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Extension of Wohl's ternary asymmetric solution model to four and *n* components

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ABSTRACT

A four-component asymmetric solution model, based on Wohl's treatment of ternary solutions, is derived from a general polynomial expansion (including up to third-degree terms) representing the excess molar free energy of a solution. This model is extended to *n* components. The derived model differs from other previously published models in the definition of the constant associated with the $X_iX_jX_k$ ($i \neq j \neq k \neq i$) terms.

INTRODUCTION

Asymmetric models of the excess thermodynamic properties of solutions are often required for the purposes of geochemical calculations. This note is concerned with the extension of Wohl's (1946, 1953) derivation for a ternary asymmetric model to 4- and *n*-component solutions. Comparison of these models to other previously published models is made. Symbols used in this note are presented in Table 1.

DERIVATION OF THE MODEL

A general expansion that describes the excess molar free energy of a four-component solution, truncated after third-degree terms, is

$$\begin{aligned} G^{ex} = {} & X_1X_2a_{12} + X_1X_3a_{13} + X_1X_4a_{14} + X_2X_3a_{23} \\ & + X_2X_4a_{24} + X_3X_4a_{34} + X_1^2X_2a_{112} + X_1X_2^2a_{122} \\ & + X_1^2X_3a_{113} + X_1X_3^2a_{133} + X_1^2X_4a_{114} + X_1X_4^2a_{144} \\ & + X_2^2X_3a_{223} + X_2X_3^2a_{233} + X_2^2X_4a_{224} \\ & + X_2X_4^2a_{244} + X_3^2X_4a_{334} + X_3X_4^2a_{344} + X_1X_2X_3a_{123} \\ & + X_1X_2X_4a_{124} + X_1X_3X_4a_{134} + X_2X_3X_4a_{234}. \end{aligned} \quad (1)$$

The a_{ij} and a_{ijk} are constants; the subscripts identify with which X_iX_j or $X_iX_jX_k$ term the constants are associated. Equation 1 is the extension of Wohl's (1946) ternary equation (Eq. 51) to a four-component solution. It differs from Wohl's (1946) Equation 51 in that the "2's" and "3's" are not included. This expansion satisfies the constraint that G^{ex} goes to zero as any mole fraction goes to 1. It is this constraint that permits deletion of terms of the type $\alpha(X_i^j)$ from Equation 1; where α is a constant, i refers to one of the components, and j is an integer of value less than 4. The above expansion is consistent with the Gibbs-Duhem relation, no matter what the values of the constants may be or what any relations of the constants to one another may be.

A more useful form of Equation 1 is one in which the constants have thermodynamic meaning. In binary systems G^{ex} may be expressed as a function $RT \ln \gamma_1^\infty$ and RT $\ln \gamma_2^\infty$, where γ_i^∞ is the activity coefficient of component "i" at infinite dilution (e.g., Froese, 1976). These are constants at a given pressure and temperature, but may be functions of P and T. If equations analogous to Equation 52a of Wohl (1946) and the expression for "C^*" of Wohl (1953) are substituted into Equation 1, then it can be shown that some of the constants in the resulting expression are the $\overline{G}^{ex\infty} = RT \ln \gamma^\infty$ for the bounding binary systems ($2.3RTA_{2\text{-}1}$ of Wohl is equivalent to $\overline{G}^{ex\infty}_{2\text{-}1}$ of this note). The remaining constants are the ternary constants as defined by Wohl (1953). The resultant expression is

$$\begin{aligned} G^{ex} = {} & X_1X_2(X_1\overline{G}^{ex\infty}_{2\text{-}1} + X_2\overline{G}^{ex\infty}_{1\text{-}2}) \\ & + X_1X_3(X_1\overline{G}^{ex\infty}_{3\text{-}1} + X_3\overline{G}^{ex\infty}_{1\text{-}3}) \\ & + X_1X_4(X_1\overline{G}^{ex\infty}_{4\text{-}1} + X_4\overline{G}^{ex\infty}_{1\text{-}4}) \\ & + X_2X_3(X_2\overline{G}^{ex\infty}_{3\text{-}2} + X_3\overline{G}^{ex\infty}_{2\text{-}3}) \\ & + X_2X_4(X_2\overline{G}^{ex\infty}_{4\text{-}2} + X_2\overline{G}^{ex\infty}_{2\text{-}4}) \\ & + X_3X_4(X_3\overline{G}^{ex\infty}_{4\text{-}3} + X_4\overline{G}^{ex\infty}_{3\text{-}4}) \\ & + X_1X_2X_3Q_{123} + X_1X_2X_4Q_{124} \\ & + X_1X_3X_4Q_{134} + X_2X_3X_4Q_{234}, \end{aligned} \quad (2)$$

where

$$\begin{aligned} Q_{ijk} = {} & [0.5(\overline{G}^{ex\infty}_{j\text{-}i} + \overline{G}^{ex\infty}_{i\text{-}j} + \overline{G}^{ex\infty}_{i\text{-}k} + \overline{G}^{ex\infty}_{k\text{-}i} + \overline{G}^{ex\infty}_{j\text{-}k} \\ & + \overline{G}^{ex\infty}_{k\text{-}j}) - C_{ijk}]. \end{aligned} \quad (3)$$

Observe that (1) the Q_{ijk} values are constants and depend on the sum of the bounding binary constants and the C_{ijk} [ternary constants as defined by Wohl (1953)] for the subsystem "i-j-k"; (2) the expression reduces to the ternary asymmetric model of Wohl (1953) if X_4 is set equal to zero; and (3) if one sets $\overline{G}^{ex\infty}_{i\text{-}j} = \overline{G}^{ex\infty}_{j\text{-}i}$, the expression reduces to binary ($X_3 = X_4 = 0$), ternary ($X_4 = 0$), and quaternary symmetric equations. It can be shown that

$$RT \ln \gamma_i = \partial[(\Sigma n_i)G^{ex}]/\partial n_i,$$

where n_i is the number of moles of the ith component. If the X_i's in Equation 2 are converted to mole ratios and then Equation 2 is multiplied by $n_1 + n_2 + n_3 + n_4$, differentiated with respect to n_1, and finally converted back to X_i's the following expression is obtained after some simplification:

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$$\begin{aligned} RT \ln \gamma_1 = {} & 2X_1(1 - X_1)[X_2\overline{G}^{ex\infty}_{2\text{-}1} + X_3\overline{G}^{ex\infty}_{3\text{-}1} + X_4\overline{G}^{ex\infty}_{4\text{-}1}] \\ & + (1 - 2X_1)[X_2^2\overline{G}^{ex\infty}_{1\text{-}2} + X_3^2\overline{G}^{ex\infty}_{1\text{-}3} + X_4^2\overline{G}^{ex\infty}_{1\text{-}4}] \\ & - 2X_2X_3[X_2\overline{G}^{ex\infty}_{3\text{-}2} + X_3\overline{G}^{ex\infty}_{2\text{-}3}] \\ & - 2X_2X_4[X_2\overline{G}^{ex\infty}_{4\text{-}2} + X_4\overline{G}^{ex\infty}_{2\text{-}4}] \\ & - 2X_3X_4[X_3\overline{G}^{ex\infty}_{4\text{-}3} - X_4\overline{G}^{ex\infty}_{3\text{-}4}] \\ & + (1 - 2X_1)[X_2X_3Q_{123} + X_2X_4Q_{124} \\ & \qquad + X_3X_4Q_{134}] \\ & - 2X_2X_3X_4Q_{234}, \end{aligned} \tag{5}$$

where the Q_{ijk} are defined by Equation 3. Expressions for components 2, 3, and 4 are obtained by suitable rotation of subscripts in Equation 5.

Table 1. Symbols

Symbol	Meaning
T	Temperature in kelvins
X_A	Mole fraction of component A
γ_A	Activity coefficient of component A; unit activity state defined as pure phase at P and T
G^{ex}	Excess molar free energy of a solution
$\overline{G}^{ex\infty}_{j\text{-}i}$	Excess partial molar free energy of component i in a binary mixture of i and j at infinite dilution
n_A	Moles of component A
C_{123}	Ternary constant for a solution of components 1, 2, and 3

Extension of the model to *n* components

Expressions for n-component systems ($n > 3$) are obtained by extending Equations 2 and 5. For the general case, the following two results are obtained (where n represents the number of components):

$$G^{ex} = \sum_{i=1}^{n-1} \sum_{\substack{j=2 \\ i<j}}^{n} X_iX_j(X_i\overline{G}^{ex\infty}_{j\text{-}i} + X_j\overline{G}^{ex\infty}_{i\text{-}j}) + \sum_{i=1}^{n-2}\sum_{j=2}^{n-1}\sum_{k=3}^{n} X_iX_jX_kQ_{ijk} \qquad (i < j < k) \tag{6}$$

and

$$\begin{aligned} RT \ln \gamma_m = {} & 2X_m(1 - X_m)\left[\sum_{\substack{i=1 \\ i\neq m}}^{n} X_i\overline{G}^{ex\infty}_{i\text{-}m}\right] \\ & + (1 - 2X_m)\left[\sum_{\substack{i=1 \\ i\neq m}}^{n} X_i^2\overline{G}^{ex\infty}_{m\text{-}i}\right] \\ & - 2\left[\sum_{\substack{i=1 \\ i\neq m}}^{n-1} \sum_{\substack{j=i+1 \\ j\neq m}}^{n} X_iX_j(X_i\overline{G}^{ex\infty}_{j\text{-}i} + X_j\overline{G}^{ex\infty}_{i\text{-}j})\right] \\ & + (1 - 2X_m)\left[\sum_{\substack{i=1 \\ i\neq m}}^{n-1} \sum_{\substack{j=i+1 \\ j\neq m}}^{n} X_iX_jQ_{mij}\right] \\ & - 2\left[\sum_{\substack{i=1 \\ i\neq m}}^{n-2} \sum_{\substack{j=i+1 \\ j\neq m\neq i}}^{n-1} \sum_{\substack{k=j+1 \\ k\neq m\neq j}}^{n} X_iX_jX_kQ_{ijk}\right] \end{aligned} \tag{7}$$

where

$$\begin{aligned} Q_{mij} = {} & [0.5(\overline{G}^{ex\infty}_{j\text{-}i} + \overline{G}^{ex\infty}_{i\text{-}j} + \overline{G}^{ex\infty}_{m\text{-}i} + \overline{G}^{ex\infty}_{i\text{-}m} \\ & + \overline{G}^{ex\infty}_{j\text{-}m} + \overline{G}^{ex\infty}_{m\text{-}j}) - C_{mij}] \end{aligned} \tag{8}$$

and

$$\begin{aligned} Q_{ijk} = {} & [0.5(\overline{G}^{ex\infty}_{j\text{-}i} + \overline{G}^{ex\infty}_{i\text{-}j} + \overline{G}^{ex\infty}_{k\text{-}i} + \overline{G}^{ex\infty}_{i\text{-}k} \\ & + \overline{G}^{ex\infty}_{j\text{-}k} + \overline{G}^{ex\infty}_{k\text{-}j}) - C_{ijk}]. \end{aligned} \tag{9}$$

Expressions for the activity coefficient of any component m can be obtained by expanding the above equation. Alternatively, one could expand for $RT \ln \gamma_1$ ($m = 1$) and then rotate subscripts. For example, for a 5-component solution where the desired expansion is for $RT \ln \gamma_3$, first expand for $RT \ln \gamma_1$ and then make the following rotations: $1 \rightarrow 3$, $2 \rightarrow 4$, $3 \rightarrow 5$, $4 \rightarrow 1$, and $5 \rightarrow 2$.

Comment on notation

For asymmetric solution models including up to third-degree terms, some authors (e.g., Berman and Brown, 1984) associate three subscripts with each parameter, even if it is a binary parameter. This is convenient because it directly relates the parameter and the mole fraction term by which it is multiplied. For example W_{122} (a binary parameter) would be multiplied by $X_1X_2X_2$. The equations derived above can be readily converted to this notation; however, this is not done since most of the geological literature uses two subscripts for binary parameters.

Discussion

Comment on other models based on Wohl's model

The four-component asymmetric model presented by Jordan et al. (1950) was based on the ternary model of Wohl (1946) that contained incorrect substitutions for the ternary constants (Wohl, 1953). Thus their model is in error. Ganguly and Saxena (1984, app.) presented a four-component model based on the revised substitutions of Wohl (1953); however, their expression should not contain $W^{4\text{-}2}$ and $W^{2\text{-}4}$ in the last term. The four- and n-component models presented here are the correct extensions of Wohl's ternary model.

The sign of the ternary constant in Equation 6 of Andersen and Lindsley (1981) is opposite to that of Wohl (1946, 1953); otherwise the models are the same. One should ensure that the sign of the ternary constant is consistent with the particular equation employed.

Comparison to other models

The expansion of Equation 10 of Benedict et al. (1945) for a four-component solution (setting $A_{iij} = A_{iji} = A_{jii} = A_{ji}$, etc.) is given in Table 2. Also given is the expression obtained from Berman and Brown's (1984) Equation 22 (using two subscripts for the binary constants) and the model derived in this note. Setting $A_{ij} = \frac{1}{3}W_{ij} = \frac{1}{3}\overline{G}^{ex\infty}_{i\text{-}j}$ and $A_{ijk} = \frac{1}{6}W_{ijk} = \frac{1}{6}Q_{ijk}$, it is seen that the expressions can be made identical. Thus, for a four- or n-component solution for which ternary data are available, the three models will provide the same values for G^{ex} and γ_i for given composition of solution, pressure, and temperature. Note that the model parameters (A, W, and $\overline{G}^{ex\infty}$

TABLE 2. Comparison of quaternary asymmetric solution models

This note*	Benedict et al. (1945)	Berman and Brown (1984)
$RT \ln \gamma_1 = 2\overline{G}^{\mathrm{ex}\infty}_{2\text{-}1} X_1 X_2(1 - X_1)$	$RT \ln \gamma_1 = 6A_{2\text{-}1} X_1 X_2(1 - X_1)$	$RT \ln \gamma_1 = 2W_{2\text{-}1} X_1 X_2(1 - X_1)$
$+ \overline{G}^{\mathrm{ex}\infty}_{1\text{-}2} X_2^2(1 - 2X_1)$	$+ 3A_{1\text{-}2} X_2^2(1 - 2X_1)$	$+ W_{1\text{-}2} X_2^2(1 - 2X_1)$
$+ 2\overline{G}^{\mathrm{ex}\infty}_{3\text{-}1} X_1 X_3(1 - X_1)$	$+ 6A_{3\text{-}1} X_1 X_3(1 - X_1)$	$+ 2W_{3\text{-}1} X_1 X_3(1 - X_1)$
$+ \overline{G}^{\mathrm{ex}\infty}_{1\text{-}3} X_3^2(1 - 2X_1)$	$+ 3A_{1\text{-}3} X_3^2(1 - 2X_1)$	$+ W_{1\text{-}3} X_3^2(1 - 2X_1)$
$+ 2\overline{G}^{\mathrm{ex}\infty}_{4\text{-}1} X_1 X_4(1 - X_1)$	$+ 6A_{4\text{-}1} X_1 X_4(1 - X_1)$	$+ 2W_{4\text{-}1} X_1 X_4(1 - X_1)$
$+ \overline{G}^{\mathrm{ex}\infty}_{1\text{-}4} X_4^2(1 - 2X_1)$	$+ 3A_{1\text{-}4} X_4^2(1 - 2X_1)$	$+ W_{1\text{-}4} X_4^2(1 - 2X_1)$
$- 2X_2X_3(X_3\overline{G}^{\mathrm{ex}\infty}_{2\text{-}3} + X_2\overline{G}^{\mathrm{ex}\infty}_{3\text{-}2})$	$- 6X_2X_3(X_3A_{2\text{-}3} + X_2A_{3\text{-}2})$	$- 2X_2X_3(X_3W_{2\text{-}3} + X_2W_{3\text{-}2})$
$- 2X_2X_4(X_4\overline{G}^{\mathrm{ex}\infty}_{2\text{-}4} + X_2\overline{G}^{\mathrm{ex}\infty}_{4\text{-}2})$	$- 6X_2X_4(X_4A_{2\text{-}4} + X_2A_{4\text{-}2})$	$- 2X_2X_4(X_4W_{2\text{-}4} + X_2W_{4\text{-}2})$
$- 2X_3X_4(X_3\overline{G}^{\mathrm{ex}\infty}_{4\text{-}3} + X_4\overline{G}^{\mathrm{ex}\infty}_{3\text{-}4})$	$- 6X_3X_4(X_3A_{4\text{-}3} + X_4A_{3\text{-}4})$	$- 2X_3X_4(X_3W_{4\text{-}3} + X_4W_{3\text{-}4})$
$+ Q_{123}X_2X_3(1 - 2X_1)$	$+ 6A_{123}X_2X_3(1 - 2X_1)$	$+ W_{123}X_2X_3(1 - 2X_1)$
$+ Q_{124}X_2X_4(1 - 2X_1)$	$+ 6A_{124}X_2X_4(1 - 2X_1)$	$+ W_{124}X_2X_4(1 - 2X_1)$
$+ Q_{134}X_3X_4(1 - 2X_1)$	$+ 6A_{134}X_3X_4(1 - 2X_1)$	$+ W_{134}X_3X_4(1 - 2X_1)$
$- 2Q_{234}X_2X_3X_4$	$- 12A_{234}X_2X_3X_4$	$- 2W_{234}X_2X_3X_4$
Where the Q_{ijk} are defined by Equation 3		

* This equation is identical to Equation 5 in the text; the first two terms of Equation 5 have been expanded for convenience.

factors, etc.) are not, in general, interchangeable. Applications must use the exact form of the equation used in the calibration of the model parameters.

The difference between the model derived here and those of Berman and Brown (1984) and Benedict et al. (1945) is in the definition of the "ternary constant" associated with the $X_iX_jX_k$ $(i \neq j \neq k \neq i)$ terms. In both of the latter models, there is only one constant associated with each term, whereas in the present model, the constant is a sum of the bounding binary constants in the "i-j-k" subsystem and the constant C_{ijk}. These relationships are summarized as follows:

$$X_iX_jX_k \times f_{ijk} \qquad (i \neq j \neq k \neq i)$$

represents the ternary terms, where, for Berman and Brown (1984) and Benedict et al. (1945),

$$f_{ijk} = \text{constant},$$

but in this note,

$$f_{ijk} = \tfrac{1}{2}\left[\sum\left(\begin{array}{c}\text{constants of}\\ \text{bounding binaries}\\ \text{for "}i\text{-}j\text{-}k\text{"}\\ \text{subsystem}\end{array}\right)\right] - \text{constant}.$$

For both the Berman and Brown (1984) model and the model presented here, the expressions for f_{ijk} result from the initial formulation of the polynomial expansion for G^{ex} [Eq. 6 of this note and Eq. 8 of Berman and Brown (1984)].

In the absence of data on ternary subsystems, the constants associated with $X_iX_jX_k$ $(i \neq j \neq k \neq i)$ terms would be set equal to zero in the models of Benedict et al. (1945) and Berman and Brown (1984); i.e., there is no estimate of ternary interactions. In the present model the C_{ijk} would be set equal to zero, and the sums of the binary constants associated with the ternary subsystem would remain as estimates of the ternary interactions.

It is important to note that one could use a more general expression for f_{ijk} instead of using either the Berman and Brown (1984) or the present expression. For example, one could use

$$f_{ijk} = \tfrac{1}{2}(z_{ij}\overline{G}^{\mathrm{ex}\infty}_{i\text{-}j} + z_{ji}\overline{G}^{\mathrm{ex}\infty}_{j\text{-}i} + z_{ik}\overline{G}^{\mathrm{ex}\infty}_{i\text{-}k} + z_{ki}\overline{G}^{\mathrm{ex}\infty}_{k\text{-}i} + z_{jk}\overline{G}^{\mathrm{ex}\infty}_{j\text{-}k} + z_{kj}\overline{G}^{\mathrm{ex}\infty}_{k\text{-}j}) - C_{ijk} \qquad (i \neq j \neq k \neq i),$$

where the z_{ij}'s are constants. In the case of Berman and Brown (1984) the z_{ij}'s are zero and $W_{ijk} = -C_{ijk}$, whereas in this note the z_{ij}'s equal unity. Other empirical methods of evaluating ternary interactions from binary data are presented by Acree (1984) and Hillert (1980).

For solutions that exhibit similar behavior, it would be useful to determine z_{ij} values that best reproduce the ternary data if the C_{ijk} values $(i \neq j \neq k \neq i)$ are set equal to zero. This would demonstrate if any empirical relationship exists among the binary constants that could be used to estimate ternary interactions in the absence of ternary data.

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