gnals on heating at ~5 deg
de with Yoder's data, within
on. Other high-pressure work
version has been noted by
966].
-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.*
elative set of data is that of
d [1960] as revised [*Boyd*
ing these data with a slight
e present results (Figure 1).
-quartz–coesite triple point
and 37 kb.
the hypothesis of a first-
Investigations of the low-
ition are very numerous;
unclear that definitive and
ve yet been obtained because
and rapid variation of ther-
eters near the inversion. For
et al. [1953] report a five-
e coefficient of thermal ex-
erval of less than 2°, slightly
ion temperature. Detailed
ntercomparison of heat ca-
pansion, and elastic moduli
thermodynamic consequences
second paper of this series
en, in preparation). It ap-
portant that these measure-
nder isothermal conditions, on
est purity.
ors have considered the high-
ion to be a first-order transi-
es for the discontinuous in-
ΔV, upon heating through the
on include (in cubic centi-
ula weight (fw)): ~0.195
evaluating earlier measure-
Majumdar et al., 1964]; 0.154
al., 1966]. Some estimates for
ge, ΔS, of the transition in-
r degree per formula weight):

~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

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

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,

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

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

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

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