

Calculations of fluid–ternary solid solution equilibria: An application of the Wilson equation to fluid–(Fe,Mn,Mg)TiO₃ equilibria at 600 °C and 1 kbar

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ABSTRACT

The Wilson equation (Wilson 1964) is applied to (Fe,Mn,Mg)TiO₃ solid solutions for obtaining the mixing properties of the ternary solid solution at 600 °C and 1 kbar. The present study utilizes data on cation exchange between (Fe,Mn)Cl_{2(aq)} and (Fe,Mn)TiO₃, between (Mn,Mg)Cl_{2(aq)} and (Mn,Mg)TiO₃, and between (Fe,Mg)Cl_{2(aq)} and (Fe,Mg)TiO₃ (Kubo et al. 1992). The molar excess Gibbs energy (G^{ex}) is the following: G^{ex} (kJ/mol) = $-7.260[X_{\text{FeTiO}_3} \ln(X_{\text{FeTiO}_3} + 1.314X_{\text{MnTiO}_3} + 0.962X_{\text{MgTiO}_3}) + X_{\text{MnTiO}_3} \ln(0.585X_{\text{FeTiO}_3} + X_{\text{MnTiO}_3} + 0.393X_{\text{MgTiO}_3}) + X_{\text{MgTiO}_3} \ln(0.406X_{\text{FeTiO}_3} + 0.371X_{\text{MnTiO}_3} + X_{\text{MgTiO}_3})]$, where X stands for the mole fraction of the subscripted component. The predicted compositions of (Fe,Mn,Mg)Cl_{2(aq)} fluids in equilibrium with the ternary solid solutions are in good agreement with the experimental values.

INTRODUCTION

The Margules equation has been used by many investigators to describe the mixing properties of mineral solid solutions (e.g., Ganguly and Saxena 1987). By means of the Margules equation, the molar excess Gibbs energy (G^{ex}) of a ternary solid solution is written as follows (e.g., Mukhopadhyay et al. 1993):

$$G^{\text{ex}} = X_1X_2(X_2W_{12} + X_1W_{21}) + X_1X_3(X_3W_{13} + X_1W_{31}) + X_2X_3(X_3W_{23} + X_2W_{32}) + X_1X_2X_3C_{123} \quad (1)$$

where X and W stand for the mole fraction of the subscripted component and the Margules parameter for the subscripted pair, respectively. The term C_{123} is the ternary interaction parameter, which is independent of the composition and the binary Margules parameters. If the ternary system consists of only symmetric regular binaries, the ternary interaction parameter is equal to zero (Mukhopadhyay et al. 1993). Otherwise, there are no reasons for assuming $C_{123} = 0$ without experimental confirmation.

As an alternative method for describing the mixing properties of multicomponent solutions, the Wilson equation (Wilson 1964) has been used for real solution mixtures. The molar excess Gibbs energy of a ternary solution is written as follows:

$$G^{\text{ex}} = -RT \sum_{i=1}^3 X_i \ln \left(\sum_{j=1}^3 A_{ij} X_j \right) \quad (2)$$

where R is the universal gas constant, T is the absolute temperature, and A_{ij} stands for the Wilson parameter for the pair of components i and j . By definition, A_{ii} is equal to 1 in Equation 2.

By an appropriate differentiation of Equation 2, the activity coefficient of component i (γ_i) is expressed as follows:

$$\ln \gamma_i = 1 - \ln \left(\sum_{j=1}^3 X_j A_{ij} \right) - \sum_{k=1}^3 \left(\frac{X_k A_{ki}}{\sum_{j=1}^3 X_j A_{kj}} \right) \quad (3)$$

The activity coefficients of the components in the ternary solution can be computed by combining the Wilson parameters for the three binary solutions whose components make up the ternary system. Thus, the main advantage of the Wilson equation is its potential applicability to the ternary solution without the ternary interaction parameter. When the number of the components is n , the equations for G^{ex} and activity coefficients can be obtained by substituting n for the limit sum 3 in Equations 2 and 3. Therefore, we can compute activity coefficients for solutions of arbitrary number of components by combining the Wilson parameters for binary mixtures.

The major drawback of the Wilson equation is its inapplicability to partially miscible solutions. Renon and Prausnitz (1968) modified the Wilson equation by introducing additional parameters to make it applicable to those mixtures. Applications of their equation (the NRTL equation) to partially miscible multicomponent mixtures might require more complicated calculations than those of the Wilson equation.

This study focuses on an application of the Wilson equation to mineral solid solutions. As an illustrative example, this study analyzes the experimental results on fluid–(Fe,Mn,Mg)TiO₃ equilibria (Kubo et al. 1992). Although there are many studies on cation exchange reactions between minerals and aqueous solutions, only a few studies deal with both binary and ternary solid solutions. The reason for choosing fluid–(Fe,Mn,Mg)TiO₃ equilibria is the availability of such experimental data. Based on the results of the three binary cation exchange experiments, the present study obtains the mixing properties of the ternary solid solution. The present study computes the compositions of (Fe,Mn,Mg)Cl_{2(aq)} in equilibria

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with (Fe,Mn,Mg)TiO₃ solid solutions and compares these computed results with the experimental data. This study also compares the Wilson equation with the Margules equation in regard to the predictability of the fluid-phase compositions.

A subsidiary purpose of the present study was to use the nonlinear programming technique of Britt and Luecke (1973) for obtaining the Wilson parameters and Gibbs energy of reactions. Although the computational technique is more complicated than ordinary linear least-square regression, the results of the calculation obey the law of mass action.

THE WILSON EQUATION

The Wilson equation is based on the Flory-Huggins equation (Flory 1941; Huggins 1941) and the concept of "local volume fraction" (Wilson 1964), both of which have been only rarely referred to in the literature of geology, mineralogy, and geochemistry. The derivation of the Flory-Huggins equation was given in detail by Flory (1944) and is not repeated here. Only the resultant Flory-Huggins equation for a ternary mixture is shown below. Thereafter, this paper derives the Wilson equation by introducing the concept of "local volume fraction" following the method of Prausnitz et al. (1986).

According to the Flory-Huggins equation, the molar Gibbs energy of mixing (G^{mixing}) is expressed as follows:

$$G^{\text{mixing}} = RT(X_1 \ln \phi_1 + X_2 \ln \phi_2 + X_3 \ln \phi_3) \quad (4)$$

where X_1 , X_2 , and X_3 stand for the mole fractions of the solvent, solute 1, and solute 2, respectively, and ϕ_1 , ϕ_2 , and ϕ_3 are the volume fractions of the solvent, solute 1, and solute 2, respectively.

Concept of "local volume fraction"

In a ternary solution being considered here, the focus is on a central molecule of type i . The probability of finding a molecule of type j , relative to finding a molecule of type i , adjacent to the central molecule is expressed in terms of the mole fraction and two Boltzmann factors:

$$\frac{X_{ji}}{X_{ii}} = \frac{X_j \exp\left(\frac{-\lambda_{ji}}{RT}\right)}{X_i \exp\left(\frac{-\lambda_{ii}}{RT}\right)} \quad (5)$$

where X_{ji} and X_{ii} stand for the mole fractions of components j and i around the central molecule of type i . The terms λ_{ji} and λ_{ii} are related to the potential energies of a j - i and an i - i pair, respectively. The ternary interaction parameter does not appear in Equation 5. It should be noted that Equation 5 considers only the nearest-neighbor molecules around the central molecule in a spherical liquid-like environment. The equation then assumes that the lattice sites on which the molecules are located could be displaced by the interaction energies between molecules.

Wilson (1964) defined the local volume fraction of component i (ϕ_{ii}) as follows:

$$\phi_{ii} = \frac{V_i X_{ii}}{V_1 X_{i1} + V_2 X_{i2} + V_3 X_{i3}} \quad (6)$$

where V_1 , V_2 , and V_3 stand for the molar volumes of the subscripted components in their pure state. It should be noted that $\phi_{i1} + \phi_{i2} + \phi_{i3}$ is not always equal to 1 (Prausnitz et al. 1986). As a result, the local volume fraction is not equivalent to the volume fraction and should be considered as a conceptual quantity in the microscale environment. The Wilson parameter (Λ_{ij}) is defined as follows:

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp\left(\frac{\lambda_{ii} - \lambda_{ij}}{RT}\right) \quad (7)$$

By the above definition, Λ_{ii} is equal to 1. By combining Equations 5 to 7, ϕ_{ii} is expressed as follows:

$$\phi_{ii} = \frac{X_{ii}}{\Lambda_{i1} X_1 + \Lambda_{i2} X_2 + \Lambda_{i3} X_3} \quad (8)$$

Wilson (1964) substituted the local volume fractions of the components, instead of their volume fractions, into the Flory-Huggins equation (Eq. 4). After rearrangement, G^{mixing} can be expressed as follows:

$$G^{\text{mixing}} = -RT\{[X_1 \ln(\Lambda_{11} X_1 + \Lambda_{12} X_2 + \Lambda_{13} X_3)] + [X_2 \ln(\Lambda_{21} X_1 + \Lambda_{22} X_2 + \Lambda_{23} X_3)] + [X_3 \ln(\Lambda_{31} X_1 + \Lambda_{32} X_2 + \Lambda_{33} X_3)] - (X_1 \ln X_1 + X_2 \ln X_2 + X_3 \ln X_3)\} \quad (9)$$

Therefore, the molar excess Gibbs energy (G^{ex}) can be derived as follows:

$$G^{\text{ex}} = G^{\text{mixing}} - RT(X_1 \ln X_1 + X_2 \ln X_2 + X_3 \ln X_3) \quad (10)$$

which is equivalent to Equation 2.

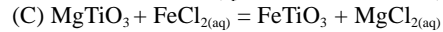
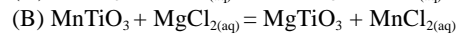
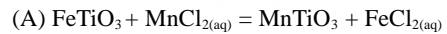
Activity coefficients of the individual components can be obtained from the partial derivatives of the excess Gibbs energy with respect to the number of moles of that component as follows:

$$\ln \gamma_i = \frac{1}{RT} \left(\frac{\partial n G^{\text{ex}}}{\partial n_i} \right)_{T,P,n_{j \neq i}} \quad (11)$$

where n and n_i stand for the total number of moles of all the components and the number of moles of component i , respectively. Using Equations 9 and 10, the activity coefficient of component i can be expressed as Equation 3.

APPLICATIONS TO FLUID-(Fe₂Mn)TiO₃, FLUID-(Mn,Mg)TiO₃, AND FLUID-(Fe,Mg)TiO₃ EQUILIBRIA

Kubo et al. (1992) carried out cation exchange experiments on the following systems at 600 °C and 1 kbar by using the method of Uchida et al. (1989):



Total molarity of metal chloride in the aqueous phase was 1.0 *M* in all their experiments. Only (Fe,Mn,Mg)TiO₃ was observed as the solid product.

By using the Wilson equation for describing the activity coefficients for the components of the solid phase, the Gibbs energy of reaction A can be written as follows:

$$\begin{aligned} \frac{\Delta G_A^0}{RT} = -\ln K = -\ln \frac{X_{\text{MnTiO}_3} \gamma_{\text{MnTiO}_3} Y_{\text{Fe}}}{X_{\text{FeTiO}_3} \gamma_{\text{FeTiO}_3} Y_{\text{Mn}}} = -\ln \frac{X_{\text{MnTiO}_3} Y_{\text{Fe}}}{X_{\text{FeTiO}_3} Y_{\text{Mn}}} \\ + \ln \frac{\Lambda_{\text{MnFe}} X_{\text{FeTiO}_3} + X_{\text{MnTiO}_3}}{X_{\text{FeTiO}_3} + \Lambda_{\text{FeMn}} X_{\text{MnTiO}_3}} + \frac{\Lambda_{\text{MnFe}} X_{\text{FeTiO}_3} - X_{\text{FeTiO}_3}}{X_{\text{FeTiO}_3} + \Lambda_{\text{FeMn}} X_{\text{MnTiO}_3}} \\ + \frac{X_{\text{MnTiO}_3} - \Lambda_{\text{MnFe}} X_{\text{MnTiO}_3}}{\Lambda_{\text{MnFe}} X_{\text{FeTiO}_3} + X_{\text{MnTiO}_3}} \end{aligned} \quad (12)$$

where K stands for the equilibrium constant and Y_{Fe} and Y_{Mn} designate the ratios of the molalities of the subscripted species to the total molality of metal chloride in the fluid phase. The Y values are expressed as follows:

$$Y_{\text{Fe}} = \frac{m_{\text{FeCl}_2(\text{aq})}}{m_{\text{FeCl}_2(\text{aq})} + m_{\text{MnCl}_2(\text{aq})} + m_{\text{MgCl}_2(\text{aq})}} \quad (13)$$

$$Y_{\text{Mn}} = \frac{m_{\text{MnCl}_2(\text{aq})}}{m_{\text{FeCl}_2(\text{aq})} + m_{\text{MnCl}_2(\text{aq})} + m_{\text{MgCl}_2(\text{aq})}} \quad (14)$$

ΔG^0 for Reaction B or C can be obtained by changing the subscripts appropriately. For example, Y_{Mg} denotes the following ratio.

$$Y_{\text{Mg}} = \frac{m_{\text{MgCl}_2(\text{aq})}}{m_{\text{FeCl}_2(\text{aq})} + m_{\text{MnCl}_2(\text{aq})} + m_{\text{MgCl}_2(\text{aq})}} \quad (15)$$

The present study ignores the ionic species and assumes that the ratios of activity coefficients of the neutral aqueous species are equal to 1. Kubo et al. (1992) reported the concentrations of the aqueous species in units of molarity. Because the present study calculates the ratios of concentrations, the conversion factor of molar scale into molal scale does not appear in Equations 13 to 15.

Values of ΔG^0 for reactions A–C and the Wilson parameters were obtained by using the following constraints:

$$\Delta G_C^0 = -(\Delta G_A^0 + \Delta G_B^0) \quad (16)$$

$$\Lambda_{\text{MgFe}} = \frac{\Lambda_{\text{MgMn}} \Lambda_{\text{MnFe}} \Lambda_{\text{FeMg}}}{\Lambda_{\text{MnMg}} \Lambda_{\text{FeMn}}} \quad (17)$$

The derivation of Equation 17 was given in Hala (1972). By imposing the above constraints on the calculations, the calculated ΔG^0 values as well as the Wilson parameters are internally consistent. For the calculation of all the values, the non-linear programming technique derived by Britt and Luecke (1973) was used in the present study. Solid and fluid compositions were also computed for each experimental data point. This study considers that the standard errors of measurements of both compositions are 0.005 in terms of mole fraction or the ratio of molality. Substitutions of the calculated compositions of the solid and fluid phases and the Wilson parameters into Equation 12 make the resultant $\ln K$ values become constant. The same is true for reactions B and C. Detailed calculation procedures are shown in the Appendix.

The results of the calculations of $\Delta G^0/RT$ and the Wilson parameters are listed in Table 1. The experimental and computed compositions are summarized in Tables 2–4. From Equation 12 and the equivalent expressions for reactions B and C, we get the following equations:

$$\frac{Y_{\text{Fe}}}{Y_{\text{Mn}}} = \exp \left[\left(-\frac{\Delta G_A^0}{RT} \right) - \ln \left(\frac{X_{\text{MnTiO}_3} \gamma_{\text{MnTiO}_3}}{X_{\text{FeTiO}_3} \gamma_{\text{FeTiO}_3}} \right) \right] \quad (18)$$

$$\frac{Y_{\text{Mn}}}{Y_{\text{Mg}}} = \exp \left[\left(-\frac{\Delta G_B^0}{RT} \right) - \ln \left(\frac{X_{\text{MgTiO}_3} \gamma_{\text{MgTiO}_3}}{X_{\text{MnTiO}_3} \gamma_{\text{MnTiO}_3}} \right) \right] \quad (19)$$

$$\frac{Y_{\text{Mg}}}{Y_{\text{Fe}}} = \exp \left[\left(-\frac{\Delta G_C^0}{RT} \right) - \ln \left(\frac{X_{\text{FeTiO}_3} \gamma_{\text{FeTiO}_3}}{X_{\text{MgTiO}_3} \gamma_{\text{MgTiO}_3}} \right) \right] \quad (20)$$

If we specify the solid compositions, activity coefficients of the components in the solid phase are determined by Equation 3. By using the activity coefficients at specific solid compositions and the ΔG^0 value for the relevant reaction, the fluid-phase compositions can be obtained from the left-hand sides of Equations 18–20. Then cation exchange isotherms for reactions A, B, and C are computed from Equations 18, 19, and 20, respectively (Figs. 1–3). The computed isotherms show good agreement with the experimental results of Kubo et al. (1992). Activities of end-member components are plotted against the mole fractions for the three binary solid solutions (Fig. 4). The (Fe,Mn)TiO₃ and (Fe,Mg)TiO₃ solid solutions show almost ideal behavior whereas (Mn,Mg)TiO₃ shows distinct nonideality.

It is possible to compute the ΔG^0 value and the Wilson parameters for each reaction and to compare the results with the internally consistent values in Table 1. Calculations on each reaction gave internally inconsistent results. Furthermore, the iterative computations often showed divergences due to the nonlinearity of the Wilson equation. Therefore, this study did not attempt to extract thermodynamic quantities from the individual exchange reactions.

Calculations of fluid-(Fe,Mn,Mg)TiO₃ equilibria

By substituting the Wilson parameters into Equation 2, the molar excess Gibbs energy of (Fe,Mn,Mg)TiO₃ solid solution at 600 °C and 1 kbar is expressed as follows.

$$\begin{aligned} G^{\text{ex}}(\text{kJ/mol}) = & -7.260[X_{\text{FeTiO}_3} \ln(X_{\text{FeTiO}_3} + 1.314X_{\text{MnTiO}_3} + \\ & 0.962X_{\text{MgTiO}_3}) \\ & + X_{\text{MnTiO}_3} \ln(0.585X_{\text{FeTiO}_3} + X_{\text{MnTiO}_3} + 0.393X_{\text{MgTiO}_3}) \\ & + X_{\text{MgTiO}_3} \ln(0.406X_{\text{FeTiO}_3} \\ & + 0.371X_{\text{MnTiO}_3} + X_{\text{MgTiO}_3})] \end{aligned} \quad (21)$$

Table 1. ΔG^0 for reactions A–C and Wilson parameters for (Fe,Mn)TiO₃, (Mn,Mg)TiO₃, and (Fe,Mg)TiO₃ solid solutions

Reaction A: $\text{FeTiO}_3 + \text{MnCl}_{2(\text{aq})} = \text{MnTiO}_3 + \text{FeCl}_{2(\text{aq})}$		
Reaction B: $\text{MnTiO}_3 + \text{MgCl}_{2(\text{aq})} = \text{MnTiO}_3 + \text{MnCl}_{2(\text{aq})}$		
Reaction C: $\text{MgTiO}_3 + \text{FeCl}_{2(\text{aq})} = \text{FeTiO}_3 + \text{MgCl}_{2(\text{aq})}$		
$\frac{\Delta G_A^0}{RT} = 1.462(0.042)$,	$\frac{\Delta G_B^0}{RT} = -0.975(0.036)$,	$\frac{\Delta G_C^0}{RT} = -0.487(0.035)$
$\Lambda_{\text{MnFe}} = 0.585(0.220)$, $\Lambda_{\text{FeMn}} = 1.314(0.370)$, $\Lambda_{\text{MgMn}} = 0.371(0.087)$		
$\Lambda_{\text{MnMg}} = 0.393(0.073)$, $\Lambda_{\text{FeMg}} = 0.962(0.213)$, $\Lambda_{\text{MgFe}} = 0.406(0.138)$		
Notes: Values in parentheses indicate the standard errors. RT is 7.260 (kJ/mol) at 600 °C.		

$$\ln \gamma_{\text{FeTiO}_3} = 1 - \ln \left(X_{\text{FeTiO}_3} + X_{\text{MnTiO}_3} \Lambda_{\text{FeMn}} + X_{\text{MgTiO}_3} \Lambda_{\text{FeMg}} \right) - \frac{X_{\text{FeTiO}_3}}{X_{\text{FeTiO}_3} + X_{\text{MnTiO}_3} \Lambda_{\text{FeMn}} + X_{\text{MgTiO}_3} \Lambda_{\text{FeMg}}} - \frac{X_{\text{MnTiO}_3} \Lambda_{\text{MnFe}}}{X_{\text{FeTiO}_3} \Lambda_{\text{MnFe}} + X_{\text{MnTiO}_3} + X_{\text{MgTiO}_3} \Lambda_{\text{MnMg}}} - \frac{X_{\text{MgTiO}_3} \Lambda_{\text{MgFe}}}{X_{\text{FeTiO}_3} \Lambda_{\text{MgFe}} + X_{\text{MnTiO}_3} \Lambda_{\text{MgMn}} + X_{\text{MgTiO}_3}} \quad (22)$$

$$\ln \gamma_{\text{MnTiO}_3} = 1 - \ln \left(X_{\text{FeTiO}_3} \Lambda_{\text{MnFe}} + X_{\text{MnTiO}_3} + X_{\text{MgTiO}_3} \Lambda_{\text{MnMg}} \right) - \frac{X_{\text{FeTiO}_3} \Lambda_{\text{FeMn}}}{X_{\text{FeTiO}_3} + X_{\text{MnTiO}_3} \Lambda_{\text{FeMn}} + X_{\text{MgTiO}_3} \Lambda_{\text{FeMg}}} - \frac{X_{\text{MnTiO}_3}}{X_{\text{FeTiO}_3} \Lambda_{\text{MnFe}} + X_{\text{MnTiO}_3} + X_{\text{MgTiO}_3} \Lambda_{\text{MnMg}}} - \frac{X_{\text{MgTiO}_3} \Lambda_{\text{MgFe}}}{X_{\text{FeTiO}_3} \Lambda_{\text{MgFe}} + X_{\text{MnTiO}_3} \Lambda_{\text{MgMn}} + X_{\text{MgTiO}_3}} \quad (23)$$

$$\ln \gamma_{\text{MgTiO}_3} = 1 - \ln \left(X_{\text{FeTiO}_3} \Lambda_{\text{MgFe}} + X_{\text{MnTiO}_3} \Lambda_{\text{MgMn}} + X_{\text{MgTiO}_3} \right) - \frac{X_{\text{FeTiO}_3} \Lambda_{\text{FeMg}}}{X_{\text{FeTiO}_3} + X_{\text{MnTiO}_3} \Lambda_{\text{FeMn}} + X_{\text{MgTiO}_3} \Lambda_{\text{FeMg}}} - \frac{X_{\text{MnTiO}_3} \Lambda_{\text{MnMg}}}{X_{\text{FeTiO}_3} \Lambda_{\text{MnFe}} + X_{\text{MnTiO}_3} + X_{\text{MgTiO}_3} \Lambda_{\text{MnMg}}} - \frac{X_{\text{MgTiO}_3}}{X_{\text{FeTiO}_3} \Lambda_{\text{MgFe}} + X_{\text{MnTiO}_3} \Lambda_{\text{MgMn}} + X_{\text{MgTiO}_3}} \quad (24)$$

By using Equation 3, activity coefficients of FeTiO₃, MnTiO₃, and MgTiO₃ in the ternary solid solution are expressed as follows:

On the basis of the above expressions of activity coefficients, the compositions of (Fe,Mn,Mg)Cl_{2(aq)} in equilibria with (Fe,Mn,Mg)TiO₃ were computed. The solid compositions were taken from the experimental results of Kubo et al. (1992). The method of Shallcross et al. (1988) was used for the present calculation. Let us define Z values as follows.

$$Z_1 = \frac{Y_{\text{Fe}}}{Y_{\text{Mn}}}, \quad Z_2 = \frac{Y_{\text{Mn}}}{Y_{\text{Mg}}}, \quad Z_3 = \frac{Y_{\text{Mg}}}{Y_{\text{Fe}}}$$

From the solid compositions, activities of the end-member components can be computed. Thus, Z₁, Z₂, and Z₃ values are obtained from Equations 18–20. If we use Z₁ and Z₂ values, Y values are calculated as follows:

$$Y_{\text{Fe}} = \frac{Z_1 Z_2}{Z_1 Z_2 + Z_2 + 1} \quad (25)$$

$$Y_{\text{Mn}} = \frac{Z_2}{Z_1 Z_2 + Z_2 + 1} \quad (26)$$

$$Y_{\text{Mg}} = \frac{1}{Z_1 Z_2 + Z_2 + 1} \quad (27)$$

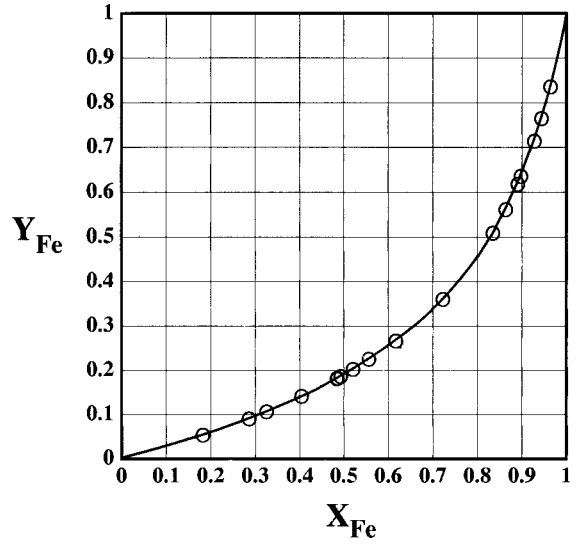


FIGURE 1. The cation exchange isotherm computed in this study (solid line) and the experimental data points (Kubo et al. 1992) for the reaction $\text{FeTiO}_3 + \text{MnCl}_{2(\text{aq})} = \text{MnTiO}_3 + \text{FeCl}_{2(\text{aq})}$. X_{Fe} and Y_{Fe} stand for the mole fraction of FeTiO₃ in the solid phase and the molality ratio defined by Equation 13.

TABLE 2. Experimental and calculated results on the cation exchange reaction $\text{FeTiO}_3 + \text{MnCl}_{2(\text{aq})} = \text{MnTiO}_3 + \text{FeCl}_{2(\text{aq})}$

Experimental results*		Calculated results†	
X_{FeTiO_3}	Y_{Fe}	X_{FeTiO_3}	Y_{Fe}
0.928	0.752	0.939	0.748
0.891	0.624	0.893	0.623
0.864	0.550	0.859	0.553
0.964	0.828	0.962	0.828
0.898	0.632	0.897	0.632
0.944	0.740	0.937	0.742
0.485	0.184	0.485	0.183
0.325	0.086	0.318	0.104
0.404	0.137	0.402	0.141
0.617	0.259	0.613	0.264
0.521	0.159	0.502	0.192
0.493	0.163	0.483	0.182
0.182	0.053	0.182	0.054
0.484	0.150	0.471	0.175
0.557	0.180	0.537	0.213
0.723	0.311	0.698	0.337
0.286	0.093	0.286	0.092
0.835	0.512	0.836	0.511

* Kubo et al. (1992).

† Calculated results of this study.

Other solutions of Y values are possible when we use the set of Z₁ and Z₃ or the set of Z₂ and Z₃. Therefore, three sets of Y values are possible. The weighted average values of fluid-phase compositions can be obtained from the following equations:

$$Y_{\text{Fe}} = \frac{X_{\text{MnTiO}_3} Z_1 Z_2}{Z_1 Z_2 + Z_2 + 1} + \frac{X_{\text{FeTiO}_3} Z_1}{Z_1 Z_3 + Z_1 + 1} + \frac{X_{\text{MgTiO}_3}}{Z_2 Z_3 + Z_3 + 1} \quad (28)$$

$$Y_{\text{Mn}} = \frac{X_{\text{MnTiO}_3} Z_2}{Z_1 Z_2 + Z_2 + 1} + \frac{X_{\text{FeTiO}_3}}{Z_1 Z_3 + Z_1 + 1} + \frac{X_{\text{MgTiO}_3} Z_2 Z_3}{Z_2 Z_3 + Z_3 + 1} \quad (29)$$

$$Y_{\text{Mg}} = \frac{X_{\text{MnTiO}_3} Z_2}{Z_1 Z_2 + Z_2 + 1} + \frac{X_{\text{FeTiO}_3}}{Z_1 Z_3 + Z_1 + 1} + \frac{X_{\text{MgTiO}_3} Z_2 Z_3}{Z_2 Z_3 + Z_3 + 1} \quad (30)$$

TABLE 3. Experimental and calculated results on the cation exchange reaction $\text{MnTiO}_3 + \text{MgCl}_{2(\text{aq})} = \text{MgTiO}_3 + \text{MnCl}_{2(\text{aq})}$

Experimental results*		Calculated results†	
X_{MnTiO_3}	Y_{Mn}	X_{MnTiO_3}	Y_{Mn}
0.480	0.716	0.480	0.722
0.456	0.692	0.450	0.715
0.528	0.745	0.530	0.735
0.707	0.775	0.705	0.781
0.136	0.559	0.140	0.555
0.581	0.761	0.584	0.748
0.339	0.666	0.334	0.680
0.046	0.410	0.064	0.404
0.605	0.769	0.609	0.754
0.663	0.780	0.666	0.769
0.147	0.524	0.127	0.538
0.914	0.846	0.894	0.872
0.295	0.669	0.296	0.666
0.081	0.484	0.093	0.478
0.168	0.553	0.151	0.568
0.320	0.649	0.311	0.672
0.393	0.648	0.379	0.695
0.908	0.861	0.897	0.875
0.813	0.768	0.793	0.813
0.743	0.797	0.744	0.794
0.356	0.706	0.361	0.690

* Kubo et al. (1992).

† Calculated results of this study.

TABLE 4. Experimental and calculated results on the cation exchange reaction $\text{MgTiO}_3 + \text{FeCl}_{2(\text{aq})} = \text{FeTiO}_3 + \text{MgCl}_{2(\text{aq})}$

Experimental results*		Calculated results†	
X_{MgTiO_3}	Y_{Mg}	X_{MgTiO_3}	Y_{Mg}
0.053	0.183	0.059	0.180
0.122	0.248	0.100	0.261
0.040	0.118	0.035	0.120
0.151	0.318	0.143	0.324
0.055	0.185	0.060	0.183
0.359	0.548	0.375	0.524
0.262	0.452	0.267	0.446
0.167	0.328	0.155	0.338
0.168	0.357	0.170	0.355
0.346	0.507	0.347	0.505
0.525	0.595	0.515	0.612
0.922	0.922	0.925	0.919
0.911	0.904	0.910	0.905
0.792	0.787	0.785	0.796
0.807	0.772	0.787	0.797
0.474	0.605	0.482	0.592
0.943	0.944	0.946	0.941
0.594	0.611	0.571	0.647
0.715	0.762	0.724	0.750
0.343	0.456	0.321	0.487
0.198	0.378	0.194	0.382
0.457	0.607	0.471	0.585
0.716	0.713	0.701	0.734
0.608	0.623	0.586	0.657
0.452	0.565	0.448	0.571
0.361	0.493	0.351	0.508
0.650	0.722	0.661	0.706

* Kubo et al. (1992).

† Calculated results of this study.

The weights correspond to the mole fractions of the components common to Z_i and Z_j .

Computed fluid compositions and the experimental results of Kubo et al. (1992) are compared in Figure 5. The agreement is generally good. Although the computed compositions deviate from the experimental compositions in the region of low Y_{Fe} , the deviations are within ± 0.08 in terms of the Y value for any component (Table 5). It can be concluded that fluid

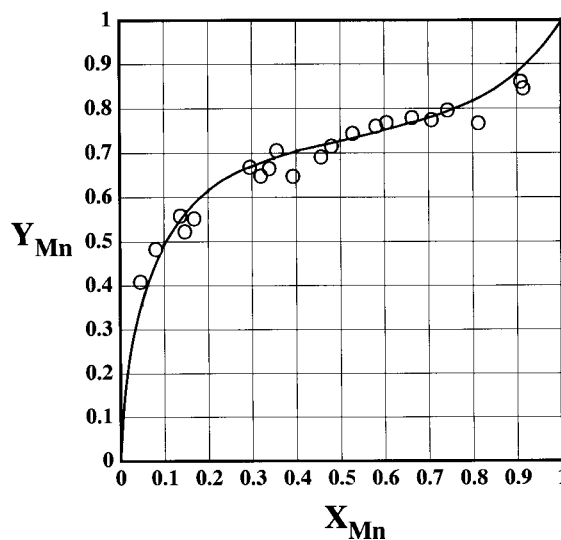


FIGURE 2. The cation exchange isotherm computed in this study (solid line) and the experimental data points (Kubo et al. 1992) for the reaction $\text{MnTiO}_3 + \text{MgCl}_{2(\text{aq})} = \text{MgTiO}_3 + \text{MnCl}_{2(\text{aq})}$. X_{Mn} and Y_{Mn} stand for the mole fraction of MnTiO_3 in the solid phase and the molality ratio defined by Equation 14.

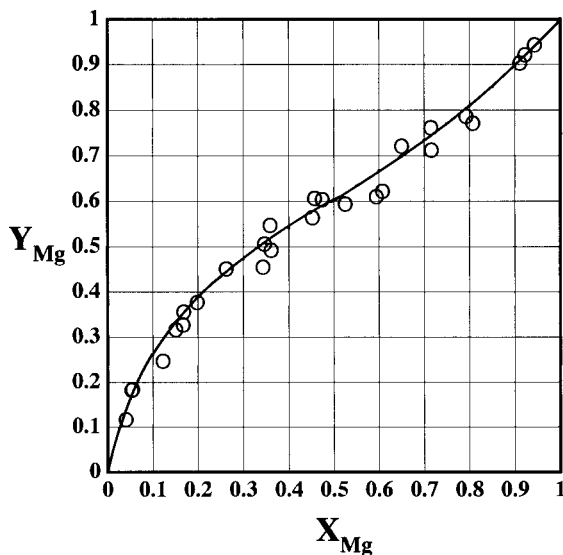


FIGURE 3. The cation exchange isotherm computed in this study (solid line) and the experimental data points (Kubo et al. 1992) for the reaction $\text{MgTiO}_3 + \text{FeCl}_{2(\text{aq})} = \text{FeTiO}_3 + \text{MgCl}_{2(\text{aq})}$. X_{Mg} and Y_{Mg} stand for the mole fraction of MgTiO_3 in the solid phase and the molality ratio defined by Equation 15.

compositions in equilibria with the ternary solid solutions may be predicted from the binary cation exchange experiments.

COMPARISON WITH THE MARGULES EQUATION

In the introduction, it was argued that the Margules equation without the ternary interaction parameter is not accurate for describing the mixing property of the ternary solid solution consisting of asymmetric binaries. The accuracy of the compo-

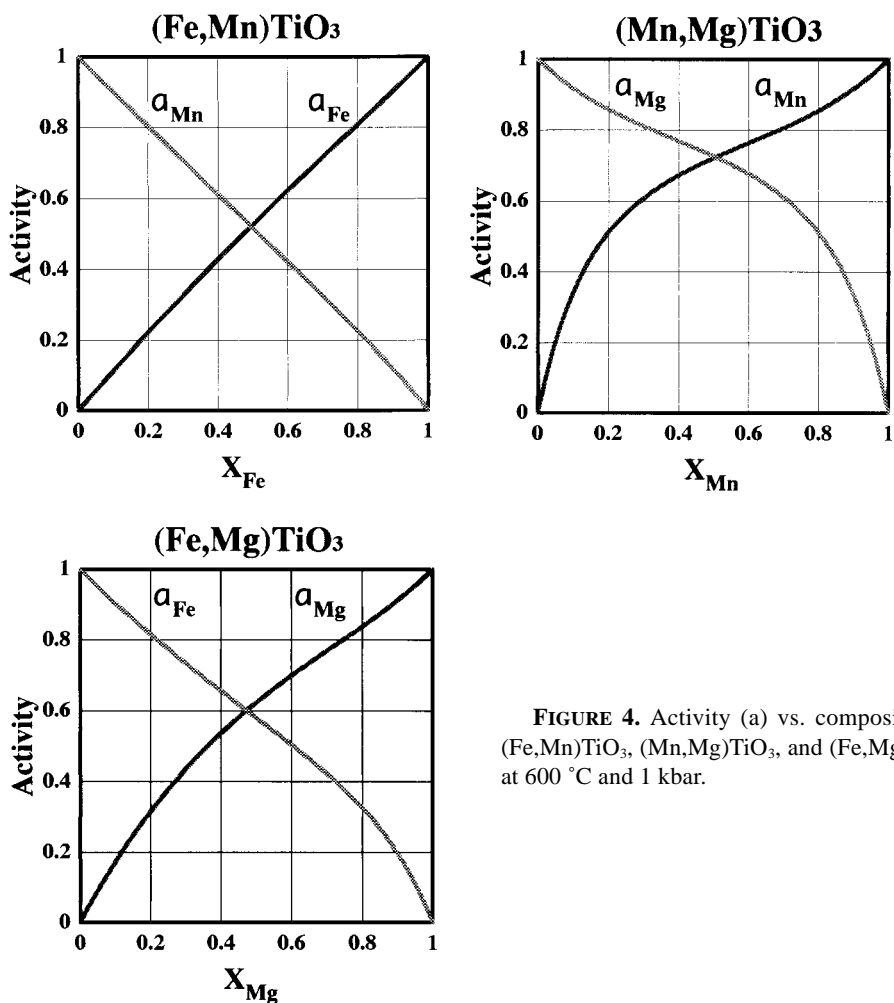


FIGURE 4. Activity (a) vs. composition (X) relations of (Fe,Mn)TiO₃, (Mn,Mg)TiO₃, and (Fe,Mg)TiO₃ solid solutions at 600 °C and 1 kbar.

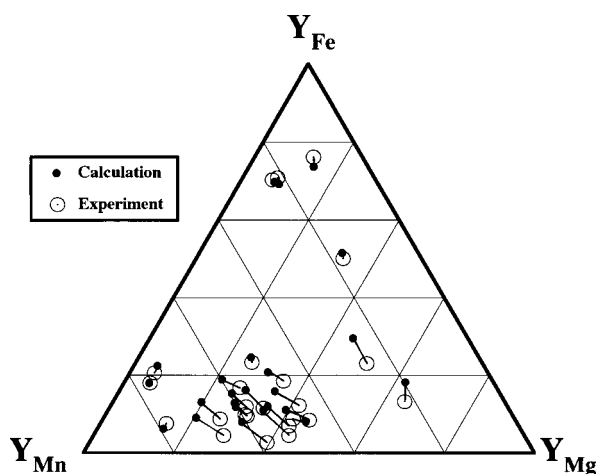


FIGURE 5. Fluid compositions in equilibria with (Fe,Mn,Mg)TiO₃ solid solutions. Fluid compositions tied by lines correspond to the same solid compositions. The experimental compositions of solid and fluid phases are taken from Kubo et al. (1992). The tie lines are omitted when the computed compositions closely agree with the experimental compositions.

sitions of the fluid phase predicted by the Margules equation and by the Wilson equation can now be compared.

By an appropriate differentiation of Equation 1, activity coefficients of components 1 and 2 in a binary solid solution are written as follows (e.g., Mukhopadhyay et al. 1993).

$$RT \ln \gamma_1 = [W_{12} + 2(W_{21} - W_{12})X_1]X_2^2 \quad (31)$$

$$RT \ln \gamma_2 = [W_{21} + 2(W_{12} - W_{21})X_2]X_1^2 \quad (32)$$

From the experimental results listed in Tables 2–4, ΔG^0 values for reactions A–C and the Margules parameters were computed for the three binary solid solutions. The constraints (Eqs. 16 and 17) were not used in the calculation. The computation of three unknowns for each reaction was carried out with the nonlinear programming technique, following the procedure shown in Appendix.

The results of the calculation are listed in Table 6. By setting $C_{123} = 0$, activity coefficients of the components in the ternary solid solution of (Fe,Mn,Mg)TiO₃ were computed on the basis of the experimental compositions of the solid phase (Table 5). Activity coefficients of the three components can be written as follows (Mukhopadhyay et al. 1993):

TABLE 5. Experimental and calculated results on the cation exchange reactions between (Fe,Mn,Mg)TiO₃ and (Fe,Mn,Mg)Cl_{2(aq)}

Experimental results*			Calculated results†		
X _{FeTiO₃}	X _{MnTiO₃}	Y _{Fe}	Y _{Mn}	Y _{Fe}	Y _{Mn}
0.919	0.056	0.704	0.228	0.699	0.225
0.924	0.027	0.762	0.108	0.738	0.118
0.367	0.317	0.095	0.590	0.129	0.599
0.916	0.054	0.709	0.214	0.693	0.217
0.498	0.062	0.230	0.257	0.296	0.253
0.424	0.315	0.119	0.580	0.153	0.593
0.428	0.270	0.115	0.544	0.162	0.558
0.340	0.315	0.099	0.592	0.119	0.601
0.504	0.318	0.168	0.569	0.189	0.596
0.489	0.199	0.185	0.464	0.208	0.486
0.376	0.189	0.122	0.461	0.159	0.495
0.230	0.293	0.027	0.580	0.080	0.607
0.297	0.206	0.069	0.510	0.120	0.530
0.397	0.429	0.087	0.654	0.131	0.672
0.278	0.218	0.045	0.522	0.110	0.545
0.301	0.495	0.045	0.667	0.091	0.704
0.576	0.221	0.233	0.510	0.247	0.503
0.489	0.480	0.180	0.763	0.180	0.763
0.564	0.409	0.206	0.740	0.225	0.723
0.248	0.031	0.132	0.223	0.182	0.195
0.782	0.043	0.501	0.174	0.516	0.167
0.219	0.660	0.076	0.779	0.062	0.792
0.159	0.118	0.087	0.492	0.080	0.466
0.249	0.159	0.084	0.458	0.111	0.494

* Kubo et al. (1992).

† Calculated results of this study.

TABLE 6. ΔG⁰ for reactions A–C and Margules parameters* for (Fe,Mn)TiO₃, (Mn,Mg)TiO₃, and (Fe,Mg)TiO₃ solid solutions

$\frac{\Delta G_A^0}{RT} = 1.513(0.058)$, $\frac{\Delta G_B^0}{RT} = -0.908(0.043)$, $\frac{\Delta G_C^0}{RT} = -0.427(0.037)$
$W_{FeMn} = 0.337(0.577)$, $W_{MnFe} = 3.254(1.661)$, $W_{MnMg} = 11.549(1.105)$, $W_{MgMn} = 10.119(0.866)$, $W_{MgFe} = 5.015(0.956)$, $W_{FeMg} = 6.227(0.707)$
Notes: Values in parentheses indicate the standard errors. RT is 7.260 (kJ/mol) at 600 °C.
* Calculated from the results on each binary reaction. Reactions A, B, and C are indicated in Table 1 and in the text.

$$RT\ln\gamma_{FeTiO_3} = W_{FeMn}X_{MnTiO_3}^2(1 - 2X_{FeTiO_3}) + 2W_{MnFe}X_{FeTiO_3}X_{MnTiO_3}(1 - X_{FeTiO_3}) - 2W_{MnMg}X_{MnTiO_3}X_{MgTiO_3}^2 - 2W_{MgMn}X_{MnTiO_3}X_{MgTiO_3} + 2W_{MgFe}X_{FeTiO_3}X_{MgTiO_3}(1 - X_{FeTiO_3}) + W_{FeMg}X_{MgTiO_3}^2(1 - 2X_{FeTiO_3}) \quad (33)$$

$$RT\ln\gamma_{MnTiO_3} = 2W_{FeMn}X_{FeTiO_3}X_{MnTiO_3}(1 - X_{MnTiO_3}) + W_{MnFe}X_{FeTiO_3}^2(1 - 2X_{MnTiO_3}) + W_{MnMg}X_{MgTiO_3}^2(1 - 2X_{MnTiO_3}) + 2W_{MgMn}X_{MnTiO_3}X_{MgTiO_3}(1 - X_{MnTiO_3}) - 2W_{MgFe}X_{FeTiO_3}X_{MgTiO_3} - 2W_{FeMg}X_{FeTiO_3}X_{MgTiO_3}^2 \quad (34)$$

$$RT\ln\gamma_{MgTiO_3} = -2W_{FeMn}X_{FeTiO_3}X_{MnTiO_3}^2 - 2W_{MnFe}X_{FeTiO_3}X_{MnTiO_3} + 2W_{MnMg}X_{MnTiO_3}X_{MgTiO_3}(1 - X_{MgTiO_3}) + W_{MgMn}X_{MnTiO_3}^2(1 - 2X_{MgTiO_3}) + W_{MgFe}X_{FeTiO_3}^2(1 - 2X_{MgTiO_3}) + 2W_{FeMg}X_{FeTiO_3}X_{MgTiO_3}(1 - X_{MgTiO_3}) \quad (35)$$

Compositions of (Fe,Mn,Mg)Cl_{2(aq)} in equilibria with (Fe,Mn,Mg)TiO₃ were computed by the same method described

before (see Equations 28 to 30). After the computation of the fluid phase compositions, the sum of the distances were obtained between the experimental compositions and the calculated compositions in the ternary system. The overall fit to the experimental data using the Wilson equation is better than with the Margules equation having no ternary interaction parameter (Σdistances = 0.00938 vs. 0.01271). Thus, the prediction of the ternary solid solution–fluid equilibria by the Wilson equation is more accurate than that by the Margules equation on the basis of data on binary cation exchange reactions.

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APPENDIX

Britt and Luecke (1973) developed a nonlinear programming technique for obtaining the parameters in various types of regression equations. Their method was used in the present study to obtain the Gibbs energy of reactions, the Wilson parameters, and the compositions of solid and fluid phases.

To avoid lengthy notations and equations, the following abbreviations are used hereafter: $B_1 = \frac{\Delta G_A^0}{RT}$, $B_2 = \Lambda_{MnFe}$, $B_3 = \Lambda_{FeMn}$, $B_4 = \frac{\Delta G_B^0}{RT}$, $B_5 = \Lambda_{MgFe}$, $B_6 = \Lambda_{MnMg}$, $B_7 = \Lambda_{FeMg}$.

Using the constraint equations shown in the text (Eqs. 16 and 17), the other two unknowns (ΔG⁰/RT for reaction C and Λ_{MgFe}) were obtained from the above seven parameters. In this study, the parameter F_1 was defined as follows for all the data points relating to reaction A:

$$F_i = B_1 + \ln \left[\frac{(1-X_i)Y_i}{X_i(1-Y_i)} \right] - \ln \left[\frac{B_2 X_i + 1 - X_i}{X_i + B_3(1-X_i)} \right] - \frac{(B_3-1)X_i}{X_i + B_3(1-X_i)} - \frac{(1-X_i)(1-B_2)}{B_2 X_i + 1 - X_i} \quad (\text{A1})$$

where X_i and Y_i stand for the calculated values of X_{FeTiO_3} and Y_{Fe} , respectively, for the i -th experimental data point. Similarly, by denoting X_i and Y_i as the calculated values of X_{MnTiO_3} and Y_{Mn} for the i -th experimental data point, F_i for reaction B is defined as follows.

$$F_i = B_4 + \ln \left[\frac{(1-X_i)Y_i}{X_i(1-Y_i)} \right] - \ln \left[\frac{B_5 X_i + 1 - X_i}{X_i + B_6(1-X_i)} \right] - \frac{(B_6-1)X_i}{X_i + B_6(1-X_i)} - \frac{(1-X_i)(1-B_5)}{B_5 X_i + 1 - X_i} \quad (\text{A2})$$

For reaction C, the following expression can be derived through the constraint equations.

$$F_i = -(B_1 + B_4) + \ln \left[\frac{(1-X_i)Y_i}{X_i(1-Y_i)} \right] - \ln \left[\frac{B_7 X_i + 1 - X_i}{X_i + \left(\frac{B_2 B_5 B_7}{B_3 B_6} \right) (1-X_i)} \right] - \frac{\left[\left(\frac{B_2 B_5 B_7}{B_3 B_6} \right) - 1 \right] X_i}{X_i + \left(\frac{B_2 B_5 B_7}{B_3 B_6} \right) (1-X_i)} - \frac{(1-X_i)(1-B_7)}{B_7 X_i + 1 - X_i} \quad (\text{A3})$$

where X_i and Y_i stand for the calculated values of X_{MgTiO_3} and

Y_{Mg} for the i -th experimental data point. In the present study, calculations were carried out under the condition that all of the F_i values should be 0, which is equivalent to the condition that $\ln K$ for each reaction becomes constant. In other words, the computed results satisfy the law of mass action.

Standard errors of the measurements of both X and Y values are assumed to be 0.005 ($= \sigma$). Then this study minimizes the value of Q , which is defined as follows:

$$Q = \frac{1}{2} \sum_i \sigma^{-2} \left[(X_i^{\text{meas}} - x_i)^2 + (Y_i^{\text{meas}} - y_i)^2 \right] \quad (\text{A4})$$

where the superscript, meas, stands for the measured value. The calculated values for solid and fluid compositions are designated as x and y , respectively.

We define L_i , which corresponds to the weight of the i -th experimental datum, as follows.

$$L_i^{(j)} = \sigma^2 \left[\left(\frac{\partial F_i^{(j)}}{\partial X_i^{(j)}} \right)^2 + \left(\frac{\partial F_i^{(j)}}{\partial Y_i^{(j)}} \right)^2 \right] \quad (\text{A5})$$

The superscript (j) designates the value at the j -th iteration. Also a matrix $C(u,v)$ and a function E_i defined below are obtained.

$$C(u,v) = \sum_i \frac{\left(\frac{\partial F_i^{(j)}}{\partial B_u^{(j)}} \right) \left(\frac{\partial F_i^{(j)}}{\partial B_v^{(j)}} \right)}{L_i^{(j)}} \quad (\text{A6})$$

$$E_i^{(j)} = \frac{F_i^{(j)} + \frac{\partial F_i^{(j)}}{\partial X_i^{(j)}} (X_i^{\text{meas}} - X_i^{(j)}) + \frac{\partial F_i^{(j)}}{\partial Y_i^{(j)}} (Y_i^{\text{meas}} - Y_i^{(j)})}{L_i^{(j)}} \quad (\text{A7})$$

Then true parameters for B_i values, b_i ($i = 1 \dots 7$), are obtained from the following simultaneous linear equation.

$$\begin{pmatrix} C(1,1) & C(1,2) & C(1,3) & C(1,4) & C(1,5) & C(1,6) & C(1,7) \\ C(2,1) & C(2,2) & C(2,3) & C(2,4) & C(2,5) & C(2,6) & C(2,7) \\ C(3,1) & C(3,2) & C(3,3) & C(3,4) & C(3,5) & C(3,6) & C(3,7) \\ C(4,1) & C(4,2) & C(4,3) & C(4,4) & C(4,5) & C(4,6) & C(4,7) \\ C(5,1) & C(5,2) & C(5,3) & C(5,4) & C(5,5) & C(5,6) & C(5,7) \\ C(6,1) & C(6,2) & C(6,3) & C(6,4) & C(6,5) & C(6,6) & C(6,7) \\ C(7,1) & C(7,2) & C(7,3) & C(7,4) & C(7,5) & C(7,6) & C(7,7) \end{pmatrix} \begin{pmatrix} B_1^{(j)} - b_1 \\ B_2^{(j)} - b_2 \\ B_3^{(j)} - b_3 \\ B_4^{(j)} - b_4 \\ B_5^{(j)} - b_5 \\ B_6^{(j)} - b_6 \\ B_7^{(j)} - b_7 \end{pmatrix} = \begin{pmatrix} \sum_i \left(\frac{\partial F_i^{(j)}}{\partial B_1^{(j)}} \right) E_i^{(j)} \\ \sum_i \left(\frac{\partial F_i^{(j)}}{\partial B_2^{(j)}} \right) E_i^{(j)} \\ \sum_i \left(\frac{\partial F_i^{(j)}}{\partial B_3^{(j)}} \right) E_i^{(j)} \\ \sum_i \left(\frac{\partial F_i^{(j)}}{\partial B_4^{(j)}} \right) E_i^{(j)} \\ \sum_i \left(\frac{\partial F_i^{(j)}}{\partial B_5^{(j)}} \right) E_i^{(j)} \\ \sum_i \left(\frac{\partial F_i^{(j)}}{\partial B_6^{(j)}} \right) E_i^{(j)} \\ \sum_i \left(\frac{\partial F_i^{(j)}}{\partial B_7^{(j)}} \right) E_i^{(j)} \end{pmatrix} \quad (\text{A8})$$

After solving Equation A8, the solid and fluid compositions are computed by the following equations.

$$X_i^{(j)} - x_i = X_i^{(j)} - X_i^{\text{meas}} + \lambda_i^{(j)} \sigma^2 \left(\frac{\partial F_i^{(j)}}{\partial X_i^{(j)}} \right) \quad (\text{A9})$$

$$Y_i^{(j)} - y_i = Y_i^{(j)} - Y_i^{\text{meas}} + \lambda_i^{(j)} \sigma^2 \left(\frac{\partial F_i^{(j)}}{\partial Y_i^{(j)}} \right) \quad (\text{A10})$$

where

$$\lambda_i^{(j)} = \frac{F_i^{(j)} + \left(\frac{\partial F_i^{(j)}}{\partial X_i^{(j)}} \right) (X_i^{\text{meas}} - X_i^{(j)}) + \left(\frac{\partial F_i^{(j)}}{\partial Y_i^{(j)}} \right) (Y_i^{\text{meas}} - Y_i^{(j)})}{L_i^{(j)}}$$

$$L_i^{(j)} = \frac{\left(\frac{\partial F_i^{(j)}}{\partial B_1^{(j)}} \right) (B_1^{\text{meas}} - b_1) + \left(\frac{\partial F_i^{(j)}}{\partial B_2^{(j)}} \right) (B_2^{\text{meas}} - b_2) + \left(\frac{\partial F_i^{(j)}}{\partial B_3^{(j)}} \right) (B_3^{\text{meas}} - b_3) + \left(\frac{\partial F_i^{(j)}}{\partial B_4^{(j)}} \right) (B_4^{\text{meas}} - b_4) + \left(\frac{\partial F_i^{(j)}}{\partial B_5^{(j)}} \right) (B_5^{\text{meas}} - b_5) + \left(\frac{\partial F_i^{(j)}}{\partial B_6^{(j)}} \right) (B_6^{\text{meas}} - b_6) + \left(\frac{\partial F_i^{(j)}}{\partial B_7^{(j)}} \right) (B_7^{\text{meas}} - b_7)}{L_i^{(j)}} \quad (\text{A11})$$

After b_i , x_i , and y_i values are obtained, those are substituted into Equations A1–A3 and A5–A7 as B_i , X_i , and Y_i . Then the newly computed F_i , E_i , and $C(u,v)$ are substituted into Equations A8–A11. Successive iterations are repeated until all of the unknowns and the compositions of solid and fluid phases are converged. The following convergence criteria were adopted as follows:

$$|B_u^{(j+1)} - B_u^{(j)}| \leq 0.00005 \quad (u = 1 \dots 7), \quad |X_i^{(j+1)} - X_i^{(j)}| \leq 0.0001, \\ |Y_i^{(j+1)} - Y_i^{(j)}| \leq 0.0001.$$