapolates reasonably well even to 2000 K and 23.773 cm³ mol⁻¹ and fits the Ackermann and Sorrell (1974) values reasonably well below 1373 K, where the X-ray measurements are not complicated by cristobalite formation. The combined extrapolations give a maximum near $K_0 = 100000$ MPa and 1650 K, which is reasonable behavior for a material with K_0 increasing with increasing T in the region accessible experimentally.

The alpha quartz-beta quartz-coesite triple point is near 1643 K and 3400 MPa, making this a convenient temperature and pressure at which to compare thermodynamic values from different equations of state for beta quartz. Table 4 compares our current values at this temperature and pressure with those from our earlier Murnaghan-Hildebrand equation of State. We do not know of any other treatment of beta quartz given in sufficient detail for inclusion in this table but we can compare our values for ΔV and ΔS for beta quartz going to coesite at 3440 MPa and 1653 K with values from Table 3 in Mirwald and Massone (Mirwald and Massone, 1980). Figures 4 and 5 show the contour lines for V and S for beta quartz. To a first approximation they are vertical and horizontal lines respectively, because the α values are small, and the slopes are $1/\alpha K$ and $\alpha VT/C_p$.

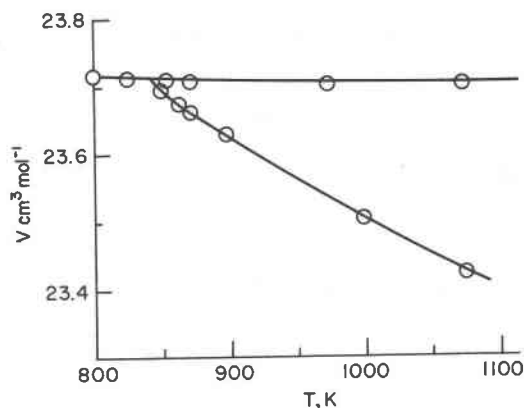


Fig. 3. Volumes of beta quartz at 0.1 MPa and at the lambda point plotted versus temperature.

Table 4. Comparison of thermodynamic values for beta quartz and coesite at high pressures and temperatures

T K	P MPa	Quartz	ref	beta quartz	coesite	ΔQ^*
1643	3400	H	**	-740206	-746483	-6277
			†	-739240	-748258	-9018
		S	**	151.50540	147.69553	-3.80987
			†	153.45105	148.05736	-5.39369
		V	**	22.96967	20.91757	-2.05210
1653	3440		†	21.69702	20.48606	-1.21096
		H	**	-738539	-744944	-6405
			†	-737578	-746712	-9134
			††			-6900
		S	**	151.08281	148.12198	-2.96083
			†	153.93282	148.49823	-5.43459
			††			-4.2
		V	**	22.96209	20.91458	-2.04751
			†	21.67548	20.48325	-1.19223
	††			-3.1		

*) change in H (J mol⁻¹), S (J mol⁻¹ K⁻¹) or V (cm³ mol⁻¹)
 **) this work
 †) Howald et al., 1985
 ††) Mirwald and Massone, 1980

Equation of state for alpha quartz

As T approaches T_λ for alpha quartz the bulk modulus approaches zero and α and C_p become infinite. The Pippard theory (Pippard, 1956) shows that the limiting slope of contour lines for both V and S is r , the slope of the equilibrium line. Thus as one approaches the lambda point the contour lines must bend and become very closely spaced. This is demonstrated in our Figures 4 and 5, and in Klement's (1968) Figure 6.

We presume Klement's contour line starting at 355°C (628 K) is for 23.0 cm³ mol⁻¹. It agrees with our line for 23.0 cm³ mol⁻¹ within ±15 K for the entire length shown.

Both volume and entropy have terms in $\theta^{0.5}$ that cannot be represented accurately by integral power series in T and P as θ approaches zero. Therefore, we have chosen a band 50 to 60 K wide below the equilibrium line in which the thermodynamic properties of alpha quartz are to be calcu-

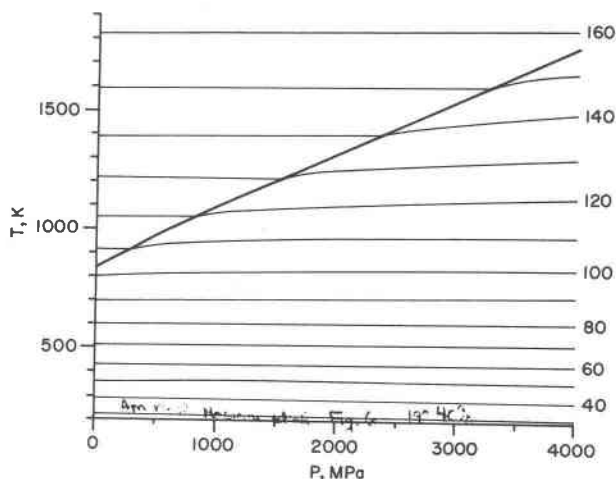


Fig. 5. Contour lines for the entropy (J mol⁻¹ K⁻¹) of quartz.

lated from the Pippard equations in the form

$$V_{\text{alpha}} = V_{\text{beta}} - (r/r_0)f(\theta) \tag{21}$$

$$S_{\text{alpha}} = S_{\text{beta}} - (1/r_0)f(\theta) \tag{22}$$

where $r = (dT/dP)_\lambda$, $r_0 = 0.265$, $\theta = T_\lambda - T$ and $f(\theta)$ is given in Table 2. We have chosen to write $(1/r_0)$ and (r/r_0) to allow for some curvature in the equilibrium line. In this case (dT/dP) drops to 0.227231 for $P > 1200$ MPa, and the r/r_0 term lets us associate this with a decrease in the ΔV of transition rather than an increase in ΔS with increasing T and P .

Our equation of state for beta quartz should extrapolate reliably to 55 and 60 K below the lambda point, and the $f(\theta)$ values in Table 2 allow us to calculate values for the volume and entropy of alpha quartz at these temperatures and a series of pressures. Fitting power series terms for the volume is fairly simple when one has reliable volume values on three edges of the region to be fitted. For alpha quartz V_0 is well known at low pressures, $K_0 = 37200$ MPa

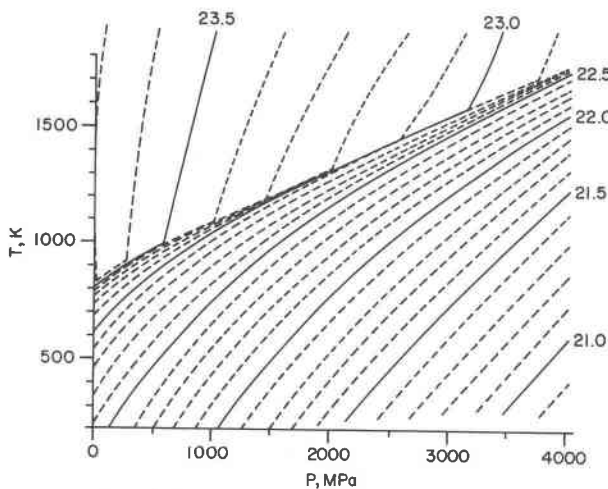


Fig. 4. Contour lines for the volume of quartz.

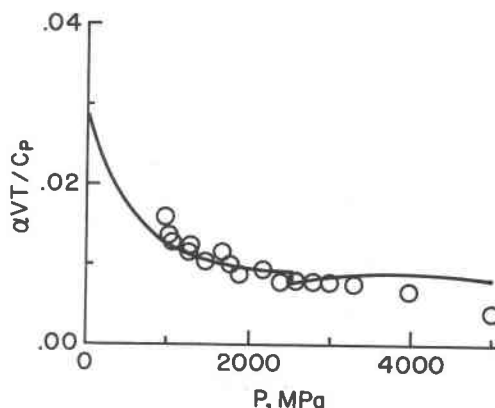


Fig. 6. Calculated and experimental values of $\alpha VT/C_p = (dT/dP)_\lambda$ at 800 K.

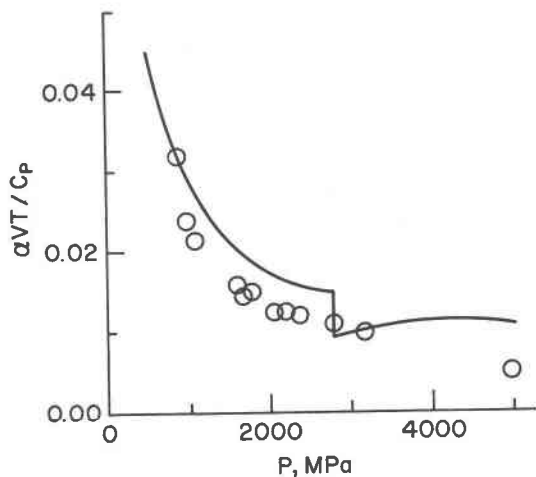


Fig. 7. Calculated and experimental (Boehler, 1982) values at 1000 K for $(dT/dP)_\lambda = \alpha VT/C_p$.

at 298.15 K (Weaver et al., 1979) (Soga, 1968) (McSkimmin et al., 1965) and the values at $\theta = 55$ and 60 give volumes and dV/dT along the upper edge of the region to be fitted. A good least-squares fit requires some estimated volumes at intermediate temperatures, but it should be easy to get these by interpolation, certainly within $\pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$. Each equation of state obtained can then be checked against the entropy values at $T_\lambda - T = 60 \text{ K}$ and against the $(dT/dP)_\lambda$ values measured at 800, and 1000 K, (Boehler, 1982). The contour lines for alpha quartz in Figures 4 and 5 are a third attempt in a series of successively better approximations.

There are two major tests of the accuracy of our final equation of state for alpha quartz beyond the reasonableness of the contour lines in Figures 4 and 5. There must be a reasonable fit about 60 K below T_λ for S and V calculations from the power series and from the Pippard equations. Table 5 shows this comparison at 3400 MPa and 1583 K. Figures 6 and 7 compare our calculations for $(dT/dP)_\lambda = \alpha VT/C_p$ with the experimental values (Boehler, 1982) as read from the published graphs.

Thermodynamic values for coesite

One principal use of reliable equations of state for alpha and beta quartz is in the interpretation of the pressure dependence of equilibria involving quartz. The quartz-coesite equilibrium has been widely studied. It provides a very stringent test of the equations of state since ΔH and ΔS are small, and even small errors can change the slope, $\Delta V/\Delta S$, drastically. The volume and bulk modulus of coesite are reliably known (Weaver et al., 1979; Levin and Prewitt, 1981).

Accurately fitting the measured equilibrium line required adjusting the C_p equation for coesite along with a whole series of successive small adjustments in its entropy and

enthalpy. Our final C_p curve

$$C_p = 9.0 E(T/800) - 1.23583 + 0.625 \\ \times 10^{-2}(T - 1000) - 0.409460 \times 10^{-5} \\ \times (T - 1000)^2 - 0.747870 \\ \times 10^{-9}(T - 1000)^3 + 0.195243 \\ \times 10^{-10}(T - 1000)^4 + .48 \times 10^6(1/T^2 - 10^6) \quad (23)$$

is plotted in Figure 8 to demonstrate that it is not unreasonably large or small anywhere in the temperature region under consideration. Our final values at 298 K for coesite are $S_{298} = 40.4672 \pm 0.2 \text{ J mol}^{-1} \text{ K}^{-1}$ and $H_{298} = \Delta H_f^\circ = -907213.9 \pm 200 \text{ J mol}^{-1}$.

This entropy value is in good agreement with the value 40.376 reported by Holm et al. (1967). The enthalpy value along with our C_p values for quartz and coesite gives $\Delta H_{970} = 1103 \pm 200 \text{ J mol}^{-1}$ for beta quartz going to coesite, compared to the published value of $2930 \pm 630 \text{ J mol}^{-1}$ (Holm et al., 1967). Recent independent measurements (Navrotsky, private communication) give 1339 J mol^{-1} . It is worth noting that a 200 J mol^{-1} shift in the enthalpy causes a substantial change in the slope and appearance of the equilibrium lines in Figure 9.

These values give good agreement between calculated and measured equilibria up to 1400 K. Above 1400 K the calculations for both alpha quartz and beta quartz going to coesite give ΔS values too negative and slope values too small to fit the reported values (Boyd and England, 1960; Mirwald and Massone, 1980). Since there must be a substantial increase in the entropy of quartz as it nears and reaches the lambda point at these pressures, just as at 0.1 MPa, the only reasonable way to accommodate higher slope values is to allow for higher entropy values for coesite at high temperatures. This could be due to either a first or second order transition, but for simplicity of calculation in

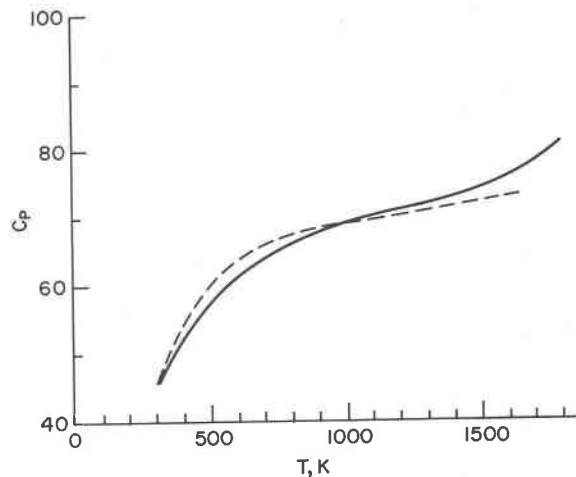


Fig. 8. Heat capacity values for coesite (solid line) and cristobalite (dashed line).

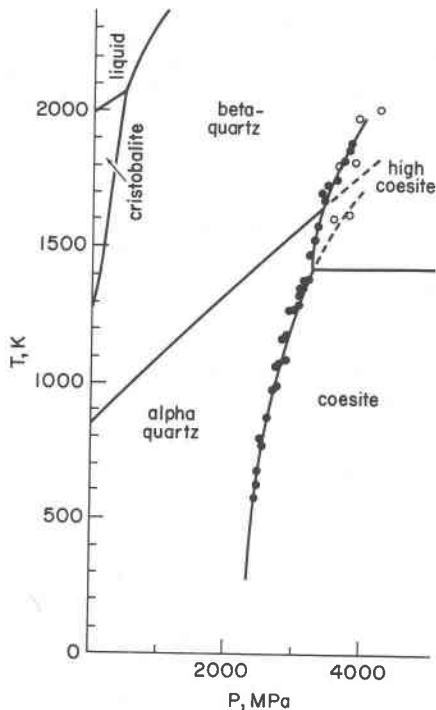


Fig. 9. Calculated phase diagram for SiO₂. The best experimental values for quartz-coesite equilibria (Boehler, 1982; Bohlen and Boetcher, 1982; Mirwald and Massone, 1980) are shown as filled circles, with the values of Boyd and England (Boyd and England, 1960) distinguished as open circles since the pressure calibration is less certain.

the absence of any direct evidence we have chosen a first order transition at 1420 K with $\Delta S = 2.5451 \pm 0.2 \text{ J mol}^{-1} \text{ K}^{-1}$. This assumed transition in coesite is shown in Figure 9, with the continuation of the quartz to low coesite calculations included as dotted lines.

Figures 6 and 7 include some calculated and experimental (Boehler, 1980) values for $\alpha VT/C_p$ in the coesite region roughly confirming the equation of state.

Thermodynamic values of cristobalite

Our first thermodynamic treatment of cristobalite (Eliezer et al., 1978) was based upon the JANAF values (Stull and Prophet, 1971) except for an increase of $0.11 \text{ J mol}^{-1} \text{ K}^{-2}$ in the entropy of cristobalite to bring the quartz-cristobalite equilibrium point to 1175 K. One major impetus for this work was concern that the Bulletin 1452 (Robie et al., 1978) values might be correct, implying that the older JANAF enthalpy could be in error by about 380 J mol^{-1} . We now have good heat capacity values for quartz, and there is reasonable agreement on the enthalpy changes in cristobalite as demonstrated in Table 6. Thus all measurements of the enthalpy differences between quartz and cristobalite can be reliably converted to ΔH_{298} between alpha quartz and low cristobalite. The ΔH_{298} values are 2636 ± 290 (Kracek et al., 1953), 2356 ± 80 (Holm et al.,

Table 5. Comparison of polynomial fit and Pippard calculations for the thermodynamic properties of alpha quartz 60 degrees below the lambda point

P	T	Material	H	S	V
MPa	K				
.1	786	beta quartz	-879756	99.91288	23.72101
		Δ	-1281	-1.548	-.41022
		alpha quartz*	-881037	98.36490	23.31079
		alpha quartz**	-881052	98.36416	23.31228
2000	1265	beta quartz	-800119	132.4389	23.18649
		Δ	-2023	-1.548	-.35175
		alpha quartz*	-802142	130.8909	22.83474
		alpha quartz**	-802356	130.8132	22.77600
3400	1583	beta quartz	-744774	148.67349	22.95617
		Δ	-2515	-1.548	-.35175
		alpha quartz*	-747289	147.12549	22.60442
		alpha quartz**	-747813	146.85953	22.54784

*) Values calculated from the beta quartz equation of state and the Pippard equations
 **) Values calculated from the alpha quartz equation of state

1967) and 1389 ± 250 (Navrotsky et al., 1980). This is much poorer agreement than shown by the quartz to glass measurements of these same workers, so the difficulty probably lies in the cristobalite samples.

We reached the decision that the entropy values of cristobalite are better known than its enthalpy, and that it is H_{298}° which should be adjusted to fit what is known of the quartz to cristobalite equilibrium. We have accepted the Richet value (Richet et al., 1982) of $S_{298}^{\circ} = 43.363 \text{ J mol}^{-1} \text{ K}^{-1}$ for low cristobalite, but their value of 1108 K for the quartz to cristobalite equilibrium is too low. Alkali silicates dissolve SiO₂ and should catalyze the transformations, and in their presence beta quartz is stable at 1141 K, and changes to tridymite around 1150 K. The equilibrium transformation to cristobalite must come at a still higher temperature. Holmquist (Holmquist, 1961) has observed the formation of cristobalite from quartz at 1163 K leaving only a 22 K interval for the equilibrium. Picking 1160 K for the equilibrium gives $H_{298}^{\circ} = -906871$ for high cristobalite and $H_{298}^{\circ} = -907915$ for low cristobalite. Thus

Table 6. Thermodynamic properties of cristobalite

	this work	*	**	***	†	††
S_{298}° †††	43.363	43.363	43.40	43.40	42.635	
H_{298}°	-907916	-907864	-908346	-908346		-908346
V_{λ}	535	525	523	543	535	
S_{600}	83.954	84.300	84.60	83.789	83.178	83.138
$H_{600}^{\circ}-H_{298}^{\circ}$	18062	18232	17973	18008	18037	17635
S_{1000}	118.216	118.167	118.61	117.80	117.36	117.69
$H_{1000}^{\circ}-H_{298}^{\circ}$	44985	44859	44735	44769	44890	44768
$H_{1000}^{\circ}-H_{1000}^{\circ}$ quartz	1456	2116	2122	1925		
$H_{298}^{\circ}-H_{298}^{\circ}$ quartz	2785	2856	2354	2354		2354

* -Richet et al., 1982
 ** -Robie et al., 1978
 *** -Stull and Prophet, 1971
 † -Mosesman and Pitzer, 1941
 †† -Eliezer et al., 1978
 ††† -S.I. units, J mol^{-1} and $\text{J mol}^{-1} \text{ K}^{-1}$ are used throughout

ΔH_{298} is 2785 ± 200 J mol⁻¹ for the alpha quartz to cristobalite transformation in good agreement with Kracek (1953), but larger than the other two values (Holm et al., 1967; Navrotsky et al., 1980).

Our heat capacity equation for high cristobalite

$$C_p = 9.0 E(T/800) - (1.49773 + 0.327610 \times 10^{-3}(T - 1000) + 0.201540 \times 10^{-5}(T - 1000)^2 + 0.601119 \times 10^{-8}(T - 1000)^3 - 0.127126 \times 10^{-11}(T - 1000)^4 + 0.48 \times 10^6(1/T^2 - 10^{-6})) \quad (24)$$

was obtained by a least squares fitting of drop calorimetric data (White, 1919; Mosesman and Pitzer, 1941; Richet et al., 1982) from 541.65 K to 1834 K. Including the Einstein term and a fixed $1/T^2$ term in the equation keeps the high power terms small enough to allow reliable extrapolation of this equation for the entire region from 400 K to 2000 K.

The different treatments for cristobalite summarized in Table 6 all give $S_{600} - S_{298}$ values between 40.3 and 41.2 J mol⁻¹ K⁻¹; however, the entropy value is still the biggest uncertainty in fixing the enthalpy of cristobalite from its equilibrium with quartz. Therefore, it was worthwhile to treat the order disorder transition in cristobalite just as we treated the alpha-beta quartz transition. The slope for the cristobalite transition in a T - P plot is 0.51 K MPa⁻¹, (Cohen and Klement, 1979) and we have

$$S_{\text{low},450} = S_{\text{high},450} - (1/r_0)(V_{\text{high},450} - V_{\text{low},450}) \quad (25)$$

with $r_0 = 0.51$. Our polynomial for the volume of high cristobalite for low pressure is

$$V = 27.4380 + 0.605751 \times 10^{-5}(T - 1000) - 0.860163 \times 10^{-8}(T - 1000)^2 + 0.156970 \times 10^{-10}(T - 1000)^3 - 0.884294 \times 10^{-14}(T - 1000)^4 \quad (26)$$

Interpolating graphically gives a volume of low cristobalite at 450 K of 26.04 cm³ (Johnson and Andrews, 1956, cited in Skinner, 1966; Leadbetter and Wright, 1976). The ΔV term is then $27.181 - 26.04 = 1.141$ cm³ mol⁻¹ for $\Delta S = 2.237$ J mol⁻¹ K⁻¹. Mosesman and Pitzer (1941) give the entropy of low cristobalite at 450 K as 63.443 J mol⁻¹ K⁻¹. Using better low temperature heat capacities corrects this to 64.194. Thus S_{450} for high cristobalite is $64.194 + 2.237 = 66.431$. Adding the results from integrating our equation for the heat capacity of high cristobalite gives the entropies of 83.954 and 118.216 J mol⁻¹ K⁻¹ at 600 K and 1000 K respectively, as shown in Table 6.

We have used a Murnaghan-Hildebrand equation of state for cristobalite (Howald, et al., 1985) with $K_{0,1000} = 14237$ MPa and $N = 6$.

Values for liquid SiO₂

The careful experimental work and literature analysis of Richet et al. (Richet et al., 1982) on liquid and glass SiO₂ provide important new data on the heat capacity of liquid SiO₂. Thus we have adopted a new equation

$$C_p = 71.0083 + 0.0184709 \cdot (T - 1000) - 0.532714 \times 10^{-5}(T - 1000)^2$$

for liquid SiO₂. The heat of fusion of cristobalite is fixed as 8621 ± 150 J mol⁻¹ at 1996 K by the measurements of ΔH for quartz to glass transitions (Kracek, 1953; Navrotsky et al., 1980), the heat capacity of SiO₂ (glass) (Richet et al., 1982), and our equations for the heat capacities of cristobalite and liquid. This compares to the choice of 8920 ± 1000 J mol⁻¹ (Richet et al., 1982). Our value for S_{2000} for liquid SiO₂ is 172.9484 J mol⁻¹ K⁻¹, in good agreement with 172.915 (Richet et al., 1982).

Figure 9 was calculated on the assumption that the bulk modulus for SiO₂ (l) is similar to that of high cristobalite, although the measured values for the glass (Birch, 1937; Ide, 1937; Wackerly, 1962) are substantially higher. Presumably both the volume and the bulk modulus will change at the glass to liquid lambda transition.

We have taken molar volumes for SiO₂ (l) from Bacon et al. (1960). As shown earlier (Richet et al., 1982) the large value of α for SiO₂ (l), 1.03×10^{-4} (Bacon et al., 1960) requires a reasonably small value for K_T , near that of cristobalite or smaller, or the calculated value of C_V for the liquid is unreasonably small.

Discussion

In view of the chemical significance of quartz it is important to have accurate well documented values for its thermodynamic properties. Thus we need a variety of independent compilations of values for quartz, and the 380 J discrepancy between the JANAF (Stull and Prophet, 1971) and Bulletin 1482 (Robie et al., 1978) values is serious. It is gratifying that independent reanalyses based on drop calorimetry (Richet et al., 1982) and on phase equilibria (this work) give overlapping ranges for $H_{1000} - H_{298}$ for quartz, 45579 ± 150 and 45452 ± 70 J mol⁻¹. The JANAF value of 45354 ± 150 is confirmed and refined, while the three lowest values in Table 1 must be discarded because they rely too heavily upon non-equilibrium C_p and DTA data.

There is now similar good agreement on the entropy of beta quartz at 1000 K: 116.215 ± 0.1 (this work), 116.02 ± 0.15 (Stull and Prophet, 1971) and 116.259 ± 0.1 J mol⁻¹ K⁻¹ (Richet et al., 1982). Similarly good agreement for cristobalite at 298 and 1000 K is shown in Table 6 between our values and those of Richet (Richet et al., 1982).

The heat of formation of coesite is now established at $H_{298}^{\circ} = -907214 \pm 200$ J mol⁻¹. The value of ΔH_{298} for alpha quartz going to coesite is thus 3486 ± 200 J mol⁻¹. Earlier published values include 2343 (Weaver et al., 1979) 5063 ± 630 (Holm et al., 1967) and two estimates by Mirwald and Massone (Mirwald and Massone, 1980) 2930 and 5067 J mol⁻¹.

It has been pointed out (Weaver et al., 1979) that the 5063 value is too large for consistency with measurements on the quartz-coesite equilibrium. However, it is necessary to have reliable equations of state for both quartz and coesite to make this argument quantitative.

There are no obvious problems with a Murnaghan-

Table 7. Polynomial equations of state for alpha and beta quartz

alpha quartz				
24.340296	3.238095 E-4	7.855450 E-7	1.018418 E-9	5.083011E-13
-1.218243E-4	-5.371956E-7	-1.357596E-9	-1.73248E-12	-8.66629E-16
1.170823 E-7	5.474543E-10	1.376992E-12	1.886086E-15	9.986443E-19
-7.99760E-11	-3.38035E-13	-8.22533E-16	-1.14072E-18	-6.00664E-22
3.031544E-14	1.203374E-16	2.743039E-19	3.586603E-22	1.754802E-25
-5.78773E-18	-2.23346E-20	-4.71042E-23	-5.49837E-26	-2.30597E-29
4.329322E-22	1.658714E-24	3.241953E-27	3.236415E-30	1.010065E-33
beta quartz				
23.701266	-.1058728E-5	.854633 E-8	-.188601E-10	.1440728E-13
-.1520712E-4	.2042034 E-7	-.519449E-10	.974922 E-13	0.714101E-16
.2441776 E-8	0.806657E-11	.1857775E-13	-.490703E-16	.492830 E-19
-.116290E-11	.3979281E-14	-.368804E-17	.917195 E-20	-.127623E-22
.2140223E-15	-.80183 E-18	.596339 E-21	-.701148E-24	.1175194E-26

$$V = C(1,1) \left[1 + \sum_{i,j} C(i,j) (T-1000) J^{i-1} P^{j-1} \right]$$

Hildebrand equation of state for cristobalite. As shown here and by Klement (1968) however, the temperature dependence of the volume for both alpha and beta quartz is unusual. The process of successive refinement to get good values of volume as functions of *T* and *P* for alpha and beta quartz was slow and difficult. At one time we hoped to be able to treat the two forms independently, and then check against the known temperatures and pressures for the lambda point. It was however, necessary to take *T*_λ as a function of pressure from the experimental data to get volumes for alpha quartz at simultaneously high temperatures and pressures. We have found the final equations of state to be very useful, and present them in full graphical detail in Figures 4 and 5 in the hope that they will be similarly valuable in the analysis of other equilibria. The full sets of 25 to 35 power series coefficients used to calculate the contour lines are given in Table 7. However, to make use of equations this complex it is helpful to have a full computer program. This can be provided as FORTRAN code on ANSI tape if the chemistry department at Montana State University is provided with a blank nine track magnetic tape or with the purchase price of the tape.

References

Ackerman, R. J. and Sorrell, C. A. (1974) Thermal Expansion and the High-Low Transformation in Quartz. I. High-Temperature X-ray Studies. *Journal Applied Crystallography*, 1, 461-467.
 Anderson, O. L. (1966) The use of ultrasonic measurements under modest pressure to estimate compression at high pressure. *Journal of the Physics and Chemistry of Solids*, 27, 547-565.
 Aslanyan, T. A. and Levanyuk, A. P. (1978) Possibility of a disproportionate phase near the α ⇌ β transition point in quartz. *Pis'ma v Zhurnal Eksperimental' noi i Teoreticheskoi Fiziki*, 28, 76-79.
 Aslanyan, T. A. and Levanyuk, A. P. (1979) On the possibility of the incommensurate phase near the α ⇌ β transition point in quartz. *Solid State Communications*, 31, 547-550.
 Aslanyan, T. A. and Levanyuk, A. P. (1984) Fluctuation effects as a cause for the incommensurate phase formation. *Ferroelectrics*, 53, 231-234.
 Bacon, J. F., Hasapis, A. A., and Wholley, J. W., Jr. (1960) Viscosity and density of molten silica and high silica content glasses. *Physics and Chemistry of Glasses*, 1, 90-98.
 Bachheimer, J. P. (1980) An anomaly in the β phase near the α - β

transition of quartz. *Journal de Physique, Lettres*, 41, L559-L561.
 Bachheimer, J. P., Bastie, P., Barnarel, J. and Dolino G. (1982) Optical observation of the interface morphology in transparent crystals (quartz, KD₂PO₄) during their first order phase transition. In H. I. Aaronson, Ed., *Proceedings of International Conference on Solid-Solid Phase transformation*, 1981, 1533-1537.
 Barin, I. and Knacke, O. (1973) *Thermochemical Properties of Inorganic Substances*. Springer-Verlag, Berlin.
 Berger, P. C., Eyraud L., Richard, M. and Riviere, R. (1966) Etude radiocristallographique de variation de volume pour quelques materiaux subissant des transformations de phase solide-solide. *Société chimique de France Bulletin*, 2, 628-633.
 Birch, F. (1937) The effect of pressure on the modulus of rigidity of several metals and glasses. *Journal of Applied Physics*, 8, 129-133.
 Boehler, R. (1982) Adiabats of quartz, coesite, olivine and magnesium oxide to 50 kbar and 1000 K, and the adiabatic gradient in the Earth's mantle. *Journal of Geophysical Research*, 87, 5501-5506.
 Bohlen, S. R. and Boettcher, A. L. (1982) The quartz ⇌ coesite transformation: a precise determination and the effects of other components. *Journal of Geophysical Research*, 87, 7073-7078.
 Boyd, F. R. and England, J. L. (1960) The quartz-coesite transition. *Journal of Geophysical Research*, 65, 749-756.
 Bragg, W. L. and Williams, E. J. (1934) The effect of thermal agitation on atomic arrangement in alloys. *Proceedings of the Royal Society of London, Series A*, 145A, 699-730.
 CODATA (1976) CODATA recommended key values for thermodynamics, 1975. Report of the CODATA Task Group on key values for Thermodynamics, 1975. *Journal of Chemical Thermodynamics*, 8, 603-605.
 Cohen, L. H. and Klement, W. Jr. (1967) High-low quartz inversion: determination to 35 kilobars. *Journal of Geophysical Research*, 72, 4245-4251.
 Cohen, L. H. and Klement, W. Jr. (1979) High-low cristobalite transitions in SiO₂, AlPO₄ and GaPO₄. Investigations by differential thermal analysis under hydrostatic pressure <6 kbar. *Philosophical Magazine*, A, 39A, 399-404.
 Cohen, L. H., Klement, W. Jr., and Adams, H. G. (1974) Yet more observations on the high-low quartz inversion: thermal analysis studies to 7 kbar with single crystals. *American Mineralogist*, 59, 1099-1104.
 Dolino, G. (1979) Elastic light scattering and birefringence measurements in the coexistence state of α and β quartz. *Journal of the Physics and Chemistry of Solids*, 40, 121-128.
 Dolino, G., Bachheimer, J. P. and Zeyen, C. M. E. (1983) Observation of an intermediate phase near the α - β transition of quartz by heat capacity and neutron scattering measurements. *Solid State Communications*, 45, 295-299.
 Dolino, G., Bachheimer, J. P., Berge, B. and Zeyen, C. M. E. (1984) Incommensurate phase of quartz: I. Elastic neutron scattering. *Journal de Physique*, 45, 361-371.
 Dolino, G., Bachheimer, J. P., Gervais, F. and Wright, A. F. (1983) The α ⇌ β transition of quartz; some current problems: order-disorder or displacive transition, thermodynamic behavior. *Bulletin de Minéralogie*, 106, 267-285.
 Eliezer, N., Howald, R. A., Marinkovic, M., and Eliezer, I. (1978) Vapor pressure measurements, thermodynamic parameters, and phase diagram for the system potassium oxide-silicon oxide at high temperature. *Journal of Physical Chemistry*, 82, 1021-1026.
 Filatov, S. K., Polyakova, I. G., Gaikovoi, A. G. and Kamentsev, I. E. (1982) X-ray diffraction determination of the changes in the

- structural parameters of quartz at the $\alpha - \beta$ transition. *Kristallografiya*, 27, 624–626 (transl. Soviet Physics Crystallography, 27, 378–379).
- Ghiorso, M. S., Carmichael, I. S. E., and Moret, L. K. (1979) Inverted high-temperature quartz. *Contributions to Mineralogy and Petrology*, 68, 307–323.
- Grimm, H. and Dörner, B. (1975) On the mechanism of the $\alpha - \beta$ transformation of quartz. *Journal of the Physics and Chemistry of Solids*, 36, 407–413.
- Holm, J. L., Kleppa, O. J. and Westrum, E. F. Jr. (1967) Thermodynamics of polymorphic transformations in silica. Thermal properties from 5 to 1070 K and pressure-temperature stability fields for coesite and stishovite. *Geochimica et Cosmochimica Acta*, 31, 2289–2307.
- Howald, R. A., Moe, A. A., and Roy, B. N. (1983) The high pressure disproportionation of spinel, $MgAl_2O_4$. *High Temperature Science*, 16, 111–121.
- Howald, R. A., Jones, R. D., Rezvani, A. B., Roy, B. N., Scanlon, M. J. and Swager, T.M. (1985) The temperature dependence of the bulk modulus. *Journal of Physical Chemistry*, 89, in press.
- Hughes, A. J. and Lawson, A. W. (1962) Cylindrical approximation and the quartz transition. *Journal of Chemical Physics*, 36, 2098–2100.
- Ide, J. M. (1937) The velocity of sound in rocks and glass as a function of temperature. *Journal of Geology*, 45, 689–716.
- Jay, A. H. (1933) The thermal expansion of quartz by X-ray measurements. *Proceedings of the Royal Society of London*, 142, 237–247.
- Johnson, W. and Andrews, K. W. (1956) An x-ray study of the inversion and thermal expansion of cristobalite. *Transactions of the British Ceramic Society*, 55, 227–236.
- Kandanoff, L. P., Gotz, W., Hamblen, D., Hecht, R., Lewis, E. A. S., Pakianskas, V. V., Royle, M., Swift, J., Aspnes, D., and Kane J. (1967) Static phenomena near critical points: theory and experiment. *Reviews of Modern Physics*, 39, 395–431.
- Kammer, E. W., Pardue, T. E. and Frissel, H. F. (1948) A determination of the elastic constants for beta quartz. *Journal of Applied Physics*, 19, 265–270.
- Kelley, K. K. (1960) Contributions to the Data on Theoretical Metallurgy. XIII. High Temperature Heat-Content, Heat-Capacity, and Entropy Data for the Elements and Inorganic Compounds. *Bulletin-United States Bureau of Mines, Bulletin* 584, 232 pp.
- Klement, W. Jr. (1968) High-low quartz inversion; approximate relations for volume and compressibility versus temperature at high pressure. *Journal of Geophysical Research*, 73, 4711–4716.
- Klement, W. Jr., and Cohen, L. H. (1968) High-low quartz inversion: thermodynamics of the lambda transition. *Journal of Geophysical Research*, 73, 2249–2259.
- Kraccck, F. C., Neuvonen, K., Burley, G. and Gordon, R. J. (1953) Contributions of thermochemical and x-ray data to the problem of mineral stability. *Carnegie Institution of Washington Yearbook*, 52, 69–73.
- Landau, L. D. and Lifshitz, E. M. (1958) *Statistical Physics*, translated by E. Peierls and R. F. Peierls, Pergamon Press Ltd., London (1958) Chapter 14 p. 453, 430–456.
- Leadbetter, A. J. and Wright, A. F. (1976) The $\alpha - \beta$ transition in the cristobalite phases of SiO_2 and $AlPO_4$. I. X-ray studies. *Philosophical Magazine*, 33, 105–112.
- LeChatelier, H. (1889) Sur la dilation du quartz. *Comptes Rendus, Academie des Sciences, Paris*, 108, 1046–1049.
- Levien, Louise and Prewitt, C. T. (1981) High-pressure crystal structure and compressibility of coesite. *American Mineralogist*, 66, 324–333.
- Levy, M., Le Guillou, J. C. and Zimm-Justin, J. (1982) *Phase Transitions*, Cargest 1980. Plenum Press, New York.
- Liebau, F. and Böhm, H. (1982) On the coexistence of structurally different regions in the low-high quartz and other displacive transformations. *Acta Crystallographica*, 38A, 252–256.
- Lord, R. C. and Morrow, J. C. (1957) Calculation of the heat capacity of α quartz and vitreous silica from spectroscopic data. *Journal of Chemical Physics*, 26, 230–232.
- Mayer, G. (1959) Doctoral thesis, University of Paris.
- Mayer, G. (1960) Recherches experimentales sur une transformation du quartz. *Rapport C.E.A. no. 1330*, 103 pp. Gil sur yvette (France).
- McSkimmin, H. J., Andreatch, P. Jr. and Thurston, R. N. (1965) Elastic moduli of quartz vs. hydrostatic pressure at 25°C and –195.8°C. *Journal of Applied Physics*, 35, 1624–1632.
- Mirwald, P. W., and Massone, H. J. (1980) The low-high quartz and quartz-coesite transition to 40 kbar between 600° and 1600°C and some reconnaissance data on the effect of $NaAlO_2$ Component on the Low Quartz Coesite Transition. *Journal of Geophysical Research*, 85B, 6983–6990.
- Moser, H. (1936) Messung der wahren spezifischen Wärme von Silber, Nickel, β -Messing, Quarzkristall und Quarzglas; zwischen + 50 und 700 C nach einer verfeinerten Method. *Physikalische Zeitschrift*, 37, 737–753.
- Mosesman, M. A., and Pitzer, K. S. (1941) Thermodynamic properties of the crystalline forms of silica. *Journal of the American Chemical Society*, 63, 2348–2356.
- Murnaghan, F. D. (1944) The compressibility of media under extreme pressures. *Proceedings of the National Academy of Sciences of the United States of America*, 30, 244–247.
- Navrotsky, A., Hon, R., Weill, D. F., and Henry, D. J. (1980) Thermochemistry of glasses and liquids in the systems $CaMgSi_2OH_6$ – $CaAl_2Si_2O_8$ – $NaAlSi_3O_8$, SiO_2 – $CaAl_2Si_2O_8$ and SiO_2 – Al_2O_3 – CaO – Na_2O . *Geochimica et Cosmochimica Acta*, 44, 1409–1423.
- Pippard, A. B. (1956) Thermodynamic relations applicable near a lambda-Transition. *Philosophical Magazine*, 1, 473–476.
- Richet, P., Bottinga, Y., Denielov, L., Petitot, J. P., and Tequi, C. (1982) Thermodynamic properties of quartz, cristobalite, and amorphous SiO_2 : drop calorimetry measurements between 1000 and 1800 K and a review from 0 to 2000 K. *Geochimica et Cosmochimica Acta* 46, 2639–2658.
- Robie, R. A. and Waldbaum, D. R. (1968) Thermodynamic properties of minerals and related substances at 298.15 K (25.0°C) and one atmosphere (1.013 bars) pressure and at higher temperatures. *Geological Survey Bulletin (United States)* 1259.
- Robie, R. A., Hemingway, B. S. and Fisher, J. R. (1978) Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures. *Geological Survey Bulletin (United States)* 1452.
- Ross, A. W. and Ter Haar, D. (1959) On the influence of Volume effects on order-disorder transitions. *Physica* 25, 343–356.
- Shirane, Gen. (1953) Incommensurate phase transitions. *Ferroelectrics*, 53, 15–24.
- Sinel'nikov, N. N. (1953). A vacuum adiabatic calorimeter and some new data on the transition of quartz. *Doklady Akademii Nauk SSSR*, 92, 369–372.
- Skinner, B. J. (1966) Thermal expansion. In S. P. Clark, Jr., Ed., *Handbook of Physical Constants*. *Memoir-Geological Society of America*, Memoir 97, 75–96.
- Soga, N. (1968) The temperature and pressure derivatives of isotropic sound velocities of α -quartz. *Journal of Geophysical Research*, 73, 827–829.

- Stull, D. R. and Prophet, H. (1971) JANAF Thermochemical Tables. National Standard Reference Data Series, NSRDS-NBS, 37, 1141 pp.
- Wackerle, J. (1962) Shock-wave compression of quartz. *Journal of Applied Physics*, 33, 922-937.
- Weaver, J. S., Chipman, D. W. and Takahashi, T. (1979) Comparison between thermochemical and phase stability data for the quartz-coesite-stishovite transformations. *American Mineralogist*, 64, 604-614.
- Westrum, E. F., (1957). Private communication to Stull and Prophet (1971).
- Westrum, E. F. Jr. (1957). The low temperature heat capacity of neutron irradiated quartz. *Travaux du IV^e Congres international du Verre, International Congress on Glass, Paris, 1956, 396-399.*

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