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A metallic solution model with adjustable parameter for describing ternary thermodynamic properties from its binary constituents

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Abstract

A metallic solution model with adjustable parameter k has been developed to predict thermodynamic properties of ternary systems from those of its constituent three binaries. In the present model, the excess Gibbs free energy for a ternary mixture is expressed as a weighted probability sum of those of binaries and the k value is determined based on an assumption that the ternary interaction generally strengthens the mixing effects for metallic solutions with weak interaction, making the Gibbs free energy of mixing of the ternary system more negative than that before considering the interaction. This point is never considered in the models currently reported, where the only difference in a geometrical definition of molar values of components is considered that do not involve thermodynamic principles but are completely empirical. The current model describes the results of experiments very well, and by adjusting the k value also agrees with those from models used widely in the literature. Three ternary systems, Mg–Cu–Ni, Zn–In–Cd, and Cd–Bi–Pb are recalculated to demonstrate the method of determining k and the precision of the model. The results of the calculations, especially those in Mg–Cu–Ni system, are better than those predicted by the current models in the literature.

Keywords: Thermodynamics; Ternary metallic solution; Excess Gibbs free energy; Solution model

1. Introduction

Predictions of the thermodynamic properties of ternary and multi-component alloys from their binary constituents based on models are very important in materials design and analysis in process metallurgy. Since the 1960s, dozens of models, which are used to calculate the thermodynamic properties, have been proposed. Among these are models by Kohler [1], Bonnier [2], Toop [3], Colinet [4], Muggianu [5], Hillert [6], Chou [7], *etc.* that are widely used. The difference between these models lies only in a geometrical definition of values of mole fraction x_i (geometric representation), which does not involve thermodynamic principles, therefore being completely empirical. In the current paper, a new model with an adjustable parameter will be derived to allow prediction of thermodynamic properties of ternary systems from its sub-binary components.

According to the regular solution model, the excess Gibbs free energy, G'^{E}, for a ternary can be expressed as the sum of those of the three sub-binary systems as follows

$$G'^{E} = G^{E}(12) + G^{E}(31) + G^{E}(23), \tag{1}$$

where $G^{E}(ij)$ is the excess Gibbs free energy of the i–j binary systems. Andersson [8] has also obtained the similar expression as equation (1) based on an assumption that

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the metallic elements can substitute for each other without any limitations in the liquid phase. It is shown that equation (1) can be used to describe approximately the properties of a ternary system from its three binary components. It can also be seen from equation (1) that each of the three sub-binary systems contributes equally to the excess Gibbs free energy, G^{E}. Actually, the contribution of each sub-binary to the ternary differs depending on the composition of the components. Perhaps, this is the reason why the traditional model cannot describe some ternary systems well. When the differing composition of the three binary systems is considered, equation (1) changes to

$$G^{E} = [1 + (m-k)x_3/3]G^{E}(12) + [1 + (n-k)x_2/3]G^{E}(31) + [1 + kx_1/3]G^{E}(23), \quad (2)$$

where $(m+n) = 3+k$ and $m/n = x_2/x_3$. The values of m and n depend on the adjustable parameter k or the k value changes with x_2/x_3. When k is designated, m and n can be determined. Equation (2) is called the adjustable parameter solution model.

It should be noted that the mole fractions x_i (ij) [or $x_j(ij)$] of the i–j binary system in the $G^{E}(ij)$ expression are used directly as those of the calculated ternary and they do not geometrically convert between the ternary system and its sub-binary systems when applying $G^{E}(ij)$ to equation (2). Compared with the conversion of mole fractions, this method is without the obvious errors.

In some previous models, an interaction parameter for the ternary, ω_{123}, is sometimes attached to equation (1) in order to perfect the expression, but ω_{123} needs be determined from experimental data for the ternary system. As a result, these models cannot be used for predicting the properties of the ternary system completely based on the properties of the binaries. In the present model, the excess Gibbs free energy for the ternary is expressed as a weighted probability sum from the binary components, that is, G^{E} can be determined based only on the properties of three sub-binary systems. Therefore, equation (2) can be used for predicting the properties of the ternary system entirely from those of its binary systems.

According to thermodynamic relationships [9] and by differentiation of equation (2) with respect to mole fraction keeping the ratio m/n (or m and n) and k constant, we obtain the partial excess molar Gibbs free energies of the given component of the system from the integral excess Gibbs free energies as follows

$$\begin{aligned} G_1^{E} =& G^{E} + (x_2+x_3)G^{E}(23)k/3 - [x_2(\partial G^{E}(23)/\partial x_2)_{x_3} + \\ & x_3(\partial G^{E}(23)/\partial x_3)_{x_2}][1 + kx_1/3] - \\ & [x_2(\partial G^{E}(12)/\partial x_2)_{x_3} + x_3(\partial G^{E}(12)/\partial x_3)_{x_2}][1 + \\ & (m-k)x_3/3] - [x_2(\partial G^{E}(31)/\partial x_2)_{x_3} + \\ & x_3(\partial G^{E}(31)/\partial x_3)_{x_2}][1 + (n-k)x_2/3] - \\ & x_2[G^{E}(31)(n-k)/3] - x_3[G^{E}(12)(m-k)/3]. \end{aligned} \quad (3a)$$

The corresponding G_2^{E} and G_3^{E} are as follows

$$\begin{aligned} G_2^{E} =& G^{E} - x_1G^{E}(23)k/3 + [(1-x_2)(\partial G^{E}(23)/\partial x_2)_{x_3} - \\ & x_3(\partial G^{E}(23)/\partial x_3)_{x_2}][1 + kx_1/3] + \\ & [(1-x_2)(\partial G^{E}(12)/\partial x_2)_{x_3} - x_3(\partial G^{E}(12)/\partial x_3)_{x_2}] \\ & [1 + (m-k)x_3/3] + [(1-x_2)(\partial G^{E}(31)/\partial x_2)_{x_3} - \\ & x_3(\partial G^{E}(31)/\partial x_3)_{x_2}][1 + (n-k)x_2/3] + \\ & (1-x_2)[G^{E}(31)(n-k)/3] - x_3[G^{E}(12)(m-k)/3], \end{aligned} \quad (3b)$$

$$\begin{aligned} G_3^{E} =& G^{E} - x_1G^{E}(23)k/3 + [-x_2(\partial G^{E}(23)/\partial x_2)_{x_3} + \\ & (1+x_3)(\partial G^{E}(23)/\partial x_3)_{x_2}][1 + kx_1/3] + \\ & [-x_2(\partial G^{E}(12)/\partial x_2)_{x_3} + (1+x_3)(\partial G^{E}(12)/\partial x_3)_{x_2}] \\ & [1 + (m-k)x_3/3] + [-x_2(\partial G^{E}(31)/\partial x_2)_{x_3} + \\ & (1+x_3)(\partial G^{E}(31)/\partial x_3)_{x_2}][1 + (n-k)x_2/3] - \\ & x_2[G^{E}(31)(n-k)/3] + (1-x_3)[G^{E}(12)(m-k)/3]. \end{aligned} \quad (3c)$$

2. Adjustable parameter

A large number of calculated ternary systems shows that the model (2) can describe the results of experiments very well by adjusting the k value. For example, for the Mg(1)–Cu(2)–Ni(3) ternary system, the model gives a set of the excess Gibbs free energies G^{E} (ij) in $J \cdot mol^{-1}$ for the three binary systems {Mg(1)–Cu(2)}, {Cu(2)–Ni(3)} and {Ni(3)–Mg(1)}, at $T = 1173$ K [7] as follows

$$G^{E}(12) = x_1x_2\{-31152.72 + 8415.79(x_1 - x_2)\}, \quad (4a)$$

$$G^{E}(23) = x_2x_3\{14301.57 - 791.97(x_2 - x_3) + 999.65(x_2 - x_3)^2\}, \quad (4b)$$

$$G^{E}(31) = -29709.64x_3x_1. \quad (4c)$$

Using equation (2) and assuming $x_2/x_3 = 1$, we can obtain a group of G^{E} curves for the ternary system with different k values, as shown in figure 1, where it can be seen

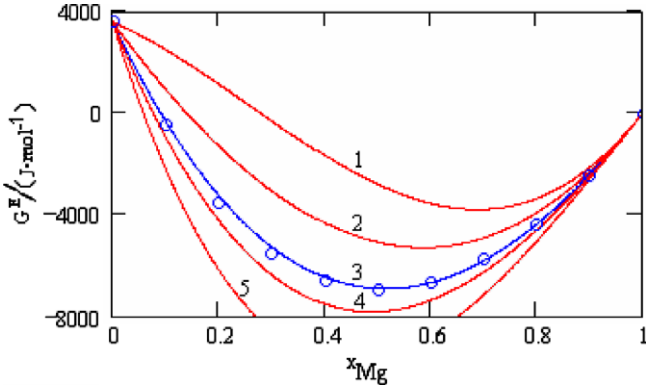

FIGURE 1. Plot of G^{E} against mole fraction magnesium for the Mg–Cu–Ni system with $x_2/x_3 = 1$ as a function of parameter k; ——, present model with different values of k: curve 1 for $k = 10$, 2 for $k = 5$, 3 for $k = 1$, 4 for $k = -1$ and 5 for $k = -5$; and o, experimental points [10].