

cision 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 ~ 26 , 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; Dache 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 five-fold 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):

~ 0.74 [Sosman, 1927, evaluating earlier measurements]; ~ 0.43 [Berger et al., 1966]. Other estimates obtained by techniques on a quartz crystal have obtained values ranging from ~ 0.1 to ~ 1.0 deg⁻¹ fw⁻³ (Kelley [1956] for the inversion, 1956; presenting the data as consistent with that the transition is first-order; K. K. Kelley, personal communication, 1966). The Clausius-Clapeyron equation, $dT/dp = \Delta V/\Delta S$, constrains the slope of the phase boundary, dT/dp , to be consistent with that of a first-order transition. The present results are in agreement with this constraint in that the initial slope is

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

for the present results. No useful approximation of the Clausius-Clapeyron equation for a first-order transition can be made that vary over a few degrees. The present results are in agreement with the experimental data of (1) or even better correlations,

$$-\left(\frac{\partial \Delta V}{\partial p} \right)_T \geq \left(\frac{dT}{dp} \right)_T$$

is made most uncertain by the large variations in $(\partial V/\partial p)_T$ near the transition. The present results may be obtained via the Clausius-Clapeyron equation for discontinuous transitions [Berger et al., 1965] or $(\partial V/\partial p)_T$ [Rosenholtz and Smith, 1965]. Any of these values for $(\partial V/\partial p)_T$ is very much in doubt.

Perhaps one of the most useful constraints on the transition is that involving the Clausius-Clapeyron equation at the high-pressure triple point. Using the available density of coesite at zero pressure [Fronde