Derivation and Consistency of the Partial Functions of a Quaternary System

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ABSTRACT

The partial thermodynamic functions of solvent and solutes of quaternary system are derived based on the Maclaurin infinite series which is expressed in terms of interaction coefficients of the integral properties of the system and subjected to appropriate boundary conditions. Derivation of the functions involves extensive integration of various geometrical series pertaining to the first order interaction coefficients and cross interaction coefficients which are independent of compositional path and also completely remove any truncational error. The thermodynamic consistency of the solute partial functions based on Maxwell relations and of solvent and solute partial functions based on Gibbs-Duhem relations have been established. The derived partials from Maclaurin Infinite series of solutes and solvent expressions leads to same functional expression in the infinite range as of derived from Margules equations. The derived logarithmic activity coefficient of the solvent and solutes are consistent with the ternary system. Using partial thermodynamic functions of solutes in the Fe-C-Ti-Si, Fe-C-Ti-Cr, FeC-Ti-Al and Fe-C-Ti-Ni systems at 1873 K, the activities of Fe, C, Ti, Si, Cr, Al and Ni are calculated in respective quaternary systems. Activity coefficient of nitrogen is calculated in Fe-Cr-V-N, Fe-Ni-V-N, Fe-Cr-Ta-N, and Fe-Ni-Ta-N quaternary systems and are in good agreement with the experimental data.

INTRODUCTION

Interaction parameter formalism based on the Maclaurin infinite series for logarithmic activity coefficient of the solute components and solvent in a solvent rich ternary system has been developed by Hajra et al. /1/. The Maclaurin infinite series of excess Gibbs energy is expanded in the neighborhood of the solvent. The series involves partial derivatives of G^{E} that are evaluated in the limit of $x_1 \rightarrow 1.0$. The partial derivatives of G^{E} are expressed in terms of the self-interactions of binary, ternary interactions of ternary and cross-interaction parameters of quaternary systems. The interaction parameter formalism is based on Maclaurin infinite series, which is expanded in the neighborhood of a solvent for the partial properties of the solutes and solvent. This formalism is exclusively useful in the dilute solutions range, but many researchers /2-10/ also tried to extend it to concentrated solutions. Schuhmann /4/ has shown that Wagner 's /2/ original suggestion is essentially valid if such an infinite series is not truncated. Since higher order interaction parameters are rarely available, activity coefficients of solutes at infinite concentrations have so far been calculated using first order parameters. Two methods have been suggested by Srikanth and Jacob /8/ toward the solution of the inexact differential equation: (a) through the introduction of special relations of interaction parameters and (b) by the use of compositional path. It may be mentioned that the compiled data available in literature do not support the validity of the special relations between the first and second order parameters.

The introduction of this compositional path is generally considered to reduce the degrees of freedom. One cannot, however, eliminate all of the compositional degrees of freedom by the application of a compositional path as one type of path may only be imposed at a time. Although there is improvement in the calculated values using this technique, the method remains as approximate as in the use of special relations between interaction parameters. Bale and Pelton /11/ had proposed unified interaction parameter formalism to predict the activity coefficient of logarithmic activity of solvent and solutes in dilute solutions based on infinite series. They are only considered up to finite order of the series and it is not a complete integration of infinite series.

In the present research, the logarithmic activity coefficients of the components which are derived based on the Maclaurin infinite series are extended to the quaternary system. The series is subjected to the appropriate boundary conditions and each of the terms are correlated to the corresponding interaction coefficients of the solvent and solutes. The partial function of the solvent and solutes are derived from the integral excess function G E. The integral function G E is denoted by

$$G^E = RT\left(x_1 \ln\gamma_1 + x_2 \ln\gamma_2 + x_3 \ln\gamma_3 + x_4 \ln\gamma_4\right) \quad (1)$$

where 1 refers to the solvent component and 2, 3 and 4 refer to the solute components of a quaternary system. Derivation of the partials of solutes and solvent involves extensive integration of the geometrical series by which they are reducible to logarithmic progression type of series. Usually it is a practice to use lower order interaction coefficients since higher order interaction terms are not well known. In the present work, we have taken, self interaction parameters in binary systems, ternary interaction parameters in ternary system and cross-interaction parameters of quaternary system to evaluate the interaction coefficients of the solutes and solvent in a quaternary system. The solute partials ln γ_2, ln γ_3 and ln γ_4 are thermodynamically consistent using maxwell relations. The functions of ln γ_1, ln γ_2, ln γ_3 and ln γ_4 are derived based on the infinite series integration and are thermodynamically consistent which is established by using Gibbs-Duhem relations. Recently, the authors /12/ have derived solvent and solute partial functions of a ternary system involving a dilute solute '2' in a 1-3 binary solvent system using Margules equations. The authors have also studied the advantages and limitations of Maclaurin and Margules equations in interpreting the thermodynamics properties of a ternary system both in the case of dilute and concentration solutions /13/. They have found that Margules equations need to be modified since the equations were divergent when higher order interactions were considered. The derived partials from modified Margules equations were convergent. The derived partials from modified Margules equations considered up to infinite series and Maclaurin equations have the same functional form.

THE FORMALISM

The Maclaurin infinite series is expressed in terms of partial properties through integral function of the system. The integral property of the system is expanded in the neighborhood of solvent component, $x_1 \rightarrow 1.0$ as:

$$G^E = \sum_{n_2=0}^{\infty}\sum_{n_3=0}^{\infty}\sum_{n_4=0}^{\infty}\frac{1}{n_2!\,n_3!\,n_4!}\left(\frac{\partial^{n_2+n_3+n_4}G^E}{\partial x_2^{n_2}\partial x_3^{n_3}\partial x_4^{n_4}}\right)_{x_1\rightarrow 1.0} \quad (2)$$

Imposing the boundary conditions: $x_2 \rightarrow 1.0$, $(G^E) \rightarrow 0$ and $(G^E)_{x_1 \rightarrow 1.0} = 0$ and the series (2) reduces to

$$\sum_{r=1}^{\infty}\frac{1}{r!}\left(\frac{\partial^r G^E}{\partial x_2^r}\right)_{x_1\rightarrow 1.0} = 0 \quad (3)$$

Similarly imposing the conditions $x_3 \rightarrow 1.0$, $(G^E) \rightarrow 0$ and $(G^E)_{x_1 \rightarrow 1.0} = 0$, and the series (2) reduces to

$$\sum_{r=1}^{\infty}\frac{1}{r!}\left(\frac{\partial^r G^E}{\partial x_3^r}\right)_{x_1\rightarrow 1.0} = 0 \quad (4)$$

Similarly imposing the conditions $x_4 \rightarrow 1.0$, $(G^E) \rightarrow 0$ and $(G^E)_{x_1 \rightarrow 1.0} = 0$, and the series (2) reduces to

$$\sum_{r=1}^{\infty}\frac{1}{r!}\left(\frac{\partial^r G^E}{\partial x_4^r}\right)_{x_1\rightarrow 1.0} = 0 \quad (5)$$

Substituting the equations (3), (4) and (5) in (2) and rearrangement of the terms gives the following expression:

$$
\begin{aligned}
G^E = {} & x_2(1-x_2)\sum_{n_2=1}^{\infty} x_2^{n_2-1}\sum_{r=1}^{n_2}\frac{1}{r!}\left(\frac{\partial^r G^E}{\partial x_2^r}\right)_{x_1\to 1.0} + x_3(1-x_3)\sum_{n_3=1}^{\infty} x_3^{n_3-1}\sum_{r=1}^{n_3}\frac{1}{r!}\left(\frac{\partial^r G^E}{\partial x_3^r}\right)_{x_1\to 1.0} \\
& + x_4(1-x_4)\sum_{n_4=1}^{\infty} x_4^{n_4-1}\sum_{r=1}^{n_4}\frac{1}{r!}\left(\frac{\partial^r G^E}{\partial x_4^r}\right)_{x_1\to 1.0} + \sum_{n_2=1}^{\infty}\sum_{n_3=1}^{\infty}\frac{1}{n_2!\,n_3!}\left(\frac{\partial^{n_2+n_3} G^E}{\partial x_2^{n_2}\partial x_3^{n_3}}\right)_{x_1\to 1.0} x_2^{n_2}x_3^{n_3} \\
& + \sum_{n_2=1}^{\infty}\sum_{n_4=1}^{\infty}\frac{1}{n_2!\,n_4!}\left(\frac{\partial^{n_2+n_4} G^E}{\partial x_2^{n_2}\partial x_4^{n_4}}\right)_{x_1\to 1.0} x_2^{n_2}x_4^{n_4} + \sum_{n_3=1}^{\infty}\sum_{n_4=1}^{\infty}\frac{1}{n_3!\,n_4!}\left(\frac{\partial^{n_3+n_4} G^E}{\partial x_3^{n_3}\partial x_4^{n_4}}\right)_{x_1\to 1.0} x_3^{n_3}x_4^{n_4} \\
& + \sum_{n_2=1}^{\infty}\sum_{n_3=1}^{\infty}\sum_{n_4=1}^{\infty}\frac{1}{n_2!\,n_3!\,n_4!}\left(\frac{\partial^{n_2+n_3+n_4} G^E}{\partial x_2^{n_2}\partial x_3^{n_3}\partial x_4^{n_4}}\right)_{x_1\to 1.0} x_2^{n_2}x_3^{n_3}x_4^{n_4}
\end{aligned}
\qquad (6)
$$

The integral excess function is subjected to repeated differentiation to obtain the relationship between interaction coefficients and the logarithmic activity coefficients of the solvent (1) and solute components (2, 3 and 4), with the restriction of dilute solution, namely $x_1 \to 1.0$ at each stage of differentiation of the following equations:

$$RT \ln \gamma_1 = G^E - x_2 \frac{\partial G^E}{\partial x_2} - x_3 \frac{\partial G^E}{\partial x_3} - x_4 \frac{\partial G^E}{\partial x_4} \quad (7)$$

$$RT \ln \gamma_2 = G^E + (1-x_2) \frac{\partial G^E}{\partial x_2} - x_3 \frac{\partial G^E}{\partial x_3} - x_4 \frac{\partial G^E}{\partial x_4} \quad (8)$$

$$RT \ln \gamma_3 = G^E - x_2 \frac{\partial G^E}{\partial x_2} + (1-x_3) \frac{\partial G^E}{\partial x_3} - x_4 \frac{\partial G^E}{\partial x_4} \quad (9)$$

and

$$RT \ln \gamma_4 = G^E - x_2 \frac{\partial G^E}{\partial x_2} - x_3 \frac{\partial G^E}{\partial x_3} + (1-x_4) \frac{\partial G^E}{\partial x_4} \quad (10)$$

Lupis and Elliott's /3/ convention for interaction coefficients is used in this paper, which are namely, (γ) for activity coefficient, and (ε, ρ, J) for the first, second and higher order interaction coefficients, respectively. According to them, $J'_{n_2 n_3 n_4}$ is defined as $\left(\frac{\partial^{n_2+n_3+n_4} \ln \gamma_i}{\partial x_2^{n_2} \partial x_3^{n_3} \partial x_4^{n_4}}\right)$ where n_2 represents the order of differentiation of $\ln \gamma_i$ for a component i with respect to x_2, order n_3 with respect to x_3 and order n_4 with respect to x_4 for a quaternary system. The different partial derivatives of G^E to the corresponding partial derivatives of the activity coefficients are known as interaction coefficients.

$$\frac{1}{RT}\left(\frac{\partial G^E}{\partial x_2}\right)_{x_1 \to 1.0} = \ln \gamma_2^{\circ}(1)$$

$$\frac{1}{RT}\left(\frac{\partial G^E}{\partial x_3}\right)_{x_1 \to 1.0} = \ln \gamma_3^{\circ}(1)$$

$$\frac{1}{RT}\left(\frac{\partial G^E}{\partial x_4}\right)_{x_1 \to 1.0} = \ln \gamma_4^{\circ}(1)$$

$$\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_2^2}\right)_{x_1 \to 1.0} = \left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{x_1 \to 1.0} = \varepsilon_2^2(1)$$

$$\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_3^2}\right)_{x_1 \to 1.0} = \left(\frac{\partial \ln \gamma_3}{\partial x_3}\right)_{x_1 \to 1.0} = \varepsilon_3^3(1)$$

$$\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_4^2}\right)_{x_1 \to 1.0} = \left(\frac{\partial \ln \gamma_4}{\partial x_4}\right)_{x_1 \to 1.0} = \varepsilon_4^4(1)$$

$$\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_2 \partial x_3}\right)_{x_1 \to 1.0} = \left(\frac{\partial \ln \gamma_2}{\partial x_3}\right)_{x_1 \to 1.0} = \varepsilon_2^3(1)$$

$$\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_2 \partial x_3}\right)_{x_1 \to 1.0} = \left(\frac{\partial \ln \gamma_3}{\partial x_2}\right)_{x_1 \to 1.0} = \varepsilon_3^2(1)$$

$$\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_2 \partial x_4}\right)_{x_1 \to 1.0} = \left(\frac{\partial \ln \gamma_4}{\partial x_2}\right)_{x_1 \to 1.0} = \varepsilon_4^2(1)$$

$$\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_2 \partial x_4}\right)_{x_1 \to 1.0} = \left(\frac{\partial \ln \gamma_2}{\partial x_4}\right)_{x_1 \to 1.0} = \varepsilon_2^4(1)$$

$$\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_3 \partial x_4}\right)_{x_1 \to 1.0} = \left(\frac{\partial \ln \gamma_4}{\partial x_3}\right)_{x_1 \to 1.0} = \varepsilon_4^3(1)$$

$$\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_3 \partial x_4}\right)_{x_1 \to 1.0} = \left(\frac{\partial \ln \gamma_3}{\partial x_4}\right)_{x_1 \to 1.0} = \varepsilon_3^4(1)$$

$$\frac{1}{RT}\left(\frac{\partial^3 G^E}{\partial x_2^3}\right)_{x_1 \to 1.0} = \left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{x_1 \to 1.0} + 2\left(\frac{\partial^2 \ln \gamma_2}{\partial x_2^2}\right)_{x_1 \to 1.0} = \varepsilon_2^2(1) + 2\rho_2^2(1)$$

$$\frac{1}{RT}\left(\frac{\partial^3 G^E}{\partial x_3^3}\right)_{x_1 \to 1.0} = \left(\frac{\partial \ln \gamma_3}{\partial x_3}\right)_{x_1 \to 1.0} + 2\left(\frac{\partial^2 \ln \gamma_3}{\partial x_3^2}\right)_{x_1 \to 1.0} = \varepsilon_3^3(1) + 2\rho_3^3(1)$$

$$\frac{1}{RT}\left(\frac{\partial^3 G^E}{\partial x_4^3}\right)_{x_1 \to 1.0} = \left(\frac{\partial \ln \gamma_4}{\partial x_4}\right)_{x_1 \to 1.0} + 2\left(\frac{\partial^2 \ln \gamma_4}{\partial x_4^2}\right)_{x_1 \to 1.0} = \varepsilon_4^4(1) + 2\rho_4^4(1)$$

$$\frac{1}{RT}\left(\frac{\partial^3 G^E}{\partial x_2^2 \partial x_3}\right)_{x_1 \to 1.0} = \left(\frac{\partial \ln \gamma_2}{\partial x_3}\right)_{x_1 \to 1.0} + \left(\frac{\partial^2 \ln \gamma_2}{\partial x_2 \partial x_3}\right)_{x_1 \to 1.0} = \varepsilon_2^3(1) + \rho_2^{(2,3)}(1)$$

$$\frac{1}{RT}\left(\frac{\partial^3 G^E}{\partial x_2^2\,\partial x_4}\right)_{x_1\to 1.0}=\left(\frac{\partial \ln\gamma_2}{\partial x_4}\right)_{x_1\to 1.0}+\left(\frac{\partial^2 \ln\gamma_2}{\partial x_2\,\partial x_4}\right)_{x_1\to 1.0}$$
$$=\varepsilon_2^4(1)+\rho_2^{(2,4)}(1)$$

$$\frac{1}{RT}\left(\frac{\partial^3 G^E}{\partial x_3^2\,\partial x_4}\right)_{x_1\to 1.0}=\left(\frac{\partial \ln\gamma_3}{\partial x_4}\right)_{x_1\to 1.0}+\left(\frac{\partial^2 \ln\gamma_3}{\partial x_3\,\partial x_4}\right)_{x_1\to 1.0}$$
$$=\varepsilon_3^4(1)+\rho_3^{(3,4)}(1)$$

$$\frac{1}{RT}\left(\frac{\partial^4 G^E}{\partial x_2^3\,\partial x_3}\right)_{x_1\to 1.0}=2\left(\frac{\partial \ln\gamma_2}{\partial x_3}\right)_{x_1\to 1.0}+2\left(\frac{\partial^2 \ln\gamma_2}{\partial x_2\,\partial x_3}\right)_{x_1\to 1.0}+\left(\frac{\partial^3 \ln\gamma_2}{\partial x_2^2\,\partial x_3}\right)_{x_1\to 1.0}$$
$$=2\varepsilon_2^3(1)+2\rho_2^{(2,3)}(1)+J_{2,1}^{(2)}$$

$$\frac{1}{RT}\left(\frac{\partial^4 G^E}{\partial x_2\,\partial x_3^3}\right)_{x_1\to 1.0}=2\left(\frac{\partial \ln\gamma_3}{\partial x_2}\right)_{x_1\to 1.0}+2\left(\frac{\partial^2 \ln\gamma_3}{\partial x_2\,\partial x_3}\right)_{x_1\to 1.0}+\left(\frac{\partial^3 \ln\gamma_3}{\partial x_2\,\partial x_3^2}\right)_{x_1\to 1.0}$$
$$=2\varepsilon_3^2(1)+2\rho_3^{(2,3)}(1)+J_{1,2}^{(3)}$$

$$\frac{1}{RT}\left(\frac{\partial^4 G^E}{\partial x_2^2\,\partial x_3^2}\right)_{x_1\to 1.0}=2\left(\frac{\partial \ln\gamma_3}{\partial x_2}\right)_{x_1\to 1.0}+2\left(\frac{\partial^2 \ln\gamma_2}{\partial x_2\,\partial x_3}\right)_{x_1\to 1.0}+\left(\frac{\partial^3 \ln\gamma_2}{\partial x_2\,\partial x_3^2}\right)_{x_1\to 1.0}$$
$$=2\varepsilon_3^2(1)+2\rho_2^{(2,3)}(1)+J_{1,2}^{(2)}$$

$$\frac{1}{RT}\left(\frac{\partial^4 G^E}{\partial x_2^2\,\partial x_3^2}\right)_{x_1\to 1.0}=2\left(\frac{\partial \ln\gamma_2}{\partial x_3}\right)_{x_1\to 1.0}+2\left(\frac{\partial^2 \ln\gamma_3}{\partial x_2\,\partial x_3}\right)_{x_1\to 1.0}+\left(\frac{\partial^3 \ln\gamma_2}{\partial x_2\,\partial x_3^2}\right)_{x_1\to 1.0}$$
$$=2\varepsilon_3^2(1)+2\rho_3^{(2,3)}(1)+J_{1,2}^{(2)}$$

$$\frac{1}{RT}\left(\frac{\partial^3 G^E}{\partial x_2\,\partial x_3\,\partial x_4}\right)_{x_1\to 1.0}=\left(\frac{\partial^2 \ln\gamma_4}{\partial x_2\,\partial x_3}\right)_{x_1\to 1.0}+\left(\frac{\partial^2 G^E}{\partial x_2\,\partial x_3}\right)_{x_1\to 1.0}$$
$$=\rho_4^{(2,3)}(1)+\varepsilon_3^2(1)$$

$$\frac{1}{RT}\left(\frac{\partial^3 G^E}{\partial x_2\,\partial x_3\,\partial x_4}\right)_{x_1\to 1.0}=\left(\frac{\partial^2 \ln\gamma_3}{\partial x_2\,\partial x_4}\right)_{x_1\to 1.0}+\left(\frac{\partial^2 G^E}{\partial x_2\,\partial x_4}\right)_{x_1\to 1.0}$$
$$=\rho_3^{(2,4)}(1)+\varepsilon_4^2(1)$$

$$\frac{1}{RT}\left(\frac{\partial^3 G^E}{\partial x_2\,\partial x_3\,\partial x_4}\right)_{x_1\to 1.0}=\left(\frac{\partial^2 \ln\gamma_2}{\partial x_3\,\partial x_4}\right)_{x_1\to 1.0}+\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_3\,\partial x_4}\right)_{x_1\to 1.0}=\rho_2^{(3,4)}(1)+\varepsilon_4^3(1)$$

$$\frac{1}{RT}\left(\frac{\partial^4 G^E}{\partial x_2^2\,\partial x_3\,\partial x_4}\right)_{x_1\to 1.0}=\left(\frac{\partial^3 \ln\gamma_2}{\partial x_2\,\partial x_3\,\partial x_4}\right)_{x_1\to 1.0}+\frac{2}{RT}\left(\frac{\partial^3 G^E}{\partial x_2\,\partial x_3\,\partial x_4}\right)_{x_1\to 1.0}=J_{1,1,1}^{(2)}+2\left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right)$$

$$\frac{1}{RT}\left(\frac{\partial^4 G^E}{\partial x_2\,\partial x_3^2\,\partial x_4}\right)_{x_1\to 1.0}=\left(\frac{\partial^3 \ln\gamma_3}{\partial x_2\,\partial x_3\,\partial x_4}\right)_{x_1\to 1.0}+\frac{2}{RT}\left(\frac{\partial^3 G^E}{\partial x_2\,\partial x_3\,\partial x_4}\right)_{x_1\to 1.0}=J_{1,1,1}^{(3)}+2\left(\rho_3^{(2,4)}(1)+\varepsilon_2^4(1)\right)$$

$$\frac{1}{RT}\left(\frac{\partial^4 G^E}{\partial x_2\,\partial x_3\,\partial x_4^2}\right)_{x_1\to 1.0}=\left(\frac{\partial^3 \ln\gamma_4}{\partial x_2\,\partial x_3\,\partial x_4}\right)_{x_1\to 1.0}+\frac{2}{RT}\left(\frac{\partial^3 G^E}{\partial x_2\,\partial x_3\,\partial x_4}\right)_{x_1\to 1.0}=J_{1,1,1}^{(4)}+2\left(\rho_4^{(2,3)}(1)+\varepsilon_2^3(1)\right)$$

$$\frac{1}{RT}\left(\frac{\partial^5 G^E}{\partial x_2^2\,\partial x_3^2\,\partial x_4}\right)_{x_1\to 1.0}=\left(\frac{\partial^4 \ln\gamma_2}{\partial x_2\,\partial x_3^2\,\partial x_4}\right)_{x_1\to 1.0}+\frac{3}{RT}\left(\frac{\partial^4 G^E}{\partial x_2\,\partial x_3^2\,\partial x_4}\right)_{x_1\to 1.0}$$
$$=J_{1,2,1}^{(2)}+3\times\left\{2\left(\rho_3^{(2,4)}(1)+\varepsilon_2^4(1)\right)+J_{1,1,1}^{(3)}\right\}$$

$$\frac{1}{RT}\left(\frac{\partial^5 G^E}{\partial x_2^2\,\partial x_3^2\,\partial x_4}\right)_{x_1\to 1.0}=\left(\frac{\partial^4 \ln\gamma_3}{\partial x_2^2\,\partial x_3\,\partial x_4}\right)_{x_1\to 1.0}+\frac{3}{RT}\left(\frac{\partial^4 G^E}{\partial x_2^2\,\partial x_3\,\partial x_4}\right)_{x_1\to 1.0}$$
$$=J_{1,2,1}^{(3)}+3\times\left\{2\left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right)+J_{1,1,1}^{(2)}\right\}$$

$$\frac{1}{RT}\left(\frac{\partial^5 G^E}{\partial x_2 \partial x_3^2 \partial x_4^2}\right)_{x_1\to 1.0} = \left(\frac{\partial^4 \ln\gamma_4}{\partial x_2 \partial x_3^2 \partial x_4}\right)_{x_1\to 1.0} + \frac{3}{RT}\left(\frac{\partial^4 G^E}{\partial x_2 \partial x_3^2 \partial x_4}\right)_{x_1\to 1.0}$$

$$= J^{(4)}_{1,2,1} + 3\times\left\{2\left(\rho_3^{(2,4)}(1)+\varepsilon_2^4(1)\right)+J^{(3)}_{1,1,1}\right\}$$

$$\frac{1}{RT}\left(\frac{\partial^5 G^E}{\partial x_2 \partial x_3^2 \partial x_4^2}\right)_{x_1\to 1.0} = \left(\frac{\partial^4 \ln\gamma_3}{\partial x_2 \partial x_3 \partial x_4^2}\right)_{x_1\to 1.0} + \frac{3}{RT}\left(\frac{\partial^4 G^E}{\partial x_2 \partial x_3 \partial x_4^2}\right)_{x_1\to 1.0}$$

$$= J^{(3)}_{1,1,2} + 3\times\left\{2\left(\rho_4^{(2,3)}(1)+\varepsilon_2^3(1)\right)+J^{(4)}_{1,1,1}\right\}$$

$$\frac{1}{RT}\left(\frac{\partial^5 G^E}{\partial x_2^2 \partial x_3 \partial x_4^2}\right)_{x_1\to 1.0} = \left(\frac{\partial^4 \ln\gamma_2}{\partial x_2 \partial x_3 \partial x_4^2}\right)_{x_1\to 1.0} + \frac{3}{RT}\left(\frac{\partial^4 G^E}{\partial x_2 \partial x_3 \partial x_4^2}\right)_{x_1\to 1.0}$$

$$= J^{(2)}_{1,1,2} + 3\times\left\{2\left(\rho_4^{(2,3)}(1)+\varepsilon_2^3(1)\right)+J^{(4)}_{1,1,1}\right\}$$

$$\frac{1}{RT}\left(\frac{\partial^5 G^E}{\partial x_2^2 \partial x_3 \partial x_4^2}\right)_{x_1\to 1.0} = \left(\frac{\partial^4 \ln\gamma_4}{\partial x_2^2 \partial x_3 \partial x_4}\right)_{x_1\to 1.0} + \frac{3}{RT}\left(\frac{\partial^4 G^E}{\partial x_2^2 \partial x_3 \partial x_4}\right)_{x_1\to 1.0}$$

$$= J^{(4)}_{2,1,1} + 3\times\left\{2\left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right)+J^{(2)}_{1,1,1}\right\}$$

$$\frac{1}{RT}\left(\frac{\partial^6 G^E}{\partial x_2^2 \partial x_3^2 \partial x_4^2}\right)_{x_1\to 1.0} = \left(\frac{\partial^5 \ln\gamma_2}{\partial x_2 \partial x_3^2 \partial x_4^2}\right)_{x_1\to 1.0} + \frac{4}{RT}\left(\frac{\partial^5 G^E}{\partial x_2 \partial x_3^2 \partial x_4^2}\right)_{x_1\to 1.0}$$

$$= J^{(2)}_{1,2,2} + 4\left[J^{(4)}_{1,2,1} + 3\times\left\{2\left(\rho_3^{(2,4)}(1)+\varepsilon_2^4(1)\right)+J^{(3)}_{1,1,1}\right\}\right]$$

$$= J^{(2)}_{1,2,2} + 4\left[J^{(3)}_{1,1,2} + 3\times\left\{2\left(\rho_4^{(2,3)}(1)+\varepsilon_2^3(1)\right)+J^{(4)}_{1,1,1}\right\}\right]$$

$$\frac{1}{RT}\left(\frac{\partial^6 G^E}{\partial x_2^2 \partial x_3^2 \partial x_4^2}\right)_{x_1\to 1.0} = \left(\frac{\partial^5 \ln\gamma_3}{\partial x_2^2 \partial x_3 \partial x_4^2}\right)_{x_1\to 1.0} + \frac{4}{RT}\left(\frac{\partial^5 G^E}{\partial x_2^2 \partial x_3 \partial x_4^2}\right)_{x_1\to 1.0}$$

$$= J^{(3)}_{2,1,2} + 4\left[J^{(4)}_{2,1,1} + 3\times\left\{2\left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right)+J^{(2)}_{1,1,1}\right\}\right]$$

$$= J^{(3)}_{2,1,2} + 4\left[J^{(2)}_{1,1,2} + 3\times\left\{2\left(\rho_4^{(2,3)}(1)+\varepsilon_2^3(1)\right)+J^{(4)}_{1,1,1}\right\}\right]$$

$$\frac{1}{RT}\left(\frac{\partial^6 G^E}{\partial x_2^2 \partial x_3^2 \partial x_4^2}\right)_{x_1\to 1.0} = \left(\frac{\partial^5 \ln\gamma_4}{\partial x_2^2 \partial x_3^2 \partial x_4}\right)_{x_1\to 1.0} + \frac{4}{RT}\left(\frac{\partial^5 G^E}{\partial x_2^2 \partial x_3^2 \partial x_4}\right)_{x_1\to 1.0}$$

$$= J^{(4)}_{2,2,1} + 4\left[J^{(2)}_{1,2,1} + 3\times\left\{2\left(\rho_3^{(2,4)}(1)+\varepsilon_2^4(1)\right)+J^{(3)}_{1,1,1}\right\}\right]$$

$$= J^{(4)}_{2,2,1} + 4\left[J^{(3)}_{2,1,1} + 3\times\left\{2\left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right)+J^{(2)}_{1,1,1}\right\}\right]$$

The above relations are labeled as (11). Substituting these relations (11) for the corresponding derivatives in the modified Maclaurin infinite series defines the integral function of the system as:

$$\frac{G^E}{RT} = x_2(1-x_2)\left[\ln\gamma_2^\circ(1) + x_2\left\{\ln\gamma_2^\circ(1) + \frac{1}{2}\varepsilon_2^2(1)\right\} + x_2^2\left\{\ln\gamma_2^\circ(1) + \frac{2}{3}\varepsilon_2^2(1) + \frac{1}{3}\rho_2^2(1)\right\} + \dots\right]$$

$$+x_3(1-x_3)\left[\ln\gamma_3^\circ(1) + x_3\left\{\ln\gamma_3^\circ(1) + \frac{1}{2}\varepsilon_3^3(1)\right\} + x_3^2\left\{\ln\gamma_3^\circ(1) + \frac{2}{3}\varepsilon_3^3(1) + \frac{1}{3}\rho_3^3(1)\right\} + \dots\right]$$

$$+x_4(1-x_4)\left[\ln\gamma_4^\circ(1) + x_4\left\{\ln\gamma_4^\circ(1) + \frac{1}{2}\varepsilon_4^4(1)\right\} + x_4^2\left\{\ln\gamma_4^\circ(1) + \frac{2}{3}\varepsilon_4^4(1) + \frac{1}{3}\rho_4^4(1)\right\} + \dots\right]$$

$$+x_2x_3\left[\frac{1}{2}\left(\varepsilon_2^3(1) + \varepsilon_3^2(1)\right) + \frac{1}{4}x_2x_3\left(\varepsilon_2^3(1) + \varepsilon_3^2(1) + \rho_2^{(2,3)}(1) + \rho_3^{(2,3)}(1) + \frac{1}{2}J_{1,2}^{(2)}\right.\right.$$

$$\left. + \frac{1}{2}J_{2,1}^{(3)}\right) + \dots + \frac{1}{2}x_2\left(\varepsilon_2^3(1) + \rho_2^{(2,3)}(1)\right) + \frac{1}{3}x_2^2\left(\varepsilon_2^3(1) + \rho_2^{(2,3)}(1) + \frac{1}{2}J_{1,2}^{(2)}\right) + \dots$$

$$\left. + \frac{1}{2}x_3\left(\varepsilon_3^2(1) + \rho_3^{(2,3)}(1)\right) + \frac{1}{3}x_3^2\left(\varepsilon_3^2(1) + \rho_3^{(2,3)}(1) + \frac{1}{2}J_{2,1}^{(3)}\right) + \dots\right]$$

$$+x_2x_4\left[\frac{1}{2}\left(\varepsilon_2^4(1) + \varepsilon_4^2(1)\right) + \frac{1}{4}x_2x_4\left(\varepsilon_2^4(1) + \varepsilon_4^2(1) + \rho_2^{(2,4)}(1) + \rho_4^{(2,4)}(1) + \frac{1}{2}J_{1,2}^{(2)}\right.\right.$$

$$\left. + \frac{1}{2}J_{2,1}^{(4)}\right) + \dots + \frac{1}{2}x_2\left(\varepsilon_2^4(1) + \rho_2^{(2,4)}(1)\right) + \frac{1}{3}x_2^2\left(\varepsilon_2^4(1) + \rho_2^{(2,4)}(1) + \frac{1}{2}J_{1,2}^{(2)}\right) + \dots$$

$$\left. + \frac{1}{2}x_4\left(\varepsilon_4^2(1) + \rho_4^{(2,4)}(1)\right) + \frac{1}{3}x_4^2\left(\varepsilon_4^2(1) + \rho_4^{(2,4)}(1) + \frac{1}{2}J_{2,1}^{(4)}\right) + \dots\right]$$

$$+x_3x_4\left[\frac{1}{2}\left(\varepsilon_3^4(1) + \varepsilon_4^3(1)\right) + \frac{1}{4}x_3x_4\left(\varepsilon_3^4(1) + \varepsilon_4^3(1) + \rho_3^{(3,4)}(1) + \rho_4^{(3,4)}(1) + \frac{1}{2}J_{1,2}^{(3)}\right.\right.$$

$$\left. + \frac{1}{2}J_{2,1}^{(4)}\right) + \dots + \frac{1}{2}x_3\left(\varepsilon_3^4(1) + \rho_3^{(3,4)}(1)\right) + \frac{1}{3}x_3^2\left(\varepsilon_3^4(1) + \rho_3^{(3,4)}(1) + \frac{1}{2}J_{1,2}^{(3)}\right) + \dots$$

$$\left. + \frac{1}{2}x_4\left(\varepsilon_4^3(1) + \rho_4^{(3,4)}(1)\right) + \frac{1}{3}x_4^2\left(\varepsilon_4^3(1) + \rho_4^{(3,4)}(1) + \frac{1}{2}J_{2,1}^{(4)}\right) + \dots\right]$$

$$+x_2x_3x_4\left[\frac{1}{3}\left(\rho_4^{(2,3)}(1) + \varepsilon_2^3(1) + \rho_3^{(2,4)}(1) + \varepsilon_2^4(1) + \rho_2^{(3,4)}(1) + \varepsilon_3^4(1)\right.\right.$$

$$+ \frac{1}{2!}\left(J_{1,1,1}^{(2)} + 2\left(\rho_2^{(3,4)}(1) + \varepsilon_3^4(1)\right)\right)x_2 + \frac{1}{2!}\left(J_{1,1,1}^{(3)} + 2\left(\rho_3^{(2,4)}(1) + \varepsilon_2^4(1)\right)\right)x_3$$

$$+ \frac{1}{2!}\left(J_{1,1,1}^{(4)} + 2\left(\rho_4^{(2,3)}(1) + \varepsilon_2^3(1)\right)\right)x_4$$

$$+ \frac{1}{2!\,2!}\left[\frac{1}{2}\left\{J_{1,2,1}^{(2)} + 3\times\left(2\left(\rho_3^{(2,4)}(1) + \varepsilon_2^4(1)\right) + J_{1,1,1}^{(3)}\right) + J_{2,1,1}^{(3)}\right.\right.$$

$$\left.\left. +3\times\left(2\left(\rho_2^{(3,4)}(1) + \varepsilon_3^4(1)\right) + J_{1,1,1}^{(2)}\right)\right\}\right]x_2x_3$$

$$+ \frac{1}{2!\,2!}\left[\frac{1}{2}\left\{J_{1,2,1}^{(4)} + 3\times\left(2\left(\rho_3^{(2,4)}(1) + \varepsilon_2^4(1)\right) + J_{1,1,1}^{(3)}\right) + J_{1,1,2}^{(3)}\right.\right.$$

$$\left.\left. +3\times\left(2\left(\rho_4^{(2,3)}(1) + \varepsilon_2^3(1)\right) + J_{1,1,1}^{(4)}\right)\right\}\right]x_3x_4$$

$$+ \frac{1}{2!\,2!}\left[\frac{1}{2}\left\{J_{1,1,2}^{(2)} + 3\times\left(2\left(\rho_4^{(2,3)}(1) + \varepsilon_2^3(1)\right) + J_{1,1,1}^{(4)}\right) + J_{2,1,1}^{(4)}\right.\right.$$

$$\left.\left. +3\times\left(2\left(\rho_2^{(3,4)}(1) + \varepsilon_3^4(1)\right) + J_{1,1,1}^{(2)}\right)\right\}\right]x_2x_4$$

$$+\frac{1}{2!2!\ 2!}\left[\frac{1}{6}\left\{J^{(2)}_{1,2,2}+4\,J^{(4)}_{1,2,1}+4\times\left\{3\times\left(2\left(\rho_3^{(2,4)}(1)+\varepsilon_2^4(1)\right)+J^{(3)}_{1,1,1}\right)\right\}\right.\right.$$
$$+J^{(2)}_{1,2,2}+4\,J^{(3)}_{1,1,2}+4\times\left\{3\times\left(2\left(\rho_4^{(2,3)}(1)+\varepsilon_2^3(1)\right)+J^{(4)}_{1,1,1}\right)\right\}$$
$$+J^{(3)}_{2,1,2}+4\,J^{(4)}_{2,1,1}+4\times\left\{3\times\left(2\left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right)+J^{(2)}_{1,1,1}\right)\right\}$$
$$+J^{(3)}_{2,1,2}+4\,J^{(2)}_{1,1,2}+4\times\left\{3\times\left(2\left(\rho_4^{(2,3)}(1)+\varepsilon_2^3(1)\right)+J^{(4)}_{1,1,1}\right)\right\}\qquad(12)$$
$$+J^{(4)}_{2,2,1}+4\,J^{(2)}_{1,2,1}+4\times\left\{3\times\left(2\left(\rho_3^{(2,4)}(1)+\varepsilon_2^4(1)\right)+J^{(3)}_{1,1,1}\right)\right\}$$
$$\left.\left.+J^{(4)}_{2,2,1}+4\,J^{(3)}_{2,1,1}+4\times\left\{3\times\left(2\left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right)+J^{(2)}_{1,1,1}\right)\right\}\right\}\right]x_2x_3x_4+\ldots\Big]$$

DERIVATION OF ln γ_2, ln γ_3 AND ln γ_4 IN TERMS OF INTERACTION COEFFICIENTS

The function ln γ_2 is derived using equations (8) and (12) and is expressed as:

$$\ln\gamma_2=(1-x_2)^2\begin{bmatrix}\ln\gamma_2^\circ(1)+2\,x_2\left(\ln\gamma_2^\circ(1)+\frac{1}{2}\varepsilon_2^2(1)\right)\\+3\,x_2^2\left(\ln\gamma_2^\circ(1)+\frac{2}{3}\varepsilon_2^2(1)+\frac{1}{3}\rho_2^2(1)\right)+\ldots\end{bmatrix}$$
$$+x_3^2\begin{bmatrix}\ln\gamma_3^\circ(1)+(2x_3-1)\left(\ln\gamma_3^\circ(1)+\frac{1}{2}\varepsilon_3^3(1)\right)\\+\left(3x_3^2-2x_3\right)\left(\ln\gamma_3^\circ(1)+\frac{2}{3}\varepsilon_3^3(1)+\frac{1}{3}\rho_3^3(1)\right)+\ldots\end{bmatrix}$$
$$+x_4^2\begin{bmatrix}\ln\gamma_4^\circ(1)+(2x_4-1)\left(\ln\gamma_4^\circ(1)+\frac{1}{2}\varepsilon_4^4(1)\right)\\+\left(3x_4^2-2x_4\right)\left(\ln\gamma_4^\circ(1)+\frac{2}{3}\varepsilon_4^4(1)+\frac{1}{3}\rho_4^4(1)\right)+\ldots\end{bmatrix}$$
$$+Z_{x_2x_3}+Z_{x_3x_4}+Z_{x_2x_4}+\ln\gamma_2'\qquad(13)$$

where $Z_{x_2x_3}, Z_{x_3x_4}, Z_{x_2x_4}$ and ln γ_2' represent the infinite series of x_2x_3, x_3x_4, x_2x_4, and $x_2x_3x_4$ terms in the ln γ_2 function. These functions are evaluated subsequently in this paper. The higher order parameters are neglected because the Gibbs energy function is evaluated in solvent range and the concentration of the solutes is small. In the ternaries 1-2-3, 1-2-4 and 1-3-4, the relations $\in_2^3(1)=\in_3^2(1), \in_2^4(1)=\in_4^2(1)$ and $\in_3^4(1)=\in_4^3(1)$ are adopted. In the quaternary 1-2-3-4, the relation between cross-interaction parameters, $\rho_2^{(3,4)}(1)+\in_3^4(1)=\rho_3^{(2,4)}(1)+\in_2^4(1)=\rho_4^{(2,3)}+\in_2^3(1)$ are adopted. The equation (13) containing $\in_2^2(1), \in_3^3(1)$ and $\in_4^4(1)$ terms may be integrated as: (Using relations (58) of Appendix A)

$$\ln\gamma_2=\ln\gamma_2^\circ(1)+x_2\varepsilon_2^2(1)+x_3\varepsilon_3^3(1)$$
$$+x_4\varepsilon_4^4(1)+\ln(1-x_3)\ \varepsilon_3^3(1)$$
$$+\ln(1-x_4)\ \varepsilon_4^4(1)+Z_{x_2x_3}+Z_{x_2x_4}+Z_{x_3x_4}+\ln\gamma_2'\qquad(14)$$

Following the convention of Lupis and Elliott /3/, the integral excess function which constitutes x_2x_3 type terms may be expressed as:

$$G^E=\frac{1}{n_2!\,n_3!}\left(\frac{\partial^{n_2+n_3}G^E}{\partial x_2^{n_2}\partial x_3^{n_3}}\right)_{x_1\to 1.0}x_2^{n_2}x_3^{n_3}\qquad(15)$$

Using the equations (8) and (15), the $Z_{x_2x_3}$ may be represented as:

$$Z_{x_2x_3}=\frac{1-(n_2+n_3)}{n_2!\,n_3!}\left(\frac{\partial^{n_2+n_3}G^E}{\partial x_2^{n_2}\partial x_3^{n_3}}\right)_{x_1\to 1.0}x_2^{n_2}x_3^{n_3}$$
$$+\frac{n_2}{n_2!\,n_3!}\left(\frac{\partial^{n_2+n_3}G^E}{\partial x_2^{n_2-1}\partial x_3^{n_3}}\right)_{x_1\to 1.0}x_2^{n_2-1}x_3^{n_3}\qquad(16)$$

Since the higher order terms are considered, $\left(\frac{\partial^{n_2+n_3} G^E}{\partial x_2^{n_2} \partial x_3^{n_3}}\right)_{x_1 \to 1.0}$ may be equated to $(n_2+n_3-2)!\epsilon_2^3(1)$ and $Z_{x_2x_3}$ may be expressed as: (See – using relations (72) of Appendix A)

$$Z_{x_2x_3} = \left(-\frac{(n_2+n_3-1)!}{n_2!n_3!} x_2^{n_2} x_3^{n_3} + \frac{(n_2+n_3-2)!}{(n_2-1)!n_3!} x_2^{n_2-1} x_3^{n_3}\right)\varepsilon_2^3(1) \quad (17)$$

The infinite series $Z_{x_2x_3}$ constitutes the terms with the following condition: $n_2 \geq 1$, $n_3 \geq 1$ and $n_2 + n_3 \geq 2$. Using these conditions, $Z_{x_2x_3}$ may be integrated as:

$$Z_{x_2x_3} = \sum_{n_3=1}^{\infty} \frac{x_3^{n_3}}{n_3} \varepsilon_2^3(1) \quad (18)$$

$$Z_{x_2x_3} = -\ln(1-x_3)\varepsilon_2^3(1) \quad (19)$$

Using a similar kind of integration, the expression $Z_{x_2x_4}$ in ln γ_2 may be expressed as:

$$Z_{x_2x_3} = -\ln(1-x_3)\varepsilon_2^3(1) \quad (19)$$

Using a similar kind of integration, the expression $Z_{x_2x_4}$ in ln γ_2 may be expressed as:

$$Z_{x_2x_4} = -\ln(1-x_4)\varepsilon_2^4(1) \quad (20)$$

The integral excess function which constitutes x_3x_4 type terms may be expressed as:

$$G^E = \frac{1}{n_3!n_4!}\left(\frac{\partial^{n_3+n_4} G^E}{\partial x_3^{n_3} \partial x_4^{n_4}}\right)_{x_1 \to 1.0} x_3^{n_3} x_4^{n_4} \quad (21)$$

Using the equations (8) and (21), the $Z_{x_3x_4}$ may be represented as:

$$Z_{x_3x_4} = \frac{1-(n_3+n_4)}{n_3!n_4!}\left(\frac{\partial^{n_3+n_4} G^E}{\partial x_3^{n_3} \partial x_4^{n_4}}\right)_{x_1 \to 1.0} x_3^{n_3} x_4^{n_4} \quad (22)$$

Since the higher order terms are considered, $\left(\frac{\partial^{n_3+n_4} G^E}{\partial x_3^{n_3} \partial x_4^{n_4}}\right)_{x_1 \to 1}$ may be equated to $(n_3+n_4-2)!\varepsilon_3^4(1)$ and $Z_{x_3x_4}$ may be expressed as;

$$Z_{x_3x_4} = -\left(\frac{(n_3+n_4-1)!}{n_3!n_4!}\right) x_3^{n_3} x_4^{n_4} \varepsilon_3^4(1) \quad (23)$$

The infinite series $Z_{x_3x_4}$ constitutes the terms with the following condition:

$n_3 \geq 1$, $n_4 \geq 1$ and $n_3 + n_4 \geq 2$.

Using these conditions $Z_{x_3x_4}$ may be integrated as:

$$Z_{x_3x_4} = -\sum_{n_3=1}^{\infty}\sum_{n_4=1}^{\infty}\left(\frac{(n_3+n_4-1)!}{n_3!n_4!}\right) x_3^{n_3} x_4^{n_4} \varepsilon_3^4(1) \quad (24)$$

$$Z_{x_3x_4} = -\ln\left(\frac{(1-x_3)(1-x_4)}{(1-x_3-x_4)}\right)\varepsilon_3^4(1) \quad (25)$$

The integral excess function which constitutes $x_2x_3x_4$ type terms may be expressed as:

$$G^E = \frac{1}{n_2!n_3!n_4!}\left(\frac{\partial^{n_2+n_3+n_4} G^E}{\partial x_2^{n_2} \partial x_3^{n_3} \partial x_4^{n_4}}\right)_{x_1 \to 1.0} x_2^{n_2} x_3^{n_3} x_4^{n_4} \quad (26)$$

Using the equations (8) and (26), the ln γ_2 may be represented as:

$$\ln\gamma_2 = \sum_{n_2=1}^{\infty}\sum_{n_3=1}^{\infty}\sum_{n_4=1}^{\infty}\left(\frac{1-(n_2+n_3+n_4)}{n_2!n_3!n_4!}\right)\left(\frac{\partial^{n_2+n_3+n_4} G^E}{\partial x_2^{n_2} \partial x_3^{n_3} \partial x_4^{n_4}}\right)_{x_1 \to 1.0} x_2^{n_2} x_3^{n_3} x_4^{n_4}$$
$$+\sum_{n_2=1}^{\infty}\sum_{n_3=1}^{\infty}\sum_{n_4=1}^{\infty}\left(\frac{n_2}{n_2!n_3!n_4!}\right)\left(\frac{\partial^{n_2+n_3+n_4} G^E}{\partial x_2^{n_2} \partial x_3^{n_3} \partial x_4^{n_4}}\right)_{x_1 \to 1.0} x_2^{n_2-1} x_3^{n_3} x_4^{n_4} \quad (27)$$

Since the higher order terms are considered, $\left(\frac{\partial^{n_2+n_3+n_4} G^E}{\partial x_2^{n_2} \partial x_3^{n_3} \partial x_4^{n_4}}\right)_{x_1 \to 1}$ may be equated to

$(n_2+n_3+n_4-2)!\left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right)$ and $\ln\gamma_2'$ may be expressed as: (See relation (82) of Appendix A and Appendix B), where $n_2>1$, $n_3\geq 1$, $n_4\geq 1$, and $n_2+n_3+n_4\geq 3$.

$$\ln\gamma_2' = \left[-\sum_{n_2=1}^{\infty}\sum_{n_3=1}^{\infty}\sum_{n_4=1}^{\infty}\left(\frac{(n_2+n_3+n_4-1)!}{n_2!\,n_3!\,n_4!}\right)x_2^{n_2}x_3^{n_3}x_4^{n_4} + \sum_{n_2=1}^{\infty}\sum_{n_3=1}^{\infty}\sum_{n_4=1}^{\infty}\left(\frac{(n_2+n_3+n_4-2)!}{(n_2-1)!\,n_3!\,n_4!}\right)x_2^{n_2-1}x_3^{n_3}x_4^{n_4}\right]\left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right)$$

$$=\left[\sum_{n_3=1}^{\infty}\sum_{n_4=1}^{\infty}\left(\frac{(n_3+n_4-1)!}{n_3!\,n_4!}\right)x_3^{n_3}x_4^{n_4}\right]\left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right)$$

$$=\left[\ln\left(\frac{(1-x_3)(1-x_4)}{(1-x_3-x_4)}\right)\right]\left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right) \tag{28}$$

Substituting the values of $Z_{x_2x_3}$, $Z_{x_3x_4}$, $Z_{x_2x_4}$, and $\ln\gamma_2'$ in the equation (13), we will get:

$$\ln\gamma_2 = \ln\gamma_2^{0} + x_2\varepsilon_2^2(1) + x_3\varepsilon_3^3(1) + x_4\varepsilon_4^4(1) + \ln(1-x_3)\left(\varepsilon_3^3(1)-\varepsilon_2^3(1)\right) + \ln(1-x_4)\left(\varepsilon_4^4(1)-\varepsilon_2^4(1)\right) - \ln\left(\frac{(1-x_3)(1-x_4)}{(1-x_3-x_4)}\right)\varepsilon_3^4(1) + \left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right)\left[\ln\left(\frac{(1-x_3)(1-x_4)}{(1-x_3-x_4)}\right)\right] \tag{29}$$

Using the similar method of integration of the series as adopted for deriving $\ln\gamma_2$ function, the expressions for $\ln\gamma_3$ and $\ln\gamma_4$ may be deduced based on equations (9) and (10) respectively as:

$$\ln\gamma_3 = \ln\gamma_3^{0} + x_2\varepsilon_2^2(1) + x_3\varepsilon_3^3(1) + x_4\varepsilon_4^4(1) + \ln(1-x_2)\left(\varepsilon_2^2(1)-\varepsilon_3^2(1)\right) + \ln(1-x_4)\left(\varepsilon_4^4(1)-\varepsilon_3^4(1)\right) - \ln\left(\frac{(1-x_2)(1-x_4)}{(1-x_2-x_4)}\right)\varepsilon_2^4(1) + \left(\rho_3^{(2,4)}(1)+\varepsilon_2^4(1)\right)\left[\ln\left(\frac{(1-x_2)(1-x_4)}{(1-x_2-x_4)}\right)\right] \tag{30}$$

$$\ln\gamma_4 = \ln\gamma_4^{0} + x_2\varepsilon_2^2(1) + x_3\varepsilon_3^3(1) + x_4\varepsilon_4^4(1) + \ln(1-x_2)\left(\varepsilon_2^2(1)-\varepsilon_4^2(1)\right) + \ln(1-x_3)\left(\varepsilon_3^3(1)-\varepsilon_4^3(1)\right) - \ln\left(\frac{(1-x_2)(1-x_3)}{(1-x_2-x_3)}\right)\varepsilon_2^3(1) + \left(\rho_4^{(2,3)}(1)+\varepsilon_2^3(1)\right)\left[\ln\left(\frac{(1-x_2)(1-x_3)}{(1-x_2-x_3)}\right)\right] \tag{31}$$

4. THERMODYNAMIC CONSISTENCY BETWEEN SOLUTE PARTIALS USING MAXWELL RELATIONS

Thermodynamic consistency of solute partials $\ln\gamma_2$, $\ln\gamma_3$, and $\ln\gamma_4$ can be established using Maxwell relations. Maxwell relations in quaternary system can be expressed from Appendix C as:

$$-\left[-2x_2\left(\frac{\partial\ln\gamma_2}{\partial x_2}\right)+(1-2x_3)\left(\frac{\partial\ln\gamma_2}{\partial x_3}\right)+(1-2x_4)\left(\frac{\partial\ln\gamma_2}{\partial x_4}\right)\right]$$
$$+\left[x_2^2\left(\frac{\partial^2\ln\gamma_2}{\partial x_2^2}\right)+(-x_3+x_3^2)\left(\frac{\partial^2\ln\gamma_2}{\partial x_3^2}\right)+(-x_4+x_4^2)\left(\frac{\partial^2\ln\gamma_2}{\partial x_4^2}\right)\right]$$
$$+\left[(-x_2+2x_2x_3)\left(\frac{\partial^2\ln\gamma_2}{\partial x_2\partial x_3}\right)+(-x_2+2x_2x_4)\left(\frac{\partial^2\ln\gamma_2}{\partial x_2\partial x_4}\right)\right.$$
$$\left.+(1-x_3-x_4+2x_3x_4)\left(\frac{\partial^2\ln\gamma_2}{\partial x_3\partial x_4}\right)\right]$$

$$
\begin{aligned}
&= -\left[(1-2x_2)\left(\frac{\partial \ln\gamma_3}{\partial x_2}\right) - 2x_3\left(\frac{\partial \ln\gamma_3}{\partial x_3}\right) + (1-2x_4)\left(\frac{\partial \ln\gamma_3}{\partial x_4}\right)\right] \\
&\quad + \left[\left(-x_2+x_2^2\right)\left(\frac{\partial^2 \ln\gamma_3}{\partial x_2^2}\right) + x_3^2\left(\frac{\partial^2 \ln\gamma_3}{\partial x_3^2}\right) + \left(-x_4+x_4^2\right)\left(\frac{\partial^2 \ln\gamma_3}{\partial x_4^2}\right)\right] \\
&\quad + \left[(-x_2+2x_2x_3)\left(\frac{\partial^2 \ln\gamma_3}{\partial x_2\partial x_3}\right) + (1-x_2-x_4+2x_2x_4)\left(\frac{\partial^2 \ln\gamma_3}{\partial x_2\partial x_4}\right)\right. \\
&\quad \left. + (-x_3+2x_3x_4)\left(\frac{\partial^2 \ln\gamma_3}{\partial x_3\partial x_4}\right)\right] \\
&= -\left[(1-2x_2)\left(\frac{\partial \ln\gamma_4}{\partial x_2}\right) + (1-2x_3)\left(\frac{\partial \ln\gamma_4}{\partial x_3}\right) - 2x_4\left(\frac{\partial \ln\gamma_4}{\partial x_4}\right)\right] \\
&\quad + \left[\left(-x_2+x_2^2\right)\left(\frac{\partial^2 \ln\gamma_4}{\partial x_2^2}\right) + \left(-x_3+x_3^2\right)\left(\frac{\partial^2 \ln\gamma_4}{\partial x_3^2}\right) + x_4^2\left(\frac{\partial^2 \ln\gamma_4}{\partial x_4^2}\right)\right] \\
&\quad + \left[(1-x_2-x_3+2x_2x_3)\left(\frac{\partial^2 \ln\gamma_4}{\partial x_2\partial x_3}\right) + (-x_4+2x_2x_4)\left(\frac{\partial^2 \ln\gamma_4}{\partial x_2\partial x_4}\right)\right. \\
&\quad \left. + (-x_4+2x_3x_4)\left(\frac{\partial^2 \ln\gamma_4}{\partial x_3\partial x_4}\right)\right]
\end{aligned}
\tag{32}
$$

In equation (32), the partial derivatives can be calculated from the solute partial functions (29), (30) and (31) and are expressed as:

$$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right) = \varepsilon_2^2(1);$$

$$\left(\frac{\partial \ln\gamma_2}{\partial x_3}\right) = \varepsilon_3^3(1) - \frac{\varepsilon_3^3(1)-\varepsilon_2^3(1)}{1-x_3} + \rho_2^{(3,4)}(1)\left[-\frac{1}{1-x_3}+\frac{1}{1-x_3-x_4}\right];$$

$$\left(\frac{\partial \ln\gamma_2}{\partial x_4}\right) = \varepsilon_4^4(1) - \frac{\varepsilon_4^4(1)-\varepsilon_2^4(1)}{1-x_4} + \rho_2^{(3,4)}(1)\left[-\frac{1}{1-x_4}+\frac{1}{1-x_3-x_4}\right];$$

$$\left(\frac{\partial^2 \ln\gamma_2}{\partial x_2^2}\right) = 0;$$

$$\left(\frac{\partial^2 \ln\gamma_2}{\partial x_3^2}\right) = -\frac{\varepsilon_3^3(1)-\varepsilon_2^3(1)}{(1-x_3)^2} + \rho_2^{(3,4)}(1)\left[-\frac{1}{(1-x_3)^2}+\frac{1}{(1-x_3-x_4)^2}\right];$$

$$\left(\frac{\partial^2 \ln\gamma_2}{\partial x_4^2}\right) = -\frac{\varepsilon_4^4(1)-\varepsilon_2^4(1)}{(1-x_4)^2} + \rho_2^{(3,4)}(1)\left[-\frac{1}{(1-x_4)^2}+\frac{1}{(1-x_3-x_4)^2}\right];$$

$$\left(\frac{\partial^2 \ln\gamma_2}{\partial x_2\partial x_3}\right) = 0; \quad \left(\frac{\partial^2 \ln\gamma_2}{\partial x_2\partial x_4}\right) = 0;$$

$$\left(\frac{\partial^2 \ln\gamma_2}{\partial x_3\partial x_4}\right) = \rho_2^{(3,4)}(1)\left[\frac{1}{(1-x_3-x_4)^2}\right];$$

$$\left(\frac{\partial \ln\gamma_3}{\partial x_2}\right) = \varepsilon_2^2(1) - \frac{\varepsilon_2^2(1)-\varepsilon_3^2(1)}{1-x_2} + \rho_3^{(2,4)}(1)\left[-\frac{1}{1-x_2}+\frac{1}{1-x_2-x_4}\right]; \quad \left(\frac{\partial \ln\gamma_3}{\partial x_3}\right) = \varepsilon_3^3(1);$$

$$\left(\frac{\partial \ln \gamma_3}{\partial x_4}\right) = \varepsilon_4^4(1) - \frac{\varepsilon_4^4(1) - \varepsilon_3^4(1)}{1-x_4} + \rho_3^{(2,4)}(1)\left[-\frac{1}{1-x_4} + \frac{1}{1-x_2-x_4}\right];$$

$$\left(\frac{\partial^2 \ln \gamma_3}{\partial x_2^2}\right) = -\frac{\varepsilon_2^2(1) - \varepsilon_3^2(1)}{(1-x_2)^2} + \rho_3^{(2,4)}(1)\left[-\frac{1}{(1-x_2)^2} + \frac{1}{(1-x_2-x_4)^2}\right]; \left(\frac{\partial^2 \ln \gamma_3}{\partial x_3^2}\right) = 0;$$

$$\left(\frac{\partial^2 \ln \gamma_3}{\partial x_4^2}\right) = -\frac{\varepsilon_4^4(1) - \varepsilon_3^4(1)}{(1-x_4)^2} + \rho_2^{(3,4)}(1)\left[-\frac{1}{(1-x_4)^2} + \frac{1}{(1-x_2-x_4)^2}\right];$$

$$\left(\frac{\partial^2 \ln \gamma_3}{\partial x_2 \partial x_3}\right) = 0; \quad \left(\frac{\partial^2 \ln \gamma_3}{\partial x_2 \partial x_4}\right) = \rho_3^{(2,4)}(1)\left[\frac{1}{(1-x_2-x_4)^2}\right]; \quad \left(\frac{\partial^2 \ln \gamma_3}{\partial x_3 \partial x_4}\right) = 0;$$

$$\left(\frac{\partial \ln \gamma_4}{\partial x_2}\right) = \varepsilon_2^2(1) - \frac{\varepsilon_2^2(1) - \varepsilon_4^2(1)}{1-x_2} + \rho_4^{(2,3)}(1)\left[-\frac{1}{1-x_2} + \frac{1}{1-x_2-x_3}\right];$$

$$\left(\frac{\partial \ln \gamma_4}{\partial x_3}\right) = \varepsilon_3^3(1) - \frac{\varepsilon_3^3(1) - \varepsilon_3^4(1)}{1-x_3} + \rho_4^{(2,3)}(1)\left[-\frac{1}{1-x_3} + \frac{1}{1-x_2-x_3}\right]; \quad \left(\frac{\partial \ln \gamma_4}{\partial x_4}\right) = \varepsilon_4^4(1);$$

$$\left(\frac{\partial^2 \ln \gamma_4}{\partial x_2^2}\right) = -\frac{\varepsilon_2^2(1) - \varepsilon_2^4(1)}{(1-x_2)^2} + \rho_4^{(2,3)}(1)\left[-\frac{1}{(1-x_2)^2} + \frac{1}{(1-x_2-x_3)^2}\right];$$

$$\left(\frac{\partial^2 \ln \gamma_4}{\partial x_3^2}\right) = -\frac{\varepsilon_3^3(1) - \varepsilon_3^4(1)}{(1-x_3)^2} + \rho_4^{(2,3)}(1)\left[-\frac{1}{(1-x_3)^2} + \frac{1}{(1-x_2-x_3)^2}\right]; \left(\frac{\partial^2 \ln \gamma_4}{\partial x_4^2}\right) = 0;$$

$$\left(\frac{\partial^2 \ln \gamma_4}{\partial x_2 \partial x_3}\right) = \rho_4^{(2,3)}(1)\left[\frac{1}{(1-x_2-x_3)^2}\right]; \quad \left(\frac{\partial^2 \ln \gamma_4}{\partial x_2 \partial x_4}\right) = 0; \quad \left(\frac{\partial^2 \ln \gamma_4}{\partial x_3 \partial x_4}\right) = 0; \tag{33}$$

Substituting relations (33) in equation (32) one obtains

$$-\left[2x_2\varepsilon_2^2(1) + (1-2x_3)\left(\varepsilon_3^3(1) - \frac{\varepsilon_3^3(1) - \varepsilon_2^3(1)}{1-x_3} + \rho_2^{(3,4)}(1)\left\{-\frac{1}{1-x_3} + \frac{1}{1-x_3-x_4}\right\}\right)\right.$$

$$\left. + (1-2x_4)\left(\varepsilon_4^4(1) - \frac{\varepsilon_4^4(1) - \varepsilon_2^4(1)}{1-x_4} + \rho_2^{(3,4)}(1)\left\{-\frac{1}{(1-x_4)} + \frac{1}{(1-x_3-x_4)}\right\}\right)\right] + x_2^2 \times 0$$

$$+ \left(-x_3 + x_3^2\right)\left(\frac{\varepsilon_3^3(1) - \varepsilon_2^3(1)}{(1-x_3)^2} + \rho_2^{(3,4)}(1)\left\{-\frac{1}{(1-x_3)^2} + \frac{1}{(1-x_3-x_4)^2}\right\}\right)$$

$$+ \left(-x_4 + x_4^2\right)\left(-\frac{\varepsilon_4^4(1) - \varepsilon_2^4(1)}{(1-x_4)^2} + \rho_2^{(3,4)}(1)\left\{-\frac{1}{(1-x_4)^2} + \frac{1}{(1-x_3-x_4)^2}\right\}\right.$$

$$+ \left(-x_2 + 2x_2x_3\right) \times 0 + \left(-x_2 + 2x_2x_4\right) \times 0$$

$$+ \left(1 - x_3 - x_4 + 2x_3x_4\right)\rho_2^{(3,4)}(1)\left\{\frac{1}{(1-x_3-x_4)^2}\right\}\Bigg)$$

$$
\begin{aligned}
= & -\left[(1-2x_2)\left(\varepsilon_2^2(1)-\frac{\varepsilon_2^2(1)-\varepsilon_2^3(1)}{1-x_2}+\rho_3^{(2,4)}(1)\left\{-\frac{1}{1-x_2}+\frac{1}{1-x_2-x_4}\right\}\right)-2x_3\varepsilon_3^3(1)\right. \\
& \left.+(1-2x_4)\left(\varepsilon_4^4(1)-\frac{\varepsilon_4^4(1)-\varepsilon_3^4(1)}{1-x_4}+\rho_3^{(2,4)}(1)\left\{-\frac{1}{(1-x_4)}+\frac{1}{(1-x_2-x_4)}\right\}\right)\right] \\
& +\left[(-x_2+x_2^2)\left(\frac{\varepsilon_2^2(1)-\varepsilon_2^3(1)}{(1-x_2)^2}+\rho_3^{(2,4)}(1)\left\{-\frac{1}{(1-x_2)^2}+\frac{1}{(1-x_2-x_4)^2}\right\}\right)+x_3^2\times 0\right. \\
& \left.+(-x_4+x_4^2)\left(-\frac{\varepsilon_4^4(1)-\varepsilon_3^4(1)}{(1-x_4)^2}+\rho_3^{(2,4)}(1)\left\{-\frac{1}{(1-x_4)^2}+\frac{1}{(1-x_2-x_4)^2}\right\}\right)\right] \\
& +(-x_3+2x_2x_3)\times 0+(-x_3+2x_3x_4)\times 0 \\
& +(1-x_2-x_4+2x_2x_4)\rho_3^{(2,4)}(1)\left\{\frac{1}{(1-x_2-x_4)^2}\right\}\Bigg) \\
= & -\left[(1-2x_2)\left(\varepsilon_2^2(1)-\frac{\varepsilon_2^2(1)-\varepsilon_2^4(1)}{1-x_2}+\rho_4^{(2,3)}(1)\left\{-\frac{1}{1-x_2}+\frac{1}{1-x_2-x_3}\right\}\right)-2x_4\varepsilon_4^4(1)\right. \\
& \left.+(1-2x_3)\left(\varepsilon_3^3(1)-\frac{\varepsilon_3^3(1)-\varepsilon_3^4(1)}{1-x_3}+\rho_4^{(2,3)}(1)\left\{-\frac{1}{(1-x_3)}+\frac{1}{(1-x_2-x_3)}\right\}\right)\right] \\
& +\left[(-x_2+x_2^2)\left(-\frac{\varepsilon_2^2(1)-\varepsilon_2^4(1)}{(1-x_2)^2}+\rho_4^{(2,3)}(1)\left\{-\frac{1}{(1-x_2)^2}+\frac{1}{(1-x_2-x_3)^2}\right\}\right)+x_4^2\times 0\right. \\
& \left.+(-x_3+x_3^2)\left(-\frac{\varepsilon_3^3(1)-\varepsilon_3^4(1)}{(1-x_3)^2}+\rho_4^{(2,3)}(1)\left\{-\frac{1}{(1-x_3)^2}+\frac{1}{(1-x_2-x_3)^2}\right\}\right)\right] \\
& +(-x_4+2x_2x_4)\times 0+(-x_4+2x_3x_4)\times 0 \\
& +(1-x_2-x_3+2x_2x_3)\rho_4^{(2,3)}(1)\left\{\frac{1}{(1-x_2-x_3)^2}\right\}\Bigg)
\end{aligned}
\tag{34}
$$

On simplification of equation (34) one gets

$$
\begin{aligned}
& -2x_2\varepsilon_2^2(1)-2x_3\varepsilon_3^3(1)-2x_4\varepsilon_4^4(1)-\varepsilon_2^3(1)-\varepsilon_2^4(1)+\rho_2^{(3,4)}(1) \\
= & -2x_2\varepsilon_2^2(1)-2x_3\varepsilon_3^3(1)-2x_4\varepsilon_4^4(1)-\varepsilon_2^3(1)-\varepsilon_3^4(1)+\rho_3^{(2,4)}(1) \\
= & -2x_2\varepsilon_2^2(1)-2x_3\varepsilon_3^3(1)-2x_4\varepsilon_4^4(1)-\varepsilon_2^4(1)-\varepsilon_3^4(1)+\rho_4^{(2,3)}(1)
\end{aligned}
$$

yielding interrelation between the ternary and quaternary interaction parameters as:

$$
\begin{aligned}
\varepsilon_2^3(1)+\rho_4^{(2,3)}(1) & = \varepsilon_2^4(1)+\rho_3^{(2,4)}(1) \\
& = \varepsilon_3^4(1)+\rho_2^{(3,4)}(1)
\end{aligned}
\tag{35}
$$

Hence, solute partials are thermodynamically consistent using Maxwell relations.

5. DERIVATION OF $\ln\gamma_1$ FUNCTION

The partial function of solvent component of the system $\ln\gamma_1$ is deduced based on equations (7) and (12) and expressed as:

$$\ln\gamma_1 = x_2\varepsilon_2^2(1)+x_3\varepsilon_3^3(1)+x_4\varepsilon_4^4(1)+\varepsilon_2^2(1)\ln(1-x_2)$$
$$+\varepsilon_3^3(1)\ln(1-x_3)+\varepsilon_4^4(1)\ln(1-x_4)-\varepsilon_2^3(1)\ln\left(\frac{(1-x_2)(1-x_3)}{(1-x_2-x_3)}\right)$$
$$-\varepsilon_3^4(1)\ln\left(\frac{(1-x_3)(1-x_4)}{(1-x_3-x_4)}\right)-\varepsilon_2^4(1)\ln\left(\frac{(1-x_2)(1-x_4)}{(1-x_2-x_4)}\right)+\ln\gamma_1' \quad (36)$$

The integral excess function which constitutes $x_2x_3x_4$ type terms may be expressed as:

$$G^E = \left(\frac{\partial^{n_2+n_3+n_4}G^E}{\partial x_2^{n_2}\partial x_3^{n_3}\partial x_4^{n_4}}\right)_{x_1\to 1.0} x_2^{n_2}x_3^{n_3}x_4^{n_4} \quad (37)$$

$\ln\gamma_1$ may be deduced from using equations (7) and (37) and $\ln\gamma_1'$ constitutes $x_2x_3x_4$ terms in the infinite series, expressed as

$$\ln\gamma_1' = -\sum_{n_2=1}^{\infty}\sum_{n_3=1}^{\infty}\sum_{n_4=1}^{\infty}\left(\frac{(n_2+n_3+n_4-1)!}{n_2!n_3!n_4!}\right)\left(\frac{\partial^{n_2+n_3+n_4}G^E}{\partial x_2^{n_2}\partial x_3^{n_3}\partial x_4^{n_4}}\right)_{x_1\to 1.0} x_2^{n_2}x_3^{n_3}x_4^{n_4} \quad (38)$$

Since the higher order terms are considered, $\left(\frac{\partial^{n_2+n_3+n_4}G^E}{\partial x_2^{n_2}\partial x_3^{n_3}\partial x_4^{n_4}}\right)_{x_1\to 1.0}$ may be equated to $(n_2+n_3+n_4-2)!\left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right)$ and $\ln\gamma_1'$ may be expressed as: (Using relation (82) of Appendix A)

$$\ln\gamma_1' = -\sum_{n_2=1}^{\infty}\sum_{n_3=1}^{\infty}\sum_{n_4=1}^{\infty}\left(\frac{(n_2+n_3+n_4-1)!}{n_2!n_3!n_4!}\right)x_2^{n_2}x_3^{n_3}x_4^{n_4}\left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right)$$
$$=-\left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right)\ln\left(\frac{(1-x_2-x_3)(1-x_2-x_4)(1-x_3-x_4)}{(1-x_2-x_3-x_4)(1-x_2)(1-x_3)(1-x_4)}\right) \quad (39)$$

Substituting the above expression of $\ln\gamma_1'$ in equation (36) yields the partial function of the solvent component $\ln\gamma_1$ of the system as:

$$\ln\gamma_1 = x_2\varepsilon_2^2(1)+x_3\varepsilon_3^3(1)+x_4\varepsilon_4^4(1)+\varepsilon_2^2(1)\ln(1-x_2)+\varepsilon_3^3(1)\ln(1-x_3)+\varepsilon_4^4(1)\ln(1-x_4)$$
$$-\varepsilon_2^3(1)\ln\left(\frac{(1-x_2)(1-x_3)}{(1-x_2-x_3)}\right)-\varepsilon_3^4(1)\ln\left(\frac{(1-x_3)(1-x_4)}{(1-x_3-x_4)}\right)-\varepsilon_2^4(1)\ln\left(\frac{(1-x_2)(1-x_4)}{(1-x_2-x_4)}\right)$$
$$-\left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right)\ln\left(\frac{(1-x_2-x_3)(1-x_2-x_4)(1-x_3-x_4)}{(1-x_2-x_3-x_4)(1-x_2)(1-x_3)(1-x_4)}\right) \quad (40)$$

6. CONSISTENCY OF $\ln\gamma_1$, $\ln\gamma_2$, $\ln\gamma_3$ AND $\ln\gamma_4$ BASED ON GIBBS-DUHEM RELATIONS

The consistency of the derived partial functions $\ln\gamma_1$, $\ln\gamma_2$, $\ln\gamma_3$, and $\ln\gamma_4$ as expressed by equations (29), (30), (31) and (40) may be deduced using the following Gibbs-Duhem equations

$$(1-x_2-x_3-x_4)\frac{\partial\ln\gamma_1}{\partial x_2}+x_2\frac{\partial\ln\gamma_2}{\partial x_2}+x_3\frac{\partial\ln\gamma_3}{\partial x_2}+x_4\frac{\partial\ln\gamma_4}{\partial x_2}=0 \quad (41)$$

$$(1-x_2-x_3-x_4)\frac{\partial\ln\gamma_1}{\partial x_3}+x_2\frac{\partial\ln\gamma_2}{\partial x_3}+x_3\frac{\partial\ln\gamma_3}{\partial x_3}+x_4\frac{\partial\ln\gamma_4}{\partial x_3}=0 \quad (42)$$

and

$$(1-x_2-x_3-x_4)\frac{\partial\ln\gamma_1}{\partial x_4}+x_2\frac{\partial\ln\gamma_2}{\partial x_4}+x_3\frac{\partial\ln\gamma_3}{\partial x_4}+x_4\frac{\partial\ln\gamma_4}{\partial x_4}=0 \quad (43)$$

It may be noted that by substituting equations (29), (30), (31) and (40) in equation (41) one obtains:

$$
\begin{aligned}
&(1-x_2-x_3-x_4)\left[-\frac{\varepsilon_2^2(1)}{1-x_2}+\varepsilon_2^2(1)+\frac{\varepsilon_2^3(1)}{1-x_2}-\frac{\varepsilon_2^3(1)}{1-x_2-x_3}+\frac{\varepsilon_2^4(1)}{1-x_2}-\frac{\varepsilon_2^4(1)}{1-x_2-x_4}\right.\\
&\left.-\left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right)\left(-\frac{1}{(1-x_2-x_3)}-\frac{1}{(1-x_2-x_4)}+\frac{1}{(1-x_2-x_3-x_4)}+\frac{1}{(1-x_2)}\right)\right]\\
&+x_2\varepsilon_2^2(1)+x_3\left[\varepsilon_2^2(1)-\frac{\left(\varepsilon_2^2(1)-\varepsilon_3^2(1)\right)}{(1-x_2)}+\rho_3^{(2,4)}(1)\left(-\frac{1}{(1-x_2)}+\frac{1}{(1-x_2-x_4)}\right)\right]\\
&+x_4\left[\varepsilon_2^2(1)-\frac{\left(\varepsilon_2^2(1)-\varepsilon_4^2(1)\right)}{(1-x_2)}+\rho_4^{(2,3)}(1)\left(-\frac{1}{(1-x_2)}+\frac{1}{(1-x_2-x_3)}\right)\right]\quad=\quad 0
\end{aligned}
\tag{44}
$$

Since all the terms in the above expression cancel each other out, consistency of the partials is maintained. Similarly, one can prove the equations (29), (30), (31) and (40) satisfy the other two Gibbs-Duhem relations given by equations (42) and (43). It may be concluded that partial functions derived based on the Maclaurin infinite series of integral excess free energy function G^{E}, are free from truncation error and are thermodynamically consistent.

7. CONSISTENCY BETWEEN THE PARTIALS OF QUATERNARY AND TERNARY SYSTEMS

In a quaternary system, if the concentration of one of the solutes tends to zero, then the partials represent the activity coefficients of the solvent and solutes in a ternary system. Hence, when $x_4 \rightarrow 0.0$, equations (29), (30) and (40) become,

$$
\begin{aligned}
\ln\gamma_2 &= \ln\gamma_2^{\circ}+x_2\varepsilon_2^2(1)+x_3\varepsilon_3^3(1)\\
&\quad+\ln(1-x_3)\left(\varepsilon_3^3(1)-\varepsilon_2^3(1)\right)
\end{aligned}
\tag{45}
$$

$$
\begin{aligned}
\ln\gamma_3 &= \ln\gamma_3^{\circ}+x_2\varepsilon_2^2(1)+x_3\varepsilon_3^3(1)\\
&\quad+\ln(1-x_2)\left(\varepsilon_2^2(1)-\varepsilon_3^2(1)\right)
\end{aligned}
\tag{46}
$$

and

$$
\begin{aligned}
\ln\gamma_1 &= x_2\varepsilon_2^2(1)+x_3\varepsilon_3^3(1)+\varepsilon_2^2(1)\ \ln(1-x_2)\\
&+\varepsilon_3^3(1)\ \ln(1-x_3)-\varepsilon_2^3(1)\ln\left(\frac{(1-x_2)(1-x_3)}{(1-x_2-x_3)}\right)
\end{aligned}
\tag{47}
$$

The equations (45), (46) and (47) are the same as equations (14), (15) and (23) given in reference /1/ respectively. Therefore, one can apply the limiting conditions on the quaternary system partials and it can be used for the ternary system.

8. APPLICABILITY AND DISCUSSION

In the present study, the logarithmic activity coefficient functions of the solvent and solutes in a quaternary system are used to calculate the cross-interaction parameters of quaternary Fe-C-i-j systems. Yuanchang *et al.* /14,15/ used silver bath iso-activity method to study the activity coefficients of two components simultaneously dissolvable in both liquid iron and liquid silver by establishing an iso-i-j-activity state for Fe-C-i-j quaternary samples through a common silver bath. In the Fe-C-i-j quaternary system, activities of i and j are constant along the iso-activity lines. Therefore, using equations (29) and (30) one obtains:

$$\ln\left(\frac{a_i}{a_j}\right) = \ln x_i + \ln\gamma_i^\circ(Fe) + x_c\varepsilon_c^c(Fe) + x_i\varepsilon_i^i(Fe) + x_j\varepsilon_j^j(Fe) + \ln(1-x_c)\left(\varepsilon_c^c(Fe) - \varepsilon_i^c(Fe)\right)$$
$$+\ln(1-x_j)\left(\varepsilon_j^j(Fe) - \varepsilon_i^j(Fe)\right) - \ln\left(\frac{(1-x_c)(1-x_j)}{(1-x_c-x_j)}\right)\varepsilon_c^j(Fe)$$
$$+\left(\rho_i^{(c,j)}(Fe) + \varepsilon_c^j(Fe)\right)\left[\ln\left(\frac{(1-x_c)(1-x_j)}{(1-x_c-x_j)}\right)\right]$$
$$-\left[\ln\gamma_j^\circ(Fe) + x_c\varepsilon_c^c(Fe) + x_i\varepsilon_i^i(Fe) + x_j\varepsilon_j^j(Fe) + \ln(1-x_c)\left(\varepsilon_c^c(Fe) - \varepsilon_j^c(Fe)\right)\right.$$
$$+\ln(1-x_i)\left(\varepsilon_i^i(Fe) - \varepsilon_j^i(Fe)\right) - \ln\left(\frac{(1-x_c)(1-x_i)}{(1-x_c-x_i)}\right)\varepsilon_c^i(Fe)$$
$$\left.+\left(\rho_j^{(c,i)}(Fe) + \varepsilon_c^i(Fe)\right)\left\{\ln\left(\frac{(1-x_c)(1-x_i)}{(1-x_c-x_i)}\right)\right\}\right] \quad (48)$$

The infinite dilution values, interaction parameter values of binary and ternary systems were taken from literature and are given in Table 1. In equation (48), a_i and a_j are constant along the iso-activity lines and $\ln\gamma_i^\circ$ and $\ln\gamma_j^\circ$ are constant at a given temperature. Therefore equation (48) can be rewritten as:

$$\rho_i^{(c,j)}(Fe)\times\ln\left(\frac{(1-x_c)(1-x_j)}{(1-x_c-x_j)}\right)$$
$$-\rho_j^{(c,i)}(Fe)\times\ln\left(\frac{(1-x_c)(1-x_i)}{(1-x_c-x_i)}\right) = f\left(x_c, x_i, x_j, const\right) \quad (49)$$

The right hand side of equation (49) has known quantity along the iso-activity lines, unknown values of cross-interaction parameters of the equation are calculated using the experimental values. Activity coefficients of solvent and solutes are predicted in the Fe-C-Ti-Al, Fe-C-Ti-Cr, Fe-C-Ti-Ni, and Fe-C-Ti-Si quaternary systems. The calculated activity coefficients of Fe, C, Ti, Al, Cr, Ni and Si are tabulated in Tables 2, 3, 4 and 5 for the respective quaternary systems. Table 6 lists the values of interaction coefficients of Cr, Ni, Ta, N and V in the constituent binaries and ternaries of the Fe-Ta-Cr-N /16/, Fe-Ta-Ni-N /16/, Fe-Cr-V-N /17/ and Fe-Ni-V-N /17/ quaternary systems at 1873 K. Using the experimental data on the activity coefficient values of nitrogen in the four quaternary systems, the interaction parameters of various components are estimated by means of regression analysis of equation (29). Using the values of activity coefficients of the components in the quaternary systems, logarithmic activity coefficient of nitrogen in the Fe-Ta-Cr-N, Fe-Ta-Ni-N, Fe-Cr-V-N, and Fe-Ni-V-N quaternary systems are calculated using equation (29). Calculated and experimental values of activity coefficient of nitrogen are given in Tables 7 to 10 and also given in Figures 1 to 4. The predicted activity coefficient values of nitrogen are in good agreement with experimental data of the Fe-Ta-Cr-N, Fe-Ta-Ni-N, Fe-Cr-V-N and Fe-Ni-V-N quaternary systems.

9. CONCLUSIONS

Expressions for the thermodynamic functions in a quaternary system, namely, $\ln\gamma_1$, $\ln\gamma_2$, $\ln\gamma_3$, and $\ln\gamma_4$ are derived based on the Maclaurin infinite series which are expressed in terms of the integral property and subjected to appropriate boundary conditions. The derivation involves extensive integration of infinite geometrical series. The derived partials are free from any truncation error and are also independent of compositional paths. The thermodynamic consistency of the partials is checked through Maxwell and the Gibbs-Duhem equations. The quaternary partials are also useful for the ternary system by applying the boundary condition that one of the solute concentrations tends to zero. Solute partial functions are used to calculate the cross-interaction parameters of the quaternary system. Using the binary, ternary interactions and the quaternary parameters of quaternary systems, the activities of solvent Fe, and solutes Al, C, Cr, Ni, Si, and Ti in the

Table 1

Values of interaction coefficients in Fe melt at 1873 K, Values in ( ) are estimated

$\ln \gamma^o_{Al}(Fe)$	= -3.54 [3]	$\ln \gamma^o_{C}(Fe)$	= -0.3567 [3]
$\ln \gamma^o_{Si}(Fe)$	= -6.645 [3]	$\ln \gamma^o_{Ti}(Fe)$	= -3.2968 [3]
$\epsilon^{Ti}_{Al}(Fe)$	= 0.93 [16]	ϵ^{C}_{C}	= 6.9 [3]
$\epsilon^{Ni}_{C}(Fe)$	= 2.9 [3]	ϵ^{Ti}_{C}	= -11.94 [15]
ϵ^{Ni}_{Ni}	= -5.46 [12]	ϵ^{Si}_{Si}	= (-25.1)
$\rho^{(Al,C)}_{Ti}(Fe)$	= (39.79)	$\rho^{(C,Ti)}_{Al}(Fe)$	= (33.16)
$\rho^{(Ti,C)}_{Cr}(Fe)$	= (246.4)	$\rho^{(Cr,Ti)}_{C}(Fe)$	= (246.4)
$\rho^{(Ni,Ti)}_{C}(Fe)$	= (975.386)	$\rho^{(C,Si)}_{Ti}(Fe)$	= (-154.5)
$\ln \gamma^o_{Cr}(Fe)$	= 0.0[3]	$\ln \gamma^o_{Ni}(Fe)$	= -0.4155 [3]
$\epsilon^{Al}_{Al}(Fe)$	= 5.6 [3]	ϵ^{C}_{Al}	= 5.3 [3]
ϵ^{Cr}_{C}	= -5.1 [3]	$\epsilon^{Cr}_{Cr}(Fe)$	= 0.0
ϵ^{Ti}_{Cr}	= 11.9 [3]	ϵ^{Ti}_{Ti}	= 4.67 [15]
$\epsilon^{Ti}_{Si}(Fe)$	= 7.96 [16]		
$\rho^{(Al,Ti)}_{C}(Fe)$	= (44.16)	$\rho^{(C,Cr)}_{Ti}(Fe)$	= (263.4)
$\rho^{(C,Ni)}_{Ti}(Fe)$	= (975)	$\rho^{(C,Ti)}_{Ni}(Fe)$	= (965.9)
$\rho^{(Si,Ti)}_{C}(Fe)$	= (-156.8)	$\rho^{(C,Ti)}_{Si}(Fe)$	= (-152.78)

Table 2

Predicted activities of Fe, Ti, Al, and C in the quaternary Fe-C-Ti-Al melt at 1873 K

X_{Ti}	X_{Al}	X_C	a_{Fe}	$a_{Ti} \times 10^4$	$a_{Al} \times 10^4$	$a_C \times 10^2$
0.0033	0.0246	0.0071	0.9629	1.3843	8.5410	0.5837
0.0044	0.0228	0.0156	0.9552	2.0628	8.2214	1.2318
0.0052	0.0210	0.0242	0.9476	2.7292	7.8964	1.8526
0.0063	0.0194	0.0329	0.9394	3.7114	7.6015	2.4517
0.0069	0.0176	0.0421	0.9317	4.5845	7.2167	3.0256
0.0080	0.0156	0.0505	0.9243	5.9368	6.6715	3.5285
0.0046	0.0366	0.0101	0.9444	2.0421	13.8314	0.8804
0.0058	0.0343	0.0227	0.9328	3.0614	13.7612	1.8958
0.0077	0.0310	0.0359	0.9209	4.8745	13.2313	2.8766
0.0085	0.0269	0.0488	0.9120	6.3853	12.1459	3.6822
0.0091	0.0242	0.0633	0.9007	8.3198	11.7897	4.4944
0.0111	0.0231	0.0770	0.8857	12.3564	12.2893	5.3027
0.0122	0.0209	0.0828	0.8808	14.6668	11.4560	5.5902

Table 3

Predicted activities of Fe, Ti, Cr, and C in the quaternary Fe-C-Ti-Cr melt at 1873 K

X_{Ti}	X_{Cr}	X_C	a_{Fe}	$a_{Ti} \times 10^4$	$a_{Cr} \times 10^2$	$a_C \times 10^2$
0.0044	0.0284	0.012	0.9525	2.9506	2.8524	0.7549
0.0052	0.0307	0.0239	0.9358	4.6459	2.9829	1.4486
0.0090	0.0315	0.0476	0.9002	13.8334	3.0718	2.8453
0.0101	0.0345	0.0602	0.8789	22.6327	3.3547	3.4855
0.0132	0.0391	0.0723	0.8469	46.7377	4.0784	4.2396
0.0123	0.0458	0.0736	0.8379	56.8916	4.6329	4.1543
0.00412	0.0171	0.0237	0.9531	2.8802	1.6331	1.4908
0.0050	0.0186	0.0346	0.9390	4.2879	1.7284	2.1059
0.0078	0.0194	0.0489	0.9178	8.9219	1.8298	2.9514
0.0095	0.0205	0.0597	0.9012	13.8065	1.9625	3.5535
0.0109	0.0221	0.0709	0.8836	20.8373	2.1493	4.1332
0.0128	0.0225	0.0818	0.8658	31.1395	2.2853	4.7346
0.0097	0.0234	0.0904	0.8663	28.9278	2.0932	4.7852

Table 4

Predicted activities of Fe, Ti, Ni, and C in the quaternary Fe-C-Ti-Ni melt at 1873 K

X_{Ti}	X_{Ni}	X_C	a_{Fe}	$a_{Ti} \times 10^3$	$a_{Ni} \times 10^2$	$a_C \times 10^2$
0.00479	0.0071	0.0138	0.9731	0.23392	0.5063	1.0248
0.005451	0.0098	0.0224	0.9595	0.34412	0.7499	1.6724
0.0063	0.01204	0.0317	0.9447	0.53236	1.0160	2.3789
0.0077	0.0137	0.0393	0.9303	0.85140	1.3093	3.0196
0.00855	0.0161	0.0479	0.9140	1.3485	1.7361	3.7388
0.0099	0.0201	0.0643	0.8801	3.5077	2.8925	5.1877
0.0084	0.00914	0.00973	0.9710	0.38106	0.6473	0.7960
0.00914	0.0125	0.024	0.9474	0.64826	1.0530	1.9931
0.0099	0.0133	0.0363	0.9290	0.99976	1.3435	2.9692
0.0109	0.0151	0.04832	0.9077	1.68046	1.8769	3.9771
0.0114	0.0178	0.0607	0.8838	3.0503	2.7210	5.0364
0.0117	0.0202	0.0729	0.8599	5.7378	3.8030	6.0505
0.0134	0.0225	0.084	0.8284	12.4259	5.9176	7.3557

Table 5

Predicted activities of Fe, Ti, Si, and C in the quaternary Fe-C-Ti-Si melt at 1873 K

X_{Ti}	X_{Si}	X_C	a_{Fe}	$a_{Ti} \times 10^4$	$a_{Si} \times 10^5$	$a_C \times 10^2$
0.0093	0.0562	0.0216	0.9068	5.9263	10.9803	2.5004
0.0083	0.0549	0.0309	0.9017	5.3837	11.5349	3.4084
0.0074	0.0530	0.0378	0.8992	4.8673	11.7508	3.9867
0.0057	0.0518	0.0500	0.8927	3.8795	12.7894	4.9590
0.0051	0.0506	0.0598	0.8870	3.5920	13.6807	5.6460
0.0046	0.0491	0.0712	0.8806	3.3936	14.8006	6.3452
0.0085	0.0307	0.0186	0.9391	4.7189	5.4343	1.7451
0.0079	0.0288	0.0275	0.9336	4.6351	5.4640	2.4460
0.00712	0.027	0.0362	0.9286	4.4853	5.4957	3.0539
0.0061	0.0254	0.0438	0.9251	4.0177	5.5086	3.5126
0.0055	0.0216	0.0537	0.9213	3.9410	5.0876	3.9940
0.0048	0.0207	0.0614	0.9169	3.6874	5.2432	4.3767
0.0041	0.0179	0.0701	0.9139	3.4459	4.9125	4.6879

Table 6

Values of interaction coefficients in iron melts at 1873 K; Values in ( ) are estimated

$\epsilon_{Cr}^{Cr}(Fe)$	=	0.0	$\epsilon_{N}^{Cr}(Fe)$	=	(-8.94)
$\epsilon_{Ni}^{Ni}(Fe)$	=	(-5.46)	$\epsilon_{N}^{Ni}(Fe)$	=	(1.391)
$\epsilon_{Ta}^{Ta}(Fe)$	=	(-218.832)	$\epsilon_{N}^{Ta}(Fe)$	=	(-27.969)
$\epsilon_{V}^{V}(Fe)$	=	(-59.392)	$\epsilon_{N}^{V}(Fe)$	=	(-21.084)
$\epsilon_{N}^{N}(Fe)$	=	0.8	$\rho_{N}^{(Ni,Ta)}(Fe)$	=	(17.617)
$\rho_{N}^{(Cr,Ta)}(Fe)$	=	(55.90)	$\rho_{N}^{(Cr,V)}(Fe)$	=	(16.27)
$\rho_{N}^{(Ni,V)}(Fe)$	=	(-1.935)			

Table 7

Logarithmic activity coefficient of nitrogen in Fe-Ta-Cr-N melts at 1873 K

wt % Fe	wt% Ta	wt% Cr	wt% N	$\log(f_N)$(Cal)	$\log(f_N)$[16]
79.77	10.0	10.0	0.23	-0.7111	-0.7239
84.83	5.0	10.0	0.17	-0.5826	-0.5835
84.85	10.0	5.0	0.15	-0.5297	-0.5294
87.86	2.0	10.0	0.14	-0.4955	-0.5174
89.89	5.0	5.0	0.11	-0.3783	-0.4083
92.91	2.0	5.0	0.09	-0.2799	-0.2969

Table 8

Logarithmic activity coefficient of nitrogen in Fe-Ta-Ni-N melts at 1873 K

wt % Fe	wt% Ta	wt% Ni	wt% N	$\log(f_N)$(Cal)	$\log(f_N)$[16]
79.92	10.0	10.0	0.08	-0.2470	-0.2407
84.91	10.0	5.0	0.09	-0.3058	-0.2960
84.95	5.0	10.0	0.05	-0.0940	-0.0714
87.96	2.0	10.0	0.04	0.00450	0.0272
89.94	5.0	5.0	0.06	-0.1427	-0.1319
92.95	2.0	5.0	0.05	-0.0386	-0.0126

Table 9

Logarithmic activity coefficient of nitrogen in Fe-Ta-V-N melts at 1873 K

wt % Fe	wt% Cr	wt% V	wt% N	$\log(f_N)$(Cal)	$\log(f_N)$[17]
79.32	10.0	10.0	0.68	-1.1859	-1.1861
84.53	5.0	10.0	0.47	-1.0307	-1.0153
82.05	10.0	7.5	0.45	-1.0265	-1.0016
87.17	5.0	7.5	0.33	-0.8515	-0.8569
84.70	10.0	5.0	0.30	-0.8467	-0.8292
89.78	5.0	5.0	0.22	-0.6548	-0.6795
87.29	10.0	2.5	0.21	-0.6485	-0.6733
92.40	5.0	2.5	0.10	-0.4421	-0.3560

Table 10
Logarithmic activity coefficient of nitrogen in Fe-Ni-V-N melts at 1873 K

wt % Fe	wt% Ni	wt% V	wt% N	$\log(f_N)$(Cal)	$\log(f_N)$[17]
84.68	5.0	10.0	0.32	−0.8519	−0.8631
79.70	10.0	10.0	0.30	−0.8213	−0.8257
87.30	5.0	7.5	0.20	−0.6556	−0.6633
82.31	10.0	7.5	0.19	−0.6224	−0.6341
89.88	5.0	5.0	0.12	−0.4420	−0.4489
84.88	10.0	5.0	0.12	−0.4063	−0.4322
92.42	5.0	2.5	0.08	−0.2121	−0.2308
87.43	10.0	2.5	0.07	−0.1744	−0.1801

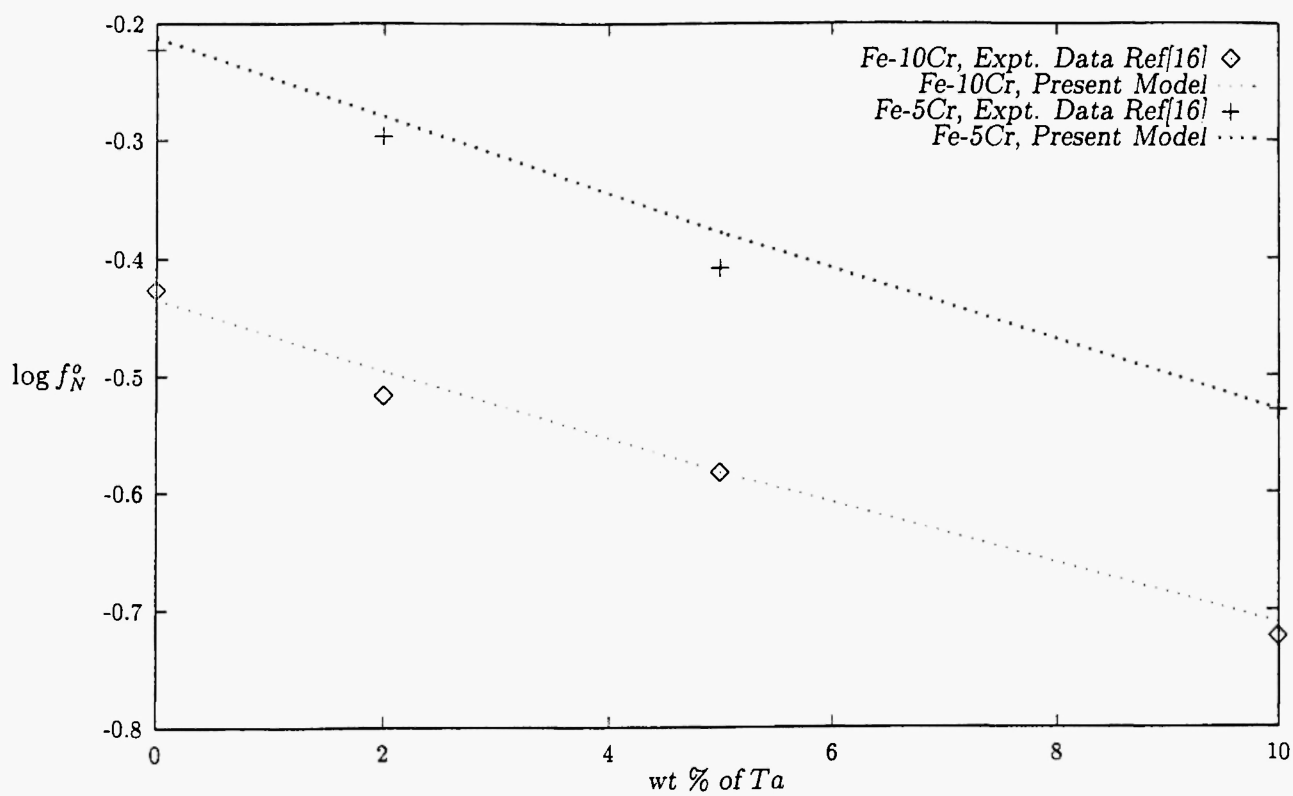

Fig. 1: The logarithmic activity coefficient of nitrogen in Fe-Ta-Cr-N alloy at 5 and 10 wt% of Cr at 1873 K.

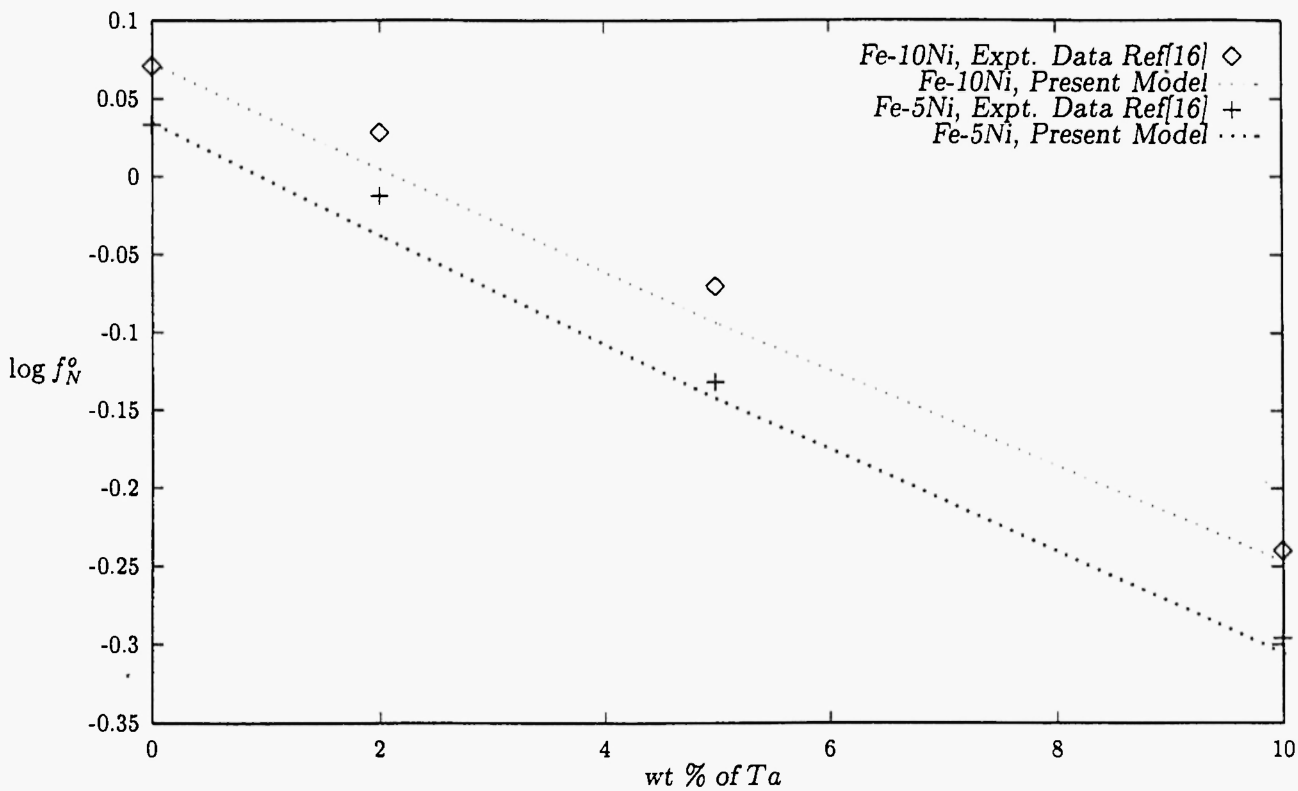

Fig. 2: The logarithmic activity coefficient of nitrogen in Fe-Ta-Ni-N alloy at 5 and 10 wt% of Ni at 1873 K.

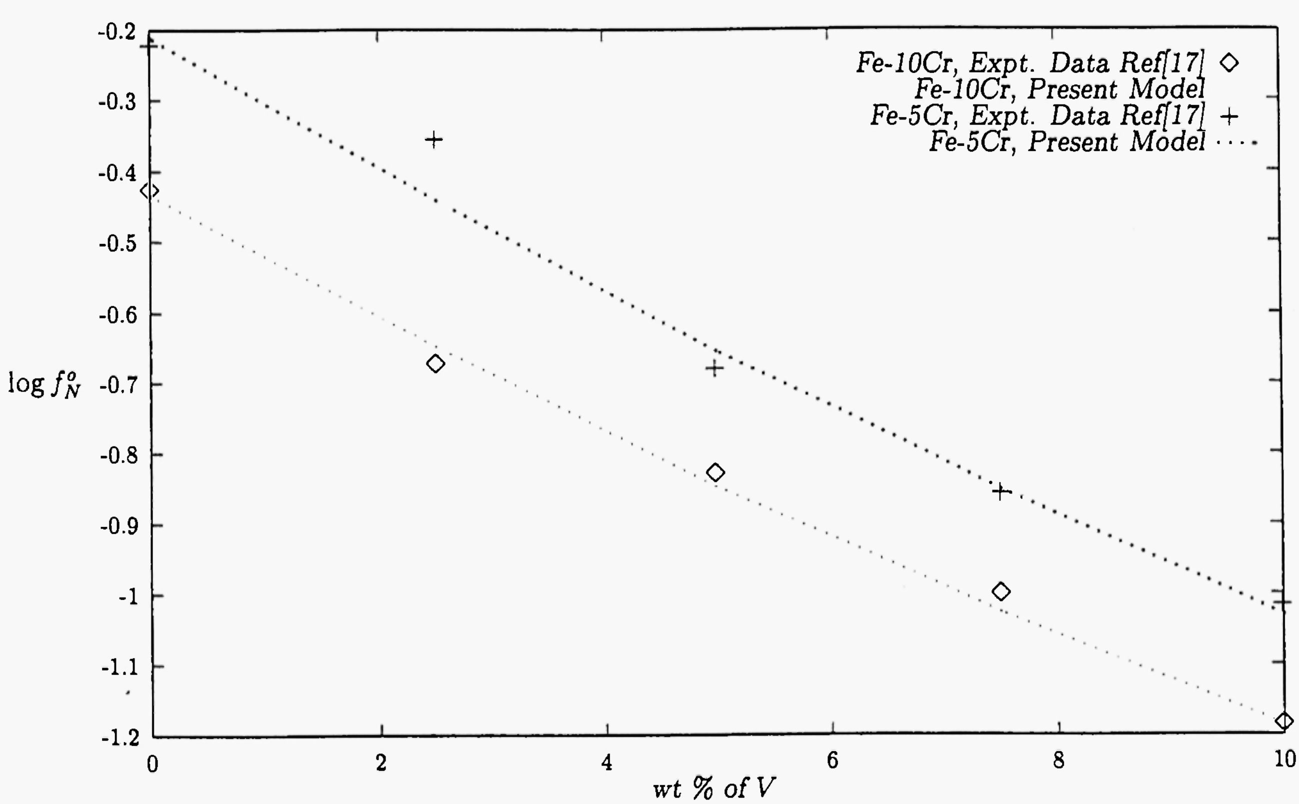

Fig. 3: The logarithmic activity coefficient of nitrogen in Fe-Cr-V-N alloy at 5 and 10 wt% of Cr at 1873 K.

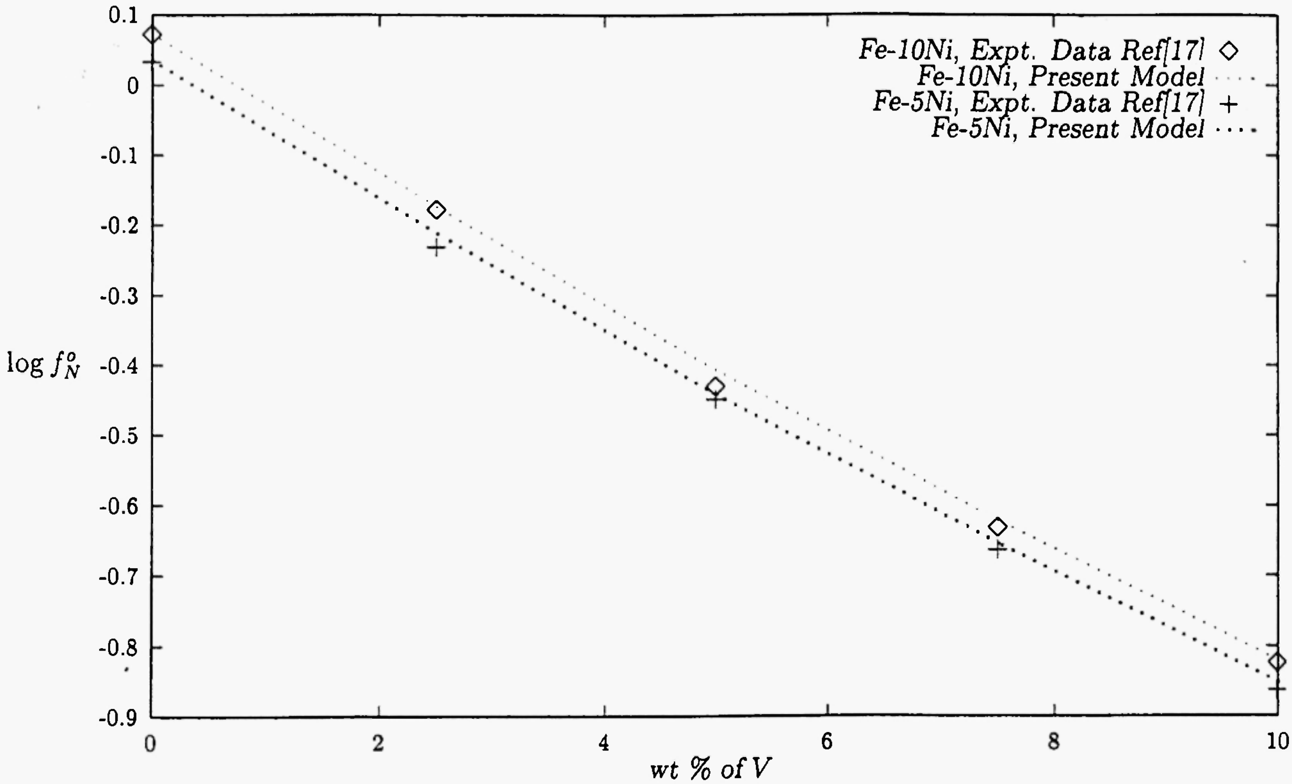

Fig. 4: The logarithmic activity coefficient of nitrogen in Fe-Ni-V-N alloy at 5 and 10 wt% of Ni at 1873 K.

Fe-Ti-Al-C, Fe-Ti-Cr-C, Fe-Ti-Ni-C and Fe-Ti-Si-C quaternary systems are calculated at 1873 K. The logarithmic activity coefficient of nitrogen is calculated in Fe-Ta-Cr-N, Fe-Ta-Ni-N, Fe-Cr-V-N, and Fe-Ni-V-N quaternary systems at 1873 K. The calculated values are in excellent agreement with the respective experimental data. The partial functions of the quaternary system derived using Maclaurin equations have the same functional form as those derived from Margules equations.

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APPENDIX A

DERIVATION OF THE RELATION

$$\frac{1}{RT}\left(\frac{\partial^{n_2} G^E}{\partial x_2^{n_2}}\right)_{x_1\to 1.0} = (n_2-2)!\ \varepsilon_2^2(1) \tag{50}$$

Using equation (10), relation (50) can be derived. Differentiating equation (10) with respect to x_2, and it can be expressed as:

$$(1-x_2)\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_2^2}\right) = \frac{\partial \ln\gamma_2}{\partial x_2} + x_3\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_2\partial x_3}\right) + x_4\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_2\partial x_4}\right) \tag{51}$$

As $x_1 \to 1.0$ and $x_2 \to 0$, $x_3 \to 0$, and $x_4 \to 0$, equation (51) reduces to

$$(1-x_2)\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_2^2}\right)_{x_1\to 1.0} = \left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)_{x_1\to 1.0} = \varepsilon_2^2(1) \tag{52}$$

Similarly, further differentiating equation (51) with respect to x_2 yields

$$(1-x_2)\frac{1}{RT}\left(\frac{\partial^3 G^E}{\partial x_2^3}\right) - \frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_2^2}\right) = \frac{\partial^2 \ln\gamma_2}{\partial x_2^2} + x_3\frac{1}{RT}\left(\frac{\partial^3 G^E}{\partial x_2^2\partial x_3}\right) + x_4\frac{1}{RT}\left(\frac{\partial^3 G^E}{\partial x_2^2\partial x_4}\right) \tag{53}$$

As $x_1 \to 1.0$ and $x_2 \to 0$, $x_3 \to 0$, and equation (53) reduces to

$$\frac{1}{RT}\left(\frac{\partial^3 G^E}{\partial x_2^3}\right)_{x_1\to 1.0} = \frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_2^2}\right)_{x_1\to 1.0} + \left(\frac{\partial^2 \ln\gamma_2}{\partial x_2^2}\right)_{x_1\to 1.0} = \varepsilon_2^2(1) + \rho_2^2(1) \tag{54}$$

Only considering first order interaction terms in equation (54), can be represented as:

$$\frac{1}{RT}\left(\frac{\partial^3 G^E}{\partial x_2^3}\right)_{x_1\to 1.0} = (3-2)!\ \varepsilon_2^2(1) = \varepsilon_2^2(1)$$

Similarly, further differentiating equation (53) with respect to x_2 yields

$$(1-x_2)\frac{1}{RT}\left(\frac{\partial^4 G^E}{\partial x_2^4}\right) - \frac{1}{RT}\left(\frac{\partial^3 G^E}{\partial x_2^3}\right) - \frac{1}{RT}\left(\frac{\partial^3 G^E}{\partial x_2^3}\right) = \frac{\partial^3 \ln\gamma_2}{\partial x_2^3} + x_3\frac{1}{RT}\left(\frac{\partial^4 G^E}{\partial x_2^3\partial x_3}\right) + x_4\frac{1}{RT}\left(\frac{\partial^4 G^E}{\partial x_2^3\partial x_4}\right) \tag{55}$$

As $x_1 \to 1.0$, $x_2 \to 0$, $x_3 \to 0$, and $x_4 \to 0$ and equation (55) reduces to

$$(1-x_2)\frac{1}{RT}\left(\frac{\partial^4 G^E}{\partial x_2^4}\right)_{x_1\to 1.0} = \frac{2}{RT}\left(\frac{\partial^3 G^E}{\partial x_2^3}\right)_{x_1\to 1.0} + \left(\frac{\partial^3 \ln \gamma_2}{\partial x_2^3}\right)_{x_1\to 1.0} \quad (56)$$

Only considering first order interaction terms in equation (56), can be represented as:

$$(1-x_2)\frac{1}{RT}\left(\frac{\partial^4 G^E}{\partial x_2^4}\right)_{x_1\to 1.0} = (4-2)!\ \varepsilon_2^2(1) = 2\ \varepsilon_2^2(1) \quad (57)$$

Similarly, one can generalize that n^{th} partial derivative of excess Gibbs energy with respective of x_2, x_3 and x_4 can be written as:

$$\frac{1}{RT}\left(\frac{\partial^{n_2} G^E}{\partial x_2^{n_2}}\right)_{x_1\to 1.0} = (n_2-2)!\ \varepsilon_2^2(1)$$
$$\frac{1}{RT}\left(\frac{\partial^{n_3} G^E}{\partial x_3^{n_3}}\right)_{x_1\to 1.0} = (n_3-2)!\ \varepsilon_3^3(1) \quad (58)$$
$$\frac{1}{RT}\left(\frac{\partial^{n_4} G^E}{\partial x_4^{n_4}}\right)_{x_1\to 1.0} = (n_4-2)!\ \varepsilon_4^4(1)$$

Derivation of the relation

$$\frac{1}{RT}\left(\frac{\partial^{n_2+n_3} G^E}{\partial x_2^{n_2}\partial x_3^{n_3}}\right)_{x_1\to 1.0} = (n_2+n_3-2)!\ \varepsilon_2^3(1) \quad (59)$$

Differentiating equation (10) with respect to x_3, on rearrangement, one obtains

$$(1-x_2)\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_2\partial x_3}\right) = \frac{\partial \ln \gamma_2}{\partial x_3} + x_3\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_3^2}\right) + x_4\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_3\partial x_4}\right) \quad (60)$$

As $x_1 \to 1.0$, $x_2 \to 0$, $x_3 \to 0$, and $x_4 \to 0$, equation (60) reduces to

$$\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_2\partial x_3}\right)_{x_1\to 1.0} = \left(\frac{\partial \ln \gamma_2}{\partial x_3}\right)_{x_1\to 1.0} = \varepsilon_2^3(1) \quad (61)$$

Further differentiating equation (60) with respect to x_2 and x_3 yields

$$(1-x_2)\frac{1}{RT}\left(\frac{\partial^4 G^E}{\partial x_2^2\partial x_3^2}\right) = \frac{2}{RT}\left(\frac{\partial^3 G^E}{\partial x_2\partial x_3^2}\right) + \left(\frac{\partial^3 \ln \gamma_2}{\partial x_2\partial x_3^2}\right) + x_3\frac{1}{RT}\left(\frac{\partial^4 G^E}{\partial x_2\partial x_3^3}\right) + x_4\frac{1}{RT}\left(\frac{\partial^4 G^E}{\partial x_2\partial x_3^2\partial x_4}\right) \quad (62)$$

Imposing boundary condition $x_1 \to 1.0$, as before, equation (62) reduces to

$$\frac{1}{RT}\left(\frac{\partial^4 G^E}{\partial x_2^2\partial x_3^2}\right)_{x_1\to 1.0} = \frac{2}{RT}\left(\frac{\partial^3 G^E}{\partial x_2\partial x_3^2}\right)_{x_1\to 1.0} + \left(\frac{\partial^3 \ln \gamma_2}{\partial x_2\partial x_3^2}\right)_{x_1\to 1.0} \quad (63)$$

Substituting corresponding interaction coefficients in equation (63) yields

$$\frac{1}{RT}\left(\frac{\partial^4 G^E}{\partial x_2^2\partial x_3^2}\right)_{x_1\to 1.0} = 2\left(\varepsilon_2^3(1)+\rho_2^{(2,3)}(1)\right)+J_{1,2}^{(2)}(1) \quad (64)$$

Using only first order interaction parameters, neglecting higher order interaction parameters, and using Wagner's relationship $\varepsilon_i^j(k)=\varepsilon_j^i(k)$ the n^{th} order excess Gibbs energy function derivatives are derived and are expressed as:

$$\frac{1}{RT}\left(\frac{\partial^4 G^E}{\partial x_2^2\partial x_3^2}\right)_{x_1\to 1.0} = 2\,\varepsilon_2^3(1) = (2+2-2)!\ \varepsilon_2^3(1) \quad (65)$$

Now differentiating equation (62) with respect to x_2, one obtains

$$(1-x_2)\frac{1}{RT}\left(\frac{\partial^5 G^E}{\partial x_2^3 \partial x_3^2}\right) = \frac{3}{RT}\left(\frac{\partial^4 G^E}{\partial x_2^2 \partial x_3^2}\right)+\left(\frac{\partial^4 \ln\gamma_2}{\partial x_2^2 \partial x_3^2}\right)$$
$$+x_3\frac{1}{RT}\left(\frac{\partial^5 G^E}{\partial x_2^2 \partial x_3^3}\right)+x_4\frac{1}{RT}\left(\frac{\partial^5 G^E}{\partial x_2^2 \partial x_3^2 \partial x_4}\right) \quad (66)$$

As $x_1 \to 1.0$, equation (66) becomes

$$\frac{1}{RT}\left(\frac{\partial^5 G^E}{\partial x_2^3 \partial x_3^2}\right) = \frac{3}{RT}\left(\frac{\partial^4 G^E}{\partial x_2^2 \partial x_3^2}\right)+\left(\frac{\partial^4 \ln\gamma_2}{\partial x_2^2 \partial x_3^2}\right) \quad (67)$$

Substituting the relation (65) in (67) and neglecting higher-order interaction parameters, one obtains

$$\frac{1}{RT}\left(\frac{\partial^5 G^E}{\partial x_2^3 \partial x_3^2}\right)_{x_1\to 1.0} = 3\times 2\ \varepsilon_2^3(1) = (3+2-2)!\ \varepsilon_2^3(1) \quad (68)$$

Similarly differentiating equation (66) with respect to x_3 and substituting the boundary condition, $x_1 \to 1.0$, one obtains

$$\frac{1}{RT}\left(\frac{\partial^6 G^E}{\partial x_2^3 \partial x_3^3}\right)_{x_1\to 1.0} = \frac{4}{RT}\left(\frac{\partial^5 G^E}{\partial x_2^2 \partial x_3^3}\right)_{x_1\to 1.0} + \left(\frac{\partial^5 \ln\gamma_2}{\partial x_2^2 \partial x_3^3}\right)_{x_1\to 1.0} \quad (69)$$

Considering only first order interaction parameters, equation (69) can be written as

$$\frac{1}{RT}\left(\frac{\partial^6 G^E}{\partial x_2^3 \partial x_3^3}\right)_{x_1\to 1.0} = \frac{4}{RT}\left(\frac{\partial^5 G^E}{\partial x_2^2 \partial x_3^3}\right)_{x_1\to 1.0} = 4\times 3\times\left(\frac{\partial^4 G^E}{\partial x_2^2 \partial x_3^2}\right)_{x_1\to 1.0} \quad (70)$$

Substituting equation (68), in equation (70) yields:

$$\frac{1}{RT}\left(\frac{\partial^6 G^E}{\partial x_2^3 \partial x_3^3}\right)_{x_1\to 1.0} = 4\times 3\times\ 2\times \varepsilon_2^3(1) = (3+3-2)!\ \varepsilon_2^3(1) \quad (71)$$

One can generalize from the equations (65), (69) and (71), n^{th} differential of excess Gibbs function with respect to x_2, x_3 and x_2, x_4 and x_3,x_4 can be written as:

$$\frac{1}{RT}\left(\frac{\partial^{n_2+n_3} G^E}{\partial x_2^{n_2} \partial x_3^{n_3}}\right)_{x_1\to 1.0} = (n_2+n_3-2)!\ \varepsilon_2^3(1)$$
$$\frac{1}{RT}\left(\frac{\partial^{n_2+n_4} G^E}{\partial x_2^{n_2} \partial x_4^{n_4}}\right)_{x_1\to 1.0} = (n_2+n_4-2)!\ \varepsilon_2^4(1) \quad (72)$$
$$\frac{1}{RT}\left(\frac{\partial^{n_3+n_4} G^E}{\partial x_3^{n_3} \partial x_4^{n_4}}\right)_{x_1\to 1.0} = (n_3+n_4-2)!\ \varepsilon_3^4(1)$$

DERIVATION OF THE RELATION

$$\frac{1}{RT}\left(\frac{\partial^{n_2+n_3+n_4} G^E}{\partial x_2^{n_2} \partial x_3^{n_3} \partial x_4^{n_4}}\right)_{x_1\to 1.0} = (n_2+n_3+n_4-2)!\left(\rho_4^{(2,3)}(1)+\varepsilon_2^3(1)\right) \quad (73)$$

Differentiation of equation (10) with respect to x_3 and x_4, and which is represented as:

$$RT\left(\frac{\partial^2 \ln\gamma_2}{\partial x_3 \partial x_4}\right) = -\left(\frac{\partial^2 G^E}{\partial x_3 \partial x_4}\right)+(1-x_2)\left(\frac{\partial^3 G^E}{\partial x_2 \partial x_3 \partial x_4}\right) -x_3\left(\frac{\partial^3 G^E}{\partial x_3^2 \partial x_4}\right)-x_4\left(\frac{\partial^3 G^E}{\partial x_3 \partial x_4^2}\right) \quad (74)$$

Imposing the boundary conditions, $x_1 \to 1.0$, $x_2 \to 0$, $x_3 \to 0$, and $x_4 \to 0$, equation (74) becomes

$$\left(\frac{\partial^3 G^E}{\partial x_2 \partial x_3 \partial x_4}\right)_{x_1\to 1.0} = RT\left(\frac{\partial^2 \ln\gamma_2}{\partial x_3 \partial x_4}\right)_{x_1\to 1.0} + \left(\frac{\partial^2 G^E}{\partial x_3 \partial x_4}\right)_{x_1\to 1.0} = (1+1+1-2)!\ \left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right) \quad (75)$$

Differentiating equation (74) with respect to x_2, one obtains

$$RT\left(\frac{\partial^3 \ln\gamma_2}{\partial x_2\partial x_3\partial x_4}\right)=-2\left(\frac{\partial^3 G^E}{\partial x_2\partial x_3\partial x_4}\right)+(1-x_2)\left(\frac{\partial^4 G^E}{\partial x_2^2\partial x_3\partial x_4}\right)-x_3\left(\frac{\partial^4 G^E}{\partial x_2\partial x_3^2\partial x_4}\right)-x_4\left(\frac{\partial^4 G^E}{\partial x_2\partial x_3\partial x_4^2}\right) \quad (76)$$

Imposing boundary condition, $x_1\to 1.0$, $x_2\to 0$, $x_3\to 0$, and $x_4\to 0$, and considering only the first order interaction parameters of ternary system and cross-interaction parameters of quaternary system, equation (76) becomes

$$\left(\frac{\partial^4 G^E}{\partial x_2^2\partial x_3\partial x_4}\right)_{x_1\to 1.0}=2\left(\frac{\partial^3 G^E}{\partial x_2\partial x_3\partial x_4}\right)_{x_1\to 1.0}=(2+1+1-2)!\left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right) \quad (77)$$

Differentiating equation (76) with respect to x_3, one obtains

$$RT\left(\frac{\partial^4 \ln\gamma_2}{\partial x_2\partial x_3^2\partial x_4}\right)=-3\left(\frac{\partial^4 G^E}{\partial x_2\partial x_3^2\partial x_4}\right)+(1-x_2)\left(\frac{\partial^5 G^E}{\partial x_2^2\partial x_3^2\partial x_4}\right)-x_3\left(\frac{\partial^5 G^E}{\partial x_2\partial x_3^3\partial x_4}\right)-x_4\left(\frac{\partial^5 G^E}{\partial x_2\partial x_3^2\partial x_4^2}\right) \quad (78)$$

Imposing the boundary conditions, $x_1\to 1.0$, $x_2\to 0$, $x_3\to 0$, and $x_4\to 0$, and considering only the first order interaction parameters of ternary system and cross-interaction parameters of quaternary system, equation (78) becomes

$$\left(\frac{\partial^5 G^E}{\partial x_2^2\partial x_3^2\partial x_4}\right)_{x_1\to 1.0}=3\left(\frac{\partial^4 G^E}{\partial x_2\partial x_3^2\partial x_4}\right)_{x_1\to 1.0}=3\times 2\left(\frac{\partial^3 G^E}{\partial x_2\partial x_3\partial x_4}\right)_{x_1\to 1.0}=(2+2+1-2)!\left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right) \quad (79)$$

Similarly, differentiating equation (78) with respect to x_4, one obtains

$$RT\left(\frac{\partial^5 \ln\gamma_2}{\partial x_2\partial x_3^2\partial x_4^2}\right)=-4\left(\frac{\partial^5 G^E}{\partial x_2\partial x_3^2\partial x_4^2}\right)+(1-x_2)\left(\frac{\partial^6 G^E}{\partial x_2^2\partial x_3^2\partial x_4^2}\right)-x_3\left(\frac{\partial^6 G^E}{\partial x_2\partial x_3^3\partial x_4^2}\right)-x_4\left(\frac{\partial^6 G^E}{\partial x_2\partial x_3^2\partial x_4^3}\right) \quad (80)$$

Imposing the boundary conditions, $x_1\to 1.0$, $x_2\to 0$, $x_3\to 0$, and $x_4\to 0$, and considering only the first order interaction parameters of ternary system and cross-interaction parameters of quaternary system, equation (80) becomes

$$\left(\frac{\partial^6 G^E}{\partial x_2^2\partial x_3^2\partial x_4^2}\right)_{x_1\to 1.0}=4\left(\frac{\partial^5 G^E}{\partial x_2\partial x_3^2\partial x_4^2}\right)_{x_1\to 1.0}=4\times 3\left(\frac{\partial^4 G^E}{\partial x_2\partial x_3\partial x_4^2}\right)_{x_1\to 1.0}=4\times 3\times 2\left(\frac{\partial^3 G^E}{\partial x_2\partial x_3\partial x_4}\right)_{x_1\to 1.0}=(2+2+2-2)!\left(\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)\right) \quad (81)$$

From the equations (75), (77), (79) and (81), one can conclude that n^{th} order partial differentiation of excess Gibbs energy function can be defined as:

$$\left(\frac{\partial^{n_2+n_3+n_4} G^E}{\partial x_2^{n_2} \partial x_3^{n_3} \partial x_4^{n_4}}\right) = (n_2+n_3+n_4-2)!\left(\rho_4^{(2,3)}(1)+\varepsilon_2^3(1)\right) \quad (82)$$

Hence the relation is proved.

APPENDIX B

The infinite series can be expressed as:

$$\sum_{n_2=2}^{\infty} \frac{(n_2-2)!}{n_2!} x_2^{n_2} = x_2 + (1-x_2)\ln(1-x_2) \quad (83)$$

$$\sum_{n_2=1}^{\infty}\sum_{n_3=1}^{\infty} \frac{(n_2+n_3-2)!}{n_2!\,n_3!} x_2^{n_2} x_3^{n_3} = \ln\left(\frac{(1-x_2)(1-x_3)}{(1-x_2-x_3)}\right) \quad (84)$$

and

$$\sum_{n_2=1}^{\infty}\sum_{n_3=1}^{\infty}\sum_{n_4=1}^{\infty} \frac{(n_2+n_3+n_4-2)!}{n_2!\,n_3!\,n_4!} x_2^{n_2} x_3^{n_3} x_4^{n_4} = \ln\left(\frac{(1-x_2-x_3)(1-x_2-x_4)(1-x_3-x_4)}{(1-x_2-x_3-x_4)(1-x_2)(1-x_3)(1-x_4)}\right) \quad (85)$$

APPENDIX C

Maxwell relations between the partials of a quaternary system

$$\left(\frac{\partial^2 \mu_2}{\partial n_3 \partial n_4}\right)_{n_1,n_2} = \left(\frac{\partial^2 \mu_3}{\partial n_2 \partial n_4}\right)_{n_1,n_3} = \left(\frac{\partial^2 \mu_4}{\partial n_2 \partial n_3}\right)_{n_1,n_4} \quad (86)$$

which can be rewritten as

$$\left(\frac{\partial^2 \ln a_2}{\partial n_3 \partial n_4}\right)_{n_1,n_2} = \left(\frac{\partial^2 \ln a_3}{\partial n_2 \partial n_4}\right)_{n_1,n_3} = \left(\frac{\partial^2 \ln a_4}{\partial n_2 \partial n_3}\right)_{n_1,n_4} \quad (87)$$

Change of the coordinates yields,

$$\left(\frac{\partial \ln a_2}{\partial n_3}\right)_{n_1,n_2} = \left(\frac{\partial \ln a_2}{\partial x_2}\right)\left(\frac{\partial x_2}{\partial n_3}\right)_{n_1,n_2} + \left(\frac{\partial \ln a_2}{\partial x_3}\right)\left(\frac{\partial x_3}{\partial n_3}\right)_{n_1,n_2} + \left(\frac{\partial \ln a_2}{\partial x_4}\right)\left(\frac{\partial x_4}{\partial n_3}\right)_{n_1,n_2} \quad (88)$$

and since

$$x_2 = \frac{n_2}{n_1+n_2+n_3+n_4}, \quad x_3 = \frac{n_3}{n_1+n_2+n_3+n_4}, \quad x_4 = \frac{n_4}{n_1+n_2+n_3+n_4} \quad (89)$$

then

$$\left(\frac{\partial x_2}{\partial n_3}\right) = -\frac{x_2}{n}, \quad \left(\frac{\partial x_3}{\partial n_3}\right) = \frac{1-x_3}{n}, \quad \left(\frac{\partial x_4}{\partial n_3}\right) = -\frac{x_4}{n} \quad (90)$$

or

$$\left(\frac{\partial x_i}{\partial n_j}\right) = -\frac{x_i}{n} \quad \text{where } i \neq j; \qquad = \frac{1-x_i}{n} \quad \text{where } i = j \quad (91)$$

Consequently,

$$\left(\frac{\partial \ln a_2}{\partial n_3}\right)_{n_1,n_2} = \frac{1}{n}\left[-x_2\left(\frac{\partial \ln a_2}{\partial x_2}\right) + (1-x_3)\left(\frac{\partial \ln a_2}{\partial x_3}\right) - x_4\left(\frac{\partial \ln a_2}{\partial x_4}\right)\right] \quad (92)$$

Substituting relation $a_2 = x_2\gamma_2$, in equation (92) one obtains

$$\left(\frac{\partial \ln \gamma_2}{\partial n_3}\right)_{n_1,n_2} = \frac{1}{n}\left[-1-x_2\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)+(1-x_3)\left(\frac{\partial \ln \gamma_2}{\partial x_3}\right)-x_4\left(\frac{\partial \ln \gamma_2}{\partial x_4}\right)\right] \quad (93)$$

Differentiating equation (93) with respect to n_4, one obtains

$$\begin{aligned}\left(\frac{\partial^2 \ln \gamma_2}{\partial n_3 \partial n_4}\right)_{n_1,n_2} = &-\frac{1}{n^2}\left[-1-x_2\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)+(1-x_3)\left(\frac{\partial \ln \gamma_2}{\partial x_3}\right)-x_4\left(\frac{\partial \ln \gamma_2}{\partial x_4}\right)\right]\\ &+\frac{1}{n}\left[\frac{x_2}{n}\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)-x_2\left\{\left(\frac{\partial^2 \ln \gamma_2}{\partial x_2^2}\right)\left(\frac{\partial x_2}{\partial n_4}\right)+\left(\frac{\partial^2 \ln \gamma_2}{\partial x_2 \partial x_3}\right)\left(\frac{\partial x_3}{\partial n_4}\right)\right.\right.\\ &\left.\left.+\left(\frac{\partial^2 \ln \gamma_2}{\partial x_2 \partial x_4}\right)\left(\frac{\partial x_4}{\partial n_4}\right)\right\}\right]+\frac{1}{n}\left[\frac{x_3}{n}\left(\frac{\partial \ln \gamma_2}{\partial x_3}\right)+(1-x_3)\left\{\left(\frac{\partial^2 \ln \gamma_2}{\partial x_2 \partial x_3}\right)\left(\frac{\partial x_2}{\partial n_4}\right)\right.\right.\\ &\left.\left.+\left(\frac{\partial^2 \ln \gamma_2}{\partial x_3^2}\right)\left(\frac{\partial x_3}{\partial n_4}\right)+\left(\frac{\partial^2 \ln \gamma_2}{\partial x_3 \partial x_4}\right)\left(\frac{\partial x_4}{\partial n_4}\right)\right\}\right]+\frac{1}{n}\left[-\frac{1-x_4}{n}\left(\frac{\partial \ln \gamma_2}{\partial x_4}\right)\right.\\ &\left.-x_4\left\{\left(\frac{\partial^2 \ln \gamma_2}{\partial x_2 \partial x_4}\right)\left(\frac{\partial x_2}{\partial n_4}\right)+\left(\frac{\partial^2 \ln \gamma_2}{\partial x_3 \partial x_4}\right)\left(\frac{\partial x_3}{\partial n_4}\right)+\left(\frac{\partial^2 \ln \gamma_2}{\partial x_4^2}\right)\left(\frac{\partial x_4}{\partial n_4}\right)\right\}\right]\end{aligned} \quad (94)$$

Substituting generalized relations (91) in equation (94) we get

$$\begin{aligned}\left(\frac{\partial^2 \ln \gamma_2}{\partial n_3 \partial n_4}\right)_{n_1,n_2} = &-\frac{1}{n^2}\left[-1-x_2\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)+(1-x_3)\left(\frac{\partial \ln \gamma_2}{\partial x_3}\right)-x_4\left(\frac{\partial \ln \gamma_2}{\partial x_4}\right)\right]\\ &+\frac{1}{n}\left[\frac{x_2}{n}\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)-x_2\left\{-\left(\frac{x_2}{n}\right)\left(\frac{\partial^2 \ln \gamma_2}{\partial x_2^2}\right)-\left(\frac{x_3}{n}\right)\left(\frac{\partial^2 \ln \gamma_2}{\partial x_2 \partial x_3}\right)\right.\right.\\ &\left.\left.+\left(\frac{1-x_4}{n}\right)\left(\frac{\partial^2 \ln \gamma_2}{\partial x_2 \partial x_4}\right)\right\}\right]+\frac{1}{n}\left[\frac{x_3}{n}\left(\frac{\partial \ln \gamma_2}{\partial x_3}\right)+(1-x_3)\left\{-\left(\frac{x_2}{n}\right)\left(\frac{\partial^2 \ln \gamma_2}{\partial x_2 \partial x_3}\right)\right.\right.\\ &\left.\left.-\left(\frac{x_3}{n}\right)\left(\frac{\partial^2 \ln \gamma_2}{\partial x_3^2}\right)+\left(\frac{1-x_4}{n}\right)\left(\frac{\partial^2 \ln \gamma_2}{\partial x_3 \partial x_4}\right)\right\}\right]+\frac{1}{n}\left[-\frac{1-x_4}{n}\left(\frac{\partial \ln \gamma_2}{\partial x_4}\right)\right.\\ &\left.-x_4\left\{-\left(\frac{x_2}{n}\right)\left(\frac{\partial^2 \ln \gamma_2}{\partial x_2 \partial x_4}\right)-\left(\frac{x_3}{n}\right)\left(\frac{\partial^2 \ln \gamma_2}{\partial x_3 \partial x_4}\right)+\left(\frac{1-x_4}{n}\right)\left(\frac{\partial^2 \ln \gamma_2}{\partial x_4^2}\right)\right\}\right]\end{aligned} \quad (95)$$

Maxwell relations in a quaternary system can be written as

$$
\begin{aligned}
&\left[2x_2\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)-(1-2x_3)\left(\frac{\partial \ln \gamma_2}{\partial x_3}\right)-(1-2x_4)\left(\frac{\partial \ln \gamma_2}{\partial x_4}\right)\right]\\
&+\left[x_2^2\left(\frac{\partial^2 \ln \gamma_2}{\partial x_2^2}\right)+\left(-x_3+x_3^2\right)\left(\frac{\partial^2 \ln \gamma_2}{\partial x_3^2}\right)+\left(-x_4+x_4^2\right)\left(\frac{\partial^2 \ln \gamma_2}{\partial x_4^2}\right)\right]\\
&+\left[(-x_2+2x_2x_3)\left(\frac{\partial^2 \ln \gamma_2}{\partial x_2 \partial x_3}\right)+(-x_2+2x_2x_4)\left(\frac{\partial^2 \ln \gamma_2}{\partial x_2 \partial x_4}\right)\right.\\
&\left.+(1-x_3-x_4+2x_3x_4)\left(\frac{\partial^2 \ln \gamma_2}{\partial x_3 \partial x_4}\right)\right]\\
=\;&\left[-(1-2x_2)\left(\frac{\partial \ln \gamma_3}{\partial x_2}\right)+2x_3\left(\frac{\partial \ln \gamma_3}{\partial x_3}\right)-(1-2x_4)\left(\frac{\partial \ln \gamma_3}{\partial x_4}\right)\right]\\
&+\left[\left(-x_2+x_2^2\right)\left(\frac{\partial^2 \ln \gamma_3}{\partial x_2^2}\right)+x_3^2\left(\frac{\partial^2 \ln \gamma_3}{\partial x_3^2}\right)+\left(-x_4+x_4^2\right)\left(\frac{\partial^2 \ln \gamma_3}{\partial x_4^2}\right)\right]\\
&+\left[(-x_3+2x_2x_3)\left(\frac{\partial^2 \ln \gamma_3}{\partial x_2 \partial x_3}\right)+(-x_3+2x_3x_4)\left(\frac{\partial^2 \ln \gamma_3}{\partial x_3 \partial x_4}\right)\right.\\
&\left.+(1-x_2-x_4+2x_2x_4)\left(\frac{\partial^2 \ln \gamma_3}{\partial x_2 \partial x_4}\right)\right]\\
=\;&\left[-(1-2x_2)\left(\frac{\partial \ln \gamma_4}{\partial x_2}\right)-(1-2x_3)\left(\frac{\partial \ln \gamma_4}{\partial x_3}\right)+2x_4\left(\frac{\partial \ln \gamma_4}{\partial x_4}\right)\right]\\
&+\left[\left(-x_2+x_2^2\right)\left(\frac{\partial^2 \ln \gamma_4}{\partial x_2^2}\right)+\left(-x_3+x_3^2\right)\left(\frac{\partial^2 \ln \gamma_4}{\partial x_3^2}\right)+x_4^2\left(\frac{\partial^2 \ln \gamma_4}{\partial x_4^2}\right)\right]\\
&+\left[(-x_4+2x_2x_4)\left(\frac{\partial^2 \ln \gamma_4}{\partial x_2 \partial x_4}\right)+(-x_4+2x_3x_4)\left(\frac{\partial^2 \ln \gamma_4}{\partial x_3 \partial x_4}\right)\right.\\
&\left.+(1-x_2-x_3+2x_2x_3)\left(\frac{\partial^2 \ln \gamma_4}{\partial x_2 \partial x_3}\right)\right]
\end{aligned}
\tag{96}
$$

As $x_1 \to 1.0$ one obtains

$$
\begin{aligned}
&-\left(\frac{\partial \ln \gamma_2}{\partial x_3}\right)-\left(\frac{\partial \ln \gamma_2}{\partial x_4}\right)+\left(\frac{\partial \ln \gamma_2}{\partial x_3 \partial x_4}\right)\\
&=-\left(\frac{\partial \ln \gamma_3}{\partial x_2}\right)-\left(\frac{\partial \ln \gamma_3}{\partial x_4}\right)+\left(\frac{\partial \ln \gamma_3}{\partial x_2 \partial x_4}\right)\\
&=-\left(\frac{\partial \ln \gamma_4}{\partial x_2}\right)-\left(\frac{\partial \ln \gamma_4}{\partial x_3}\right)+\left(\frac{\partial \ln \gamma_4}{\partial x_2 \partial x_3}\right)
\end{aligned}
\tag{97}
$$

or

$$-\varepsilon_2^3(1)-\varepsilon_2^4(1)+\rho_2^{(3,4)}(1)=-\varepsilon_3^2(1)-\varepsilon_3^4(1)+\rho_3^{(2,4)}(1)=-\varepsilon_4^2(1)-\varepsilon_4^3(1)+\rho_4^{(2,3)}(1)$$
$$\rho_2^{(3,4)}(1)+\varepsilon_3^4(1)=\rho_3^{(2,4)}(1)+\varepsilon_2^4(1)=\rho_4^{(2,3)}(1)+\varepsilon_2^3(1) \qquad (98)$$

Equation (98) is the reciprocal relation between cross-interaction parameters in a quaternary system.