(coefficient of p^2 term); polynomials of order >2 yielded only negligible improvement in the curve fitting and are thus not necessary. Only when data from run 3 (below) were separated into adjacent ranges and curves fitted to each range were polynomials of order >2 occasionally found to be significant.

Run 1 was primarily exploratory; from 30-some data on heating and cooling cycles respectively, the initial slope was $\sim 26._2$ deg kbar^{-1}, with a standard error of $\sim 0.5°$ and the initial curvature was essentially zero (<0.1 deg kbar^{-2}). Run 2 was meant primarily to investigate the effect of considerably smaller sample size on the peculiar thermal analysis signal and also to collect more closely spaced data; from 60-some data on heating and cooling cycles respectively, the initial slope was $\sim 26._8$ deg kbar^{-1}, with a standard error of $\sim 0.5°$ and initial curvature (d^2T/dp^2) ~ -0.2 deg kbar^{-2}. For run 3, thermal contact between thermocouple and sample was enhanced by use of the silver conductive paint. Yet more data, more closely spaced, were obtained, particularly at the lower pressures. From 70-some data on heating and cooling cycles respectively, the initial slope was $\sim 26._0$ deg kbar^{-1}, with a standard error $\sim 0.12°$ and negligible curvature. Systematic deviations from this fit were noted below ~ 0.3 kbar, and regression analyses showed that somewhat better fits could be obtained if the data below 0.8, 0.6, or 0.4 kbar were fitted by one curve and those above by another. The curves for the higher pressure data essentially coincided with the curve obtained for all the data, whereas the curves for the lower pressure data suggested higher initial slopes and greater curvatures ($d^2T/dp^2 < 0$). Run 3 can also be considered as a search for the existence of a "hitch" in the inversion such as KvGtH (1973) interpreted from their data. It is not clear whether fitting curves to piecewise sections of data, or even to overlapping sections, is a method for discovering "hitches."

Because data at the lower pressures are perforce more important for comparison with the various thermodynamic data at 1 bar, run 4 was intended to improve the statistical reliability of the results at the lower pressures and to try to pin down existence and characteristics of a "hitch," if any, in the trajectory of the inversion below 1 kbar. The initial slope thus obtained from 50-some data on heating and cooling respectively were $28._6$ deg kbar^{-1} with a standard error of 0.08°, and the curvature (d^2T/dp^2) ~ -4 deg kbar^{-2}.

Thus the results from run 4, the most intensive investigation thus far of the range below 1 kbar, suggest greater initial slope and curvature than indicated hitherto by the data at higher pressures. It is hoped that the very recent recalibration of the 1 and 3 kbar pressure gauges is sufficient precaution to insure confidence in the pressures given here. Thermocouple calibrations are, of course, another problem. It is believed that the calibrations most relevant to the present experiments should be made *in situ; in situ* calibrations at 1 bar have been made with the Curie point of iron (Cohen and Klement, 1973) and with the solid-liquid transition of lead (Cohen and Klement, 1974) but do not seem to be accurate enough for the present experiments. Nothing in the present experiments suggests drastic variations for the chromel-alumel thermocouples, beyond the instabilities already recognized (Potts and McElroy, 1961) for these materials. Although the effect of pressure on emf of chromel-alumel thermocouples is considered to be considerably smaller than for Pt–Pt + 10% Rh thermocouples over the present p-T range (Getting and Kennedy, 1970), it is worthwhile to examine what seems to be the variation within the range of the present experiments. According to Getting and Kennedy (1970), the maximum correction voltage may be of the order of 20 μV (observed temperatures $\sim 1/2°$ higher than actual), increasing from zero at 1 bar and then decreasing to zero again and changing arithmetical sign at higher pressures; more details for the variation are not known (see also Freud and LaMori, 1971). Unfortunately, a correction of $\sim 1/2°$ at, say, 0.5 kbar yields an apparent initial slope ~ 1 deg kbar^{-1} higher than actual, which is the suggested sign of direction of the variation of the present data at the lowest pressures as compared to the data for all pressures.

If one applies approximate corrections (Getting and Kennedy, 1970) for the effects of pressure on the emf of Pt–Pt + 10% Rh thermocouples to the KvGtH (1973) data, it becomes moot as to whether there is nonzero curvature; likewise the slope above 1 kbar becomes $\gtrsim 26$ deg kbar^{-1}. Whether there is actually a hitch in the trajectory of the transition for their samples depends upon the requisite knowledge of pressure and of temperature and the manner in which the data are reduced and interpreted. The KvGtH (1973) report of an initial slope as low as ~ 15 deg kbar^{-1} is not corroborated in the present work, or elsewhere.

Until more convincing experiments can be carried out, it is suggested that (1) there is no evidence yet for the initial slope of the high-low quartz inversion being sample-dependent; (2) the initial slope is $\gtrsim 26$ deg $kbar^{-1}$, with ~ 28 deg $kbar^{-1}$ being a suggested upper limit; (3) considering uncertainties in the pressure effects on thermocouples, there is no evidence yet that the curvature is nonzero within the 7 kbar range of the present experiments.

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References

American Society for Testing and Materials (1963) Appendix, In *Temperature-Electromotive Force (emf) Tables for Thermocouples.* ASTM Designation **E230-63,** 59 p.

Bates, F., and F. P. Phelps (1927–8) A suggested new base point on the thermometric scale and the $\alpha \rightleftharpoons \beta$ inversion of quartz. *U. S. Natl. Bur. Stand. Sci. Pap.* **22,** 315–327.

Coe, R. S., and M. S. Paterson (1969) The α-β inversion in quartz: a coherent phase transition under nonhydrostatic stress. *J. Geophys. Res.* **74,** 4921–4948.

Cohen, L. H., and W. Klement (1967) High-low quartz inversion: determination to 35 kilobars. *J. Geophys. Res.* **72,** 4245–4251.

———, and ——— (1973) Determination of the high-low inversion in berlinite ($AlPO_4$) to 6 kbar. *Am. Mineral.* **58,** 796–798.

———, and ——— (1974) Investigation to 6 kbar of the lambda and solid-liquid transitions in sodium nitrate. *J. Chem. Eng. Data,* **19,** 210–211.

Dadson, R. S., and R. G. P. Grieg (1965) Fixed points on the scale of high pressures: the freezing pressure of mercury at 0°C. *Brit. J. Appl. Phys.* **16,** 1711–1718.

Freud, P. J., and P. N. Lamori (1971) Pressure dependence of the thermoelectric power of thermocouple materials. p. 67–75 In, E. C. Lloyd, Ed., *Accurate Characterization of the High-Pressure Environment. U. S. Natl. Bur. Stand., Spec. Publ.* **326.**

Getting, I. C., and G. C. Kennedy (1970) Effect of pressure on the emf of chromel-alumel and platinum-platinum 10% rhodium thermocouples. *J. Appl. Phys.* **41,** 4552–4562.

Gibson, R. E. (1928) The influence of pressure on the high-low inversion of quartz. *J. Phys. Chem.* **32,** 1197–1205.

Goldsmith, J. R., and H. C. Heard (1961) Subsolidus phase relations in the system $CaCO_3$–$MgCO_3$. *J. Geol.* **69,** 45–74.

Höchli, U. T. (1970) Ultrasonic investigation of the first-order α-β phase transition in quartz. *Solid State Commun.* **8,** 1487–1490.

Keith, M. L., and O. F. Tuttle (1952) Significance of variation in the high-low inversion of quartz. *Am. J. Sci. Bowen Vol.* 203–280.

Koster van Groos, A. F., and J. P. ter Heege (1973) The high-low quartz transition up to 10 kilobar pressure. *J. Geol.* **81,** 717–724.

Klement, W., and L. H. Cohen (1968) High-low quartz inversion: thermodynamics of the lambda transition. *J. Geophys. Res.* **73,** 2249–2259.

McElroy, D. L. (1958) Progress report I—thermocouple research report. *U. S. Atomic Energy Comm. Rep.* Ornl-**2467,** 87 p.

Potts, J. F., and D. L. McElroy (1961) Thermocouple research to 1000°C—final report. *U. S. Atomic Energy Comm. Rep.* Ornl-**2773,** 158 p.

Smyth, F. H., and L. H. Adams (1923) The system, calcium oxide-carbon dioxide. *J. Am. Chem. Soc.* **45,** 1167–1184.

Sosman, R. B. (1965) *The Phases of Silica.* New Brunswick, New Jersey, Rutgers University Press, 388 p.

Yoder, H. S. (1950) High-low quartz inversion up to 10,000 bars. *Trans. Am. Geophys. Union,* **31,** 827–835.

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