Calculations of fluid–ternary solid solution equilibria: An application of the Wilson
equation to fluid–\((\text{Fe, Mn, Mg})\text{TiO}_3\) equilibria at 600 °C and 1 kbar

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ABSTRACT

The Wilson equation (Wilson 1964) is applied to \((\text{Fe, Mn, Mg})\text{TiO}_3\) 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 \((\text{Fe, Mn})\text{Cl}_{2(aq)}\) and \((\text{Fe, Mn})\text{TiO}_3\), between \((\text{Mn, Mg})\text{Cl}_{2(aq)}\)
and \((\text{Mn, Mg})\text{TiO}_3\), and between \((\text{Fe, Mg})\text{Cl}_{2(aq)}\) and \((\text{Fe, Mg})\text{TiO}_3\) (Kubo et al. 1992). The molar excess
Gibbs energy \((G^e)\) is the following: \(G^e\) (kJ/mol) = −7.260\([X_{\text{FeTiO}_3}\ln(X_{\text{FeTiO}_3} + 1.314X_{\text{MgTiO}_3} + 0.962X_{\text{MnTiO}_3})]
+ X_{\text{MgTiO}_3}\ln(0.585X_{\text{FeTiO}_3} + X_{\text{MnTiO}_3} + 0.393X_{\text{MgTiO}_3}) + X_{\text{MnTiO}_3}\ln(0.406X_{\text{FeTiO}_3} + 0.371X_{\text{MgTiO}_3}
+ X_{\text{MnTiO}_3})]\), where \(X\) stands for the mole fraction of the subscripted component. The predicted compositions of
\((\text{Fe, Mn, Mg})\text{Cl}_{2(aq)}\) 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 \((G^e)\) of a ternary solid solution is written as follows (e.g., Mukhopadhyay et al. 1993):

\[
G^e = X_iX_j(X_iW_{12} + X_jW_{21}) + X_iX_k(X_iW_{13} + X_kW_{31}) + X_jX_k(X_jW_{23} + X_kW_{32}) + X_iX_jX_kC_{123}
\]  

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:

\[
G^e = -RT\sum_{i=1}^{3} X_i \ln \left( \sum_{j=1}^{3} \gamma_i \gamma_j X_j \right)
\]  

where \(R\) is the universal gas constant, \(T\) is the absolute temperature, and \(\gamma_i\) stands for the Wilson parameter for the pair of components \(i\) and \(j\). By definition, \(\gamma_i = 1\) in Equation 2.

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

\[
\ln \gamma_i = 1 - \ln \left( \sum_{k=1}^{3} X_k A_{ik} \right) - \sum_{j=1}^{3} X_j \frac{A_{ij}}{\sum_{k=1}^{3} X_k A_{ik}}
\]

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 \(G^e\) 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–\((\text{Fe, Mn, Mg})\text{TiO}_3\) 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–\((\text{Fe, Mn, Mg})\text{TiO}_3\) 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 \((\text{Fe, Mn, Mg})\text{Cl}_{2(aq)}\) in equilibria.