

From the Lindemann relation,

$$\frac{1}{3V} \left(\frac{\partial V}{\partial p} \right) - \frac{1}{2T} \left(\frac{\partial T}{\partial p} \right) + \frac{1}{\vartheta} \left(\frac{\partial \vartheta}{\partial p} \right) = 0, \quad (9)$$

if the "constant" is indeed assumed to be constant.

For the calculation of the relative variation in the Debye temperature with pressure,

$$\frac{1}{\vartheta} \left(\frac{\partial \vartheta}{\partial p} \right)_{300^\circ\text{K}} = -\frac{1}{3V} \left(\frac{\partial V}{\partial p} \right)_{300^\circ\text{K}} + \frac{1}{v_m} \left(\frac{\partial v_m}{\partial p} \right)_{300^\circ\text{K}}, \quad (10)$$

where v_m is the averaged velocity of sound. This velocity variation with pressure is most conveniently computed from the observed elastic moduli variation by the method presented by Anderson¹⁹; although this method is less accurate than several others proposed, the over-all uncertainty in the calculation is perhaps not much more than the ca. 2% uncertainty in the elastic moduli data. Taking the zero-pressure, 300°K elastic moduli for copper from Schmunk and Smith,²⁰ for silver from Bacon and Smith²¹ and from Neighbours and Alers²² and for gold from Neighbours and Alers²² and from Daniels and Smith,¹⁸ $(1/v_m)(\partial v_m/\partial p)_{300^\circ\text{K}}$ is estimated as 3.9 for Cu, 6.8 for Ag, and 7.3 for Au in units of (Mbar)⁻¹. The elastic moduli for these solid elements are not known near the melting points, but may be assumed to be similar to (or slightly less than) the 300°K values. Then, from Eqs. (9) and (10), $(1/2T)(dT/dp)$ should be approximately equal to $(1/v_m)(\partial v_m/\partial p)_{300^\circ\text{K}}$. However, the experimental values for $(1/2T)(dT/dp)$ are ~1.5 for Cu, ~2.4±0.1 for Ag, and ~2.4 for Au, in units of (Mbar)⁻¹. Thus, from the viewpoint of the Lindemann relation, the observed increase of the melting point with pressure is from two to three times too small. Since this conclusion is based

on an analysis of 300°K data, there is a possibility that better agreement might be achieved with high-temperature elastic moduli data. It is unlikely, however, that such large discrepancies could be removed without anomalously large variations in the moduli as temperature is increased.

Despite the extensive theoretical treatments, mostly by Gilvarry²³ and recently by Babb,²⁴ the Simon equation has not proved to be reliable in estimating the courses of melting curves; it seems to be at best a convenient two-parameter representation for data over an explored interval. The inadequacies in the theoretical derivations of the Simon equation are probably due mostly to the inadequacies of the Lindemann relation. In addition to the outright failures for the several elements with liquids more dense than the solids along the melting curves, the above calculations suggest that little confidence can be vested in the relation even insofar as elements as "normal" as copper, silver, and gold are concerned. The great difficulty of course is that this relation effectively ignores the properties of the liquid by imputing to it a structure rigidly related to that of the solid. This is in inadequate agreement with the data (Table I) which indicate volume changes of fusion of 4.60±0.15%, 5.23±0.12% and 5.2–5.7% for copper, silver and gold, respectively.

ACKNOWLEDGMENTS

One of us (W. K.) gratefully acknowledges a fellowship from the Miller Institute. Support from the Committee on Research, University of California, Berkeley is acknowledged by L. H. C. Dr. H. L. Luo kindly supplied the high-purity copper and gold. Thanks are due to Dr. A. Jayaraman for comments on the manuscript. Partial financial support was provided by ONR Metallurgy Branch Nonr 233(53).

¹⁹ O. L. Anderson, *J. Phys. Chem. Solids* **24**, 909 (1963).

²⁰ R. E. Schmunk and C. S. Smith, *Acta Met.* **8**, 396 (1960).

²¹ R. Bacon and C. S. Smith, *Acta Met.* **4**, 337 (1956).

²² J. R. Neighbours and G. A. Alers, *Phys. Rev.* **111**, 707 (1958).

²³ J. J. Gilvarry, *Phys. Rev.* **102**, 308 (1955); **102**, 317 (1955); **102**, 325 (1955); **102**, 331 (1955); **103**, 1700 (1956); **104**, 908 (1956).

²⁴ S. E. Babb, *J. Chem. Phys.* **38**, 2743 (1963).