

# Calculation of physicochemical properties in molten melts

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**Abstract:** The physicochemical properties of melts are very important for controlling metallurgical processes and designing new processes. However, it is difficult to obtain them in terms of the experiments due to the system studied with higher melting temperature, under corrosion environment and with a larger number of components. Therefore, most of physicochemical data came from theoretical calculation in the light of very limited experiment measurements. The theoretical calculation can be classified into three categories: physical model, empirical model as well as semi-empirical and semi-theoretical model, among which the last one is most popular and has provided most part of data required by research and industrial applications. In this report, the progresses of semi-empirical and semi-theoretical model in China have been summarized, that can further be divided into three types of methods: (i) geometrical model, (ii) semi-empiric model (computing the system property based on the melts structure information) and (iii) the model correlating two different kinds of properties, as a result one can calculate one physicochemical property based on another property. Concerning the geometric model, the stress will be put on our new generation model that has been demonstrated more reasonable and accurate than that of the traditional geometric model in terms of a statistical thermodynamic analysis and practical calculating examples. The significance of the third method, i.e. the relation between two different physicochemical properties has been discussed. Finally, the advantages and disadvantages of these three methods have also been compared that will be beneficial for the model selection and model developing for high temperature molten systems.

**Keywords:** Molten melts, physicochemical properties, solution model

## 1. Introduction

In metallurgical processes the molten melt have played a very important role, which, either acts as a reactant or as a byproduct directly participates in the metallurgy reactions. Therefore, the physicochemical properties of melts are extremely important to the quality of metallurgical products. On the other hand, for the metallurgical industry one has to consider the energy consuming and environment pollution that leads us to research new metallurgical processes. Producing higher quality metallurgical products and designing new processes for metallurgical industry to make metallurgical process more friendly to the environment is the task of metallurgists in this new era. For this purpose the physicochemical data of melts is the basic condition required in researches.

It is essential to acquire physicochemical properties from experimental measurements; nevertheless, it is also well

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known that the metallurgical experiments are difficult to perform due to the higher temperature environment, caustic atmosphere and a large number of complicated multicomponent systems. Accordingly, the theoretical calculation will play a key role in obtaining the physicochemical data for melts. The essential of theoretical method is calculating physicochemical properties from other known data that involve various kinds of data, for instance, microscopic information such as atomic or molecular information, the structure information or macroscopic information like viscosity, entropy, heat capacity,...etc. Based on the different kind of known data, the theoretical method can be categorized into three kinds of calculation models: (i) physical model, (ii) empirical model, (iii) semi-empirical and semi-theoretical model. The physical model is to calculate the physicochemical data based on the information in atomic or molecular level. The advantage of this method is that it has a clear physic picture and explicit physical meaning, but the application is limited in a narrow range. The empirical method correlated the physicochemical properties with an assumed mathematical formula directly with certain parameters; this method can find application in many practical problems but without physical meaning. Between the above two models the semi-empirical and semi-theoretical model can combine the advantages of above two methods and find more applications in practical systems. We will stress on this method in this paper.

There are many semi-empirical and semi-theoretical methods, among which our focus will be set on the following three kinds of methods that are active recently in China. The first method is calculating physicochemical data of melts for a multicomponent system based on the information of all corresponding binaries. This model is also named as so-called “geometrical model” ; The second one is to correlate the physicochemical data required with a special accessory function such as basicity, optical basicity...and so forth that are closely related to the microcosmic properties such as molecular structure, interact force between molecules and atoms,...etc. The third one is correlating the required physicochemical property with another physicochemical property directly, from which we can find one property from another or vice versa. In the following sections we will discuss the progress of each method that had made progresses in China recently.

## **2. Geometrical model**

As mentioned above, the geometrical model is a kind of model which can calculate the physicochemical properties of higher order multicomponent system based on the properties of corresponding binaries[1-9]. Since there are a lot of binary data available and their results are more reliable than that of any other properties. This method will bring us more reliable results, besides, different from other semi-empirical and semi-theoretical methods that will be discussed later section, this method will also give us the data available in a large range of composition area that will make possible to calculate the phase diagram in a whole composition range. Accordingly, the geometrical model will find more applications.

### **2.1 The definition of geometric model**

The earliest idea of geometrical model was coming from thermodynamic calculation. It is assumed that, the Excess Gibbs Free Energy of mixing of a ternary system can be expressed as a combination of Excess Gibbs Free Energy of

mixing of three corresponding binaries with a probability weights  $W_{12}, W_{23}, W_{31}$  as follows[8-12].

$$\Delta G_{123}^E = W_{12}\Delta G_{12}^E + W_{23}\Delta G_{23}^E + W_{31}\Delta G_{31}^E \quad (1)$$

where  $\Delta G_{123}^E$  represents the ternary Excess Gibbs free energy of mixing,  $\Delta G_{12}^E, \Delta G_{23}^E, \Delta G_{31}^E$  binary Gibbs free energy of mixing

$$W_{12} = \frac{X_1 X_2}{X_{1(12)} X_{2(12)}}, W_{23} = \frac{X_2 X_3}{X_{2(23)} X_{3(23)}}, W_{31} = \frac{X_3 X_1}{X_{3(31)} X_{1(31)}} \quad (2)$$

where the upper case  $X_{i(j)}, X_{j(i)}$  represent the mole fraction of i and j in a i-j binary solution respectively and lower case  $X_1, X_2, X_3$  represent the mole fractions of components 1,2,3 in a ternary system respectively.

Based upon the above regulation, it is clear that the geometrical model is a kind of “phenomenological theory”. The core of this method is that, the property of a ternary or multicomponent system can be expressed as the combination of properties of its corresponding binaries[8, 10-12]. When the representative binary points have been selected for each corresponding binaries, the property of multicomponent system will be fixed according to Eqs(1) and (2).

## 2.2 The traditional geometrical models and their problems.

According to the discussion mentioned in the previous paragraph, the different selection of binary representative points will lead to different geometrical model. Hillert[7] has divided the geometrical model into two categories: symmetrical and asymmetrical models. In 1989, Chou and Chang[9] have summarized hundreds and hundreds kind of traditional geometrical model and given symmetrical and asymmetrical model a formal definition, that is, “A model shall be referred to as a symmetric model if the ternary Gibbs free energy of mixing can be expressed in terms of its three binary Gibbs free energies of mixing at the same kind of selected composition and the same kind of assigned probability weight for all three binaries. All other cases shall be deemed as asymmetric.” [9] Actually, it is a summary for all traditional geometrical models.

In the CALPHAD XXIII meeting of 1993, Chou has pointed out that all traditional geometrical models have fatal defects: they are unreasonable in theory and not executable in practical performance in our computer era. After that Chou has published many papers to prove his pointview[10-12]. Since then more and more examples have demonstrated the correctness of this analysis[13-19]. At present, we like to prove the incorrectness of the traditional geometrical model from another angle.

The fatal defect of the traditional geometrical model is that, the selection of binary representative composition is fixed and not related to the third component. On the other words, for a ternary system A-B-C, the selection of binary representative point for system A-B is independent of component “C”, no matter this C is ‘C’, ‘C’ or ‘C’” the selected point for A-B binary will be no change (ref Fig.1). Obviously, it is incorrect, it can be imaged that if the component “C” is identical with component “B”, this ternary system will be reduced to a binary system A-B at the selected point “D”,

on contrary, if the component “C” is identical with component “A”, the system will also be reduced to a binary system A-B, but in this case the selected point should be located at point “E”(see Fig.2). It is clear now the traditional geometrical model cannot meet these two requirements due to the unchangeable selection for the binary representative point.

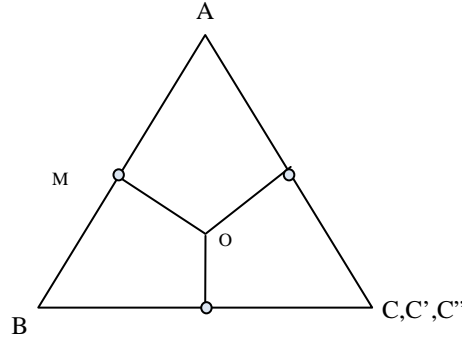


Fig.1 The binary selected point of traditional geometrical model  
(the selected binary points never change no matter what kind of the third component C)

### 2.3 The new generation geometrical model and its reasonability

The relations between the selected binary composition and ternary composition for the new generation geometric model are[10-12]

$$X_{i(ij)}^k = (x_i + x_k \xi_{ij}^k) \quad (3)$$

$$X_{j(ij)}^k = (x_j + x_k (1 - \xi_{ij}^k)) \quad (4)$$

where  $\xi_{ij}^k$  is called as “similarity coefficient” that can be obtained in terms of

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

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

$$\eta(ij, ik) = \int_{X_i=0}^{X_i=1} (\Delta G_{ij}^E - \Delta G_{ik}^E)^2 dX_i \quad (6)$$

where i, j, k denote three components respectively.

For a ternary A-B-C system (here i=A, j=B, k=C), when the third component C is identical with component “B” (“k” will be equal to “j”), according to Eq.(7)  $\eta(ij, ik) = 0$ , thus, the binary selected point should be going to “D” (Fig.2), while the third component “C” is identical with component “A”, similarly, the selected binary point should go to “E”, it is a reasonable conclusion. Therefore, the new generation geometric model is reasonable theoretically.

The correctness of the new generation geometric model actually can be explained through the statistical thermodynamics. It has been proved that, as long as one considers that, the potential energy of each pair of molecules is

also affected by all other molecules existing in the solution, one may obtain the form of our new generation geometric model. It is a long demonstration that will be published in our future work.

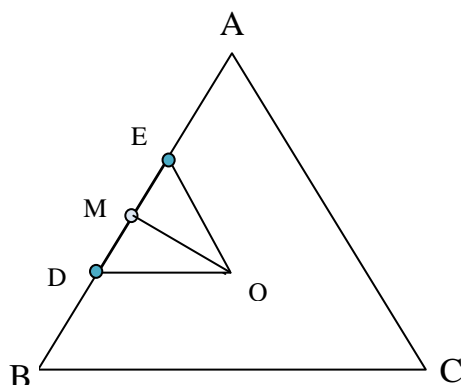


Fig.2 The selected binary point in the new generation geometric model are related to the third component (when the “C” is identical with B, the selected binary point will move to D, while the “C” is identical A, the selected binary point will move to E )

#### 2.4 Recent progress of new generation geometric model

The geometric models originally were applied to the calculation of phase diagrams and thermodynamic functions only. In the 1980s, our group in the University of Science and Technology Beijing has extended this method to calculate other physicochemical properties and obtain a great success, since then, more physicochemical properties have been tested[20, 21]. Why the geometrical model can be extended from calculating thermodynamic properties to calculating physicochemical data? From a different point of view to see the geometric model, one will find that, the approach of geometric model actually is a kind of method to calculate central area data in terms of the boundary data, since a multicomponent system is surrounded by its all binary boundaries. The calculated result is depended on the geometrical point of all known data. Based on this point of view, it is reasonable to assume that the geometric model can be used to estimate either thermodynamic property or the physicochemical properties. Our practice and all other scientist researchers have proved this point is correct. At present geometric models have been used to calculate, viscosity, conductivity, surface tension,...and many other physicochemical properties.

Since the geometric model can also be regarded as the calculation from boundary data to estimate the central area data. If the known data are not available in the whole binary system, the geometric models cannot make their calculation in the area without known data. In the history, an option could be adopted, that is, extrapolating the binary data from known data area to that of unknown data area after assuming that these data are metastable. Of course this treatment is very rough.

In order to solve the problem mentioned above, a mass triangle method has been developed by us, based on which one can calculate the physicochemical properties from any boundary where the corresponding data are available[22]. Recently, this method has further been extended to the multicomponent system where the known data are only in some discrete points[23].The meaning of this new development is significant since most of metallurgical systems are

multicomponent system with high melting point, where the experimental data are very limited.

### 3. Physicochemical properties and structure information of melts

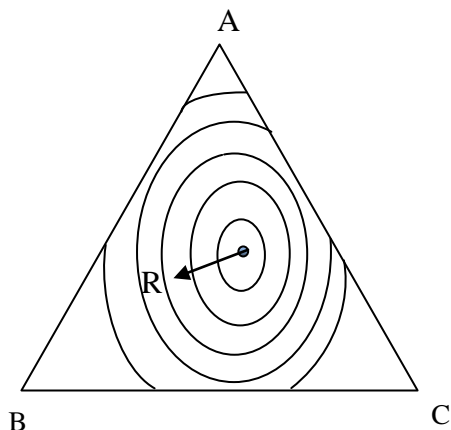


Fig. 3 Schematic diagram of contour lines of physicochemical property

As we discuss above, the geometric model is established on the base of phenomenological theory. It is simple and can find more applications in practical systems. Nevertheless, the physical picture of this method is not clear and physical meaning for some parameters is not significant. On contrary, the first principle calculation can offer a very clear physical picture, but the data provided in this method are not very useful, which also require a complicated calculation. It is natural to think, can we combine the merits of these two methods to fast obtain the required data for metallurgical processes. It is possible since the data for high temperature processes permit a certain range of error. In the following paragraphs, we will introduce some methods of this kind of treatment.

The basic idea of this method is, any kind of physicochemical properties in a ternary or higher order system can be expressed for a series of contour lines (or contour surface, Fig.3), that can be expressed as a function of temperature and composition, for instance, the viscosity of solution and be expressed as

$$\eta = f(T, x_1, x_2, \dots, x_n, ) \quad (7)$$

Of course, based on the experimental data or calculated data, one may find this formula through data regression. Nevertheless, it is not the way we are going to do; instead, we try to find this formula based on the structure information of melts. For example, we find a function  $R = R(x_1, x_2, \dots, x_n)$  in terms of structure information and from which, we have

$$\eta = \eta(T, R) \quad (8)$$

How to find R based on the structure information that needs physical knowledge. In the following paragraphs we will give some example

### 3.1 Electrical conductivity of aluminosilicate melts

The electrical conductivity of aluminosilicate melts increases as increasing temperature providing that the electron conductivity can be neglected. So, the temperature dependence of electrical conductivity could be described by the Arrhenius law as Eq.(10).

$$\sigma = A_{\sigma} \exp(-E_{\sigma} / RT) \quad (9)$$

where  $A_{\sigma}$  is a pre-exponent,  $\Omega^{-1} \cdot \text{cm}^{-1}$ ;  $E_{\sigma}$  is the activation energy,  $\text{J} / \text{mol}$ ;  $R$  is the universal gas constant,  $8.314 \text{ J} / (\text{mol} \cdot \text{K})$ ; and  $T$  is the absolute temperature,  $\text{K}$ . Therefore, the main task of modelling electrical conductivity is to find a reasonable expression to correlate activation energy with chemical composition. It is found that[24] the activation energy can be expressed as the linear addition of mole fraction of each component to some extent, as expressed in Eq.(11).

$$E_{\sigma} = \sum x_i E_i \quad (10)$$

where  $x_i$  is the mole fraction of component  $i$ ;  $E_i$  is the parameter corresponding to component  $i$ ,  $\text{J} / \text{mol}$ .

For the  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$  system, the activation energy of electrical conductivity can also be expressed as the linear function of optical basicity corrected by Mills[25] after considering the charge compensation effect of  $\text{Al}^{3+}$  ion[26], as shown Eqs. (12) and (13).

$$E_{\sigma} = m \cdot \Lambda^{corr} + n \quad (11)$$

$$\Lambda^{corr} = \frac{1.0 \times (x_{\text{CaO}} - x_{\text{Al}_2\text{O}_3}) + 0.78 \times x_{\text{MgO}} + 0.6 \times 3 \times x_{\text{Al}_2\text{O}_3} + 0.48 \times 2 \times x_{\text{SiO}_2}}{(x_{\text{CaO}} - x_{\text{Al}_2\text{O}_3}) + x_{\text{MgO}} + 3 \times x_{\text{Al}_2\text{O}_3} + 2 \times x_{\text{SiO}_2}} \quad (12)$$

where  $\Lambda^{corr}$  is the corrected optical basicity;  $m$  and  $n$  are constants.

### 3.2 Viscosity of melts

Recently, we have derived a structurally-based viscosity model to describe the viscosity variation of aluminosilicate melts with composition[27-30]. In this model, a simple method is proposed to calculate the numbers of different types of oxygen ions classified by the different cations bonded with oxygen, which is used to characterize the influence of composition on viscosity. When dealing with the aluminosilicate melts containing several basic oxides, the priority order is established for different cations to charge compensate  $\text{Al}^{3+}$  ions, according to the coulombic force between cation and oxygen anion. The method of calculating numbers of different types of oxygen ions can be found in our previous papers[27-30].

The temperature dependence of viscosity is calculated by Arrhenius equation,

$$\ln \eta = \ln A_{\eta} + E_{\eta} / RT \quad (13)$$

where  $\eta$  is the viscosity, Poise;  $A_{\eta}$  is the pre-exponent factor, Poise;  $E_{\eta}$  is the activation energy,  $\text{J/mol}$ . The

temperature compensation effect is considered,

$$\ln A_\eta = k(E - 572516) - 17.47 \quad (14)$$

For multicomponent system  $\sum M_x O_y - \text{SiO}_2$ , the value of parameter  $k$  is assumed to be the linear addition of that of the binary systems  $M_x O_y - \text{SiO}_2$  with the re-normalized mole fractions of oxides  $M_x O_y$  as the weighting factors,

$$k = \frac{\sum_{i,i \neq \text{SiO}_2} (x_i k_i)}{\sum_{i,i \neq \text{SiO}_2} x_i} \quad (15)$$

The activation energy of viscosity in Eq.(14) is expressed as follows,

$$E_\eta = \frac{572516 \times 2}{n_{\text{O}_{\text{Si}}} + \alpha_{\text{Al}} n_{\text{O}_{\text{Al}}} + \sum \alpha_{\text{Al},i} n_{\text{O}_{\text{Al},i}} + \sum \alpha_{\text{Si}}^i n_{\text{O}_{\text{Si}}^i} + \sum \alpha_{\text{Al},i}^j n_{\text{O}_{\text{Al},i}^j} + \sum \alpha_i n_{\text{O}_i}} \quad (16)$$

where  $n$  is the mole number and  $\alpha$  describes the deforming ability of bond around the corresponding oxygen ion. The first, second, third, fourth, fifth, sixth terms in the denominator are the contributions of bridging oxygen  $\text{O}_{\text{Si}}$ , bonded with  $\text{Si}^{4+}$  ion; oxygen  $\text{O}_{\text{Al}}$ , bonded with  $\text{Al}^{3+}$  ion not charge compensated; bridging oxygen  $\text{O}_{\text{Al},i}$ , bonded with  $\text{Al}^{3+}$  ion charge compensated by cation  $i$ ; non-bridging oxygen  $\text{O}_{\text{Si}}^i$ , bonded with  $\text{Si}^{4+}$  ion and metal cation  $i$ ; non-bridging oxygen  $\text{O}_{\text{Al},i}^j$ , bonded with metal cation  $j$  and  $\text{Al}^{3+}$  ion charge compensated by cation  $i$ ; free oxygen  $\text{O}_i$ , bonded with metal cation  $i$ , respectively.

The model provides a good description of the viscosity behavior varied with composition and temperature. Meanwhile, it could also give a satisfy interpretation to the abnormal phenomenon[31] that viscosity increases when adding  $\text{K}_2\text{O}$  to  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  melt within a certain composition range.

We measured the effect of  $\text{K}_2\text{O}$  on viscosity in  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  melt with low content of  $\text{Al}_2\text{O}_3$ [32], and it is found from the experimental results that viscosity first increases then decreases with increasing content of  $\text{K}_2\text{O}$ , with the maximum viscosity occurring in the field of  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3 > 1$  [9]. Our viscosity model can also well describe this phenomenon.

#### 4. Relation between different physicochemical properties

In the nature, it is possible that there exist some relations between two physicochemical properties, such as, molar density and molar volume, the diffusion coefficient and velocity of molecule, ..., etc. If this relation has been found, that will be meaningful, since we can calculate one property from another, especially when the required property is difficult to obtain either from experiment or from theoretical calculation. The relation between electrical conductivity and viscosity is one of example for this situation. It is well known that both electrical conductivity and viscosity are related to the molecular or atomic motion. It is expected that they might exist some relation between these two properties.



Both the temperature dependences of electrical conductivity and viscosity can be described by the Arrhenius law as Eqs. (10) and (14), so

$$\ln \eta + n \ln \sigma = \ln A_\eta + n \ln A_\sigma + (E_\eta - nE_\sigma) / RT \quad (8)$$

For a fixed system, if there is a constant “ $n$ ” always fulfilling the condition of  $E_\eta - nE_\sigma = 0$  regardless of composition, logarithm of viscosity will be the linear function of logarithm of electrical conductivity. We have published a series of work on the relation between electrical conductivity and viscosity [33-35]. It is found that the logarithm of viscosity varies linearly with the logarithm of electrical conductivity. The linear relations are different for MO-SiO<sub>2</sub> (M=Mg, Ca, Sr, Ca, Fe, Mn) system and M<sub>2</sub>O-SiO<sub>2</sub> (M=Li, Na, K) system, which are mainly determined by the valences of metal cations [33], as shown in Fig. 4.

MO-SiO<sub>2</sub> system:

$$\ln \eta = 0.15 - 1.10 \ln \sigma \quad (9)$$

M<sub>2</sub>O-SiO<sub>2</sub> system:

$$\ln \eta = 4.02 - 2.87 \ln \sigma \quad (10)$$

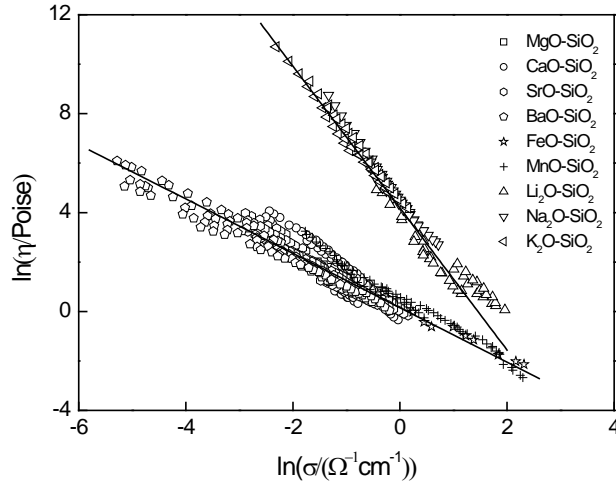


Fig.4 The relation between viscosity and electrical conductivity for MO-SiO<sub>2</sub> and M<sub>2</sub>O-SiO<sub>2</sub> binary system

For  $\sum M_x O$ -SiO<sub>2</sub> melt, when the valences of all metal cations are divalent (or univalent), the relation between viscosity and electrical conductivity is the same as that of MO-SiO<sub>2</sub> system (or M<sub>2</sub>O-SiO<sub>2</sub> system). For  $\sum M_2 O$ - $\sum MO$ -SiO<sub>2</sub> system containing both MO and M<sub>2</sub>O oxides, the coefficients of the linear relation between the logarithm of viscosity and the logarithm of electrical conductivity can be obtained from the linear addition of coefficients for MO-SiO<sub>2</sub> and M<sub>2</sub>O-SiO<sub>2</sub> systems, with the weight factors from the re-normalized mole fractions of basic oxides  $\sum MO$  and  $\sum M_2 O$ , as expressed in Eqs. (11-13) [12].

$$\ln \eta = m - n \ln \sigma \quad (11)$$

$$m = \frac{4.02 \sum_i x_{(M_2O)_i} + 0.15 \sum_j x_{(MO)_j}}{\sum_i x_{(M_2O)_i} + \sum_j x_{(MO)_j}} \quad (12)$$

$$n = \frac{2.87 \sum_i x_{(M_2O)_i} + 1.10 \sum_j x_{(MO)_j}}{\sum_i x_{(M_2O)_i} + \sum_j x_{(MO)_j}} \quad (13)$$

It is also found that  $Al_2O_3$  has little effect on the relation between viscosity and electrical conductivity. The relation for  $\sum M_xO-SiO_2$  melt can be approximately applied to  $\sum M_xO-Al_2O_3-SiO_2$  melt[33].

## 5. Discussion and Conclusion

(1) With the concern of energy crises and the environment pollution, the metallurgical industry has been confronted with a serious challenge. Therefore, designing new processes is a significant subject in the process metallurgy. As a result the physicochemical data become a very important and urgent issue.

(2) The metallurgical melts is a kind of caustic and high temperature solution, with which the experiments are not easy to conduct, therefore, the theoretical calculation will become more and more important in acquiring physicochemical data.

(3) In the theoretical calculation, the first principle method has a clear physic picture and substantial meaning for the relevant parameters, nevertheless, this calculation is complicated and the results obtained are very limited that are usable for practical processes. The semi-empirical and semi-theoretical method should play a very important role in offering data for practical systems.

(4) Geometric model is a kind of semi-empirical and semi-theoretical method for calculating the physicochemical properties in multicomponent systems based on their corresponding binaries. Since there are many reliable binary data, this method will play and continue to play an important role in acquiring data for multicomponent melts.

(5) The traditional geometric models have a series of defects, such as, theoretically unreasonable (cannot reduce to a binary system when two components are identical in a ternary system), requiring human interference in arranging the components for the model, not executable in computerization...etc.

(6) The new generation geometric model can overcome all defects of traditional geometric models due to correctly assuming that the selected binary representative point for the model will closely relate to the third component. With more data obtained from experimental measurements or/and theoretical calculation, and more accurate results obtained from high level instrument or software, the advantages of new generation geometrical model should be shown clearly.

(7) The semi-empirical method associated with the melts structure and microscopic information will greatly simplify the calculation for physicochemical data of melts, besides, it will also promote the insight of the melts.

### Acknowledgement

The authors wish to thank the Chinese Natural Science Foundation for their kind support under the contract 51174022, also to the State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, for their kind of support.

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