

A Model Description of the Thermochemical and Thermophysical Properties of Multicomponent Slags

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ABSTRACT

The modelling of Metallurgical processes require an understanding of the fundamental properties of slags. A knowledge of the thermodynamic properties of slags is imperative for optimal operations in different Metallurgical processes.

A mathematical model has been developed with the aim to predict the thermodynamical properties of the liquid phase in multicomponent slag systems using only the experimental information from the corresponding binary subsystems. The model uses Temkins description of the entropy of ionic melts coupled with Lumsden's description of silicate and aluminate melts, where the ionic melts are considered as an oxygen-ion matrix with the cations including Si^{4+} distributed in it. To enable this type of representation, a hypothetical standard state for silica has been adopted, wherein the SiO_2 network is completely dissociated into Si^{4+} and O^{2-} ions. Only the next nearest neighbour interaction between different cations in the presence of oxygen ions are considered in description of the solution thermodynamics. The excess Gibbs energies are described by means of Redlich-Klister polynomials.

In the case of multicomponent systems containing Al_2O_3 , CaO , FeO , MgO , MnO and SiO_2 , the agreement between the model prediction and the experimental values has been found, in general, satisfactory within the limits of experimental uncertainties. With a similar structure, the slag viscosities has also been successfully modelled for six component slags.

The model description is also used in linking thermodynamic information with slag viscosities. The viscosities of ternary silicates have been predicted from binary viscosities using thermodynamic data.

1. Introduction

Although great efforts have been put forward all over the world to determine the thermodynamic properties of slags, researchers and engineers very often find that there are still too few data available for the slag systems of interest to the industry. The industrial slags are always multicomponent in nature and in most of industrial practices, slag compositions vary with time. The need for thermodynamic models to describe the equilibrium conditions in oxide melts has been magnified during the last years when the demand for cleaner steel and better process control has increased. Models that have the ability to describe the thermodynamics of ternary and multicomponent systems using experimental information from the ingoing binary sub systems are of particular importance.

Thermodynamic models of molten silica containing slags could be classified into two major groups, namely structure-based models [1-3] and empirical or semi empirical models [4-9]. It is well known that all Si atoms are tetrahedrally bonded to four oxygen atoms in a silicate melt. As the concentration of SiO_2 increases, the SiO_4^{4-} tetrahedra start to join together forming dimers $\text{Si}_2\text{O}_7^{6-}$, trimers $\text{Si}_3\text{O}_{10}^{8-}$, cyclic polymers and even three dimensional network of bridged silicate tetrahedra. While the structure based models, as for example, the pioneering work by Masson [1] may provide an insight into the relationship between the thermodynamic properties and the slag structures, the lack of structural information of the silicate melts has greatly hindered the progressing of this kind of approaches. On the other hand, empirical or semi empirical models based on experimental data have more extensively been used in practice. The ionic two-sub-lattice model developed by Hillert et al [4] and the IRSID model developed by Gaye et al [5] are, to some extent, in line with this consideration. However, difficulties are encountered in the choice of the suitable species and estimating their abundance[10]. An alternative approach is to consider a silicate melt as a matrix of oxygen ions with different cations including Si^{4+} distributed in it. This approach was originally proposed by Lumsden [6]. By combining the approaches of Temkin [11], Lumsden [6] and Hillert et al [4], a thermodynamic model for ionised melts has been develop in the present laboratory [12-17].

The aim with the present model is to describe the oxide activities in multicomponent slag systems using solely the experimental information from the corresponding binary subsystems. Successful model predictions have been made in several ternary systems [13-16] using solely the experimental information from the corresponding binary subsystems.

The application of the model was later extended to multicomponent melts including six oxide components, Al_2O_3 , CaO , FeO , MgO , MnO and SiO_2 [17]. Experimental data are available in literature for the systems CaO-FeO-MgO-SiO_2 , $\text{Al}_2\text{O}_3\text{-CaO-MgO-SiO}_2$, $\text{Al}_2\text{O}_3\text{-FeO-MnO-SiO}_2$ and $\text{Al}_2\text{O}_3\text{-CaO-FeO-MgO-MnO-SiO}_2$ systems, model calculations for these systems have been carried out in order to examine the validity of the model calculations. To exemplify the results of the comparison between experimental values and the results from model calculations only the results from the $\text{Al}_2\text{O}_3\text{-CaO-MgO-SiO}_2$ and $\text{Al}_2\text{O}_3\text{-CaO-FeO-MgO-MnO-SiO}_2$ systems are presented. Detailed description of the results for all of the the multicomponent systems can be found in the earlier publication [17]. Examples of model predications for some typical slag

compositions, relevant to the Swedish steel industry, used in the blast furnace (BF), electric arc furnace (EAF) and ladle furnace (LF) are also presented.

The viscosities of ionic melts depend on the movements of ionic species, which, in turn, are determined by the bonding as well as the configuration in the liquid. Dependency on the interionic bond strengths (enthalpy factor) and the distribution of the ions in the melt (entropy factor) can also be found with the thermodynamic properties such as the molar Gibbs energy and molar volume (density) of a liquid. While the two kinds of dependencies could be quite different, natural correlation between the two could still be expected. This has been evidently demonstrated in the case of substitutional metallic melts [18,19]. The present approach is to establish this link so that viscosities in a binary silicate system of the type MO-YO-SiO₂ can be estimated from the viscosities of the corresponding silicates MO-SiO₂ and YO-SiO₂ using the thermodynamic Gibbs energy of mixing [20]. For this purpose, the thermodynamic model developed in the present laboratory was used. The good agreement observed between the calculated viscosities and the experimental data in the CaO-FeO-SiO₂, CaO-MgO-SiO₂, CaO-MnO-SiO₂ and FeO-MnO-SiO₂, ternary silicate systems indicates that this approach can be successfully to predict the viscosities of ternary silicate melts [20].

2. Model description

According to this model, an oxide melt is considered to consist of a matrix of oxygen ions with various cations distributed in it. The presence of basic cations such as Ca²⁺, Fe²⁺, Mg²⁺ and Mn²⁺ along with Si⁴⁺ will distort the oxygen matrix and determine the configuration of the ionic melt and the bond energies between different ions. The configuration of the ions and the bond energies will be functions of composition and temperature. By picturing the oxide melts in this manner, the difficulties in choosing the anionic species and the fractions of the same are avoided. While there are mutual effects between the cations and oxygen ions, the thermodynamic properties of the solution can be formulated by the consideration of the next nearest neighbour interactions, namely the interactions between the cations when oxygen ions are present. In a system containing *m* different oxides, C₁O_{a1}, C₂O_{a2}, ..., C_iO_{ai}, ..., C_mO_{am}, the cations can be grouped together:

$$(C_1^{v_1}, C_2^{v_2}, \dots, C_i^{v_i}, \dots, C_m^{v_m})_p (O^{2-})_q \quad (1)$$

where C^{vi} stands for cations, the superscript *vi* denotes the electrical charge. Even Si⁴⁺ ion is included in the cation group. *p* and *q* in equation (1) are stoichiometric coefficients and can be calculated by the following equations:

$$p = \sum_{i=1 \text{ to } m} X_{C_i O_{a_i}} \cdot c_i \quad (2)$$

$$q = \sum_{i=1 \text{ to } m} X_{C_i O_{a_i}} \cdot a_i \quad (3)$$

where $X_{C_i O_{a_i}}$ is the mole fraction of the oxide C_iO_{ai}. Following the line of the above consideration, the thermodynamic properties of mixing can be formulated as functions of the interactions between different cations in the presence of O²⁻. It is logical to use ionic fractions to

describe the composition of a melt. The ionic fraction of cation y_i within the cation grouping is defined as:

$$y_{Ci} = \frac{N_{Ci}}{\sum_{j=1 \text{ to } m} N_{Cj}} \quad (4)$$

where N_i is the number of cation Ci^{vi} and the summation covers all the cations including Si^{4+} . The integral Gibbs energy of a solution can be expressed as:

$$G^m = \sum X_{Ci_{ci}O_{ai}} G_{Ci_{ci}O_{ai}}^o + RTp \sum (y_{Ci} \ln y_{Ci}) + G^E \quad (5)$$

where $G_{Ci_{ci}O_{ai}}^o$ represents the standard Gibbs energy of oxide $Ci_{ci}O_{ai}$. R stands for the gas constant and T is the temperature in Kelvin. As only oxygen ions occur in the anionic group, the second term that corresponds to Temkin's expression [11] for ideal entropy of mixing, consists of only the contribution from the cation group. G^E in equation (5) stands for the excess Gibbs energy of mixing due to the interactions between different cations in the presence of oxygen ions.

The present description of silicate melts necessitates the assumption that the silicate network is completely dissociated into Si^{4+} and O^{2-} ions and even any aluminate complex to Al^{3+} and O^{2-} ions. In the case of silicates, the complete dissociation of the network to individual ions requires the introduction of a hypothetical standard state from the three dimensional network to totally dissociated Si^{4+} and O^{2-} ions. The Gibbs energy change for the standard state change from pure SiO_2 (network) to ionic SiO_2 (consisting Si^{4+} and O^{2-}) has been evaluated by Lumsden [6]. Based on the silica saturated liquidus in the $FeO-SiO_2$ system, he deduced the Gibbs energy change for the fusion of silica:

$$SiO_2(solid) = SiO_2(\text{liquid consisting of } Si^{4+} \text{ and } O^{2-}) \quad (6)$$

$$\Delta G_6 = 35600 - 7.53T \quad (\text{J/mole}) \quad (7)$$

A calculation based on the activities of FeO in the $FeO-SiO_2$ system was made to estimate the Gibbs energy change for reaction (6). A value of 22000 J/mole was obtained for ΔG_6 in the temperature range of 1533-1673K [13]. Comparison of this value with the value according to equation (7) in the same temperature range shows very good agreement. The choice of the $FeO-SiO_2$ binary for the evaluation is due to the consideration that this system has been studied most extensively and the agreement between the experimental data reported by different research groups is very good. Moreover, the liquid phase has very wide composition range, which is necessary for reliable calculation. However, no attempt was made to evaluate ΔG_6 as a function of temperature, since the activity of FeO does not show very strong temperature dependence in the $FeO-SiO_2$ system. Instead, equation (7) was adopted.

The excess Gibbs energy term, G^E is expressed as function of both temperature and composition:

$$G^E = f(T, y_{\text{Si}^{4+}}) + \sum_{i=1 \text{ to } m-1} \left(\sum_{j=i+1 \text{ to } m} y_{\text{Ci}} y_{\text{Cj}} \Omega^{\text{Ci,Cj}(O)} \right) \quad (8)$$

$\Omega^{\text{Ci,Cj}(O)}$ in equation (8) represents the interaction between cations Ci^{vi} and Cj^{vj} when O^{2-} ions are present. This interaction is described by Redlich-Klister polynomials as a function of temperature and composition:

$$\begin{aligned} \Omega^{\text{Ci,Cj}(O)} = & \Omega_1^{\text{Ci,Cj}(O)} + \Omega_2^{\text{Ci,Cj}(O)} T + \left(\Omega_3^{\text{Ci,Cj}(O)} + \Omega_4^{\text{Ci,Cj}(O)} T \right) (y_{\text{Ci}} - y_{\text{Cj}}) + \\ & \left(\Omega_5^{\text{Ci,Cj}(O)} + \Omega_6^{\text{Ci,Cj}(O)} T \right) (y_{\text{Ci}} - y_{\text{Cj}})^2 + \dots \end{aligned} \quad (9)$$

The function, $f(T, y_{\text{Si}^{4+}})$ in equation (8) is introduced in order to compensate for the fact that the excess Gibbs energy is not zero when the composition of the melt is approaching pure silica; but does not really correspond to pure SiO_2 for which the hypothetical standard state for silica is adopted. The term $f(T, y_{\text{Si}^{4+}})$ would be expected to have strong dependence on the composition in the liquids of high silica content but to a less extent in the liquids of low silica content. Even in the composition range with about 55 mass pct silica, the composition dependence of $f(T, y_{\text{Si}^{4+}})$ might still be considerable. The dependence of this function on composition would only be negligible when the silica content is lower than the orthosilicate composition ($y_{\text{Si}^{4+}} = \frac{1}{3}$). Below this silica content, the silicate network would almost be broken down completely into SiO_4^{4-} tetrahedra, so that $f(T, y_{\text{Si}^{4+}})$ could be treated as constant. Hence, this function is assumed arbitrarily as zero when $y_{\text{Si}^{4+}} \leq \frac{1}{3}$. On the basis of the experimental information of a number of binary silicate systems including the Al_2O_3 - SiO_2 , the following expression was found to provide a good description for the function $f(T, y_{\text{Si}^{4+}})$,

$$f(T, y_{\text{Si}^{4+}}) = 0, \quad \text{with} \quad y_{\text{Si}^{4+}} \leq \frac{1}{3} \quad (10a)$$

and

$$f(T, y_{\text{Si}^{4+}}) = A \cdot (y_{\text{Si}}^* - y_{\text{Si}})^3 \quad \text{with} \quad y_{\text{Si}^{4+}} \geq \frac{1}{3} \quad (10b)$$

where

$$y_{\text{Si}}^* = \frac{1}{3} \quad (11)$$

and

$$A = \frac{\Delta G_6}{(y_{\text{Si}}^* - 1)^3} \quad (12)$$

The activity coefficient of $\text{Ci}_{\text{ci}}\text{O}_{\text{ai}}$, according to Temkin's theory [11], is related to the activity coefficient of the corresponding cation, C_{Ci} , which in turn, can be expressed by the partial excess Gibbs energy of the same species:

$$\gamma_{\text{Ci}_{ci} \text{O}_{ai}} = \gamma_{\text{Ci}}^{ci} \cdot \gamma_{\text{O}}^{ai} = \gamma_{\text{Ci}}^{ci} = \exp \left[\frac{G_{\text{Civi}+}^E}{RT} \right] \quad (13)$$

The present approach is very similar to that suggested by Hillert et al in his thermodynamic representation [4]. It is noted that only binary interaction terms are present in the excess Gibbs energy of mixing, since the model aims at the prediction of thermodynamic properties of high-order systems using solely the information of binary systems. The interaction term $\Omega_{ij}^{(O)}$ can be evaluated using the experimental data for activities in the $\text{Ci}_{ci}\text{O}_{ai}$ - $\text{Cj}_{cj}\text{O}_{aj}$ binary system. In other words, the binary interaction parameters in equation (9) can be optimised using available experimental information. The choice of the Ω parameters in the use of equation (9) would depend on the system studied. In general, the first three to four parameters are sufficient to provide good model calculations for a binary system.

3. Model predictions for higher order systems

Only limited thermodynamic data can be found in the literature for multicomponent silicate systems presumably due to the experimental difficulties associated with the measurements. As a literature survey revealed that the experimental data regarding the oxide activities were available for the systems CaO-FeO-MgO-SiO_2 , $\text{Al}_2\text{O}_3\text{-CaO-MgO-SiO}_2$, $\text{Al}_2\text{O}_3\text{-FeO-MnO-SiO}_2$ and $\text{Al}_2\text{O}_3\text{-CaO-FeO-MgO-MnO-SiO}_2$, model calculations were carried out in these systems in order to examine the reliability of the model in predicting the activities in higher order systems. In this paper, as already mentioned only the $\text{Al}_2\text{O}_3\text{-CaO-MgO-SiO}_2$ and $\text{Al}_2\text{O}_3\text{-CaO-FeO-MgO-MnO-SiO}_2$ systems will be discussed. A detailed description of the model calculations for ternary as well as for multicomponent systems can be found in the earlier publications [13-17]. The binary interaction parameters used in the model calculations are listed in Table I.

Rein and Chipman [21,22] investigated the SiO_2 activities in the $\text{Al}_2\text{O}_3\text{-CaO-MgO-SiO}_2$ system for the 10 mass pct MgO, 20 mass pct MgO and 30 mass pct MgO planes at 1873 K by equilibrating slags with liquid Fe-Si-C alloys in graphite or SiC crucibles. The iso-activity contours of SiO_2 were constructed by the authors based on the measurements of four compositions in each plane. Their results are reproduced in Figures 1a-c for the planes of 10 mass pct MgO, 20 mass pct MgO and 30 mass pct MgO, respectively. The compositions of the experimentally studied slags are also presented in these figures. Unfortunately, raw data for the activities of these slags were not provided in the original publications [21,22]. The calculated iso-activity lines using the present model are incorporated in these figures for comparison.

The calculated activities of silica in the regions close to the experimental points agree very well with the results of Rein and Chipman [21,22]. It is only in the regions away from the experimental compositions that the model predictions show deviation from the suggested activity contours. It should be admitted that the uncertainties possibly involved with the $\text{Ca}^{2+}\text{-Mg}^{2+}$ interaction parameters, obtained from the ternary CaO-MgO-SiO_2 system [17], might introduce some uncertainties in the model predictions, especially at higher MgO contents.

Kalyanram et al [23] studied the CaO activities at 1773 K in the Al_2O_3 -CaO-MgO-SiO₂ system using the equilibrium between gas containing SO₂ and slag sample. A comparison between the experimentally obtained and calculated CaO activities at constant MgO content (mass pct MgO=10) is presented in Figure 2. Considering the extremely low activity values, the agreement between the values predicted by the model and the experimental results can be considered reasonable.

Ohita and Suito [24,25] as well as Seo and Suito [26] investigated the Al_2O_3 , FeO, MnO and SiO₂ activities in the Al_2O_3 -CaO-FeO-MgO-MnO-SiO₂ system with low concentrations of both FeO and MnO (below 2 mass pct). Slag-metal equilibration technique was employed. The experiments were conducted in either CaO or MgO crucibles at 1873 K. Figure 3a-b present the comparisons between the calculated and experimental activities of alumina and silica respectively at 1873 K for the plane with 20 mass pct Al_2O_3 in the pseudo quaternary Al_2O_3 -CaO-MgO-SiO₂ system. Similar comparisons for the plane with 40 mass pct Al_2O_3 are presented in Figures 4a-b. It should be mentioned that in view of the small amounts of FeO (0.07 to 1.2 mass pct) and MnO (0.2 to 1.9 mass pct) present in these slags, for the sake of convenience, the contents of FeO and MnO were neglected in the comparisons of silica and alumina activities.

It is seen in these figures that the scatter in the results of these experimental studies [24-26] is considerable. In general, the calculated results agree with the experimental data within the uncertainty limits. However, the calculated alumina activities in the plane of 20 mass pct Al_2O_3 , Figure 3a, are lower than the experimental values.

Comparisons between experimentally reported and predicted activities of FeO and MnO are presented in Figures 5a-b, respectively. The error bars associated with the experimental data, which were reported by Ohita and Suito [25] are also included in the same figures.

As shown by the error bars, the experimental uncertainties are, in many cases larger than the activity values themselves. While the calculated FeO activities generally agree with the experimental data within the uncertainty limits, there is no clear trend in the case of MnO activities. However, both model predictions and experimental results indicate that the manganese oxide activities in the slags are all below 0.025.

4. Application of the thermodynamic model for the estimation of slag viscosities

Thermodynamic properties of a liquid slag represent the bonding characteristics of the melt, which, in turn, depend on the interactions of different species. On other hand, viscous movement in an ionic melts is also dependent on the interionic bonding in the liquid phase. Seetharaman and Du Sichen [18,19] have proposed a correlation to estimate the viscosities of binary substitutional liquid alloys using the Gibbs energy of mixing. Their approach has further been extended to the ternary silicate melts having two basic oxides, MO and YO [20].

Richardson [27] suggested that a ternary silicate solution having two basic oxides, MO and YO could be considered as a solution of two silicates of equal metal oxide to silica ratio, viz. $z\text{MO}\cdot\text{SiO}_2$ and $z\text{YO}\cdot\text{SiO}_2$. Only the next-nearest-neighbour interactions between M^{2+} and Y^{2+}

would be important in this approach. In line with this approach, Seetharaman et al [20] proposed the build up of the Gibbs activation energy surface for the viscosities of $z\text{MO} \cdot \text{SiO}_2$ and $z\text{YO} \cdot \text{SiO}_2$ mixtures, which is reproduced in Figure 6.

Based on Figure 6, the following expression to calculate the Gibbs energy of viscous flow in a ternary silicate system MO-YO-SiO_2 at constant mole fraction of silica was suggested:

$$\Delta G^* = U_{\text{MO}} \cdot \Delta G_{z\text{MO-SiO}_2}^* + U_{\text{YO}} \cdot \Delta G_{z\text{YO-SiO}_2}^* + \Delta^E G^* \quad (14)$$

where U_{MO} and U_{YO} are defined as

$$U_{\text{MO}} = \frac{x_{\text{MO}}}{x_{\text{MO}} + x_{\text{YO}}} \quad (15a)$$

and

$$U_{\text{YO}} = \frac{x_{\text{YO}}}{x_{\text{MO}} + x_{\text{YO}}} \quad (15b)$$

The terms $\Delta G_{z\text{MO-SiO}_2}^*$ and $\Delta G_{z\text{YO-SiO}_2}^*$ in equation (14) represent the Gibbs activation energies in the binary MO-SiO_2 and YO-SiO_2 systems respectively at a constant mole fraction of silica. The term $\Delta^E G^*$ in equation (14) stands for the deviation of the Gibbs activation energy from linearity. On the basis of examination of a number of ternary silicate systems, namely CaO-FeO-SiO_2 , CaO-MgO-SiO_2 , CaO-MnO-SiO_2 and FeO-MnO-SiO_2 , Seetharaman et al [20] suggested that this term could be related to the Gibbs energy of mixing, ΔG^E by the expression:

$$\Delta^E G^* = 3 \cdot x_{\text{MO}} \cdot x_{\text{YO}} \cdot (1 - x_{\text{SiO}_2}) \cdot \Delta G^E \quad (28)$$

The application of the proposed correlation to the liquid slags in the systems, FeO-MnO-SiO_2 , FeO-MgO-SiO_2 , CaO-FeO-SiO_2 , CaO-MnO-SiO_2 and CaO-MgO-SiO_2 has shown very promising results [20]. Figure 7 presents the comparison of the estimated iso-viscosity contours with the experimental data for the system CaO-FeO-SiO_2 [20].

5. Discussion

The difference between the use of equation (1) and the formulation of silicate melts using complex anionic species, like SiO_4^{4-} , is a simplified only the way of looking at the nature of the ionic solutions. The model based on equation (1) pictures an ionic solution as an oxygen anion matrix with different cations including Si^{4+} distributed in it. The occurrence and the fractions of the complex ions SiO_4^{4-} , $\text{Si}_2\text{O}_7^{6-}$, $\text{Si}_3\text{O}_{10}^{8-}$, cyclic polymers and even three dimensional network of bridged silicate tetrahedra will of course determine the oxygen matrix and the distribution of the cations. However, the experimental information is far from sufficiency to support model calculations for the fractions of the polymers in multicomponent melts. The present approach avoids the difficulties in attributing the effect of mixing to two unknown factors, namely the

nature and fractions of the polymers as well as the interactions between them. Instead, only the interactions between different cations in the presence of O^{2-} are considered. The fractions of the cations can easily be calculated from the mole fractions of the component oxides. Since the next-nearest neighbour interactions are considered as functions of composition, the structural factors of the ionic liquid are included in the interactions mathematically.

The good agreement between the results of model calculation and the experimental data in the binary systems indicates the reliability of the model in extrapolating and interpolating experimental data in the case of both silicate and alumina-containing systems. The comparison of the model predictions with the experimental data in the case of ternary and multicomponent systems further shows that the model can well be applied to predict the oxide activities of multicomponent slags with reasonable uncertainty limits [13-17].

Using the model, the oxide activities of different iron-making and steel-making slags could be predicted. The slag compositions for different industrial processes differ greatly. In Table II, some typical slag compositions, relevant to the Swedish steel industry, used in the blast furnace (BF), electric arc furnace (EAF) and ladle furnace (LF) are presented. As an example of the model calculations, the effect of the replacement of SiO_2 by CaO on the activities of alumina in the case of BF, EAF and LF slags is illustrated in Figure 8. In the calculation for each type of slag, the contents of the other components given in Table II were kept constant.

It is seen in Figure 8 that the activity of alumina is lower in EAF slag than in BF slag at the same mass pct CaO /mass pct SiO_2 ratio. It is also seen that an increase of the mass pct CaO /mass pct SiO_2 ratio leads to a considerable decrease of the alumina activity, irrespective of the type of the slag. However, the decrease in alumina activity with the increasing mass pct CaO /mass pct SiO_2 ratio is more profound in the case of BF and EAF slags. Thus the model calculations would provide the researchers and the engineers a useful tool for gaining an insight into the processes. For example, in the case of LF slags, the increase of the ratio (mass pct CaO /mass pct SiO_2) from 4 to 7 would decrease the alumina activity from about 0.08 to about 0.03. This decrease would be beneficial for deoxidation process. Further increase of the ratio (mass pct CaO /mass pct SiO_2) would have less effect on the decrease the alumina activity.

6. Summary

In the present work, a mathematical model has been developed to predict thermodynamic properties in multicomponent slag systems. The model pictures oxide melts including silicate solutions as an O^{2-} matrix with different cations distributed in it. It avoids the difficulties in choosing the complex ionic species and the evaluation of their fractions. Only the next nearest neighbour interactions, viz. the interactions between different cations in the presence of oxygen are considered to be important in the solutions thermodynamics. The model has the ability to describe high order systems using solely experimental information from the corresponding binary subsystems. Thermodynamic calculations have been performed for molten slags in a number of multicomponent systems containing Al_2O_3 , CaO , FeO , MgO , MnO and SiO_2 . The predicted oxide activities have been compared with the available literature experimental data. In general, the model predications have been found satisfactory when compared with the

experimental values. However, the calculated activities differed somewhat from the reported values in some cases. Either the uncertainties involved in the experiments or the uncertainties associated with some of the model parameters obtained from inadequate experimental information or even both may be the reason for the disagreement. Examples of model predications for some typical slag compositions, relevant to the Swedish steel industry, used in the blast furnace (BF), electric arc furnace (EAF) and ladle furnace (LF) have been presented.

The applicability of the model in estimating the viscosities of ternary silicate melts from the binaries using the thermodynamic information of the ternary melt has been demonstrated. The model is expected to be a powerful tool in the modelling of metallurgical processes.

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Tables

Table I

Binary interactions variables used in the model calculations.

Variable	Expression
$\Omega^{AlCa(O)}$	$-125997 + 6594.66 \cdot (y_{Al} - y_{Ca}) - 44390 \cdot (y_{Al} - y_{Ca})^2$
$\Omega^{AlFe(O)}$	$-8049.18 - 18775.2 \cdot (y_{Al} - y_{Fe})$
$\Omega^{AlMg(O)}$	$-7049.76 - 4.30 \cdot T - 30313.22 \cdot (y_{Al} - y_{Mg})$
$\Omega^{AlMn(O)}$	$-22165.1 - 13054.5 \cdot (y_{Al} - y_{Mn}) + 13408 \cdot (y_{Al} - y_{Mn})^2$
$\Omega^{AlSi(O)}$	$-10256.9 + 27248.2 \cdot (y_{Al} - y_{Si}) - 10811.9 \cdot (y_{Al} - y_{Si})^2$
$\Omega^{CaFe(O)}$	$-45175.2 + 10819 \cdot (y_{Ca} - y_{Mn}) + 5804.6 \cdot (y_{Ca} - y_{Mn})^2$
$\Omega^{CaMg(O)}$	-80961.3
$\Omega^{CaMn(O)}$	$-45175.2 + 10819 \cdot (y_{Ca} - y_{Mn}) + 5804.6 \cdot (y_{Ca} - y_{Mn})^2$
$\Omega^{CaSi(O)}$	$-42988.5 - 113.356 \cdot T + (-414694 + 145.133 \cdot T) \cdot (y_{Ca} - y_{Si})$ $-37739 \cdot (y_{Ca} - y_{Si})^2$
$\Omega^{FeMg(O)}$	$-45175.2 + 10819 \cdot (y_{Fe} - y_{Mg}) + 5804.6 \cdot (y_{Fe} - y_{Mg})^2$
$\Omega^{FeMn(O)}$	0
$\Omega^{FeSi(O)}$	$-17609.3 - 30373.2 \cdot (y_{Fe} - y_{Si}) + 36090.7 \cdot (y_{Fe} - y_{Si})^2$
$\Omega^{MgMn(O)}$	0
$\Omega^{MgSi(O)}$	$-126521 - 79099.6 \cdot (y_{Mg} - y_{Si}) - 28086.2 \cdot (y_{Mg} - y_{Si})^2$
$\Omega^{MnSi(O)}$	$-89638.2 + 10.574 \cdot T - 35278.3 \cdot (y_{Mn} - y_{Si}) +$ $+ 43013.3 \cdot (y_{Mn} - y_{Si})^2$

Table II

Some typical slag compositions of the blast furnace (BF), electric arc furnace (EAF) and ladle furnace (LF) processes used in Sweden.

Compositions in mass pct			
Oxide	BF	EAF	LF
Al ₂ O ₃	13	10	33.5
CaO	32	40	53.5
FeO	2	15	0.6
MgO	17	9	6
MnO	2	5	0.4
SiO ₂	34	21	6

Figure captions

- Figure 1a. Comparison between iso-activity lines of SiO_2 suggested by Rein and Chipman [21,22] and calculated by the present model at 1873 K in the Al_2O_3 -CaO-MgO- SiO_2 system in the 10 mass pct MgO plane.
- Figure 1b. Comparison between iso-activity lines of SiO_2 suggested by Rein and Chipman [21,22] and calculated by the present model at 1873 K in the Al_2O_3 -CaO-MgO- SiO_2 system in the 20 mass pct MgO plane.
- Figure 1c. Comparison between iso-activity lines of SiO_2 suggested by Rein and Chipman [21,22] and calculated by the present model at 1873 K in the Al_2O_3 -CaO-MgO- SiO_2 system in the 30 mass pct MgO plane.
- Figure 2. Calculated iso-activity lines of CaO by the present model and experimental [23] values at 1773 K in the Al_2O_3 -CaO-MgO- SiO_2 system in the 10 mass pct MgO plane.
- Figure 3a. Calculated iso-activity lines of Al_2O_3 by the present model and experimental [24-26] values at 1873 K in the pseudo quaternary Al_2O_3 -CaO-MgO- SiO_2 system for the 20 mass pct Al_2O_3 plane.
- Figure 3b. Calculated iso-activity lines of SiO_2 by the present model and experimental [24-26] values at 1873 K in the pseudo quaternary Al_2O_3 -CaO-MgO- SiO_2 system for the 20 mass pct Al_2O_3 plane.
- Figure 4a. Calculated iso-activity lines of Al_2O_3 by the present model and experimental [24-26] values at 1873 K in the pseudo quaternary Al_2O_3 -CaO-MgO- SiO_2 system for the 40 mass pct Al_2O_3 plane.
- Figure 4b. Calculated iso-activity lines of SiO_2 by the present model and experimental [24-26] values at 1873 K in the pseudo quaternary Al_2O_3 -CaO-MgO- SiO_2 system for the 40 mass pct Al_2O_3 plane.
- Figure 5a. Comparison between calculated and experimentally [24,25] obtained FeO activities in the Al_2O_3 -FeO-MgO-MnO- SiO_2 system.
- Figure 5b. Comparison between calculated and experimentally [24,25] obtained MnO activities in the Al_2O_3 -FeO-MgO-MnO- SiO_2 system.
- Figure 6. Gibbs activation energy surface for the viscosities of MO-YO- SiO_2 mixtures [20].
- Figure 7. Comparison between the estimated iso-viscosity contours with the experimental data at 1723K in the CaO-FeO- SiO_2 system [20].
- Figure 8. The activities of Al_2O_3 for some typical slag compositions in BF, EAF and LF slags as a functions of the ratio mass pct CaO/ mass pct SiO_2 .

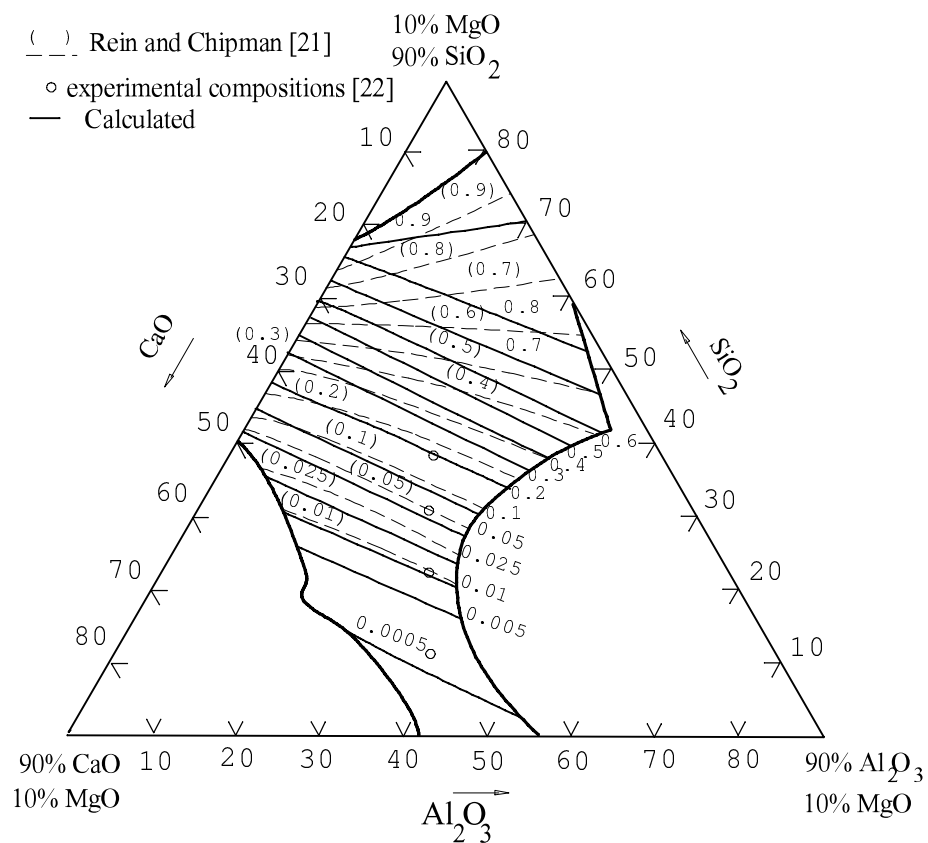


Figure 1a. Comparison between iso-activity lines of SiO₂ suggested by Rein and Chipman [21,22] and calculated by the present model at 1873 K in the Al₂O₃-CaO-MgO-SiO₂ system in the 10 mass pct MgO plane.

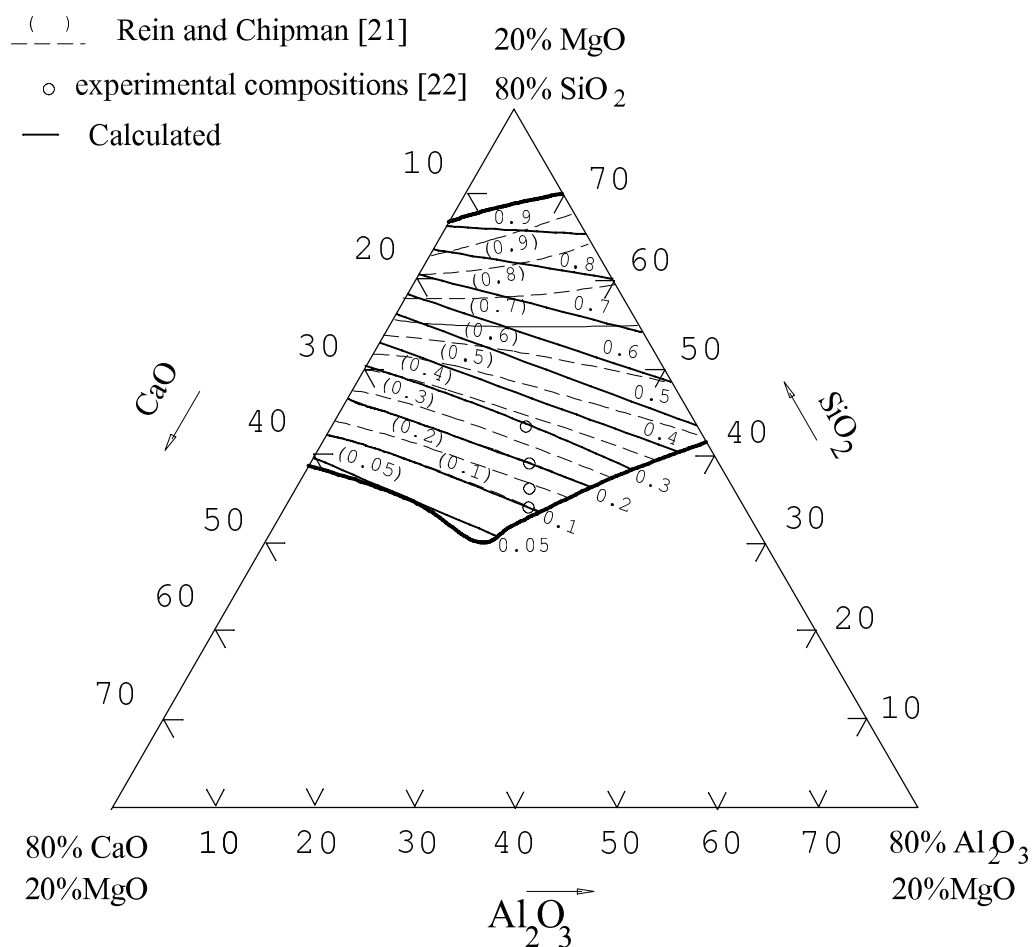


Figure 1b. Comparison between iso-activity lines of SiO₂ suggested by Rein and Chipman [21,22] and calculated by the present model at 1873 K in the Al₂O₃-CaO-MgO-SiO₂ system in the 20 mass pct MgO plane.

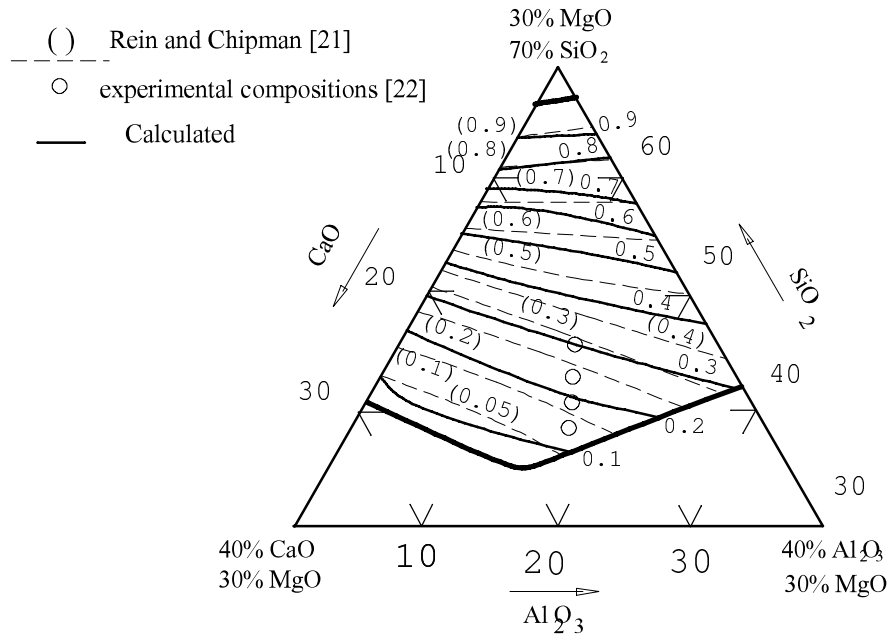


Figure 1c. Comparison between iso-activity lines of SiO₂ suggested by Rein and Chipman [21,22] and calculated by the present model at 1873 K in the Al₂O₃-CaO-MgO-SiO₂ system in the 30 mass pct MgO plane.

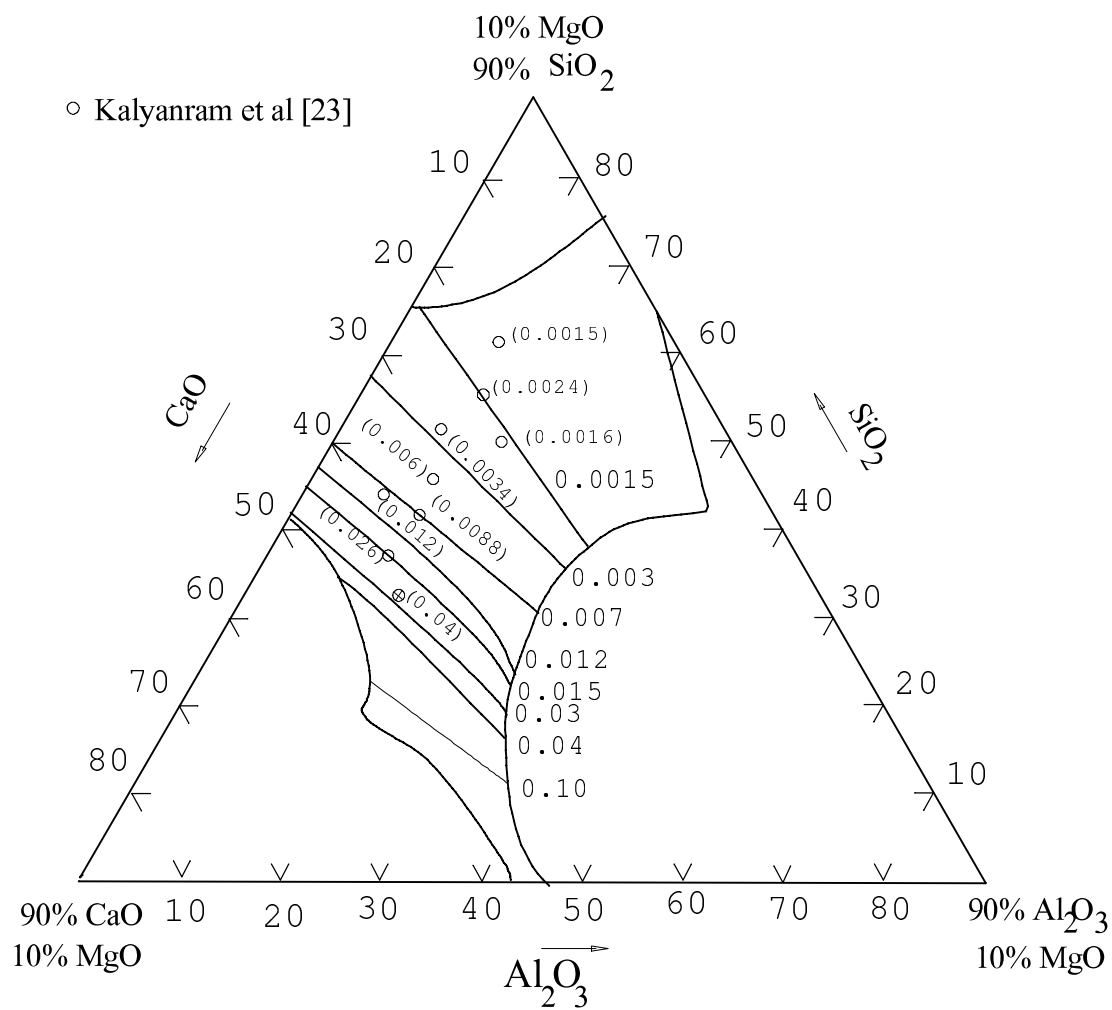


Figure 2. Calculated iso-activity lines of CaO by the present model and experimental [23] values at 1773 K in the Al_2O_3 -CaO-MgO-SiO₂ system in the 10 mass pct MgO plane.

□ Ohita and Suito [24,25]

□ Seo and Suito [26]

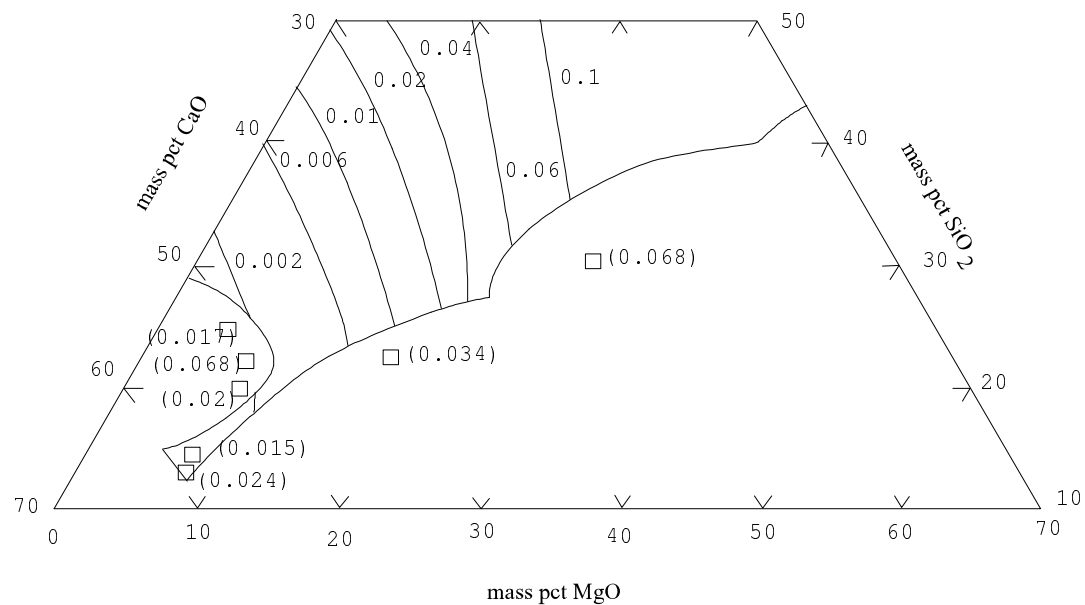


Figure 3a. Calculated iso-activity lines of Al_2O_3 by the present model and experimental [24-26] values at 1873 K in the pseudo quaternary Al_2O_3 -CaO-MgO-SiO₂ system for the 20 mass pct Al_2O_3 plane.

□ Ohita and Suito [24,25]

□ Seo and Suito [26]

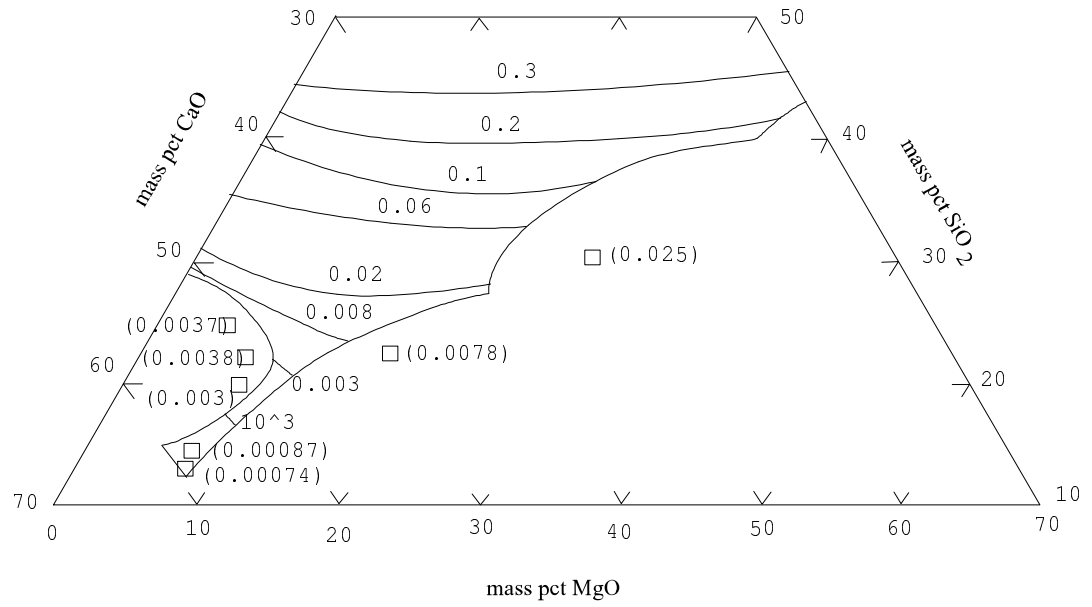


Figure 3b. Calculated iso-activity lines of SiO_2 by the present model and experimental [24-26] values at 1873 K in the pseudo quaternary Al_2O_3 - CaO - MgO - SiO_2 system for the 20 mass pct Al_2O_3 plane.

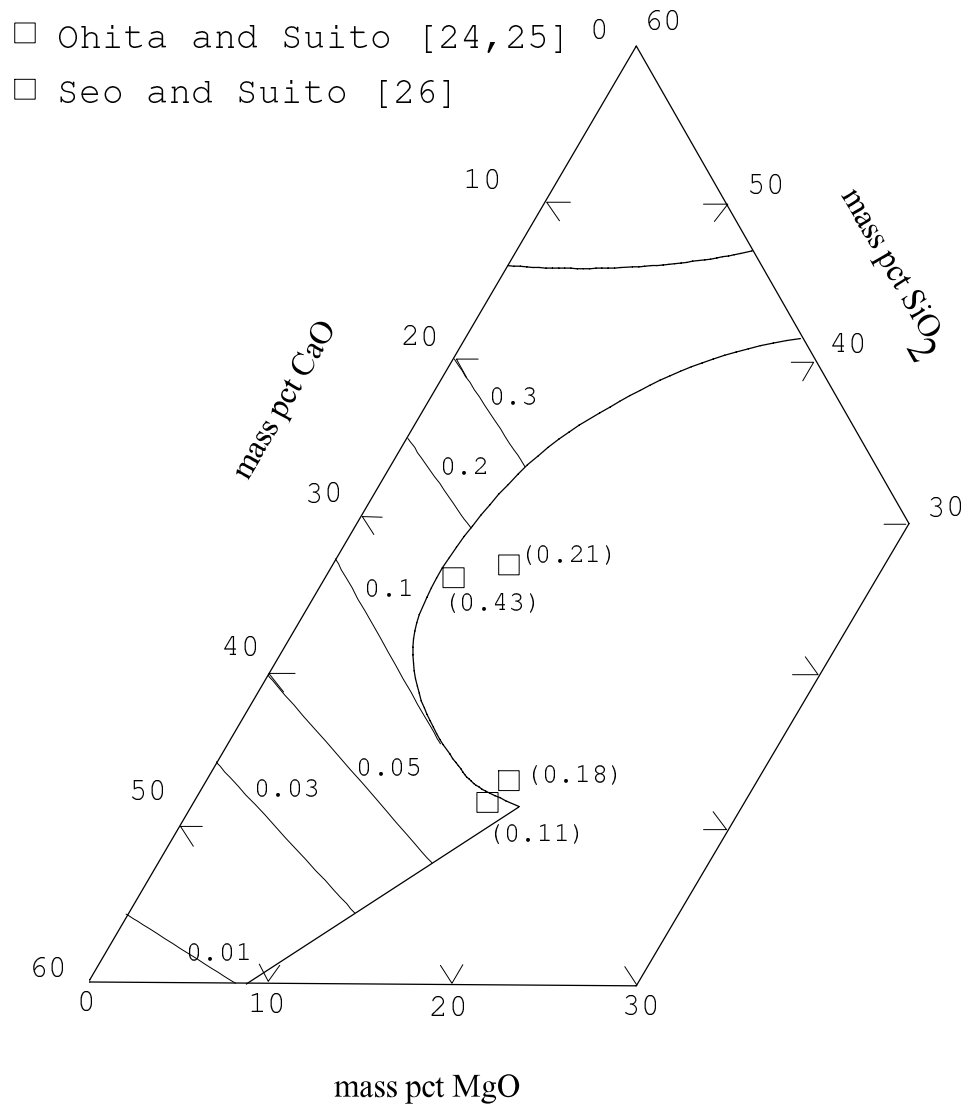


Figure 4a. Calculated iso-activity lines of Al_2O_3 by the present model and experimental [24-26] values at 1873 K in the pseudo quaternary Al_2O_3 -CaO-MgO-SiO₂ system for the 40 mass pct Al_2O_3 plane.

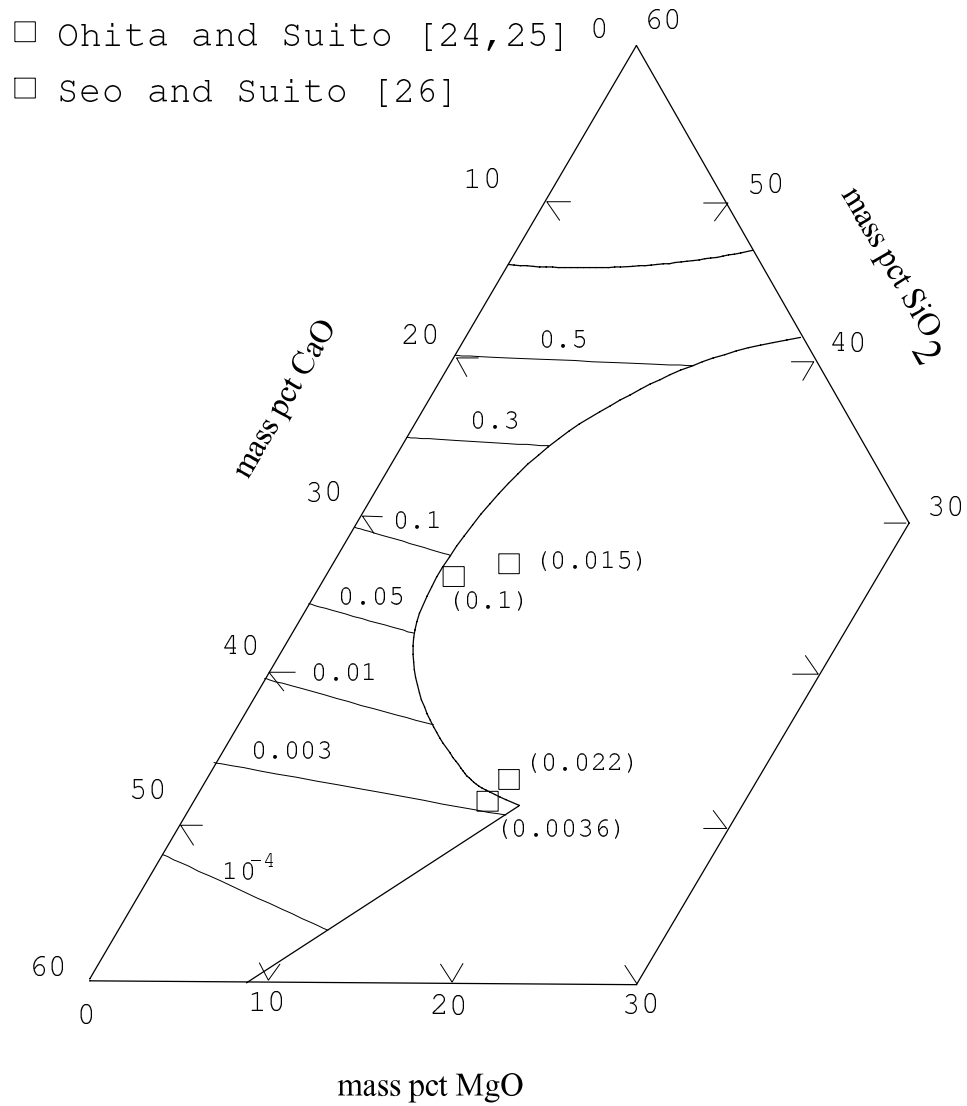


Figure 4b. Calculated iso-activity lines of SiO₂ by the present model and experimental [24-26] values at 1873 K in the pseudo quaternary Al₂O₃-CaO-MgO-SiO₂ system for the 40 mass pct Al₂O₃ plane.

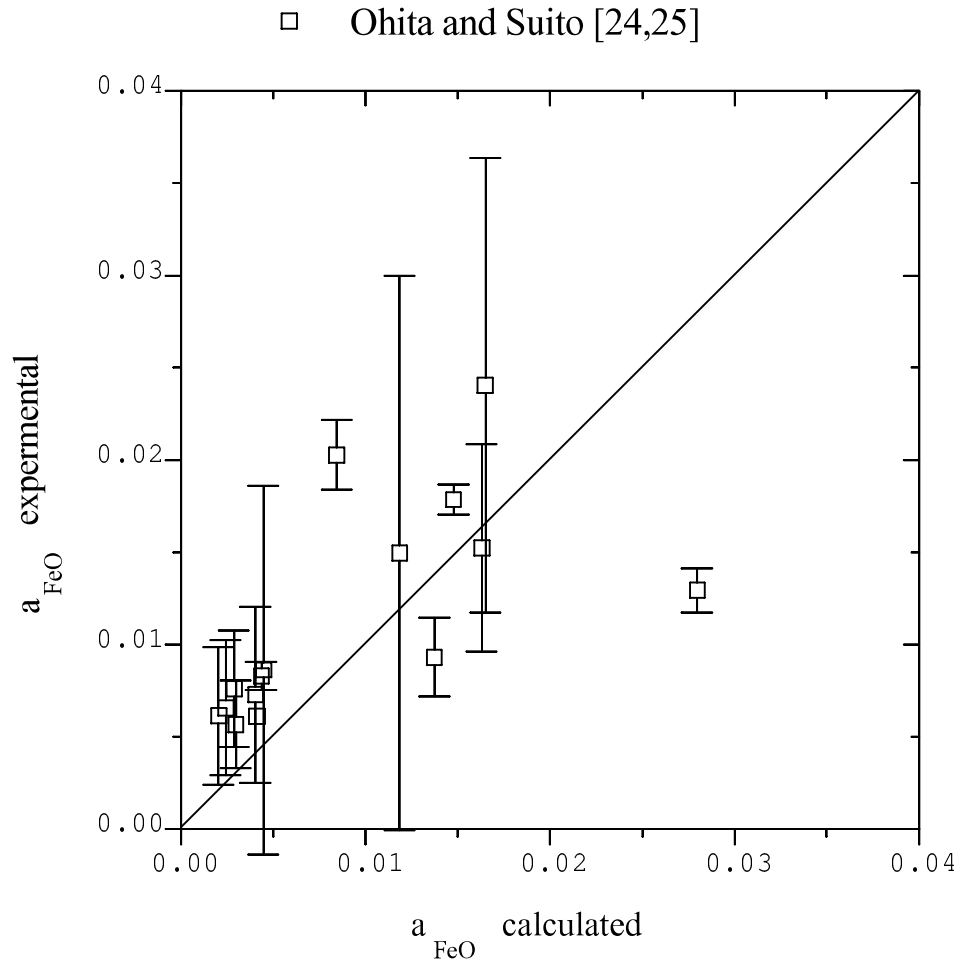


Figure 5a. Comparison between calculated and experimentally [24,25] obtained FeO activities in the Al_2O_3 -FeO-MgO-MnO-SiO₂ system.

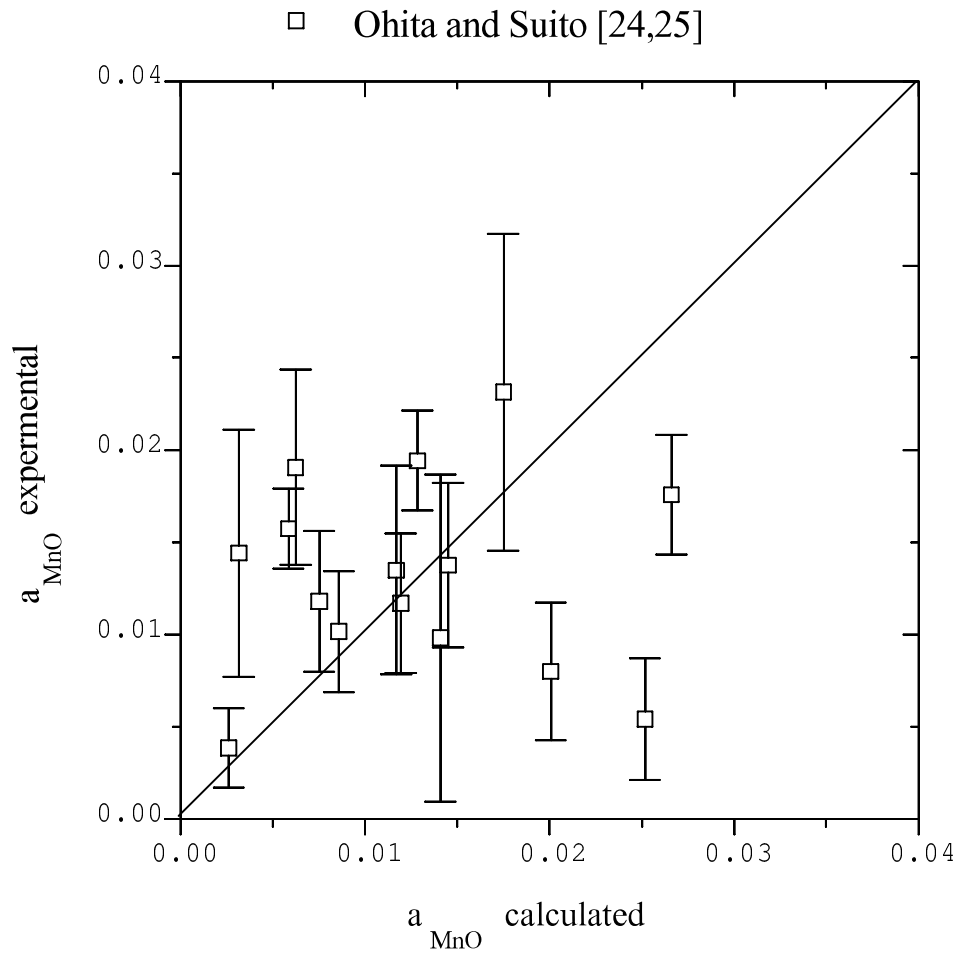


Figure 5b. Comparison between calculated and experimentally [24,25] obtained MnO activities in the Al_2O_3 -FeO-MgO-MnO-SiO₂ system.

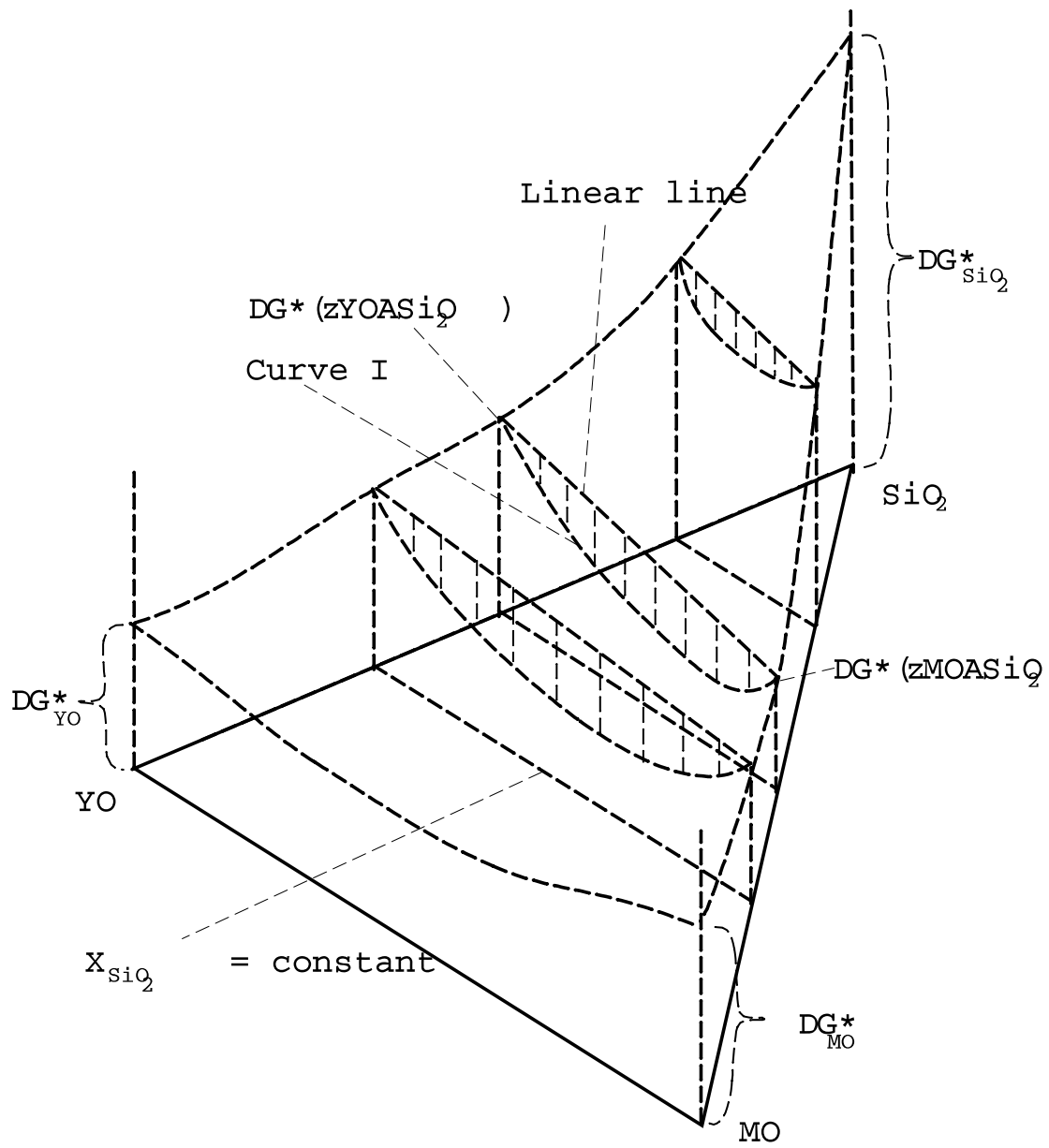


Figure 6. Gibbs activation energy surface for the viscosities of MO-YO-SiO₂ mixtures [20].

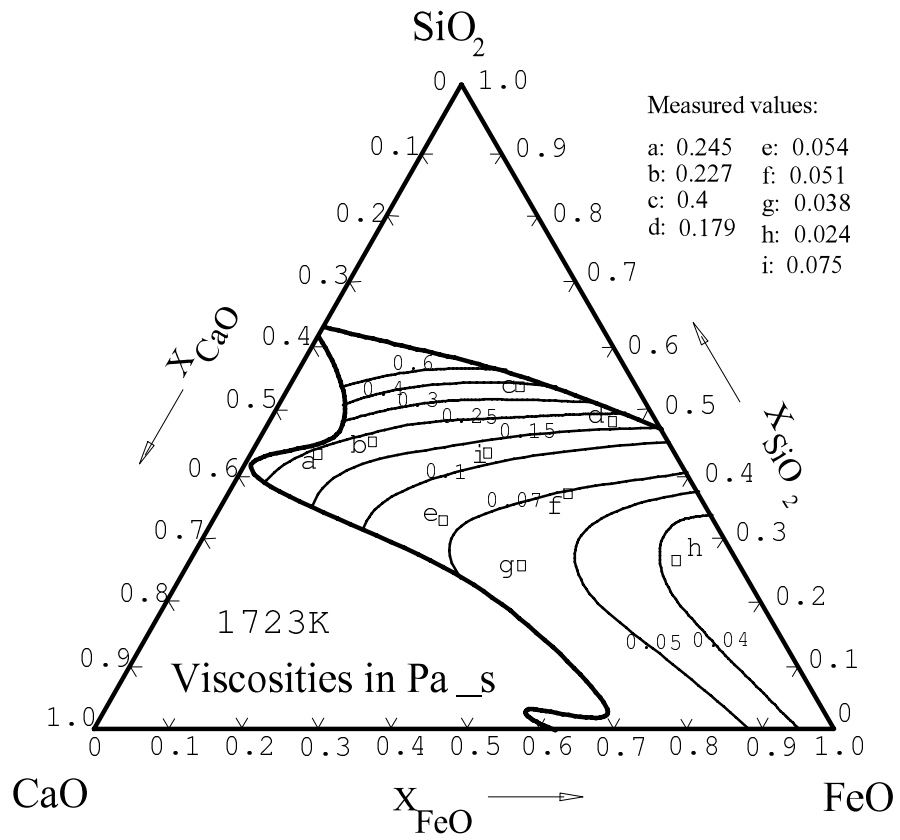


Figure 7. Comparison between the estimated iso-viscosity contours with the experimental data at 1723K in the CaO-FeO-SiO₂ system [20].

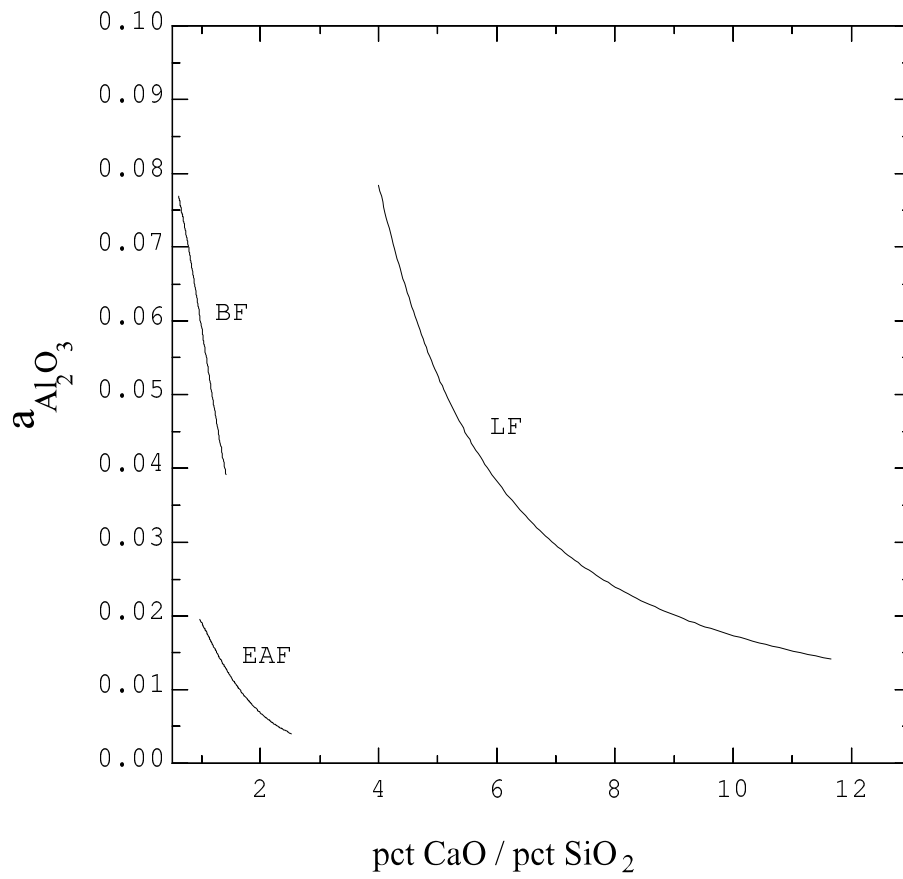


Figure 8. The activities of Al_2O_3 for some typical slag compositions in BF, EAF and LF slags as a functions of the ratio mass pct CaO/ mass pct SiO_2 .