

## Subregular model for multicomponent solutions

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### ABSTRACT

The subregular Margules model is applied here to quaternary solutions in order to derive equations for excess properties ( $G^{xs}$ ,  $V^{xs}$ , etc.) and partial molar excess properties ( $RT \ln \gamma_i$ , etc.) for components in the mixture. Formulae generalizing the subregular model to arbitrary numbers of components and expressions for higher derivatives of the free energy, for use in binode and spinode location, are also presented. The derivation indicates that ternary mixing parameters exist independent of their component binaries. It is therefore impossible to estimate ternary interaction coefficients having knowledge only of the mixing properties of the binaries. Quaternary and higher-order coefficients are not required for multicomponent subregular solutions.

### INTRODUCTION

The subregular or asymmetric mixing model has been used extensively in the geological, metallurgical, and chemical literature. In geological systems, phases containing four or more components are common, and, as discussed by Andersen and Lindsley (1981), the extension of the subregular model to these systems is not intuitively obvious and most attempts in the literature are in error. The formulation for a binary (e.g., Thompson, 1967) is straightforward, and the derivation for ternary subregular solutions given by Andersen and Lindsley (1981) (after Wohl, 1946) is a clear exposition of the problems and pitfalls that arise in multicomponent systems. Although Andersen and Lindsley's ternary equation is correct, all currently available derivations of the subregular model for quaternary and more complex solutions are, as far as we are aware, incorrect. Jordan et al. (1950) presented an expression for the activity coefficient in a quaternary solution that must be wrong because relabeling of any two of the component indices does not yield an equivalent equation. Typographic errors mar the expressions of Currie and Curtis (1976) and Ganguly and Saxena (1987). In addition, Currie and Curtis erroneously suggested that ternary interaction coefficients can be derived from the properties of the binaries (Chu and Sposito, 1981). Andersen and Lindsley (1988) gave the correct expression for  $G^{xs}$ , but their equation for  $RT \ln \gamma$  must be in error since it does not reduce to the correct expression for the binaries. Lastly, a concise formulation for asymmetric mixing-model parameters has been suggested by Berman and Brown (1984, 1987), but this results in interdependent symmetric and asymmetric interaction parameters in ternary and higher-order systems.

In view of these errors and ambiguities, our intention is to present a correct derivation of excess mixing properties in quaternary subregular solutions that will serve as a useful reference. We feel that the derivation here is

correct, and we argue that it is. Furthermore, the extension to even more complex solutions may be written down without further derivation. The development, while tedious, is clear so that others may verify the result.

### DERIVATION

The formalism of Thompson (1967) is followed. This involves expressing the excess molar property, for example,  $G^{xs}$ , as a suitably truncated power series<sup>1</sup> in the  $n - 1$  (in this case,  $4 - 1 = 3$ , with  $X_1$  eliminated) independent mole fractions of the mixing end-members:

$$G^{xs} = (K) + a_2X_2 + a_3X_3 + a_4X_4 + b_{22}X_2^2 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{33}X_3^2 + b_{34}X_3X_4 + b_{44}X_4^2 + c_{222}X_2^3 + c_{223}X_2^2X_3 + c_{224}X_2^2X_4 + c_{333}X_3^3 + c_{332}X_3^2X_2 + c_{334}X_3^2X_4 + c_{444}X_4^3 + c_{442}X_4^2X_2 + c_{443}X_4^2X_3 + c_{234}X_2X_3X_4. \quad (1)$$

Successive substitution of  $X_1 = 1$ ,  $X_2 = 1$ ,  $X_3 = 1$ ,  $X_4 = 1$  (with the other  $X_i = 0$ ) yields, since  $G^{xs} \equiv 0$  at each pure end-member composition,

$$K = 0, \\ a_2 = -b_{22} - c_{222}, \\ a_3 = -b_{33} - c_{333}, \\ a_4 = -b_{44} - c_{444}.$$

Substituting these relations, Equation 1 becomes

$$G^{xs} = b_{22}X_2(X_2 - 1) + b_{33}X_3(X_3 - 1) + b_{44}X_4(X_4 - 1) + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 + c_{222}X_2(X_2^2 - 1) + c_{333}X_3(X_3^2 - 1)$$

<sup>1</sup> The convention for power series coefficient labels follows that of Currie and Curtis (1976), not that of Thompson (1967).

$$\begin{aligned}
& + c_{444}X_4(X_4^2 - 1) \\
& + c_{223}X_2^2X_3 + c_{332}X_2X_3^2 + c_{224}X_2^2X_4 \\
& + c_{442}X_2X_4^2 + c_{334}X_3^2X_4 \\
& + c_{443}X_3X_4^2 + c_{234}X_2X_3X_4. \quad (2)
\end{aligned}$$

In order to convert this expression into one containing the familiar Margules parameters  $W_{ij}$  and  $W_{ji}$ , all terms need to be made third order in mole fractions of the endmembers.

Since in a binary the interaction coefficients  $W_{ij}$  and  $W_{ji}$  contain the products  $X_iX_j^2$  and  $X_jX_i^2$ , extension to multicomponent systems requires the same third-order forms. Additionally, the third-order terms should contain products of more than one mole fraction:  $X_i^3$  terms are forbidden since they do not represent a mole-fraction product of either a binary or a ternary interaction coefficient. These requirements guide the remaining substitutions to bring Equation 2 into its final form. First, the  $X_i(X_i^2 - 1)$  terms are brought to mixed products by substitution of

$$\begin{aligned}
& \left[ 1 - \sum_{j \neq i} X_j \right]^2 \text{ for } X_i^2: \\
G^{\text{XS}} = & b_{22}X_2(X_2 - 1) + b_{33}X_3(X_3 - 1) + b_{44}X_4(X_4 - 1) \\
& + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 \\
& + c_{222}X_2(X_2^2 + 2X_4X_3 + 2X_4X_1 - 2X_4 \\
& \quad + X_3^2 + 2X_3X_1 - 2X_3 + X_1^2 - 2X_1) \\
& + c_{223}X_3X_2^2 + c_{332}X_3^2X_2 + c_{224}X_4X_2^2 + c_{442}X_4^2X_2 \\
& + c_{333}X_3(X_3^2 + 2X_4X_2 + 2X_4X_1 - 2X_4 \\
& \quad + X_2^2 + 2X_2X_1 - 2X_2 + X_1^2 - 2X_1) \\
& + c_{334}X_4X_3^2 + c_{443}X_4^2X_3 \\
& + c_{444}X_4(X_4^2 + 2X_3X_2 + 2X_3X_1 - 2X_3 \\
& \quad + X_2^2 + 2X_2X_1 - 2X_2 + X_1^2 - 2X_1) \\
& + c_{234}X_2X_3X_4. \quad (3)
\end{aligned}$$

Next, terms involving  $X_i(X_i - 1)$  are brought to third order by substitution of  $-\sum_{j \neq i} X_j$  for  $(X_i - 1)$  and by multiplication of these substituted terms and others that contain second-order terms in  $X_i$  by  $X_1 + X_2 + X_3 + X_4$  (which is equal to 1). This produces

$$\begin{aligned}
G^{\text{XS}} = & -X_1^2X_2(b_{22} + c_{222}) - X_1^2X_3(b_{33} + c_{333}) \\
& - X_1^2X_4(b_{44} + c_{444}) \\
& - X_2^2X_1(b_{22} + 2c_{222}) - X_3^2X_1(b_{33} + 2c_{333}) \\
& - X_4^2X_1(b_{44} + 2c_{444}) \\
& + X_2^2X_3(-b_{33} + b_{23} - b_{22} - c_{333} + c_{223} - 2c_{222}) \\
& + X_2^2X_4(-b_{44} + b_{24} - b_{22} - c_{444} + c_{224} - 2c_{222}) \\
& + X_3^2X_2(-b_{33} + b_{23} - b_{22} - 2c_{333} + c_{332} - c_{222}) \\
& + X_3^2X_4(-b_{44} + b_{34} - b_{33} - 2c_{444} + c_{334} - c_{333}) \\
& + X_4^2X_2(-b_{44} + b_{24} - b_{22} - 2c_{444} + c_{442} - c_{222}) \\
& + X_4^2X_3(-b_{44} + b_{34} - b_{33} - 2c_{444} + c_{443} - c_{333}) \\
& + X_1X_2X_3(-2b_{33} + b_{23} - 2b_{22} - 2c_{333} - 2c_{222}) \\
& + X_1X_2X_4(-2b_{44} + b_{24} - 2b_{22} - 2c_{444} - 2c_{222}) \\
& + X_1X_3X_4(-2b_{44} + b_{34} - 2b_{33} - 2c_{444} - 2c_{333})
\end{aligned}$$

$$\begin{aligned}
& + X_2X_3X_4(-2b_{44} + b_{34} - 2b_{33} + b_{24} + b_{23} - 2b_{22} \\
& \quad - 2c_{444} - 2c_{333} - 2c_{222} + c_{234}). \quad (4)
\end{aligned}$$

Equation 4 contains four ternary terms (involving  $X_1X_2X_3$ ,  $X_1X_3X_4$ , etc.). As noted by Andersen and Lindsley (1981), these are functions of both second-degree *symmetric* coefficients ( $b_{ii}$ ,  $b_{ij}$ ) and third-degree *asymmetric* coefficients ( $c_{ijk}$ , etc.) in the original power-series expansion, which is undesirable. With some effort, the portions of the ternary terms involving  $b_{ii}$  and  $b_{ij}$  can be distributed into the binary terms. To do this, all  $b_{ij}$  terms multiplying  $X_iX_jX_k$  need to be converted into  $X_iX_j^2$  and  $X_jX_i^2$  terms, which will include them in the *binary* subregular products. Equation 4 already contains the asymmetric binary interaction coefficients, the use of which simplifies the following algebra. Applying Equation 4 to each of the binaries in turn and using the definition for a binary asymmetric quantity,<sup>2</sup>

$$G^{\text{XS}} = X_iX_j^2W_{ij} + X_jX_i^2W_{ji},$$

we obtain

$$\begin{aligned}
W_{12} & = -b_{22} - 2c_{222}, \\
W_{21} & = -b_{22} - c_{222}, \\
W_{13} & = -b_{33} - 2c_{333}, \\
W_{31} & = -b_{33} - c_{333}, \\
W_{14} & = -b_{44} - 2c_{444}, \\
W_{41} & = -b_{44} - c_{444}, \\
W_{23} & = -b_{33} + b_{23} - b_{22} - 2c_{333} + c_{332} - c_{222}, \\
W_{32} & = -b_{33} + b_{23} - b_{22} - c_{333} + c_{223} - 2c_{222}, \\
W_{24} & = -b_{44} + b_{24} - b_{22} - 2c_{444} + c_{442} - c_{222}, \\
W_{42} & = -b_{44} + b_{24} - b_{22} - c_{444} + c_{224} - 2c_{222}, \\
W_{34} & = -b_{44} + b_{34} - b_{33} - 2c_{444} + c_{443} - c_{333}, \\
W_{43} & = -b_{44} + b_{34} - b_{33} - c_{444} + c_{334} - 2c_{333}.
\end{aligned}$$

In Equation 4 the factors of the  $X_1X_2X_3$  term involving  $b$  are  $(-2b_{33} + b_{23} - 2b_{22})$ . The definitions of the  $W_{ij}$  terms reveal

$$\begin{aligned}
b_{22} & = W_{12} - 2W_{21}, \\
b_{33} & = W_{13} - 2W_{31}, \\
c_{222} & = W_{21} - W_{12}, \\
c_{333} & = W_{31} - W_{13},
\end{aligned}$$

$$\begin{aligned}
W_{23} + W_{32} & = 2b_{23} - 2(b_{33} + b_{22}) - 3(c_{333} + c_{222}) \\
& \quad + (c_{223} + c_{332}),
\end{aligned}$$

yielding

<sup>2</sup> The subscript convention for  $W$  follows Wohl (1946) and Andersen and Lindsley (1981) and is opposite to that of Thompson (1967). Subscripts farther to the right denote higher powers of  $X$ ; the interaction coefficient  $W_{ij}$  applies to the mole fraction product  $X_iX_j^2$ , whereas  $W_{ji}$  applies to  $X_jX_i^2$ . Thus,  $W_{ij}$ , for example, is the excess partial molar free energy of  $i$  infinitely diluted in  $j$ .

$$b_{23} = \frac{1}{2}(W_{23} + W_{32}) + (W_{13} - 2W_{31} + W_{12} - 2W_{21}) \\ + \frac{1}{2}(W_{21} - W_{12} + W_{31} - W_{13}) - \frac{1}{2}(c_{223} + c_{332}).$$

Therefore,

$$(-2b_{33} + b_{23} - 2b_{22}) = -\frac{1}{2}(c_{223} + c_{332}) \\ + 3(W_{21} - W_{12}) \\ + \frac{1}{2}(W_{21} + W_{12}) \\ + 3(W_{31} - W_{13}) \\ + \frac{1}{2}(W_{31} + W_{13}) \\ + \frac{1}{2}(W_{23} + W_{32}) \\ = -\frac{1}{2}(c_{223} + c_{332}) + 3c_{333} \\ + \frac{1}{2}(W_{21} + W_{12}) \\ + 3c_{222} + \frac{1}{2}(W_{31} + W_{13}) \\ + \frac{1}{2}(W_{23} + W_{32}).$$

Returning to the terms multiplying  $X_1X_2X_3$ , substituting the above result, and using the expressions for  $c_{222}$  and  $c_{333}$ ,

$$X_1X_2X_3(-2b_{33} + b_{23} - 2b_{22} - 2c_{333} - 2c_{222}) \\ = X_1X_2X_3[c_{333} + c_{222} - \frac{1}{2}(c_{223} + c_{332})] \\ + X_1X_2(\frac{1}{2}X_3)W_{21} + X_1X_2(\frac{1}{2}X_3)W_{12} \\ + X_1X_3(\frac{1}{2}X_2)W_{31} + X_1X_3(\frac{1}{2}X_2)W_{13} \\ + X_2X_3(\frac{1}{2}X_1)W_{32} + X_2X_3(\frac{1}{2}X_1)W_{23}.$$

This factors the  $X_1X_2X_3$  term. The first term on the right-hand side defines the ternary constant  $W_{123}$ , in which no  $b_{ij}$  coefficients appear, and all of the  $b_{ij}$  terms have been transformed into terms involving the binary coefficients  $W_{ij}$ . The remaining three ternary products are disaggregated into their ternary and binary interaction coefficients in analogous fashion.

After eliminating the binary coefficients from the ternary mole-fraction products and collecting like  $W_{ij}$  terms, the complete expression for excess  $G$  is

$$G^{\text{XS}} = X_1X_2[X_2 + \frac{1}{2}(X_3 + X_4)]W_{12} \\ + X_1X_2[X_1 + \frac{1}{2}(X_3 + X_4)]W_{21} \\ + X_1X_3[X_3 + \frac{1}{2}(X_2 + X_4)]W_{13} \\ + X_1X_3[X_1 + \frac{1}{2}(X_2 + X_4)]W_{31} \\ + X_1X_4[X_4 + \frac{1}{2}(X_2 + X_3)]W_{14} \\ + X_1X_4[X_1 + \frac{1}{2}(X_2 + X_3)]W_{41} \\ + X_2X_3[X_3 + \frac{1}{2}(X_1 + X_4)]W_{23} \\ + X_2X_3[X_2 + \frac{1}{2}(X_1 + X_4)]W_{32} \\ + X_2X_4[X_4 + \frac{1}{2}(X_1 + X_3)]W_{24} \\ + X_2X_4[X_2 + \frac{1}{2}(X_1 + X_3)]W_{42} \\ + X_3X_4[X_4 + \frac{1}{2}(X_1 + X_2)]W_{34} \\ + X_3X_4[X_3 + \frac{1}{2}(X_1 + X_2)]W_{43} \\ + X_1X_2X_3W_{123} + X_1X_2X_4W_{124} \\ + X_1X_3X_4W_{134} + X_2X_3X_4W_{234}, \quad (5)$$

where the  $W_{ij}$  and  $W_{ijk}$  terms are

$$W_{12} = -b_{22} - 2c_{222}, \\ W_{21} = -b_{22} - c_{222},$$

$$W_{13} = -b_{33} - 2c_{333}, \\ W_{31} = -b_{33} - c_{333}, \\ W_{14} = -b_{44} - 2c_{444}, \\ W_{41} = -b_{44} - c_{444}, \\ W_{23} = -b_{33} + b_{23} - b_{22} - 2c_{333} + c_{332} - c_{222}, \\ W_{32} = -b_{33} + b_{23} - b_{22} - c_{333} + c_{223} - 2c_{222}, \\ W_{24} = -b_{44} + b_{24} - b_{22} - 2c_{444} + c_{442} - c_{222}, \\ W_{42} = -b_{44} + b_{24} - b_{22} - c_{444} + c_{224} - 2c_{222}, \\ W_{34} = -b_{44} + b_{34} - b_{33} - 2c_{444} + c_{443} - c_{333}, \\ W_{43} = -b_{44} + b_{34} - b_{33} - c_{444} + c_{334} - 2c_{333}, \\ W_{123} = c_{222} + c_{333} - \frac{1}{2}(c_{223} + c_{332}), \\ W_{124} = c_{222} + c_{444} - \frac{1}{2}(c_{224} + c_{442}), \\ W_{134} = c_{333} + c_{444} - \frac{1}{2}(c_{334} + c_{443}), \\ W_{234} = c_{222} + c_{333} + c_{444} + c_{234} \\ - \frac{1}{2}(c_{223} + c_{332} + c_{224} + c_{442} + c_{334} + c_{443}) \\ = c_{234} + W_{123} + W_{134} + W_{124} + W_{12} \\ - W_{21} + W_{13} - W_{31} + W_{14} - W_{41}.$$

The binary  $W$  terms are repeated here for a complete collection of binary and ternary interaction coefficient definitions.

Setting  $c_{ijk} = 0$  yields the symmetric ternary expression given by Wohl (1946), and setting  $X_4, X_3 = 0$  and  $W_{ij} = W_{ji}$  successively recovers the ternary and binary asymmetric and symmetric regular solution expressions given by Wohl (1946).

The generalization of Equation 5 to an arbitrary number of components,  $n$ , is

$$G^{\text{XS}} = \sum_{i=1}^n \sum_{j>i}^n X_iX_j \left\{ W_{ij} \left[ X_j + \frac{1}{2} \sum_{\substack{k \neq i \\ k \neq j}}^n X_k \right] \right. \\ \left. + W_{ji} \left[ X_i + \frac{1}{2} \sum_{\substack{k \neq i \\ k \neq j}}^n X_k \right] \right\} \\ + \sum_{i=1}^n \sum_{j>i}^n \sum_{k>j}^n X_iX_jX_k W_{ijk}. \quad (5')$$

Activity coefficients are derived from Equation 5 following Wohl (1946),

$$RT \ln \gamma_i = \left[ \frac{\partial}{\partial n_i} \left( \sum_j n_j \right) G^{\text{XS}} \right]_{T,P,n_k \neq i}.$$

It is helpful to recall that

$$N \frac{\partial X_i}{\partial n_j} = \begin{cases} (1 - X_i) & \text{if } i = j \\ -X_i & \text{if } i \neq j \end{cases}, \quad \text{where } N = \sum_k n_k.$$

Only the result of the derivation is given since the intermediate expressions are cumbersome and are not illuminating:

$$RT \ln \gamma_1 = \frac{1}{2}W_{12}X_2[1 - X_1 + X_2 + 2X_1(X_1 - X_2 - 1)] \\ + \frac{1}{2}W_{21}X_2[1 - X_1 - X_2 - 2X_1 \\ \cdot (X_1 - X_2 - 1)] \\ + \frac{1}{2}W_{13}X_3[1 - X_1 + X_3 + 2X_1$$

$$\begin{aligned}
& \cdot (X_1 - X_3 - 1)] \\
& + \frac{1}{2} W_{31} X_3 [1 - X_1 - X_3 - 2X_1 \\
& \quad \cdot (X_1 - X_3 - 1)] \\
& + \frac{1}{2} W_{14} X_4 [1 - X_1 + X_4 + 2X_1 \\
& \quad \cdot (X_1 - X_4 - 1)] \\
& + \frac{1}{2} W_{41} X_4 [1 - X_1 - X_4 - 2X_1 \\
& \quad \cdot (X_1 - X_4 - 1)] \\
& + W_{23} X_2 X_3 (X_2 - X_3 - \frac{1}{2}) \\
& + W_{32} X_3 X_2 (X_3 - X_2 - \frac{1}{2}) \\
& + W_{24} X_2 X_4 (X_2 - X_4 - \frac{1}{2}) \\
& + W_{42} X_4 X_2 (X_4 - X_2 - \frac{1}{2}) \\
& + W_{34} X_3 X_4 (X_3 - X_4 - \frac{1}{2}) \\
& + W_{43} X_4 X_3 (X_4 - X_3 - \frac{1}{2}) \\
& + W_{123} X_2 X_3 (1 - 2X_1) + W_{124} X_2 X_4 (1 - 2X_1) \\
& + W_{134} X_3 X_4 (1 - 2X_1) \\
& - 2W_{234} X_2 X_3 X_4.
\end{aligned} \tag{6}$$

Activity coefficients for the remaining three components may be obtained by cyclic permutation of indices (1→2, 2→3, 3→4, 4→1). As before, setting  $X_3, X_4 = 0$  recovers the binary asymmetric activity coefficient expression, and further setting  $W_{ij} = W_{ji}$  recovers the symmetric binary activity coefficients given by Wohl (1946), Equations 5a and 39a, respectively. The terms multiplying each  $W_{ij}$  can be independently differentiated and verified individually. The generalization of Equation 6 to an arbitrary number of components,  $n$ , is

$$\begin{aligned}
RT \ln \gamma_1 &= \sum_{j>1}^n \frac{X_j}{2} \\
& \cdot \{ W_{1j} [1 - X_1 + X_j + 2X_1(X_1 - X_j - 1)] \\
& \quad + W_{j1} [1 - X_1 - X_j - 2X_1(X_1 - X_j - 1)] \} \\
& + \sum_{i>1}^n \sum_{j>i}^n X_i X_j \\
& \cdot \{ W_{ij} (X_i - X_j - \frac{1}{2}) + W_{ji} (X_j - X_i - \frac{1}{2}) \\
& \quad + W_{1ij} (1 - 2X_1) \} \\
& - 2 \sum_{i>1}^n \sum_{j>i}^n \sum_{k>j}^n W_{ijk} X_i X_j X_k.
\end{aligned} \tag{6'}$$

#### BINODES AND SPINODES IN THE SUBREGULAR MODEL

When mixing in a multicomponent system is nonideal, phase separation may occur, giving rise to binodes separating coexisting phases. Within each binode is contained the spinodal surface, separating unstable and metastable regions. As other authors have reported, the spinode is the easier of the two to determine (Meijering, 1950, 1951; Prigogine and Defay, 1954; Barron, 1978). The spinodal surface is defined by the general equation  $\det(\mathbf{A}) = 0$  (Bernard et al., 1967), with the elements of matrix  $\mathbf{A}$  defined as

$$A_{lm} = \frac{\partial^2 G}{\partial X_l \partial X_m}.$$

$\mathbf{A}$  is a  $(n-1)$  by  $(n-1)$  matrix since one of the  $X_i$  terms is redundant;  $X_n = 1 - \sum_{i=1}^{n-1} X_i$ , for example.  $G$  is the system free energy, with

$$G = \sum_{i=1}^n X_i \mu_i, \quad \mu_i = \mu_i^0 + RT \ln X_i + RT \ln \gamma_i. \tag{7}$$

Each component's ideal contribution to the free energy is given by the first two terms of  $\mu_i$ , and the nonideal portion is the last term. The standard state chemical potential,  $\mu_i^0$ , is not compositionally dependent and so will not contribute to any  $A_{lm}$ . The second term will contribute either  $RT \left( \frac{1}{X_n} \right)$  to  $A_{lm}$  or  $RT \left( \frac{1}{X_n} + \frac{1}{X_m} \right)$  to  $A_{mm}$ . The third term, when summed over all  $X_i$ , is  $G^{XS}$  and so will contribute  $\frac{\partial^2 G^{XS}}{\partial X_l \partial X_m}$  to  $A_{lm}$ . Collecting these parts, the elements of  $\mathbf{A}$  are then

$$\begin{aligned}
A_{lm} &= RT \left( \frac{1}{X_n} + \frac{\delta_{lm}}{X_m} \right) \\
& + \sum_{i=1}^n \sum_{j>i}^n (D_i^n D_j^{ln} + D_j^n D_i^{mn}) \\
& \cdot \left\{ W_{ij} \left[ X_j + \frac{1}{2} \sum_{\substack{k \neq i \\ k \neq j}}^n X_k \right] \right. \\
& \quad \left. + W_{ji} \left[ X_i + \frac{1}{2} \sum_{\substack{k \neq i \\ k \neq j}}^n X_k \right] \right\} \\
& + \sum_{i=1}^n \sum_{j>i}^n (D_i^n X_j + D_j^n X_i) \\
& \cdot \left\{ W_{ij} \left[ D_j^{mn} + \frac{1}{2} \sum_{\substack{k \neq i \\ k \neq j}}^n D_k^{mn} \right] + W_{ji} \left[ D_i^{mn} + \frac{1}{2} \sum_{\substack{k \neq i \\ k \neq j}}^n D_k^{mn} \right] \right\} \\
& + \sum_{i=1}^n \sum_{j>i}^n (D_i^{mn} X_j + D_j^{mn} X_i) \\
& \cdot \left\{ W_{ij} \left[ D_j^{ln} + \frac{1}{2} \sum_{\substack{k \neq i \\ k \neq j}}^n D_k^{ln} \right] + W_{ji} \left[ D_i^{ln} + \frac{1}{2} \sum_{\substack{k \neq i \\ k \neq j}}^n D_k^{ln} \right] \right\} \\
& + \sum_{i=1}^n \sum_{j>i}^n \sum_{k>j}^n W_{ijk} \{ X_i [D_j^n D_k^{mn} + D_k^n D_j^{mn}] \\
& \quad + X_j [D_i^n D_k^{mn} + D_k^n D_i^{mn}] \\
& \quad + X_k [D_i^n D_j^{mn} + D_j^n D_i^{mn}] \},
\end{aligned} \tag{8}$$

where

$$D_i^{ln} = \delta_{lm} - \delta_{in}, \quad \delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases}.$$

Note that  $n$  has been designated the dependent mole frac-

tion in these formulae. To locate the spinode, one approach is to determine the temperature at which a given composition lies on a spinode (Barron, 1978). After determining the spinodal temperatures for a series of compositions, the spinode at a given temperature may be obtained by contouring the various temperatures calculated. An elegant formalism exists to determine the spinodal temperature, given a composition (Barron, 1985). A can be partitioned into its temperature-dependent and temperature-independent portions, giving  $A = H - TS$ . Segregating the terms of A in this way, the spinode's temperature is given by the highest eigenvalue of  $S^{-1}H$ . This is a well-understood problem in linear algebra that numerical techniques may solve easily. Spinode location at a given temperature is, in essence, a problem of contouring a given temperature within a field of temperatures at known compositions.

The eigenvector corresponding to the eigenvalue at a given composition is related to the tie-lines giving the compositions of the coexisting phases across the binode. This eigenvector,  $X^s$ , indicates a compositional direction of zero curvature of the free-energy surface at the composition and temperature. Though subparallel to the tie-lines crossing the binodal surface that mantles the spinode, this vector is distinct. However, where the spinodal and binodal surfaces coincide at the consolute point, this vector is parallel to the binodal tie-lines and is a fair approximation to them in the vicinity of the consolute point. Therefore, binodal tie-lines can be approximately determined, at temperatures near the consolute point, while the spinode is being located.

Not only the curvature, but the change in the curvature of the free-energy surface is zero in the direction  $X^s$  at the consolute point (Prigogine and Defay, 1954). This aids in location of the consolute point, provided the directional derivative of A in direction  $X^s$  at composition  $X^s$ ,  $X^s \cdot (X^s \cdot \nabla A|_{X^s}) \cdot X^s$ , is known.  $\nabla A$  is a three-dimensional matrix whose components are given by

$$\begin{aligned} (\nabla A)_{q|lm} = & RT \left( \frac{1}{X_n^2} - \frac{\delta_{qm}\delta_{lm}}{X_m^2} \right) \\ & + \sum_{i=1}^n \sum_{j>i}^n (D_i^n D_j^{mn} + D_j^n D_i^{mn}) \\ & \cdot \left\{ W_{ij} \left[ D_j^{qn} + \frac{1}{2} \sum_{\substack{k \neq i \\ k \neq j}}^n D_k^{qn} \right] \right. \\ & \left. + W_{ji} \left[ D_i^{qn} + \frac{1}{2} \sum_{\substack{k \neq i \\ k \neq j}}^n D_k^{qn} \right] \right\} \\ & + \sum_{i=1}^n \sum_{j>i}^n (D_i^n D_j^{qn} + D_j^n D_i^{qn}) \\ & \cdot \left\{ W_{ij} \left[ D_j^{mn} + \frac{1}{2} \sum_{\substack{k \neq i \\ k \neq j}}^n D_k^{mn} \right] \right. \end{aligned}$$

$$\begin{aligned} & \left. + W_{ji} \left[ D_i^{mn} + \frac{1}{2} \sum_{\substack{k \neq i \\ k \neq j}}^n D_k^{mn} \right] \right\} \\ & + \sum_{i=1}^n \sum_{j>i}^n (D_i^{mn} D_j^{qn} + D_j^{mn} D_i^{qn}) \\ & \cdot \left\{ W_{ij} \left[ D_j^n + \frac{1}{2} \sum_{\substack{k \neq i \\ k \neq j}}^n D_k^n \right] \right. \\ & \left. + W_{ji} \left[ D_i^n + \frac{1}{2} \sum_{\substack{k \neq i \\ k \neq j}}^n D_k^n \right] \right\} \\ & + \sum_{i=1}^n \sum_{j>i}^n \sum_{k>j}^n W_{ijk} \\ & \cdot \{ D_i^{qn} [D_j^n D_k^{mn} + D_k^n D_j^{mn}] \\ & + D_j^{qn} [D_i^n D_k^{mn} + D_k^n D_i^{mn}] \\ & + D_k^{qn} [D_i^n D_j^{mn} + D_j^n D_i^{mn}] \}. \end{aligned} \quad (9)$$

Note that only the first term of  $\nabla A$  is compositionally dependent. If  $X^s$  is normalized to a unit vector, the curvature along  $X^s$  at  $X^s$  is

$$X^s \cdot (X^s \cdot \nabla A|_{X^s}) \cdot X^s = \sum_{l=1}^{n-1} X_l^s \sum_{m=1}^{n-1} X_m^s \sum_{q=1}^{n-1} X_q^s A_{qlm},$$

where  $X_q^s$  are the individual components of  $X^s$  and  $\nabla A$  has been evaluated at composition  $X^s$ . These formulae allow one to calculate a temperature at which a given composition lies on a spinode as well as to check whether the composition represents a consolute point, since the change in curvature will be zero there. The directional derivative may also be used to follow the spinodal locus at a given temperature once a point on the spinode is found.

## DISCUSSION

The derivation of Equation 6 shows that quaternary and higher-order constants do not occur when more than three components join in a subregular solution, contrary to the assertion of Ganguly and Saxena (1987) following their Equation 2.12. Such constants would only pertain to mole-fraction products such as  $X_i X_j X_k X_l$  with ( $i \neq j \neq k \neq l$ ), yet the power series (Eq. 1) is truncated before these terms appear, as dictated by a subregular model. Extension of Equation 5 to more components only adds new binary  $W_{ij}$  terms and new ternary  $W_{ijk}$  terms for the  $\binom{n}{2}$  binary combinations and the  $\binom{n}{3}$  ternary combinations of mole fractions.

Berman and Brown (1984, 1987) developed a compact formulation for excess quantities, substantially simplifying the formulae. Their starting point is the set of third-order mole fraction products in the power-series expansion (Eq. 4). The power-series coefficients multiplying these products define their interaction parameters, re-

ferred to here as  $W_{ijk}^{BB}$ , giving  $W_{12}^{BB} = -b_{22} - c_{222}$ , for example. In a three-component system, there is one ternary constant,  $W_{123}^{BB} = -2b_{33} + b_{23} - 2b_{22} - 2c_{333} - 2c_{222}$ . Defined this way, the ternary interaction coefficient depends on both the symmetric and asymmetric properties of the binary since it involves both  $b$  and  $c$  coefficients (see Eq. 1). The liberty to set this parameter to an arbitrary value, e.g., zero, must be available to the modeler in the absence of data on ternary behavior. Yet doing so implies an unwarranted relation between symmetric and asymmetric parameters in this definition. Were  $W_{123}^{BB}$  set to zero, a relation between binary 1-2 and 1-3 properties (through  $b_{22}$ ,  $c_{222}$ ,  $b_{33}$ , and  $c_{333}$ ) and binary 2-3 properties (through  $b_{23}$ ) must hold and probably constitutes a contradiction within the solution-model parameters. Andersen and Lindsley (1981) advised against this definition of interaction parameters, suggesting instead that the binary-related coefficients be factored out of those of the ternary. This approach, which we have followed, yields more complex expressions but no contradiction internal to the model if the ternary parameters are set arbitrarily.

Algebraic manipulation of the definitions of the  $W_{ij}$  and  $W_{ijk}$  terms can readily yield expressions for some of the power-series coefficients. For example,  $(W_{21} - W_{12}) = c_{222}$ , and  $(W_{23} - W_{32}) = c_{222} + c_{333} + (c_{223} - c_{332})$ . This exercise affords some insight into the properties of ternary and higher-order solutions. First, suppose that in a ternary solution, each of the constituent binaries are symmetric. What implications does this have for the properties for the ternary interaction coefficient? In general, one would probably treat this case by truncating the power series for  $G^{XS}$  (Eq. 1) after the second-order terms. This yields the well-known equation for a ternary regular solution in which no ternary term *can* appear,

$$G^{XS} = X_1X_2W_{12} + X_2X_3W_{23} + X_1X_3W_{13}.$$

The fact that each binary is symmetric does not, however, require that there is no ternary constant. From the definition of a symmetric binary, we obtain  $W_{12} = W_{21}$ ,  $W_{13} = W_{31}$ , and  $W_{23} = W_{32}$ . Using these definitions and our expression for the third-order expansion yields  $c_{222} = 0$ ,  $c_{333} = 0$ ,  $c_{332} - c_{223} = c_{333} - c_{222}$ , or that  $c_{332} = c_{223}$ . From the definition of  $W_{123}$ ,

$$\begin{aligned} W_{123} &= c_{222} + c_{333} - \frac{1}{2}(c_{223} + c_{332}), \\ &= (W_{21} - W_{12}) + (W_{31} - W_{13}) \\ &\quad - \frac{1}{2}(c_{223} + c_{332}) \\ &= -c_{223} \\ &= -c_{332}. \end{aligned} \quad (10)$$

Thus,  $W_{123}$  is not required to be zero even though all the binaries are symmetric. Therefore, no statement about the magnitude of the ternary interaction coefficient can be made on the basis of the symmetry of the binaries; an independent measurement of ternary properties must be made to determine  $c_{223}$  (and  $W_{123}$ ). If binary 1-2 is not symmetric, then its  $W_{12}$  and  $W_{21}$  terms can yield values for the power-series coefficient  $c_{222}$  through the difference

$(W_{21} - W_{12})$ . The same result obtains: knowledge of the binaries sheds no light on the properties of the ternary constant  $W_{123}$ .

Ternary properties yield no information on binary properties either. Suppose a value were known for the ternary constant  $W_{123}$ . Through Equation 10 there is a relation among  $W_{123}$ ,  $(W_{21} - W_{12})$ , and  $(W_{31} - W_{13})$ , but it involves the power-series coefficients  $c_{223}$  and  $c_{332}$ , of which nothing is known unless values for  $(W_{21} - W_{12})$  and  $(W_{31} - W_{13})$  are known as well. Moreover, if  $W_{123}$ ,  $(W_{21} - W_{12})$ , and  $(W_{31} - W_{13})$  are all known, these do not supply adequate information to extract  $W_{23}$  or  $W_{32}$ , since these coefficients also involve  $b_{23}$ .

Collectively, these observations show that ternary constants exist independently of the properties of the constituent binaries, contrary to Currie and Curtis's assertion (Currie and Curtis, 1976). Wohl has suggested (Jordan et al., 1950) that an estimate for the ternary interaction parameter is afforded by (Ganguly and Saxena, 1984, 1987)

$$W_{123} \approx \frac{1}{2}[(W_{21} - W_{12}) + (W_{13} - W_{31}) + (W_{32} - W_{23})]. \quad (11)$$

The definition for  $W_{123}$  indicates, however, that an approximation to  $c_{223} + c_{332}$  is needed to approximate  $W_{123}$  (see Eq. 10), yet Equation 11 contains the term  $(W_{32} - W_{23})$ , which yields  $c_{223} - c_{332}$ . Thus, Equation 11 is essentially ad hoc and cannot in any way be regarded as applying an unequivocal constraint on the magnitude of  $W_{123}$ .

The observation that the ternary constants exist independently of the binary coefficients makes good crystallochemical sense. Binary interaction coefficients only account for the forces arising between pairs of molecules. A ternary interaction parameter represents new interactions involving triplets of different molecular species, unrelated to pair-wise behavior. Although it may be true that ternary interaction parameters are, in general, negligible, this says only that pair-wise interactions dominate, not that triplet interactions cannot arise, nor that they are necessarily insignificant when they do arise.

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