

$$\frac{d(K/K_0)}{dP} = m + \frac{a^2(K_0' - m)}{(P + a)^2} \quad (2)$$

We assume, with Anderson, that K_0 and K_0' will be determined from ultrasonic measurements at low or moderate pressures. We require $m > 0$ and $a > 0$. By appropriate choice of the positive parameters a and m , the resulting pressure-volume relation can be made to fit the data and at the same time predict reasonable behavior on the entire range $P > 0$, even when $K_0' < 0$. If $m = K_0'$, both this relation and Keane's reduce to Murnaghan's formula.

Equation 2 is only one of many possibilities of functions that would be suitable. A few other possibilities are noted in Appendix A. There is no strong reason for choosing equation 2 over the others. In this connection, it should be emphasized that the pressure-volume relation in the range of available data is relatively insensitive to departures of the bulk modulus $K(P)$ from its initial tangent. The initial tangent to the curve $K(P)$ versus P can be obtained rather precisely, but it would be wrong to attach any great significance to a function $K(P)$ simply because the resulting pressure-volume relation agrees with the available data.

CHOICE OF PARAMETERS

By differentiation of equation 2,

$$\frac{d^2(K/K_0)}{dP^2} = -\frac{2a^2(K_0' - m)}{(P + a)^3}$$

Defining C to be the value of this derivative at $P = 0$, we obtain

$$C \equiv K_0 K_0'' = -\frac{2(K_0' - m)}{a} \quad (3)$$

Here K_0'' is the value of d^2K/dP^2 at $p = 0$. We have required $a > 0$ and $m > 0$ in order to obtain reasonable behavior on $P > 0$. Since $a > 0$, C and $[K_0' - m]$ must be of opposite sign. This means that $m > K_0'$ if $C > 0$ and $m < K_0'$ if $C < 0$.

Now m is the value of dK/dP in the limit as $p \rightarrow \infty$. Since this limit can never be attained experimentally, we are free to choose any $m \geq 0$ that fits the available data. However, some theoretical guidance is provided by the theory of solids. For example, Landau and Lifshitz [1958] state that for a sufficiently compressed substance, the effect of the interaction of its

atomic electrons with the nuclei becomes insignificant, and the substance may be regarded as a degenerate perfect Fermi electron gas, for which the value of dK/dp in the nonrelativistic and extreme relativistic approximations is 5/3 and 4/3, respectively. It should be noted that these values apply only at extremely high pressures. According to the same source, the value 5/3 is for 10^{17} atm $\gg p \gg 5 \times 10^5 Z^{1/3}$ atm, where Z is some average atomic number of the substance, whereas the value 4/3 is for $p \gg 10^{17}$ atm. For sodium ($Z = 11$) the inequality for the value 5/3 becomes $10^{17} \gg p \gg 1.5 \times 10^6$ atm. This range is far above the range of any experimental data and probably even above the range where extrapolations are needed! The highest value of pressure found in compiling the present comparisons is a shock wave point at 1.5×10^6 atm for aluminum oxide. Birch [1963] has estimated the pressure at the center of the earth to be of the order of 3.4 Mb. In general, it is considered normal for dK/dp to decrease slowly in a monotone fashion as the pressure increases. Equation 2 provides the monotone behavior, but the leveling off of dK/dp to within a few per cent of the value m takes place at pressures p of the order of $10aK_0$, which, for reasonable values of a , is very low compared with 10^{12} atm. Therefore, in order to simulate the expected behavior over the pressure range where the extrapolation is desired, it is not unlikely that the best m to use in equation 2 should be substantially larger than 5/3. This is not a very sensitive point, however, since the parameter a (or C) remains undetermined, and the initial value of the second derivative, given by equation 3, can still be adjusted by proper choice of a .

The values of the first two pressure derivatives of the bulk modulus at $P = 0$ and the limiting value of the first derivative as $P \rightarrow \infty$ may be matched to the corresponding values from the Keane equation by using the same values of K_0' and m in the two equations and setting $a = 2/K_0'$, or, equivalently, $C = -K_0'(K_0' - m)$. A similar match to the Birch equation with $K_0' = 4$ [Birch, 1938, 1952], requires $m = 7/3$ and $C = -35/9$, whereas for $K_0' \neq 4$, a match requires $m = 3$ and $C = -K_0'^2 + 7K_0' - 143/9$.

In the comparisons to be presented here, we arbitrarily chose $m = 5/3$ when $C < 0$, and

or C and K_0' both positive.

$$m - K_0' = \frac{2}{[K_0']^2}$$

This expression was obtained by setting the derivative of K_0' to the smallest value that would allow K_0' to fall to zero on $-a < P < 0$. The condition $C \ll K_0'^2$. The condition $C \ll K_0'^2$ continuously to zero on $P < 0$ is an 'instability' condition. It is automatically satisfied whenever $K_0' > 0$, but is not considered essential for extrapolating on $P > 0$, but is of other guidance, it seemed a reasonable criterion for relating the parameters, say m and C , when $C < 0$. The idea that m is the smallest value that allows K_0' to fall from the feeling that K_0' needed to avoid a singularity in this case, is likely to give a value too large to be a correct value of dK/dp as $p \rightarrow \infty$.

When $K_0' < 0$, as for vitreous silica, formulas including those of Keane necessarily predict $K_0' > 0$ on $P > 0$. Although this is a catastrophe, and could be avoided by a more advantageous choice of K_0' , $K_0' < 0$ could be presumed a transition, through which K_0' should not be continued. It is interesting to note that the same such an instability to be avoided by a sufficiently high positive value of K_0' is illustrated in Figure 1 versus P for three different values of $K_0' = -6.5$ and $m = 1$. This applies to vitreous silica [Anderson, 1961].

COMPRESSION

The next task is to relate pressure, subject to equation 1, to the bulk modulus

$$K = \frac{1}{V} = \frac{1}{\left[\frac{mP^2}{2} + (1 + \frac{C}{K_0'}) \right]}$$