Thermodynamic Evaluation of the Surface Tension of Molten CaO–SiO_2–Al_2O_3 Ternary Slag

Ja-Yong CHOI and Hae-Geon LEE
Formerly Graduate Student, Department of Materials Science and Engineering, Pohang University of Science and Technology, now at the STS Research Group, Technical Research Laboratories, POSCO, Pohang, 790-785 Korea.
1) Department of Materials Science and Engineering, Pohang University of Science and Technology, Pohang, 790-784 Korea.
(Received on June 25, 2001; accepted in final form on November 27, 2001)

The surface tension of CaO–SiO_2–Al_2O_3 system at 1 873 K was computed using a modified Butler’s equation, and by making use of critically evaluated ionic surface distances of pure oxides involved in the system. For CaO–SiO_2 and CaO–Al_2O_3 binary systems, the computed results are in good agreement with the experimental results reported by other researchers. For CaO–SiO_2–Al_2O_3 ternary system, the surface tension in a wide range of liquid compositional range was computed and the results were favorably compared with the experimental results reported in the literature. It was found that the surface tension increases with decreasing SiO_2, and with increasing CaO or Al_2O_3. For a given SiO_2 content, the surface tension was relatively independent of the CaO/Al_2O_3 ratio. An iso-surface tension diagram has been suggested for liquid CaO–SiO_2–Al_2O_3 solutions.

KEY WORDS: surface tension; CaO; SiO_2; Al_2O_3; temperature coefficient.

1. Introduction

Thermodynamic databases have been used for the construction of phase diagrams and the calculation of chemical equilibria, and the calculation results with the aid of thermodynamic databases showed good agreements with the experimental results. However, the thermodynamic databases have not been widely applied to the prediction of physicochemical properties such as surface tension.

There have been some reports for the surface tension calculations of molten oxide mixtures. Tanaka et al. calculated the surface tension of binary mixture using modified Butler’s equation and thermodynamic database. Nakajima calculated the surface tension of molten slag using Prigogine’s model and the parameter obtained by fitting the experimental surface tension results previously reported. In the present study, the surface tensions of molten CaO–SiO_2–Al_2O_3 ternary systems are calculated using a modified Butler’s equation and thermodynamic database, and by making use of critically evaluated ionic surface distances of pure oxides involved in the system.

2. Thermodynamic Modeling for Surface Tension

Among various models suggested by previous researchers for the prediction of surface tension of liquid solutions, the present work is based on Butler’s equation.

2.1. Butler’s Equation

Butler derived the equation of surface tension of liquid solutions in terms of activity at the surface and at the bulk phase by assuming equilibrium between a bulk phase and a hypothetical surface phase. Butler’s equation for an A–B binary solution is given by Eq. (1).

$$\sigma = \sigma_A + \frac{RT}{A_X} \ln \frac{f^A_B f^B_A}{f^A_A f^B_B} + \frac{RT}{A_B} \ln \frac{f^B_A f^B_B}{f^A_B f^B_A}$$

where $\sigma$: surface tension of the binary mixture, $\sigma_i$: surface tension of pure component $i$, $R$: gas constant, $T$: temperature, $A_i$: molar surface area of component $i$, $f_i$: activity coefficient of component $i$, $N_i$: mole fraction of component $i$.

Superscript B: bulk, Superscript S: surface.

$A_i$ can be obtained by Eq. (2):

$$A_i = N_i^{1/3} V_i^{2/3}$$

where $N_i$ is Avogadro number, $V_i$ molar volume of pure liquid $i$, $L$ correction factor resulting from the surface structure. The value of $L$ in Eq. (2) is usually set to be 1.091 for liquid metals assuming closed packed structures. However there has not been any exact information on the value of $L$ for ionic melts. Tanaka et al. set $L$ to 1 for the molten salts and ionic oxide mixtures.

Separating the ideal term and the excess term in Eq. (1),

$$\sigma = \sigma_A + \frac{RT}{A_X} \ln \frac{f^A_B f^B_A}{f^A_A f^B_B} + \frac{1}{A_X} \Gamma^{\text{ex}}_A(T, N^S_B) - \frac{1}{A_A} \Gamma^{\text{ex}}_B(T, N^S_B)$$

1. Introduction

Thermodynamic databases have been used for the construction of phase diagrams and the calculation of chemical equilibria, and the calculation results with the aid of thermodynamic databases showed good agreements with the experimental results. However, the thermodynamic databases have not been widely applied to the prediction of physicochemical properties such as surface tension.

There have been some reports for the surface tension calculations of molten oxide mixtures. Tanaka et al. calculated the surface tension of binary mixture using modified Butler’s equation and thermodynamic database. Nakajima calculated the surface tension of molten slag using Prigogine’s model and the parameter obtained by fitting the experimental surface tension results previously reported. In the present study, the surface tensions of molten CaO–SiO_2–Al_2O_3 ternary systems are calculated using a modified Butler’s equation and thermodynamic database, and by making use of critically evaluated ionic surface distances of pure oxides involved in the system.

2. Thermodynamic Modeling for Surface Tension

Among various models suggested by previous researchers for the prediction of surface tension of liquid solutions, the present work is based on Butler’s equation.

2.1. Butler’s Equation

Butler derived the equation of surface tension of liquid solutions in terms of activity at the surface and at the bulk phase by assuming equilibrium between a bulk phase and a hypothetical surface phase. Butler’s equation for an A–B binary solution is given by Eq. (1).

$$\sigma = \sigma_A + \frac{RT}{A_X} \ln \frac{f^A_B f^B_A}{f^A_A f^B_B} + \frac{RT}{A_B} \ln \frac{f^B_A f^B_B}{f^A_B f^B_A}$$

where $\sigma$: surface tension of the binary mixture, $\sigma_i$: surface tension of pure component $i$, $R$: gas constant, $T$: temperature, $A_i$: molar surface area of component $i$, $f_i$: activity coefficient of component $i$, $N_i$: mole fraction of component $i$.

Superscript B: bulk, Superscript S: surface.

$A_i$ can be obtained by Eq. (2):

$$A_i = N_i^{1/3} V_i^{2/3}$$

where $N_i$ is Avogadro number, $V_i$ molar volume of pure liquid $i$, $L$ correction factor resulting from the surface structure. The value of $L$ in Eq. (2) is usually set to be 1.091 for liquid metals assuming closed packed structures. However there has not been any exact information on the value of $L$ for ionic melts. Tanaka et al. set $L$ to 1 for the molten salts and ionic oxide mixtures.

Separating the ideal term and the excess term in Eq. (1),

$$\sigma = \sigma_A + \frac{RT}{A_X} \ln \frac{f^A_B f^B_A}{f^A_A f^B_B} + \frac{1}{A_X} \Gamma^{\text{ex}}_A(T, N^S_B) - \frac{1}{A_A} \Gamma^{\text{ex}}_B(T, N^S_B)$$
where $G_{i}^{E,S}$ and $G_{i}^{EB}$ are partial excess Gibbs free energy of $i$ in the surface phase and in the bulk phase, respectively.

Tanaka et al.\textsuperscript{2)} considered the size effect in term of mixing entropy in Butler’s equation (Eq. (3)) by using ionic distances of A ($d_{A}$) and B ($d_{B}$) in the A–B binary system. Modified Butler’s equation can then be expressed as follows:

\[
\sigma=\sigma_{A}^{+}+\frac{RT}{A_{A}}\ln \frac{N_{A}^{S}}{N_{B}^{S}}+\frac{1}{A_{A}}G_{i}^{E,S}(T,N_{i}^{S})-\frac{1}{A_{A}}G_{i}^{EB}(T,N_{i}^{B}) \]

\[
=\sigma_{B}^{+}+\frac{RT}{A_{B}}\ln \frac{N_{B}^{S}}{N_{A}^{S}}+\frac{1}{A_{B}}G_{i}^{E,S}(T,N_{i}^{S})-\frac{1}{A_{B}}G_{i}^{EB}(T,N_{i}^{B}) \]

\[
\tag{4}
\]

where

\[
D_{i}^{S}=\sum_{j}N_{j}^{S}d_{ij}^{S} \quad \text{and} \quad D_{i}^{B}=\sum_{j}N_{j}^{B}d_{ij}^{B}(i=A \text{ or } B)
\]

2.2. Excess Free Energy of the Surface

For the alkali-halide system, Lumsden\textsuperscript{8)} calculated the heat of mixing of binary alkali–halide mixtures, and the heat of mixing was found to be proportional to the potential energy of mixing due to the non-polar London force and the polarization energy. Provided that the excess Gibbs free energy is mainly determined by the electric field arising from the polarization which is generated by the different ions having the same or different charge sign, the excess free energy can be obtained by partial differentiation of the heat of mixing and have the following proportionality with ionic distances. According to Lumsden,\textsuperscript{5)}

\[
G_{i}^{EB}=RT \ln f_{i}=k(1-N_{i})^{2} \propto \alpha Z(1-N_{i})^{2}\left(\frac{z_{i}}{(d_{i}^{B})^{2}}-\frac{z_{j}}{(d_{i}^{S})^{2}}\right)^{2}
\]

\[
\tag{5}
\]

where $k$ is the proportionality factor, the polarizability, $Z$ coordination number, and $z_{i}$ valency of cation of $i$.

Therefore the excess Gibbs free energy of $i$ in the bulk phase can be expressed by Eq. (6).

\[
G_{i}^{EB}(T,N_{i}^{B}) \propto \alpha Z^{B}(1-N_{i}^{B})^{2}\left(\frac{z_{i}}{(d_{i}^{B})^{2}}-\frac{z_{j}}{(d_{j}^{B})^{2}}\right)^{2}
\]

\[
\tag{6}
\]

If the excess Gibbs free energy in the surface has the same function of temperature and compositions as that in the bulk, the excess Gibbs free energy of $i$ in the surface phase can be expressed in a similar way.\textsuperscript{8,10)}

\[
G_{i}^{EB}(T,N_{i}^{S}) \propto \alpha (Z^{S})^{2}(1-N_{i}^{S})^{2}\left(\frac{z_{i}}{(\xi_{i}^{B}d_{i}^{B})^{2}}-\frac{z_{j}}{(\xi_{j}^{B}d_{j}^{B})^{2}}\right)^{2}
\]

\[
\tag{7}
\]

where $(Z^{S})^{2}$ is the apparent coordination number in the surface under consideration of surface relaxation and $\zeta_{i}$ is the ratio of the ionic distance in the surface phase to that in the bulk phase ($\frac{Z_{i}}{d_{i}^{S}/d_{i}^{B}}$).

Suppose that $G_{i}^{EB}(T,N_{i}^{S})$ represents the excess free energy if the bulk concentration of B had a value of $N_{B}^{S}$. Then the ratio of $G_{i}^{EB}(T,N_{i}^{S})$ to $G_{i}^{EB}(T,N_{i}^{B})$ can be then expressed as follows:

\[
\frac{G_{i}^{EB}(T,N_{i}^{S})}{G_{i}^{EB}(T,N_{i}^{B})} = \beta \left(\frac{z_{i}}{(\xi_{i}^{B}d_{i}^{B})^{2}}-\frac{z_{j}}{(\xi_{j}^{B}d_{j}^{B})^{2}}\right)^{2}
\]

\[
\tag{8}
\]

where $\beta=(Z^{S})^{2}/Z^{B}$.

If the surface relaxation is not considered in the coordination number and ionic distance, the calculated results on the surface tension of molten ionic solutions including molten slags did not agree with the experimental values.\textsuperscript{1)} Therefore the surface relaxation structure as well as the coordination number should be considered in order to evaluate the surface tension of molten slag. This was pointed out by Tanaka et al. and almost the same relations in Eqs. (5)–(7) was applied to express the effect of the surface relaxation structure on the excess Gibbs energy in the surface.\textsuperscript{1,2)}

The ratio ($\beta$) has the relationship with the heat of evaporation and the surface tension for the pure substance $i$ as seen by Eq. (9).\textsuperscript{4)}

\[
\sigma_{i,j}=(-1-\beta)\Delta H_{i,j}
\]

\[
\tag{9}
\]

Tanaka et al.\textsuperscript{4)} found that $\beta_{i}$ is equal to 0.94 for the alkali–halides. In addition, the value of $\beta_{i}$ for a pure oxide was found from the relationship between heat of vaporization ($\Delta H_{i,v}$) and melting point ($T_{m}$) for the alkali-halides since the value of heat of evaporation is unknown for oxides.\textsuperscript{11)} The relationship between $\Delta H_{i,v}$ (1/mol) and $T_{m}$ is obtained from the regression analysis and the result is expressed as follows:

\[
T_{m}=5.02\times10^{-3}\Delta H_{i,v}
\]

\[
\tag{10}
\]

Substituting Eq. (10) into Eq. (9) gives

\[
\sigma_{i,j}=\frac{(1-\beta_{i})}{5.02\times10^{-3}}T_{m,j}
\]

\[
\tag{11}
\]

The ratio ($\beta_{i}$) of the coordination number in the surface to that in the bulk can be calculated from Eq. (11), and the results are listed in Table 1.

For the rock-salt structured alkali metal–halides mixture, the coordination number ratio ($\beta$) is independent of the component consisting of binary mixture because the coordination number is equal for all components. Contrary to most alkali metal–halides having a rock-salt structure,\textsuperscript{8)} the crystal structure of oxides differs from oxide to oxide. For example, CaO and MgO have a rock-salt structure, Al$_{2}$O$_{3}$ corundum structure, and a-$\alpha$-quartz (SiO$_{2}$) trigonal structure. In order to accommodate the fact that different oxides may have different crystal structures, the term $\beta$ may be modified in the form given in Eq. (12), assuming that the coordination number of oxide mixtures is affected by the crystal structure and the relative amount of each oxide.
Table 1. Surface tension, molar volume, ionic distance and ratio of coordination number in the surface to that in the bulk.

<table>
<thead>
<tr>
<th></th>
<th>Surface tension($\sigma_s$) (mN/m)</th>
<th>Molar volume($V_f$) (m$^3$/mol)</th>
<th>Ionic distance($d_s$) (Å)</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>645.2 – 0.097(T – 2873)</td>
<td>20.71[1+1×10$^{-3}$(T−1773)]×10$^{-4}$</td>
<td>2.40</td>
<td>0.9242</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>243.2 × 0.031[T]</td>
<td>27.51[1+1×10$^{-4}$(T−1773)]×10$^{-4}$</td>
<td>1.63</td>
<td>0.9396</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>721.2 – 0.078(T – 2313)</td>
<td>14.15[1+1×10$^{-7}$(T−1773)]×10$^{-4}$</td>
<td>1.93</td>
<td>0.9095</td>
</tr>
</tbody>
</table>

$$\sigma = \sigma_A + RT \ln \frac{D_A}{D_B} + \frac{1}{A_A} F_{A-B}^{A} \left( T, N_B^S \right)$$

$$= \sigma_B + RT \ln \frac{D_B}{D_A} + \frac{1}{A_B} F_{A-B}^{B} \left( T, N_B^S \right)$$

$$\beta = (\beta_N^S + \beta_N^B)$$ ...........................................(12)

Substituting Eqs. (8) and (12) into Eq. (4),

$$\frac{\sigma_A}{A_A} \ln \frac{D_A}{D_B} + \frac{1}{A_A} F_{A-B}^{A} \left( T, N_B^S \right)$$

$$= \frac{\sigma_B}{A_B} \ln \frac{D_B}{D_A} + \frac{1}{A_B} F_{A-B}^{B} \left( T, N_B^S \right)$$

$$= \frac{1}{A_B} \sum_{i,j} \zeta_{i,j} = \sum_{i,j} \left( \frac{z_i}{d_i} - \frac{z_j}{d_j} \right)^2$$

$$= \frac{1}{A_B} \sum_{i,j} \zeta_{i,j} = \sum_{i,j} \left( \frac{z_i}{d_i} - \frac{z_j}{d_j} \right)^2$$

where

$$F_{i,j} = (\beta_N^S + \beta_N^B) \left( \frac{z_i}{d_i} - \frac{z_j}{d_j} \right)^2$$

2.3. Surface Rumpling and Relaxation of Pure Oxide

Sawada et al. calculated the mean-square displacement of ions on the (001) surface of ionic crystals with a rock-salt structure, with particular reference to sodium halide crystals by extending the method of the self-consistent Einstein model, and they found that all sodium halides have nearly the same degree of rumpling, i.e. about 3 % contraction at the surface (\(\zeta=0.97\)). Tanaka et al. assumed that the value of 0.97 for \(\zeta\) also applied to the salts and ionic oxides. For oxides such as SiO$_2$, Al$_2$O$_3$, and CaO which are commonly encountered in metallurgical systems, however, care must be paid in evaluating the rumpling behavior of these oxides because the crystal structures of these oxides may not be the same as that of halides.

SiO$_2$ has various crystal structures, for example \(\alpha\)-cristobalite (tetragonal-P4$_2$), \(\beta\)-cristobalite (cubic-Fd3m), keatite (tetragonal-P4$_2$), \(\alpha\)-quartz (trigonal-P3$_2$), \(\beta\)-quartz (hexagonal-P6$_2$), coesite (P21/a), and stishovite (P4$_2$/mm). Therefore the bond length and the bond angles are different with crystal structure. Most data of bond length in the surface are obtained from the solid-state computer modeling. Koudriachova et al. investigated several possible reconstructions of the (001) \(\alpha\)-quartz surface by using a combinatorial approach of classical and \textit{ab initio} molecular dynamics. At high temperature, the reconstruction of \(\alpha\)-quartz (RQ3) was produced, where RQ3 represents a true ground state. This structure contains only 4-coordinated silicon atoms and 2-coordinated oxygens. The six-membered rings are rebuilt on the surface and the Si–O distance was found to be 1.59 Å on the surface. The Si–O distance in bulk was found to be 1.63×10$^{-10}$m. Therefore the \(\zeta_{SiO_2}\) is 0.9755, i.e. 2.45 % contraction.

Aluminum oxide crystallizes in the corundum structure. Along the (0001) direction, it is composed of hexagonal close-packed oxygen layers. The oxygen layers alternate with two metal layers, very close to each other, which contain metal atoms in octahedral environments. There have been numerous studies on the (001) surface of \(\alpha\)-Al$_2$O$_3$ single crystals. The surface of \(\alpha\)-Al$_2$O$_3$ is terminated with a single Al layer, which is in agreement with electrostatic considerations. Strong relaxations take place at the surface layer; and hence the interplanar spacings are shortened. However, the oxygen atoms in the second layer move laterally (bond length conservative motion), so the Al–O bond length is only 4.5–6.1 % contracted.

Then \(\zeta_{Al_2O_3}\) is about 0.947.

Study on the characterization of the corresponding CaO(100) surface is few. Alfonso et al. obtained the surface rumpling of CaO by \textit{ab initio} total-energy calculations. The cations move outward and the anions move inward from their bulk positions. Therefore the surface are rumpled by \(-0.6\sim1.0\%\) and then the interplanar spacing becomes to be lengthened by about 0.8 %. The Ca–O bond length can be assumed to be lengthened by 0.8 %. Then \(\zeta_{CaO}\) is about 1.008.

3. Application of the Model

The modified Butler’s equation, Eq. (4), enables the calculation of surface tension of liquid solutions to be possible, provided that various terms involved in the equation be known or obtainable. Sample calculations have been made for various binary combinations and a ternary one of CaO–SiO$_2$–Al$_2$O$_3$ oxide system. Physico-chemical data and parameters used in the calculation are listed in Table 1. The basic technique for the calculation was that

1) The surface concentration of each component is first
chosen arbitrarily for a given liquid solution.

2) The surface tension is calculated from each component’s point of view using Eq. (4).

3) The above procedure is repeated until surface tension values calculated from different components agree with each other.

Thermodynamic data for the calculation were obtained from the thermodynamic software, ChemSage®. In the calculation Eq. (13) was employed for the ratio of the coordination number ($b$). For the ratio of the ionic distance in the surface to that in the bulk, $z_i$, for each oxide, the value evaluated in the previous section was used.

3.1. CaO–SiO$_2$ System

Figure 1 shows the surface tension of the liquid CaO–SiO$_2$ system computed by the present study at 1 873 K, together with experimental results reported in the literature. It also includes results computed using models suggested by Tanaka et al. and by Nakajima. Considering the extent of scatter of the experimental data one can assume that all three models are in reasonably good agreement with the experimental results. It should be noted that in the approach of Tanaka et al. the ionic distances for all components was assumed identical. Nakajima used Prigogine’s equation given below to calculate the surface tension.

$$
\sigma = \sum_{i=1}^{n} \sigma_i N_i^B + \sum_{i=1}^{n} \sum_{j=i+1}^{n} W_{ij} N_i^B N_j^B
$$

$$
\frac{\partial \sigma}{\partial T} = \sum_{i=1}^{n} \left( \frac{\partial \sigma}{\partial T} \right)_p N_i^B
$$

where $W_{ij} = m \omega_{ij} / \rho_i$.

$m$: coordination number related parameter,

$\omega_{ij}$: mixing energy.

The parameter $W_{ij}$ was obtained by fitting experimental results reported by various investigators. In this regard Nakajima’s approach may be considered semi-empirical.

It is seen in Fig. 1 that the surface tension decreases with increasing the mole fraction of SiO$_2$.

The temperature coefficient of surface tension was also evaluated in the temperature range of 1 773 to 1 873 K and the results are given in Fig. 2. An increase of the temperature coefficient with increasing SiO$_2$ content is visible, but the extent of dependence on the composition is rather small. Nakajima’s result is not much different from the present one, and shows a similar increasing trend with increasing SiO$_2$. However, experimental data reported by several investigators given in Fig. 2 show a large disagreement with each other not only in the value of the coefficient, but also in the dependence on the composition. King reported that the temperature coefficient was very small and showed a slightly increasing trend with increasing the SiO$_2$ content. Mukai et al. showed that the temperature coefficient was very small and practically independent of the SiO$_2$ content and of the oxygen potential in the atmosphere. On the other hand, Ono et al. reported that under the inert atmosphere with Ar gas the temperature coefficient was positive and decreased with increasing SiO$_2$ content, but negative and increased with increasing SiO$_2$ content under the oxidizing atmosphere with O$_2$. Gunji et al. reported that the coefficient was negative and increased with increasing the SiO$_2$ content approaching zero at around 55 mol% of SiO$_2$. In summary, although the experimental data reported by various investigators are different from each other, the results computed based on the first principles in the present study can be considered to be representative of the experimental results.

3.2. CaO–Al$_2$O$_3$ System

Figure 3 shows the surface tension of CaO–Al$_2$O$_3$ system at 1 873 K. Included in the figure are experimental results reported in the literature and also results of three different modeling works. The result obtained by keeping the ionic distance at the surface ($\zeta$) constant at 0.97 for all oxides as some previous investigators did is seen to give a large disagreement with the experimental results—see the broken dashed line in Fig. 3. The result by Nakajima given with a dash-dotted line, appears to reasonably well represent the experimental results which exhibit a scatter. This
agreement may not be surprising because the Prigogine’s model that Nakajima employed for the calculation in fact utilized all these experimental data in finding the empirical parameter $W_{ij}$ see Eq. (14). The solid line in the figure is the result obtained from the method that is proposed in the present study. Considering that the calculation done in the present study was purely theoretical based only on the first principles, the agreement of the present calculation with the experimental data can be regarded remarkable. Experimental results of surface tension measured at 2 473 K by Elyutin et al.39) are also included in Fig. 3. It is of interest to notice that the dependence of the surface tension with composition shows a similar trend with that computed in the present study at 1 973 K in which the surface relaxation and rumpling was taken into consideration. The temperature coefficient of surface tension evaluated in the present study is given in Fig. 4, together with reported experimental data. It is seen that the agreement of the present prediction with the reported values is poor. It must be noted however that the compositional dependence of the temperature coefficient obtained in the present study at 1 873 K shows a quite similar trend with the experimental results at 2 473 K39) which cover a wide range of composition.

4. Surface Tension of Ternary Systems

4.1. Model Development

Modified Butler’s equation can be rewritten for a ternary $i$–$j$–$k$ system as follows:

$$
\sigma = \sigma_i + \frac{RT}{A_i} \ln \frac{D_j^S}{D_j^B} + \frac{1}{A_j} F_{i-j-k}^{E,B} \sigma_j (T, N_j^S, N_k^S) - \frac{1}{A_j} \sigma_j (T, N_j^B, N_k^B) \nonumber
$$

$$
= \sigma_i + \frac{RT}{A_j} \ln \frac{D_j^S}{D_j^B} + \frac{1}{A_j} F_{i-j-k}^{E,B} \sigma_j (T, N_j^S, N_k^S) - \frac{1}{A_j} \sigma_j (T, N_j^B, N_k^B) 
$$

where $F_{i-j-k}^E$ is the ternary pre-factor of $i$ in $i$–$j$–$k$ ternary system.

For calculation of the surface tension of a ternary system, evaluation of both ternary excess free energy in the bulk and the ternary pre-factor is required. For a ternary bulk the excess free energy can be determined by a usual thermodynamic approach. In the present study it is determined using ChemSage database. For the ternary surface, however, the pre-factor defined in Eq. (13) for binary systems must be expanded for a ternary system.

Consider an $i$–$j$–$k$ ternary system in which all the components have a same coordination number. Probabilities of $i$–$j$ and $i$–$k$ pairs can then be given by Eqs. (16) and (17), respectively:

$$
P_{ij} = \frac{N_i N_j}{N_i^S + N_j^S} \tag{16}
$$

$$
P_{ik} = \frac{N_i N_k}{N_i^S + N_k^S} \tag{17}
$$

where $P_{ij}$ and $P_{ik}$ are probabilities of $i$–$j$ and $i$–$k$ pairs in the $i$–$j$–$k$ ternary system.

The ternary pre-factor of $i$, $F_{i-j-k}^{E,B}$ may be assumed to be affected only by $i$–$j$ and $i$–$k$ pairs, not by $j$–$k$ pairs. Then probabilities of $i$–$j$ and $i$–$k$ pairs without taking consideration $j$–$k$ pairs into consideration, $P'_{ij}$ and $P'_{ik}$, respectively, can be given as follows:

$$
P_{ij}' = \frac{P_{ij}}{P_{ij} + P_{ik}} = \frac{N_j}{N_j + N_k} \tag{18}
$$
It is now assumed that the ternary pre-factor for component \( i \), \( F_{i-j-k} \), is a linear extension of the binary pre-factors, \( F_{i-j} \) and \( F_{i-k} \), but weighted by their respective pair probabilities:

\[
P_{i-j-k} = \frac{P_i}{P_j + P_k} = \frac{N_k}{N_j + N_k} \tag{19}
\]

\[
F_{i-j-k} = P_{i-j} F_{i-j} + P_{i-k} F_{i-k} = \frac{N_j^s}{N_j^s + N_k^s} F_{i-j} + \frac{N_k^s}{N_j^s + N_k^s} F_{i-k} \tag{20}
\]

Similar to the binary surface tension calculation, the surface tension for a ternary solution can be obtained by varying the surface contents, until three equations in Eq. (15) yield the same value of the surface tension.

### 4.2. Application to CaO–SiO₂–Al₂O₃ System

**Figure 5** shows the surface tension of CaO–SiO₂–Al₂O₃ ternary system at 1873 K, together with the experimental results reported in the literature. Various lines are the results computed using Eq. (15) for different CaO/SiO₂ ratios as indicated in the index of the figures. Thermodynamic information required for the computation was obtained from a thermodynamic software ChemSage. It is seen from the figure that the surface tension increases with increasing the Al₂O₃ content for a given CaO/SiO₂ ratio, and also increases with increasing CaO/SiO₂ ratio for a given Al₂O₃ content. The computed results are compared with the work of Gunji et al.\(^{27}\) in Fig. 5(a) and with the work of Mukai et al.\(^{28}\) in Fig. 5(b). It is seen that the reported values support the general trend of compositional dependence of the surface tension predicted in the present work. The prediction in the present work shows a good agreement with the work of Gunji et al.\(^{27}\) at high CaO/SiO₂ ratios, whereas it is in line with the work of Mukai et al.\(^{28}\) at low CaO/SiO₂ ratios. It should be noted that the surface tension values reported by these two works for the same system differ to a large extent.

**Figure 6** shows the effect of SiO₂ on the surface tension for a given CaO/Al₂O₃ ratio. Experimental results reported by various researchers are also superimposed in the figure.
It reveals that the surface tension decreases with increasing the SiO$_2$ content for a given CaO/Al$_2$O$_3$ ratio, and that the CaO/Al$_2$O$_3$ ratio hardly affects the surface tension. As for CaO/Al$_2$O$_3$ ratio of 1.8 the prediction in the present work shows an excellent agreement with the values reported by various researchers. For the case of CaO/Al$_2$O$_3$ ratio of 2.2, two sets of report are available in the literature, one by Smolyarenko et al. and the other by Evseev et al. and unfortunately they are vastly different from each other as seen in Fig. 6. It is noted that the present prediction is nicely located in the middle of these two. In addition, the present calculation results show a good agreement with the Nakajima’s results obtained by Prigogine’s model and the parameter ($W_{ij}$) obtained by fitting the previously reported experimental results.

Figure 7 shows the effect of Al$_2$O$_3$ on the surface tension for a given CaO content. It is seen that the surface tension increases with increasing Al$_2$O$_3$ content and that CaO addition increases the surface tension for a given Al$_2$O$_3$ content. Nakajima’s work and the experimental data reported in the literature, which are superimposed in the figure, show a good agreement with the present prediction.

Using the model represented by Eq. (15) the surface tension of liquid CaO–SiO$_2$–Al$_2$O$_3$ system was computed for various compositions, and the results are given in Fig. 8. In Fig. 9 the prediction in the present work is compared in the form of iso-surface tension lines with those reported in the literature. As seen in the previous discussions, disagreement to some extents that exists among experimental results is understandable. However, the present prediction shows a slightly different result on the effect of Al$_2$O$_3$ from those experimental data: the present work shows the surface tension being roughly independent of CaO/Al$_2$O$_3$ for a given SiO$_2$ content, whereas those reported by Gunji et al. and Mukai et al. shows decrease in the surface tension with increasing Al$_2$O$_3$ for a given SiO$_2$ content. This disagreement in the trend warrants further work.

In summary, it can be considered that the prediction in the present work is well representative of the surface tension of the CaO–SiO$_2$–Al$_2$O$_3$ ternary system, especially if taking into account the fact that there are large inherent experimental uncertainties and disagreement of the reported values of the surface tension among investigators.

5. Conclusion

The surface tension of CaO–SiO$_2$–Al$_2$O$_3$ system at 1 873 K was computed using a modified Butler’s equation. The computed results were critically compared with experimental results reported in the literature. For CaO–SiO$_2$ and CaO–Al$_2$O$_3$ binary systems, the present prediction is in good agreement with the experimental results reported by other researchers. For CaO–SiO$_2$–Al$_2$O$_3$ ternary system, the surface tension in a wide range of liquid compositional range was computed and the results were favorably compared with the experimental results reported in the litera-
ture. It was found that the surface tension increases with decreasing SiO$_2$, and with increasing CaO or Al$_2$O$_3$. For a given SiO$_2$ content, the surface tension was relatively independent of the CaO/Al$_2$O$_3$ ratio. An iso-surface tension diagram has been suggested for liquid CaO–SiO$_2$–Al$_2$O$_3$ solutions.

REFERENCES