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Extrapolation Formula for Finding the Volume of Solids at High Pressures

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A formula is proposed for extrapolating from data taken at low or moderate pressures to the high pressures that exist in the interior of the earth and planets. The formula, which predicts the curve of reduced volume v/v_0 versus reduced pressure $P \equiv p/K_0$, follows from integration of the following assumed expression for the pressure derivative of the bulk modulus $K \equiv -v\, dp/dv$

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

When $m = K_0'$, the formula reduces to the well-known Murnaghan relation, which is itself remarkably successful. In general, there is an improvement on the Murnaghan relation because the above expression allows the derivative to change from its initial value K_0' to a more realistic value m as $P \to \infty$. The Keane equation, $d(K/K_0)/dP = m + (K_0' - m)/(K/K_0)$, has this same property, but with the disadvantage of behaving unreasonably if $K_0' < 0$. To apply our formula, K_0' is determined from low-pressure ultrasonic data (0 to 6 kb), m is fixed at some reasonable value, and the remaining parameter is then determined by trial and error to fit the high-pressure data that are available. Rough estimates of the initial value of the second pressure derivative of the bulk modulus can be obtained in this way. As examples, the formula is fitted to experimental data that are already in the literature on aluminum oxide, α-quartz, magnesium, potassium, sodium, and lead.

Introduction

A few years ago, *Anderson* [1966] emphasized that the extrapolation formula of *Murnaghan* [1944], which is based on the assumption of a linear pressure dependence of the bulk modulus, is remarkably successful in predicting the volume of a solid at high pressures. More recently, *Anderson* [1968] pointed to the need for an improved formula and recommended the Keane equation [*Keane*, 1954]. In the present paper, we give a formula that has the advantage of the Keane equation while incorporating an additional parameter for increased flexibility.

The Keane equation can be obtained by integration from

$$\frac{d(K/K_0)}{dP} = m + \frac{K_0' - m}{K/K_0} \qquad (1)$$

where $P = p/K_0$, p being the pressure, K is the bulk modulus, K_0 its value at zero pressure,

K_0' its first pressure derivative evaluated at zero pressure, and m the value of the first pressure derivative in the limit as $K \to \infty$. Anderson's recommendation is to determine K_0 and K_0' from ultrasonic data taken at low pressures, and m from shock wave data at higher pressures. This procedure gives an excellent fit to the available experimental data. Whenever K_0' and m are both positive, the extrapolation behaves reasonably on the entire range $P > 0$. However, if K_0' is negative, the Keane equation predicts unreasonable behavior in that it forces K to go to zero at some positive pressure.

There is a class of materials, mainly certain glasses, where K_0' is negative, although dK/dp becomes positive and behaves normally at sufficiently high pressures. This class includes vitreous silica [*McSkimin* as cited by *Anderson*, 1961], obsidian [*Manghnani et al.*, 1968], germania glass [*Soga*, 1969], and vycor [*Manghnani and Benzing*, 1969]. The previous extrapolation formulas do not handle this class at all.

The present proposal is to take

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

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 $p \to \infty$. 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 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 $\gg p \gg 5 \times 10^5 Z^{10/3}$ atm, where Z is some average atomic number of the substance, whereas the value 4/3 is for $p \gg 10$ atm. For sodium ($Z = 11$) the inequality for the value 5/3 becomes $10^{17} \gg p \gg 1.5 \times 10$ 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 $P \to \infty$ 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 $C = -K_0'^2 + 7 K_0' - 143/9$.

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

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C and K_0' both positive we used

$$m - K_0' = \frac{C}{2[K_0' - (2C)^{1/2}]} \quad (4)$$

This expression was obtained as an approxima-
on to the smallest value of m that allowed K
fall to zero on $-a < P < 0$, assuming
$\ll K_0'^2$. The condition that K drop con-
nuously to zero on $P < 0$ may be regarded as
n 'instability' condition. It is satisfied auto-
atically whenever $K_0' > 0$ and $C < 0$. It is
ot considered essential for the purpose of extra-
olating on $P > 0$, but in the absence of any
ther guidance, it seemed to be a reasonable
riterion for relating the two adjustable param-
ters, say m and C, when K_0' and C are both
ositive. The idea that m should be near the
mallest value that allows this instability fol-
ws from the feeling that the condition $m >$
K_0', needed to avoid a singularity on $P > 0$ in
this case, is likely to give an m that is already
too large to be a correct limiting value of
dK/dp as $p \rightarrow \infty$.

When $K_0' < 0$, as for vitreous silica, many
formulas including those of Murnaghan and
Keane necessarily predict an instability ($K \leq$
0) on $P > 0$. Although this may not be a great
catastrophe, and could even be represented as
advantageous (because an actual material with
$K' < 0$ could be presumed to undergo a phase
transition, through which the extrapolation
should not be continued analytically), it is in-
teresting to note that the present formula allows
such an instability to be avoided by choosing
a sufficiently high positive value for C. This
is illustrated in Figure 1, which shows K/K_0
versus P for three different values of C with
$K_0' = -6.5$ and $m = 1$. The value $K_0' = -6.5$
applies to vitreous silica [McSkimin as cited by
Anderson, 1961].

COMPRESSION EQUATION

The next task is to relate the volume v to the
pressure, subject to equation 2 and the defini-
on of the bulk modulus

$$K = -v \, dp/dv \quad (5)$$

Fig. 1. Determining the value of C that en-
sures reasonable behavior of K on $p > 0$ for the
anomalous case, vitreous silica ($K_0' < 0$) (see
text).

Let $V = v/v_0$. Then

$$K/K_0 = -V \, dP/dV \quad (6)$$

As an abbreviation in equation 2, let $A = a(K_0' - m)$. Then the integral of equation 2 is

$$\frac{K}{K_0} = -V \frac{dP}{dV} = 1 + A + mP - \frac{aA}{P + a} \quad (7)$$

where the constant of integration has been
determined to make $K = K_0$ at $P = 0$. From
(7)

$$V = \exp\left[-\int \frac{dP}{\left(1 + A + mP - \frac{aA}{P + a}\right)}\right] \quad (8)$$

The evaluation of the integral in the expres-
sion above, subject to $V = 1$ when $P = 0$
(Given in Appendix B), gives us

$$V = \left\{\left[\frac{a}{mP^2 + (1 + A + am)P + a}\right] \cdot \left[\frac{4am + 2mP[(q)^{1/2} + (1 + A + am)]}{4am - 2mP[(q)^{1/2} - (1 + A + am)]}\right]^{(1+A-am)/(q)^{1/2}}\right\}^{1/2m} \quad (9)$$
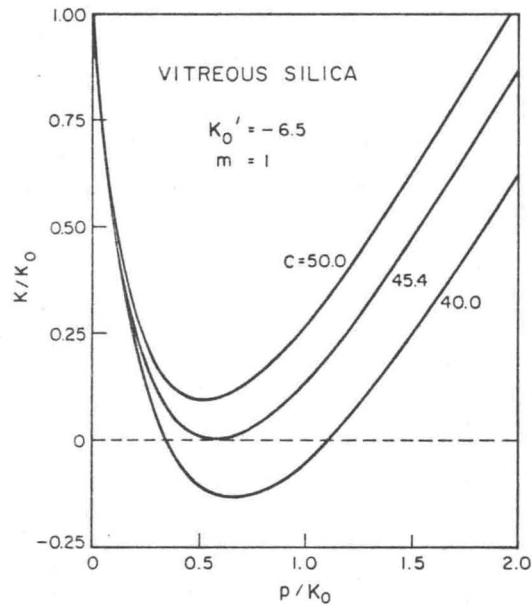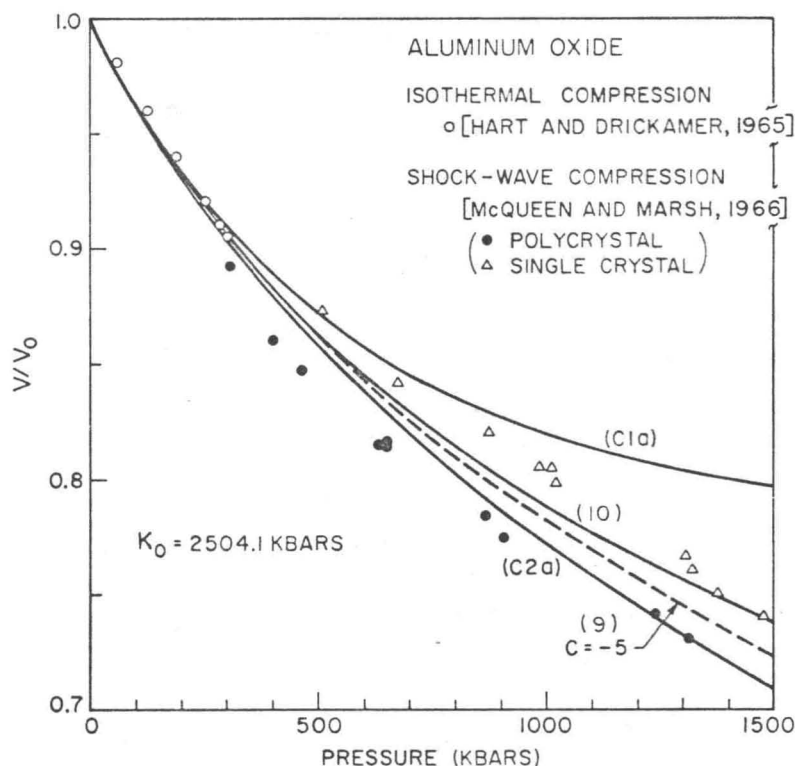
Fig. 2.

Figures 2–7 give a comparison of extrapolated and measured values of volume ratio v/v_0 versus pressure for aluminum oxide, α-quartz, magnesium, potassium, sodium, and lead; the curves are marked with the numbers of the extrapolation formulas given in the text.

where $q = (1 + A + am)^2 - 4am$.

For the case $C = K_0 K_0'' = 0$, the integration of the expression for the bulk modulus (equation 7 with $A = 0$ and $m = K_0'$) leads to the 'extrapolation formula' for V due to *Murnaghan* [1944]

$$V = [1 + K_0'P]^{-1/K_0'} \qquad (10)$$

RESULTS OF CALCULATIONS

The results of the calculations based upon equations 9 and 10 for aluminum oxide, α-quartz, magnesium, potassium, sodium, and lead are compared with experimental data in Figures 2–7. In these figures the solid curve is a plot of equation 10, whereas the dashed curve refers to equation 9. The additional solid curves, labeled C1a and C2a, are derived from the exponential formulas discussed in Appendix C.

The calculations were based on values of K_0 and K_0' compiled by *Anderson* [1966]. These

are listed in Table 1. For equation 9, $m = 5/3$ was chosen for $C < 0$, whereas for $C > 0$ the approximation given by equation 4 was used to determine m; the value of K_0'' was chosen (by trial and error) to provide reasonable agreement with the experimental compression data. The sources of the data are cited in the figures.

An error in K_0' will clearly affect the apparent value of K_0'' needed for a good fit. For this reason, it is important to have a reliable value of K_0' before any confidence can be placed in an estimate of K_0''. For example, a relatively small error in K_0' may very well account for the unexpected difference (in sign of K_0'') between sodium and potassium. Similarly, taking account of a possible difference in K_0' between monocrystalline and polycrystalline aluminum oxide would be very likely to affect the conclusions concerning C.

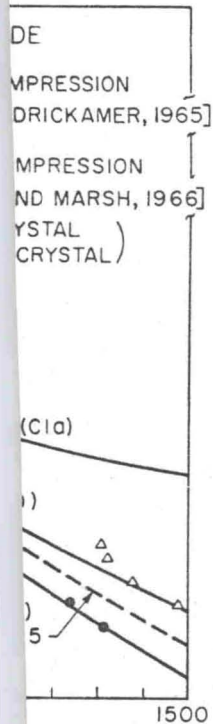For aluminum oxide, α-quartz, and magnesium (Figures 2–4), the disparity between the ex-

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ND MARSH, 1966]
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lues of volume ratio v/v_0
m. sodium, and lead; the
given in the text.

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provide reasonable agreemen
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mental data permits the choice of C to vary
derably. In the case of aluminum oxide
$= +5$ and $C = -15$ would provide a
sonable fit of the single-crystal and poly-
tal shock wave data, respectively. We have
sen $C = -5$ ($K_0'' = -2 \times 10^{-12}$ cm²/dyne)
represent an average fit, but we certainly
uld not attach any particular significance to
choice of C in view of the available data,
ch seem to indicate that the single-crystal
polycrystal behave somewhat differently.
this case the calculated curves are based on
determined from the ultrasonic data for
crystalline material. For α-quartz $C = 10$
$K_0'' = 27 \times 10^{-12}$ cm²/dyne) provides a rea-
uable fit of the shock wave data, whereas the
gh-pressure isothermal data suggest a smaller

value of C for a fit. For magnesium, Figure 4,
$C = \pm 2$ ($K_0'' = \pm 5.8 \times 10^{-12}$ cm²/dyne) ac-
commodates the scatter between the high pres-
sure isothermal compression data.

The calculated curve for potassium (Figure
5) shows good agreement with experimental
data by picking $C = -0.6$ ($K_0'' = -17.8 \times 10^{-12}$ cm²/dyne). Strangely, a positive value of
C was required to fit the experimental data of
the other alkali metal, sodium. In Figure 6 the
calculated curve for sodium with $C = 1.5$
($K_0'' = 24.3 \times 10^{-12}$ cm²/dyne) provides a very
good fit of the experimental data to high pres-
sures.

In Figure 7 the agreement between calculated
and experimental data for lead is quite good
over the entire pressure range for a value of

Fig. 3.

MAGNESIUM

ISOTHERMAL COMPRESSION
o [CLENDENEN AND DRICKAMER, 1964]
• [DRICKAMER ET. AL., 1966]
△ [BRIDGMAN, 1948a]

SHOCK-WAVE COMPRESSION
□ [RICE, McQUEEN AND WALSH, 1958]

$K_0 = 344.04$ KBARS
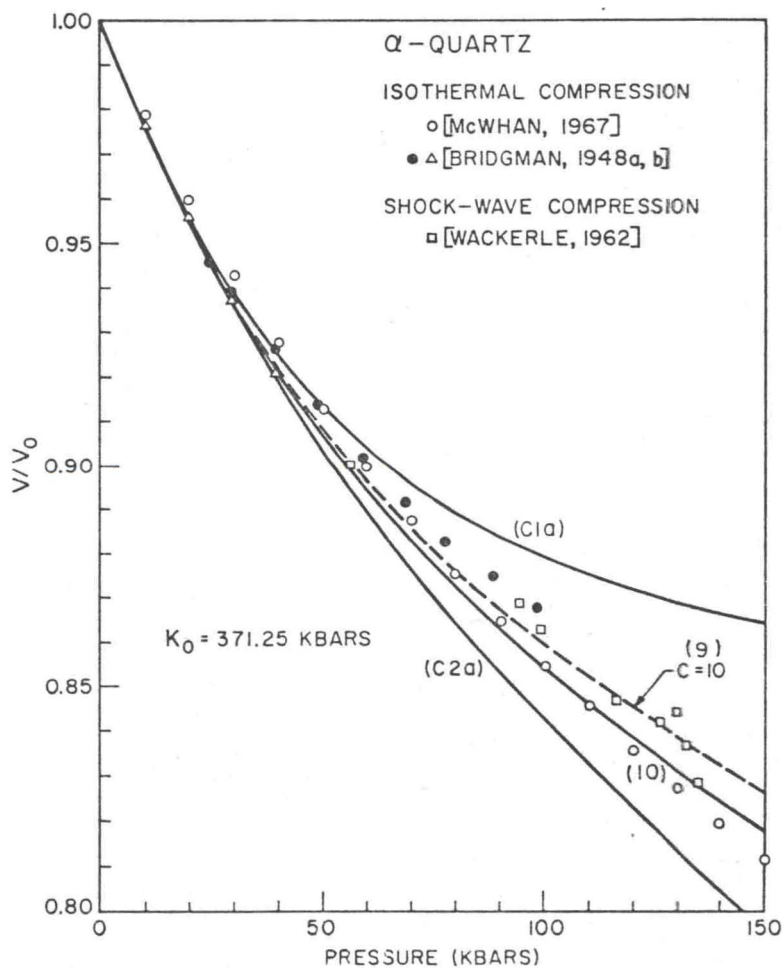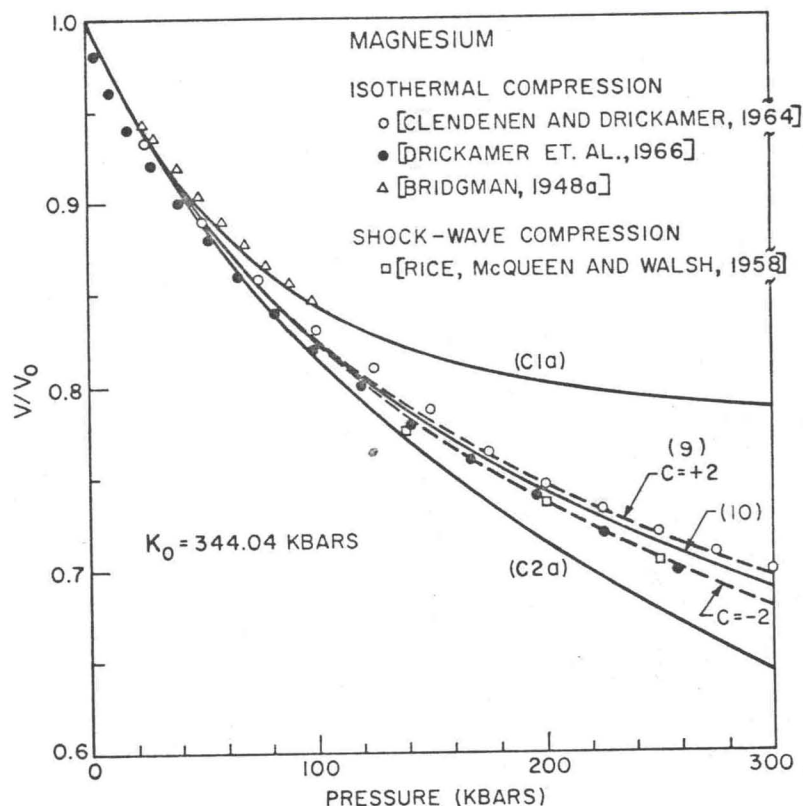
Fig. 4.

$C = -2$, corresponding to $K_0'' = -4.8 \times 10^{-12}$ cm^2/dyne. In spite of the impressive agreement, it should be mentioned that a phase transition at about 160 kb makes questionable any extrapolation from the low-pressure region into the high-pressure region.

The effect of varying m is shown in Figure 8 where we have plotted the calculated curves for aluminum oxide out to 5000 kb. Using values of m equal to 1, 2, and 3, equation 9 is plotted for $C = -1$. In addition, we have plotted the curves for $m = 4.2, 5.2, 6.2,$ and $C = +1.0$. One can readily observe that the six curves are distinguishable only for extreme pressures. Also, as $C \to 0$ for given K_0' and m, either $a \to \infty$ or $K_0' = m$, and in both cases the limiting expression for K/K_0 becomes independent of m. We may therefore conclude that the value of m does not appreciably affect the volume calculation when $|C|$ is small.

As a final point of interest, Figure 9 compares typical results from equation 9 with re-

sults based on a quadratic approximation to the bulk modulus, given by

$$\frac{K}{K_0} = 1 + K_0'P + \tfrac{1}{2}CP^2$$

The extrapolation formula predicted by this quadratic approximation is obtained in a manner similar to that given in Appendix B for equation 7. That is

$$V = \exp\left[-\int \frac{dP}{\tfrac{1}{2}CP^2 + K_0'P + 1}\right]$$

$$= \left\{\frac{[CP + K_0' + (r)^{1/2}][K_0' - (r)^{1/2}]}{[CP + K_0' - (r)^{1/2}][K_0' + (r)^{1/2}]}\right\}^{1/(r)^{1/2}} \quad (11)$$

where $r = (K_0')^2 - 2C > 0$. For $r = 0$ and $r < 0$ the volume equation becomes

$$V = \exp\left(\frac{2}{CP + K_0'} - \frac{2}{K_0'}\right) \quad (11a)$$

and

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D DRICKAMER, 1964]
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a]

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(9)
C=+2
(10)

C=-2

300

a quadratic approximation to
given by

$$= 1 + K_0'P + \tfrac{1}{2}CP^2$$

tion formula predicted by
roximation is obtained in a m
that given in Appendix B
at is

$$\int \frac{dP}{\tfrac{1}{2}CP^2 + K_0'P + 1} \Bigg]$$

$$\frac{K_0' + (r)^{1/2}][K_0' - (r)^{1/2}]}{K_0' - (r)^{1/2}][K_0' + (r)^{1/2}]} \Bigg\}$$

$$_0')^2 - 2C > 0. \text{ For } r = 0$$
ume equation becomes

$$\left(\frac{2}{CP + K_0'} - \frac{2}{K_0'} \right)$$

$$\exp \left\{ \frac{2}{(-r)^{1/2}} \left[\tan^{-1} \frac{K_0'}{(-r)^{1/2}} \right.\right.$$

$$\left.\left. - \tan^{-1} \frac{CP + K_0'}{(-r)^{1/2}} \right] \right\} \qquad (11b)$$

pectively. We note from the figure that both
ations predict similar values of compression
r a considerable pressure range. For nega-
e values of C, equation 11 exhibits an in-
tion point, corresponding to the maximum
ue of K at the positive pressure $P = -K_0'/C$,
d at another finite positive pressure

$$P = -\left[\frac{K_0' + (r)^{1/2}}{C} \right]$$

e bulk modulus and volume are both zero. In
dition, for positive values of C, equations 11,
a, and 11b tend to the limits

$$\left[\frac{K_0' - (r)^{1/2}}{K_0' + (r)^{1/2}} \right]^{1/(r)^{1/2}}, \ \exp\left[-\frac{2}{K_0'} \right],$$

and

$$\exp \left[\frac{2}{(-r)^{1/2}} \tan^{-1} \frac{K_0'}{(-r)^{1/2}} - \frac{\pi}{(-r)^{1/2}} \right]$$

respectively, as $P \rightarrow \infty$. Nevertheless, these
equations usually predict reasonable behavior
beyond the range of experimental data. The
behavior predicted by this quadratic approxi-
mation to the bulk modulus has been discussed
also by *Macdonald* [1969] in a recent review
paper on equations of state.
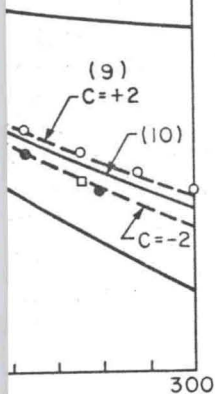
APPENDIX A. SOME OTHER POSSIBILITIES

There are many expressions that may be
suitable for representing the bulk modulus as
a function of pressure. To put equation 2 in a
more general setting, we write

$$\frac{d(K/K_0)}{dP} = m + \frac{a_1}{P + a} + \frac{a_2}{(P + a)^2} \qquad (A1)$$

When one solves for a_1 and a_2 in terms of K_0',
C, m, and a, the results are

$$a_1 = a^2C + 2a(K_0' - m) \qquad (A2)$$

POTASSIUM
ISOTHERMAL COMPRESSION
o ● [BRIDGMAN, 1948a, b]
△ [MONFORT AND SWENSON, 1965]
SHOCK-WAVE DATA
□ [RICE, McQUEEN AND WALSH, 1958]

(C1a)

(C2a)

(10)

(9)
C = -0.6
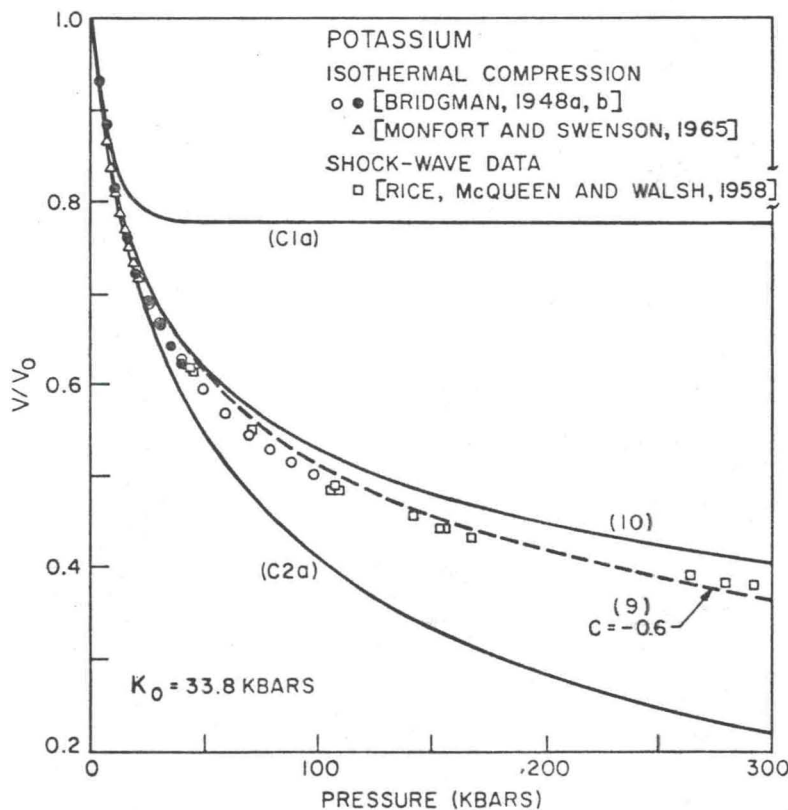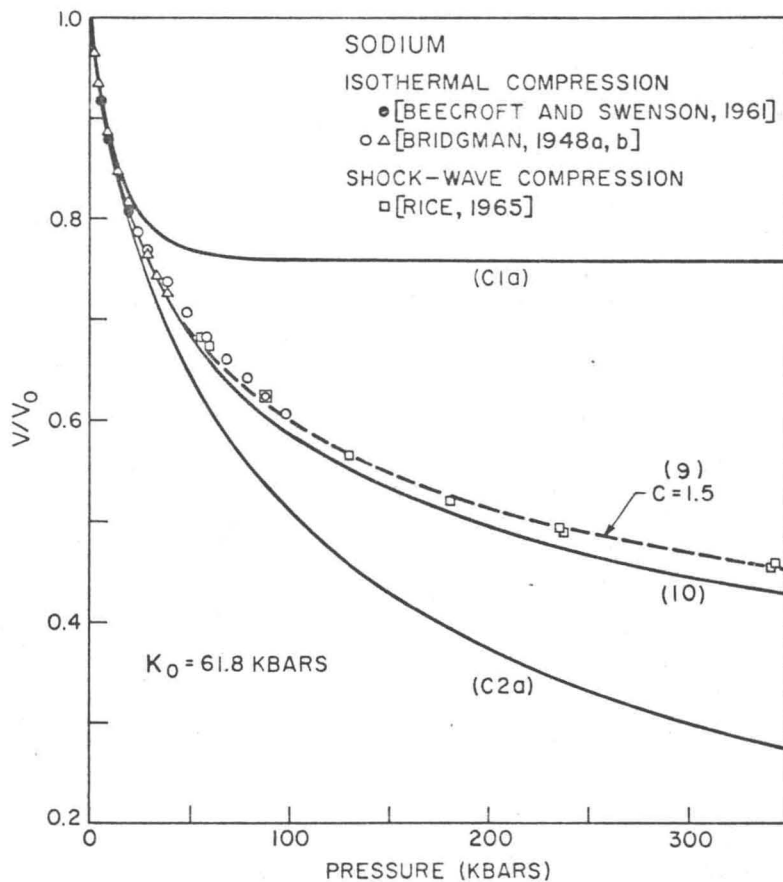
K_0 = 33.8 KBARS

V/V₀

PRESSURE (KBARS)

Fig. 5.

Fig. 6.

$$a_2 = -a^3 C - a^2(K_0' - m) \qquad (A3)$$

If C satisfies equation 3, then $a_1 = 0$ and $a_2 = a^2(K_0' - m)$, in which case equation A1 reduces to equation 2. Having an additional parameter, equation A1 has considerably more freedom, as manifested by the fact that C and $(K_0' - m)/a$ can be varied independently. For example, one can have $m = K_0'$ with $C \neq 0$ or $C = 0$ with $m \neq K_0'$. A possible method of use of equation A1 would be to choose two parameters sensibly but somewhat arbitrarily, say $m = 4$ and $a = 1$, determine K_0' and C for fitting to data, and then use the formula for the purpose of extrapolation.

Equation A1 will be recognized as part of a Laurent series. One may also consider a more general term of the form $a_n(P + a)^{-n}$. For example, we could write

$$\frac{d(K/K_0)}{dP} = m + \frac{a_n}{(P + a)^n} \qquad (A4)$$

Equation 2 then appears as the special case in which $n = 2$. The special case $n = 1$ is also the special case of (A1) in which $a_2 = 0$. With $n = 1$, $a = 1/K_0'$, and $a_1 = 1 - (m/K_0')$, equation A4 gives the result of substituting the Murnaghan expression for K/K_0 into the right-hand side of the Keane equation, equation 1.

Some other possibilities are

$$\frac{d(K/K_0)}{dP} = m + \frac{b}{\log(P + a)} \qquad (A5)$$

and

$$\frac{d(K/K_0)}{dP} = m + \frac{c}{(P + a)\log(P + a)} \qquad (A6)$$

APPENDIX B. EXTRAPOLATION FORMULA FOR
COMPRESSION FROM EQUATION 7

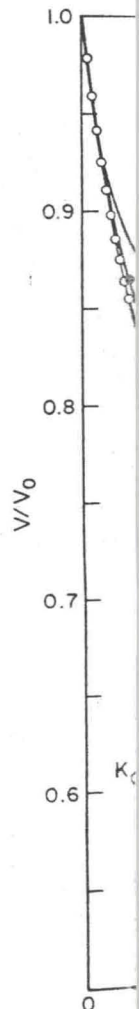By replacing dP in equation 8 with $d(P + a)$, see that it is of the form

$$V = \exp\left[-\int \frac{x\,dx}{bx^2 + cx + d}\right]$$

The integral in the exponent is

$$\frac{1}{2b}\ln(bx^2 + cx + d) - \frac{c}{2b}\int \frac{dx}{bx^2 + cx + d} \quad (B1)$$

where

$$b = m, \qquad m > 0$$

$$c = (1 + A - am)$$

$$d = -aA$$

In writing the expression for

$$\int \frac{dx}{bx^2 + cx + d} \quad (B2)$$

it is of interest to know the sign of $q = c^2 - 4bd$; that is, we have $q = (1 + A - am)^2 + 4amA > 0$ if a, A, and m are all positive. This is the usual case since ordinarily $(K_0' - m) > 0$ and $C = (K/K_0)_0'' < 0$, and this requires

Fig. 7.

TABLE 1.   Data

Material	K_0, kb	K_0'
α-SiO_2	371.25	6.33
Al_2O_3	2504.1	4.00
Mg	344.04	4.07
K	33.8	3.98
Na	61.8	3.59
Pb	416.0	6.30

$a > 0$ and $A > 0$ (equation 3). For the case $(K_0' - m) < 0$ the parameters a and A are of opposite sign, and q is clearly > 0. We also need to know whether $2bx + c > (q)^{1/2}$. To answer this question, note that

$$q = (1 + A - am)^2 + 4amA$$

$$= (1 + A + am)^2 - 4am \qquad (B3)$$

and

$$2bx + c = 2m(P + a) + (1 + A - am)$$

$$= (1 + A + am) + 2mP$$

Clearly, for $C < 0$, $(q)^{1/2} < (1 + A + am)$ therefore $2bx + c > (q)^{1/2}$ for all $P \geq 0$. In this case equation B2 is appropriately written in the logarithmic form

$$\frac{1}{(q)^{1/2}} \ln \left[\frac{(1 + A + am) + 2mP - (q)^{1/2}}{(1 + A + am) + 2mP + (q)^{1/2}} \right]$$
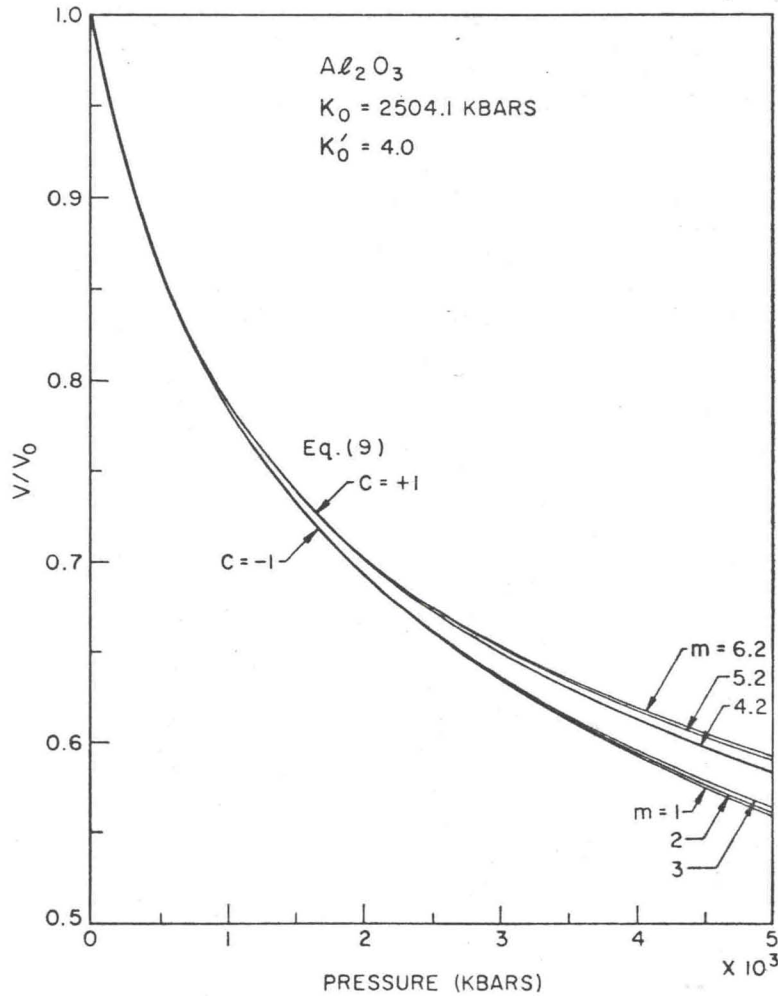
$$(B4$$

Fig. 8.   Effect of varying m on extrapolated values of v/v_0 versus pressure for aluminum oxide.

$$- am)^2 + 4am\,A$$

$$+ am)^2 - 4am$$

$$P + a) + (1 + A \dots$$

$$- A + am) + 2mP$$

$$0, (q)^{1/2} < (1 + A + \dots$$

$$\; > (q)^{1/2} \text{ for all } P \geq 0$$

B2 is appropriately written

form

$$+ am) + 2mP - (q)^{\dots}$$
$$+ am) + 2mP + (q)^{\dots}$$
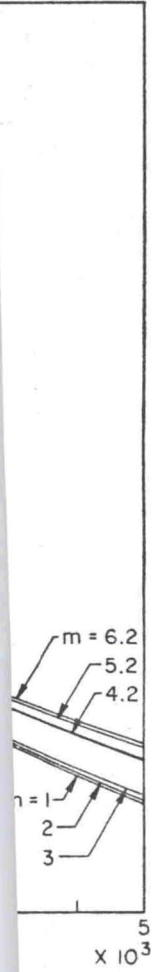
answer the question for $C > 0$, $(K_0' - m) <$ write equation B3 for q with $A = (\dots - m)$, $a = -2(K_0' - m)/C$:

$$\left[1 - \frac{2(K_0' - m)^2}{C} - \frac{2m(K_0' - m)}{C}\right]^2$$

$$+ \frac{8m(K_0' - m)}{C}$$

$$= \left[1 + \frac{2K_0'(m - K_0')}{C}\right]^2$$

$$- \frac{8m(m - K_0')}{C} \qquad (B5)$$

note that both the second term and the square root of the first term in the above expression are positive; therefore, $2bx + c > \dots$ for all $P \geq 0$, and we again use the logarithmic form (Equation B4) to evaluate equation B2.

After having evaluated the integral, equation B1, for both cases subject to $V = 1$ when $= 0$ we then write the equation for V (equation 9).

APPENDIX C

As has been emphasized by *Anderson* [1966], the success of Murnaghan's equation 10 is spectacular because the entire curve of K/K_0 versus K_0 is determined by a single parameter K_0'. Moreover, this parameter is not adjusted to fit
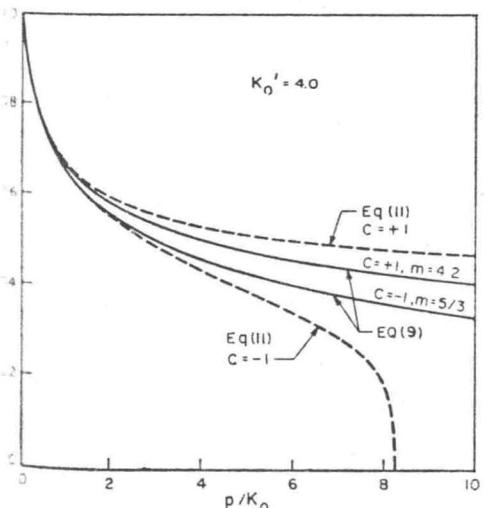
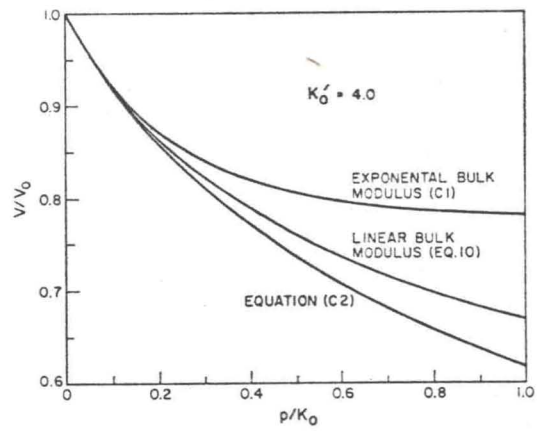9. Comparison of extrapolation formulas for $C = \pm 1$ (see text).

Fig. 10. Comparison of extrapolation formulas based on the linear and exponential assumptions for the bulk modulus (see text).

all the data, but only the low pressure ultrasonic data on wave transit times versus p. (This is presumed to give, after calculations using thermal data to convert from adiabatic to isothermal values of dK/dp, the true limit of dK/dp as $p \to 0$.) It was desired to see whether a one-parameter fit (in which the parameter is the initial value of dK/dp) is sensitive to the assumption of exact linearity of K. To gain some insight into this question, we have compared V predicted from the linear assumption (given by equation 10) with V predicted from each of two exponential formulas.

$$\frac{K}{K_0} = \exp\left(\frac{K_0'p}{K_0}\right) \qquad (C1)$$

$$\frac{K}{K_0} = \exp\left(\frac{K_0'p}{K}\right) \qquad (C2)$$

With K given by equation 6 the above expressions can be integrated to obtain the required formulas for the volume ratio. From (C1),

$$V = \exp\left\{\frac{1}{K_0'}\left[\exp\left(-K_0'P\right) - 1\right]\right\} \qquad (C1a)$$

and from (C2)

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

$$P = \frac{1}{K_0'}\left(\frac{K}{K_0}\ln\frac{K}{K_0}\right) \qquad (C2a)$$

The assumption (C2) leads to the above pair of equations C2a, from which calculations can

be made by picking values of K/K_0 and calculating the corresponding values of V and P. It is, of course, possible, by eliminating K/K_0, to obtain a formula connecting P and V directly. The result is

$$P = \frac{S}{K_0'} e^s \tag{C2b}$$

$$S = \ln \frac{K}{K_0} = -1 + \left[1 + 2K_0' \ln\left(\frac{1}{V}\right)\right]^{1/2}$$

If $K_0' = 0$ the linear, quadratic, and exponential equations reduce to $K = K_0$ yielding the same limiting function

$$V = \exp(-P) \tag{C3}$$

It should be noted, however, that equations 10, 9, and C2a lead to the limiting behavior $V \to 0$ as $P \to \infty$, whereas equation C1a unrealistically predicts $V \to \exp(-1/K_0')$.

The results of calculations based on the linear and two exponential assumptions are plotted in Figure 10 for the case $K_0' = 4$, a typical value. At $P = 1$, the values of V are 0.671, 0.785, and 0.618 from (10), (C1), and (C2), respectively. On the other hand, the values of K itself are respectively $5K_0$, $54.5K_0$, and $3.33K_0$. It must be concluded that comparison of volume ratios (or density ratios) in the range $0 < p/K_0 < 1$ is not a highly sensitive test of the behavior of the bulk modulus. This is to be expected, of course, because the volume changes are relatively small. Nevertheless, it seems worthwhile to emphasize this point because of the large changes in K that can possibly accompany small changes in the density.

We remark that even crude measurements of wave velocity in a material that is initially compressed to say 0.8 of its original volume should give more information concerning the behavior of the bulk modulus than can be obtained from relatively precise volume measurements.

As further illustrations, calculations based on the exponential assumptions for α-quartz, aluminum oxide, magnesium, potassium, sodium, and lead are added to Figures 2–7. It is certainly clear that a linear pressure dependence of the bulk modulus gives better agreement than an exponential one.

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