Representation of Excess Thermodynamic Properties of Ternary Systems Using Interaction Parameters

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A ternary function has been developed based on the Maclaurin infinite series, which is expressed in the neighborhood of each of the pure components of the system. Each of the series is subjected to various boundary conditions. The ternary function is based on the summation of these series. In the process of converting the terms of these infinite series to the corresponding infinite dilution constants and interaction parameters, the ternary function also distinguishes between the binary and ternary interaction parameters of the system. The truncation of the infinite series pertaining to the binary and ternary interaction terms is adjusted by a suitable technique which is described in the text. The function is thermodynamically consistent and capable of interpreting properties of the ternary system.

I. INTRODUCTION

THE development of the interaction parameter formalism[1,2] is based on the expansion of the Maclaurin infinite series in terms of the partial property in the neighborhood of a solvent component of a system. Although the parameters are originally intended to be useful for interpretation of properties for dilute solutions, attempts have been made by several researchers to extend the approach to concentrated solutions.[3,4] Schuhmann[3] has shown that Wagner's original suggestion[1] is essentially valid if such an infinite series is not truncated. Since higher order interaction parameters are rarely available for systems of practical interest, activity coefficients of solutes at finite concentrations have so far been calculated using the first-order parameters. Two methods have been suggested by Srikanth and Jacob[7] toward solution of the inexact differential equation: (a) through the introduction of the special relations of the interaction parameters and (b) by the use of suitable compositional paths. It should be mentioned that an extensive critical survey of the experimental data of the first- and second-order parameters has been compiled in the literature;[8–12] their evaluation does not support the validity of the special relations between the first- and second-order parameters. A constant compositional path, such as $x_i = k$ or $x_i/x_j = \mathrm{k}$, may be employed, as suggested by them,[7] toward the solution of the problem. One cannot eliminate all of the compositional degrees of freedom by the application of a compositional path. Hence, the method remains inconsistent from a thermodynamic viewpoint as in the case of the use of the special relations between parameters. Two important aspects which emerge from the discussion are (a) thermodynamic consistency and (b) the capability of interpreting experimental data beyond the dilute solution range. It should be mentioned that the Maclaurin infinite series may either be expressed by an integral or a partial property in the neighborhood of a component of a system. Since a partial may be readily derived from the other using the Gibbs-Duhem relation for a binary system, the choice of an integral or a partial property for expressing the Maclaurin series does not restrict the thermodynamic consistency due to truncation of the series. In the case of a ternary or a higher order system, the truncated Maclaurin series based on the partial property of the system has been shown to limit the thermodynamic consistency.[3,7] It should be mentioned that these observations are made with respect to the Maclaurin series which is expressed in the vicinity of a component of a system. Before one considers the applicability of a function beyond the dilute solution range, it must satisfy certain boundary conditions. For integral excess properties of a ternary system, these conditions are

$$(x) \qquad \Delta G^{XS} \rightarrow 0 \quad \text{as } X_1 \rightarrow 1.0$$

$$(y) \qquad \Delta G^{XS} \rightarrow 0 \quad \text{as } X_2 \rightarrow 1.0$$

$$(z) \qquad \Delta G^{XS} \rightarrow 0 \quad \text{as } X_3 \rightarrow 1.0$$

Using similar arguments, as mentioned with respect to the binaries, it may be noted that Darken's equations[5,6] satisfy the Gibbs-Duhem relation and, therefore, they are thermodynamically consistent. The equation satisfies condition (x) and will satisfy (y) and (z) for a ternary system if the solute components also behave regularly. The quadratic formalism may be quite useful in representing excess thermodynamic properties in dilute multicomponent solutions for simple systems. From the above arguments, it follows that it may be necessary to adopt the Maclaurin infinite series based on the integral property which is expressed in the neighborhood of each of the components of the system. Furthermore, it is easy to obtain the partials from the integral function for a ternary or a higher order system, as the truncation may be controlled by repeated differentiation. It may also be noted that the derived partials from such an integral function are automatically thermodynamically consistent. The above-mentioned boundary conditions and their applications at the various stages of the treatment, as adopted in the present research, are discussed in detail in the text along with the development of the function.

II. GENERALIZED APPROACH TO TERNARY SYSTEMS

Although the Maclaurin infinite series is normally expressed in terms of the partial properties, in the present

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work, as already outlined, it has been expressed through the integral function of the system. Furthermore, apart from expressing the Maclaurin infinite series in the vicinity of $X_1 \rightarrow 1.0$, the series representations are also included as $X_2 \rightarrow 1.0$ and $X_3 \rightarrow 1.0$. These three separate representations of the Maclaurin infinite series may then be expressed as

$$\begin{aligned}\Delta G^{XS} = {} & (\Delta G^{XS})_{X_1\rightarrow 1.0} + \left(\frac{\partial \Delta G^{XS}}{\partial X_2}\right)_{X_1\rightarrow 1.0} X_2 \\ & + \frac{1}{2}\left(\frac{\partial^2 \Delta G^{XS}}{\partial X_2^2}\right)_{X_1\rightarrow 1.0} X_2^2 \\ & + \frac{1}{3!}\left(\frac{\partial^3 \Delta G^{XS}}{\partial X_2^3}\right)_{X_1\rightarrow 1.0} X_2^3 + \ldots \\ & + \left(\frac{\partial \Delta G^{XS}}{\partial X_3}\right)_{X_1\rightarrow 1.0} X_3 + \frac{1}{2}\left(\frac{\partial^2 \Delta G^{XS}}{\partial X_3^2}\right)_{X_1\rightarrow 1.0} X_3^2 \\ & + \frac{1}{3!}\left(\frac{\partial^3 \Delta G^{XS}}{\partial X_3^3}\right)_{X_1\rightarrow 1.0} X_3^3 + \ldots \\ & + \left(\frac{\partial^2 \Delta G^{XS}}{\partial X_2 \partial X_3}\right)_{X_1\rightarrow 1.0} X_2 X_3 \\ & + \frac{1}{2}\left(\frac{\partial^3 \Delta G^{XS}}{\partial X_2^2 \partial X_3}\right)_{X_1\rightarrow 1.0} X_2 X_3^2 + \ldots \end{aligned} \qquad [1]$$

in the vicinity of $X_1 \rightarrow 1.0$ of a ternary system. The representation based on the Maclaurin series as $X_2 \rightarrow 1.0$ may be denoted as

$$\begin{aligned}\Delta G^{XS} = {} & (\Delta G^{XS})_{X_2\rightarrow 1.0} + \left(\frac{\partial \Delta G^{XS}}{\partial X_1}\right)_{X_2\rightarrow 1.0} X_1 \\ & + \frac{1}{2}\left(\frac{\partial^2 \Delta G^{XS}}{\partial X_1^2}\right)_{X_2\rightarrow 1.0} X_1^2 + \frac{1}{3!}\left(\frac{\partial^3 \Delta G^{XS}}{\partial X_1^3}\right)_{X_2\rightarrow 1.0} X_1^3 \\ & + \ldots + \left(\frac{\partial \Delta G^{XS}}{\partial X_3}\right)_{X_2\rightarrow 1.0} X_3 \\ & + \frac{1}{2}\left(\frac{\partial^2 \Delta G^{XS}}{\partial X_3}\right)_{X_2\rightarrow 1.0} X_3^2 \\ & + \frac{1}{3!}\left(\frac{\partial^3 \Delta G^{XS}}{\partial X_3^3}\right)_{X_2\rightarrow 1.0} X_3^3 \\ & + \ldots + \left(\frac{\partial^2 \Delta G^{XS}}{\partial X_1 \partial X_3}\right)_{X_2\rightarrow 1.0} X_1 X_3 \\ & + \frac{1}{2}\left(\frac{\partial^3 \Delta G^{XS}}{\partial X_1^2 \partial X_3}\right)_{X_2\rightarrow 1.0} X_1^2 X_3 \\ & + \frac{1}{2}\left(\frac{\partial^3 \Delta G^{XS}}{\partial X_1 \partial X_3^2}\right)_{X_2\rightarrow 1.0} X_1 X_3^2 + \ldots \end{aligned} \qquad [2]$$

The series in the neighborhood of $X_3 \rightarrow 1.0$ may be expressed as

$$\begin{aligned}\Delta G^{XS} = {} & (\Delta G^{XS})_{X_3\rightarrow 1.0} + \left(\frac{\partial \Delta G^{XS}}{\partial X_1}\right)_{X_3\rightarrow 1.0} X_1 \\ & + \frac{1}{2}\left(\frac{\partial^2 \Delta G^{XS}}{\partial X_1^2}\right)_{X_3\rightarrow 1.0} X_3 + \frac{1}{3!}\left(\frac{\partial^3 \Delta G^{XS}}{\partial X_1^3}\right)_{X_3\rightarrow 1.0} X_1^3 \\ & + \ldots + \left(\frac{\partial \Delta G^{XS}}{\partial X_2}\right)_{X_3\rightarrow 1.0} X_2 \\ & + \frac{1}{2}\left(\frac{\partial^2 \Delta G^{XS}}{\partial X_2^2}\right)_{X_3\rightarrow 1.0} X_2^2 + \frac{1}{3!}\left(\frac{\partial^3 \Delta G^{XS}}{\partial X_2^3}\right)_{X_3\rightarrow 1.0} X_2^3 \\ & + \ldots + \left(\frac{\partial^2 \Delta G^{XS}}{\partial X_1 \partial X_2}\right)_{X_3\rightarrow 1.0} X_1 X_2 \\ & + \frac{1}{2}\left(\frac{\partial^3 \Delta G^{XS}}{\partial X_1^2 \partial X_2}\right)_{X_3\rightarrow 1.0} X_1^2 X_2 \\ & + \frac{1}{2}\left(\frac{\partial^3 \Delta G^{XS}}{\partial X_1 \partial X_2^2}\right)_{X_3\rightarrow 1.0} X_1 X_2^2 + \ldots \end{aligned} \qquad [3]$$

The process of converting the above derivatives in the Maclaurin series represented by Eqs. [1] through [3] to the corresponding interaction parameters involves repeated differentiation of the equations relating to the partials and the integral excess quantities of ternary systems with the application of relevant dilute solution restrictions.[13]

These equations along with their respective dilute solution restrictions are summarized as

$$\ln \gamma_1 = \frac{\Delta G^{XS}}{RT} - X_2\left(\frac{\partial \Delta G^{XS}}{\partial X_2}\right)\frac{1}{RT} - X_3\left(\frac{\partial \Delta G^{XS}}{\partial X_3}\right)\frac{1}{RT} \qquad [4]$$

$$\begin{aligned}\ln \gamma_2 = {} & \frac{\Delta G^{XS}}{RT} + (1 - X_2)\left(\frac{\partial \Delta G^{XS}}{\partial X_2}\right)\frac{1}{RT} \\ & - X_3\left(\frac{\partial \Delta G^{XS}}{\partial X_3}\right)\frac{1}{RT}\end{aligned} \qquad [5]$$

$$\begin{aligned}\ln \gamma_3 = {} & \frac{\Delta G^{XS}}{RT} - X_2\left(\frac{\partial \Delta G^{XS}}{\partial X_2}\right)\frac{1}{RT} \\ & + (1 - X_3)\left(\frac{\partial \Delta G^{XS}}{\partial X_3}\right)\frac{1}{RT}\end{aligned} \qquad [6]$$

for the dilute solution restriction $X_1 \rightarrow 1.0$ which is used at each stage of differentiation for correlating the derivatives of Eq. [1] to the corresponding interaction parameters. With the restriction of $X_2 \rightarrow 1.0$, the following equations are used in converting the derivatives of Eq. [2]:

$$\begin{aligned}\ln \gamma_1 = {} & \frac{\Delta G^{XS}}{RT} + (1 - X_1)\left(\frac{\partial \Delta G^{XS}}{\partial X_1}\right)\frac{1}{RT} \\ & - X_3\left(\frac{\partial \Delta G^{XS}}{\partial X_3}\right)\frac{1}{RT}\end{aligned} \qquad [7]$$

$$\begin{aligned}\ln \gamma_2 &= \frac{\Delta G^{XS}}{RT} - X_1\left(\frac{\partial \Delta G^{XS}}{\partial X_1}\right)\frac{1}{RT} \\ &\quad - X_3\left(\frac{\partial \Delta G^{XS}}{\partial X_3}\right)\frac{1}{RT} \qquad [8]\end{aligned}$$

$$\begin{aligned}\ln \gamma_3 &= \frac{\Delta G^{XS}}{RT} - X_1\left(\frac{\partial \Delta G^{XS}}{\partial X_1}\right)\frac{1}{RT} \\ &\quad + (1 - X_3)\left(\frac{\partial \Delta G^{XS}}{\partial X_3}\right)\frac{1}{RT} \qquad [9]\end{aligned}$$

Application of restriction $X_3 \rightarrow 1.0$ at each stage of differentiation of the following equations:

$$\begin{aligned}\ln \gamma_1 &= \frac{\Delta G^{XS}}{RT} + (1 - X_1)\left(\frac{\partial \Delta G^{XS}}{\partial X_1}\right)\frac{1}{RT} \\ &\quad - X_2\left(\frac{\partial \Delta G^{XS}}{\partial X_2}\right)\frac{1}{RT} \qquad [10]\end{aligned}$$

$$\begin{aligned}\ln \gamma_2 &= \frac{\Delta G^{XS}}{RT} - X_1\left(\frac{\partial \Delta G^{XS}}{\partial X_1}\right)\frac{1}{RT} \\ &\quad + (1 - X_2)\left(\frac{\partial \Delta G^{XS}}{\partial X_2}\right)\frac{1}{RT} \qquad [11]\end{aligned}$$

$$\begin{aligned}\ln \gamma_3 &= \frac{\Delta G^{XS}}{RT} - X_1\left(\frac{\partial \Delta G^{XS}}{\partial X_1}\right)\frac{1}{RT} \\ &\quad - X_2\left(\frac{\partial \Delta G^{XS}}{\partial X_2}\right)\frac{1}{RT} \qquad [12]\end{aligned}$$

leads to necessary correlations between the derivatives of the Maclaurin series, as represented by Eq. [3], to the corresponding interaction parameters of the ternary system.

From the above treatment of conversion of the derivatives, it is clear that each of the two initial series involved in Eqs. [1] through [3] belongs exclusively to those of the constituent binaries and the rest are specific ternary interaction parameters. In this treatment, it is interesting to note that the properties of a binary system may be regarded as a summation of binary contributions and, specifically, the ternary ones.

The following boundary conditions are imposed on Eq. [1]:

as $X_2 \rightarrow 1.0, \qquad \Delta G^{XS} \rightarrow 0$

$$\sum_{r=1}^{\infty} \frac{1}{r!}\left(\frac{\partial^r \Delta G^{XS}}{\partial X_2^r}\right)_{X_1 \rightarrow 1.0} = 0$$

and as $X_3 \rightarrow 1.0, \qquad \Delta G^{XS} \rightarrow 0$

$$\sum_{r=1}^{\infty} \frac{1}{r!}\left(\frac{\partial^r \Delta G^{XS}}{\partial X_3^r}\right)_{X_1 \rightarrow 1.0} = 0$$

Using these relations and converting the derivatives to the corresponding interaction parameters, Eq. [1] reduces to

$$\begin{aligned}\frac{\Delta G^{XS}}{RT} &= X_2(1 - X_2)\left\{\ln \gamma^0_{2(1)} + X_2\left[\ln \gamma^0_{2(1)} + \frac{1}{2}\varepsilon^2_{2(1)}\right]\right. \\ &\qquad + X_2^2\left[\ln \gamma^0_{2(1)} + \frac{2}{3}\varepsilon^2_{2(1)}\right. \\ &\qquad \left.\left. + \frac{1}{3}\rho_2^2(1)\right] + \ldots\right\} \\ &\quad + X_3(1 - X_3)\left\{\ln \gamma^0_{3(1)} + X_3\left[\ln \gamma^0_{3(1)} + \frac{1}{2}\varepsilon_2^2(1)\right]\right. \\ &\qquad + X_3^2\left[\ln \gamma^0_{3(1)} + \frac{2}{3}\varepsilon^3_{3(1)}\right. \\ &\qquad \left.\left. + \frac{1}{3}\rho^3_{3(1)}\right] + \ldots\right\} \\ &\quad + X_2X_3\{\varepsilon^3_{2(1)} + \ldots\} \qquad [13]\end{aligned}$$

Similarly, on imposing conditions $X_1 \rightarrow 1.0$ and $X_3 \rightarrow 1.0$, the following equations are obtained as

$$\sum_{r=1}^{\infty} \frac{1}{r!}\left(\frac{\partial^r \Delta G^{XS}}{\partial X_1^r}\right)_{X_2 \rightarrow 1.0} = 0$$

and

$$\sum_{r=1}^{\infty} \frac{1}{r!}\left(\frac{\partial^r \Delta G^{XS}}{\partial X_3^r}\right)_{X_2 \rightarrow 1.0} = 0$$

Using these relations, Eq. [2] may be represented as

$$\begin{aligned}\frac{\Delta G^{XS}}{RT} &= X_1(1 - X_1)\left\{\ln \gamma^{\circ}_{1(2)} + X_1\left[\ln \gamma^{\circ}_{1(2)} + \frac{1}{2}\varepsilon^1_{1(2)}\right]\right. \\ &\qquad + X_1^2\left[\ln \gamma^{\circ}_{1(2)} + \frac{2}{3}\varepsilon^1_{1(2)}\right. \\ &\qquad \left.\left. + \frac{1}{3}\rho_1^1(2)\right] + \ldots\right\} \\ &\quad + X_3(1 - X_3)\left\{\ln \gamma^{\circ}_{3(2)} + X_3\left[\ln \gamma^{\circ}_{3(2)} + \frac{1}{2}\varepsilon^3_{3(2)}\right]\right. \\ &\qquad + X_3^2\left[\ln \gamma^{\circ}_{3(2)} + \frac{2}{3}\varepsilon_3^3(2)\right. \\ &\qquad \left.\left. + \frac{1}{3}\rho_3^3(2)\right] + \ldots\right\} \\ &\quad + X_1X_3\{\varepsilon_3^1(2) + \ldots\} \qquad [14]\end{aligned}$$

Equation [3] may similarly be transformed through the use of equations

$$\sum_{r=1}^{\infty} \frac{1}{r!}\left(\frac{\partial^r \Delta G^{XS}}{\partial X_1^r}\right)_{X_3 \rightarrow 1.0} = 0$$

and

$$\sum_{r=1}^{\infty}\frac{1}{r!}\left(\frac{\partial^r \Delta G^{XS}}{\partial X_2^r}\right)_{X_3\to 1.0} = 0$$

for conditions $X_1 \to 1.0$ and $X_2 \to 1.0$, respectively. Equation [3] may be written by use of the above equations as

$$\begin{aligned}\frac{\Delta G^{XS}}{RT} = {} & X_1(1-X_1)\Bigg\{\ln\gamma^0_{1(3)} + X_1\Bigg[\ln\gamma^0_{1(3)} + \frac{1}{2}\varepsilon^1_{1(3)}\Bigg] \\ & + X_1^2\Bigg[\ln\gamma^0_{1(3)} + \frac{2}{3}\varepsilon^1_{1(3)} \\ & + \frac{1}{3}\rho^1_1(3)\Bigg] + \ldots\Bigg\} \\ & + X_2(1-X_2)\Bigg\{\ln\gamma^0_{2(3)} + X_2\Bigg[\ln\gamma^0_{2(3)} + \frac{1}{2}\varepsilon^2_{2(3)}\Bigg] \\ & + X_2^2\Bigg[\ln\gamma^0_{2(3)} + \frac{2}{3}\varepsilon^2_{2(3)} \\ & + \frac{1}{3}\rho^2_2(3)\Bigg] + \ldots\Bigg\} \\ & + X_1X_2\{\varepsilon^1_2(3) + \ldots\}\end{aligned} \quad [15]$$

Since two of the initial series in Eqs. [13] through [15] belong to those of the constituent binaries, as already mentioned, the following approximations are used in respect of them as

For 1-2 binary, $X_1(1 - X_1) = X_2(1 - X_2) = X_1X_2$
For 1-3 binary, $X_1(1 - X_1) = X_3(1 - X_3) = X_1X_3$
For 2-3 binary, $X_3(1 - X_2) = X_3(1 - X_3) = X_2X_3$

The summation of Eqs. [13] through [15] yields integral excess free energy of mixing of the ternary system as

$$\begin{aligned}\frac{\Delta G^{XS}(\text{ternary})}{RT} = {} & X_1X_2\Bigg\{\ln\gamma^0_{2(1)} + X_2\Bigg(\ln\gamma^0_{2(1)} + \frac{1}{2}\varepsilon^2_{2(1)}\Bigg) \\ & + X_2^2\Bigg(\ln\gamma^0_{(1)} + \frac{2}{3}\varepsilon^2_2(1) \\ & + \frac{1}{3}\rho^2_2(1)\Bigg) + \ldots \\ & + \ln\gamma^0_{1(2)} + X_1\Bigg(\ln\gamma^0_{1(2)} \\ & + \frac{1}{2}\varepsilon^1_1(2)\Bigg) \\ & + X_1^2\Bigg(\ln\gamma^0_{1(2)} + \frac{2}{3}\varepsilon^1_1(2) \\ & + \frac{1}{3}\rho^1_1(2)\Bigg) + \ldots\Bigg\} \\ & + X_1X_3\Bigg\{\ln\gamma^0_{3(1)} + X_3\Bigg(\ln\gamma^0_{3(1)} \\ & + \frac{1}{2}\varepsilon^3_3(1)\Bigg) \\ & + X_3^2\Bigg(\ln\gamma^0_{3(1)} + \frac{2}{3}\varepsilon^3_3(1) \\ & + \frac{1}{3}\rho^3_3(1)\Bigg) + \ldots \\ & + \ln\gamma^0_{1(3)} + X_1\Bigg(\ln\gamma^0_{1(3)} \\ & + \frac{1}{2}\varepsilon^1_1(2)\Bigg) \\ & \cdot X_1^2\Bigg(\ln\gamma^0_{1(3)} + \frac{2}{3}\varepsilon^1_1(3) \\ & + \frac{1}{3}\rho^1_1(3)\Bigg) + \ldots\Bigg\} \\ & + X_2X_3\Bigg\{\ln\gamma^0_{2(3)} + X_2\Bigg(\ln\gamma^0_{2(3)} \\ & + \frac{1}{2}\varepsilon^2_2(3)\Bigg) \\ & + X_2^2\Bigg(\ln\gamma^0_{2(3)} + \frac{2}{3}\varepsilon^2_2(3) \\ & + \frac{1}{3}\rho^2_2(3)\Bigg) + \ldots \\ & + \ln\gamma^0_{3(2)} + X_3\Bigg(\ln\gamma^0_{3(2)} \\ & + \frac{1}{2}\varepsilon^3_3(2)\Bigg) \\ & + X_3^2\Bigg(\ln\gamma^0_3(2) + \frac{2}{3}\varepsilon^3_3(2) \\ & + \frac{1}{3}\rho^3_3(2)\Bigg) + \ldots\Bigg\} \\ & + X_2X_3(\varepsilon^3_{2(1)} + \ldots) \\ & + X_1X_2(\varepsilon^2_1(3) + \ldots) \\ & + X_1X_3(\varepsilon^3_{1(2)} + \ldots)\end{aligned} \quad [16]$$

The binary contributions involved in Eq. [16] satisfy the following boundary conditions:

(a) ΔG^{XS} (ternary) → ΔG^{XS} 1-2 binary as $X_3 \to 0$
(b) ΔG^{XS} (ternary) → ΔG^{XS} 1-3 binary as $X_2 \to 0$
(c) ΔG^{XS} (ternary) → ΔG^{XS} 2-3 binary as $X_1 \to 0$

However, the specific ternary interaction terms should tend toward zero for each of the above boundary conditions. They are bound by the following necessary condition which is expressed as

$$\begin{aligned}\frac{\Delta G^{XS}\,(\text{ternary}) - \Delta G^{XS}\,(\text{binaries})}{X_1X_2X_3}&\\ = \varepsilon_2^3 X_1 + \varepsilon_2^1 X_3 + \varepsilon_1^3 X_2 &\qquad [17]\end{aligned}$$

This, however, involves truncation of the higher order terms of the series depicted in Eq. [16] with respect to the specific interaction effect of the ternary system. Necessary adjustments with respect to them by use of equations based on differentiation of the excess integral function of the ternary system will be discussed in the subsequent sections.

Assessment of the Binary Function

It should be noted that the binary functions, as expressed in Eq. [16], consist of infinite terms of the original Maclaurin series. In this section, truncation of these series is discussed by application of relevant boundary conditions. As an example, the form of function of the binary 1-2 system is considered in this section. This may be represented from Eq. [16] as

$$\begin{aligned}\frac{\Delta G^{XS}\,(1\text{-}2)}{\mathrm{R}T} = X_1X_2\Big\{&\ln \gamma^0_{2(1)} + X_2\left(\ln \gamma^0_{2(1)} + \frac{1}{2}\,\varepsilon^2_2(1)\right)\\ &+ X_2^2\left(\ln \gamma^0_{2(1)} + \frac{2}{3}\,\varepsilon^2_{2(1)} + \frac{1}{3}\,\rho^2_2(1)\right)\\ &+ \ldots + \ln \gamma^0_{1(2)}\\ &+ X_1\left(\ln \gamma^0_{1(2)} + \frac{1}{2}\,\varepsilon^1_1(2)\right)\\ &+ X_1^2\Big(\ln \gamma^0_{1(2)} + \frac{2}{3}\,\varepsilon^1_1(2)\\ &+ \frac{1}{3}\,\rho^1_1(2)\Big) + \ldots\Big\}\end{aligned}\qquad [18]$$

For the binary system,

$$\text{as } X_2 \rightarrow 0 \quad \text{and } X_1 \rightarrow 1.0, \qquad \frac{\Delta G^{XS}\,(1\text{-}2)}{X_1X_2} \rightarrow \ln \gamma^0_2(1)$$

Imposing the condition on Eq. [18], one obtains

$$\begin{aligned}\ln \gamma^0_{2(1)} = \ln \gamma^0_{2(1)} + \ln \gamma^0_{1(2)} &+ \left(\ln \gamma^0_{1(2)} + \frac{1}{2}\,\varepsilon^1_1(2)\right)\\ &+ \left(\ln \gamma^0_{1(2)} + \frac{2}{3}\,\varepsilon^1_1(2) + \frac{1}{3}\,\rho^1_1(2)\right) + \ldots\end{aligned}$$

i.e.,

$$\begin{aligned}\ln \gamma^0_{1(2)} = &- \left(\ln \gamma^0_{1(2)} + \frac{1}{2}\,\varepsilon^1_1(2)\right)\\ &- \left(\ln \gamma^0_{1(2)} + \frac{2}{3}\,\varepsilon^1_1(2) + \frac{1}{3}\,\rho^1_1(2)\right)\end{aligned}$$

Similarly, by imposing the condition

$$\frac{\Delta G^{XS}\,(1\text{-}2)}{X_1X_2} \rightarrow \ln \gamma^0_{1(2)} \quad \text{as } X_1 \rightarrow 0 \quad \text{and } X_2 \rightarrow 1.0$$

one obtains the following series which is expressed as

$$\begin{aligned}\ln \gamma^0_{2(1)} = &- \left(\ln \gamma^0_{2(1)} + \frac{1}{2}\,\varepsilon^2_2(1)\right)\\ &- \left(\ln \gamma^0_{2(1)} + \frac{2}{3}\,\varepsilon^2_2(1) + \frac{1}{3}\,\rho^2_2(1)\right) - \ldots\end{aligned}$$

Substituting the above equations in Eq. [18], one obtains the following form of function, neglecting higher order terms as

$$\begin{aligned}\frac{\Delta G^{XS}\ 1\text{-}2}{\mathrm{R}T} = X_1X_2\Big\{&\ln \gamma^0_{2(1)} + X_2(\ln \gamma^0_{1(2)} - \ln \gamma^0_{2(1)})\\ &+ X_2(1 - X_2)\Big[2 \ln \gamma^0_{2(1)} + \frac{1}{2}\,\varepsilon^2_2(1)\\ &+ 4 \ln \gamma^0_1(2) + \varepsilon^1_1(2) + X_2\Big(2 \ln \gamma^0_{2(1)}\\ &- 2 \ln \gamma^0_{1(2)} + \frac{1}{2}\,\varepsilon^2_2(1) - \frac{1}{2}\,\varepsilon^1_1(2)\Big)\Big]\Big\}\end{aligned}\qquad [19]$$

Since truncation of higher order terms is unavoidable, it is necessary to adjust Eq. [19] by the following conditions while retaining the above functional form

$$\left(\frac{d\Delta G^{XS}}{dX_1}\right)_{X_2\rightarrow 1.0} \frac{1}{\mathrm{R}T} = \ln \gamma^0_{1(2)}$$

$$\left(\frac{d\Delta G^{XS}}{dX_2}\right)_{X_1\rightarrow 1.0} \frac{1}{\mathrm{R}T} = \ln \gamma^0_{2(1)}$$

$$\left(\frac{d^2\Delta G^{XS}}{dX_1^2}\right)_{X_2\rightarrow 1.0} \frac{1}{\mathrm{R}T} = \varepsilon^1_1(2)$$

$$\left(\frac{d^2\Delta G^{XS}}{dX_2^2}\right)_{X_1\rightarrow 1.0} = \varepsilon^2_2(1)$$

By use of the above sets of equations, Eq. [19] transforms to

$$\begin{aligned}\frac{\Delta G^{XS}\,(1\text{-}2)}{\mathrm{R}T} = X_1X_2\Big\{&X_1 \ln \gamma^0_{2(1)} + X_2 \ln \gamma^0_{1(2)}\\ &+ X_2(1 - X_2)\\ &\cdot\Big[X_1\Big(\frac{1}{2}\,\varepsilon^2_2(1) - \ln \gamma^0_{1(2)}\\ &+ 2 \ln \gamma^0_{2(1)}\Big)\\ &+ X_2\Big(\frac{1}{2}\,\varepsilon^1_1(2) + 2 \ln \gamma^0_{1(2)}\\ &- \ln \gamma^0_{2(1)}\Big)\Big]\Big\}\end{aligned}\qquad [20]$$

Applicability of the equation in interpreting thermodynamic properties of various binary systems is described elsewhere.[14] Adopting an exactly similar form of binary function for the 2-3 and 1-3 binaries from Eqs. [16], [17], and [20], ΔG^{XS} of the ternary system may be expressed as

$$\begin{aligned}
\frac{\Delta G^{XS}}{\mathrm{R}T} = {} & X_1X_2\Bigg[X_1 \ln \gamma^0_{2(1)} + X_2 \ln \gamma^0_{1(2)} \\
& + X_1X_2\Bigg\{X_1\Bigg(\frac{1}{2}\,\varepsilon^2_2(1) - \ln \gamma^0_{1(2)} \\
& + 2 \ln \gamma^0_{2(1)}\Bigg) \\
& + X_2\Bigg(\frac{1}{2}\,\varepsilon^1_1(2) + 2 \ln \gamma^0_{1(2)} \\
& - \ln \gamma^0_{2(1)}\Bigg)\Bigg\}\Bigg] \\
& + X_1X_3\Bigg[X_1 \ln \gamma^0_{3(1)} + X_3 \ln \gamma^0_{1(3)} \\
& + X_1X_3\Bigg\{X_1\Bigg(\frac{1}{2}\,\varepsilon^3_3(1) - \ln \gamma^0_{1(3)} \\
& + 2 \ln \gamma^0_{3(2)}\Bigg) \\
& + X_3\Bigg(\frac{1}{2}\,\varepsilon^1_1(3) + 2 \ln \gamma^0_{1(3)} \\
& - \ln \gamma^0_{3(1)}\Bigg)\Bigg\}\Bigg] \\
& + X_2X_3\Bigg[X_2 \ln \gamma^0_{3(2)} + X_3 \ln \gamma^0_{2(3)} \\
& + X_2X_3\Bigg\{X_2\Bigg(\frac{1}{2}\,\varepsilon^3_3(2) - \ln \gamma^0_{2(3)} \\
& + 2 \ln \gamma^0_{3(2)}\Bigg) \\
& + X_3\Bigg(\frac{1}{2}\,\varepsilon^2_{2(3)} + 2 \ln \gamma^0_{2(3)} \\
& - \ln \gamma^0_{3(2)}\Bigg)\Bigg\}\Bigg] \\
& + X_1X_2X_3(\varepsilon^3_{2(1)}X_1 + \varepsilon^2_1(3)X_3 + \varepsilon^3_1(2)X_2 + \ldots)
\end{aligned} \qquad [21]$$

Equation [21] satisfies the following boundary conditions:

ΔG^{XS} (ternary) → ΔG^{XS} 1,2 binary as $X_3 \rightarrow 0$
ΔG^{XS} (ternary) → ΔG^{XS} 1,3 binary as $X_2 \rightarrow 0$
ΔG^{XS} (ternary) → ΔG^{XS} 2,3 binary as $X_1 \rightarrow 0$

It should further be noted that for each of the above conditions, the ternary interaction terms tend toward zero. However, as implied earlier, application of Eq. [17] involves truncation of the series related to the specific ternary interaction terms in Eq. [16]. Necessary adjustments are now, therefore, required to make Eq. [21] thermodynamically consistent. Let the ternary function be redesignated by Eq. [22], retaining the assessed functional form as in Eq. [21] as

$$\begin{aligned}
\frac{\Delta G^{XS}}{\mathrm{R}T} = {} & X_1X_2\{a_1X_1 + a_2X_2 + X_1X_2(a_3X_1 + a_4X_2)\} \\
& + X_1X_3\{a_5X_1 + a_6X_3 + X_1X_3(a_7X_1 + a_8X_3)\} \\
& + X_2X_3\{a_9X_2 + a_{10}X_3 + X_2X_3(a_{11}X_2 + a_{12}X_3)\} \\
& + X_1X_2X_3\{a_{13}X_1 + a_{14}X_2 + a_{15}X_3\}
\end{aligned} \qquad [22]$$

Since a ternary isothermal integral function consists of two compositional variables, the partial differentiation of the excess integral property followed by the application of relevant dilute solution restrictions involves prior transformation of the equation into two variable functions. The following sets of equations may then be derived by differentiating the integral excess function of Eq. [22] repeatedly and by applying appropriate dilute solution restrictions at each stage of differentiation as

$$\left(\frac{\partial \Delta G^{XS}}{\partial X_2}\right)_{X_1\rightarrow 1.0} \frac{1}{\mathrm{R}T} = \ln \gamma^0_{2(1)} = a_1$$

$$\left(\frac{\partial^2 \Delta G^{XS}}{\partial X_2^2}\right)_{X_1\rightarrow 1.0} \frac{1}{\mathrm{R}T} = \varepsilon^2_2(1) = -4a_1 + 2a_2 + 2a_3$$

$$\left(\frac{\partial \Delta G^{XS}}{\partial X_3}\right)_{X_1\rightarrow 1.0} \frac{1}{\mathrm{R}T} = \ln \gamma^0_{3(1)} = a_5$$

$$\left(\frac{\partial^2 \Delta G^{XS}}{\partial X_3^2}\right) \frac{1}{\mathrm{R}T} = \varepsilon^3_3(1) = -4a_5 + 2a_6 + 2a_7$$

$$\left(\frac{\partial \Delta G^{XS}}{\partial X_1}\right)_{X_2\rightarrow 1.0} \frac{1}{\mathrm{R}T} = \ln \gamma^0_{1(2)} = a_2$$

$$\left(\frac{\partial^2 \Delta G^{XS}}{\partial X_1^2}\right)_{X_2\rightarrow 1.0} \frac{1}{\mathrm{R}T} = \varepsilon^1_1(2) = -4a_2 + 2a_1 + 2a_4$$

$$\left(\frac{\partial \Delta G^{XS}}{\partial X_3}\right)_{X_2\rightarrow 1.0} \frac{1}{\mathrm{R}T} = \ln \gamma^0_{3(2)} = a_9$$

$$\left(\frac{\partial^2 \Delta G^{XS}}{\partial X_3^2}\right)_{X_2\rightarrow 1.0} \frac{1}{\mathrm{R}T} = \varepsilon^3_3(2) = -4a_9 + 2a_{10} + 2a_{11}$$

$$\left(\frac{\partial \Delta G^{XS}}{\partial X_1}\right)_{X_3\rightarrow 1.0} \frac{1}{\mathrm{R}T} = \ln \gamma^0_{1(3)} = a_6$$

$$\left(\frac{\partial^2 \Delta G^{XS}}{\partial X_1^2}\right)_{X_3\rightarrow 1.0} \frac{1}{\mathrm{R}T}\, \varepsilon^1_1(3) = -4a_6 + 2a_5 + 2a_8$$

$$\left(\frac{\partial \Delta G^{XS}}{\partial X_2}\right)_{X_3\to 1.0}\frac{1}{\mathrm{R}T} = \ln \gamma^0_{2(3)} = a_{10}$$

$$\left(\frac{\partial^2 \Delta G^{XS}}{\partial X_2^2}\right)_{X_3\to 1.0}\frac{1}{\mathrm{R}T} = \varepsilon^2_2(3) = -4a_{10} + 2a_9 + 2a_{12}$$

$$\left(\frac{\partial^2 \Delta G^{XS}}{\partial X_2 \partial X_3}\right)_{X_1\to 1.0}\frac{1}{\mathrm{R}T} = \varepsilon^3_2(1) = -2a_1 - 2a_5 + a_{13}$$

$$\left(\frac{\partial^2 \Delta G^{XS}}{\partial X_3 \partial X_1}\right)_{X_2\to 1.0}\frac{1}{\mathrm{R}T} = \varepsilon^1_3(2) = -2a_2 - 2a_9 + a_{14}$$

$$\left(\frac{\partial^2 \Delta G^{XS}}{\partial X_1 \partial X_2}\right)_{X_3\to 1.0}\frac{1}{\mathrm{R}T} = \varepsilon^1_2(3) = -2a_6 - 2a_{10} - a_8 + a_{15}$$

The empirical constants a_1 through a_{15} may be expressed through the infinite dilution constants and interaction parameters. Solutions of the above equations yield the following relations:

$$a_1 = \ln \gamma^0_{2(1)}; \qquad a_2 = \ln \gamma^0_{1(2)}$$

$$a_3 = \frac{1}{2}\,\varepsilon^2_2(1) + 2 \ln \gamma^0_{2(1)} - \ln \gamma^0_{1(2)}$$

$$a_4 = \frac{1}{2}\,\varepsilon^1_1(2) + 2 \ln \gamma^0_{1(2)} - \ln \gamma^0_{2(1)}$$

$$a_5 = \ln \gamma^0_{3(1)}; \qquad a_6 = \ln \gamma^0_{1(3)}$$

$$a_7 = \frac{1}{2}\,\varepsilon^3_3(1) + 2 \ln \gamma^0_3(1) - \ln \gamma^0_{1(3)}$$

$$a_8 = \frac{1}{2}\,\varepsilon^1_1(3) + 2 \ln \gamma^0_{1(3)} - \ln \gamma^0_{3(1)}$$

$$a_9 = \ln \gamma^0_{3(2)}; \qquad a_{10} = \ln \gamma^0_{2(3)}$$

$$a_{11} = \frac{1}{2}\,\varepsilon^3_3(2) + 2 \ln \gamma^0_{3(2)} - \ln \gamma^0_{2(3)}$$

$$a_{12} = \frac{1}{2}\,\varepsilon^2_2(3) + 2 \ln \gamma^0_{2(3)} - \ln \gamma^0_{3(2)}$$

$$a_{13} = \varepsilon^3_{2(1)} + 2 \ln \gamma^0_{2(1)} + 2 \ln \gamma^0_{3(1)}$$

$$a_{14} = \varepsilon^1_3(2) + 2 \ln \gamma^0_{1(2)} + 2 \ln \gamma^0_{3(2)}$$

$$\begin{aligned} a_{15} = {} & \varepsilon^2_1(3) + 2 \ln \gamma^0_{1(3)} + 2 \ln \gamma^0_{2(3)} + \frac{1}{2}\,\varepsilon^1_1(3) \\ & + 2 \ln \gamma^0_{1(3)} - \ln \gamma^0_{3(1)} \end{aligned}$$

It should be noted that constants a_1 through a_{12} match exactly as expected to those of corresponding binary functions, as expressed in Eq. [21]. The constants pertaining to specific ternary interaction, however, differ due to the truncational effects, as mentioned earlier. It is to be noted that necessary adjustments as described are required to transform the normally acceptable analytical ternary function to one based on interaction parameters. Substituting the above relations into Eq. [22], the resulting ternary functions may then be expressed as

$$\begin{aligned} \frac{\Delta G^{XS}}{\mathrm{R}T} = {} & X_1X_2\biggl[X_1 \ln \gamma^0_{2(1)} + X_2 \ln \gamma^0_{1(2)} \\ & + X_1X_2\biggl\{X_1\biggl(\frac{1}{2}\,\varepsilon^2_2(1) - \ln \gamma^0_{1(2)} \\ & + 2 \ln \gamma^0_{2(1)}\biggr) \\ & + X_2\biggl(\frac{1}{2}\,\varepsilon^1_1(2) + 2 \ln \gamma^0_{1(2)} \\ & - \ln \gamma^0_{2(1)}\biggr)\biggr\}\biggr] \\ & + X_1X_3\biggl[X_1 \ln \gamma^0_{3(1)} + X_3 \ln \gamma^0_{1(3)} \\ & + X_1X_3\biggl\{X_1\biggl(\frac{1}{2}\,\varepsilon^3_3(1) - \ln \gamma^0_{1(3)} \\ & + 2 \ln \gamma^0_{3(1)}\biggr) \\ & + X_3\biggl(\frac{1}{2}\,\varepsilon^1_1(3) + 2 \ln \gamma^0_{1(3)} \\ & - \ln \gamma^0_{3(1)}\biggr)\biggr\}\biggr] \\ & + X_2X_3\biggl[X_2 \ln \gamma^0_{3(2)} + X_3 \ln \gamma^0_{2(3)} \\ & + X_2X_3\biggl\{X_2\biggl(\frac{1}{2}\,\varepsilon^3_{3(2)} - \ln \gamma^0_{2(3)} \\ & + 2 \ln \gamma^0_{3(2)}\biggr) \\ & + X_3\biggl(\frac{1}{2}\,\varepsilon^2_2(3) + 2 \ln \gamma^0_{2(3)} \\ & - \ln \gamma^0_{3(2)}\biggr)\biggr\}\biggr] \\ & + X_1X_2X_3\biggl\{X_1(\varepsilon^3_2(1) + 2 \ln \gamma^0_{2(1)} + 2 \ln \gamma^0_{3(1)}) \\ & + X_2(\varepsilon^1_3(2) + 2 \ln \gamma^0_{1(2)} + 2 \ln \gamma^0_{3(2)}) \\ & + X_3\biggl(\varepsilon^2_1(3) + 2 \ln \gamma^0_1(3) \\ & + 2 \ln \gamma^0_{2(3)} + \frac{1}{2}\,\varepsilon^1_1(3) + 2 \ln \gamma^0_{1(3)} \\ & - \ln \gamma^0_{3(1)}\biggr)\biggr\} \end{aligned} \qquad [23]$$

The constants pertaining to the specific interaction effect are seen to differ as a result of the truncational effect, as described earlier. These adjustments are required to make the function, Eq. [23], thermodynamically consistent. Thermodynamic consistency of a ternary function is determined by any two of its partials,[2] such as,

$$-X_2 \frac{\partial \ln \gamma_2}{\partial X_2} + (1 - X_3) \frac{\partial \ln \gamma_2}{\partial X_3} = -X_3 \frac{\partial \ln \gamma_3}{\partial X_3} + (1 - X_2) \frac{\partial \ln \gamma_3}{\partial X_2} \quad [24]$$

It may be shown that the partials of the integral function represented by Eq. [23], which may be deduced through Eqs. [7] and [8], for example, will automatically satisfy consistency (Eq. [24]).

III. APPLICABILITY OF EQUATION [23]

Although all of the necessary binary parameters may be evaluated by regressional analysis of the respective experimental excess property using Eq. [20], it is normally difficult to obtain the specific interaction parameters in the neighborhood of each of the pure components for various systems. Equation [23] has been used to interpret thermodynamic properties of the Fe-Cr-Ni system at 1873 K. Gilby and St. Pierre[15] have measured thermodynamic properties of the system using Knudsen effusion mass spectrometry and analysis of the condensed vapor phase. The infinite dilution constants and first-order interaction parameters for the Ni-Cr and Fe-Cr

Table I. Evaluation of Binary Parameters

The Ni-Fe System, 1873 K

	Regressional Values Based on Eq. [20]	Hultgren *et al.*[16]
$\ln \gamma_{Fe}^{0}$ (Ni)	−1.0212	−1.0356
$\ln \gamma_{Ni}^{0}$ (Fe)	−0.4988	−0.4828
ε_{Ni}^{Ni} (Fe)	+1.92	—
ε_{Fe}^{Fe} (Ni)	+1.85	—

Comparison between integral excess values computed by Eq. [20] and those of the experimental data[16]

X_{Ni}		0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$-\Delta G^{XS}$	J · mol	668.27	1238.18	1797.13	2335.97	2778.9	3013.3	2919.75	2401.65	1415.38
$-\Delta G^{XS}$, Ref. 15	J · mol	665.5	1246.8	1803.5	2326.3	2765.6	3016.6	2928.8	2401.6	1414.19

The Ni-Cr system, 1873 K

	Regressional Values Based on Eq. [20]	Gilby and St. Pierre[15]
$\ln \gamma_{Cr}^{0}$ (Ni)	− 1.0424	−0.77
ln Ni (Cr)	− 2.4809	—
ε_{Cr}^{Cr} (Ni)	1.61	1.85
ε_{Ni}^{Ni} (Cr)	21.60	—

Comparison between integral excess values computed by Eq. [20] and those of the experimental data[15]

X_{Cr}		0.01	0.03	0.05	0.1	0.2	0.3	0.4	0.5
$-\Delta G_{calc}^{XS}$	$J \cdot mol^{-1}$	160.99	473.38	769.98	1424.26	2286.45	2577.21	2499.48	2339.90
$-\Delta G_{exptl}^{XS}$, Ref. 14	$J \cdot mol^{-1}$	161.65	482.95	748.47	1412.26	2337.32	2560.05	2477.83	2351.15

The Fe-Cr system, 1873 K

	Regressional Values
$\ln \gamma_{Cr}^{0}$ (Fe)	−0.1384
$\ln \gamma_{Fe}^{0}$ (Cr)	−0.4281
ε_{Fe}^{Fe} (Cr)	1.277
ε_{Cr}^{Cr} (Fe)	−0.2742

Comparison between computed values and the Hultgren data[16]

X_{Fe}		0.4	0.5	0.6	0.7	0.8	0.9
$-\Delta G_{calc}^{XS}$	$J \cdot mol^{-1}$	1204.57	1134.57	971.31	746.50	491.11	234.0
$-\Delta G^{XS}$, Ref. 16	$J \cdot mol^{-1}$	1204.99	1133.86	970.69	748.93	489.52	234.30

Table II. Comparison between the Computed Integral Excess Values of the Fe-Cr-Ni System at 1873 K and the Experimental Data[15]

$X_1 = \text{Ni}$	$X_2 = X_{\text{Fe}}$	$X_3 = X_{\text{Cr}}$	$-\Delta G^{XS}_{\text{calc}}$ by Eq. [23] J · mol^{-1}	$-\Delta G^{XS}_{\text{exptl}}$, Ref. 15 J · mol^{-1}
0.293	0.657	0.050	1962.16	1963.13
0.490	0.460	0.050	2943.24	2733.05
0.688	0.262	0.050	3070.62	2696.79
0.794	0.156	0.050	2509.76	2075.78
0.851	0.099	0.050	1993.30	1760.04
0.897	0.053	0.050	1477.23	1336.20
0.182	0.718	0.100	1432.69	1130.93
0.293	0.607	0.100	2127.23	1900.57
0.485	0.415	0.100	3097.10	3084.06
0.692	0.208	0.100	3136.19	3144.86
0.743	0.157	0.100	2891.54	2745.79
0.795	0.105	0.100	2523.55	2436.40
0.847	0.053	0.100	2035.04	2112.37

systems are determined by regressional analysis of the excess integral values, as reported by Hultgren *et al.*,[16] and those for the Ni-Cr system are evaluated with respect to the experimental data of Gilby and St. Pierre.[15] Table I lists these evaluated parameters along with the data available in the literature.[15,16] The table also lists the computed and experimental values of the integral excess properties of the binary systems for the purpose of comparison. In this calculation, $\varepsilon^{\text{Fe}}_{\text{Cr}}(\text{Ni})$ and $\varepsilon^{\text{Ni}}_{\text{Cr}}(\text{Fe})$ are, respectively, taken to be 2.19 and 0, as indicated by the authors.[15] In the absence of any other data for $\varepsilon^{\text{Ni}}_{\text{Fe}}(\text{Cr})$, it has been assumed to be zero for the purpose of the present ternary calculation. Table II lists the computed values of the integral excess properties of the Fe-Cr-Ni system at 1873 K using Eq. [23] along with the experimental values.[15] Table I shows that an excellent agreement exists between these two sets of values.

IV. CONCLUSIONS

A ternary function has been deduced based on the Maclaurin infinite series which is expanded in the neighborhood of each of the pure components of the system. These series are subjected to appropriate boundary conditions, as described in this article. The truncation of the infinite series pertaining to the constituent binaries and that of the specific interaction terms are controlled by repeated differentiation of the excess function with the application of relevant dilute solution restrictions at each stage of differentiation. The function is thermodynamically consistent and capable of interpreting thermodynamic properties of the Fe-Cr-Ni system at 1873 K.

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