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High-Low Quartz Inversion: Determination to 35 Kilobars

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The high–low quartz inversion has been determined over the range 6 to 35 kb by means of differential thermal analysis in piston-cylinder apparatus, with chromel-alumel, Platinel II, and Pt versus Pt + 10% Rh thermocouples. The transition temperature initially rises at the rate of $\sim$26 deg kb^{-1}; the curvature, $-d^2T/dp^2$, is less than $\sim$0.4 deg kb^{-2}, in contrast with the reports of Gibson and of Yoder for the inversion at lower pressures. Comparison with selected data for the quartz–coesite transition suggests an intersection with the high-low quartz inversion near $\sim$1400°C and $\sim$37 kb. The several thermodynamic constraints involved if the inversion is first order (and this is not established at present) are discussed in the context of the present results.

Introduction. The many zero pressure investigations of the high–low quartz inversion and the associated physical properties have made this transition a classic problem. Further understanding of this geologically and technologically important material requires determination of its properties at elevated pressures, as well as at zero pressure. Because of the importance of the problem and the desire to examine further the thermodynamics of the inversion, an attempt was made to extend the determination of the inversion to higher pressures and to sort out the diverging data of *Gibson* [1928] and *Yoder* [1950]. This paper reports an investigation of the transition in the range 6 to 35 kb by differential thermal analysis (DTA) with three different types of thermocouples. There is an uncertainty in the accurate location of the phase boundary because of the lack of reliable corrections for the effects of pressure on thermocouple emf. Nevertheless, the concordance of the present results, obtained with the several thermocouples, is sufficient for using these data in a detailed discussion of the thermodynamics of the transition.

Experiments and results. Pressure was generated in a piston-cylinder apparatus, with a furnace design similar to that described by *Klement et al.* [1966]. Single-crystal specimens were cut from the sample of natural quartz used by *Kennedy et al.* [1962]. For each experiment two crystals, 4.6 mm in diameter and $\sim$0.7 mm thick, were placed together in the plane normal to the furnace axis. A butt-welded thermocouple junction (0.3 mm wire) was positioned between the crystals in a groove $\sim$0.5 mm wide. The reference junction was separated from the butt-weld by the crystal thickness plus $\sim$0.4 mm of talc. Sleeves of boron nitride or alsimag insulated the thermocouple-sample assembly from the graphite heater. Talc or boron nitride was used in the rest of the furnace.

The temperature difference across the sample (i.e., between the thermocouples) was only several degrees, for constant power input, over the entire experimental range. Temperature was varied at rates of $\sim$2 to 20 deg sec^{-1}. DTA signals appeared to be much the same as those observed for melting and solid-solid first-order transitions [*Cohen et al.*, 1966*a*]. Reproducibilities of ±2° were frequently obtained in a given run for both heating and cooling signals; no systematic differences in the temperatures of the signals on heating or cooling were observed.

Accurate knowledge of pressure requires pre-

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cise corrections for friction [*Cohen et al.*, 1966*a*; *Klement et al.*, 1966]. By careful manipulation of the applied (i.e. ram) pressure, attempts were made to ensure that the piston was moving in on an increasing pressure cycle and out on a decreasing pressure cycle regardless of temperature cycling across the transition. By assuming friction to be symmetrical, 'true' values of pressure were obtained by averaging the applied pressures on compression and decompression cycles for given transition temperatures. The double-value of friction was, in all cases, $\lesssim$1.5 kb. For a number of runs, failure occurred before data could be obtained on decompression, and friction corrections were made according to other runs in this investigation.

In the run with chromel-alumel thermocouples, several compression and decompression cycles were made (in an almost ideal run), and reproducibility was clearly demonstrated, even though the thermocouples were briefly taken up to 1200°C. Friction corrections were accurately determined and varied up to ~1.5 kb double-value at the highest pressures. The data (Figure 1) are believed precise to ±6°C and accurate to ±0.5 kb. Because of mechanical failure on decompression, it was difficult to obtain data below ~5 kb.

Several runs were made with Platinel II thermocouples [*Zysk*, 1963] (Figure 1), but these thermocouples invariably failed on decompression.

Data from the runs with Pt versus Pt +

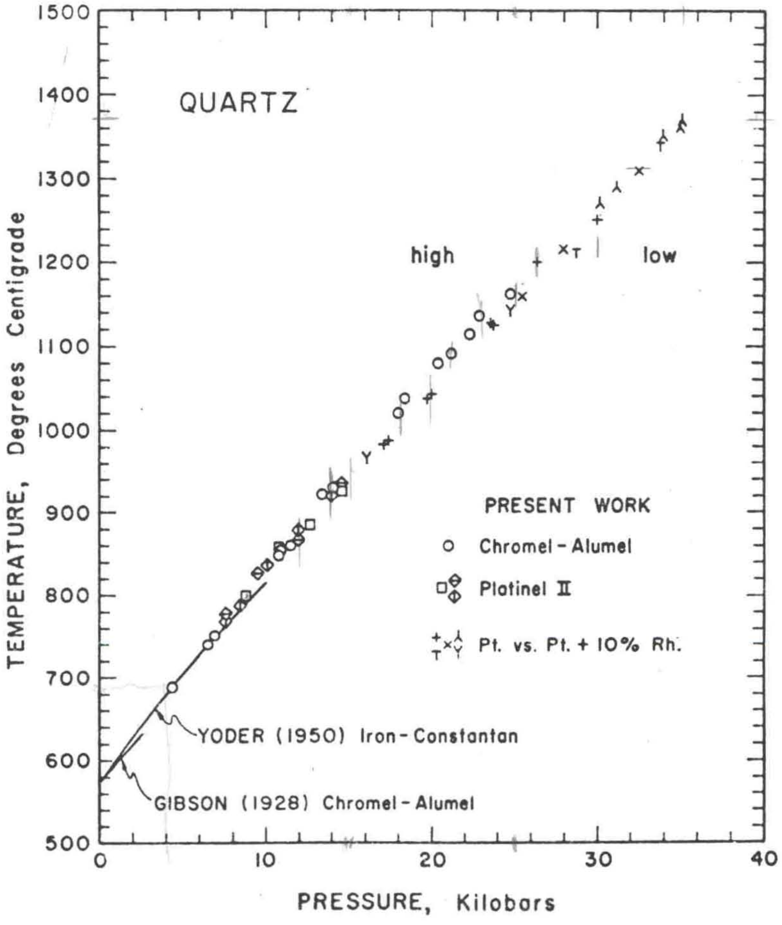

Fig. 1. Experimental data for the high-low quartz inversion. Interpolation equations given by *Gibson* [1928] and *Yoder* [1950] are used to plot their results. For the present work, each symbol represents a separate determination.

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10% Rh thermocouples are also shown in Figure 1. Accurate data on decompression were obtained in several of the runs and the double-value of friction was ∼1.5 kb. The greatest problem in these experiments at the highest pressures and temperatures was the disappearance of the thermal arrests, a phenomenon not encountered at the lower pressures and temperatures and not yet understood. In the vicinity of the sample, one may expect contaminants such as water from the decomposition of talc and carbon from the graphite heating sleeve. The quartz-water phase relations at elevated pressures [*Kennedy et al.*, 1962; *Ostrovsky*, 1966] do not suggest any mechanism for the inconsistent vanishing of the arrests. The data of *Keith and Tuttle* [1952] indicate that solid solution of small amounts of impurities may cause a large change in temperature of the inversion, but no such change in inversion temperature was detected within the precision of the present measurements. Evidence of 'stuffed' high quartz was sought in X-ray patterns [*Schreyer and Schairer*, 1961], but none was detected. Examination of the samples after the runs often indicated carbon around the thermocouples; attempts to 'getter' this carbon were made by placing an 0.05-mm-thick molybdenum sheet between sample and graphite sleeve, but there was no clear success here either.

The data (Figure 1) obtained in the runs using Pt versus Pt + 10% Rh thermocouples may be assigned a precision of better than ±10° and an accuracy of ±1 kb.

Since the temperature-measuring thermocouple was placed in a groove between two thin disks of quartz crystal, there may be some question as to whether pressure on the sample near the thermocouple was the same as the applied pressure elsewhere in the furnace. The thin disks readily crushed around the thermocouple. All experiments were in a hydrous environment, since the heating element in the furnace was placed next to talc which dehydrates below ∼830°C [*Kitahara et al.*, 1966] for the pressures involved here. *Griggs and Blacic* [1965] and *Griggs* [1966] have demonstrated that the strength of quartz is markedly reduced at elevated temperatures in the presence of water. The ∼20-kb compressive strength of anhydrous quartz at 5-kb confining pressure and 800°C [*Griggs et al.*, 1960] is reduced by more than an order of magnitude under similar conditions, as determined in shearing experiments, if the quartz is originally hydrous or is hydrated during the experiment. Apparently, therefore, no salient problems connected with the strength of quartz were involved in the present experiments, since the results from separate runs were in consonance and in general agreement with other high-pressure investigations under dissimilar conditions (see below).

In addition to absence of detectable variation in transition temperature with heating/cooling rate and the absence of any systematic difference between temperatures of heating and cooling signals ('hysteresis'), the following observations can be recorded: cycling in temperature across the transition as many as 10–20 times at a given pressure did not change the transition temperature, within experimental error; deterioration of the signals in many of the runs appeared to proceed gradually with time, as well as with increasing temperature (and pressure); annealing, for as long as 10–20 min as much as 200° above and below the transition, had little effect on the nature and temperature of the arrest; the over-all durations of the runs were less than 2–3 hr.

Intercomparison of the data (Figure 1) obtained with the several thermocouples suggests consistency and concordance, within the experimental error, although no attempts were made to correct for the effects of pressure on thermocouple emf. The most recent and extensive investigations of these effects [*Hanneman and Strong*, 1965, 1966] have been seriously questioned [*Cohen et al.*, 1966*b*], and the problem remains unresolved; qualitatively and tentatively it has been suggested [e.g., *Hanneman and Strong*, 1965] that pressure only slightly alters the emf for chromel-alumel (compared with the zero pressure calibration), whereas a somewhat larger subtractive correction may be involved for Pt versus Pt + 10% Rh thermocouples. There do not seem to have been any investigations for the Platinel series thermocouples, but the present results suggest behavior similar to chromel-alumel.

The zero pressure transition temperature is taken as ∼573–574°C for the present samples and hysteresis, effect of rate of temperature change is ignored as being beyond the precision of this investigation. The chromel-alumel run suggests an initial slope for the transition of $\sim 26 \pm 1$ deg kb^{-1}, which is approximately corroborated by the Platinel II data (Figure 1). The maximum 'curvature' deduced from all the data (Figure 1) is $d^2T/dp^2 \sim -0.4$ deg kb^{-2}. The present results disagree somewhat with those of *Gibson* [1928] and *Yoder* [1950] as to slope and especially as to curvature.

Comparison with previous reports. Gibson [1928], using chromel-alumel thermocouples for DTA under carbon dioxide pressure, gave for the phase boundary

$$T(p) - T(p = 0) \approx -0.31 + 21p + 0.86p^2$$

for T in degrees and p in kilobars, up to 2.64 kb. Gibson describes some difficulties with thermal gradients, especially below 0.7 kb. If only Gibson's data above 0.7 kb are considered, very nearly a straight line, of slope more in line with the present results, can be fitted.

Yoder [1950], using iron-constantan thermocouples for DTA under argon pressure, gave for the phase boundary

$$T(p) - T(p = 0) \approx -1.6 + 28.71p - 0.4284p^2$$

up to 10 kb. Recent discussions [*Babb,* 1963; *Boren et al.,* 1965] suggest that errors in pressure via calibration of the manganin coil may be $\sim 1\%$. More serious problems are probably involved in the corrections for the effects of pressure on iron-constantan thermocouples (which Yoder believed to be less than 0.5°C). In the vicinity of 0–100°C, the pressure effect on the thermal emf is large (compared with many other thermocouple elements) for constantan [*Bridgman,* 1918; *Bundy,* 1961] and perhaps complex for iron [*Bridgman,* 1918]. It is believed that significant, but presently unknown, corrections must be made for the effects of pressure on emf of iron-constantan thermocouples. These corrections might be most important at the upper end of Yoder's experimental range; below ~ 4 kb, Yoder's data can be fitted with an essentially straight line of slope $\sim 26._7$ deg kb^{-1}, in good agreement with the present results.

T. Takahashi (personal communication, 1963), using chromel-alumel thermocouples for DTA with powdered quartz in a tetrahedral press, obtained signals on heating at ~ 5 deg min^{-1}, which coincide with Yoder's data, within the claimed precision. Other high-pressure work on the quartz inversion has been noted by *Dickinson* [1964, 1966].

Low-quartz–high-quartz–coesite triple point. Among the numerous investigations of the quartz-coesite transition [*MacDonald,* 1956; *Dachille and Roy,* 1959; *Boyd and England,* 1960; *Yasukawa,* 1963; *Takahashi,* 1963; *Kitahara and Kennedy,* 1964; *Bell et al.,* 1965; *Boyd et al.,* 1966], the following data are selected for the transition at high temperatures: the best absolute position is the 1400°C, 37.5 (±0.2) kb value obtained with Pt versus Pt + 10% Rh thermocouples by *Boyd et al.* [1966]; the best relative set of data is that of *Boyd and England* [1960] as revised [*Boyd et al.,* 1966]. Combining these data with a slight extrapolation of the present results (Figure 1), the low-quartz–high-quartz–coesite triple point occurs near 1400°C and 37 kb.

Consequences of the hypothesis of a first-order transition. Investigations of the low-high quartz transition are very numerous; nevertheless, it is unclear that definitive and consistent data have yet been obtained because of the complexity and rapid variation of thermophysical parameters near the inversion. For example, *Strelkov et al.* [1953] report a fivefold increase in the coefficient of thermal expansion over an interval of less than 2°, slightly below the transition temperature. Detailed evaluation and intercomparison of heat capacity, thermal expansion, and elastic moduli data and their thermodynamic consequences will occupy the second paper of this series (Klement and Cohen, in preparation). It appears especially important that these measurements be made, under isothermal conditions, on material of the highest purity.

Many investigators have considered the high-low quartz inversion to be a first-order transition. Some estimates for the discontinuous increase in volume, ΔV, upon heating through the low–high transition include (in cubic centimeters per formula weight (fw)): ~ 0.195 [*Sosman,* 1927, evaluating earlier measurements]; ~ 0.11 [*Majumdar et al.,* 1964]; 0.154 ± 14 [*Berger et al.,* 1966]. Some estimates for the entropy change, ΔS, of the transition include (in joules per degree per formula weight):

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-quartz–coesite triple point. erous investigations of the nsition [*MacDonald,* 1956; , 1959; *Boyd and England,* 1963; *Takahashi,* 1963; *Kita-* 1964; *Bell et al.,* 1965; the following data are se- sition at high temperatures: position is the 1400°C, 37.5 obtained with Pt versus Pt mocouples by *Boyd et al.* lative set of data is that of d [1960] as revised [*Boyd* ining these data with a slight e present results (Figure 1). -quartz–coesite triple point and 37 kb.

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~0.74 [*Sosman,* 1927, evaluating earlier measurements]; ~0.43 [*Majumdar et al.,* 1964]. *Berger et al.* [1965] used thermogrammatic techniques on a variety of samples and obtained values ranging from ~0.5 to ~1.0 J deg^{-1} fw^{-3} (*Kelley* [1960] tabulates a finite ΔS for the inversion, but this is a manner of presenting the data and does not mean to imply that the transition is considered as first order (K. K. Kelley, personal communication).)

The Clausius-Clapeyron equation, $dT/dp = \Delta V/\Delta S$, constrains estimates of ΔV and ΔS to be consistent with the initial slope of the phase boundary, $dT/dp = 26 \pm 1$ deg kb^{-1}. For any first-order transition, there is a further constraint in that the initial curvature

$$\frac{d^2T}{dp^2} = \frac{1}{\Delta S}\left\{\left(\frac{\partial \Delta V}{\partial p}\right)_T + 2\left(\frac{dT}{dp}\right)\left(\frac{\partial \Delta V}{\partial T}\right)_p - \left(\frac{dT}{dp}\right)^2 \frac{\Delta C_p}{T}\right\} \tag{1}$$

For the present results, $-d^2T/dp^2 \lesssim 0.4$ deg kb^{-2}. No useful application of the Clausius-Clapeyron equation to the high-low quartz transition can be made with ΔS and ΔV values that vary over a factor of 2. Initial slopes calculated from the quantities tabulated span the experimentally determined value. Application of (1) or even *Bridgman*'s [1931] empirical correlations,

$$-\left(\frac{\partial \Delta V}{\partial p}\right)_T \geq \left(\frac{dT}{dp}\right)\left(\frac{\partial \Delta V}{\partial T}\right)_p \geq \left(\frac{dT}{dp}\right)^2\left(\frac{\Delta C_p}{T}\right) \tag{2}$$

is made most uncertain because of the rapid variations in $(\partial V/\partial p)_T$, $(\partial V/\partial T)_p$, and C_p as the transition is approached. Various bounds may be obtained via (2), using published estimates for discontinuities in C_p/T [e.g., *Berger et al.,* 1965] or $(\partial V/\partial T)_p$ [e.g., *Sosman,* 1927; *Rosenholtz and Smith,* 1941], but the worth of any of these values for the possible discontinuities is very much in doubt.

Perhaps one of the most experimentally accessible constraints on the possible first-order transition is that involving trajectories of phase boundaries at the high-quartz–low-quartz–coesite triple point. Using 2.93 g cm^{-3} as the probable density of coesite at room temperature and zero pressure [*Frondel,* 1962, pp. 310 and 314], ΔV (low quartz → coesite) ~2.2 cm^3 fw^{-1} and a similar value may be assumed near the triple point. The 'averaged dT/dp,' ('quartz'-coesite) is ~9 deg kb^{-1} [*Boyd and England,* 1960, et seq.]. To a good approximation, the difference in slope between the high-quartz–coesite and low-quartz–coesite phase boundaries, dT/dp (high-quartz–coesite) $-dT/dp$ (low-quartz–coesite) $\equiv \Delta dT/dp$, is

$$\Delta \frac{dT}{dp} \approx \frac{\Delta V(\text{low} \rightarrow \text{high quartz})}{\Delta V(\text{low quartz} \rightarrow \text{coesite})} \cdot \frac{dT}{dp}(\text{`quartz'-coesite}) \tag{3}$$

From (3) and an average value (see above) for ΔV (low → high quartz), $-\Delta\, dT/dp \sim 0.6$ deg kb^{-1}. The best high-pressure data presently available [*Boyd and England,* 1960] are inadequate, however, to detect a kink of such magnitude in the quartz-coesite phase boundary.

In the authors' opinion, conclusive proof for first-order behavior of the high-low quartz transition is lacking. In any case, the most spectacular variations in the thermophysical properties near the inversion indicate a lambda transition, the thermodynamics of which is discussed in a forthcoming paper (Klement and Cohen, in preparation).

Geological implications. For the several temperature distributions within the crust and upper mantle calculated by *Clark and Ringwood* [1964], all the proposed temperature-depth curves lie within the field of low quartz; nevertheless, regions of significantly elevated temperatures, as well as magmas, may be well within the stability field of high quartz. A number of equilibrium reactions involving quartz intersect the low–high quartz inversion curve. If definite criteria were available to distinguish quartz that has passed through the inversion from quartz that has not, then comparison of reaction curves with the data for quartz may give additional constraints on the paragenesis of the assemblage being considered. *Frondel* [1962, p. 119] has summarized the problem of inversion criteria as follows: 'The question arises whether a given natural quartz crystal or anhedron originally crystallized as low-quartz or as high-quartz. . . . In general the criteria as afforded by natural material are negative in so far as the identification of high-quartz is concerned.'

Further investigation may, however, provide inversion criteria [e.g., *Barsanov and Gur'yeva*, 1963]. Clearly the establishment of such criteria would contribute to the development of petrogenetic grids.

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