PREDICTION OF PHYSICOCHEMICAL PROPERTIES IN MULTICOMPOENT MOLTEN SYSTEM

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ABSTRACT

In this paper, a method has been suggested to predict thermodynamic or other physicochemical properties based on some limited discrete data in a multicomponent system. This issue is particular significant to the metallurgical system since the available data are very limited for a multicomponent system due to the difficulty of experimental measurement and no any effective calculation method is available up to now.

INTRODUCTION

With the progress of science and technology and the requirement of automatization in industry, there is an increasing demand for physicochemical properties of molten salt and slag in metallurgical industry and researches. However, it is difficult to measure the physicochemical properties for the system concerned due to its high melting point and caustic environment in experiments. This issue becomes extremely acute with the increasing of number of components in the considered systems. Fortunately the progress of computer technique gives us a calculation approach to solve this problem. Nevertheless, this calculation has to be restricted in the system where the related binary data are known [1, 2, 3, 4, 5], otherwise, considerable errors will be introduced. What is more serious is that, if the known data are limited in couple of points not a range of data in a multicomponent system, that will be very difficult to calculate properties in an area interested for material scientists. In this paper a new method has been introduced to analyze what are the minimum data required for calculating a specified multicomponent system and how to compute a physicochemical property. The significance of this work is that it will enlarge the capability of geometrical model to a new level and utilize the available experimental data sufficiently.

Development of Geometrical Model and its Limitation

With the progress of science and technology and the requirement of automatization in industry, there is an increasing demand for physicochemical properties of molten salt and slag in metallurgical industry and researches. However, it is difficult to measure the physicochemical properties for the system concerned due to its high melting point and caustic environment in experiments. This issue becomes extremely acute with the increasing of number of components in the considered systems. Fortunately the progress of computer technique gives us a calculation approach to solve this problem. Nevertheless, this calculation has to be restricted in the system where the related binary data are known [1, 2, 3, 4, 5], otherwise, considerable errors will be introduced. What is more serious is that, if the known data are limited in couple of points not a range of data in a multicomponent system, that will be very difficult to calculate properties in an area interested for material scientists. In this paper a new method has been introduced to analyze what are the minimum data required for calculating a specified multicomponent system and how to compute a physicochemical property. The significance of this work is that it will enlarge the capability of geometrical model to a new level and utilize the available experimental data sufficiently.

Development of Geometrical Model and its Limitation

The original idea of geometrical model can be backward to the raising of regular solution model proposed by Hieldbrand in 20's of last century [6, 7, 8], in which the Excess Gibbs Free Energy for a binary system "ij",ΔG_{ij}^{E}, can be expressed as

$$\Delta G_{ij}^{E} = \alpha_{ij} X_{i(ij)} X_{j(ij)} \tag{1}$$

where upper case $X_{i(ij)}$, $X_{j(ij)}$ represent the mole fraction of i and j in a i-j binary solution respectively and α_{ij} is a constant depending on i-j binary itself. Based on Equation 1 it is easy to prove that for a ternary system the Excess Gibbs Free Energy of mixing can be expressed as [9]:

$$\Delta G^{E}_{123} = \alpha_{12}\, x_1 x_2 + \alpha_{23}\, x_2 x_3 + \alpha_{31}\, x_3 x_1 \tag{2}$$

where lower case x_1, x_2, x_3 represent the mole fractions of components 1,2,3 in a ternary system respectively. Equation 2 can be rewritten as the following form

$$\Delta G^{E}_{123} = W_{12}\Delta G^{E}_{12} + W_{23}\Delta G^{E}_{23} + W_{31}\Delta G^{E}_{31} \tag{3}$$

where

$$W_{12} = \frac{x_1 x_2}{X_{1(12)} X_{2(12)}},\ W_{23} = \frac{x_2 x_3}{X_{2(23)} X_{3(23)}},\ W_{31} = \frac{x_3 x_1}{X_{3(31)} X_{1(31)}} \tag{4}$$

The above equations give us a very interesting message, that is, the Excess Gibbs Free Energy of mixing of a ternary system can be expressed as a combination of Excess Gibbs Free Energy of three corresponding binaries as long as one selecting the Equation 4 as their probability weights. On the other words, one can predict the Excess Gibbs Free Energy of mixing of a ternary system based only on binary's information. The premise of the above conclusion is relied on the regular solution model. It is noted that the Equation 3 is a general form, in which no any specific point in binary system needs to be selected as long as the regular solution model equation is fulfilled.

However, most of practical solutions do not fulfill the regular solution, in order to keep Equation 3, one has to select different binary representative point to express the W_{ij} and ΔG^{E}_{ij}, thus a series of models appeared, such as, Kolher model [10], Muggianu model [11], Hillert model [12], Toop model [13], Chou model [2], etc. In 1989 Chou and Chang [1] had given a summary for this kind of model and pointed out that how many possible potential combinations there would be and how to select them. We called this kind of model as the old generation geometrical model. The advantages of these model is the binary solution won't be restricted in "regular solution". Nevertheless, all these old generation models have two defects, they are, (i) it is well known that the old generation model could be divided into two categories: symmetrical model and asymmetrical model, for symmetrical model it is not reasonable from the point of view of the theoretical consideration since the ternary system can not reduce to a binary system even the two components from a ternary system are exactly identical; (ii) for the asymmetrical model, it needs the human interference for arranging three components to three apexes of a ternary composition triangle. These two inherent defects are not only unreasonable but also prevent us from the application of the geometrical model in this computer era. In 1995 Chou [3] has proposed a new generation geometrical model that can overcome these two inherent defects after introducing so called "symmetrical coefficient [3, 5] $\xi^{<k>}_{i(ij)}$", that is

$$\xi^{<k>}_{i(ij)} = \frac{\eta(ij,ik)}{\eta(ij,ik) + \eta(ji,jk)} \tag{5}$$

where $\eta(ij,ik)$ is called "the deviation sum of squares" which is defined as

$$\eta(\mathrm{ij},\mathrm{ik}) = \int_{X_i=0}^{X_i=1} (\Delta G^{E}_{ij} - \Delta G^{E}_{ik})^2 \, dX_i \tag{6}$$

At present one may calculate the Excess Gibbs Free Energy of mixing of a ternary system in terms of Equation 3 without the trouble of the above two defects as long as the Wij is calculated from the "symmetrical coefficient $\xi^{<k>}_{i(ij)}$". Let us call this model as the new generation geometrical model to distinguish the old one.

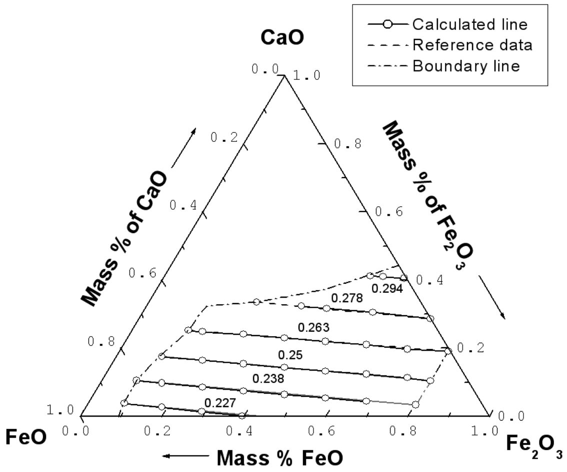

Figure 1: Specific volume of CaO-FeO-Fe_2O_3 at 1873 K (x10^{-3} m^3/Kg)

Though the new generation geometrical model has solved the defects exsisting in the tradition geometrical model, it is noted that like all old geometrical models the new generation geometrical model can not be used in a system with a limited homogenous phase region either. Since for a limited homogenous phase the binary subsystem information is not available. To overcome this problem, Chou *et al.* [14] have proposed a new model, which does not have to use subsystem information. Instead, the limited data on the boundary of the homogenous region have been used to calculate the properties within the boundary. Figure 1 shows the calculation results of specific volume of CaO-FeO-Fe_2O_3 at 1873 K (x10^{-3} m^3/Kg) that is calculated in terms of this mass triangle model.

Figure 2 is another successful example that used the mass triangle method to calculate the surface tension of the MnO—CaO—SiO_2 ternary system at 1500°C. The common point of these two systems is that they are all limited solubility solution at the specific temperature and phase boundaries can not cover the binary subsystem.

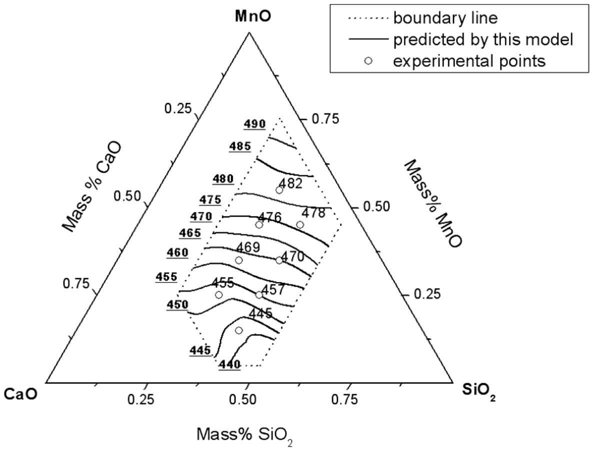

Figure 2: The calculated iso- surface tension (mN·m^{-1}) lines of the MnO—CaO—SiO_2 ternary system at 1500°C

From the above description, we have successfully treated the calculation of geometrical model for the case with known condition of binary data and/or the data along a closed boundary within a composition triangle based on the form of Equation 3. At present, one would like to further know if the known condition is not a series of continue data in the binaries or along a closed boundaries within a composition triangle but only couple of discrete points scattering within a ternary or multicomponent system, in this case what kind of information one can obtain and how to extract these information.

These topics are particularly meaningful for the high order multicomponent system since the available data for it are always very limited. We will treat this subject here now.

Calculating Properties based on Discrete Data

Figure 4 is a schematic diagram showing the relation between the required calculated point "O" with eight discrete experimental points in a quaternary system, in which the solid black points represent the experimental data, the circle point "O" represents the calculated point.

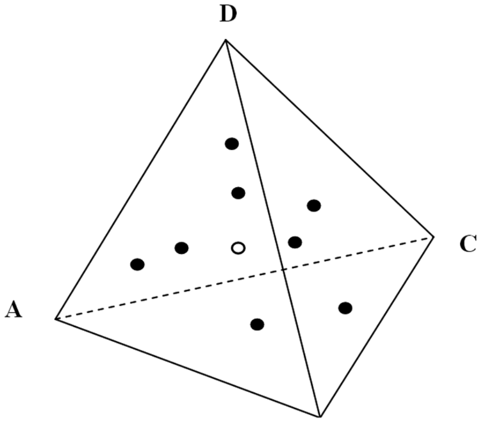

Figure 3: A schematic diagram explaining how to calculate point "O" from 8 discrete data points in a quaternary system

For a general case, assuming that there are total "n" experimental points in a "m" components system,($n \geq m$). Let us select any m points from n points. The physicochemical property of point "O"calculated from m selected points can be expressed as

$$G_o = W_1G_1 + W_2G_2 + W_3G_3 + \ldots + W_mG_m \tag{7}$$

where Wj represents the probability weight that can be solved from the following simultaneous equations

$$\begin{aligned}
x_1^o &= W_1 x_{11} + W_2 x_{12} + \ldots + W_m x_{1m} \\
x_2^o &= W_1 x_{21} + W_2 x_{22} + \ldots + W_m x_{2m} \\
x_3^o &= W_1 x_{31} + W_2 x_{32} + \ldots + W_m x_{3m} \\
&\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\
x_m^o &= W_1 x_{m1} + W_2 x_{m2} + \ldots + W_m x_{mm}
\end{aligned} \tag{8}$$

where $x_1^o, x_2^o, \dots, x_m^o$ represent the mole fraction of the point "O", the physicochemical property of which, G_o, is required to be calculated.

DISCUSSION

- If the number of experiment data points n is great than that of component m, namely n≥m,under this situation,one may select any m points from n data points to calculate the physicochemical property. Since there are totally C_n^m combinations, therefore, we should have many calculated results.One may take an average value as the final result.
- Please note, it is possible that the calculated W_j could be a negative value that may cause big error due to extrapolation. Under this situation, an approximate method is suggested below: Let us give up these points with a negative probability weight from the consideration of calculation and re-calculating the W_j all over again in terms of the following equation,

$$W_j^{'} = \frac{W_{pj}}{W_{p1} + W_{p2} + W_{p3} + \dots + W_{pm}} \tag{9}$$

where W_{pj} represent the probability weight of point "j" which has positive value and $W_j^{'}$ is new probability weight. Thus Equation 7 becomes

$$G_O = W_1^{'}G_1 + W_2^{'}G_2 + W_3^{'}G_3 + \cdots + W_{m-q}^{'}G_{m-q} \tag{10}$$

where q is the number of negative probability weight.

This is an approximate method for the calculation point containing negative probability weight value more approximate approaches are possible that will be discussed in our future paper.

Application to the Practical System

Table 1 lists the experimental results of density for $CaO\text{-}FeO\text{-}Fe_2O_3\text{-}MnO\text{-}SiO_2$ quinary system [15]. At present let us calculate the density of composition of $CaO{:}FeO{:}Fe_2O_3{:}MnO{:}SiO_2$ = 12.1: 33.2: 2.26:16.4:34.6 since the density of this point is already known, that is equal to 3.5 g/cm^3.

Table 1: Density of $CaO\text{-}FeO\text{-}Fe_2O_3\text{-}MnO\text{-}SiO_2$ quinary system at 1673 K

Data point	CaO (wt%)	FeO (wt%)	Fe_2O_3 (wt%)	MnO (wt%)	SiO_2 (wt%)	Density (mg/cm^3)
A	33.4	16.3	2.06	10	38.2	3.4
B	34.2	11.5	0.97	15.2	37	3.5
C	35.5	5.85	0	19.8	38.4	3.4
D	11.6	30.2	3.9	17.2	35.6	3.54
E	15.7	32.7	2	12.1	36.2	3.6
F	20.3	35	2	5.6	35.8	3.4

Let us take A, B, D, E, F five points as a source data to calculate the density of point "O" after solving the simultaneously Equation 8, one found that the probability weight of point "A" has a negative value, therefore this point should be ruled out from our consideration. We have to re-calculate the probability weight according to Equation 9 and calculate the density in terms of Equation 10 that is 3.492 very close to the experimental value of 3.5 g/cm^3.

CONCLUSIONS

Extracting physicochemical properties from limited discrete data points is a very significant work due to the shortage of experimental data in the system with high order multicomponent especially for metallurgical systems with high melting point. Current calculation methods can not offer an effective approach for it. The method introduced in this paper has filled up this gap. It is expected that this method will play a useful role in this topic in future. We will also introduce more methods in future.

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