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A General "Geometric" Thermodynamic Model for Multicomponent Solutions

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Abstract. Several "geometric" models have been proposed for estimating thermodynamic properties of a ternary solution from optimized data for its binary subsystems. The most common are the Kohler, Muggianu, Kohler/Toop, and Muggianu/Toop models. The latter two are "asymmetric" in that one component is singled out, whereas the first two are "symmetric". The use of a symmetric model when an asymmetric model is more appropriate can often give rise to errors. There are 64 possible simple geometric models for a ternary system. Equations are developed to calculate the thermodynamic properties of an *N*-component solution (*N*>3) in a rational manner while permitting complete flexibility to choose any of the 64 possible geometric models for any ternary subsystem. An improved general functional form for "ternary terms" in the excess Gibbs energy expression is also proposed.

Introduction

Over thirty years ago, Larry Kaufman introduced the use of "geometric" models to CALPHAD. This article presents a generalization of this concept.

The molar excess Gibbs energy of a binary system with components 1 and 2 is often expressed as:

$$g_{12}^{E} = \alpha_{12} X_1 X_1 \qquad (1)$$

where X_1 and X_2 are the mole fractions and α_{12} is a parameter which, under the assumptions of regular solution theory, is equal to the energy of forming two moles of (1-2) nearest-neighbor pairs according to:

$$(1-1)+(2-2) = 2(1+2) \qquad (2)$$

where (i - j) represents a first-nearest-neighbor pair.

The term α_{12} is often expanded as a polynomial in the mole fractions:

$$\alpha_{12} = \sum_{i\geq 0} \sum_{j\geq 0} q_{12}^{ij} X_1^i X_2^j \qquad (3)$$

where the q_{12}^{ij} are empirical coefficients which may be temperature dependent. Eq (3) is frequently re-arranged into "Redlich-Kister" form:

$$\alpha_{12} = \sum_{i\geq 0}^{i} L_{12} \left(X_1 - X_2\right)^i \qquad (4)$$

This is done because the coefficients ${}^{i}L_{12}$ tend to be less strongly correlated than the coefficients q_{12}^{ij}. Clearly the set of coefficients q_{12}^{ij} can be calculated from the set of ${}^{i}L_{12}$ and vice versa.

For ternary systems, several "geometric" models may be proposed. Some of these are illustrated in Fig 1. In each model, g^E in the ternary solution at a composition point p is estimated from the excess Gibbs energies in the three binary subsystems at points *a*, *b* and *c* by the equation:

$$g^E = X_1X_2\alpha_{12(a)} + X_2X_3\alpha_{23(b)} + X_3X_1\alpha_{31(c)} + (\textit{ternary terms}) \qquad (5)$$

where $\alpha_{12(a)}$, $\alpha_{23(b)}$ and $\alpha_{31(c)}$ are the binary "α-functions" evaluated at points *a* , *b* and c. The "ternary terms" are polynomial terms which are identically zero in the three binary subsystems. The empirical coefficients of these ternary terms may be chosen in order to fit ternary experimental data. However, these ternary coefficients should be small. That is, Eq (5) with no ternary terms should provide a reasonable first estimate of g^E in the ternary solution.

If, at a given temperature, all three binary α-functions are constant, independent of composition, then all geometric models are clearly identical. The Kohler [1] and Muggianu [2] models in Figs 1a and 1c are "symmetric" models, whereas the Kohler/Toop [3] and Muggianu/Toop [4] models in Figs 1b and 1d are "asymmetric" models inasmuch as one component (component 1 in Figs 1b and 1d) is singled out. In these two asymmetric models, α_{12} and α_{31} are assumed to be constant along lines where X_1 is constant. That is, replacing component 2 by component 3 is assumed to have no effect on the energy, α_{12} , of forming (1-2) nearest-neighbor pairs as in Eq (2), and similarly for (3-1) pairs. An asymmetric model is thus more physically reasonable than a symmetric model if components 2 and 3 are chemically similar while component 1 is chemically different, as for example in the systems SiO_2-CaO-MgO, S-Fe-Cu, Na-Au-Ag, $AlCl_3$-NaCl-KCl, etc. (where the asymmetric component has been written first in each example).

When g^E is large and α_{12} and α_{31} depend strongly upon composition, a symmetric and an asymmetric model will give very different results. As an example, consider a solution with $\alpha_{12} = \alpha_{31} = -50(1-X_1)$ kJ/mol and $\alpha_{23} = 0$. That is, the binary solutions 1-2 and 3-1 have identical properties and the 2-3 solution is ideal. Clearly, one would expect g^E in the ternary system to be nearly constant at constant X_1 as is predicted by the asymmetric models. However, when the symmetric Kohler model is applied to this solution, an obviously incorrect region of immiscibility is calculated as shown in Fig. 2. Similar incorrect results are obtained with the symmetric Muggianu model.

Therefore, we disagree with the current tendency to use the symmetric Muggianu model for nearly all solutions. In many systems, an asymmetric model is more appropriate and can result in very different ternary Gibbs energy functions.

As well as the four models illustrated in Figs 1a to 1d, many other geometric models might be proposed. Two of these are shown in Figs. 1e and 1f. In general, rather than speaking of a model for a ternary 1-2-3 system, we should instead define the approximation used for each of the three α_{ij} functions. For example, in Figs 1e and 1f a "Kohler type" approximation is used for α_{23} and a "Muggianu-type" approximation is used for α_{31}. For α_{12}, a "Toop-type" approximation along lines of constant X_1 is used in Fig. 1e, while a "Toop-type" approximation along lines of constant X_2 is used in Fig. 1f. Since each function α_{ij} can be approximated in four different ways, there are 64 such possible geometric ternary models. However, probably only the four models in Figs 1a to 1d are of practical importance.

Suppose that data for the three binary subsystems of a ternary system have been optimized to give binary coefficients q_{mn}^{ij} of Eq (3) or ${}^{i}L_{mn}$ of Eq (4) and that we wish to estimate g^E in the ternary solution by means of Eq (5) having chosen which type of approximation we wish to use for each of the three α_{ij} functions.

Suppose, for example that we have chosen to use a Kohler-type approximation for α_{12} as in Fig. 1a. Along the line *ap* in Fig. 1a, the ratio $X_2/(X_1+X_2)$ is constant. Furthermore, this ratio is equal to X_2 at point *a* where $(X_1+X_2)=1$. Therefore, the function $\alpha_{12(a)}$ in Eq (5) can be written:

$$\alpha_{12(a)} = \sum_{i\geq 0}\sum_{j\geq 0} q_{12}^{ij}\left(\frac{X_1}{X_1+X_2}\right)^i\left(\frac{X_2}{X_1+X_2}\right)^j \tag{6}$$

where the q_{12}^{ij} are the binary coefficients of Eq. (3). Alternatively, if the 1-2 binary system was optimized with a Redlich-Kister expansion, then $\alpha_{12(a)}$ in Eq (5) is written:

$$\alpha_{12(a)} = \sum_{i\geq 0} {}^{i}L_{12}\left(\frac{X_1-X_2}{X_1+X_2}\right)^i \tag{7}$$

where the ${}^{i}L_{12}$ are the binary coefficients of Eq. (4). That is, $\alpha_{12(a)}$, as given in Eq (6) or (7), is constant along the line *ap* in Fig 1a. Similarly, if we have chosen to use Kohler-type approximations for α_{23} and α_{31}, then these would be written in terms of the ratios $X_3/(X_2+X_3)$ and $X_3/(X_3+X_1)$ respectively.

Suppose instead that we have chosen to approximate α_{12} by a Toop-type approximation along lines of constant X_1 as in Figs 1b, 1d and 1e. In this case, $\alpha_{12(a)}$ is set constant along these lines of constant X_1 by means of the substitution:

$$\alpha_{12(a)} = \sum_{i\geq 0}\sum_{j\geq 0} q_{12}^{ij}\, X_1^i\,(1-X_1)^j \tag{8}$$

$$\text{or}\quad \alpha_{12(a)} = \sum_{i\geq 0} {}^{i}L_{12}\left(X_1-(1-X_1)\right)^i = \sum_{i\geq 0} {}^{i}L_{12}\,(2X_1-1)^i \tag{9}$$

Finally, suppose that we have chosen to approximate α_{12} by a Muggianu-type approximation as in Fig. 1c. We note that (X_1-X_2) is constant along the line *ap* in Fig. 1c. Hence, if α_{12} in the binary system has been expressed by a Redlich-Kister polynomial as in Eq (4) then, as was pointed out by Hillert [4], Eq (4) can be substituted directly into Eq (5) with no change. Because of this particularly simple substitution, the Muggianu model is sometimes referred to as the "Muggianu-Redlich-Kister model". However, this is a misnomer. The use of the Muggianu model does not require that the binary α-functions be expressed as Redlich-Kister polynomials. If α_{12} is expressed as a general polynomial as in Eq (3), then we note that the functions $(1+X_1-X_2)/2$ and $(1-X_1+X_2)/2$ are both constant along the line *ap* in Fig. 1c, and that these are equal to X_1 and X_2 respectively in the 1-2 binary system. Hence, in order that $\alpha_{12(a)}$ be constant along the line *ap* we make the substitution:

$$\alpha_{12(a)} = \sum_{i\geq 0}\sum_{j\geq 0} q_{12}^{ij}\left(\frac{1+X_1-X_2}{2}\right)^i\left(\frac{1-X_1+X_2}{2}\right)^j \tag{10}$$

Conversely, the use of the Kohler or Kohler/Toop models does not preclude expressing the binary α-functions as Redlich-Kister polynomials, as has just been shown in Eqs (7) and (9). Hence, the choice between using the Kohler or Muggianu approximations is not related to the use of Redlich-Kister polynomials.

Extension to Multicomponent Solutions

A database for a multicomponent solution of $N > 3$ components is developed by first evaluating/optimizing available data for the binary subsystems to obtain binary coefficients of Eqs (3) or (4). Next, an appropriate geometrical model is chosen for each ternary subsystem and, if ternary experimental data are available, ternary terms are included in Eq (5) and their coefficients are determined by optimization.
Before these coefficients can be used to estimate properties of the N-component system however, a rational method of extending the Kohler, Muggianu and Toop approximations to multicomponent solutions must be devised. The equations must reduce to the model equations chosen for each of the ternary subsystems, and should be completely flexible in permitting any one of the 64 possible geometric models to be chosen for any one of the ternary subsystems.

In our own database development work, we tend to shun the Muggianu approximation, for reasons discussed in our earlier publication [5]. Hence, we mainly use either the Kohler (Fig. 1a) or Kohler/Toop (Fig. 1b) models. In our earlier publication [5] we developed a general method for extending these two models to N-component solutions. However, other researchers have evaluated and optimized many ternary systems using the Muggianu model, and we would like to be able to combine their coefficients for some ternary subsystems with our own coefficients for other ternary subsystems into one multicomponent database. Therefore, in the present publication we develop a general and completely flexible extension of the Kohler-Muggianu-Toop geometric formalism to N-component systems which permits each ternary subsystems to be treated by any of the 64 possible models. We begin with the binary α_{ij} functions. Ternary terms are discussed in a later section.

The method is best illustrated by means of an example. Consider a 5-component system in which a choice of models for the ternary subsystems has been made as illustrated in Fig. 3. For instance, the α_{12} function is given in the 1-2-3 system by a Toop-type approximation at constant X_2, in the 1-2-4 system by a Toop-type approximation at constant X_1 , and in the 1-2-5 system by a Kohler-type approximation..
We now define

$$\xi'_{ij} = X_i + \sum_k X_k \qquad (11)$$

where the summation is over all components k of *i-j-k* ternary solutions in which α_{ij} is given by a Toop-type approximation along lines of constant X_j. In the example of Fig. 3:

$$\begin{aligned}
\xi_{12} &= X_1 + X_3 & \xi_{21} &= X_2 + X_4 \\
\xi_{13} &= X_1 & \xi_{31} &= X_3 + X_4 \\
\xi_{14} &= X_1 & \xi_{41} &= X_4 + X_2 + X_3 + X_5 \\
\xi_{15} &= X_1 & \xi_{51} &= X_5 + X_4 \\
\xi_{23} &= X_2 & \xi_{32} &= X_3 + X_1 \\
\xi_{24} &= X_2 + X_3 & \xi_{42} &= X_4 \\
\xi_{25} &= X_2 & \xi_{52} &= X_5 \\
\xi_{34} &= X_3 & \xi_{43} &= X_4 + X_2 + X_5 \\
\xi_{35} &= X_3 + X_2 & \xi_{53} &= X_5 + X_4 \\
\xi_{45} &= X_4 & \xi_{54} &= X_5
\end{aligned} \qquad (12)$$

The significance of these variables is as follows. The choice of a Toop-type approximation for α_{12} in the 1-2-3 and 1-2-4 subsystems means that α_{12}, the energy of forming (1-2) nearest-neighbor pairs, is assumed to remain constant as component 1 is replaced by component 3 in the 1-2-3 ternary system and as component 2 is replaced by component 4 in the 1-2-4 system. Hence, in the multicomponent system it is reasonable to assume that α_{12} should remain constant at constant $\xi_{12} = (X_1 + X_3)$ and at constant $\xi_{21} = (X_2 + X_4)$ when all other mole fractions (X_5 in

this case) are held constant. Similarly, α_{31} should remain constant at constant $\xi_{13} = X_1$, and at constant $\xi_{31} = (X_3 + X_4)$ when X_2 and X_5 are held constant; and similarly for the other α_{ij} functions.

We see from Fig. 3 that in the 1-2-5 system α_{12} is given by a Kohler-type approximation. That is, α_{12} is constant along lines of constant ratio $X_2/(X_1 + X_2)$ in this subsystem. In the case of α_{23} , we see that this function is given by a Kohler-type approximation in both the 2-3-4 and 2-3-5 subsystems where α_{23} is constant along lines of constant ratio $X_3/(X_2 + X_3)$. For such functions α_{ij} which are given in all ternary subsystems by either Toop-type or Kohler-type (but never Muggianu-type) approximations, it is thus reasonable to approximate α_{ij} in the N-component system by replacing X_i and X_j in Eq (3) or Eq (4) by the functions $\xi_{ij}/(\xi_{ij} + \xi_{ji})$ and $\xi_{ji}/(\xi_{ij} + \xi_{ji})$ respectively. This reduces to the correct expressions for α_{12} and α_{23} in all ternary subsystems in Fig. 3 as can be verified by substitution of Eqs (12) into these functions.

The function α_{35} is given by a Muggianu-type approximation in the 1-3-5 system where it is constant along lines of constant $(X_3 - X_5)$. Similarly, α_{31} is given by a Muggianu-type approximation in the 1-2-3 and 1-3-5 systems where it is constant along lines of constant $(X_1 - X_3)$. For such functions α_{ij} which are given in all ternary subsystems by either Toop-type or Muggianu-type (but never Kohler-type) approximations, it is thus reasonable to approximate α_{ij} in the N-component system by replacing $(X_i - X_j)$ of Eq (4) by $(\xi_{ij} - \xi_{ji})$, or by replacing X_i and X_j of Eq (3) by $(1 + \xi_{ij} - \xi_{ji})/2$ and $(1 - \xi_{ij} + \xi_{ji})/2$ respectively. Again, this reduces to the correct expressions or α_{35} and α_{31} in all ternary subsystems.

Finally, for the general case of function such as α_{15} and α_{25} which may be given by Kohler-type, Muggianu-type and Toop-type approximations in the ternary subsystems, we first define

$$\sigma_{ij} = \sigma_{ji} = 1 - \sum_k X_k \qquad (13)$$

where the summation is over all components k of ternary subsystems *i-j-k* in which α_{ij} is given by a Kohler-type approximation. In the example of Fig. 3:

$$\begin{aligned}
\sigma_{12} &= 1 - X_5 & \sigma_{24} &= 1 - X_1 - X_5 \\
\sigma_{13} &= 1 & \sigma_{25} &= 1 - X_1 \\
\sigma_{14} &= 1 & \sigma_{34} &= 1 \\
\sigma_{15} &= 1 - X_2 & \sigma_{35} &= 1 \\
\sigma_{23} &= 1 - X_4 - X_5 & \sigma_{45} &= 1 - X_1 - X_3
\end{aligned} \qquad (14)$$

We then write α_{ij} by replacing X_i and X_j in Eq (3) by the functions $\left(1 + \frac{\xi_{ij} - \xi_{ji}}{\sigma_{ij}}\right)\Big/2$ and $\left(1 + \frac{\xi_{ji} - \xi_{ij}}{\sigma_{ij}}\right)\Big/2$ respectively, or by replacing $(X_i - X_j)$ of Eq (4) by $(\xi_{ij} - \xi_{ji})/\sigma_{ij}$.

That is, for the case of α_{12} :

$$\alpha_{12} = \sum_{i \geq 0} \sum_{j \geq 0} q_{12}^{ij} \left(\frac{1 + \frac{\xi_{12} - \xi_{21}}{\sigma_{12}}}{2}\right)^i \left(\frac{1 + \frac{\xi_{21} - \xi_{12}}{\sigma_{12}}}{2}\right)^j \qquad (15)$$

$$\text{or } \alpha_{12} = \sum_{i\geq 0} {}^{i}L_{12}\left(\frac{\xi_{12}-\xi_{21}}{\sigma_{12}}\right)^{i} \tag{16}$$

These general expressions reduce to the correct expressions for α_{ij} in all ternary subsystems. Note also that if α_{ij} is given by only Toop-type and Muggianu-type (but never by Kohler-type) approximations, then $\sigma_{ij}=1$. If α_{ij} is given by only Toop-type and Kohler-type (but never by Muggianu-type) approximations, then $\sigma_{ij}=\left(\xi_{ij}+\xi_{ji}\right)$. By making these substitutions into Eqs (15) and (16) it can be seen that the general equations reduce to these two limiting cases which were discussed above.

Ternary Terms

If experimental ternary data are available, then these may be included in the optimization to give empirical "ternary terms" in Eq (5). These terms are identically zero in all binary subsystems. Terms such as

$$q_{123}^{ijk}X_1^iX_2^jX_3^k \tag{17}$$

where $i\geq 1, j\geq 1$ and $k\geq 1$ and q_{123}^{ijk} is an empirical coefficient, are generally used. However, such terms have little theoretical justification. Furthermore, it is not clear how such ternary terms should be extrapolated into systems of four or more components.

In our previous article [5] we proposed the use of ternary terms which are designed to represent the effect of a third component, 3, upon the energy α_{12} of the pair exchange reaction Eq (2). If α_{12} is given by a Kohler-type approximation in the 1-2-3 ternary system as in Fig. 1a, then we proposed ternary terms of the form:

$$X_1X_2\left(q_{12(3)}^{ijk}\left(\frac{X_1}{X_1+X_2}\right)^{i}\left(\frac{X_2}{X_1+X_2}\right)^{j}X_3^k\right) \tag{18}$$

where $i\geq 0, j\geq 0$ and $k\geq 1$. Alternatively, this could be written in Redlich-Kister form as:

$$X_1X_2\left[{}^{ik}L_{12(3)}\left(\frac{X_1-X_2}{X_1+X_2}\right)^{i}X_3^k\right] \tag{19}$$

where the ${}^{ik}L_{12(3)}$ are ternary coefficients.

If α_{12} is given in the 1-2-3 ternary system by a Toop-type approximation along lines of constant X_1 as in Figs 1b and 1d, then we proposed to represent the effect of component 3 upon α_{12} by terms of the form:

$$X_1X_2\left(q_{12(3)}^{ijk}\left(X_1\right)^{i}\left(1-X_1\right)^{j}\left(\frac{X_3}{X_2+X_3}\right)^{k}\right) \tag{20}$$

or in Redlich-Kister form as:

$$X_1X_2\left[{}^{ik}L_{12(3)}\left(2X_1-1\right)^{i}\left(\frac{X_3}{X_2+X_3}\right)^{k}\right] \tag{21}$$

In the previous publication we proposed, for the sake of simplicity, to use the ternary terms of Eqs (18) and (19) also in the case where α_{12} is given by a Muggianu-type approximation. However, in order to give more flexibility, we now propose, in such cases, to include terms of the form:

$$X_1X_2\left[{}^{ik}L_{12(3)}\left(X_1-X_2\right)^{i}X_3^k\right] \tag{22}$$

or alternatively:

$$X_1 X_2 \left(q_{12(3)}^{ijk} \left(\frac{1+X_1-X_2}{2} \right)^i \left(\frac{1-X_1+X_2}{2} \right)^j X_3^k \right) \tag{23}$$

Note that in any ternary system 1-2-3, three types of ternary terms may thus be included: terms giving the effect of component 3 upon α_{12} as in Eqs (18) to (23); terms giving the effect of component 1 upon α_{23}; and terms giving the effect of component 2 upon α_{31}

For extending these ternary terms into the N-component system, we propose the following:

(i) If α_{12} in the 1-2-3 system is given by a Kohler-type or a Muggianu-type approximation, then the following ternary terms may be included:

$$X_1 X_2 \left[q_{12(3)}^{ijk} \left(\frac{1+\frac{\xi_{12}-\xi_{21}}{\sigma_{12}}}{2} \right)^i \left(\frac{1+\frac{\xi_{21}-\xi_{12}}{\sigma_{12}}}{2} \right)^j X_3 \left(1-\xi_{12}-\xi_{21}\right)^{k-1} \right] \tag{24}$$

$$\text{or } X_1 X_2 \left[{}^{ik}L_{12(3)} \left(\frac{\xi_{12}-\xi_{21}}{\sigma_{12}} \right)^i X_3 \left(1-\xi_{12}-\xi_{21}\right)^{k-1} \right] \tag{25}$$

(ii) If α_{12} in the 1-2-3 system is given by a Toop-type approximation along lines of constant X_1, then the following ternary terms may be included:

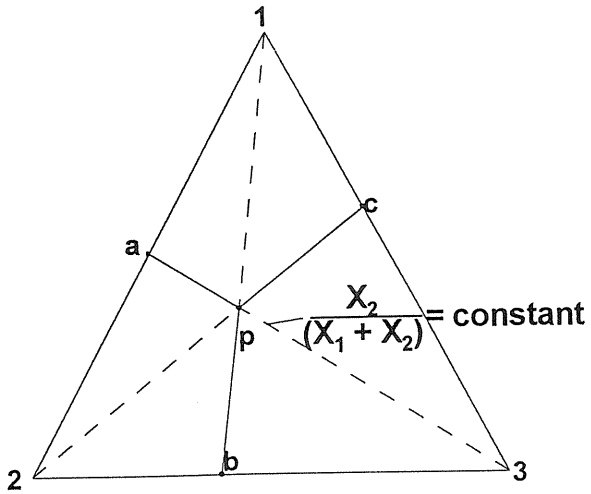
$$X_1 X_2 \left[q_{12(3)}^{ijk} \left(\frac{1+\frac{\xi_{12}-\xi_{21}}{\sigma_{12}}}{2} \right)^i \left(\frac{1+\frac{\xi_{21}-\xi_{12}}{\sigma_{12}}}{2} \right)^j \left(\frac{X_3}{\xi_{21}} \right) \left(1-\frac{X_2}{\xi_{21}} \right)^{k-1} \right] \tag{26}$$

$$\text{or } X_1 X_2 \left[{}^{ik}L_{12(3)} \left(\frac{\xi_{12}-\xi_{21}}{\sigma_{12}} \right)^i \left(\frac{X_3}{\xi_{21}} \right) \left(1-\frac{X_2}{\xi_{21}} \right)^{k-1} \right] \tag{27}$$

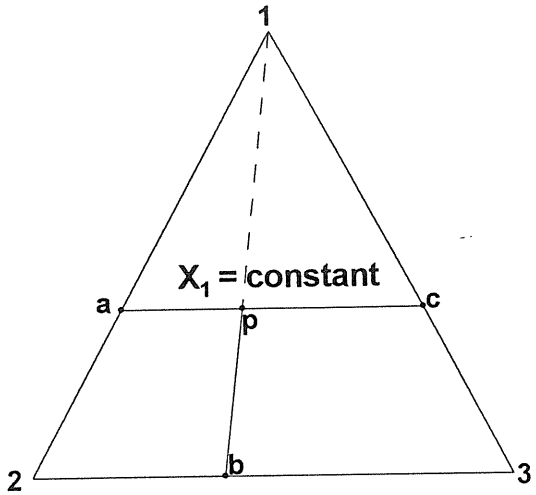
Eqs (24) to (27) reduce to Eqs. (18) to (23) in the 1-2-3 ternary system. The justification for using the factor $X_3 \left(1-\xi_{12}-\xi_{21}\right)^{k-1}$ rather than simply X_3^k in Eqs (24) and (25) and the factor $\left(\frac{X_3}{\xi_{21}} \right) \left(1-\frac{X_2}{\xi_{21}} \right)^{k-1}$ rather than simply $\left(\frac{X_3}{X_2+X_3} \right)^k$ in Eqs. (26) and (27) was discussed previously [5].

Discussion

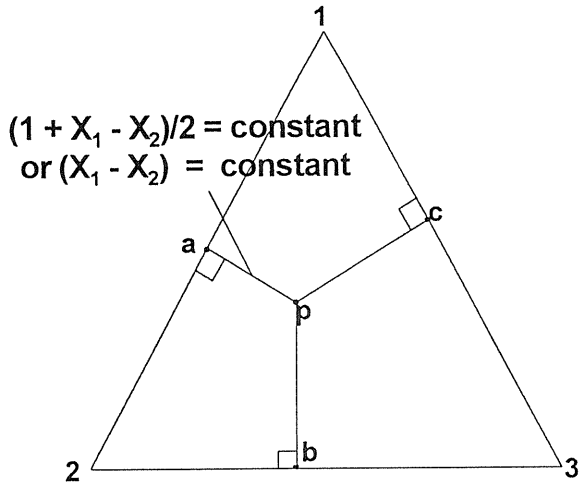
The present generalization permits several geometric models to be combined in one multicomponent database. For example, many ternary systems have already been evaluated/optimized with the Muggianu model. If future optimizations of other ternary systems are performed with the Kohler or Toop models, then these can all be immediately combined in one large multicomponent database. No re-optimization will be required. Hence, the fact that certain subsystems have already been optimized with one model does not mean that other models cannot be used for other subsystems.



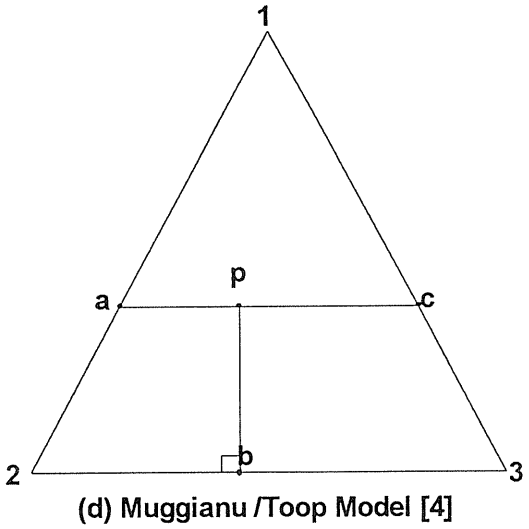
(a) Kohler Model [1]



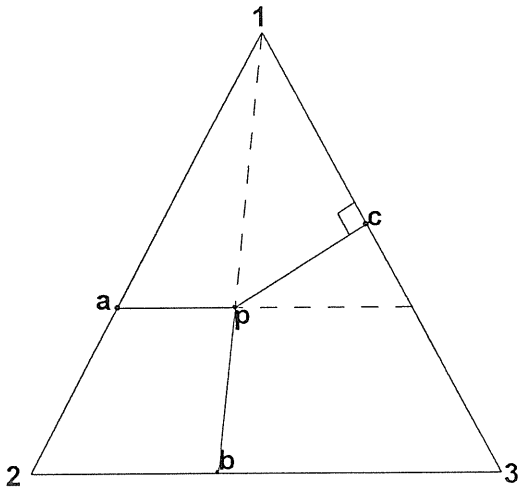
(b) Kohler / Toop Model [2]



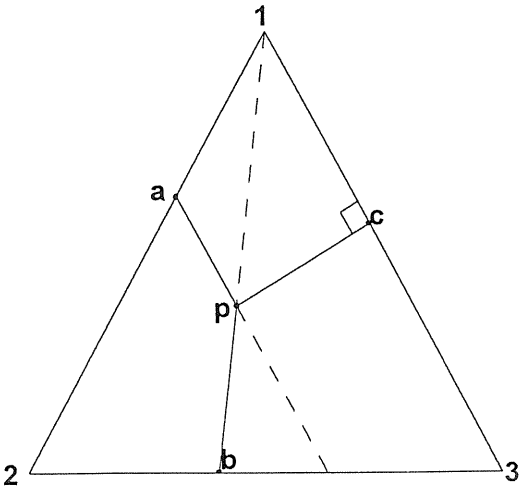
(c) Muggianu Model [3]



(d) Muggianu /Toop Model [4]



(e) A Weird Model



(f) Another Weird Model

Fig.1: Some "geometric" models for estimating ternary thermodynamic properties from optimized binary data.

Clearly, for sublattice models such as the Compound Energy Formalism, the equations developed here apply to each sublattice.

All the considerations and equations in the present article also apply when short-range ordering is taken into account by using the modified quasichemical model in the pair approximation [6]. In this model, the excess Gibbs energy in a binary system is given as $g_{12}^{E} = \alpha_{12} X_{12}$, where X_{12} is the fraction of nearest-neighbor pairs which are (1-2) pairs. However, the energy change α_{12} of the pair exchange reaction (2) in a binary system is expressed as a polynomial just as in Eqs (3) or (4). The configurational entropy of mixing is then written as a function of the concentrations of the different nearest-neighbor pairs, and the equilibrium pair fractions are calculated by minimizing the Gibbs energy [6]. For estimating ternary properties from the binary coefficients, the values of the α-functions in the ternary solution are assumed to be equal to the values $\alpha_{12(a)}$, $\alpha_{23(b)}$ and $\alpha_{31(c)}$ in the binary solutions according to the geometric models as in Fig. 1.

The equations derived in the present article are for the integral excess Gibbs energy. The partial excess Gibbs energies of the components can easily be calculated therefrom. A particularly useful form of the equation for calculating the partial properties from the integral property was discussed previously [5].

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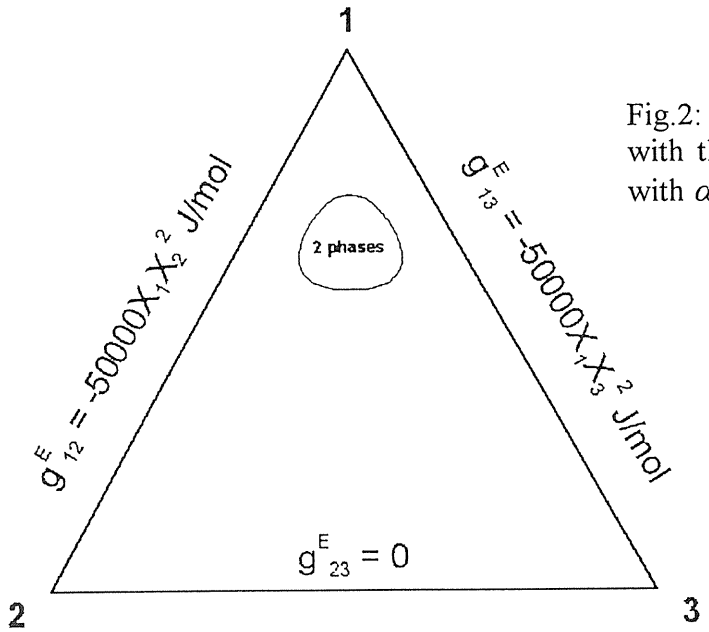

Fig.2: Spurious immiscibility gap calculated with the Kohler model at 973 K in a solution with $\alpha_{12} = \alpha_{31} = -50(1-X_1)$ kJ/mol and $\alpha_{23} = 0$.

5-Component Solution

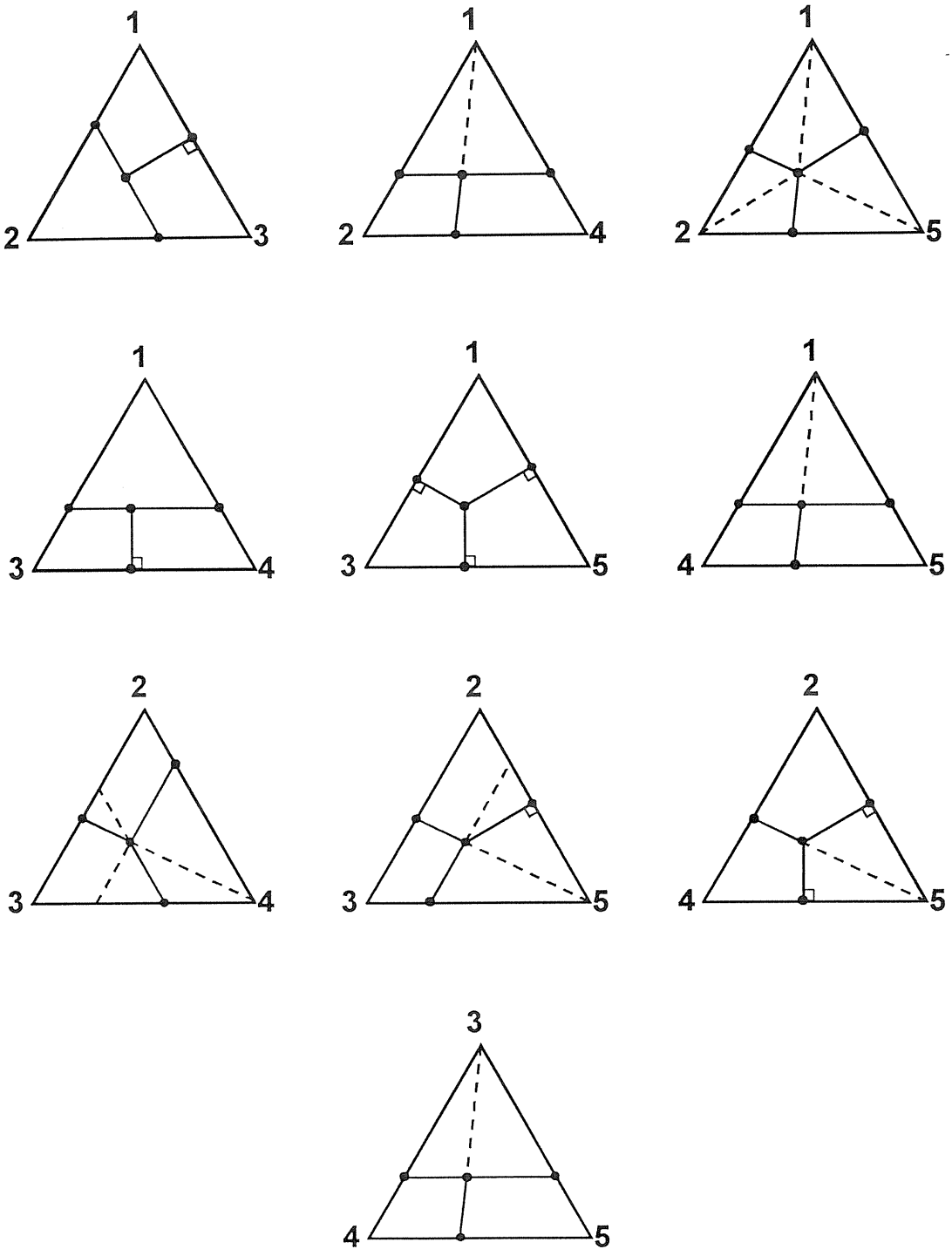

Fig.3: A 5-component solution showing the geometric models chosen for all ternary subsystems.