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Compression of Mercury at High Pressure*,†

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An exact method of computing volume changes under high pressure from acoustic-wave-velocity measurements is developed. It is applicable to large as well as small compressions. To illustrate the application of the method, precision ultrasonic-velocity measurements made in mercury at pressures up to 13 kbar for three temperatures have been used to compute V as a function of T and P. The volume is determined to an accuracy of better than 0.01% at each pressure and temperature. An analytical expression for the pressure dependence of the volume in which all coefficients are expressed in terms of the bulk modulus and its derivatives is developed and shown to give a better representation of the P–V data than many of the equations now in use.

INTRODUCTION

A FUNDAMENTAL problem in high-pressure research is the determination of the equation of state of condensed materials. One experimental approach to this problem is direct measurement of the volume as a function of pressure. Various methods have been devised for this. For liquids Bridgman has used a piezometer,[1,2] a piston-displacement method,[3–5] and a sylphon-bellows device[6–9] which employs a potentiometric length-measuring technique. The piezometer yielded volumes accurate to about 0.1%, the piston-displacement method to about 1%, and the sylphon bellows to a few hundredths of 1%. For solids Bridgman used a linear-compression technique[10,11] where the change in length of samples relative to that of pure iron is measured and, again, the piston-displacement method.[12–16] These methods have been refined by other investigators. Cutler *et al.*[17] and Boelhouwer[18] modified the sylphon-bellows technique by employing an external linear-differential transformer to measure the bellows motion. Doolittle *et al.*[19] determined the change in volume of a liquid by following the motion of a float at its surface with an external linear-differential transformer. Accuracies of the order of 0.01% are attained. To measure compression in solids to very high pressures, a Debye–Scherrer x-ray powder pattern of a sample compressed in an anvil device has been used. A review of the earlier x-ray techniques is given by Jamieson and Lawson[20]; newer methods are described by Barnett and Hall[21] and Perez-Albuerne, Forsgren, and Drickamer.[22] A common problem in the x-ray methods is that pressure determination is difficult so that the volume results obtained are accurate to only about 1%. For compression measurements to ultrahigh pressure (megabars), the shock-wave method is used. Deal[23] has given a review of the techniques involved. The question of accuracy is a difficult one here, but it is certainly not better than 1% of the volume.

In all of the experimental methods enumerated above, volume is measured directly as a function of pressure. An alternative approach, inherently capable of yielding higher accuracy, is to measure the pressure dependence of the compressibility and then obtain volume as a function of pressure by integration. The compressibility and its pressure dependence may be measured to high accuracy by acoustic methods. In 1949 Lazarus[24] initiated development of the techniques necessary for making sonic-velocity measurements to high pressure. In his work on the elastic constants of cubic single crystals he assumed the samples changed length as though they had constant compressibility. In 1957 Cook[25] described a method of obtaining accurate volume results from high-pressure sonic-velocity data. He employed the less restrictive assumption that the ratio of the isothermal and adiabatic compressibilities is a constant. This approximation is reliable when the com-

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