A Structural Molar Volume Model for Oxide Melts Part II: Li$_2$O-Na$_2$O-K$_2$O-MgO-CaO-MnO-PbO-Al$_2$O$_3$-SiO$_2$ Melts—Ternary and Multicomponent Systems

ERIC THIBODEAU, AIMEN E. GHERIBI, and IN-HO JUNG

A structural molar volume model based on the silicate tetrahedral Q-species has been developed to accurately predict the molar volume of molten oxides. In this study, the molar volumes of ternary and multicomponent melts in the Li$_2$O-Na$_2$O-K$_2$O-MgO-CaO-MnO-PbO-Al$_2$O$_3$-SiO$_2$ system are reviewed and compared with the predicted molar volumes from the newly developed structural model. The model can accurately predict the molar volumes using binary model parameters without any ternary or multicomponent parameters. The nonlinear behavior in the molar volume of silicate melts is well predicted by the present model.

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I. INTRODUCTION

IN the Part I of this series, a structural molar volume model for binary melts was introduced. The model is based on the silicate Q^n species which are calculated from the Modified Quasichemical Model[1] with optimized thermodynamic data from FactSage FToxid database.[2] All the unary and binary experimental data were critically reviewed based on experimental technique and the molar volume parameters of unary oxide component and binary Q^n species were optimized to reproduce the experimental data.

As Part II of this series, the predictive ability of the present molar volume model is demonstrated for ternary and multicomponent melts without any additional model parameters. All experimental data of the ternary and multicomponent melts in Li$_2$O-Na$_2$O-K$_2$O-MgO-CaO-MnO-PbO-Al$_2$O$_3$-SiO$_2$ system are reviewed, and the comparison of the predicted values from the present model with experimental data is presented.

II. STRUCTURAL MOLAR VOLUME MODEL

The structural molar volume model is based on the molar volume of different Q-species. As discussed in the Part I, silicate tetrahedral Q^n species where $n = 0$ to 4 are calculated from the Modified Quasichemical Model (MQM)[1] with optimized thermodynamic model parameters (stored in FactSage FToxid database[2]). The amounts of different Q^n species for the binary silicate melt can be calculated considering the bond fractions of bridged oxygen O^0, broken oxygen O$^-$, and free oxygen O^{2-}. In the MQM, the bridged, broken, and free oxygen for example in a MO-SiO$_2$ melt are described as Si-Si, M-Si, and M-M pairs, respectively. This is demonstrated in Part I. The same approach was used to calculate the Q^n species for ternary and multicomponent melts. Of course, in the ternary and multicomponent melt, the broken oxygen can be generated by different network modifiers, and the total number of all broken oxygens is counted in the calculation of Q^n species.

The molar volumes of the ternary and higher order melts are predicted from the unary and binary model parameters by first calculating the quantity of each Q^n species for a given melt and performing a linear extrapolation from the binary parameters weighted by the quantity of each M-Si pairs:

$$V_m = n_{Q^4}(a_{SiO_2} + b_{SiO_2}T) + \sum_{n=0}^{3} n_{Q^n} \frac{\sum_i x_{Si-i}(a_{ni} + b_{ni}T)}{\sum_i x_{Si-i}}$$
$$+ n_t \sum_i \sum_j x_{i-j}(a_{i-j} + b_{i-j}T) \qquad [1]$$

where n_{Q^n} and n_t are the amount of Q^n species and total number of oxygen in 1 mol of liquid, and i and j are cations of network modifiers. x_{Si-i} and x_{i-j} are bond fractions of broken oxygen (Si$-i$ pairs) and free oxygen (i–j pairs) in 1 mol of liquid. The molar volume parameters of pure SiO$_2$ ($a_{SiO_2} + b_{SiO_2}T$), $Q^n(a_{nM} + b_{nM}T)$, where $n = 0$ to 3, and MO ($a_{M-M} + b_{M-M}T$) are obtained by the optimization of the molar volume of binary MO-SiO$_2$ melt. The last term in Eq. [1] incorporates the effect of free oxygen species. The molar volume of M_i–M_j ($a_{i-j} + b_{i-j}T$) is the average of the molar volume of M_i–M_i ($a_{i-i} + b_{i-i}T$) and M_j–M_j ($a_{j-j} + b_{j-j}T$).

It should be noted that Al$_2$O$_3$, an amphoteric component, is treated as a network modifier in the present

ERIC THIBODEAU, Graduate Student, and IN-HO JUNG, Associate Professor, are with the Department of Mining and Materials Engineering, McGill University, 3610 University Street, Montreal, QC, H3A 0C5, Canada. Contact e-mail: in-ho.jung@mcgill.ca AIMEN E. GHERIBI, Research Associate, is with the Department of Mining and Materials Engineering, McGill University, and also with the Centre de Recherche en Calcul Thermochimique, Departement de Genie Chimique, Ecole Polytechnique de Montreal, C.P. 6079, Succ. Centre-ville, Montreal, QC, H3C3A7, Canada.
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model. As seen in Part I of this study, the molar volumes of the CaO-Al$_2$O$_3$ and MgO-Al$_2$O$_3$ melts change linearly with composition which can be described by the last term in Eq. [1]. Therefore, no additional complication like Q-species was required for Al$_2$O$_3$. In the case of alkali oxide, A$_2$O, A$_2$ was used as a cation unit (for example, Na$_2$ instead of Na) in the model.

The structure of silicate melts of ternary and higher order system can be calculated at a given composition and temperature from the MQM with thermodynamic database. This structural change is automatically taken into account in the molar volume calculations as described in Eq. [1].

III. PREDICTION OF MOLAR VOLUME IN TERNARY AND HIGHER ORDER SYSTEMS

The present structural molar volume model can predict the molar volume of ternary and higher order molten oxides from unary and binary model parameters without additional parameters. In the prediction, the structures of melts (Q^i species and free oxides) are calculated from the FToxid thermodynamic database.[2]

In the following sections, each ternary system is examined individually. A ternary plot is shown to illustrate the composition ranges studied. To show the accuracy of the model, an experimental data *vs* prediction plot (1 to 1 plot) is also shown with 2 pct error bars. Some key systems are further examined by showing pseudo-binary sections to illustrate the trends in the experimental data and the model predictions. The results from the linear model of Lange and Carmichael[3] are also shown as dashed lines for comparison. All compositions are in mole percent unless otherwise specified. All the systems examined and the associated references are shown in Table I.

A. *Ternary Alkali Silicate Melts*

1. *Li$_2$O-Na$_2$O-SiO$_2$ system*
The ternary Li$_2$O-Na$_2$O-SiO$_2$ system was studied along two different iso-composition joins as shown in Figure 1(a). Din[5] used the SBA technique while Golovin and Dertev[8] used the DBA technique. Bockris et al.[4] examined a single composition with equi-molar Li$_2$O and Na$_2$O using the DBA technique and Sasek and Lisy[6] did the same using the SBA technique. All available experimental data were measured in the high silica region and are consistent with each other. The present model can predict all the results within ~1 pct error as shown in Figure 1(b). To better illustrate the prediction of the present model, two joins are examined in Figure 2 (constant SiO$_2$ and constant Na$_2$O). The present model and the linear model are nearly identical across the constant silica join. They are nearly equivalent along the constant Na$_2$O join in the high silica region, but the present model predicts a higher molar volume in the Li$_2$O-Na$_2$O system because the molar volumes of Li$_2$O and Na$_2$O in the present model are much higher than those in the linear model of Lange and Carmichael.

2. *Li$_2$O-K$_2$O-SiO$_2$ system*
The Li$_2$O-K$_2$O-SiO$_2$ system was examined along a single silica join by Sasek and Lisy[6] using the SBA method. Bockris et al.[4] examined a single composition. The accuracy of the model and corresponding compositions are shown in Figure 3. The composition closer to the K$_2$O-SiO$_2$ binary system by Sasek and Lisy (circled) showed nonlinear behavior with temperature.

3. *Na$_2$O-K$_2$O-SiO$_2$ system*
The ternary Na$_2$O-K$_2$O-SiO$_2$ system was examined by three research groups. Sasek and Lisy[6] used the SBA method, while the other two research groups, Dertev and Golovin[8] and Lange and Carmichael[11], used the DBA method. Dertev and Golovin examined an iso-SiO$_2$ join and found the molar volume increases linearly from the Na$_2$O to the K$_2$O side. All the experimental data are predicted within 1 pct error, as shown in Figure 4.

B. *Ternary Lead Oxide Silicate Melts*

The ternary lead oxide silicates have been studied in very few works. Nearly all the publications were produced by Japanese research groups using the SBA method and published graphically. In addition, the majority of the data were obtained from a single research group (Hino et al.[15,19] and Ejima et al.[10]). The results in the PbO-SiO$_2$ system by Hino et al. are not considered to be the most accurate (as shown in Part I) so there is a somewhat consistent difference between the experimental data and present predictions.

Suginohara et al.[9] also performed measurements in the PbO-SiO$_2$ system with small additions (<5 mol pct) of other oxides, but the results have been omitted as accurate data extraction was not possible from the figures provided in their paper.

1. *Li$_2$O-PbO-SiO$_2$ system*
This ternary system was studied by Ejima et al.[10] along two joins (50 mol pct SiO$_2$ and equi-molar PbO:SiO$_2$) using the SBA method. The compositions measured and the model accuracy can be seen in Figure 5. The molar volume along the two joins is examined in Figure 6. The results suggest a linear decrease in molar volumes with increasing Li$_2$O concentration at constant SiO$_2$, which is well predict by the present model. At higher Li$_2$O concentrations of the PbO/SiO$_2$ = 1 section the experimental data shows a significant deviation from the linear trend. This abrupt change seems unlikely because it would require a significant structural change in the liquid. This might have occurred due to the formation of a solid phase. Similar observations were made in other alkali bearing lead oxide systems.

2. *Na$_2$O-PbO-SiO$_2$ system*
The molar volume of the Na$_2$O-PbO-SiO$_2$ system was examined by Hino et al.[15] (the same research group examined the Li$_2$O-PbO-SiO$_2$ system) and published their results graphically. A single composition at multiple temperatures was also measured by Kostanyan and Karapetyan.[14] Both research groups used a SBA method. As shown in Figure 7, the molar volume data by Kostanyan

Table I. Summary of Molar Volume Studies for Ternary Oxide Melts

Oxide Components	References (Year: Authors)	Method	Presentation
$Li_2O-Na_2O-SiO_2$	1956: Bockris et al.[4]	DBA	equation
	1968: Din[5]	SBA	table
	1972: Sasek and Lisy[6,7]	SBA	table
	1973: Dertev and Golovin[8]	DBA	graph
$Li_2O-K_2O-SiO_2$	1956: Bockris et al.[4]	DBA	equation
	1972: Sasek and Lisy[6,7]	SBA	table
$Li_2O-MgO-SiO_2$	1972: Sasek and Lisy[10,11]	SBA	table
$Li_2O-CaO-SiO_2$	1972: Sasek and Lisy[10,11]	SBA	table
$Li_2O-PbO-SiO_2$	1962: Sugionohara et al.[9]	SBA	graph
	1970: Ejima et al.[10]	SBA	graph
$Na_2O-K_2O-SiO_2$	1972: Sasek and Lisy[6,7]	SBA	table
	1973: Dertev and Golovin[8]	DBA	graph
	1987: Lange and Carmichael[11]	DBA	table
$Na_2O-MgO-SiO_2$	1960: Adachi et al.[12]	SD	table
	1968: Din[5]	SBA	table
	1973: Dertev and Golovin[8]	DBA	graph
	1972: Sasek and Lisy[6,7]	SBA	table
$Na_2O-CaO-SiO_2$	1960: Adachi et al.[12]	SD	table
	1966: Coenen[13]	SBA	graph
	1968: Din[5]	SBA	table
	1973: Dertev and Golovin[8]	DBA	graph
	1972: Sasek and Lisy[6,7]	SBA	table
$Na_2O-MnO-SiO_2$	1960: Adachi et al.[12]	SD	table
$Na_2O-PbO-SiO_2$	1962: Sugionohara et al.[9]	SBA	graph
	1967: Kostanyan and Karapetyan[14]	SBA	equation
	1968: Hino et al.[15]	SBA	graph
$Na_2O-Al_2O_3-SiO_2$	1960: Adachi et al.[12]	SD	table
	1966: Coenen[13]	SBA	graph
	1966: Riebling[16]	SBA	equation
	1979: Nelson and Carmichael[17]	DBA	equation
	1986: Stein et al.[18]	DBA	table
$K_2O-MgO-SiO_2$	1972: Sasek and Lisy[10,11]	SBA	table
$K_2O-CaO-SiO_2$	1972: Sasek and Lisy[10,11]	SBA	table
	1979: Nelson and Carmichael[17]	DBA	equation
	1987: Lange and Carmichael[17]	DBA	table
$K_2O-PbO-SiO_2$	1962: Sugionohara et al.[9]	SBA	graph
	1967: Kostanyan and Karapetyan[14]	SBA	equation
	1969: Hino et al.[19]	SBA	graph
$K_2O-Al_2O_3-SiO_2$	1987: Lange and Carmichael[11]	DBA	table
$MgO-CaO-SiO_2$	1955: Ermolaeva and Ogneupory[20]	MBP	table
	1979: Nelson and Carmichael[17]	DBA	equation
	1982: Licko and Danek[21]	SBA	equation
	1987: Lange and Carmichael[11]	DBA	table
	1989: Taniguchi[22]	DBA	table
	1992: Konche et al.[23]	DBA	table
$MgO-PbO-SiO_2$	1962: Sugionohara[9]	SBA	graph
	1977: Ouchi et al.[24]	DBA	table
$MgO-Al_2O_3-SiO_2$	1955: Ermolaeva and Ogneupory[20]	MBP	table
	1964: Riebling[25]	SBA	equation
$CaO-MnO-SiO_2$	1978: Kekelidze et al.[26]	SD	table
	1978: Segers et al.[27]	SBA	equation
	2012: Lee et al.[28]	SBA	equation
$CaO-PbO-SiO_2$	1962: Sugionohara et al.[9]	SBA	graph
	1977: Ouchi et al.[24]	DBA	table
$CaO-Al_2O_3-SiO_2$	1955: Ermolaeva and Ogneupory[20]	MBP	table
	1959: Barrett and Thomas[29]	MBP	table
	1965: Kammel et al.[30]	DBA	table
	1965: Smolyarenko et al.[31]	MBP	table
	1967: Evseev and Filippov[32]	MBP	table
	1968: Bochorishvili and Yyakobashvili[33]	MBP	table
	1969: Sokolov et al.[34]	MBP	table
	1971: Krinochkin et al.[35]	SD	table

Oxide Components	References (Year: Authors)	Method	Presentation
	1985: Yakushev et al.[36]	MBP	table
	1987: Lange and Carmichael[11]	DBA	table
	1989: Taniguchi[22]	DBA	table
	1992: Konche et al.[23]	DBA	table
	1995: Courtial and Dingwell[37]	DBA	table
	2007: Magidson et al.[38]	MBP	equation
	2010: Muhmood and Seetharaman[39]	MBP	table
Li₂O-CaO-Al₂O₃	1968: Bochorishvili and Yyakobashvili[33]	MBP	table
Na₂O-CaO-Al₂O₃	1968: Bochorishvili and Yyakobashvili[33]	MBP	table
K₂O-CaO-Al₂O₃	1968: Bochorishvili and Yyakobashvili[33]	MBP	table
MgO-CaO-Al₂O₃	1955: Ermolaeva and Ogneupory[20]	MBP	table
	1965: Smolyarenko et al.[31]	MBP	table
	1967: Evseev and Filippov[32]	MBP	table
	1968: Bochorishvili and Yyakobashvili[33]	MBP	table
	1977: Zielinski and Sikora[40]	MBP	table
	2013: Li et al.[41]	SBA	equation

Method DBA: double bob archimedean, SDA: single bob archimedean, MBP: maximum bubble pressure, SD: sessile drop.
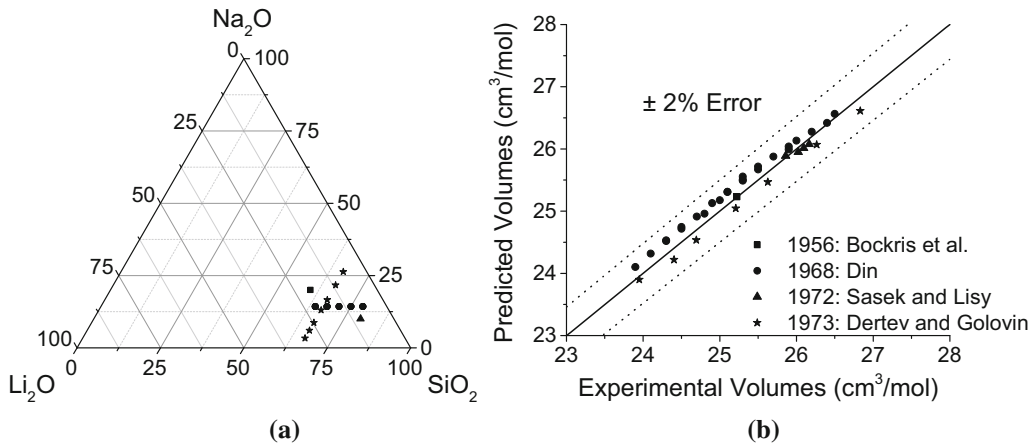
Fig. 1—The ternary Li₂O-Na₂O-SiO₂ system: (a) compositions examined and (b) model accuracy.[4–8]
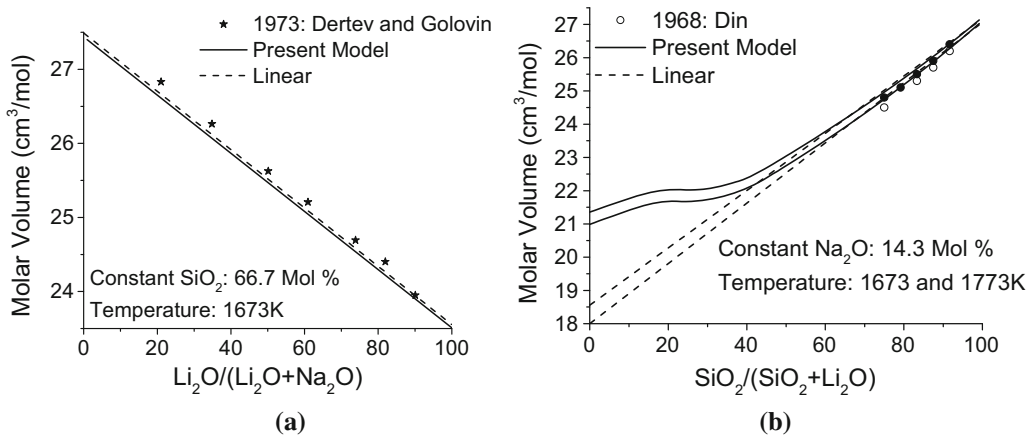
Fig. 2—The molar volume in the Li₂O-Na₂O-SiO₂ across the (a) SiO2 = 66.7 mol pct[8] and (b) Na₂O = 14.3 mol pct joins.[5] [filled symbols at 1673 K (1400 °C) and open symbols at 1773 K (1500 °C)].

and Karapetyan are much higher than the data by Hino et al. The predicted molar volumes are closer to the data by Hino et al. and the increasing trend in molar volume with increasing Na₂O content is well replicated. The scatter in the data is significant across both joins (constant SiO₂ and equi-molar ratio of PbO and SiO₂) as shown in Figure 8.
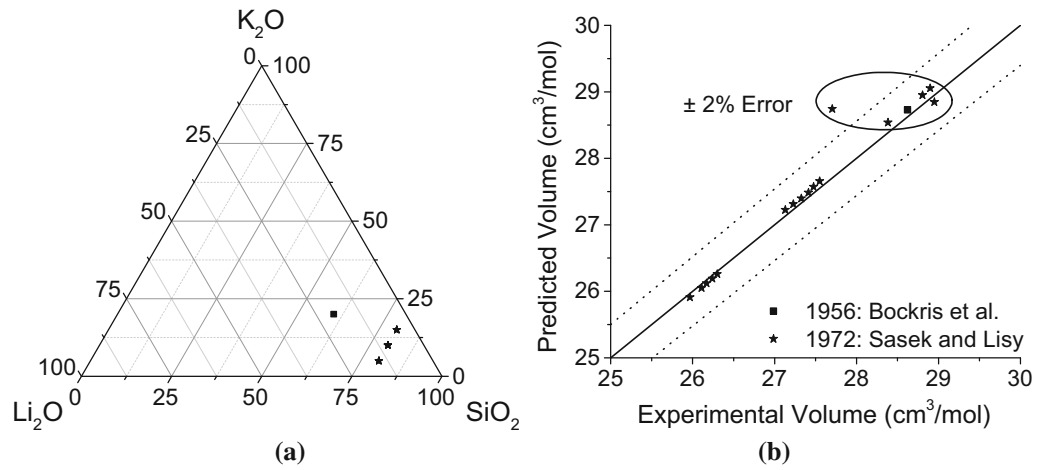
Fig. 3—The ternary Li_2O-K_2O-SiO_2 system: (a) compositions examined and (b) model accuracy.[4,6] Additional information concerning the circled data is mentioned in the text.
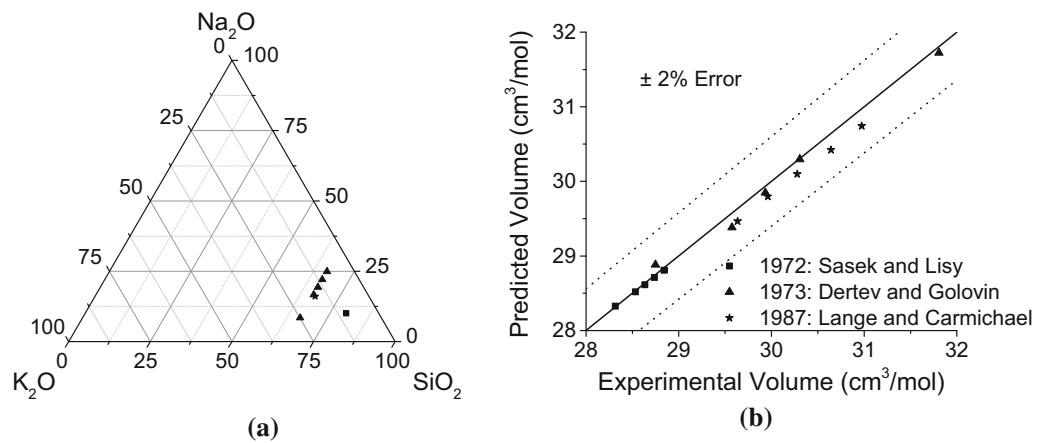

Fig. 4—The ternary Na_2O-K_2O-SiO_2 system: (a) compositions examined and (b) model accuracy.[6,8,11]
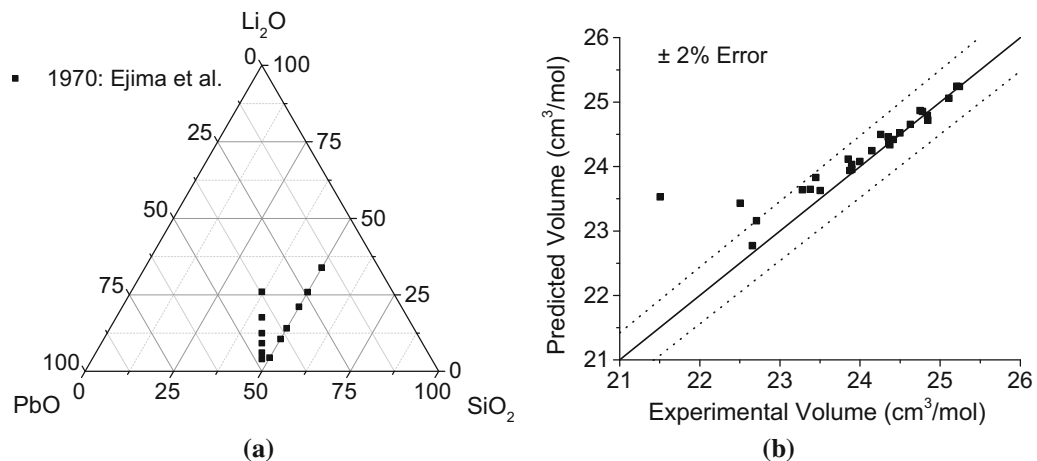
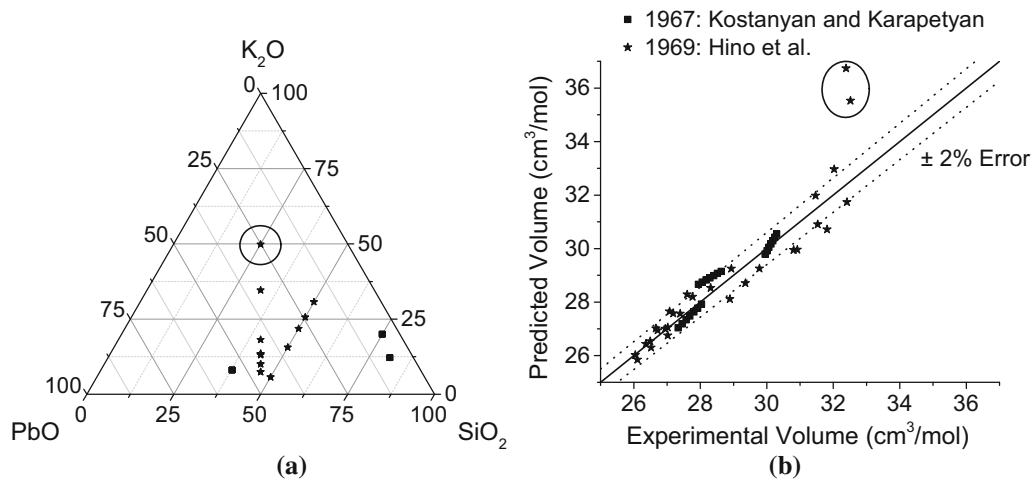Fig. 5—The ternary Li_2O-PbO-SiO_2 system: (a) compositions measured and (b) model accuracy.[10]

3. K_2O-PbO-SiO_2 system

Kostanyan and Karapetyran[14] and Hino et al.[19] also examined the potassium oxide-containing system. The experimental data and the present model agree moderately well. The investigated compositions and the model accuracy are shown in Figure 9. The molar volume across two joins (50 pct SiO_2 and equi-molar PbO:SiO_2) increases with the addition of K_2O, which are
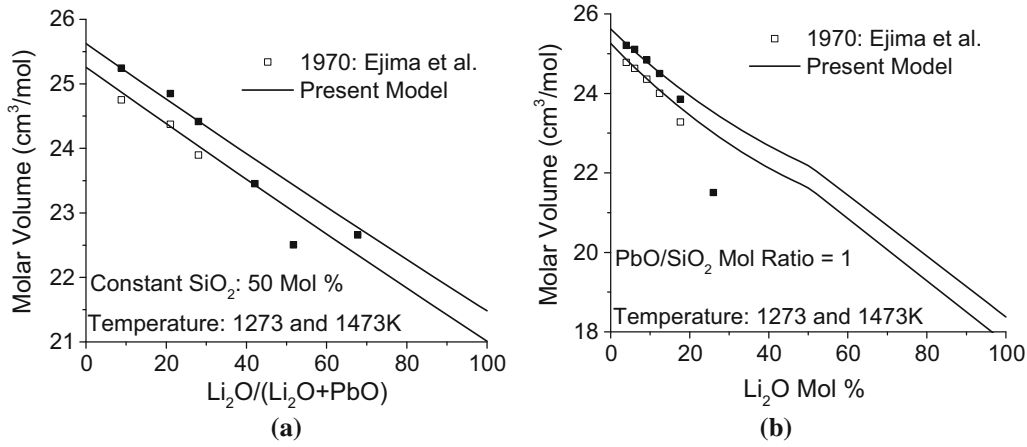
Fig. 6—The molar volume in the Li_2O-PbO-SiO_2 system across the (a) SiO_2 = 50 mol pct and (b) PbO/SiO_2 = 1 joins[10] [filled symbols at 1473 K (1200 °C) and open symbols at 1273 K (1000 °C)].
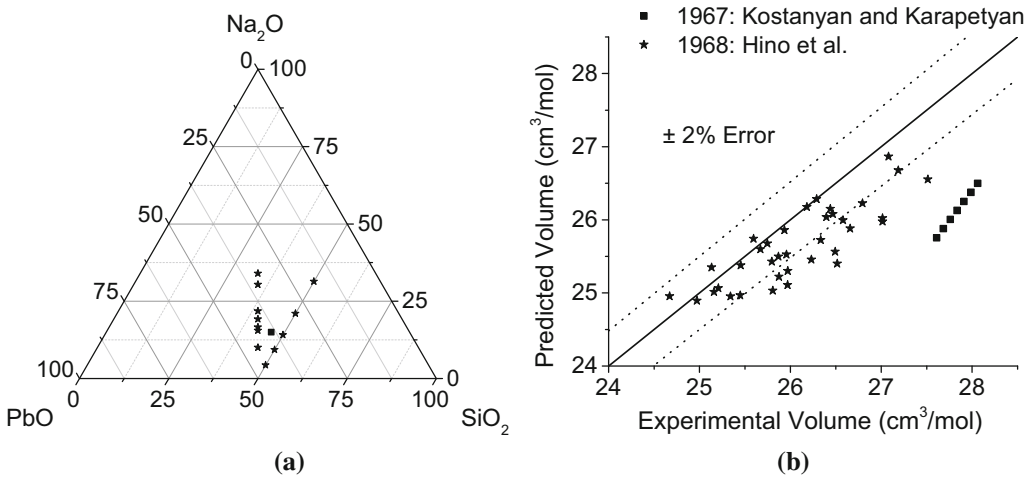
Fig. 7—The ternary Na_2O-PbO-SiO_2 system: (a) compositions measured and (b) model accuracy.[14,15]
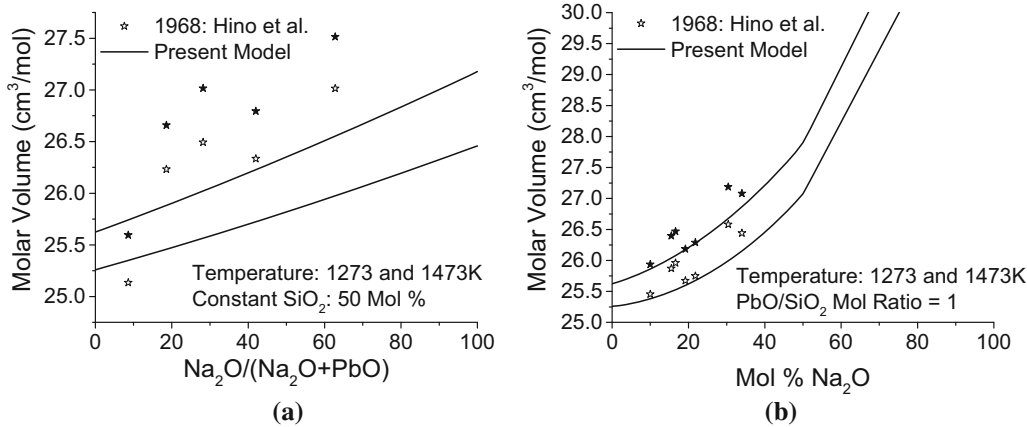
Fig. 8—The molar volume in the Na_2O-PbO-SiO_2 system across the (a) SiO_2 = 50 mol pct and (b) PbO/SiO_2 = 1 joins[15] [filled symbols at 1473 K (1200 °C) and open symbols at 1273 K (1000 °C)].

well predicted by the present model as shown in Figure 10. The one experimental point at 50 pct K_2O circled in Figure 9, deviated largely from the linear trend

of the experimental data and suggests a negative thermal expansion: their data were likely measured sub-liquidus, but no phase diagram information is available.

Fig. 9—The ternary K_2O-PbO-SiO_2 system: (a) compositions examined and (b) model accuracy.[14,19] Additional information concerning the circled data is mentioned in the text.
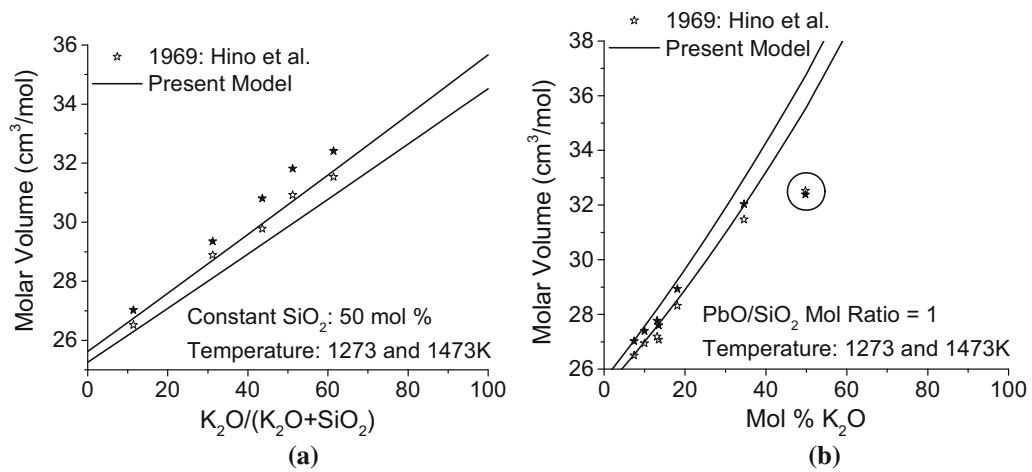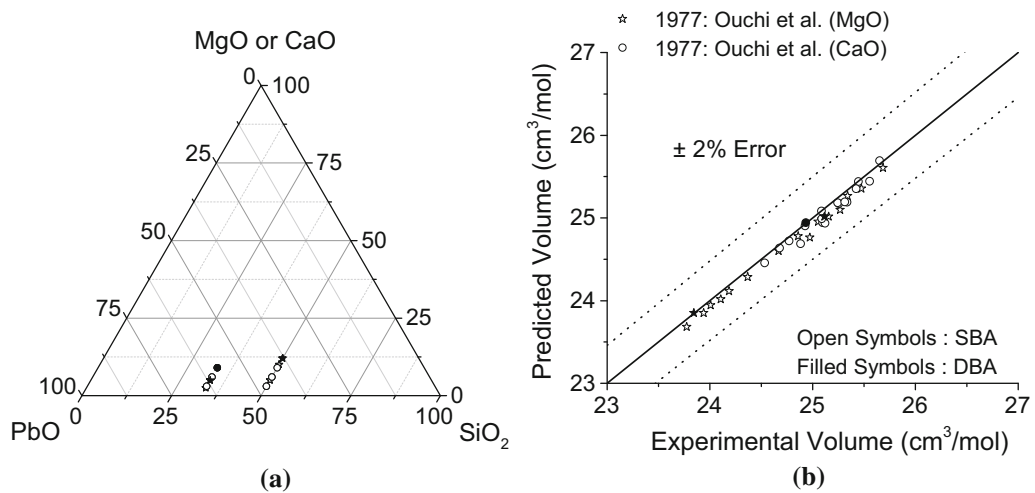

Fig. 10—The molar volume in the K_2O-PbO-SiO_2 system across the (a) SiO_2 = 50 mol pct and (b) PbO/SiO_2 = 1 joins[19] [filled symbols at 1473 K (1200 °C) and open symbols at 1273 K (1000 °C)].

Fig. 11—The ternary MgO-PbO-SiO_2 and CaO-PbO-SiO_2 systems: (a) compositions examined and (b) model accuracy.[24] Open symbols represent SBA measurements and filled symbols represent DBA measurements.
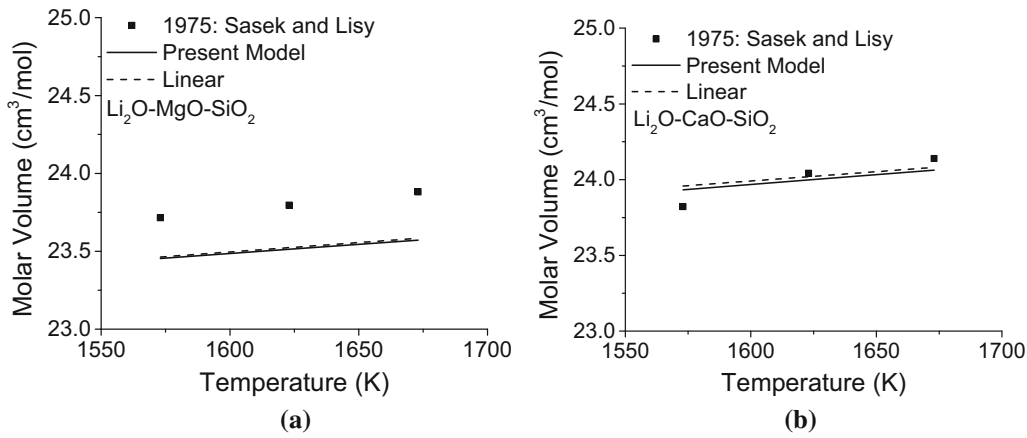
Fig. 12—The molar volume for the (a) ternary Li_2O-MgO-SiO_2 and (b) ternary Li_2O-CaO-SiO_2 systems at various temperatures with a composition of 72.22 SiO_2-9.72 Li_2O-18.06 MgO or CaO in mol pct.[6]

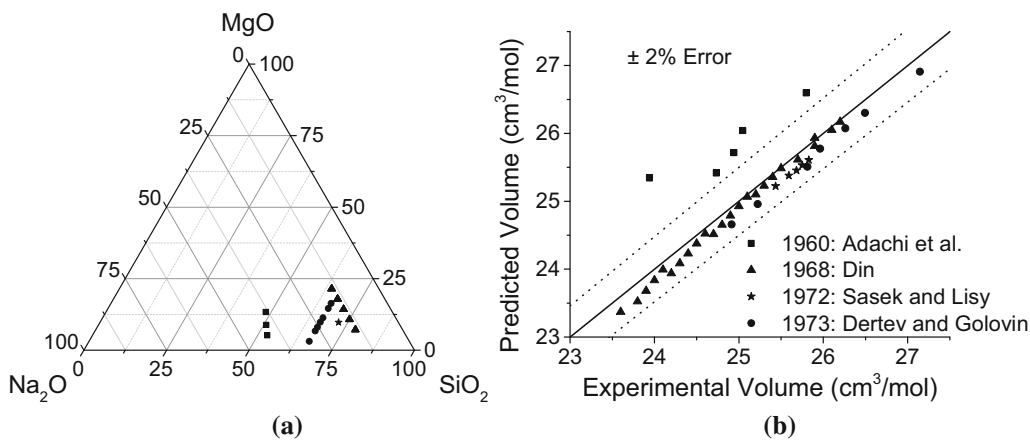

Fig. 13—The ternary Na_2O-MgO-SiO_2 system: (a) compositions examined and (b) model accuracy.[5,7,8,12]

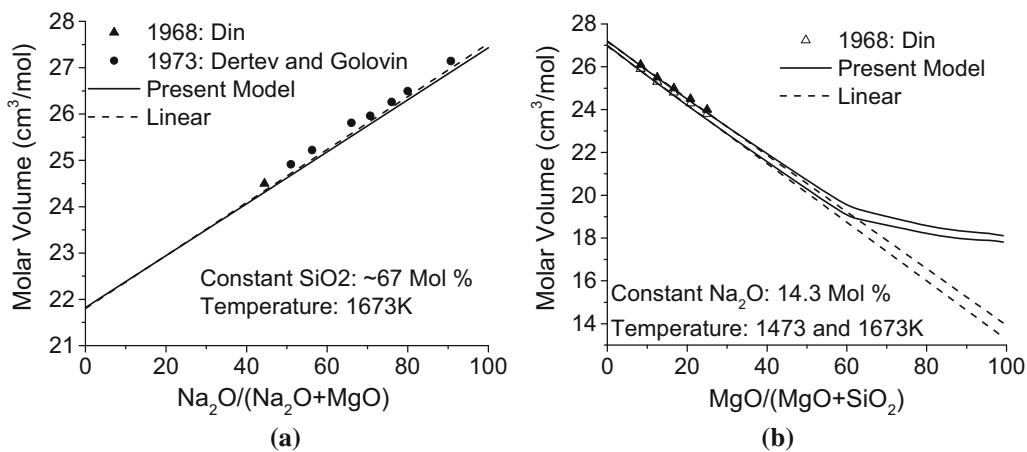Fig. 14—The molar volume in the Na_2O-MgO-SiO_2 system across the (a) SiO_2 = ~67 mol pct[5,8] and (b) Na_2O = 14.3 mol pct [filled symbols at 1673 K (1400 °C) and opened at 1473 K (1200 °C)][5] joins.

4. MgO-PbO-SiO₂ and CaO-PbO-SiO₂ systems

The molar volume of the PbO-SiO_2 system with MgO or CaO additions were studied by Ouchi et al.[24] using a single bob method for the majority of measurements and the double bob method to determine the corrections required. Additions of up to 12 mol pct MgO or CaO were made. The molar volume decreased linearly with increasing CaO or MgO content. The present model is
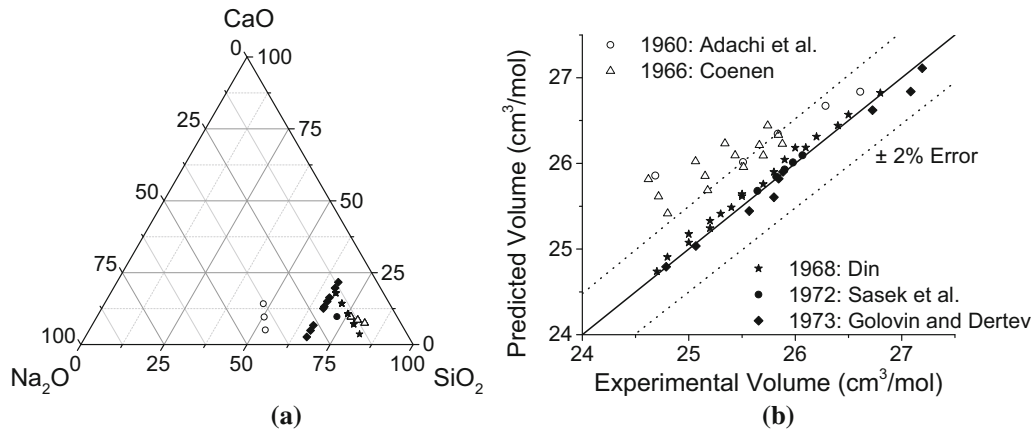
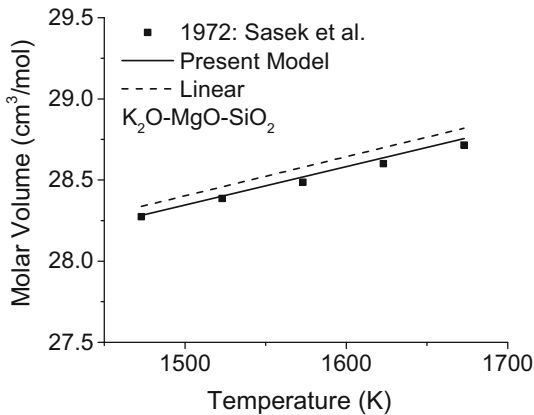Fig. 15—The ternary Na_2O-CaO-SiO_2 system: (a) compositions examined and (b) model accuracy.[5,7,8,12,13]

Fig. 16—The molar volume of the ternary K_2O-MgO-SiO_2 system at various temperatures at a composition of 72.22 SiO_2-9.72 K_2O-18.06 MgO[7] in mol pct.

able to predict all the experimental data within 1 pct error. Ouchi et al. also examined the effect of BaO, SrO, and NiO additions to the PbO-SiO_2 system. In all cases, a linear molar volume change with oxide addition was observed along constant silica joins. The compositions examined in the MgO-PbO-SiO_2 and CaO-PbO-SiO_2, and model accuracy are shown in Figure 11.

C. Ternary Alkali Alkali-Earth Silicate Melts

1. Li_2O-MgO-SiO_2 and Li_2O-CaO-SiO_2 systems
The lithium silicate systems with either MgO or CaO additions have not been studied in depth. Only one composition was studied (72.22 SiO_2-9.72 Li_2O-18.06 MgO or CaO by mole percent) by Sasek et al.[6] using the SBA method at multiple temperatures. Both the linear model and the present model provide similar results and can predict the experimental data within a 1 pct error limit as shown in Figure 12.

2. Na_2O-MgO-SiO_2 system
The Na_2O-MgO-SiO_2 system was studied in four independent works. The measurements by Adachi et al.[12] were performed using the sessile drop (SD) method. Their results are not considered to be accurate

based on experimental technique and inconsistency with other measurements. The remaining data obtained from Din,[5] Sasek and Lisy,[6] and Dertev and Golovin[8] are consistent with each other and are well predicted, as shown in Figure 13. Din et al.[42] published the same results of Din.[5] Two binary sections were examined in more detail: in Figure 14, the constant 66.7 mol pct silica join and the constant 14.3 mol pct Na_2O join are shown. The results from the linear model and the present model are nearly equivalent in the high SiO_2 region and are in good agreement with the experimental data. They provide different extrapolations at the low-SiO_2 region due to the different molar volumes of pure MgO and Li_2O used in the two models.

3. Na_2O-CaO-SiO_2 system
The Na_2O-CaO-SiO_2 system was studied in similar composition ranges as the Na_2O-MgO-SiO_2 system as shown in Figure 15. The work by Din,[5,42] Sasek and Lisy,[6] and Dertev and Golovin[8] are in good agreement with each other and are well predicted. Like the Na_2O-MgO-SiO_2 system, the results of Adachi et al.[12] (SD method) are less reliable. The results of Coenen[13] using the SBA method were inconsistent with the results of Din at the similar compositions. Dertev and Golovin reported a linear decrease in molar volume at 66.7 pct SiO_2 with replacement of Na_2O by CaO, which are well predicted by the present model and the linear model.

4. K_2O-MgO-SiO_2 system
Only one composition was examined in this ternary system by Sasek et al.[6] using the SBA method: 72.22 SiO_2-9.72 K_2O-18.06 MgO in mol pct. The experimental data as a function of temperature are well predicted by the present model as shown in Figure 16. Nearly the same results are obtained by the linear model. Both models predict the experimental temperature dependence.

5. K_2O-CaO-SiO_2 system
Only two compositions were examined in this ternary system: Sasek and Lisy[6] (72.22 SiO_2-9.72 K_2O-18.06 CaO in mol pct) using the SBA method and Lange and Carmichael[11] (59.52 SiO_2-9.97 K_2O-30.51 CaO in mol pct) using the DBA method. Both datasets are well
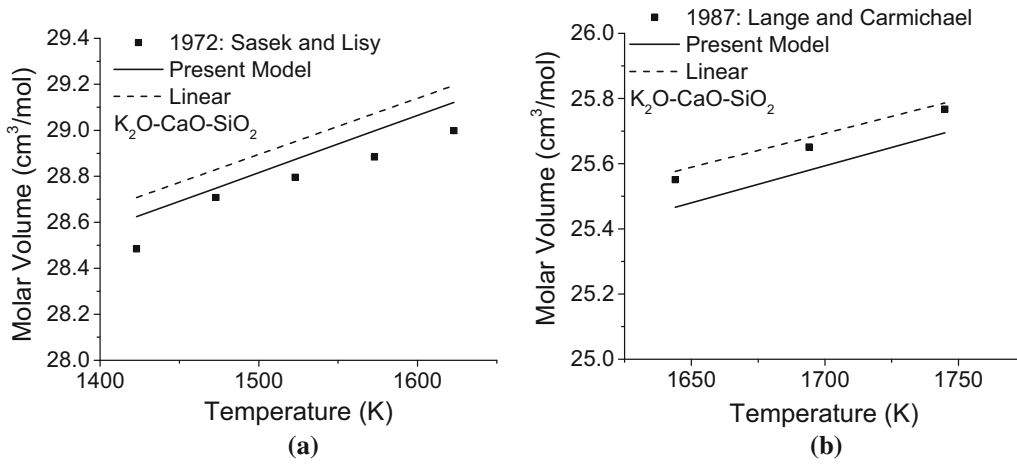
Fig. 17—The molar volume of the ternary K_2O-CaO-SiO_2 system at various temperatures at a composition of (*a*) 9.72 K_2O-18.06 CaO-72.22 SiO_2[6] and (*b*) 9.97 K_2O-30.51 CaO-59.52 SiO_2 in mol pct.[11]
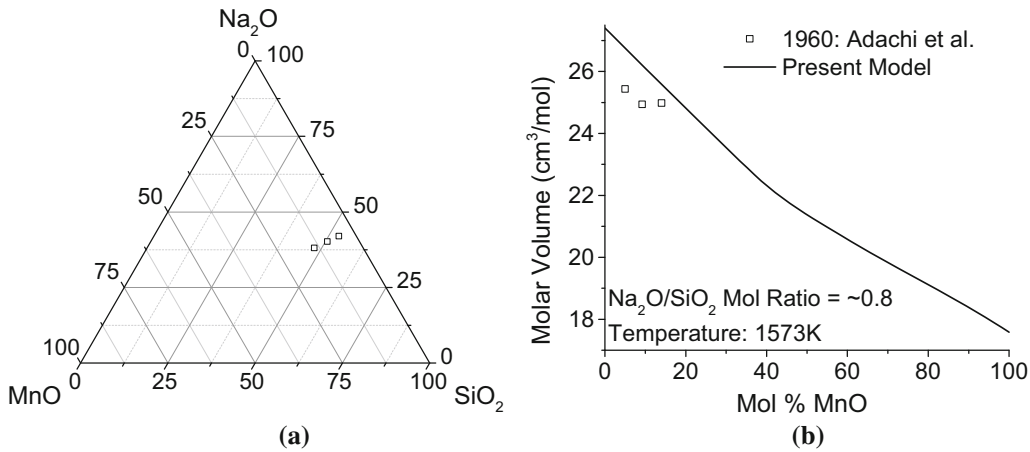

Fig. 18—The ternary Na_2O-MnO-SiO_2 system: (*a*) compositions examined and (*b*) the Na_2O/SiO_2 = 0.8 join.[12]

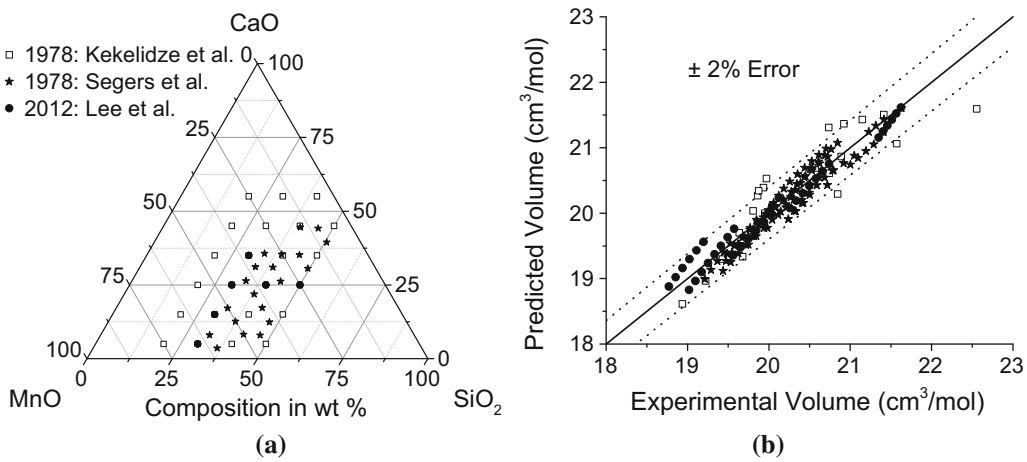Fig. 19—The ternary CaO-MnO-SiO_2 system: (*a*) compositions examined and (*b*) model accuracy.[26–28]
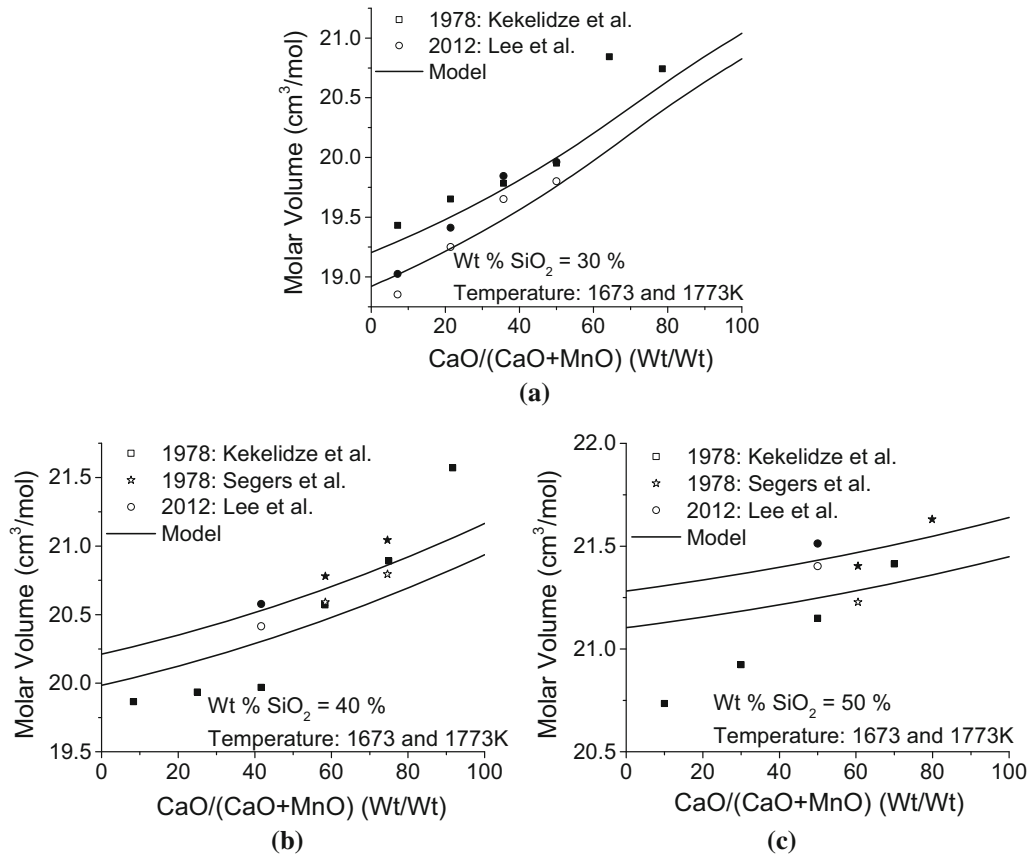
(a)

(b)

(c)

Fig. 20—The molar volume in the CaO-MnO-SiO₂ system across the (*a*) 30 wt pct, (*b*) 40 wt pct, and (*c*) 50 wt pct silica joins.[26–28] Open symbols are at 1673 K (1400 °C) and filled symbols are at 1773 K (1500 °C).
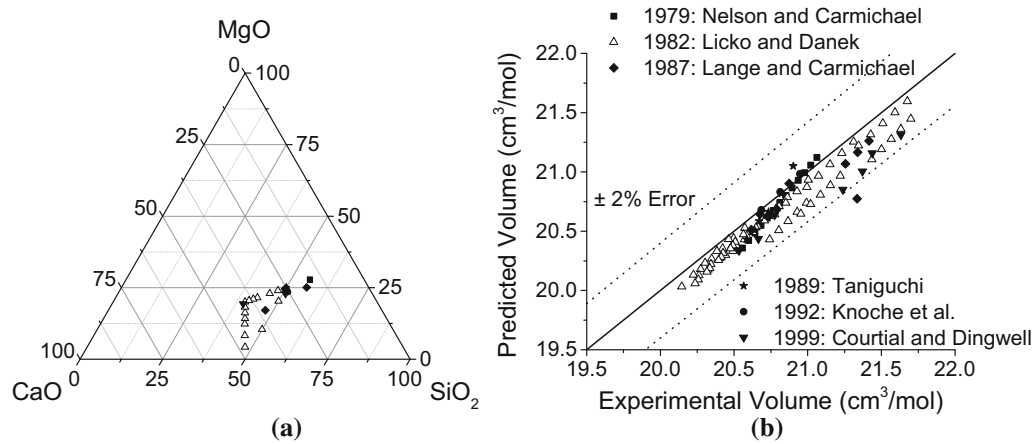

(a)

(b)

Fig. 21—The ternary MgO-CaO-SiO₂ system: (*a*) compositions examined and (*b*) model accuracy.[11,17,22,23,43]

predicted by the present model as a function of temperature as shown in Figure 17.

D. *Ternary Manganese Oxide-Containing Systems*

Relatively few measurements have been made in the manganese containing systems with the exception of the CaO-MnO-SiO₂ system. In addition, there is no experimental data using the DBA technique. Only imaging

techniques and SBA technique which are prone to systematic errors have been used.

1. *Na₂O-MnO-SiO₂ system*

This is the only known alkali system containing manganese oxide studied. Adachi *et al.*[12] examined three compositions. The predictions from the present model are higher than the experimental data, as shown in Figure 18. The accuracy of the work of Adachi
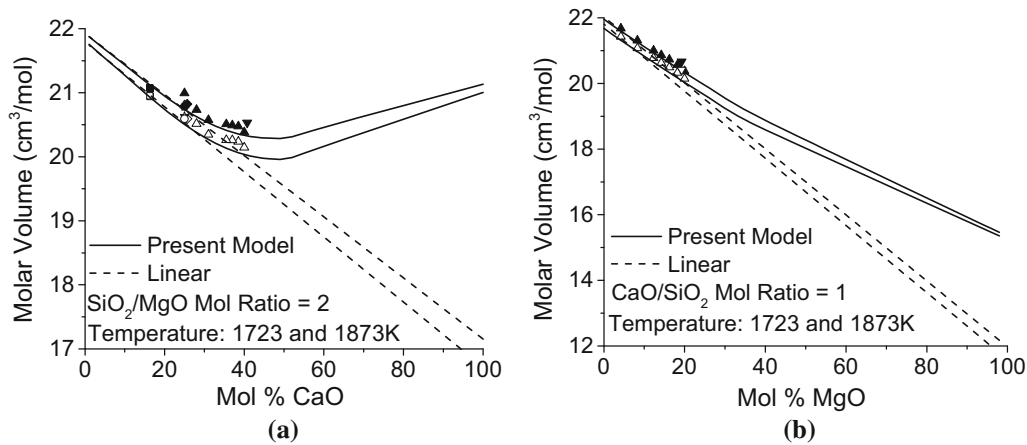
Fig. 22—The molar volume in the MgO-CaO-SiO$_2$ system across the (a) SiO$_2$/MgO = 2 and (b) CaO/SiO$_2$ = 1 joins. The legend is the same Fig. 21, and open and filled symbols represent 1723 K (1450 °C) and 1873 K (1600 °C), respectively.
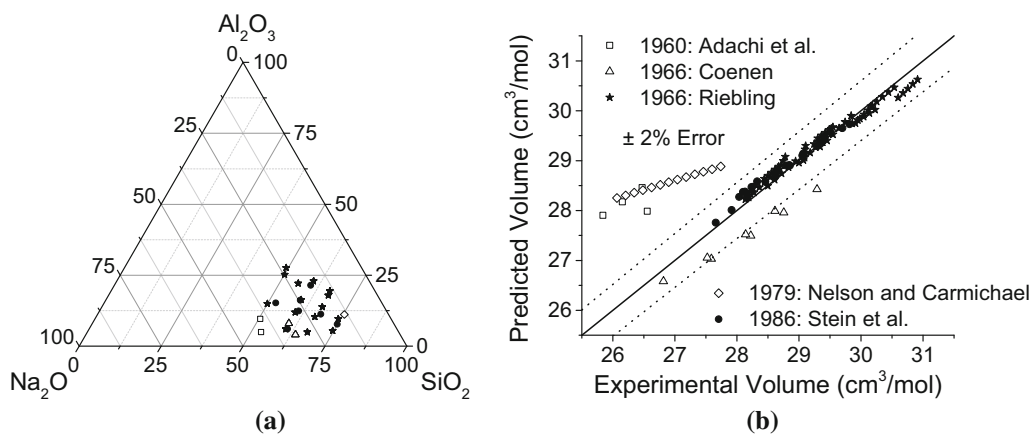

Fig. 23—The ternary Na$_2$O-Al$_2$O$_3$-SiO$_2$ system: (a) compositions examined and (b) model accuracy.[12,13,16–18]

et al.[12] using the SD technique was questioned in several systems. The molar volume of the Na$_2$O-SiO$_2$ system extrapolated from the results by Adachi et al. are noticeably lower than the experimental data of the Na$_2$O-SiO$_2$ system as examined in Part I of this series.

2. CaO-MnO-SiO$_2$ system

The CaO-MnO-SiO$_2$ system has been well studied. It was examined by Kekelidze et al.[26] (SD method), Segers et al.[27] (SBA method), and more recently by Lee et al.[28] (SBA method). Segers et al. and Lee et al. provided their results in the form of equations with temperature limits, while Kekelidze et al. made measurements at a temperature of 1773 K (1500 °C) and tabulated their results. The measurements of Kekelidze et al. span a wide composition range; however, some of the lowest silica content measurements were made below the liquidus. All three datasets are in good agreement with each other, but the data of Kekelidze are the least consistent. All experimental data are well predicted by the present model and are within 2 pct error as shown in Figure 19.

To further examine this system, three iso-SiO$_2$ sections with 30, 40, and 50 wt pct of SiO$_2$ are presented in Figure 20. Molar volume increases with replacement of MnO with CaO at iso-SiO$_2$ concentrations. These sections illustrate the agreement between authors and the accuracy of the present model. As mentioned above, the results of Kekelidze et al. are the least consistent.

E. Ternary Alkali-Earth Silicate Melts

1. MgO-CaO-SiO$_2$ system

The MgO-CaO-SiO$_2$ system is one of the most important metallurgical and geological systems. This system was investigated by Licko and Danek[21] along two pseudo-binary joins (CaMgSi$_2$O$_6$-Ca$_2$MgSi$_2$O$_7$ and CaSiO$_3$-Ca$_2$MgSi$_2$O$_7$) using a SBA technique. The remaining authors[11,17,22,23,43] used the more accurate DBA technique. The examined compositions and the accuracy of the present model can be seen in Figure 21. The experimental data are slightly under-predicted. The deviation from the experimental results of Licko and Danek may be attributed to the SBA
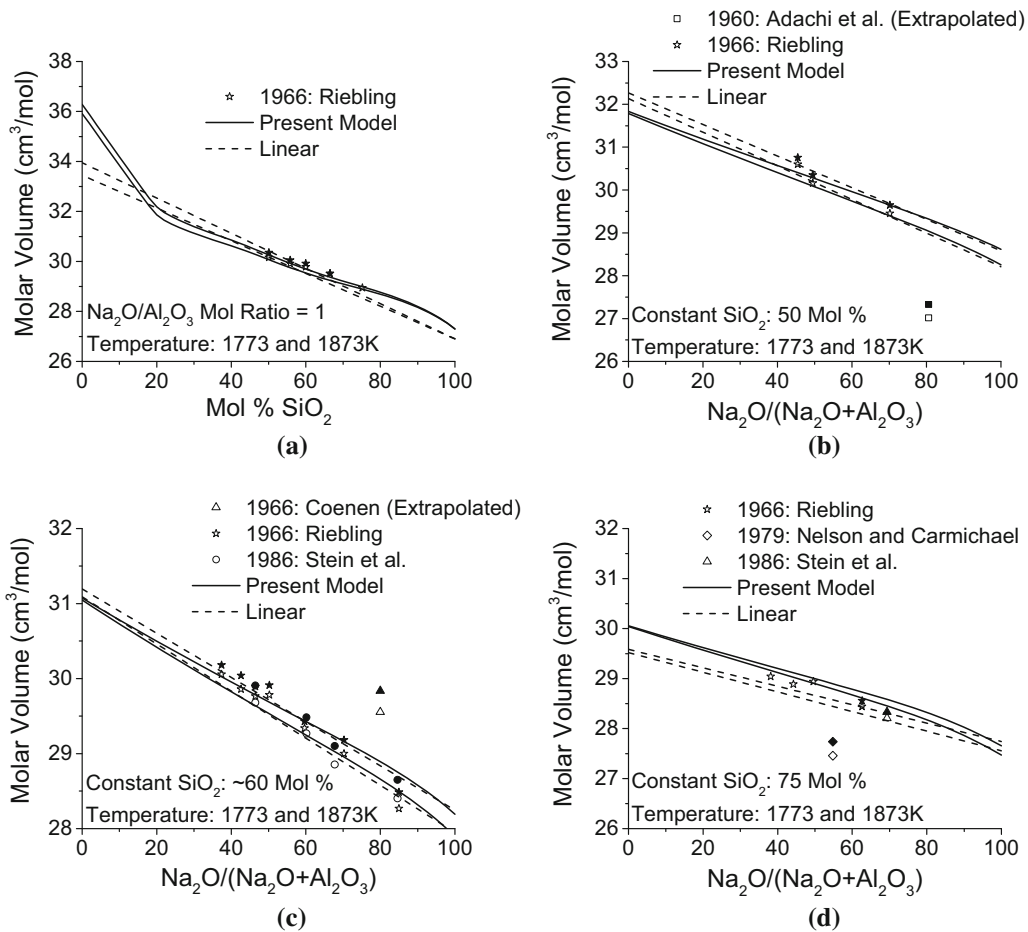
Fig. 24—The molar volume in the Na₂O-Al₂O₃-SiO₂ system at (a) Na₂O/Al₂O₃ = 1, (b) 50 mol pct silica, (c) ~60 mol pct silica, and (d) 75 mol pct silica [filled symbols at 1873 K (1600 °C) and open symbols at 1773 K (1500 °C)].[12,13,16–18]
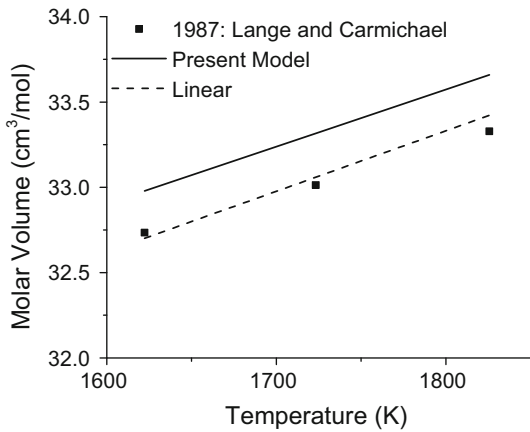

Fig. 25—The molar volume of the ternary K₂O-Al₂O₃-SiO₂ system (65.84 SiO₂, 5.6 Al₂O₃, 28.56 K₂O mol pct) as a function of temperature.[11]

technique. The data of Courtial and Dingwell[43] are the least well predicted by the present model (approaching 2 pct deviation). However, it was noted previously that their measurements deviated from those of Tomlinson et al.[44] in both the binary MgO and CaO silicate

systems which were used to calibrate the binary model parameters of the present model (see Part I). The two joins are further examined in Figure 22 and demonstrate the predicted trends. The present model provides better accuracy than the linear model of Lange and Carmichael,[3] as can be seen in Figure 22(a).

F. Ternary Alumino-Silicate Melts

Alumino-silicate melts have received a fair amount of attention by the modeling community due to the possibility of significant changes in structure as a function of composition. Bottinga et al.[45] devised a model which attempted to incorporate nonlinear trends as a function of the changes in coordination of aluminum. In the present model, nonlinear trends in the molar volume of alumina were introduced in the SiO₂-Al₂O₃ system. Because of the importance of these alumino-silicate systems, many isopleths are illustrated to prove the accuracy of predictions of the present model.

1. Na₂O-Al₂O₃-SiO₂ system

The sodium containing alumino-silicate system was extensively studied by Riebling et al.[16] using a SBA
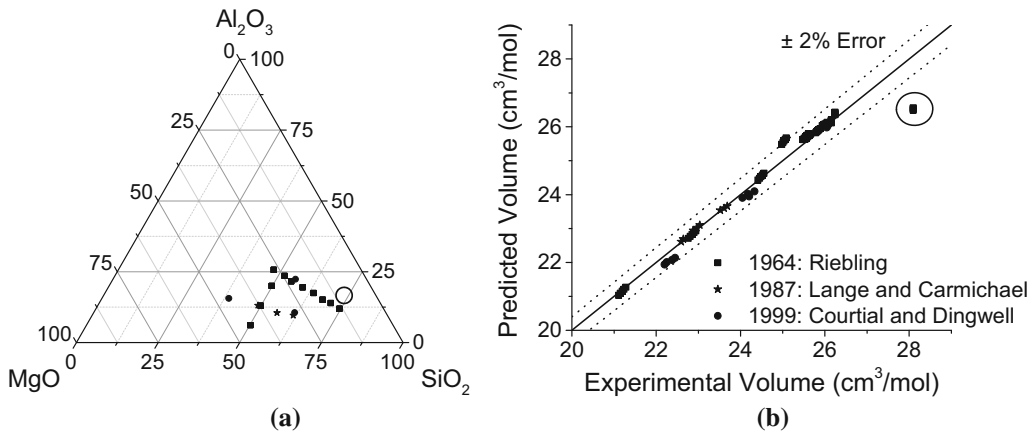
Fig. 26—The ternary MgO-Al$_2$O$_3$-SiO$_2$ system: (a) compositions examined and (b) model accuracy.[11,25,43] Additional information concerning the circled data is mentioned in the text.
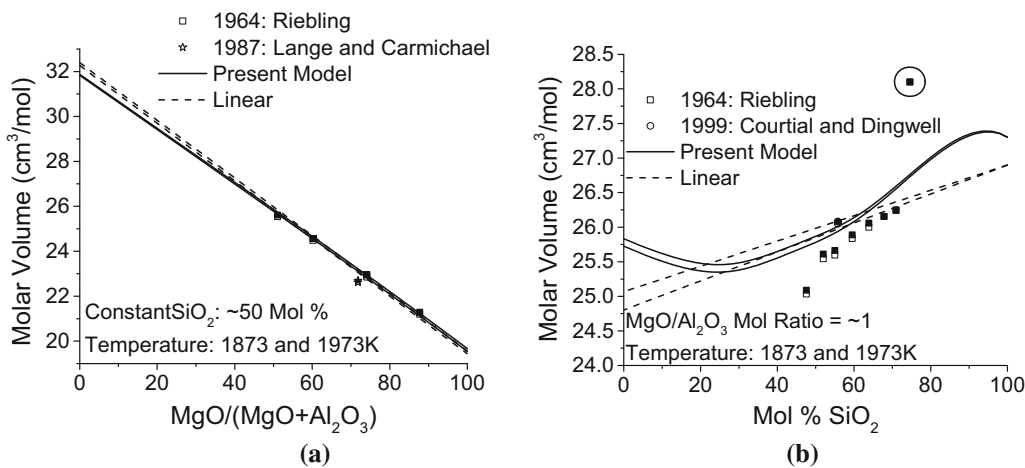

Fig. 27—The molar volume in the MgO-Al$_2$O$_3$-SiO$_2$ system across the (a) SiO$_2$ = 50 mol pct and (b) MgO/Al$_2$O$_3$ = 1 joins.[11,25,43] Additional information concerning the circled data is mentioned in the text [filled symbols at 1973 K (1700 °C) and opened symbols at 1873 K (1600 °C)].

technique. The measurements were performed along constant silica joins in addition to along the Na$_2$O/Al$_2$O$_3$ = 1 join. Adachi *et al.*[12] (SD), Coenen[13] (SBA), Nelson and Carmichael[17] (DBA), and Stein *et al.*[18] (DBA) also investigated the molar volume of this ternary system using various techniques. All experimental compositions are plotted in Figure 23 along with the model accuracy. The molar volume changes in the sections with Na$_2$O/Al$_2$O$_3$ = 1, and iso-SiO$_2$ (50, 60, 75 pct) are also plotted in Figure 24. The results of Stein *et al.*[18] (DBA) are believed to be the most accurate and are comparable to those of Riebling within ~0.5 pct. Along the Na$_2$O/Al$_2$O$_3$ = 1 section, significant curvature is predicted due to the restrictions on the Na$_2$O-SiO$_2$ system. These two sets of data are very well predicted by the present model as shown in Figures 23 and 24. The experimental data of Adachi *et al.* and Nelson and Carmichael are lower than the data by Riebling and Stein *et al.* The results of Coenen are systematically higher than the predicted values from present model. Both the present model and the linear

model of Lange and Carmichael predict similar values in the high SiO$_2$ region.

2. K$_2$O-Al$_2$O$_3$-SiO$_2$ system

A single composition was examined by Lange and Carmichael[11] (65.84 SiO$_2$, 5.6 Al$_2$O$_3$, 28.56 K$_2$O mol pct) in this ternary system using the DBA method. The experimental data are compared with the values predicted from the present model and the linear model of Lange and Carmichael[3] in Figure 25. Both models can well predict the experimental data.

3. MgO-Al$_2$O$_3$-SiO$_2$ system

The MgO-Al$_2$O$_3$-SiO$_2$ system was systematically studied by Riebling[25] with a SBA method. Measurements by Lange and Carmichael[11] and Courtial and Dingwell[43] were performed using the DBA method. The experimental compositions are shown in Figure 26. The change in molar volume at an iso-SiO$_2$ sections (50 pct SiO$_2$) and a section with MgO/Al$_2$O$_3$ = 1 by Riebling are compared with the predicted data in this
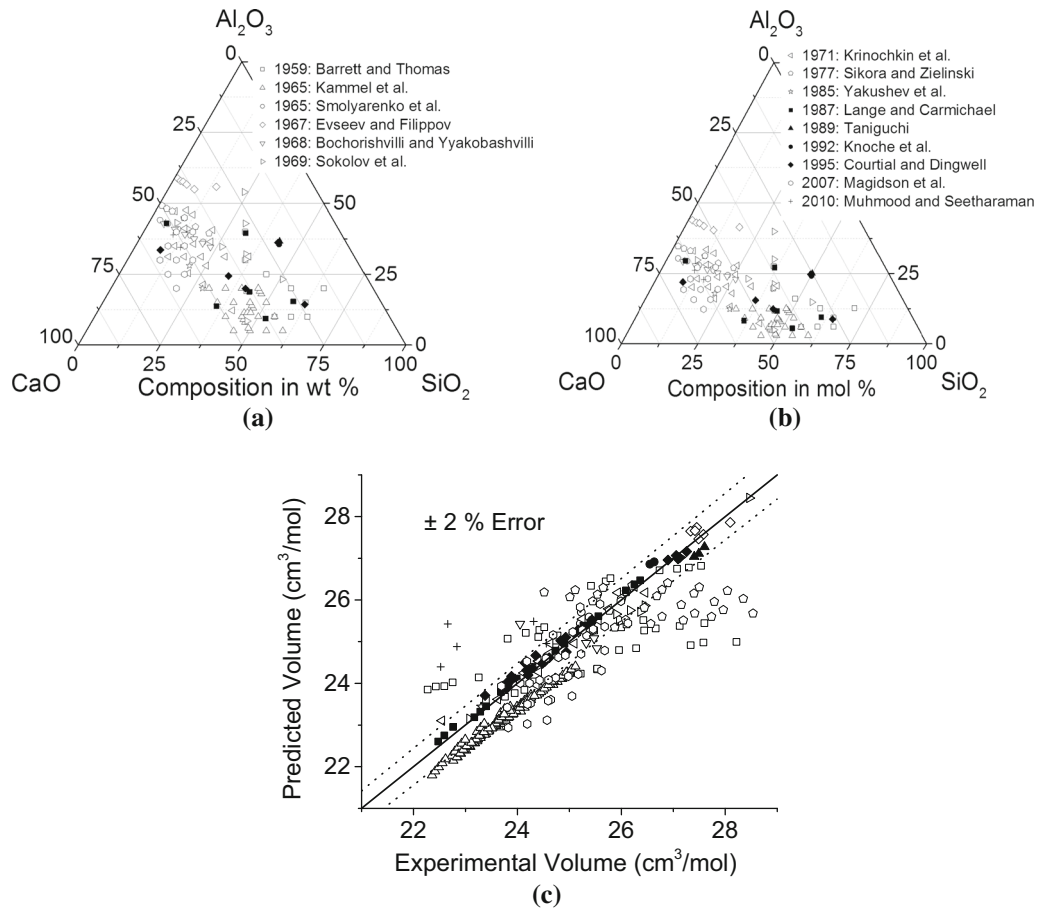
Fig. 28—The ternary CaO-Al$_2$O$_3$-SiO$_2$ system: (*a*) compositions examined in weight percent, (*b*) compositions examined in mole percent, and (*c*) model accuracy.[11,22,23,30,32,33,37,38,40]

study in Figure 27. All the results are reasonably well predicted except for the highest silica content measurements of Riebling (even higher than pure SiO$_2$), circled in Figures 26 and 27.

4. *CaO-Al$_2$O$_3$-SiO$_2$ system*

The CaO-Al$_2$O$_3$-SiO$_2$ system has been investigated extensively. Unfortunately, there is considerable disagreement in the available experimental data. The experimental compositions (in both mole and weight percent) along with the model accuracy are shown in Figure 28. The most comprehensive studies have been performed using the less accurate experimental techniques. Kammel *et al.*[30] (SBA) investigated the change in molar volume of this ternary system at various iso-CaO content joins. However, their data are systematically higher than the results of more accurate DBA measurements by Lange and Carmichael,[11] Taniguchi,[22] Knoche *et al.*,[23], and Courtial and Dingwell.[37] The measurements in the silica poor region are performed primarily using the MBP technique,[32,33,38,40] with questionable accuracy.

The change in molar volume at constant CaO (30, 40, 45, 50 wt pct CaO) are shown in Figure 29. The molar CaO/Al$_2$O$_3$ = 1 join is shown in Figure 30. All the DBA measurement results are well predicted within a 2 pct

error limit. The trends in the results by Kammel *et al.*[30] are well reproduced although systematically higher than the predictions of the present model. Comparing the present model with the linear model by Lange and Carmichael,[3] the predictions are similar in the high silica region but the model of Lange and Carmichael predicts a significantly lower molar volumes in the silica poor regions. Along the molar CaO/Al$_2$O$_3$ = 1 join, both models predict approximately the same molar volumes at 50 mol pct SiO$_2$ content but the present model suggests significant curvature with silica content resulting from the curvatures observed in molar volumes of the Al$_2$O$_3$-SiO$_2$ and CaO-SiO$_2$ systems.

G. *Ternary Aluminate Melts*

Several silica free aluminate systems were examined in the literature. Bochorishvili and Yakobashvili[33] examined the effect of oxide addition to a Al$_2$O$_3$-CaO melt (45 wt pct Al$_2$O$_3$-55 wt pct CaO). Additions of Li$_2$O, Na$_2$O, K$_2$O, MgO, or SiO$_2$ were made and the density change was measured using the MBP method. The alkali bearing systems are not shown due to very limited data but are reasonably well predicted by the present model, considering the error associated with the MBP technique.
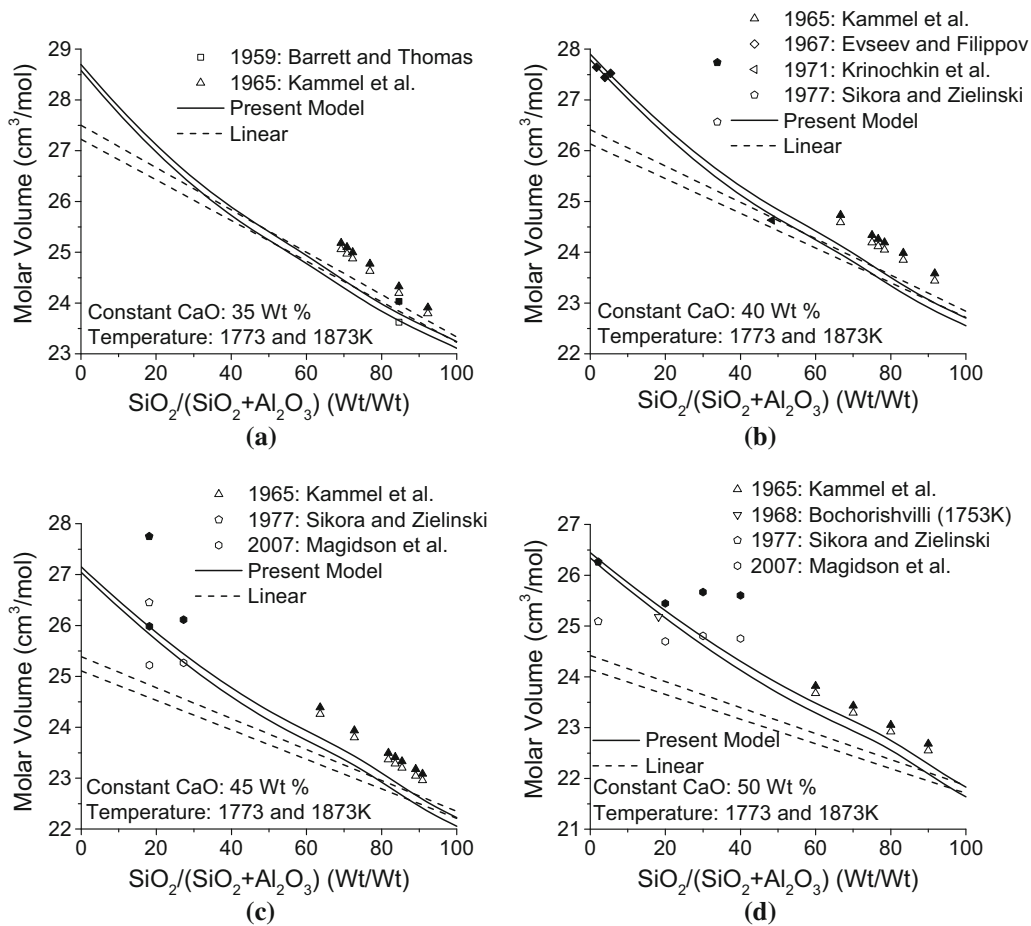
Fig. 29—The molar volume in the CaO-Al$_2$O$_3$-SiO$_2$ system across the (*a*) 35 wt pct, (*b*) 40 wt pct, (*c*) 45 wt pct, and (*d*) 50 wt pct CaO joins [filled symbols at 1873 K (1600 °C) and opened at 1773 K (1500 °C)].[11,22,23,30,32,33,37,38,40]
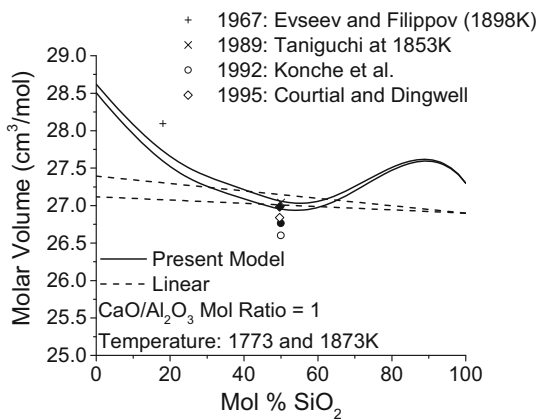

Fig. 30—The molar volume in the CaO-Al$_2$O$_3$-SiO$_2$ system along the SiO$_2$-CaAl$_2$O$_4$ join[22,23,32,37] [filled symbols at 1873 K (1600 °C) and opened at 1773 K (1500 °C)].

The MgO-CaO-Al$_2$O$_3$ system was examined by several research groups.[32,33,40,41] The difficulties with this system are primarily associated with the high melting temperatures. The compositions examined are shown in Figure 31(a). Most of the experimental data were measured up to 5 wt pct MgO composition. The accuracy of the experimental data is questionable with relatively large inconsistencies because all measurements were made using the MBP method except that of Li *et al*.[41] who used a SBA technique. It was found that the data of Li *et al*. are questionable; they made no correction for surface tension and the magnitude of their density results suggests an incredibly dense melt. The data of Li *et al*. are completely inconsistent with the molar volume data of the binary CaO-Al$_2$O$_3$. The 5 wt pct MgO join is shown in Figure 32 and illustrates the significant disagreement with this dataset. Therefore, the results by Li *et al*.[41] and by Xu *et al*.[46] from the same research group were not considered in this study. The linear model of Lange and Carmichael[3] differs from the prediction of the present model mainly because of different molar volume data of CaO, but it is not significantly different in the region of experimental studies.

H. *Higher Order Systems*

Molar volumes of multicomponent melts were examined for consistency and to ensure that the predictions remained reasonable. The components of the
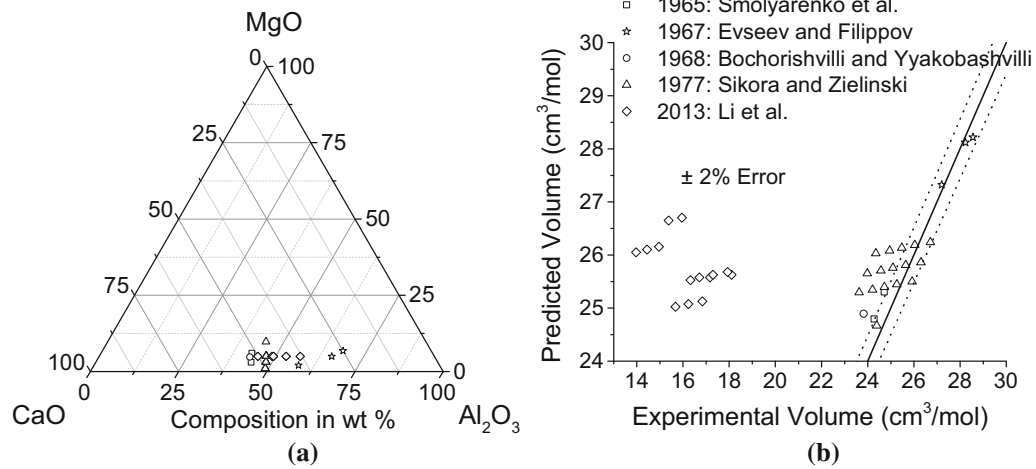
Fig. 31—The ternary MgO-CaO-Al$_2$O$_3$ system: (a) compositions examined and (b) model accuracy.[31–33,40,41]
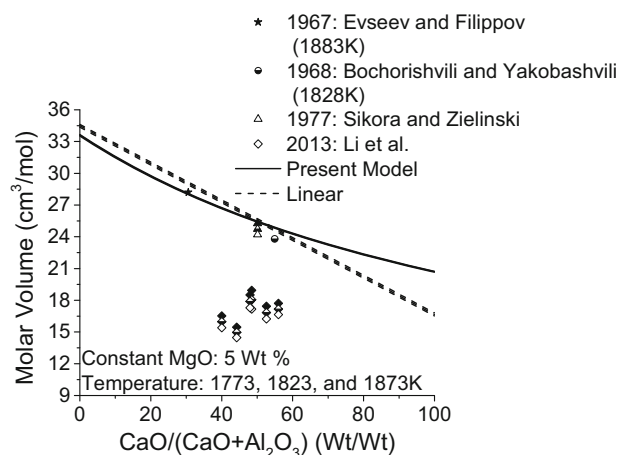

Fig. 32—The molar volume in the MgO-CaO-Al$_2$O$_3$ system across the MgO = 5 wt pct join[32,33,40,41] [filled symbols at 1873 K (1600 °C), half-filled symbols at 1823 K (1550 °C) and open symbols at 1773 K (1500 °C)].

multicomponent systems and the experimental methods are listed in Table II. The prediction accuracy of the present model for several higher order systems can be assessed in Figure 33. The data points with filled symbols are the most accurate studies using the DBA technique and are well predicted.

The MgO-CaO-Al$_2$O$_3$-SiO$_2$ system was investigated by Smolyarenko et al.[31] (MBP) Winterhager et al.[47] (SBA), Dzhincharadze et al.[48] (SD), Yakushev et al.[36] (MBP), Taniguchi[22] (DBA), and Courtial and Dingwell[43] (DBA). Coenen[13] (SBA) studied the Na$_2$O-CaO-Al$_2$O$_3$-SiO$_2$ system. Kekelidze et al.[26] (SD) studied a few compositions in the CaO-MnO-SiO$_2$ system with small additions of Al$_2$O$_3$ which are not well predicted. Nelson and Carmichael[17] (DBA) studied various compositions in multiple quaternary and higher order systems, and the accuracy of their results is uncertain considering the discrepancies observed in several of the lower order systems (ex: Na$_2$O-SiO$_2$).

Lange and Carmichael[11] (DBA) also studied various compositions in various higher order systems. Magidson et al.[38] (MBP) studied various Na$_2$O-CaO-Al$_2$O$_3$-SiO$_2$ melts and are not well reproduced; however, they quoted a large error of 4 to 5 pct with their measurements.

I. Predictions for Iso-molar Volume Contours of Ternary and Quaternary Systems

Iso-molar volume contour plots were calculated in this section to provide some insight into the molar volume behavior of several important ternary and quaternary systems based purely on the predictions made by the present structural molar volume model. The model assumes a single liquid melt. That is, no liquid miscibility gap or solids were considered. All the diagrams are presented in weight percent.

The predicted iso-molar volume contours for the CaO-Al$_2$O$_3$-SiO$_2$ system at 1873 K (1600 °C) are presented in Figure 34(a). According to the prediction, the molar volume of the slag with constant CaO to Al$_2$O$_3$ ratio gradually decreases with increasing SiO$_2$ content up to approximately 50 pct and then begins to increase again above 50 wt pct SiO$_2$. This type of inflection is also demonstrated in Figure 30. Adding Al$_2$O$_3$ into CaO-SiO$_2$ slags increases the molar volume monotonically. The molar volume of the CaO-Al$_2$O$_3$-SiO$_2$ system with 10 wt pct MgO is predicted in Figure 34(b). The addition of 10 wt pct MgO does not change the general trend of the iso-contours. However, MgO addition decreases the overall molar volume with a more pronounced effect in the Al$_2$O$_3$-rich region. The addition of 10 wt pct Na$_2$O to the CaO-Al$_2$O$_3$-SiO$_2$ system is predicted in Figure 34(c). An increase in molar volume is predicted, with a more significant increase in the CaO rich region.

Iso-molar volume contour for the CaO-MgO-SiO$_2$ system are predicted in Figure 35(a). Up to approximately 50 wt pct SiO$_2$, the molar volume linearly decreases with the addition of MgO regardless of the CaO/SiO$_2$ ratio (basicity). Above 50 wt pct SiO$_2$, the replacement of CaO by MgO at a given SiO$_2$ content

Oxide Components	References (Year: Authors)	Method	Presentation
MgO-CaO-Al$_2$O$_3$-SiO$_2$	1965: Smolyarenko et al.[31]	MBP	table
Na$_2$O-CaO-Al$_2$O$_3$-SiO$_2$	1966: Coenen[13]	SBA	graph
MgO-CaO-Al$_2$O$_3$-SiO$_2$	1966: Winterhager et al.[47]	SBA	table
CaO-MnO-Al$_2$O$_3$-SiO$_2$	1978: Kekelidze et al.[26]	SD	table
MgO-CaO-Al$_2$O$_3$-SiO$_2$	1979: Dzhincharadze et al.[48]	SD	table
Various	1979: Nelson and Carmichael[17]	DBA	equation
(Na$_2$O)-(K$_2$O)-MgO-CaO-Al$_2$O$_3$-SiO$_2$	1985: Yakushev et al.[36]	MBP	table
Various	1987: Lange and Carmichael[11]	DBA	table
MgO-CaO-Al$_2$O$_3$-SiO$_2$	1989: Taniguchi[22]	DBA	table
MgO-CaO-Al$_2$O$_3$-SiO$_2$	1999: Courtial and Dingwell[43]	DBA	table
Na$_2$O-CaO-Al$_2$O$_3$-SiO$_2$	2007: Magidson et al.[38]	MBP	table

Method DBA: double bob archimedean, SDA: single bob archimedean, MBP: maximum bubble pressure, SD: sessile drop.
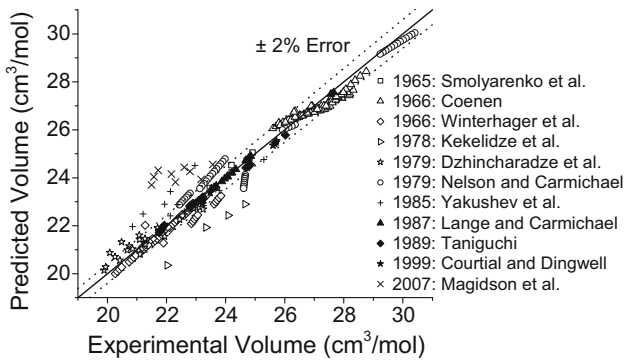

Fig. 33—The accuracy of the present model in quaternary and higher order systems without iron oxide.[11,13,17,22,26,31,36,38,43,47,48]

more significantly decreases the molar volume of the melt. The effect of a 10, 20, and 30 wt pct Al$_2$O$_3$ addition in the CaO-MgO-SiO$_2$ system is predicted in Figures 34(b) through (d). No significant change in iso-contour trend is observed. A general increase of 1 cm^3/mol per 10 wt pct Al$_2$O$_3$ addition is predicted in all compositions.

Iso-molar volume contours for the CaO-MnO-SiO$_2$ system are predicted in Figure 36(a). The general trend is similar to that of the CaO-MgO-SiO$_2$ system. However, the molar volume is almost constant with changing SiO$_2$ content above 50 wt pct SiO$_2$. That is, the replacement of CaO by MnO does not significantly change the molar volume. Like the CaO-MgO-SiO$_2$ system with Al$_2$O$_3$ addition, a 10 wt pct addition of Al$_2$O$_3$ increases the molar volume of the CaO-MnO-SiO$_2$ system by approximately 1 cm^3/mol, as shown in Figure 36(b).

The molar volume of alkali oxide alumino-silicate systems are predicted in Figure 37. The molar volume of alkali oxides changes significantly between Li$_2$O, Na$_2$O, and K$_2$O, which significantly changes the iso-contour trends in each ternary system. The molar volume of pure Li$_2$O at 1773 K (1500 °C) is predicted to be 19.37 cm^3/mol which is significantly lower than that of Al$_2$O$_3$ and SiO$_2$, and therefore, it induces a decreasing molar volume trend with increasing Li$_2$O content in the

Li$_2$O-Al$_2$O$_3$-SiO$_2$ system. On the other hand, K$_2$O has a significantly higher molar volume of 53.50 cm^3/mol at 1773 K (1500 °C) and therefore increases the molar volume of the K$_2$O-Al$_2$O$_3$-SiO$_2$ system with increasing K$_2$O content. In the case of Na$_2$O-Al$_2$O$_3$-SiO$_2$ system, as Na$_2$O is predicted to have a volume of 35.86 cm^3/mole, a similar volume as Al$_2$O$_3$ at 1773 K (1500 °C), the molar volume of the Na$_2$O-Al$_2$O$_3$ system is approximately constant and the addition of SiO$_2$ in the Na$_2$O-Al$_2$O$_3$ system decreases the molar volume.

IV. DISCUSSIONS

There are a few systems that have very little or no experimental data in the binary systems that are deemed accurate enough to calibrate the binary systems required for extrapolations. For example, the MnO bearing systems are all measured using SBA measurements which may have systematic errors. In addition, few measurements have been made in the binary MnO-SiO$_2$ system. The temperature dependence of this system requires improvement as is apparent during the examination of the CaO-MnO-SiO$_2$ extrapolation. There is still disagreement in the experimental data of the Al$_2$O$_3$-SiO$_2$ system. The measurements of Aksay et al.[49] have been questioned, the accuracy of the results of Anisimov et al.[50] is uncertain, and the single measurement of Courtial and Dingwell[37] did not provide further insight concerning the accuracy of either of these datasets. More accurate experiments are necessary to resolve the disagreement.

As shown in the part I of this study, a large change in the composition dependency of molar volume $\left(\frac{\partial V}{\partial X_{SiO_2}}\right)$ and thermal expansivity $(\partial/(\partial X\,SiO_2)(\partial V/\partial T))$ is predicted in many binary silicate melt near the orthosilicate composition ($X_{SiO_2} = 0.33$). This molar volume behavior of binary silicate melt also results in nonlinear behavior of molar volume in ternary and multicomponent melts. For example, the predicted iso-molar volume contours in Figure 34 through Figure 37 clearly show nonlinear behavior of molar volume. In particular, a
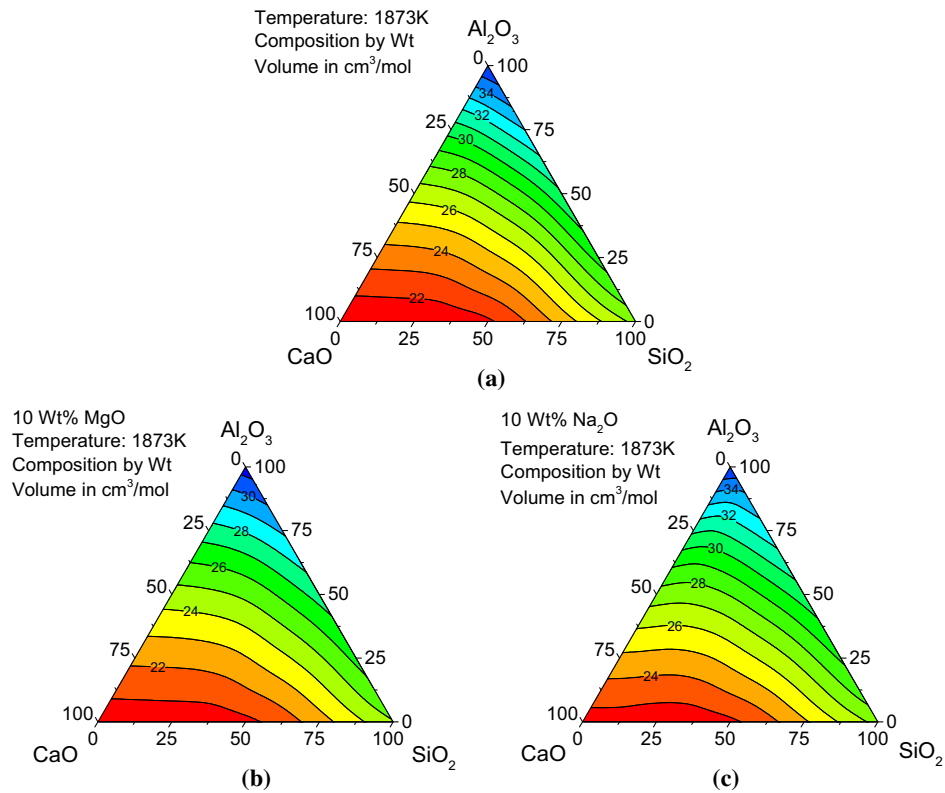
Fig. 34—Predicted molar volume contours of (*a*) the ternary CaO-Al₂O₃-SiO₂ system. (*b*) CaO-Al₂O₃-SiO₂ system with 10 wt pct MgO and (*c*) 10 wt pct Na₂O at 1873 K (1600 °C).
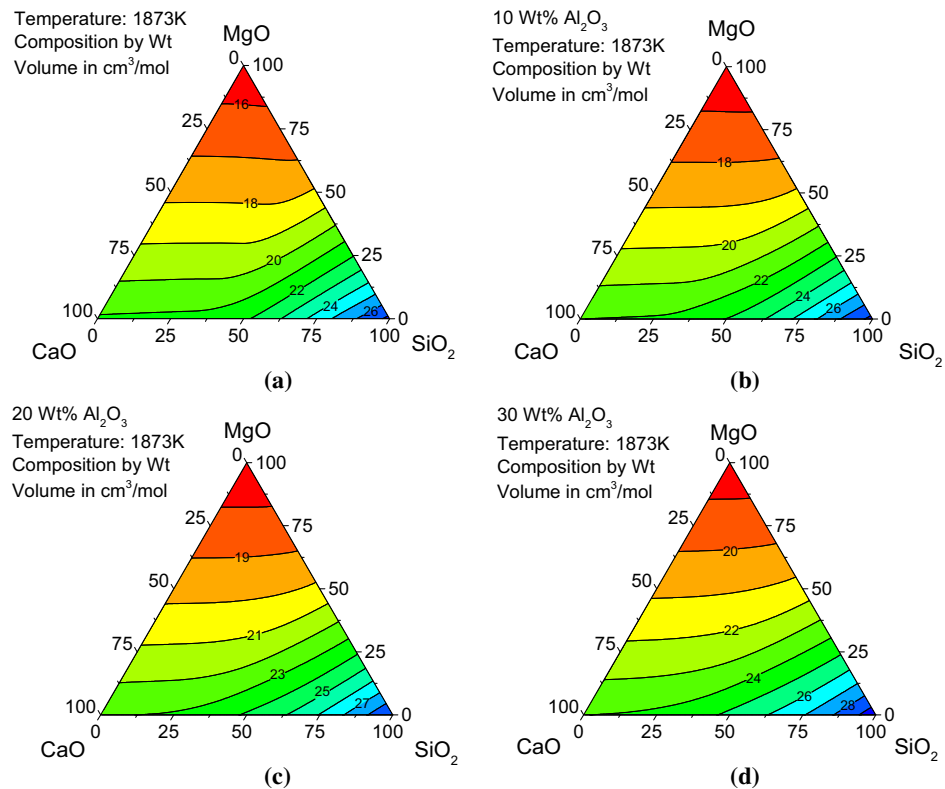

Fig. 35—Predicted molar volume contours of (*a*) the ternary CaO-MgO-SiO₂ system and CaO-MgO-SiO₂ system with (*b*) 10 wt pct Al₂O₃, (*c*) 20 wt pct Al₂O₃, and (*d*) 30 wt pct Al₂O₃ at 1873 K (1600 °C).
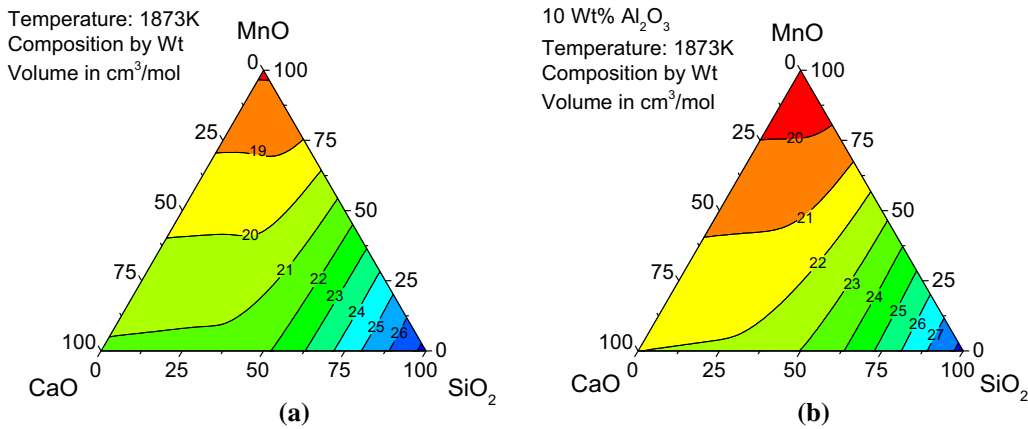
Fig. 36—Predicted molar volume contours of (a) the ternary CaO-MnO-SiO$_2$ system and (b) CaO-MnO-SiO$_2$ system with 10 wt pct Al$_2$O$_3$ at 1873 K (1600 °C).
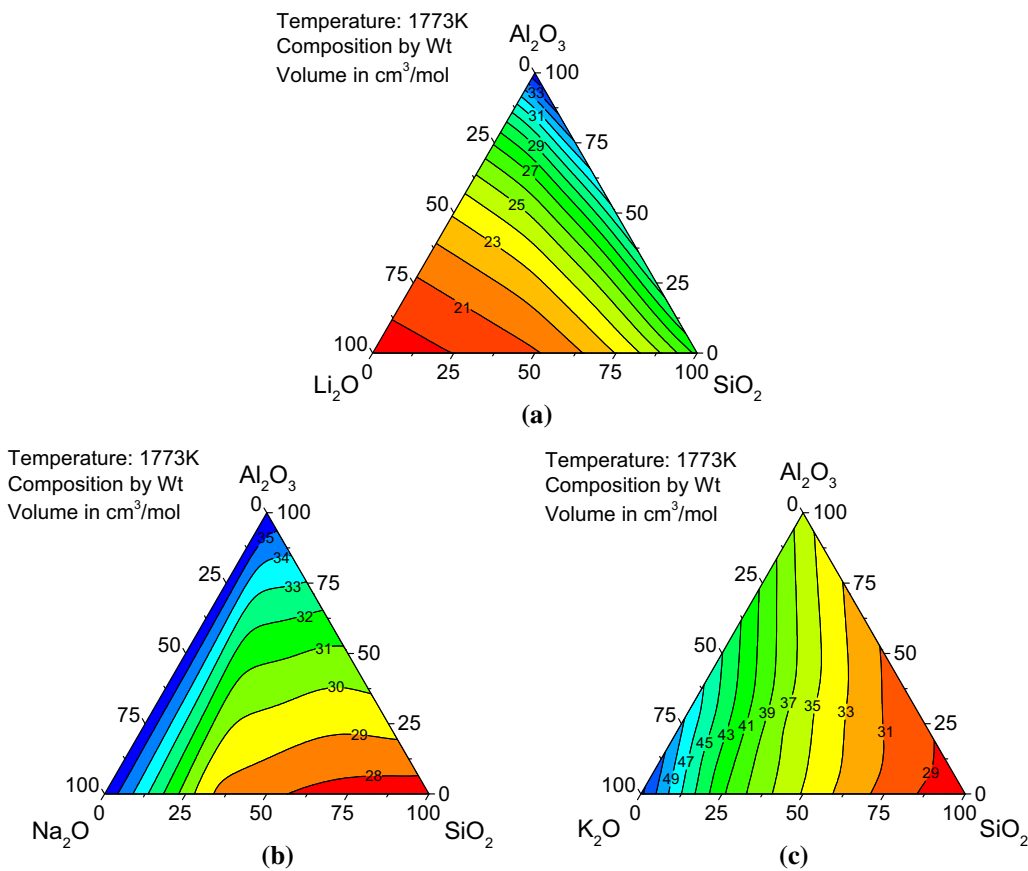

Fig. 37—Predicted molar volume contours of (a) ternary Li$_2$O-Al$_2$O$_3$-SiO$_2$ system, the (b) ternary Na$_2$O-Al$_2$O$_3$-SiO$_2$ system, and the (c) K$_2$O-Al$_2$O$_3$-SiO$_2$ system 1773 K (1500 °C).

minimum in molar volume can be predicted in CaO-Al$_2$O$_3$-SiO$_2$-based melts at constant CaO/Al$_2$O$_3$ join. Unfortunately, few experimental data are available for the validation of such predicted behavior at low SiO$_2$ region due to experimental difficulties, (i) high melting temperatures in the systems containing CaO and MgO, and (ii) high vaporization tendency in the systems containing alkali oxides. The molar volume data in the

MgO-CaO-SiO$_2$ system across the SiO$_2$/MgO = 2 (see Figure 22) shows this trend.

The present structural model can reproduce the molar volume of binary aluminate melts and ternary and multicomponent alumina containing melts which was poorly predicted by the linear model of Lange and Carmichael.[3] However, it should be noted that the treatment of Al$_2$O$_3$ in the present model would be over

simplification of the nature of Al_2O_3 in liquid slag. Aluminum is known to have various coordinations in oxide melts[45] but was simplified as a network modifier connected to three nearest neighboring oxygens. The molar volumes of ternary alumino-silicate melts show more nonlinear behavior than other systems. Although the present model can reasonably predict the experimental data within experimental scatter, it might require additional ternary parameters. From the structural view point, it may be required to consider the possibility of associated formation like $NaAlO_2$ and $Ca_{0.5}AlO_2$ in liquid slags like the case for structural viscosity model.[51] This should be further investigated with the availability of more accurate experimental data covering wide composition ranges.

V. SUMMARY

A structural molar volume model was applied to calculate the molar volume of ternary and multicomponent molten slags of the Li_2O-Na_2O-K_2O-MgO-CaO-MnO-PbO-Al_2O_3-SiO_2 system. After the amount of different silicate tetrahedral Q-species in ternary and multicomponent slag are obtained from the quasichemical bond fractions computed from the Modified Quasichemical Model with the FactSage FToxid database, the molar volume of a liquid slag can be calculated using this structural information and unary and binary molar volume parameters. The present model accurately predicted the molar volume of the Li_2O-Na_2O-K_2O-MgO-CaO-MnO-PbO-Al_2O_3-SiO_2 melts at any composition and temperature under 1 atmosphere pressure without any additional ternary parameters. In particular, nonlinear molar volume behavior of liquid slag was well predicted which was impossible from a linear molar volume model.

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