Theoretical prediction for the validity of isothermal EOS for geophysical minerals

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ABSTRACT
The validity of equation-of-state (EOS) of geophysical minerals is very important for various scientific fields including geophysics, material science and high-pressure physics. In the present work we have calculated pressure \( P \), isothermal bulk modulus \( K'_T \), first pressure derivative of isothermal bulk modulus \( K'_T \) and second order pressure derivative of isothermal bulk modulus in terms of \( K'_T K_T \) for MgO and Al2O3, using different equation of state. Using the values of these parameters we have computed the values of Gruneisen parameter \( \gamma \) corresponding to different values of \( V/V_0 \) and graphs are plotted for Gruneisen parameter \( \gamma \) vs. \( V/V_0 \) for MgO and Al2O3. From these plots it is clear that the Brennan-Stacey and Shanker EOS is compatible both low and high compression ranges for calculating Gruniesen parameter where as Vinet EOS is not compatible for calculating the Gruniesen parameter at low compression ranges.

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Introduction
Knowledge of the \( P-V-T \) equation-of-state EOS of relevant materials is very important for scientific investigations in the various fields including geophysics, material science and high-pressure physics [1, 2]. Experimentally, the EOS of a material can be determined by both static diamond anvil cell DAC [3] and dynamic shock wave experiments [4-5] at high pressures and temperatures. Alternatively, the pressure, especially under high pressure and high temperature conditions, can be obtained from the diffraction line shifts in a standard material which is mixed with the sample and whose equation-of-state EOS of relevant standard materials is one of the most basic information required for pressure calibration.

The purpose of the present study is to assess the validity of some important Equation of states (EOS) for mantle minerals. A comparison of the result for P-V relationships, bulk modulus, its pressure derivative and Gruneisen parameter has been presented with those obtained from Brennan and Stacey EOS [6], Shanker EOS [9, 10] and Vinet EOS [11-13] at different compression ranges.

In present paper an attempt has been made for theoretical prediction of validity of three different phenomenological isothermal EOS viz. Shanker EOS, Vinet EOS and Brennan-Stacey EOS to determine the compression dependence pressure of two different mantle minerals viz. MgO and Al2O3.

Theory
The derivation of equation of state (EOS) of a thermodynamic system is based on a fundamental theorem which equates the negative of pressure to the isothermal volume derivative of a Helmholtz free energy function \( F \). The function \( F \) consists of two terms in the case of solids, the first of which represents the potential energy of a non-vibrating lattice while the second owes its origin to the pressure of the thermal vibrations.

An EOS can be derived from the volume derivative of lattice potential energy by using the relation:

\[
P = -\left( \frac{dW}{dV} \right)
\]

where \( W \) for an ionic crystal can be written as the sum of electrostatic energy and short range overlap repulsive energy.

Using the free volume formula [7] for the Gruneisen parameter \( \gamma \) and assuming that the Gruneisen parameter \( \gamma \) is proportional to volume, Brennan and Stacey obtained an EOS [6, 8] which is given as:

\[
P = \frac{3K_0 \left( \frac{V}{V_0} \right)^{\frac{4}{3}}}{(3K_0 - 5)} \left[ \exp \left( \frac{3K_0 - 5}{3} \left( \frac{V}{V_0} \right) \right) - 1 \right]
\]

(1)
On the basis of Born lattice theory taking the volume derivative of short range force constant Shanker obtained a equation of state known as Shanker EOS \([9,10]\) which are as:

\[
P = \frac{3K_0}{(3K_0 - 8)} \left[ \left(1 - \frac{1}{t} + \frac{2}{t^2}\right) \exp \left(1 - y\right) + \left(y + \frac{1}{t} - \frac{2}{t^2}\right) \exp \left(1 - y\right) \right]
\]

where,

\[y = 1 - \frac{V}{V_0}\] and \[t = K_0 - \frac{8}{3}\]

Vinet proposed a new equation of state on account of relating binding energy with inter-atomic distances known as Vinet EOS \([11-13]\) given as-

\[
P = 3K_0 x^{-2} \exp \left(\eta(1-x)\right)
\]

Where,

\[x = \left(\frac{V}{V_0}\right)^{1/3}\] and \[\eta = \frac{3}{2}(K_0' - 1)\]

Expression for isothermal bulk modulus corresponding to equation (1), (2) and (3) can be obtained by using the relation, \(K_T = -V \frac{\partial P}{\partial V}\), are given as under:

\[
K_T = \frac{4}{3} P + K_0 \left(\frac{V}{V_0}\right)^{1/3} \exp \left(K_0' - \frac{5}{3} \left(1 - \frac{V}{V_0}\right)\right)
\]

\[
K_T = \frac{4}{3} P + K_0 \left(\frac{V}{V_0}\right)^{4/3} \exp \left(K_0' - \frac{8}{3} \left(1 - \frac{V}{V_0}\right)\right)
\]

\[
K_T = K_0 x^{-2} \left[1 + \left(1 + \eta x(1-x)\right)\right] \exp \eta(1-x)
\]

The first order pressure derivative of isothermal bulk modulus \(K_T'\) can be obtained by using the relation \(K_T = \frac{\partial K_T}{\partial P}\),

\[
K_T' = \frac{16}{9} \frac{P}{K_T} + \frac{1}{3} \frac{4P}{3K_T} \left[\left(\frac{K_0' - 5}{3}\right) \left(\frac{V}{V_0}\right) + \frac{5}{3}\right]
\]

\[
K_T' = \frac{16}{9} \frac{P}{K_T} + \frac{1}{3} \frac{4P}{3K_T} \left[\left(\frac{K_0' - 8}{3}\right) \left(\frac{V}{V_0}\right) + \frac{8}{3}\right]
\]

\[
K_T' = \frac{1}{3} \left[\frac{x(1-\eta) + 2\eta x^2}{1 + (\eta x + 1)(1-x)} + \eta x + 2\right]
\]

The corresponding expression for second order pressure derivative of isothermal bulk modulus \(K_T''\), obtained from further derivation of expression for \(K_T'\), corresponding to three different EOS, on making further derivation of (7), (8) and (9) we obtain \(K_T''\), in terms of \(K_T, K_T'\) given as follows:

\[
K_T K_T' = \frac{4}{3} \left(1 - \frac{PK_T}{K_T}\right) \left[\frac{V}{V_0} \left(K_0' - \frac{5}{3}\right) + \frac{5}{3}\right] - \left(V \frac{K_0' - 5}{3}\right) \left(1 - \frac{4}{3} \frac{P}{K_T}\right)
\]

\[
K_T K_T' = \frac{4}{3} \left(1 - \frac{PK_T}{K_T}\right) \left[\frac{V}{V_0} \left(K_0' - \frac{8}{3}\right) + \frac{8}{3}\right] - \left(V \frac{K_0' - 8}{3}\right) \left(1 - \frac{4}{3} \frac{P}{K_T}\right)
\]
\[ K_T K_T' = \frac{-x}{9} \left[ \left\{ (1-\eta) + 4 \eta x \right\} - \left\{ 3K_T - \eta x - 2 \right\} \left( \eta - 2 \eta x - 2 \right) + \eta \right] \] (12)

Borton and Stacey find correlation for Gruneisen Parameter \( \gamma \) [14,15], leading to-

\[ \gamma = \left( \frac{1}{2} \right) K_T' - \frac{1}{6} - \frac{f}{3} \left( 1 - \frac{1}{3} \left( \frac{P}{K_T} \right) \right) \]

Where, \( f = 2.35 \) a constant, \( K_T \) is isothermal bulk modulus and \( K_T' \) is the first pressure derivative of isothermal bulk modulus.

**Result and Discussion:**

In the present work we did calculations for pressure \( P \), isothermal bulk modulus \( K_T \), first pressure derivative of isothermal bulk modulus \( K_T' \) and second order pressure derivative of isothermal bulk modulus in terms of \( K_T K_T' \) for geophysical minerals viz. MgO and Al\(_2\)O\(_3\) by using Brennan Stacey, Shanker and Vinet Equation of States. All the three equation of state contains only two parameters \( K_0 \) and \( K_0' \) both at zero pressure. These values of \( K_0 \) and \( K_0' \) have been recommended by Anderson. The value of input parameters \( K_0 \) and \( K_0' \) are given in Table-1, taken from literature [16, 17].

The values of pressure \( P \) (GPa) for different geophysical minerals were computed for given increments of \( V/V_0 \) by using equation (1), (2) and (3). Using the value of pressure \( P \) (GPa) as computed above, the value of isothermal bulk modulus \( K_T \) has been calculated by using equation (4), (5) and (6). Substituting these values of \( P \) and \( K_T \) in equation (7), (8) and (9) the value of first order pressure derivative of \( K_T \) i.e. \( K_T' \) has been obtained. Further substituting the values of \( P \), \( K_T \) and \( K_T' \) in equation (10), (11) and (12) second order pressure derivative of \( K_T \) i.e. \( K_T'' \) has been calculated in terms of \( K_T K_T' \). The values of different parameters calculated with the use of Brennan-Stacey EOS is given by \( P \) (a), \( K_T \) (a), \( K_T' \) (a), \( K_T K_T' \) (a) and \( \gamma \) (a); values calculated with the use of Shanker EOS is designated with the suffix (b) as \( P \) (b), \( K_T \) (b), \( K_T' \) (b), \( K_T K_T' \) (b) and \( \gamma \) (b) and suffix (c) corresponding to Vinet EOS viz. \( P \) (c), \( K_T \) (c), \( K_T' \) (c), \( K_T K_T' \) (c) and \( \gamma \) (c).

We have plotted the graphs for \( P \) vs \( V/V_0 \), displayed in Fig. (1-2), \( P \) vs \( K_T \) displayed in Fig. (3-4), \( P \) vs \( K_T' \) displayed in Fig. (5-6), \( P \) vs \( K_T K_T' \) displayed in Fig. (7-8) and \( \gamma \) vs \( V/V_0 \) displayed in Fig. (9-10) for different geophysical minerals. From graph we observe that as \( V/V_0 \rightarrow 0 \), \( P \) goes to infinity. Isothermal bulk modulus increases regularly and continuously with increase in pressure. Pressure derivative of isothermal bulk modulus \( K_T \) i.e. \( K_T' \) decreases progressively with the increase in pressure and \( K_T K_T' \) is always negative.

The expression \( \gamma /\Omega \) leads to equation of straight line \( (y = mx+c) \). Hence the graph between Gruniesen parameter \( \gamma \) vs. \( \Omega \) must be a straight line which strongly supports the Brennan-Stacey EOS and Shanker EOS both under low and high compression where as Vinet EOS is applicable only at high compression ratio. Thus it is concluded that Brennan-Stacey and Shanker EOS is compatible at both low and high compression ranges for calculating Gruniesen parameter where as Vinet EOS is incompatible for calculating the Gruniesen parameter at low compression ranges.

![Figure 1: MgO](image1.png)

![Figure 2: Al\(_2\)O\(_3\)](image2.png)

**Figure (1-2):** The variation of pressure \( P \) versus \( V/V_0 \) by using Brennan-Stacey EOS, Shanker EOS and Vinet EOS for geophysical minerals viz. MgO, Al\(_2\)O\(_3\) and Olivine.
Figure (3-4): The variation of pressure $P$ versus $KT$ by using Brennan-Stacey EOS, Shanker EOS and Vinet EOS for geophysical minerals viz. MgO, Al$_2$O$_3$ and Olivine

Figure (5-6): The variation of pressure $P$ versus $K_T^-$ by using Brennan-Stacey EOS, Shanker EOS and Vinet EOS for geophysical minerals viz. MgO, Al$_2$O$_3$ and Olivine

Figure (7-8): The variation of pressure $P$ versus $K_T^-$ by using Brennan-Stacey EOS, Shanker EOS and Vinet EOS for geophysical minerals viz. MgO, Al$_2$O$_3$ and Olivine

Figure (9-10): The variation of $\gamma$ versus $V/V_0$ by using Brennan-Stacey EOS, Shanker EOS and Vinet EOS for geophysical minerals viz. MgO, Al$_2$O$_3$ and Olivine
### Table-1: Input values of $K_0$ and $K'_0$ for geophysical minerals

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### Table-2: Calculated values of different parameters for MgO

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### Table-3: Calculated values of different parameters for Al₂O₃

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