

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

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  $\gg p \gg 5 \times 10^8 Z^{1/3}$  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  $10^{17} \gg p \gg 1.5 \times 10^9$  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  $1.5 \times 10^6$  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

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

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

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

COMPRESSION

The next task is to relate the pressure, subject to equation 2, to the bulk modulus

$$K = \frac{K_0}{1 - \frac{C}{mP^2 + (1 + m)P}}$$