Modified Ghiorso equation of state for CaMgSi$_2$O$_6$ silicate melt at 1673 K

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Ghiorso has recently developed a functional form for an equation of state (EOS) of molten silicate liquids. The EOS is designed for application over a wide range of melt compositions which can be used from reference conditions to very high pressures. It is emphasized here that the Ghiorso EOS does not satisfy the thermodynamic boundary conditions at infinite pressure. Ghiorso EOS has been modified to make it consistent with the Stacey thermodynamics at extreme compression. Various relationships between the compression ratio ($V/V_0$) and pressure $P$ have been studied for the silicate melt CaMgSi$_2$O$_6$ at 1673 K. The pressure-volume isothermal relationship, isothermal bulk modulus $K$ and its pressure derivative have been calculated using five different forms of EOS viz. Birch Murnaghan third order EOS, Vinet-Rydberg EOS, Stacey EOS, Ghiorso EOS and the modified Ghiorso EOS. It is found that the modified Ghiorso EOS developed in the present study gives the satisfactory results which is in good agreement with the Stacey reciprocal-$K^\prime$ EOS.

Keywords: Equation of state, Bulk modulus, Isothermal pressure-volume relationship, Silicate melt

1 Introduction

An equation of state (EOS) of a system describes the relationships among thermodynamic variables such as pressure, temperature, and volume. The EOS is fundamentally important in studying the properties of materials under high pressures and at high temperature. The ability to quantify the thermodynamic properties of silicate melts at elevated pressures, is essential for a detailed understanding of the generation of magmas in the interiors earth and other planetary bodies. A simple empirical, volume explicit EOS has been developed by Ghiorso for use in describing the volumetric properties of silicate melts that exhibit large thermal expansivities and strongly non-linear, pressure dependent compressibilities. The Ghiorso EOS is intended to account for the volumetric properties of liquids whose structural configurations do not vary with pressure and temperature.

For performing calculations with the help of an EOS for a material at high pressures, we need the parameters $K_0$, $K'_0$ and $K''_0$ which represent the bulk modulus, first order pressure derivative, and second order pressure derivative of bulk modulus, respectively, all at zero pressure. It has been emphasized by Stacey that a critical test of an EOS can be made by studying the variation of $K'=dK/dP$ with pressure or compression ($V/V_0$). The $P$-$V$ relationships reveal that the volume decreases continuously with the increase in pressure. The bulk modulus also increases with the increase in pressure but its pressure derivative $K'$ decreases with the increase in pressure. In the limit of infinite pressure ($P \rightarrow \infty$) or extreme compression ($V \rightarrow 0$), the pressure derivative of bulk modulus $K'$ approaches a constant value equal to $K''_\infty$, such that:

$$\frac{1}{K''_\infty} = \left(\frac{P}{K'_\infty}\right)_\infty$$

Eq. (1) is satisfied at infinite pressure by all such equations of state for which $K''_\infty$ is greater than zero. According to the Thomas-Fermi model, $K''_\infty$ must be equal to 5/3. However, it has been shown by Stacey that the Thomas-Fermi model is not relevant for materials at extreme compression ($V \rightarrow 0$ at $P \rightarrow \infty$). Although $K''_\infty$ is an important equation of state parameter which should be used as an adjustable parameter. The thermodynamics of solids formulated by Stacey reveals that $K''_\infty$ must be greater than 5/3 and also that $K''_\infty$ should be different for different solids. It is emphasized in the present study, that although the Ghiorso EOS represents the volume as an explicit function of pressure, so that this EOS is more suitable to study the volumetric properties of materials, but extreme compression behaviour exhibited by this EOS is not consistent with the thermodynamic theory. A modified form of the Ghiorso EOS is presented which is shown to be...
compatible with thermodynamically consistent Stacey-reciprocal $K'$ EOS. A comparison of the results for the $P$-$V$ relationships, bulk modulus and its pressure derivative has been presented with those obtained from the Birch-Murnaghan third order EOS, Vinet-Rydberg EOS and the original Ghiorso EOS.

2 Method of Analysis

Expressions for pressure $P$, isothermal bulk modulus $K$ and pressure derivative of $K$, $K'=dK/dP$ obtained from the different EOS are given below:

(i) Birch-Murnaghan third order EOS

\[ P = \frac{3}{2} K_0 \left[ x^7 - x^5 \right] \left[ 1 + \frac{3}{4} (K'_0 - 4) (x^2 - 1) \right] \] \hspace{1cm} \ldots(2)

\[ K = \frac{1}{2} K_0 \left[ 7 x^7 - 5 x^5 \right] + \frac{3}{8} K_0 (K'_0 - 4) \times (9 x^9 - 14 x^7 + 5 x^5) \] \hspace{1cm} \ldots(3)

\[ K' = \frac{K'_0}{8K} \left[ (K'_0 - 4) (81 x^9 - 98 x^7 + 25 x^5) + \frac{4}{9} (49 x^7 - 25 x^5) \right] \] \hspace{1cm} \ldots(4)

where $x = \left( \frac{V}{V_0} \right)^{1/3}$

(ii) Vinet-Rydberg EOS

\[ P = 3 K_0 x^2 (1 - x) \exp[\eta(1 - x)] \] \hspace{1cm} \ldots(5)

\[ K = K_0 x^2 \left[ 1 + (1 - x)(1 - \eta x) \exp[\eta(1 - x)] \right] \] \hspace{1cm} \ldots(6)

and

\[ K' = \frac{1}{3} \left[ \frac{x(1 - \eta) + 2 \eta x^2}{1 + (\eta x + 1)(1 - x)} + \eta x + 2 \right] \] \hspace{1cm} \ldots(7)

where $x = \left( \frac{V}{V_0} \right)^{1/3}$

and $\eta = \frac{3}{2} (K'_0 - 1)$

(iii) Stacey reciprocal $K'$-EOS

\[ \ln \left( \frac{V}{V_0} \right) = \left( \frac{K'_0}{K_0} - 1 \right) \frac{P}{K} + \frac{K'_0}{K_0} \ln \left( 1 - \frac{K}{K'_0} \right) \] \hspace{1cm} \ldots(8)

\[ \frac{K}{K_0} = \left( 1 - \frac{P}{K} \right)^{-K_0/K'_0} \] \hspace{1cm} \ldots(9)

\[ \frac{1}{K} = \frac{1}{K_0} + \left( 1 - \frac{K'_0}{K_0} \right) \frac{P}{K} \] \hspace{1cm} \ldots(10)

(iv) Ghiorso EOS is

\[ \frac{V}{V_0} = \frac{1 + AP + BP^2}{1 + aP + bP^2} \] \hspace{1cm} \ldots(11)

\[ \frac{1}{K} = - \frac{A + 2BP}{(1 + AP + BP^2)} + \frac{a + 2bP}{(1 + aP + bP^2)} \] \hspace{1cm} \ldots(12)

\[ K' = \frac{2B}{(1 + AP + BP^2)} - \frac{(A + 2BP)^2}{(1 + AP + BP^2)^2} + \frac{(a + 2bP)^2}{(1 + aP + bP^2)^2} \] \hspace{1cm} \ldots(13)

where $A, B, a$ and $b$ are constants and their values are determined from the boundary condition, $V=V_0$ at $P=0$, using the values of $K_0$, $K'_0$ and $K''_0$. The expression for $K''=d^2K/dP^2$ is obtained by differentiating Eq. (13) with respect to $P$.

(v) The modified Ghiorso EOS

\[ \frac{V}{V_0} = \frac{1 + AP}{(1 + aP + bP^2)^t} \] \hspace{1cm} \ldots(14)

\[ \frac{1}{K} = - \frac{A}{1 + AP} + \frac{t(a + bP)}{(1 + aP + bP^2)} \] \hspace{1cm} \ldots(15)

\[ \frac{K'}{K_0} = - \frac{A^2}{(1 + AP)^2} + \frac{t(a + 2bP)^2}{(1 + aP + bP^2)^2} - \frac{2t b}{(1 + aP + bP^2)^t} \] \hspace{1cm} \ldots(16)

where $A, a, b$ and $t$ are constants and their values are determined from the boundary condition, $V=V_0$ at $P=0$, using the values of $K_0$, $K'_0$ and $K''_0$. The expression for $K''=d^2K/dP^2$ is obtained by differentiating Eq. (16) with respect to $P$.

Eqs (2-4) based on the Birch-Murnaghan third order EOS satisfy the boundary conditions $V=V_0$ at $P \to 0$ and $V \to 0$ at $P \to \infty$, and Eq. (1). For the Birch-Murnaghan third Order EOS, value of $K'_0=3$ satisfies the Stacey thermodynamic constraint viz. $K''_0 \to 5/3$. Eqs (5-7) based on the Vinet-Rydberg EOS satisfy the boundary conditions and Eq. (1), but the Stacey thermodynamic constraint ($K''_0 \to 5/3$) is not satisfied because for this EOS $K''_0 \to 2/3$. Eqs (8-10) based on the Stacey reciprocal $K'$-EOS satisfy the boundary
conditions and Eq. (1). Eqs (11-12) based on the Ghiorso EOS satisfy the boundary condition \( V \rightarrow V_0 \) at \( P \rightarrow 0 \), but it does not satisfy the boundary conditions at extreme compression, i.e. \( V \rightarrow 0 \) at \( P \rightarrow \infty \). For the Ghiorso EOS, we have \( K'_\infty \rightarrow \infty \) and \( (P/K)_\infty \rightarrow 0 \) which are inconsistent with the thermodynamics. This EOS is, therefore, not suitable. Also it gives a finite volume at \( P \rightarrow \infty \).

\[
\frac{V_\infty}{V_0} = \frac{B}{b} \quad \ldots (17)
\]

Values of constants \( B \) and \( b \) when used in Eq. (17) reveal that \( V_\infty \) remains one third of \( V_0 \) for the silicate melt under study.

### 3 Results and Discussion

We have predicted isothermal pressure-volume relationships, the isothermal bulk modulus \( K \), and its first pressure derivative \( K' = dK/dP \) for \( \text{CaMgSi}_2\text{O}_6 \) (diopside) at 1673 K. The calculations have been performed for a wide range of pressures up to 60 GPa. In the present case this is very high pressure because it is more than double of the bulk modulus equal to 25.8 GPa for the material under study. The input data used in calculations are given in Table 1. The values of \( K_0K''_0 \) have been obtained from the stacey relationship:\(^9\)

\[
K_0K''_0 = -K'_0(k'_0 - K'_\infty) \quad \ldots (18)
\]

and the ratio \( K'_\infty/K'_0 = 3/5 \) as found in the recent studies\(^{10,11}\). The values of \( P \) versus \( V \), \( K \) versus \( P \) and \( K' \) versus \( P \) are shown in Figs 1-3. The results for

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(a)</th>
<th>(b)</th>
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<tr>
<td>( K_0 ) (GPa)</td>
<td>25.8</td>
<td>25.8</td>
</tr>
<tr>
<td>( K'_0 )</td>
<td>4.6</td>
<td>4.6</td>
</tr>
<tr>
<td>( K_0K''_0 )</td>
<td>-</td>
<td>-8.5</td>
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<tr>
<td>( A ) (GPa(^{-1}))</td>
<td>0.1192</td>
<td>0.1394</td>
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<tr>
<td>( B ) (GPa(^{-2}))</td>
<td>1.077x10(^{-3})</td>
<td>-</td>
</tr>
<tr>
<td>( a ) (GPa(^{-1}))</td>
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<td>0.270</td>
</tr>
<tr>
<td>( b ) (GPa(^{-2}))</td>
<td>3.0x10(^{-3})</td>
<td>0.0164</td>
</tr>
<tr>
<td>( t )</td>
<td>-</td>
<td>0.66</td>
</tr>
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Table 1 — Values of input parameters\(^2\) used in calculations [Values given in column (a) are for Ghiorso EOS and in column (b) for the modified Ghiorso EOS]
Fig. 2 — Plots between bulk modulus $K$ and pressure $P$ for CaMgSi$_2$O$_6$ at $T=1673$ K based on different EOS (a) Ghiorso EOS (b) Birch-Murnaghan third order EOS (c) Stacey EOS (d) Modified Ghiorso EOS and (e) Vinet-Rydberg EOS from top to bottom.

Fig. 3 — Plots between pressure derivative of bulk modulus $K'$ and pressure $P$ for CaMgSi$_2$O$_6$ at $T=1673$ K based on different EOS (a) Ghiorso EOS (b) Birch-Murnaghan third order EOS (c) Modified Ghiorso EOS (d) Stacey EOS and (e) Vinet-Rydberg EOS from top to bottom.
isothermal bulk modulus and pressure derivative of bulk modulus reveal that the Birch-Murnaghan third order EOS and the original Ghiorso EOS deviate much at high pressures from those determined with the help of the Vinet-Rydberg EOS, Stacey EOS and the modified Ghiorso EOS. Although the Vinet-Rydberg EOS gives good agreement with the Stacey EOS, it does not satisfy the thermodynamic constraint $(K'_\infty > 5/3)$. On the other hand, the modified Ghiorso EOS is consistent with the thermodynamics and also with the Stacey reciprocal-$K'$ EOS.

In the present study, we have thus modified the Ghiorso EOS in such a manner that its drawbacks are removed, but its special feature, viz. volume expressed as an explicit function of pressure, is retained. It should be emphasized that the modified EOS thus presented here satisfies the boundary conditions viz. $V = V_0$ at $P = 0$ and $V \to 0$ at $P \to \infty$. The main shortcoming of the original Ghiorso EOS (Eq. 11) is that it gives finite value of $V = V_\infty$ in the limit of infinite pressure (Eq. 17). Other important point is regarding the variation of pressure derivative of bulk modulus $K' = dK/dP$ with pressure. It should be mentioned that $K'$ is a higher derivative property depending on the third derivative of potential energy, its variation with pressure provides a more critical test of an EOS. The experimental data and theoretical studies$^{10,11}$ reveal that $K'$ decreases regularly and continuously with the increase in pressure for all materials up to extreme compression. This behaviour is exhibited by all the equations of state under study except the original Ghiorso EOS Fig. 3.

According to the Ghiorso EOS, $K'$ decreases first with the increase in pressure for a limited range of pressures and then starts to increase rapidly with the further increase in pressure becoming infinitely large at higher pressures. This finding based on the Ghiorso EOS that $K'_\infty \to \infty$ in the limit of infinite pressure is not consistent with the thermodynamics of solids at extreme compression$^{10,11}$. This deficiency is removed in the present study by modifying the Ghiorso EOS. For the modified EOS, $K'$ decreases continuously with the increase in pressure and attains a finite value given below:

$$K'_\infty = \frac{1}{(2t - 1)}$$ …(19)

In the present case, $t = 0.66$ which gives $K'_\infty = 3.125$ this value of $K'_\infty$ is greater than 5/3, and therefore satisfies the thermodynamic constraint$^{10,11}$. It should be mentioned that the Roy-Roy$^{14}$ EOS gives the following expression for the P-V relationship:

$$\frac{V}{V_0} = \left[1 + aP(1 + bP) c \right]^{-1}$$ …(20)

where $a = \frac{1}{K_0}$, $b = \frac{(1 - K'_0)}{2cK_0}$ and $c = \left( \frac{1}{K'_\infty} \right)^{-1}$.

Eq. (20) yields results which are very similar to those found in the present study from the modified Ghiorso EOS. This is mainly because the Roy-Roy EOS is also consistent with the stacey thermodynamic formualation$^{15,16}$.

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References