

of the important results of should extend to pressures measurements of the ultra- The range of validity is on of accuracy of the bulk re derivatives.

s on the right of (16) con- empirical) quadratic equa- per is called the quadratic

$$\left(\frac{P}{B_0}\right)^2: \text{quadratic,} \quad (20)$$

$$\left(\frac{P}{B_0}\right)^2 - n\left(\frac{P}{B_0}\right)^3: \text{cubic.} \quad (21)$$

ed the quartic polynomial. re entirely determined by data, and they converge to at low pressures. Thus, at adric form (20) satisfac- ta. At a pressure where it e cubic is required (but the to duplicate the data. In s inadequate, and finally a here the quartic itself is

and q , a problem must be ated to the assumption of s because n and q include as a term involving B_0'' . measurements indicate B_0'' r three figures, the magni- e enough that $B_0 B_0''$ is not y. However, we take as an er that $B_0 B_0''$ and $B_0^2 B_0'''$ t all terms in B_0'' and B_0''' dropped. This assumption future experimental and he data discussed in this a special case for n and q

$$3B_0' + 2(B_0')^2 \quad (22)$$

$$11(B_0')^2 + 6(B_0')^3. \quad (23)$$

The definitions (22) and (23) requiring that B_0'' and B_0''' are negligibly small is, of course, consistent with the assumption of linearity between bulk modulus and pressure and is contained in (5). The results of this paper can be regarded as a test on (5): We compare measurements of V/V_0 at high pressure with equations based upon (5) and evaluated with acoustic data.

4. THE LOGARITHMIC COMPRESSION EQUATION

Equation (16) is an expansion around data taken at $P = 0$. It is also possible to use (5) to obtain the compression equation by integration.

In 1944, MURNAGHAN⁽¹⁸⁾ defined and integrated (5) to find

$$P = \frac{B_0}{B_0'} \left\{ \left(\frac{V_0}{V} \right)^{B_0'} - 1 \right\}. \quad (24)$$

There are references to various derivations as "the Murnaghan equation", but this important contribution of Murnaghan has been neglected in the recent literature of equations of state. Cook and Rogers produced, apparently independently, a variant of (24) 19 years later.⁽¹⁹⁾ However, we recognize the original derivation, which is hereafter referred to as the Murnaghan logarithmic equation. From (24)

$$\ln \left(\frac{V_0}{V} \right) = \frac{1}{B_0'} \ln \left\{ B_0' \left(\frac{P}{B_0} \right) + 1 \right\}. \quad (25)$$

It turns out, as we shall show, that (25) describes the compression of compressible solids like NaCl better than the quartic polynomial, (16), at very high pressures, but there is no difference for modest pressures. For incompressible solids like MgO, the advantage of (25) over (16) is slight at pressures in the 200- to 300-kbar region.

A 1% error in B_0' changes the extrapolated volume at $P = B_0$ by less than $\frac{1}{2}\%$.

It is instructive to compare (25) to another equation in wide use⁽²⁰⁾ called the Birch equation of state.

$$P = \frac{3B_0}{2} \left\{ \left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right\}. \quad (26)$$

This equation is for the special case $B_0' = 4$; for B_0' different from 4 it is more complicated but still useful.⁽²⁰⁾ The difference between (25) and (26)

arises because of the different expansions used. In the Birch derivation, the Helmholtz free energy (or strain energy) is expanded in powers of linear strain, and (26) results from using the first three terms and taking $B_0' = 4$. In the Murnaghan logarithmic derivation, the bulk modulus is expanded in powers of pressure, and all but the linear term is ignored. It turns out, as could be expected, that the pressure evaluated from the two equations is equal up to a pressure corresponding to a certain value of the parameter V/V_0 —which is about 0.85—and divergence only occurs at very high compression.

5. THE ADIABATIC-ISOTHERMAL TRANSFORMATIONS

An important numerical computation must be made before (16) or (25) can be evaluated from acoustic data. It appears worthwhile to give in detail the adiabatic-isothermal transformations and the results for several solids.

B_0 is found from B_0 by using (3). The determination of B_0' is more involved. The equations have been derived by OVERTON,⁽²¹⁾ and are presented in a modified form:

$$\begin{aligned} B_0' &= B_0' + T\alpha\gamma \left(\frac{B_0}{B_0'} \right) \left[1 - \frac{2}{\alpha B_0} \left(\frac{\partial B_0}{\partial T} \right)_P - 2B_0' \right] \\ &\quad + \left[T\alpha\gamma \left(\frac{B_0}{B_0'} \right) \right]^2 \left[B_0' - 1 - \frac{1}{\alpha^2} \left(\frac{\partial \alpha}{\partial T} \right)_P \right] \\ &= B_0' + 1\text{st correction term} + 2\text{nd correction term} \end{aligned} \quad (27)$$

Overton found that the 1st correction term was positive for the materials he considered,⁽²¹⁾ and the 2nd term positive or negative but quite small. However, either correction term can be positive or negative, and in the case of cadmium, B_0' is smaller than B_0 .

In (27) all terms are given by the measurements except possibly $(\partial B_0/\partial T)_P$. If adiabatic measurements versus temperature are available, then following (3) and taking $d\gamma/dT = 0$, we have

$$\begin{aligned} \left(\frac{\partial B_0}{\partial T} \right)_P &= \left(\frac{\partial B_0}{\partial T} \right)_P / (1 + T\alpha\gamma) \\ &\quad - \frac{B_0}{T} \frac{T\alpha\gamma}{[1 + T\alpha\gamma]^2} \left\{ 1 + \frac{(\partial \alpha/\partial T)_P}{\alpha/T} \right\}. \end{aligned} \quad (28)$$