

PHYSICOCHEMICAL PROPERTIES OF TERNARY SLAG SYSTEMS-A MODELLING APPROACH

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ABSTRACT

The present work describes a new approach to the estimation of the properties of ternary slags from the respective binaries. The novelty of the present approach is that it can be applied to both systems with complete solubility in liquid state as well as to those with limited ternary solubilities. The method is equally successful for thermochemical as well as for thermophysical properties of ternary slags. Several successful applications of this new model in predicting viscosity, surface tension, density have been demonstrated in the case of a number of ternary slags in liquid state, as for example, ReO_y - CaF_2 - SiO_2 (where Re is a rare earth metal), SiO_2 - TiO_2 - MnO , SiO_2 - CaO - Al_2O_3 , BaO - FeO - Fe_2O_3 , SiO_2 - MnO - CaO etc. The method has also been extended to predications for electrical conductivities and sulphide capacities. One of the salient features of this approach is that it can be applied to both ternary systems with a limited solubility area as well those that exhibit total miscibility in the entire composition range. In view of all of applications of this new method, the mass triangle model offers really a powerful and efficient tool for estimation various properties of molten system based only on limited experimental information.

INTRODUCTION

The understanding and optimization of the metallurgical processes require access to accurate data of the thermophysical and thermochemical properties of slag systems. There are a number of models for computing the thermodynamic properties of slag systems. The Kapoor-Frohberg-Gaye model, often referred to as IRSID model [1], the Pelton-Blander model [2] and the KTH model [3, 4, 5, 6] are a few examples of semi-empirical correlations used often in connection with slag thermodynamics. In the case of thermophysical properties, the efforts have mainly been focused on viscosities of slags, for which a number of models are available. A unified approach to estimate both thermochemical as well as thermophysical properties of multicomponent slags is still to be developed. Such a model would enable computation of slag properties which would be mutually compatible enabling less empiricism in process simulations.

The present work describes a new approach to the estimation of the properties of ternary slags from the boundary. The method [7, 8, 9, 10], referred to as the mass triangle model is an approach similar to those of Köhler [11], Maggiano [12] and Jacob [13] approaches reaching out to ternary compositions from the binaries using geometric relationships. One of the salient features of this approach is that it can be applied to both ternary systems with a limited solubility area as well those that exhibit total miscibility in the entire composition range. Several thermophysical properties of ternary systems, such as viscosity, density, surface tension etc. have been evaluated by this approach. Good agreements have been proved that this method is comprehensive and flexible.

MODEL DESCRIPTION

The model has been described in detail in earlier publications [7, 8, 9, 10]. Only a brief outline of the model is presented here in order to provide a landmark for the readers before the model is applied to calculate the various thermophysical properties of molten slag systems.

The basic idea of geometrical model is to obtain the ternary system information from binary systems. Mass triangle model belongs to this group. Consider a ternary system 1-2-3 with miscible gap inside. As shown in Figure 1, there are two cases when the miscible gap appeared which may or may not interact with binary systems.

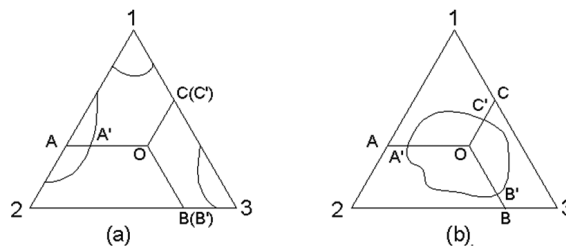


Figure 1: Schematic graph of ternary system with a miscible gap

Following the idea of geometrical models, this new method performs the ternary calculation from the coordinate boundary ones. Instead of using the binary boundaries, the property of a ternary point in homogenous area is expressed as the combination of three boundary points and their weight probability as Equation (1). It should be noted that the weight probability of each boundary point is designed by the ratio of two triangle areas. However, the assignments of three boundary points are not restricted, here, and Chou's selecting way is chosen for example.

$$P_O = \frac{S_{\Delta OB'C'}}{S_{\Delta A'B'C'}} P_{A'} + \frac{S_{\Delta A'OC'}}{S_{\Delta A'B'C'}} P_{A'} + \frac{S_{\Delta A'B'O}}{S_{\Delta A'B'C'}} P_{A'} \tag{1}$$

The area of each triangle is easily computed from the determinate compositions of three points like Equation (2). That means that we may perform the calculation based on the limited experimental data.

$$W_A = \frac{S_{\Delta OB'C'}}{S_{\Delta A'B'C'}} = \frac{\begin{vmatrix} x_1^O & x_2^O & x_3^O \\ x_1^{B'} & x_2^{B'} & x_3^{B'} \\ x_1^{C'} & x_2^{C'} & x_3^{C'} \end{vmatrix}}{\begin{vmatrix} x_1^{A'} & x_2^{A'} & x_3^{A'} \\ x_1^{B'} & x_2^{B'} & x_3^{B'} \\ x_1^{C'} & x_2^{C'} & x_3^{C'} \end{vmatrix}} \tag{2}$$

It is necessary to note that the whole area must be homogenous. Therefore, a program has been developed in present work, and various thermophysical properties of molten slags have been investigated.

SLAG PROPERTIES APPLICATIONS

Thermophysical and thermochemical properties of molten melts have received considerable attention for a long time, because they play important role in slag/metal reactions in metallurgical processes. Model calculation is presented for ternary system where the results could be compared to experimental data.

Surface Tension

In the case of evaluating surface tension, MnO-CaO-SiO₂ system (1823 K) has been selected in order to demonstrate to validity of the mass triangle model. As shown in Figure 2, the predictions of surface tension are plotted, along with the experimental data points [14]. In order to validate the prediction of surface tension contour by mass triangle model, the surface tension of eight points which have the same compositions as the experimental data within this area are compared with the measured value shown in Table 1. Both results show good agreement with each other.

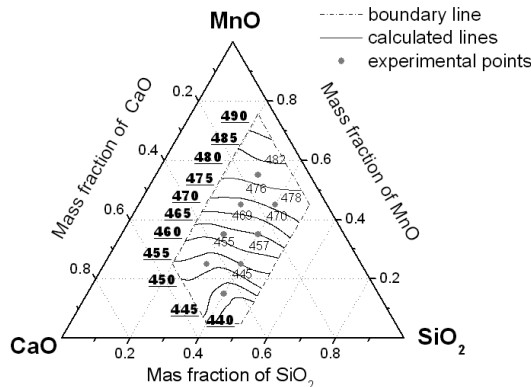


Figure 2: Surface tension (mN·m⁻¹) of MnO-CaO-SiO₂ at 1773 K

interfacial properties, come from the Slag Atlas [6] for a temperature of 1600°C, and are listed in Table 1.

Table 1: Comparison of surface tension of MnO-CaO-SiO₂ at 1773 K

x(SiO ₂)	x(MnO)/ x(MnO)+x(CaO)	Experimental values [14]	Calculation values
0.3	0.78571	482	451.811
	0.64286	476	462.544
	0.35714	455	473.014
	0.5	469	482.167
0.4	0.41667	457	442.979
	0.58333	470	455.14
	0.75	478	465.007
	0.25	445	476.321

Density

With regard to density, the isodensity curves of BaO-FeO-Fe₂O₃ has been predicted at three different temperatures. For similarity, only the case at 1673 K has been indicated here in Figure 3. Based on the limited information from experiment [15], the tendency of density of BaO-FeO-Fe₂O₃ has been reported. There are also three points inside for validation. The error analysis is presented in Table 2.

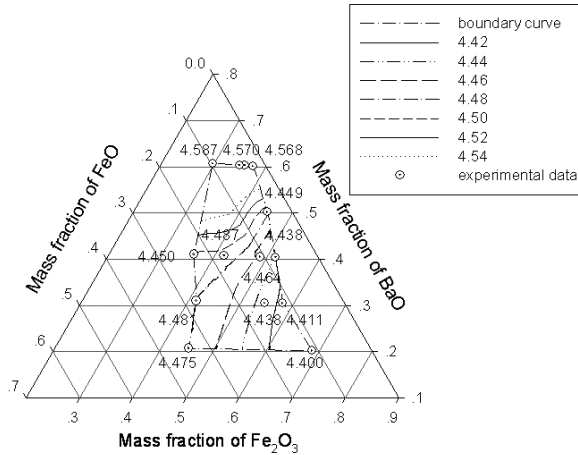


Figure 3: density (g·cm⁻³) of BaO-FeO-Fe₂O₃ at 1673K

Table 2: Comparison of calculation density with experimental values [15] at 1673-1873K

Composition			Density (g/cm ³)								
(Mass fraction)			1673 K			1773 K			1873 K		
BaO	FeO	Fe ₂ O ₃	Exp.	Cal.	Err. %	Exp.	Cal.	Err. %	Exp.	Cal.	Err. %
0.408	0.174	0.418	4.487	4.468	-0.43	4.460	4.492	0.72	4.434	4.440	0.13
0.405	0.107	0.487	4.464	4.433	-0.71	4.446	4.450	0.10	4.430	4.412	-0.40
0.306	0.149	0.546	4.438	4.413	-0.56	4.421	4.432	0.25	4.399	4.388	-0.25

Viscosity

The iso-viscosity of RE_xO_y - SiO_2 - CaF_2 has been calculated in the region of CaF_2 rich at 1873 K shown in Figure 4. The viscosity of this system is strongly dependent on the composition of SiO_2 , High content of silicate leads to polymerization which would result in the increases in viscosity. In the Figure 4, the curves represented the calculation viscosity, as well as the literature points [16].

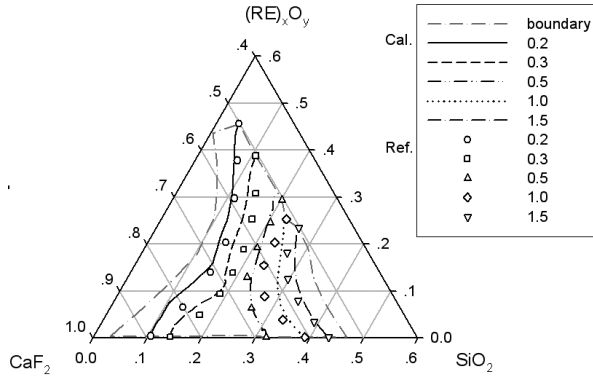


Figure 4: viscosity (Pa·s) of CaF_2 - SiO_2 - $(RE)_xO_y$ at 1873 K

Electrical Conductivity

The measurements on the electrical conductivity of CaO - SiO_2 - MgO have been carried out by Kawahara *et al.* [17] in 1978, and Licko *et al.* in 1983 [18] The data from different sources exhibit a very good consistency. In order to verify the accuracy of this new method, the electrical conductivity curves of SiO_2 - CaO - MgO ternary system at 1823 K are calculated using the above approach and presented in Figure 5, along with the contours reported in the literature [17]. As shown in Figure 5, the electrical conductivity of CaO - SiO_2 - MgO depends largely on the amount of silicate. And the contribution of CaO to the electrical conductivity of slags is similar to that of MgO . At high content of silicate, the electrical conductivity of CaO - SiO_2 - MgO increases slightly with increasing MgO content.

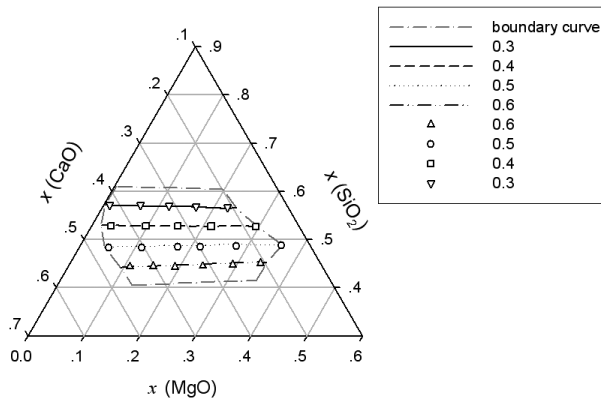


Figure 5: electrical conductivity ($\Omega^{-1}\cdot cm^{-1}$) of SiO_2 - CaO - MgO at 1823K

Sulphide Capacity

The concept of sulphide capacity (C_s), originally defined by Fincham and Richardson is frequently used to describe the solubility of sulphur at low partial pressures of oxygen. The slag with a high C_s will hold sulphur more strongly than the one with low C_s . Therefore, it is very meaningful in iron and steelmaking process. The sulphide capacity of CaO-SiO₂-MgO at 1873 K has been evaluated and shown in Figure 6, along with the experimental data [19]. It can be found that the sulphide capacity will increase with the decrease of content of SiO₂.

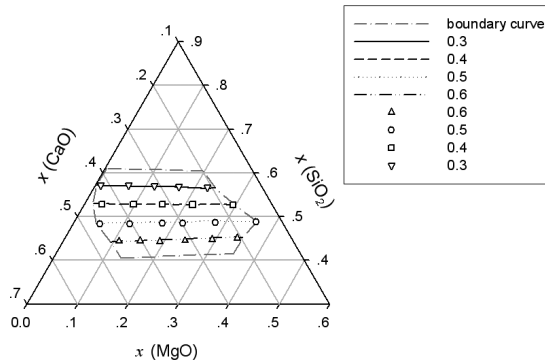


Figure 6: Sulphide capacity of CaO-SiO₂-MgO at 1873 K

DISCUSSION AND SUMMARY

From the applications mentioned above, it can be found that this method is an efficient tool for computing various thermophysical and thermochemical properties. It is different from the traditional geometrical model in that the probability weights are normalized to unity. Moreover, it does not restrict the boundary as real physical phase boundary. One may select an imaginary boundary arbitrarily according to the data in literature and ascertain that it is homogenous area inside.

It has earlier been proved that the mass triangle model had been successfully used to treat the calculation of surface tension and density in the system with a limited solubility area. In this paper, we have further proved the possibility of extending this method to calculate a variety of thermophysical and thermochemical properties in ternary system with a miscible gap, such as electrical conductivity, sulphide capacity etc.

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