Application of general solution model in estimating thermodynamic and other physical properties of multicomponent metal systems

Dragana Živković[a#], Živan Živković[a] and Kuo Chih Chou[b]

[a] University of Belgrade, Technical Faculty, Bor, Serbia

[b] University of Science and Technology Beijing, Department of Physical Chemistry, Beijing, China

Abstract: The application of general solution model in estimating thermodynamic and other physical properties (viscosities, surface tension, density i.e.) of multi-component metallic systems are presented in this paper based on different examples. The agreement between the calculated and experimental data indicates to successful use of mentioned model in predicting thermodynamic and other physical properties of multicomponent systems.

Keywords: general solution model, calculation, thermodynamics, physical properties, multicomponent systems

1. Introduction

Current models used to predict ternary thermodynamic properties from binaries [1-4] assume that the selected binary compositions in a ternary model are independent of ternary considered. As a result, it requires human interference for selecting models and arranging components to three apexes of a triangle, and lead to a result unacceptable in some limiting cases.

On the basis of a reasonable assumption, that the selected binary compositions are closely related to the ternary itself, a general solution model has been suggested [5-8], being more reasonable in theoretic point of view, more reliable in practical application and more realistic to use in computerized thermodynamic and physical properties, as well as phase diagram calculation.

The application of general solution model in estimating thermodynamic and other physical properties in the case of ternary metal systems - viscosities, surface tension, density, i.e., are presented in this paper based on literature relevant examples.

2. Theoretical fundamentals

According to Hillert [1], several traditional methods, representing the ternary thermodynamic properties based on three corresponding binary systems, are classified into two categories: symmetrical – Kohler [2], Muggianu [3], and asymmetrical – Toop [4], Hillert [1].

Beside these traditional methods, a general solution model has been provided [5,6], breaking down the boundary between symmetrical and asymmetrical models.

The basic equations of this model are given as follows [5,6]:

$$\Delta Z^E = x_1x_2\,(A^o{}_{12} + A^1{}_{12}\,(x_1\text{-}x_2) + A^2{}_{12}\,(x_1\text{-}x_2)^2) + x_2x_3\,(A^o{}_{23} + A^1{}_{23}\,(x_2\text{-}x_3) + A^2{}_{23}\,(x_2\text{-}x_3)^2) + x_3x_1\,(A^o{}_{31} + A^1{}_{31}\,(x_3\text{-}x_1) + A^2{}_{31}\,(x_3\text{-}x_1)^2) + f x_1x_2x_3 \quad \text{... (1)}$$

where A^{o}_{ij}, A^{1}_{ij}, A^{2}_{ij} are parameters for binary system "ij", independent of composition, only relying on temperature, which have been used in the regular type equation:

$$\Delta Z^{E}_{ij} = X_i X_j [A^{o}_{ij} + A^{1}_{ij} (X_i - X_j) + A^{2}_{ij} (X_i - X_j)^2 + ... + A^{n}_{ij} (X_i - X_j)^2] \quad ... (2)$$

where X_i and X_j indicate the mole fraction of component “i” and “j” in “ij” binary system. The function *f* is the ternary interaction coefficient expressed by

$$f = (2\xi_{12} -1)\{A^{2}_{12} [(2\xi_{12} -1)x_3 + 2(x_1-x_2)] + A^{1}_{12}\} + (2\xi_{23} -1)\{A^{2}_{23} [(2\xi_{23} -1)x_1 + 2(x_2-x_3)] + A^{1}_{23}\} + (2\xi_{31} -1)\{A^{2}_{31} [(2\xi_{31} -1)x_2 + 2(x_3-x_1)] + A^{1}_{31}\} , \quad ... (3)$$

where ξ_{ij} are the similarity coefficients defined by η_i called the deviation sum of squares:

$$\xi_{ij} = \eta_i / (\eta_i + \eta_j) \quad ... (4)$$

where

$$\eta_I = \int_{X_i=0}^{X_i=1} (\Delta Z^{E}_{12} - \Delta Z^{E}_{13})^2 dX_1$$

$$\eta_{II} = \int_{X_i=0}^{X_i=1} (\Delta Z^{E}_{21} - \Delta Z^{E}_{23})^2 dX_2$$

$$\eta_{III} = \int_{X_i=0}^{X_i=1} (\Delta Z^{E}_{31} - \Delta Z^{E}_{32})^2 dX_3 \quad , \quad ... (5)$$

and

$$X_{1(12)} = x_1 + x_3\xi_{12}$$

$$X_{2(23)} = x_2 + x_1\xi_{23}$$

$$X_{3(31)} = x_3 + x_2\xi_{31} \quad . \quad ... (6)$$

In all given equations, ΔZ^{E} and ΔZ^{E}_{ij} correspond to the integral molar excess property for ternary and binary systems, respectively, while x_1, x_2, x_3 correspond to the mole fraction of components in investigated ternary system.

3. Results and Discussion

General solution model (GSM) has been applied many times for predicting thermodynamic and physical properties of different ternary systems. Some of characteristic cases will be collected in this paper – according to thermodynamic properties and for physical properties, separately.

3.1. Thermodynamic properties predicted by GSM

Some examples from literature [9-14] are shown in order to present successful application of general solution model in thermodynamic properties predicting.

In the frame of investigation of Bi–Cu–Sn alloys thermodynamics [9], comparison between the results obtained experimentally [10] and predicted by GSM was given, as shown in Fig.1.

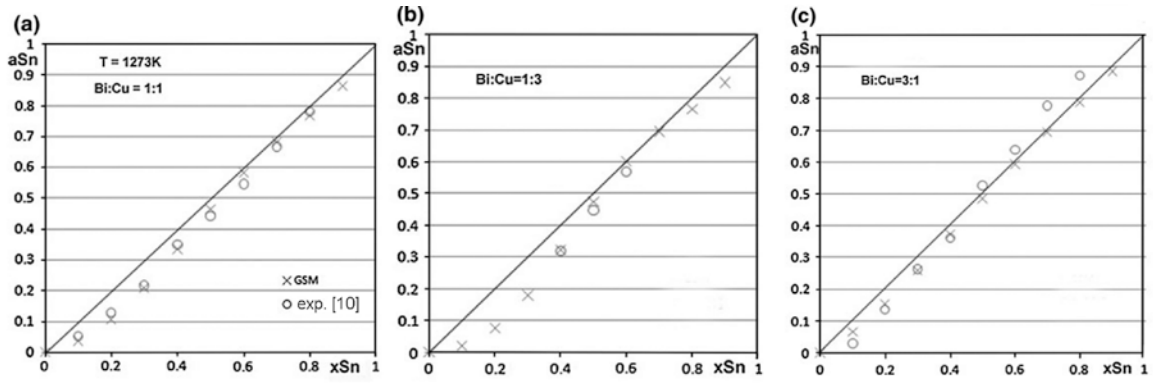

Fig.1. Comparison between tin activities in Bi-Cu-Sn system obtained experimentally [10] and predicted by GSM (taken from Ref.[9])

According to [11], thermodynamic calculation of Zn–Al–Ga system was performed parallel with calorimetric investigations and the results were compared, as shown in Fig.2. The results of thermodynamic study of Ag-In-Sn system [12], with comparative review of experimental data and calculation by different predicting methods, are presented in Fig.3.

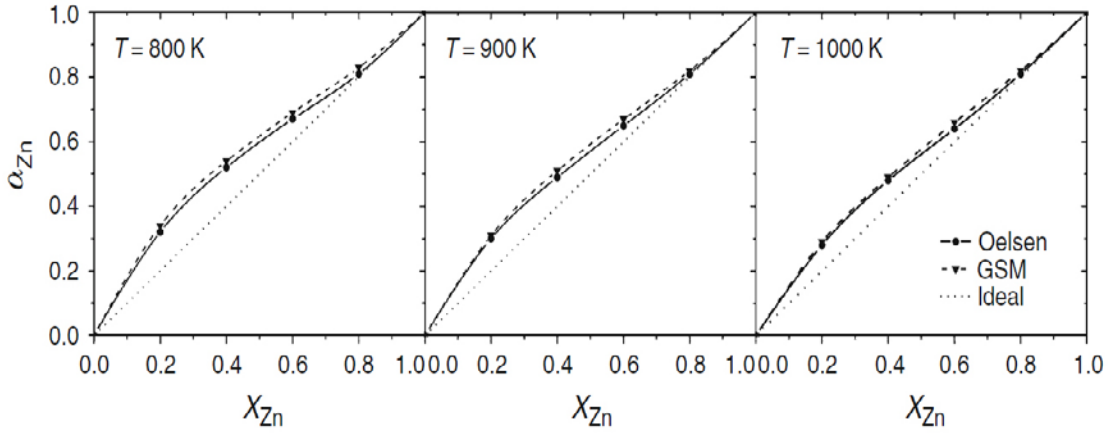

Fig.2. Comparison between zinc activities in Zn-Al-Ga system obtained experimentally and predicted by GSM (taken from Ref.[11])

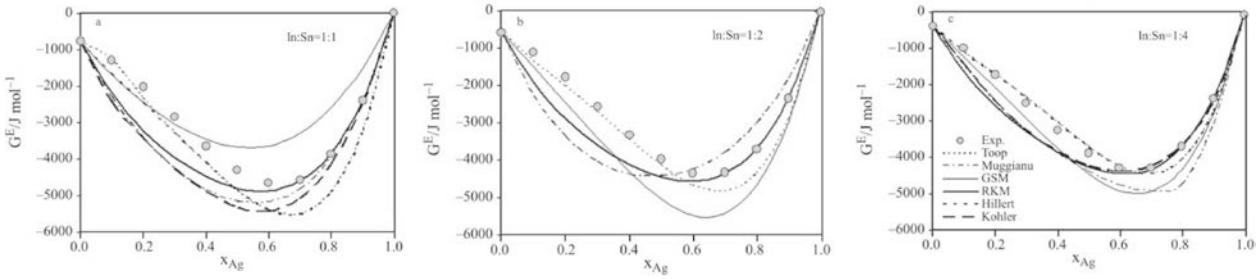

Fig.3. Comparison between integral molar Gibbs energies in Ag-In-Sn system obtained experimentally [13] and predicted by GSM and other geometric models (taken from Ref.[12])

The application of GSM was examined in [5], where experimentally obtained results [14] were compared with Bonnier and GSM predicting calculation, Fig.4.

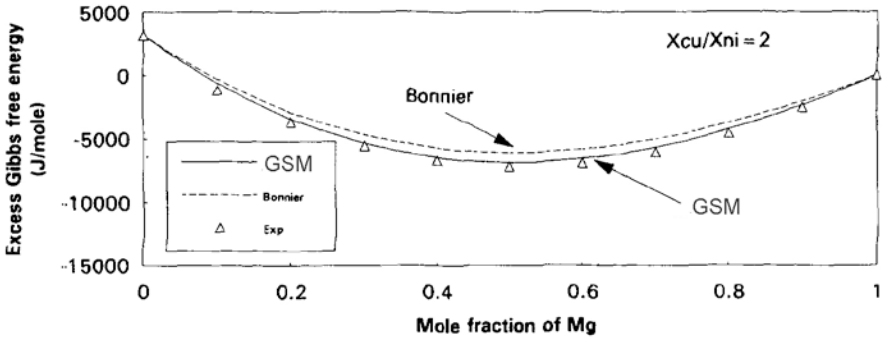

Fig.4. Comparison between integral molar Gibbs energies in Cu-Mg-Ni system obtained experimentally [14] and predicted by GSM and Bonnier model (taken from Ref.[5])

As can be seen from given literature examples [5,9,11,12], there is an excellent agreement between thermodynamic quantities obtained by different experimental methods and predicted values by general solution model. When different thermodynamic predicting methods are used, general solution model shows best agreement with experiments, which is confirmed in additional relevant literature [15-18], also. That is due to the fact that general solution model can overcome the inherent defects for both current symmetrical and asymmetrical models, and therefore it can give reliable predicted data.

3.2. Physical properties predicting using GSM

General solution model is also used for predicting of physical properties, such as viscosities, surface tensions, molar volumes, based on known binary data for the subsystems included. The references [20-24] indicate to reliable prediction in these cases, too.

Surface tension determination using GSM [19,20] and comparison with experiments [21,22] are given for the examples from literature [19,20] in Figs.5 and 6, respectively.

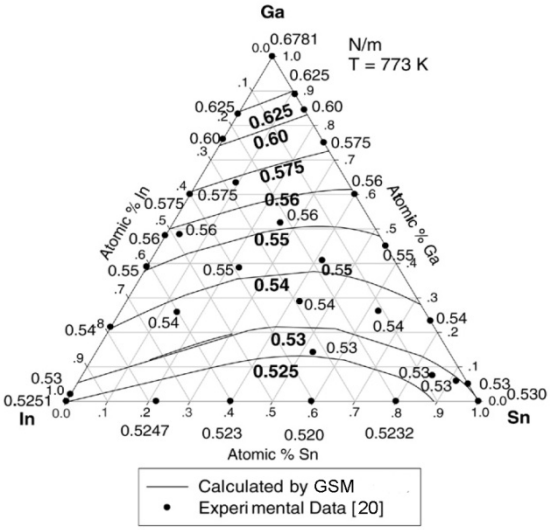

Fig.5. Comparison between surface tensions in Ga-In-Sn system obtained experimentally [20] and predicted by GSM model (taken from Ref.[19])

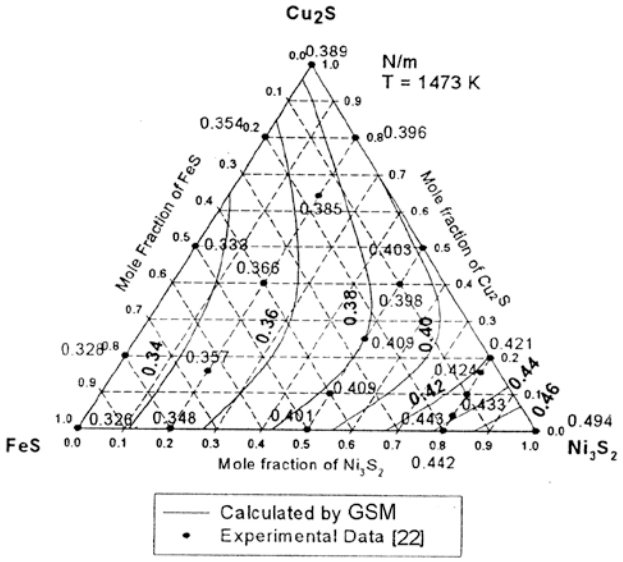

Fig.6. Comparison between surface tensions in Ga-In-Sn system obtained experimentally [22] and predicted by GSM model (taken from Ref.[21])

The viscosities of ternary Ag-Cu-Au liquid alloys were calculated using general solution model, also [7,23]. The comparison of such obtained data with experimental ones for Ag-Cu-Au [24], for the section with xAg:xCu=0.543, is shown in Fig.7. More, GSM application in predicting molar volumes of Ga-Bi-X (X = Sn, In) liquid alloys is given in Ref. [25], showing excellent agreement with available experimental data.

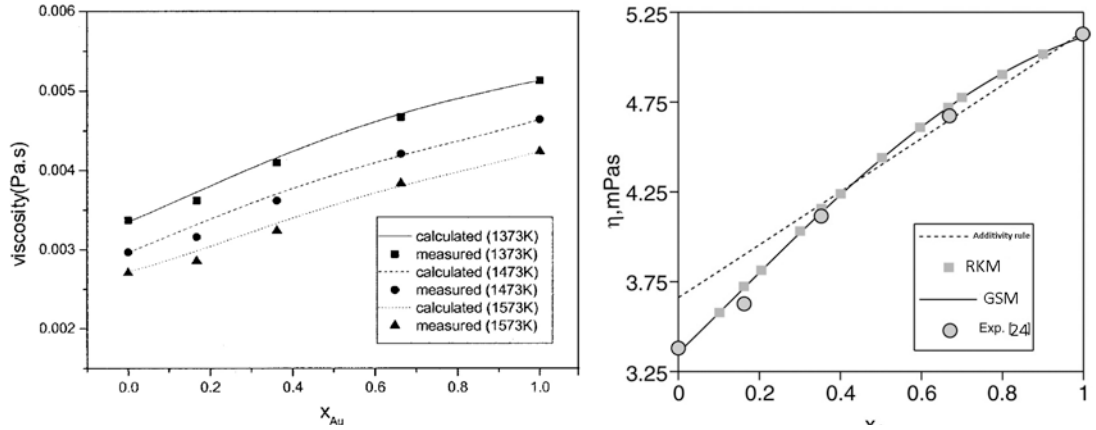

Fig.7. Comparison between visciosities in Ag-Cu-Au system obtained experimentally [24] and predicted by GSM model (taken from Refs.[7] – (a) and [23]- (b))

Similarly to thermodynamic predicting, general solution model has been already verified and approved as reliable one in many different cases, as presented. The lack of experimental data for these quantities, as well as simple and easy application of GSM, should be taken into account as the most important advantages among other well known models.

4. Conclusions

As can be seen from numerous examples presented in this paper, general solution model has been proved in practical examples as the correct and accurate model for predicting thermodynamic and physical properties of ternary systems. Important advantage of this model is its simplicity comparing to other kind of models, according to which only binary data for the subsystems are to be known. Also, general solution model can overcome the inherent defects for both current symmetrical and asymmetrical models, giving not only a more reliable data, but also making the computerization possible for estimating thermodynamic properties and calculating phase diagrams - especially for ternary and, also, other multicomponent systems.

Acknowledgement

The authors from Serbia are grateful to the Ministry of Education and Science of the Republic of Serbia for support under Project $N^0$172037.

References

[1] M. Hillert, *Calphad*, 4 (1980) 1.
[2] F. Kohler, *Monatsh.Chem*., 91 (1960) 738.
[3] Y. M. Muggianu, M. Gambino, J. P. Bross, *J.Chimie Physique*, 72 (1975) 83.
[4] G. W. Toop, *Trans.Met.Soc. AIME*, 233 (1965) 850.
[5] K. C. Chou, *Calphad*, 19(3) (1995) 315.

[6] K. C. Chou, W. C. Li, F. Li, M. He, *Calphad*, 20 (1996) 395.

[7] X.M. Zhong, Y.H. Liu, K.C. Chou, X.G. Lu, D. Živković, Ž. Živković, *Journal of Phase Equilibria*, 24 (1) (2003) 7.

[8] G.H. Zhang, K.C. Chou, *Journal of Solution Chemistry*, 39 (2010) 1200.

[9] D. Živković, D. Minić, D. Manasijević, N. Talijan, I. Katayama, A. Kostov, *Mater Sci: Mater Electron*, 22 (2011) 1130.

[10] M. Kopyto, G. Garzel, L. Zabdyr, *J. Min. Metall. Sect. B-Metall*, 45(1) (2009) 95.

[11] Lj.Balanović, D. Živković, A. Mitovski, D. Manasijević, Ž. Živković, *J Therm Anal Calorim*, 103 (2011) 1055.

[12] D. Živković, A. Milosavljević, A. Mitovski, B. Marjanović, *Journal of Thermal Analysis and Calorimetry*, 89 (1) (2007) 137.

[13] T. Miki, N. Ogawa, T. Nagasaka and M. Hino, Mater., Trans. JIM, 42 (2001) 732.

[14] T. Gnanasekaran, H. Ipser, *Metallurgical and Materials Transactions B*, 25B (1994) 67.

[15] G.Klančnik, J.Medved, *Materiali in Tehnologije*, 45 (4) (2011) 317.

[16] N.Milcheva, J. Romanowska, G. Vassilev, *Central European Journal of Chemistry*, 9 (1) (2011) 149.

[17] I.Katayama, D. Živković, R. Novaković, H. Yamashita, *International Journal of Materials Research*, 99 (12) (2008) 1330.

[18] S.Knott, Z.Li, A.Mikula, *Thermochimica Acta***,** 470 (1-2) (2008) 12.

[19] L. Yan, S. Zheng, G. Ding, G. Xu, Z. Qiao, *Calphad*, 31 (2007) 112.

[20] Z. Qiao, L. Yan, Z. Cao, Y. Xie, *Journal of Alloys and Compounds*, 325 (2001) 180.

[21] Kh.I. Ibragimov, R.Kh. Dadashev, S.M. Yushaev, *Poverkh. Natya.Plotno. Troin. Metall. Sistem. V. Ki: Teploprov. Diffuz. Tekhnol.*, Prots.Riga. Rizhsk. Politekhn. Int-t. (1977) pp. 29.

[22] M. Kucharski, S.W. Ip, J.M. Toguri, *Can. Metallurgical Q.*, 33 (3) (1994) 197.

[23] D. Živković, D. Manasijević, *Calphad*, 29 (2005) 312–316.

[24] E. Gebhardt, G. Worwag, *Z. Metallkd.*, 43 (1952) 106.

[25] D. Živković, R. Novaković, I. Katayama, D. Manasijević, *International Journal of Materials Research***,** 101 (11) (2010) 1432.