A New Method for Evaluating Some Thermophysical Properties for Ternary System

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(Received June 20, 2008: final form July 7, 2008)

ABSTRACT

In our earlier papers, we have presented a new method, named the mass triangle model, for calculating physicochemical properties in the ternary system within a limited solubility area. This model was shown to be superior to traditional geometrical models in the computation of ternary data from the known data for the corresponding binaries. In the present paper, the authors extend this method to a ternary system where the entire compositional area inside the ternary triangle is homogeneous. The successful application of this new method to the estimation of surface tension and density has been demonstrated in the case of the system Ni_3S_2-FeS-Cu_2S at 1473K with mean square root error of ±1.83%, ±4.33% respectively, compared with the experimental results.

Keywords: geometrical models, thermophysical properties, ternary system

1. INTRODUCTION

During the past decades, geometric models /1-17/, such as Toop model /1/, Hillert model /2/, Kohler model /3/, Muggianu model /4/, Chou model /7/, new general solution model put forward by Chou *et al* /10/ have met with different degrees of success in predicting thermodynamic properties and calculating phase diagrams for ternary and multicomponent systems. This is attributed to the simplicity and effectiveness of such an approach. Further, the calculations require information only from the binary systems, which is relatively easy to obtain. It is to be noted that the reliable application of these models is limited to homogeneous ternary systems. If the systems exhibit a partial solubility area, this kind of calculations is found to introduce considerable errors, especially when the solubility area is so small that this homogeneous phase field cannot intersect with binary edges in a composition triangle. In order to solve this problem, successful attempts have been made in our previous papers /18-20/, in which a new model, named the Mass Triangle Model, has been presented to calculate the physicochemical properties for a small solubility area in a ternary system where such calculations cannot be carried out by a traditional geometrical model. Good agreement between the calculation results and the experimental data presented in these publications demonstrated that this new model was significant for evaluating properties in a ternary system with a limited solubility area. Based on these successful applications in limited solubility area, it was felt necessary to test the performance of this model in the case of a system with complete solubility area and compare with the result obtained from tradition geometrical model. If successful, the Mass Triangle Model would prove to be a valuable unified thermodynamic tool that can be applied to both homogeneous as well as multiphase ternary systems works. With the advancements in the modeling of metallurgical processes, the property measurements are extended to thermophysical properties such as viscosities, surface tensions and densities. In the present paper, the new model is applied to predict the surface tension and density in the case of the ternary test system

Ni_3S_2-FeS-Cu_2S at 1473K from the experimental data corresponding to the binaries.

2. THEORETICAL ANALYSIS

For a ternary system 1-2-3 with a complete solubility, the ternary properties can be calculated through a combination of three binary properties in combination with weight probability values assigned at selected binary points. According to the method of selecting binary points suggested by Chou /10, 18/, the three binary compositions are chosen in terms of the following procedure:

Through the ternary composition point O (**Fig. 1**) three straight lines are drawn parallel to three binary composition lines 23, 31 and 12 respectively, i.e. OA, OB and OC in the figure. These three lines intersect binary edges at points A, B, C respectively. Thus, the composition relationships between point O and three points A, B, C can be expressed as follows:

$$x_O^1 = x_A^1, \quad x_O^2 = x_B^2, \quad x_O^3 = x_C^3 \tag{1}$$

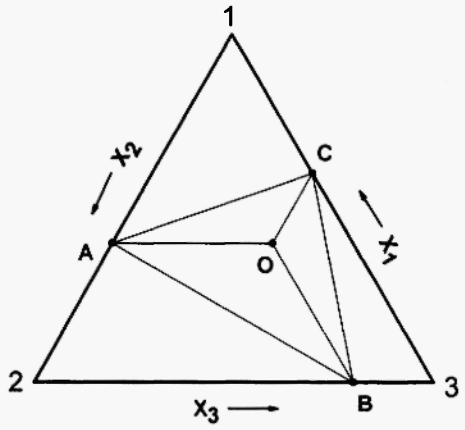


Fig. 1: Schematic diagram of mass triangle model in ternary system

If the calculated property is surface tension, the equation for the ternary surface tension according to mass triangle model can be expressed as follows

$$\sigma_O = W_A\sigma_A + W_B\sigma_B + W_C\sigma_C \tag{2}$$

where σ_A, σ_B, and σ_C, denote the surface tensions at points A, B and C respectively, while W_A, W_B and W_C are the respective weight factors. The symbols of $S_{\Delta OBC}$, $S_{\Delta OCA}$, $S_{\Delta OAB}$ and $S_{\Delta ABC}$ represent the areas of triangles ΔOBC, ΔOCA, ΔOAB and ΔABC respectively. The weight factors of W_A, W_B and W_C can be calculated in the following way

$$W_A = S_{\Delta OBC} / S_{\Delta ABC} \tag{3}$$

$$W_B = S_{\Delta OCA} / S_{\Delta ABC} \tag{4}$$

$$W_C = S_{\Delta OAB} / S_{\Delta ABC} \tag{5}$$

Since the area of the triangle can be expressed in terms of the coordinate of mole fractions of corresponding components 1, 2, 3,the probability weight at points A, B, C can be expressed as follows

$$W_A = \begin{vmatrix} x_1^O & x_2^O & x_3^O \\ x_1^B & x_2^B & x_3^B \\ x_1^C & x_2^C & x_3^C \end{vmatrix} / \begin{vmatrix} x_1^A & x_2^A & x_3^A \\ x_1^B & x_2^B & x_3^B \\ x_1^C & x_2^C & x_3^C \end{vmatrix} \tag{6}$$

$$W_B = \begin{vmatrix} x_1^O & x_2^O & x_3^O \\ x_1^C & x_2^C & x_3^C \\ x_1^A & x_2^A & x_3^A \end{vmatrix} / \begin{vmatrix} x_1^A & x_2^A & x_3^A \\ x_1^B & x_2^B & x_3^B \\ x_1^C & x_2^C & x_3^C \end{vmatrix} \tag{7}$$

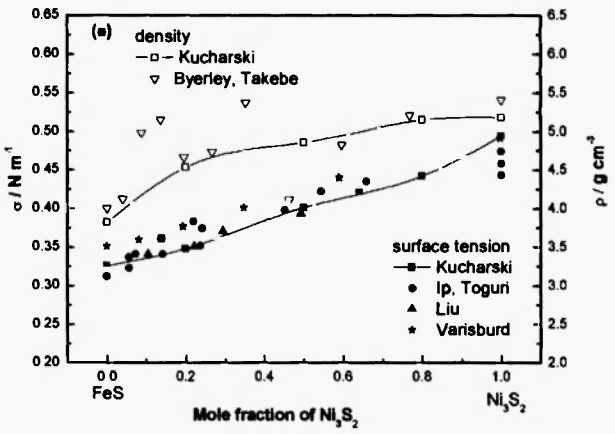
$$W_C = \begin{vmatrix} x_1^O & x_2^O & x_3^O \\ x_1^A & x_2^A & x_3^A \\ x_1^B & x_2^B & x_3^B \end{vmatrix} / \begin{vmatrix} x_1^A & x_2^A & x_3^A \\ x_1^B & x_2^B & x_3^B \\ x_1^C & x_2^C & x_3^C \end{vmatrix} \tag{8}$$

3. APPLICATION

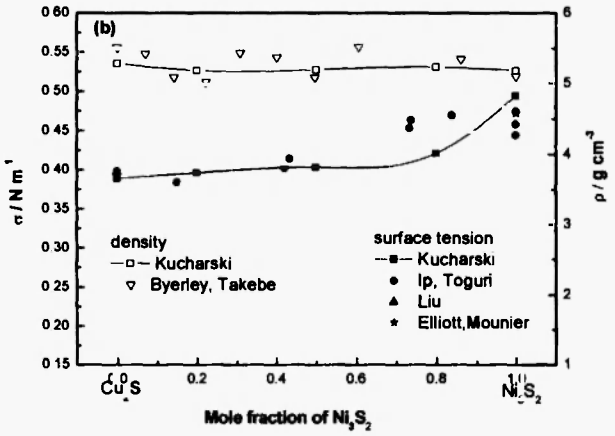
Knowledge of the surface tensions and densities of sulphide liquid mattes containing Cu_2S, FeS, Ni_3S_2 is a prerequisite to understand flash smelting and converter processes for the production of nickel and copper. However, the literature data of surface tension and density for the systems mentioned above are scattered and insufficient. To the best knowledge of the present authors, the only systematic measurement of surface

tension and density of molten Ni_3S_2-FeS-Cu_2S mattes is due to Kucharski *et al.* /21/. These authors have taken extreme precautions in their experiments for the measurements of the above-mentioned properties along pseudo-binary lines at 1473K. The maximum bubble pressure method was employed by these authors with a deviation of ±2.5% between independent measurements. In order to evaluate the accuracy of their data, comparisons of the values reported by Kucharski *et al.* with other literature data /22-29/ have been carried out by the present authors and the comparison results are illustrated in **Fig. 2**. In the case of the system FeS-Ni_3S_2, the surface tension values reported by Kucharski *et al.* /21/ are in reasonable agreement with the values reported by Byerley and Takabe /22/. The same is true in the case of the densities in these systems. In the case of the binary system Cu_2S-Ni_2S_3, the values for both surface tension as well as densities reported by Kucharski *et al.*/21/ can be seen to be in agreement with those reported by Byerley and Takabe /22/ except at the high Ni_3S_2 end. In the case of the system FeS-Cu_2S, the surface tension values reported by Kucharski *et al.* /21/ deviate from the reported results of both Tokumoto *et al.* /23/ as well as Vanyukov /24/. The different density measurement results by these two groups also exhibit a difference. The estimation of the ternary properties of the ternary system Ni_3S_2-FeS-Cu_2S from the binaries requires a mutual consistency between the data for the three binaries involved. Thus, the present authors found the best choice of binary date for the estimations of surface tension and density by the mass triangle model in the case of the ternary system Ni_3S_2-FeS-Cu_2S was to utilize the corresponding binary data reported by Kucharski *et al.* /21/.

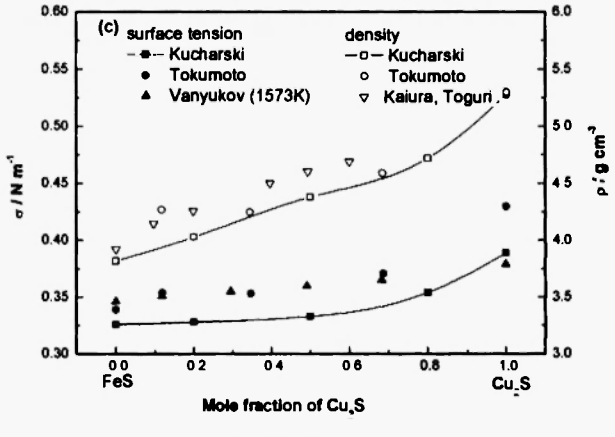
In analogy with thermodynamic calculations, even in the case of thermophysical properties such as surface tension or density, the excess properties can be expressed by the difference between real properties and ideal properties in a binary system. In the application of mass triangle model in a composition triangle, two types of calculations were employed in the present work, *viz.*: one is based on excess surface tension on binary boundary, and the other on the actual surface tension of three binaries. In the present paper, the results of both kinds of calculations have been performed.



(a) FeS-Ni_3S_2



(b) Cu_2S-Ni_3S_2



(c) FeS-Cu_2S

Fig. 2: Comparison of surface tension and density of three binary systems at 1473K.

3.1 Calculation in terms of excess property

Based on the experimental data reported by Kucharski *et al.* /21/, the excess surface tensions σ^E and excess densities ρ^E of three binaries in Ni_3S_2-FeS-Cu_2S at 1473K were calculated as shown in **Fig. 3 a**, σ^E, and **b**, ρ^E. It is easily found that the deviations of the excess properties in Ni_3S_2-FeS binary are different from the other two binaries Cu_2S-FeS, Ni_3S_2-Cu_2S. In the case of surface tensions, the FeS- Ni_3S_2 system shows an irregular pattern with the increasing of FeS. In the case of excess density, on the other hand, the values show a positive deviation. In order to describe the σ^E and ρ^E of three binaries by mathematical formulae, the power series regression was adopted in the present work fit the excess property data for three binary systems,. The coefficients thus evaluated are listed in **Table 1** and **Table 2**.

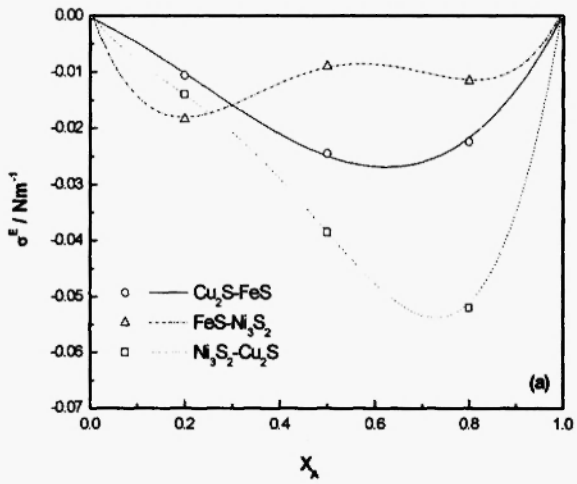
Table 1
Power series regression coefficients for excess surface tension of Cu_2S-FeS, FeS-Ni_3S_2, Ni_3S_2-Cu_2S at1473K

binary	x_ix_j	$x_ix_j(x_i)$	$x_ix_j(x_i^2)$	R^2
Cu_2S-FeS	-0.05078	-0.06596	-0.05696	0.99875
FeS-Ni_3S_2	-0.231837	0.712514	-0.64168	1
Ni_3S_2-Cu_2S	-0.497057	0.976394	-0.58056	1

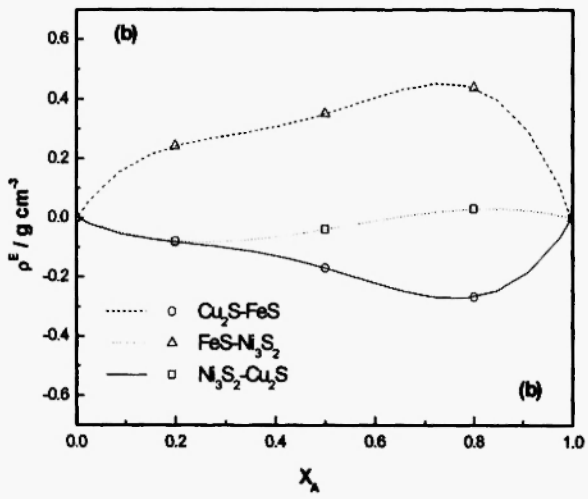
Table 2
Power series regression coefficients for excess density of Cu_2S-FeS, FeS-Ni_3S_2, Ni_3S_2-Cu_2S at1473K

binary	x_ix_j	$x_ix_j(x_i)$	$x_ix_j(x_i^2)$	R^2
Cu_2S-FeS	-0.098	-0.06146	-0.01424	1
FeS-Ni_3S_2	-0.036	0.035417	-0.16042	1
Ni_3S_2-Cu_2S	-0.154	0.197917	-0.14514	1

With the excess properties along the binary boundaries, the surface tension and density of the Ni_3S_2-FeS-Cu_2S at 1473K are calculated for the whole composition triangle and are presented in Fig. 3 together with experimental results reported in literature. Considering the experimental error of ±2.5%, one may conclude that the model evaluation is in reasonably good agreement with the experimental results. With the excess properties along the binary boundaries, the surface tension and density of the Ni_3S_2-FeS-Cu_2S at 1473K are calculated for the whole composition triangle, which are presented in **Fig.** 4 together with experimental results reported in literature. Considering the experimental error of ±2.5%, one may conclude that the model evaluation is in reasonably good agreement with the experimental results.

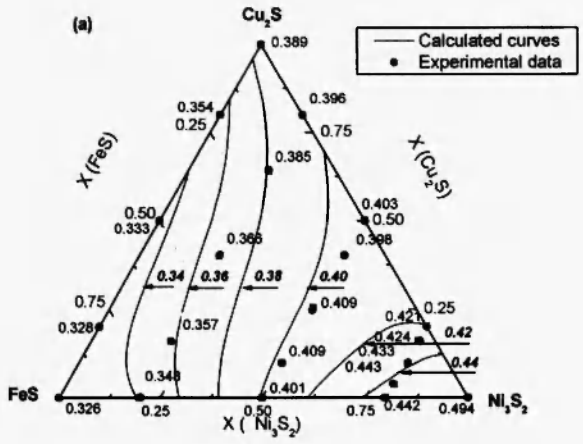


(a) Excess surface tension

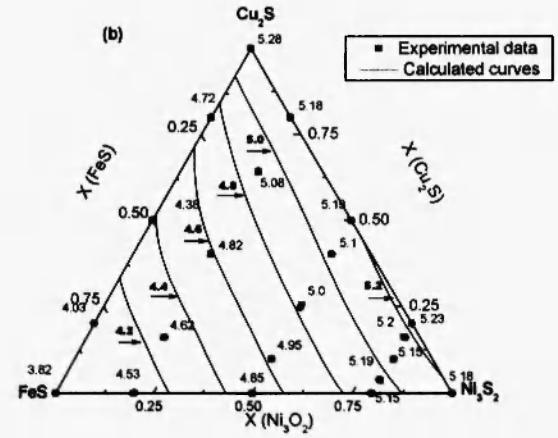


(b) Excess density

Fig. 3: Excess properties of the Ni_3S-FeS, FeS-Cu_2S, Cu_2S-Ni_3S_2 binaries at 1473K.



(a) iso-surface tension

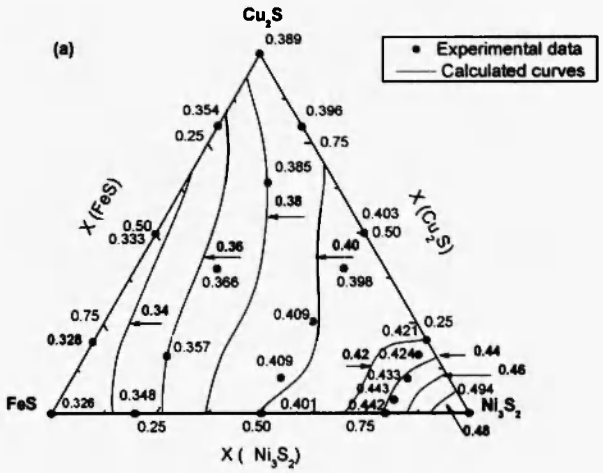


(b) iso-density

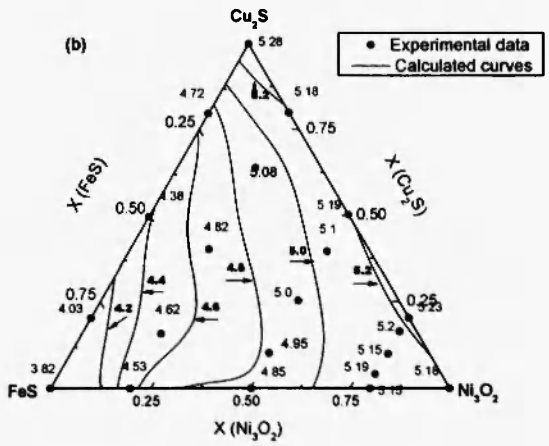
Fig. 4: Calculated properties in molten Ni_3S_2-FeS-Cu_2S system at 1473K from excess boundary.

3.2 Calculated from real data of surface tension and density in binaries

As mentioned above, for the mass triangle model, it also can be applied in terms of the actual property data from three binary boundaries directly. **Figure 5** illustrates the calculated results in terms of real binary properties for surface tension and density in Ni_3S_2-FeS-Cu_2S system at 1473K respectively, along with the experimental data measured. In these calculations, the spine interpolate function is used.



(a) is-surface tension



(b) iso-density

Fig. 5: Calculated properties in molten Ni_3S_2-FeS-Cu_2S system at 1473K from actual properties.

4. DISCUSSION

In order to evaluate the validity of the mass triangle model for the ternary system with complete solubility, nine experimental points along three pseudo-binary lines were picked up for comparison. It is also of interest to know which of the two boundary data, excess or the actual property, would give better results. The detailed comparisons are listed in **Table 3**.

Table 3
Comparison of the calculation results with the experiments

Composition in mole fraction			Experimental Results /21/		Surface tension / $N \cdot m^{-1}$		Density / $g \cdot cm^{-3}$	
Ni_3S_2	FeS	Cu_2S	σ /N · m	ρ /g · cm^{-3}	By excess	By real	By excess	By real
0.2	0.16	0.64	0.385	5.08	0.381	0.381	4.89	4.9
0.5	0.1	0.4	0.398	5.1	0.404	0.406	5.04	5.02
0.8	0.04	0.16	0.424	5.2	0.429	0.432	5.16	5.17
0.2	0.4	0.4	0.366	4.82	0.369	0.367	4.59	4.65
0.5	0.25	0.25	0.409	5.0	0.403	0.398	4.83	4.93
0.8	0.1	0.1	0.433	5.15	0.437	0.442	5.06	5.12
0.2	0.64	0.16	0.357	4.62	0.358	0.361	4.28	4.53
0.5	0.4	0.1	0.409	4.95	0.403	0.397	4.63	4.84
0.8	0.16	0.04	0.443	5.19	0.444	0.444	4.96	5.13
Relative difference (± %)			2.5	2.5	*1.09*	*1.83*	*4.33*	*2.11*

It is clear from Table 3 that the relative errors of the mass triangle model, when applied to the calculation of surface tension and density, are within the experimental error of 2.5%, except in the calculation by using excess density, where the errors were as high as 4.33%. In view of this, it should be reasonable to expect that the mass triangle method can be applied for calculating physicochemical properties for ternary systems with a completely homogeneous area.

It is found that, if the binary points are selected by using the method suggested by Chou /10,18/, the model calculation will be simplified since the relations between A, B, C and point "O" are straight-forward, from which one can find a simple fornula to calculate the triangle areas. This can be represented as

$$S_{\Delta ABC} = \sqrt{3}\begin{vmatrix} x_1^A & x_2^A & x_3^A \\ x_1^B & x_2^B & x_3^B \\ x_1^C & x_2^C & x_3^C \end{vmatrix}/4 = \sqrt{3}\begin{vmatrix} x_1^O & 1-x_1^O & 0 \\ 0 & x_2^O & 1-x_2^O \\ 1-x_3^O & 0 & x_3^O \end{vmatrix}/4 = \sqrt{3}(x_1^O x_2^O + x_2^O x_3^O + x_3^O x_1^O)/4 \quad (9)$$

$$S_{\Delta OBC} = \sqrt{3}\begin{vmatrix} x_1^O & x_2^O & x_3^O \\ x_1^B & x_2^B & x_3^B \\ x_1^C & x_2^C & x_3^C \end{vmatrix}/4 = \sqrt{3}\begin{vmatrix} x_1^O & x_2^O & x_3^O \\ 0 & x_2^O & 1-x_2^O \\ 1-x_3^O & 0 & x_3^O \end{vmatrix}/4 = \sqrt{3}x_1^O x_2^O/4 \quad (10)$$

$$S_{\Delta OCA} = \sqrt{3}\begin{vmatrix} x_1^O & x_2^O & x_3^O \\ x_1^C & x_2^C & x_3^C \\ x_1^A & x_2^A & x_3^A \end{vmatrix}/4 = \sqrt{3}\begin{vmatrix} x_1^O & x_2^O & x_3^O \\ 1-x_3^O & 0 & x_3^O \\ x_1^O & 1-x_1^O & 0 \end{vmatrix}/4 = \sqrt{3}x_2^O x_3^O/4 \quad (11)$$

$$S_{\Delta OAB} = \sqrt{3}\begin{vmatrix} x_1^O & x_2^O & x_3^O \\ x_1^A & x_2^A & x_3^A \\ x_1^B & x_2^B & x_3^B \end{vmatrix}/4 = \sqrt{3}\begin{vmatrix} x_1^O & x_2^O & x_3^O \\ x_1^O & 1-x_1^O & 0 \\ 0 & x_2^O & 1-x_2^O \end{vmatrix}/4 = \sqrt{3}x_3^O x_1^O/4 \quad (12)$$

Thus the probability weight will be reduced to:

$$W_{A'} = x_1^O x_2^O /(x_1^O x_2^O + x_2^O x_3^O + x_3^O x_1^O) \quad (13)$$

$$W_{B'} = x_2^O x_3^O /(x_1^O x_2^O + x_2^O x_3^O + x_3^O x_1^O) \quad (14)$$

$$W_{C'} = x_3^O x_1^O /(x_1^O x_2^O + x_2^O x_3^O + x_3^O x_1^O) \quad (15)$$

As we discussed in the previous section, there are two methods used for calculating the physico-chemical properties in the mass triangle model: one is based on the actual property and the other is on the excess property. Comparing the results in **Figs. 4** and **5**, it can be seen that the two methods have very similar tendency for both surface tension and density of this system at 1473K, though there is still a slight difference with respect to the absolute values. Surface tension increases with the increase of Ni_3S_2 content, and decreases with the addition of FeS. In view of the fact that only one ternary system has been tried in the present work, however, it is hard to judge which kind of boundary data, excess or actual property will be more appropriate for such calculations in general. Considering only the simplicity of calculation, the actual property boundary will definitely be advantageous in data treatment.

There are two methods that can be used to calculate the physicochemical properties for a solution: these are the general geometrical model /16-17/ and the mass triangle model /18/. It has already been found that the former is suitable for the solution with completely homogenous area, while the latter is suitable for a solution with a limited solubility. Our calculation in this paper shows that the mass triangle model is working very well even for the calculation of surface tension and density in the Ni_3S_2-FeS-Cu_2S system, which exhibits a complete solution in liquid phase at 1473K. Thus, the mass triangle approach provides a generalized approach towards the computation of thermophysical properties of ternary and higher order system.

5. CONCLUSION

It has earlier been proved that the mass triangle model had been successfully used to treat the calculation of properties in the system with a limited solubility area. In this paper, we have further proved the possibility of extending this method to ternary system where the whole system is homogeneous. The application of the mass triangle model to the calculation of surface tension of the Ni_3S_2-FeS-Cu_2S mattes at 1473K showed that this method can obtain good results in comparison with the experimental data.

ACKNOWLEDGEMENTS

The authors would like to express their thanks to Chinese National Science Foundation for their kind financial support under contracts No: 50774004 (NSFC)

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