

volume at $P=0$, and k , ξ , and r are parameters which can be related to B'_0 , the pressure derivative of the bulk modulus at $P=0$, i.e.,

$$k=r-1=B'_0 \text{ and } 4\xi=12-3B'_0. \quad (6)$$

Of these equations, the Tait equation allows the volume to go to zero at a finite pressure (MacDonald, 1966). Because of this and because it generally does not fit experimental data on solids at high pressures as well as some of the other equations, it will not be developed further, except to say that it follows from an integration assuming that the isothermal bulk modulus is a linear function of pressure (Anderson, 1966), i.e.,

$$B = -V_0 \left(\frac{\partial P}{\partial V} \right)_T = B_0 + B'_0 P. \quad (7)$$

A more detailed analysis of the Tait equation has been recently given by MacDonald (1966).

The Birch equation has been used in the form of equation (3) with one arbitrary parameter or in the form (4) with two arbitrary parameters. This equation is derived from the theory of finite strain under the assumption that the total strain energy can be expanded as $E = \sum a_n \epsilon^n$, where ϵ is the hydrostatic strain in an isotropic solid. Equation (4) follows if $a_n = 0$ for all $n \geq 4$ and equation (3) follows for $a_n = 0$ for all $n \geq 3$. This assumption, as well as the use of finite strain theory, has been discussed by Knopoff (1963). The equation should be a rather good representation of the pressure volume isotherm at $T=0$, for a cubic crystal in a hydrostatic environment for not too large a strain. Birch estimates that it can give good results for relatively large strain for materials in which ξ is small (Birch, 1952). Bernardes and Swenson (1963) observe that the experimental data for the alkali metals at low temperatures fit the Birch equation with small values of ξ , but that slight deviations from this equation appear along higher temperature isotherms. Gilvarry (1957) notes that equation (3) requires that the initial value of the Gruneisen constant at zero pressure must equal 11/6, which, of course, is not satisfied by all solids. This indicates that the two parameter equation (4) is necessary to insure that the P - V relation has the correct initial curvature at zero pressure. This second constant is related to the third-order elastic constants and should be kept in Birch's equation for often the third-order elastic constants are comparable to the second-order elastic constants. Recent high pressure measurements (McWhan, 1967) indicate $\xi = -0.40$ for MgO, $\xi = -1.02$ for NaCl, and $\xi = -1.74$ for alpha-quartz. We will hereafter consider only equation (4) when referring to the Birch equation.

The Murnaghan equation, derived by Murnaghan from the theory of finite strain (Murnaghan, 1937) is an approximation in which the instantaneous bulk modulus $B = -V \left(\frac{\partial P}{\partial V} \right)_T$, where $V = V(P)$, is assumed to vary

only linearly with pressure. Murnaghan refers to it as integrated linear theory (Murnaghan, 1951). It also involves the assumptions that the strain is small and isotropic and the pressure is hydrostatic. The parameters B_0 and $k = B'_0$ can be determined from measurements at zero pressure or they can be left arbitrary and chosen to give the best fit to a set of measurements of P versus V . The best fit to measured data is obviously obtained if both parameters are allowed to be arbitrary. Quite reasonable fits can be obtained, however, by using ultrasonically determined values of B_0 leaving only one arbitrary parameter to vary to give the best fit. The value k has been related to the Gruneisen parameter; i.e., $k = 2\gamma + 1/3$, or the initial pressure derivative of the bulk modulus, B'_0 . Rarely does one find the relation between k and γ to hold but recently Anderson (1966) has shown that precise ultrasonic measurements at rather low pressures will give values of B_0 and B'_0 which allows Murnaghan's equations to represent high pressure isotherms fairly well if the compression is not too large. Many authors (see MacDonald, 1966; and Cook and Rogers, 1963) have proposed equations of state that are nothing more than Murnaghan's equation in a different form and with different labeling of the parameters.

Murnaghan allowed both parameters to vary arbitrarily and was able to fit Bridgman's compression measurements to 100 kbar on Na to within 1.5 percent in V/V_0 . He also observed that the arbitrary coefficients varied considerably depending upon the region of the data used to determine them. He concluded that this indicates that the equation is only an approximation to the truth and that higher order approximations should be considered. A second order theory was also given by Murnaghan (1951) which allows the pressure derivative of the bulk modulus to vary with pressure. He also concluded that this was not accurate enough for the large compression of Na and concluded that the third order elastic constants were very important for large compression.

Recently Rose (1967) extended the expansion of the instantaneous bulk modulus to terms of order P^2 .

$$B = \left(-V \frac{dP}{dV} \right)_T = B_0 + B'_0 P + B''_0 P^2/2. \quad (8)$$

Integrating (8) along on isotherm yields the equation of state

$$P = \frac{-2B_0 \tan \left[\sqrt{\frac{2B_0 B''_0 - B_0'^2}{2}} \left(\ln V/V_0 \right) \right]}{\sqrt{(2B_0 B''_0 - B_0'^2)} + B'_0 \tan \left[\sqrt{\frac{2B_0 B''_0 - B_0'^2}{2}} \ln V/V_0 \right]}. \quad (9)$$

The coefficients in (8) can be expressed in terms of 2nd, 3rd, and 4th order single crystal elastic constants

as defined by Brugger (1964). For a cubic ($m3m$ symmetry) crystal one obtains (Ghate, 1966; Thurston, 1967)

$$B_0 = (c_{11} + 2c_{12})/3$$

$$B'_0 = -(c_{111} + 6c_{112} + 2c_{123})/9B_0, \text{ and}$$

$$B''_0 = (c_{1111} + 8c_{1112} + 6c_{1122} + 12c_{1123} - 2c_{11} - 15B_0 - 9B_0 B'_0)/27B_0^2. \quad (10)$$

The bulk moduli must be converted from adiabatic to isothermal to use in static equations of state. Experimental pressure dependence of the elastic constants have been measured for several materials (Lazarus, 1949; Hughes and Kelly, 1953; Bateman, et al., 1961; Daniels and Smith, 1963; Miller and Smith, 1964; Chang, 1965; Bogardus, 1965; Bartels and Schuele, 1965; Chechile, 1967; Koliwad, et al., 1967).

In principle, Bridgman's equation, equation (1), can fit any analytic compression curve if the expansion is carried out to enough parameters. However, the use of several terms may cause the curve to have anomalous variations related to the scatter in the data and not to fundamental compressibility. One should not use more parameters than is justified by the accuracy of the data. For rather incompressible materials two parameters seem sufficient to fit the data. But an equation of four parameters is not good enough for the alkali metals (Bridgman, 1958).

Gilvarry (1957, 1956) has given an equation of state which will generate many of the proposed isothermal equations of state for solids

$$P = (n - m)^{-1} B_0 [(V_0/V)^n - (V_0/V)^m] \quad (11)$$

where n and m are constants. There is no theoretical basis for this equation but it can be made to fit a wide class of P - V relations by varying the parameters m and n and is equivalent to equations (2) and (3) for given choices of m and n .

Comparisons of these empirical equations of state with experiment are not always too conclusive in that there is often a great deal of scatter and experimental uncertainty in the experiments. *In many cases any or all of these equations of state might be argued as valid representations because they fit the data to within the experimental accuracy.* The experimental techniques are being improved so that experimentally we are just now beginning to be able to discriminate among the proposed equations. There is a more serious problem, however, and that is the accuracy in the pressure measurement itself in the experimental equations of state. Over the years the proposed pressure scale has changed considerably and there are still large differences between the pressure scales used by some experimenters and considerable uncertainty in the pressure measurement. It is hoped that some of the guess work can be removed by the use of equations of state.

Recent work (McWhan, 1967), using x-rays to detect volume change, indicates that the bulk modulus is not

linear with pressure and that the simple two-parameter, Murnaghan equation, equation (2), will always yield too large a pressure for a given compression. This equation, however, will yield reliable pressure to within 3 percent for $V/V_0 > 0.9$, i.e., where terms of higher order than linear in equation (8) can be neglected. However, for these small compressions, equations (2) and (4) will give the same results and the Birch equation appears to be valid to higher compression and is thus preferable. One advantage of the Murnaghan equation is its simple form, while still making a valuable interpolation tool at low pressures. A comparison of pressure differences determined from the Birch and Murnaghan equations versus compression for several values of B'_0 is given in figure 3. It will be noted that the Murnaghan equation always predicts a larger pressure than the Birch equation for any value of B'_0 . If one expands the bulk modulus calculated from (4) in a power series of P , one finds $B''_0 = -(B'_0{}^2 - 7B'_0 + 143/9)/B_0$, which is always negative and never zero.

Two experiments which definitely favor the Birch equation (4) over the Murnaghan equation (2) have

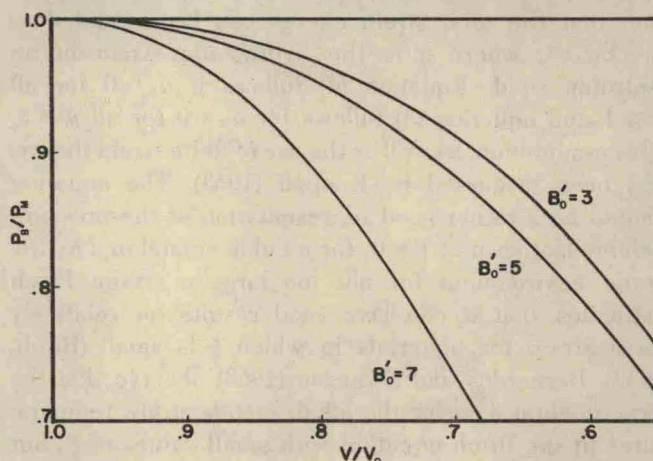


FIGURE 3. Ratio of pressures from the Birch to the Murnaghan equations.

recently been completed (McWhan, 1967; Weaver, et al., 1967). In these experiments, MgO and NaCl, two materials with very different compressibilities, were intimately mixed in a high pressure x-ray cell and their lattice parameters simultaneously measured at various pressures. If the pressure was then calculated from the MgO compression using (2) or (4), which agreed to within 1 percent to 300 kbar, the P - V relation of NaCl agreed with (4) to within 10 percent but definitely disagreed with (2). McWhan used results of Bartels and Schuele (1965) for B_0 and B'_0 for NaCl. Better agreement with (4) would follow if the results of Chang (1965) were used for B'_0 , i.e., isothermal $B'_0 = 5.18 \pm .09$.

It was concluded that the Birch equation (4) was the most reliable of these two parameter equations considered. It should also be added, however, that all the equations based on the theory of finite strain are valid only for cubic crystals in hydrostatic media.