

signals on heating at ~ 5 deg
side with Yoder's data, within
son. Other high-pressure work
inversion has been noted by
[1966].

High-quartz-coesite triple point.
Numerous investigations of the
inversion [MacDonald, 1956;
1959; Boyd and England,
1963; Takahashi, 1963; Kita-
1964; Bell et al., 1965;
the following data are se-
position at high temperatures:
position is the 1400°C, 37.5
obtained with Pt versus Pt
thermocouples by Boyd et al.
relative set of data is that of
[1960] as revised [Boyd
fitting these data with a slight
the present results (Figure 1).
High-quartz-coesite triple point
and 37 kb.

Test of the hypothesis of a first-
Investigations of the low-
inversion are very numerous;
unclear that definitive and
have yet been obtained because
and rapid variation of ther-
parameters near the inversion. For
et al. [1953] report a five-
the coefficient of thermal ex-
interval of less than 2°, slightly
inversion temperature. Detailed
intercomparison of heat cap-
expansion, and elastic moduli
thermodynamic consequences
second paper of this series
then, in preparation). It ap-
important that these measure-
under isothermal conditions, on
best purity.

Authors have considered the high-
inversion to be a first-order transi-
criteria for the discontinuous in-
 ΔV , upon heating through the
then include (in cubic centi-
mole weight (fw)): ~ 0.195
evaluating earlier measure-
Majumdar et al., 1964]; 0.154
et al., 1966]. Some estimates for
ge. ΔS , of the transition in-
ter degree per formula weight):

~ 0.74 [Sosman, 1927, evaluating earlier meas-
urements]; ~ 0.43 [Majumdar et al., 1964].
Berger et al. [1965] used thermogrammatic
techniques on a variety of samples and ob-
tained values ranging from ~ 0.5 to ~ 1.0 J
 $\text{deg}^{-1} \text{fw}^{-3}$ (Kelley [1960] tabulates a finite ΔS
for the inversion, but this is a manner of pre-
sented 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 con-
straint in that the initial curvature

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

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 cal-
culated from the quantities tabulated span the
experimentally determined value. Application
of (1) or even Bridgman's [1931] empirical
correlations,

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

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 esti-
mates 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 discontinu-
ities is very much in doubt.

Perhaps one of the most experimentally ac-
cessible 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 prob-
able density of coesite at room temperature and
zero pressure [Fron del, 1962, pp. 310 and 314],

ΔV (low quartz \rightarrow coesite) $\sim 2.2 \text{ cm}^3 \text{fw}^{-1}$ and
a similar value may be assumed near the triple
point. The 'averaged dT/dp ' ('quartz'-coesite)
is $\sim 9 \text{ deg kb}^{-1}$ [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-co-
esite) $\equiv \Delta dT/dp$, is

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

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

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 dis-
cussed in a forthcoming paper (Klement and
Cohen, in preparation).

Geological implications. For the several tem-
perature distributions within the crust and
upper mantle calculated by Clark and Ring-
wood [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 dis-
tinguish quartz that has passed through the
inversion from quartz that has not, then com-
parison of reaction curves with the data for
quartz may give additional constraints on the
paragenesis of the assemblage being considered.
Fron del [1962, p. 119] has summarized the
problem of inversion criteria as follows: 'The
question arises whether a given natural quartz
crystal or anhedral originally crystallized as
low-quartz or as high-quartz. . . . In general the
criteria as afforded by natural material are