Thermodynamics of Oxygen and Sulfur in Ternary Liquid Alloys

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ABSTRACT

The Margules equation is used in interpreting the excess Gibbs energies of several ternary systems. In the present study the activity coefficient of a dilute solute, 2, in a binary solvent 1-3 is interpreted using the Margules equation for a ternary system. The formalism is based on Gibbs energy interaction parameters which is deduced from the integral function of a ternary system. The derived expression is used to interpret logarithmic activity coefficient of oxygen in seven metallic systems and of sulfur in three metallic systems. The present study calculations of logarithmic activity coefficient of solute are compared with the available experimental data. Self interaction parameters of the solutes are derived from the partial functions of solutes along the constant compositional path. A thermodynamic formalism based on Maclaurin infinite series is used in interpreting excess Gibbs energy of a ternary system. An expression for logarithmic activity coefficient and self-interaction parameter of oxygen were derived using Maclaurin infinite series equations using same conditions as mentioned for the Margules equations. The derived equations are based on Maclaurin infinite series used successfully to deduce the thermodynamics of self-interaction of oxygen as a interstitial atom in two metallic systems. The predicted thermodynamic parameter values using Maclaurin infinite series and Margules equations, were found to be in excellent agreement with the available experimental data and also our predictions are far more accurate than the predictions made by other models.

INTRODUCTION

In most of the pyrometallurgical high temperature processes, interactions of solutes such as oxygen, nitrogen, and sulfur, with the solvent atoms are very important during refining processes. Numerous theories have been developed, mainly using statistical or quasichemical equations /1-25/ to interpret the thermodynamics of solutes in multicomponent alloy systems. Wagner /4/ developed one energy parameter ideal solvent model based on the activity coefficient of solutes compositional dependence. He used one energy interaction term which was not able to account for interaction energy parameters for the same solute concentration at different solvent compositions and also it was ineffective in predicting the interaction parameters of solutes in strongly interacting systems. Several researchers /10-16/, tried to extend this formalism to strongly interacting systems. Wagner's one energy parameter has been modified to two energy parameter terms by Chiang and Chang /10/ to better fit the experimental data. Using quasichemical equations,

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Jacob and Alcock /3/ proposed a model to predict the activity coefficient of solute in ternary systems. They were not able to predict activity coefficients accurately because they did not use first order Gibbs energy interaction parameters in their formalism. Coordinate cluster theories were developed based on general statistical mechanical theories by Blander *et al.* /13,14/, to evaluate activity coefficients of dilute solutes in multicomponent systems. The theory could accommodate the earlier proposed theories /1-4,7,21-26/, but it could not calculate the self-interaction between the solutes.

Holcomb and St. Pierre /17/ proposed one parameter exponential form of expression for log *f(solute)*, to predict the thermodynamic nature of solute in one solvent system. However, it could not predict the same in the case of one solute and two solvents system, since the formalism does not consider the first order interaction parameter of the second solvent. In this study, we have developed a formalism for predicting the activity coefficient and self-interaction parameters of a solute in a ternary system, using Margules equations and Maclaurin infinite series. Using both the models, activity coefficients of oxygen and sulfur in several ternary systems and self-interaction parameter of oxygen in two ternary systems are calculated. Table 1 gives a clear picture of the advantages and limitations of both the models for all oxygen and sulfur systems. In addition, the thermodynamic nature of the solutes and solvents in solvent rich ternary and quaternary systems using both models is presented in Table 1.

Chang *et al.* /22/ and Gokcen *et al.* /23-27/ used cubic Margules equations for calculating the excess molar Gibbs energy, G^E, which is the basis for deriving logarithmic activity coefficient of solute in a ternary system. In the present study, we considered fourth-order

Table 1
Comparison between Margules and Maclaurin Thermodynamic Models

	Margules equations	Maclaurin equations
Order of Equation	4	5
No. of Parameters in:		
(i) Excess Gibbs energy equation	12	15
(ii) Activity Coefficient equation	5	7
(iii) Self-Interaction equation	5	13
Prediction of Activity Coefficients in	Oxide and Sulfide Systems	
Pb-O-Cu	Excellent	Excellent
Pb-O-Bi	Excellent	Good
Cu-O-Ag	Poor	Good
Fe-O-Cu	Poor	Good
Ag-O-Sn	Good	Good
Pb-O-Sn	Good	Good
Ag-O-Pb	Good	Excellent
Ag-S-Sn	Excellent	Excellent
Ag-S-Pb	Good	Good
Cu-S-Ag	Excellent	Excellent
Self-Interaction Parameter		
Cu-O-Pb	Excellent	Excellent
Pb-O-Bi	Excellent	Good

Excellent: <5% deviation; Good: 5% to 10 %deviation; Poor: >15 % deviation w.r.t. experimental Values

Margules equations for the prediction of the excess molar Gibbs energy, G^E, logarithmic activity coefficient of solute and self-interaction parameter of solute in several melts. In the present study, using the Maclaurin infinite series model, component 2 is taken as a solute in the ternary system. The model takes into account interactions between 1 and 2, 3 and 2, and solubilities of 2 in 1 and 3 and also phase equilibria between the binaries. The model predicts the thermodynamic properties of solute in ternary system and also predicts the primary interactions from the experimental data. Calculated thermodynamic properties using these primary interaction values are in excellent agreement with the experimental values.

FORMULATION OF MODEL USING MARGULES EQUATIONS

The fourth-order Margules equation is derived to represent excess Gibbs thermodynamic functions of ternary systems and is expressed as /28/:

$$\begin{aligned} G^E &= RTx_1x_2\left[\left(A_{21}x_1 + A_{12}x_2\right) + B_{12}x_1^2x_2^2\right. \\ &+ x_1x_3\left(A_{31}x_1 + A_{13}x_3\right) \\ &+ B_{13}x_1^2x_3^2 + x_2x_3\left(A_{32}x_2 + A_{23}x_3\right) + B_{23}x_2^2x_3^2 \\ &\left.+ x_1x_2x_3\left(A_{21} + A_{13} + A_{32} + C_1x_1 + C_2x_2 + C_3x_3\right)\right] \end{aligned} \tag{1}$$

where A_{21}, A_{12}, B_{12}, A_{31}, A_{31}, B_{13}, A_{32}, A_{23}, B_{23}, are binary parameters and C_1, C_2, C_3 are ternary parameters. The partial excess property of solute 2 in the ternary system is related to the integral function through the following relation:

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

Since ternary integral function consists of two compositional variables, the partial differentiation of equation (1) which gives $\frac{\partial G^E}{\partial x_2}$ and $\frac{\partial G^E}{\partial x_3}$ involves prior transformation of the above equation into a two variable function. The partial derivatives based on equation (2) are expressed as:

$$\begin{aligned} &\ln\gamma_2\,(alloy) \\ &= x_3^2\left[A_{23} + 2x_2\left(A_{32} - A_{23} + B_{23}\right) - 3B_{23}x_2^2\right] \\ &+ x_1^2\left[A_{21} + 2x_2\left(A_{12} - A_{21} + B_{12}\right) - 3B_{12}x_2^2\right] \\ &+ x_1x_3\left[A_{32} + A_{21} - A_{13} + 2x_2\left(A_{12} - A_{21}\right)\right. \\ &+ 2x_1\left(A_{13} - A_{31}\right) - 3B_{13}x_1x_3 + C_2x_2\left(2 - 3x_2\right) \\ &\left.+ C_3x_3\left(1 - 3x_2\right) + C_1x_1\left(1 - 3x_2\right)\right] \end{aligned} \tag{3}$$

The thermodynamic behavior of solute 2 in a 1-2-3 alloy is developed at $x_2 \rightarrow 0$, i.e solute concentration compared to solvent is very low. While substituting $x_2 = 0$ in equation (3) one gets

$$\begin{aligned} &\ln\gamma_2\,(alloy) \\ &= x_3^2A_{23} + x_1^2A_{21} + x_1x_3\left[A_{32} + A_{21} - A_{13}\right. \\ &\left.+ 2x_1\left(A_{13} - A_{31}\right) - 3B_{13}x_1x_3 + C_3x_3 + C_1x_1\right] \end{aligned} \tag{4}$$

Imposing boundary conditions in equation (4), the following coefficients are obtained:

when

$$x_1 \rightarrow 1.0,\quad \ln\gamma_2(alloy) \rightarrow \ln\gamma_2(1) \text{ and } A_{21} = \ln\gamma_2(1)$$

when

$$x_3 \rightarrow 1.0,\quad \ln\gamma_2(alloy) \rightarrow \ln\gamma_2(3)$$

and

$$A_{23} = \ln\gamma_2(3)$$

and

$$A_{32} + A_{21} - A_{13} + C_3 = P_{int}$$

$$2A_{13} - 2A_{31} + C_1 - C_3 = Q_{int}$$

$$-3B_{13} = R_{int}$$

where P_{int}, Q_{int} and R_{int} are Margules interaction coefficients. Substitution of the above coefficients in equation (4), and rearranging terms, the logarithmic activity coefficient of the solute can be written as:

$$\begin{aligned} &\ln\gamma_2 = \ln\gamma_2(1)\,x_1^2 + \gamma_2(3)\,x_3^2 + \\ &x_1x_3\left(P_{int} + Q_{int}x_1 + R_{int}x_1x_3\right) \end{aligned} \tag{5}$$

SELF-INTERACTION PARAMETERS USING MARGULES EQUATIONS

Self-Interaction Parameter is defined as

$$\varepsilon_2^2(alloy) = \left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{x_2 \to 0} \tag{6}$$

Imposing the boundary conditions /28/ for incorporating the constant compositional path for differentiation:

$$\left(\frac{\partial x_1}{\partial x_2}\right)_{0<x_1<1.0} = \frac{-x_1}{x_1 + x_3} \tag{7}$$

$$\left(\frac{\partial x_3}{\partial x_2}\right)_{0<x_3<1.0} = \frac{-x_3}{x_1 + x_3} \tag{8}$$

where $x_1 + x_3 = 1$ when $x_2 \to 0$, and the self-interaction parameter is given as:

$$\begin{aligned}
&\varepsilon_2^2(alloy) && (9)\\
&= 2x_1^2\left(A_{12} - 2A_{21} + B_{12}\right) + 2x_3^2\left(A_{32} - 2A_{23} + B_{23}\right)\\
&-2x_1x_3\Big[\left(A_{12} + 2A_{21} - A_{13} - A_{12} - C_2\right)\\
&+3x_1\left(A_{13} - A_{31} + C_1/2\right) - 6x_1x_3B_{13} + 1.5x_3C_3\Big]
\end{aligned}$$

and imposing boundary conditions as:

when

$x_1 \to 1.0, \qquad \varepsilon_2^2(alloy) \to \varepsilon_2^2(1)$

and

$x_3 \to 1.0, \qquad \varepsilon_2^2(alloy) \to \varepsilon_2^2(3)$

The coefficients are reduced as:

$$2\left(A_{12} - 2A_{21} + B_{12}\right) = \varepsilon_2^2(1)$$
$$2\left(A_{32} - 2A_{23} + B_{23}\right) = \varepsilon_2^2(3)$$

and

$$-2\left(A_{32} + 2A_{21} - A_{13} - A_{12} - C_2 + 1.5C_3\right) = P_{self},$$
$$-6\left(A_{13} - A_{31} + 0.5C_1 - 1.5C_3\right) = Q_{self}, \text{ and}$$
$$12B_{13} = R_{self},$$

where P_{self}, Q_{self} and R_{self} are Margules self-interaction parameters.

The self-interaction parameter of a solute may be written as:

$$\begin{aligned}
\varepsilon_2^2(alloy) &= x_1^2\varepsilon_2^2(1) + x_3^2\varepsilon_2^2(3)\\
&+x_1x_3\left(P_{self} + Q_{self}x_1 + R_{self}x_1x_3\right)
\end{aligned} \tag{10}$$

FORMULATION OF MODEL USING MACLAURIN INFINITE SERIES

Hajra and Mazumdar /28/ proposed a four parameter binary function based on Maclaurin infinite series, which adequately describes the excess integral values of various binary systems. The function is represented by

$$\frac{G^E}{RT} = x_1x_2\left\{a_1x_1 + a_2x_2 + x_1x_2\left(a_3x_1 + a_4x_2\right)\right\} \tag{11}$$

This equation describes the properties of the 1-3 binary system. Since a ternary system consists of 1-2, 1-3, and 2-3 binaries, the integral excess function (Hajra /29/) of the ternary system is expressed as:

$$\begin{aligned}
\frac{G^E}{RT} &= x_1x_2\left\{a_1x_1 + a_2x_2 + x_1x_2\left(a_3x_1 + a_4x_2\right)\right\}\\
&+x_1x_3\left\{a_5x_1 + a_6x_3 + x_1x_3\left(a_7x_1 + a_8x_3\right)\right\}\\
&+x_2x_3\left\{a_9x_2 + a_{10}x_3 + x_2x_3\left(a_{11}x_2 + a_{12}x_3\right)\right\}\\
&+x_1x_2x_3\left\{a_{13}x_1 + a_{14}x_2 + a_{15}x_3\right\}
\end{aligned} \tag{12}$$

where x_1, x_2 and x_3 represent mole fractions of 1, 2 and 3 respectively in the 1-2-3 system, a_1 to a_{12} are binary parameters and a_{13}, a_{14} and a_{15} are ternary parameters. Logarithmic activity coefficient of solute, 2, can be evaluated using partial function (2) and partial derivatives of G^E (equation (12)) with respect to x_2 and x_3 and substituted in equation (2) and rearranged as:

$$
\begin{aligned}
\ln \gamma_2 = {} & \\
& (1-x_2-x_3)\left[a_1(1-x_2-x_3)(1-2x_2)+2a_2x_2(1-x_2)\right. \\
& +x_2(1-x_2-x_3)\{2a_3(1-x_2-x_3)(1-2x_2) \\
& \left.+a_4x_2(3-4x_2)\}\right] \\
& -2x_3(1-x_2-x_3)\left[a_5(1-x_2-x_3)+a_6x_3\right. \\
& \left.+2x_3(1-x_2-x_3)\{(1-x_2-x_3)a_7+x_3a_8\}\right] \\
& +x_3\left[2x_3(1-x_2)a_9+x_3(1-2x_2)a_{10}\right. \\
& \left.+x_2x_3\{x_2(3-4x_2)a_{11}+2x_3(1-2x_2)a_{12}\}\right] \\
& +x_3(1-x_2-x_3)\{(1-x_2-x_3)(1-3x_2)a_{13} \\
& +x_{22}(2-3x_2)a_{14} \\
& +x_3(1-3x_2)a_{15}\}
\end{aligned}
\tag{13}
$$

Investigation into the nature of the ternary parameters are derived through the following equations

$$\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_2 \partial x_3}\right)_{x_1 \to 1.0} = \varepsilon_2^3(1) = -2a_1 - 2a_5 + a_{13}$$

$$\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_1 \partial x_3}\right)_{x_2 \to 1.0} = \varepsilon_1^3(2) = -2a_2 - 2a_9 + a_{14}$$

$$\frac{1}{RT}\left(\frac{\partial^2 G^E}{\partial x_1 \partial x_2}\right)_{x_3 \to 1.0} = \varepsilon_1^2(3) = -2a_6 - 2a_{10} + a_{15}$$

The thermodynamic behavior of solute 2 in 1-2-3 alloys is developed using an appropriate boundary condition:

$$
\begin{aligned}
(\ln \gamma_2)_{x_2 \to 0} = {} & \\
& a_1(1-x_3)^2 - -2x_3(1-x_3)\left[a_5(1-x_3)\right. \\
& \left.+a_6x_3+2x_3(1-x_3)\{(1-x_3)a_7+x_3a_8\}\right]+x_3^2a_{10} \\
& +x_3(1-x_3)^2a_{13}+x_3^2(1-x_3)a_{15}
\end{aligned}
\tag{14}
$$

The values of ternary parameters a_{13} and a_{15} are calculated through the following equations.

$$a_{13} = \varepsilon_2(1) + 2a_1 + 2a_5$$

$$a_{15} = \varepsilon_1^2(3) + 2a_6 + 2a_{10}$$

Parameters a_1 and a_{10} are given by

$$a_1 = \ln \gamma_2^0(1)$$

$$a_{10} = \ln \gamma_2^0(3)$$

The parameters a_5 to a_8 are calculated through the regressional analysis of Gibbs energy function of 1-3 system.

DERIVATION OF SELF-INTERACTION PARAMETER USING MACLAURIN INFINITE SERIES

The self-interaction parameter is defined in equation (6). While differentiating equation (13) along the constant compositional paths given by equations (7) and (8), the self-interaction parameter can be expressed as:

$$
\begin{aligned}
\varepsilon_2^2(alloy) = {} & \\
& -2a_1x_1(1+x_1)+2a_2x_1+2a_3x_1^3 \\
& +4x_1x_3\left[a_5x_1+a_6x_3+5x_1x_3\{a_7x_1+a_8x_3\}\right] \\
& +2a_9x_3-2a_{10}x_3(1+x_3)+2a_{12}x_3^3 \\
& -x_1x_3\left[5a_{13}x_1+2a_{14}+5a_{15}x_3\right]
\end{aligned}
\tag{15}
$$

As $x_1 \to 1.0$

$$\varepsilon_2^2(1) = -4a_1 + 2a_2 + 2a_3 \tag{16}$$

Similarly $x_3 \to 1.0$

$$\varepsilon_2^2(3) = 2a_9 - 4a_{10} + 2a_{12} \tag{17}$$

APPLICABILITY OF EQUATIONS AND PHYSICOCHEMICAL INTERPRETATION

In the present study, we have used Margules and Maclaurin infinite series models to predict the activity coefficient and self-interaction parameter of solute has been studied. The Margules equations are used to interpret the thermodynamic behavior of solutes in ternary system. Logarithmic activity coefficient of solute is derived using fourth-order Margules equation and partial functions. As the order of Margules equation increases, it improves accuracy of predicted thermodynamic properties. In the derived equation logarithmic activity coefficient of 2 (soulte) in 1 ($\ln\gamma_2^0(1)$) and 3($\ln\gamma_2^0(3)$) only considered and remaining parameters are evaluated based on experimental data. The resultant equation is able to predict logarithmic activity coefficient of 2 (soulte) in several ternary melts. The data of logarithmic activity coefficients and Margules coefficients for several systems are presented in Table 2.

The expression for the self-interaction parameter of solute is developed by differentiating solute partial functions with respect to solute concentrations and applying boundary conditions. Self-interaction parameters of 2 (solute) in 1 $\left(\varepsilon_1^1(2)\right)$ and in 3 $\left(\varepsilon_3^2(2)\right)$ are considered in the equation and other parameters are evaluated using experimental data. The resultant equation is able of interpreting self-interaction parameter of oxygen in several ternary melts. For calculations of self-interaction of oxygen in Pb-O-Bi /31/ and Pb-O-Cu /32/ systems, the binary oxygen self-interaction parameters $\left(\varepsilon_2^2(1)\right)$, $\left(\varepsilon_2^2(3)\right)$ and Margules coefficients are required. These Margules coefficients are calculated from the experimental data, which are given in Table 3.

In the 1-2-3 system, calculations using Maclaurin infinite series, the thermodynamics of binary 1-3 system have been calculated using four-parameter equation (11). Using binary thermodynamic parameters and also with ternary interactions of the system values, γ_2^0 values are predicted. No regressional analysis has been carried out with respect to experimental data for the systems in order to calculate activity coefficient of solutes. The values of the interaction parameters are given in Table 4. For binary systems 1-3 data has been

Table 2

Activity coefficients and Margules Coefficients of Oxygen in the Melts

Pb-O-Bi at 1173 K /31/	Pb-O-Cu at 1473 K /32/	
$\ln\gamma_O^o(Pb) = -6.14$	$\ln\gamma_O^o(Pb) = -3.69$	
$\ln\gamma_O^o(Bi) = -4.42$	$\ln\gamma_O^o(Cu) = -1.55$	
$P_{int} = -13.80$	$P_{int} = -9.930$	
$Q_{int} = 1.56$	$Q_{int} = -0.787$	
$R_{int} = 0.44$	$R_{int} = 3.902$	
x_1 = Pb	x_1 = Pb	
Pb-O-Sn at 1023 K /33/	Pb-O-Sn at 1223 K /33/	
$\ln\gamma_O^o(Sn) = -13.77$	$\ln\gamma_O^o(Sn) = -10.30$	
$\ln\gamma_O^o(Pb) = -8.4$	$\ln\gamma_O^o(Pb) = -5.65$	
$P_{int} = -26.90$	$P_{int} = -20.73$	
$Q_{int} = -12.12$	$Q_{int} = -10.16$	
$R_{int} = 22.22$	$R_{int} = 19.07$	
x_1 = Pb	x_1 = Pb	
Ag-O-Pb at 1273 K /34/	Ag-O-Sn at 1373 K /35,36/	Ag-O-Sn at 1473 K /35,36/
$\ln\gamma_O^o(Ag) = 3.8182$	$\ln\gamma_O^o(Sn) = -8.158$	$\ln\gamma_O^o(Sn) = -7.483$
$\ln\gamma_O^o(Pb) = -5.091$	$\ln\gamma_O^o(Ag) = 4.0$	$\ln\gamma_O^o(Ag) = 4.03$
$P_{int} = -10.02$	$P_{int} = -15.59$	$P_{int} = -12.47$
$Q_{int} = -16.46$	$Q_{int} = -24.10$	$Q_{int} = -23.43$
$R_{int} = 36.12$	$R_{int} = 35.42$	$R_{int} = 28.70$
x_1 = Ag	x_1 = Ag	x_1 = Ag

Table 3

Self-Interaction and Margules Coefficients of Oxygen in the Binary Melts

Pb-O-Bi at 1173 K /31/	Pb-O-Cu at 1473 K /32/
$\epsilon_o^o(Pb) = -6.14$	$\epsilon_o^o(Pb) = -1.288$
$\epsilon_o^o(Bi) = -17.0$	$\epsilon_o^o(Cu) = -8.0$
$P_{self} = 458.2$	$P_{self} = 155.0$
$Q_{self} = 24.5$	$Q_{self} = -50.6$
$R_{self} = 0.3$	$R_{self} = 0.1$
$x_1 = \mathrm{Pb}$	$x_1 = \mathrm{Pb}$

calculated from the regressional analysis of experimental values and the evaluated expressions of the interaction parameters as function of temperature are given in Table 5. In this model, first order Gibbs energy parameter of oxygen in both the pure metals is taken into account. Parameter a_i represents the logarithmic activity coefficient of solute in 1 and a_{10} represents the logarithmic activity coefficient of solute in 3 and parameters a_{13} and a_{15} constitute the first order Gibbs energy parameters in equation (14). For systems Ag-O-Pb /34/, Ag-O-Sn /35,36/, Cu-O-Ag /35-38/, Fe-O-Cu /39,40/, Pb-O-Sn /33/, Ag-S-Pb /41/ and Cu-S-Ag /42/,

Table 4

Activity Coefficients and Interaction Parameters of Oxygen and Sulfur in the Binary Melts. Values in ( ) are estimated using Maclaurin Equations

Pb-O-Bi at 1173 K /31/	Pb-O-Cu at 1473 K /32/	
$\ln \gamma_O^o(Pb) = -6.14$	$\ln \gamma_O^o(Pb) = -3.69$	
$\ln \gamma_O^o(Bi) = -4.42$	$\ln \gamma_O^o(Cu) = -1.55$	
$\epsilon_O^{Bi}(Pb) = 0.05$	$\epsilon_O^{Cu}(Pb) = -2.7$	
$\epsilon_O^{Pb}(Bi) = -6$	$\epsilon_O^{Pb}(Cu) = -7.7$	
Ag-O-Pb at 1273 K /34/	Ag-O-Sn at 1373 K /35/	Ag-O-Sn at 1473 K /36/
$\ln \gamma_O^o(Ag) = 3.8182$	$\ln \gamma_O^o(Sn) = -8.158$	$\ln \gamma_O^o(Sn) = -7.483$
$\ln \gamma_O^o(Pb) = -5.091$	$\ln \gamma_O^o(Ag) = 4.0$	$\ln \gamma_O^o(Ag) = 4.03$
$\epsilon_O^{Pb}(Ag) = (-22)$	$\epsilon_O^{Ag}(Sn) = (-44)$	$\epsilon_O^{Ag}(Sn) = (-38)$
$\epsilon_O^{Ag}(Pb) = (4.0)$	$\epsilon_O^{Sn}(Ag) = (8.8)$	$\epsilon_O^{Sn}(Ag) = (7.0)$
Cu-O-Ag at 1373 K /37,38/	Cu-O-Ag at 1473 K /37,38/	
$\ln \gamma_O^o(Cu) = -2.1282$	$\ln \gamma_O^o(Cu) = -1.645$	
$\ln \gamma_O^o(Ag) = 4.0$	$\ln \gamma_O^o(Ag) = 4.03$	
$\epsilon_O^{Ag}(Cu) = (-3)$	$\epsilon_O^{Ag}(Cu) = (2.0)$	
$\epsilon_O^{Cu}(Ag) = (-21)$	$\epsilon_O^{Cu}(Ag) = (-27)$	
Fe-O-Cu at 1873 K /39,40/	Pb-O-Sn at 1023 K /33/	Pb-O-Sn at 1223 K /33/
$\ln \gamma_O^o(Fe) = -4.559$	$\ln \gamma_O^o(Sn) = -13.77$	$\ln \gamma_O^o(Sn) = -10.30$
$\ln \gamma_O^o(Cu) = -0.0813$	$\ln \gamma_O^o(Pb) = -8.4$	$\ln \gamma_O^o(Pb) = -5.65$
$\epsilon_O^{Cu}(Fe) = (1.0)$	$\epsilon_O^{Sn}(Pb) = (-18)$	$\epsilon_O^{Sn}(Pb) = (-15)$
$\epsilon_O^{Fe}(Cu) = (-22.0)$	$\epsilon_O^{Pb}(Sn) = (2.0)$	$\epsilon_O^{Pb}(Sn) = (1.5)$
Ag-S-Sn at 1223 /41/	Ag-S-Pb at 1100 K /41/	Cu-S-Ag at 1473 K /42/
$\ln \gamma_S^o(Ag) = -6.2260$	$\ln \gamma_S^o(Ag)=-7.0$	$\ln \gamma_S^o(Cu) = -2.89$
$\ln \gamma_S^o(Sn) = -7.7217$	$\ln \gamma_S^o(Pb)=-8.47$	$\ln \gamma_S^o(Ag) = -0.75$
$\epsilon_S^{Sn}(Ag)=(2.6)$	$\epsilon_S^{Pb}(Ag)=(-2.8)$	$\epsilon_S^{Ag}(Cu) = 0.1$
$\epsilon_S^{Ag}(Sn)=(1.8)$	$\epsilon_S^{Ag}(Pb)=(-1.4)$	$\epsilon_S^{Cu}(Ag) = -4.4$

Table 5

Interaction Parameter Expressions of the Binary Systems

Ag-Pb System /43/ where x_1=Pb and x_2=Ag	$a_1 = -654.826/T + 0.937$
	$a_2 = 1855.680/T - 1.419$
	$a_3 = 14319.51/T - 10.190$
	$a_4 = -4038.129/T + 4.165$
Ag-Sn System /44/ where x_1=Ag and x_2=Sn	$a_1 = 152.2961/T - 2.788874$
	$a_2 = -4616.760/T - 1.306$
	$a_3 = 6219.121/T - 6.398$
	$a_4 = 8143.825/T - 3.211$
Cu-Ag System /45/ where x_1=Cu and x_2=Ag	$a_1 = 2.678 - 0.001{*}T$
	$a_2 = 2.927 + 0.001{*}T$
	$a_3 = -0.105 + 0.001{*}T$
	$a_4 = -0.684 - 0.004{*}T$
Fe-Cu System /46,47/ where x_1=Cu and x_2=Fe	$a_1 = 3.547 - 7.915E\text{-}04{*}T$
	$a_2 = 11.321 - 4.82E\text{-}03{*}T$
	$a_3 = 10.215 - 5.733E\text{-}03{*}T$
	$a_4 = -36.537 + 1.902E\text{-}02{*}T$
Pb-Bi System /48,49/ where x_1=Bi and x_2=Pb	$a_1 = 4.341E\text{-}03$
	$a_2 = -0.579 + 337.483/T$
	$a_3 = -3.752E\text{-}02$
	$a_4 = -1.309 + 812.760/T$
Pb-Cu System /50/ where x_1=Cu and x_2=Pb	$a_1 = 6141.098/T - 2.002688$
	$a_2 = 2633.078/T$
	$a_3 = -5269.640/T + 2.364$
	$a_4 = -1075.106/T$
Pb-Sn System /51/ where x_1=Sn and x_2=Pb	$a_1 = 594.768/T + 0.198$
	$a_2 = 618.932/T + 0.304$
	$a_3 = 101.129/T - 8.480E\text{-}02$
	$a_4 = -269.134/T + 0.225$

Table 6

Interaction Parameter Values of Pb-O-Cu at 1473 K using Maclaurin equations

a_1	=	-1.551	$\ln\gamma_O^o(Cu)$	=	-1.551
a_2	=	30.277	$\ln\gamma_{Cu}^o(CuO)$	=	30.277
a_3	=	-37.242	$\epsilon_O^O(Cu)$	=	-7.727
a_5	=	2.166	$\ln\gamma_{Pb}^o(Cu)$	=	2.166
a_6	=	1.787	$\ln\gamma_{Cu}^o(Pb)$	=	1.787
a_7	=	-1.213	$\epsilon_{Pb}^{Pb}(Cu)$	=	-7.517
a_8	=	-0.729	$\epsilon_{Cu}^{Cu}(Pb)$	=	-4.277
a_9	=	17.938	$\ln\gamma_{Pb}^o(PbO)$	=	17.938
a_{10}	=	-3.688	$\ln\gamma_O^o(Pb)$	=	-3.688
a_{12}	=	-25.959	$\epsilon_O^O(Pb)$	=	-1.288
a_{13}	=	-6.467	$\epsilon_O^{Cu}(Pb)$	=	-2.7
a_{14}	=	-132.115	$\epsilon_O^{Pb}(Cu)$	=	-7.7
a_{15}	=	-6.504	$\epsilon_{Cu}^{Pb}(PbO - CuO)$	=	-228.546

Table 7

Interaction Parameter Values of Pb-O-Bi at 1173 K using Maclaurin equations

a_1	=	-6.14	$\ln\gamma_O^o(Pb)$	=	-6.14
a_2	=	4.329	$\ln\gamma_{Pb}^o(PbO)$	=	4.329
a_3	=	-20.609	$\epsilon_O^O(Pb)$	=	-8.00
a_5	=	4.34E-03	$\ln\gamma_{Bi}^o(Pb)$	=	4.34E-03
a_6	=	-0.291	$\ln\gamma_{Pb}^o(Bi)$	=	-0.291
a_7	=	-3.75E-02	$\epsilon_{Bi}^{Bi}(Pb)$	=	-0.675
a_8	=	-0.616	$\epsilon_{Pb}^{Pb}(Bi)$	=	-5.73E-02
a_9	=	1.421	$\ln\gamma_{Bi}^o(BiO)$	=	1.421
a_{10}	=	-4.42	$\ln\gamma_O^o(Bi)$	=	-4.42
a_{12}	=	-18.761	$\epsilon_O^O(Bi)$	=	-17
a_{13}	=	-12.221	$\epsilon_O^{Bi}(Pb)$	=	0.05
a_{14}	=	8.068	$\epsilon_O^{Pb}(Bi)$	=	-6
a_{15}	=	-15.423	$\epsilon_{Bi}^{Fb}(BiO - PbO)$	=	-3.433

the first order Gibbs energy parameter is calculated based on the experimental results because of larg uncertainity in the reported values as a function of temperature.

For calculations of self-interaction of oxygen using Maclaurin infinite series in Pb-O-Cu and Pb-O-Bi systems, the parameters a_2, a_3, a_9, a_{12} and a_{14} are required. These parameters are calculated through the regression analysis of experimental data. Tables 6 and 7 show the values of coefficients from a_1 to a_3, a_5 to a_{10} and a_{12} to a_{15} obtained for the Pb-O-Bi system at 1173 K /31/ and Pb-O-Cu system at 1473 K /32/ respectively. It also includes the interaction parameter values of the Pb-Cu, Pb-Bi binaries, solute infinite dilution and also interaction in the binary dilute melt. In the present work, experimental data of the Pb-O-Bi system at 1173 K /31/ and the Pb-O-Cu system at 1473 K /32/ were analyzed to determine the activity coefficient at infinite dilution and self interaction parameter of oxygen.

The activity coefficient of oxygen at infinite dilution, ln γ_O^0, in the following systems Cu-O-Ag at 1373 K and 1473 K /35-38/, Fe-O-Cu at 1873 K /39,40/, Ag-O-Sn at 1373 K and 1473 K /35,36/, Pb-O-Sn at 1023 K and 1223 K /33/, and Ag-O-Pb at 1273 K /34/ and activity coefficient of sulfur at infinite dilution, ln γ_S^0, in the systems Ag-S-Sn at 1223 K /41/, Ag-S-Pb at 1100 K /41/, and Cu-S-Ag at 1473 K /42/ were calculated. The calculated values of ln γ_O^0 and ln γ_S^0 as a function of mole fraction of one of the binary components in the respective ternary systems are shown in Figures 1 to 8 and Figures 9 to 11 respectively using Maclaurin and Margules equations and are compared with the experimental data as well as the calculated data

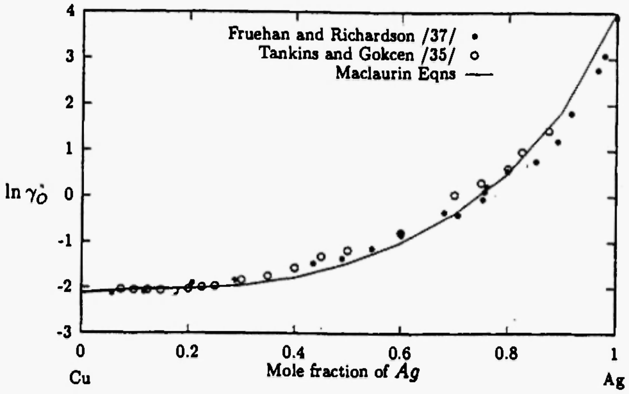

Fig. 3: Calculated and experimental values of oxygen infinite dilute value in Cu-Ag melts at 1373 K.

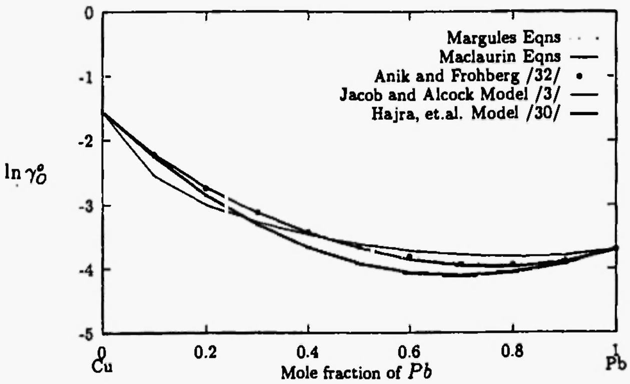

Fig. 1: Calculated and experimental values of the activity coefficient of oxygen at infinite dilution in Pb-Cu binary solvent melts at 1473K.

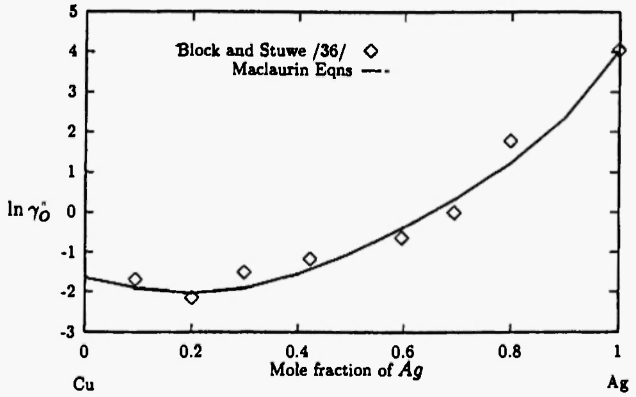

Fig. 4: Calculated and experimental values of oxygen infinite dilute value in Cu-Ag melts at 1473 K.

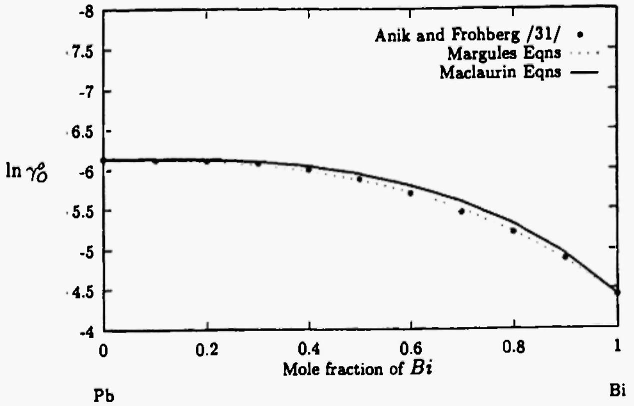

Fig. 2: Calculated and experimental values of oxygen infinite value in Pb-Bi melts at 1173 K.

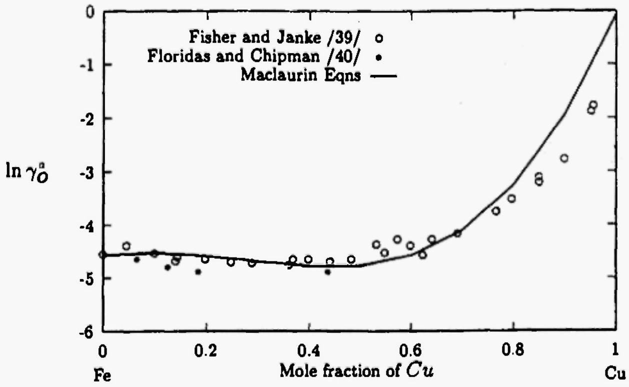

Fig. 5: Calculated and experimental values of oxygen infinite dilute value in Fe-Cu melts at 1873 K.

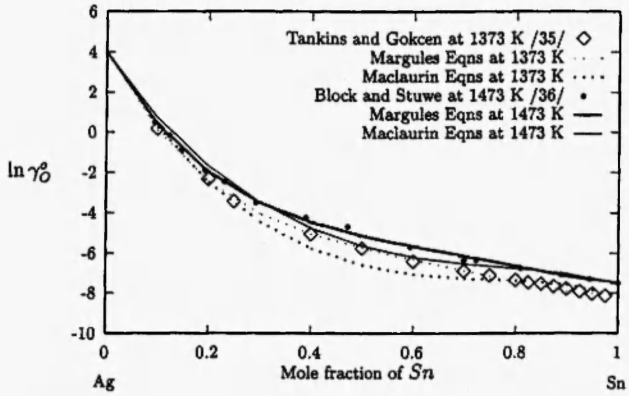

Fig. 6: Calculated and experimental values of oxygen infinite dilute value in Ag-Sn melts at 1373 K and 1473 K.

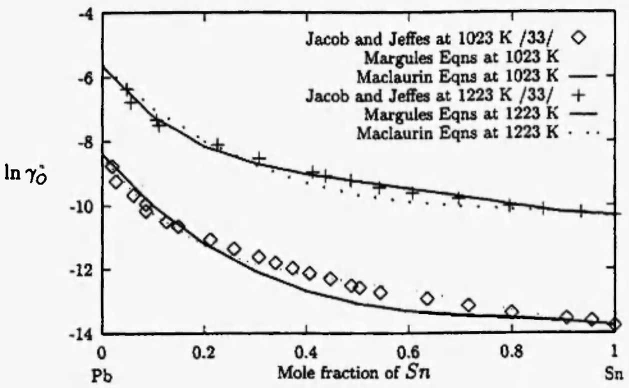

Fig. 7: Calculated and experimental values of oxygen infinite dilute value in Pb-Sn melts at 1023 K and 1223 K.

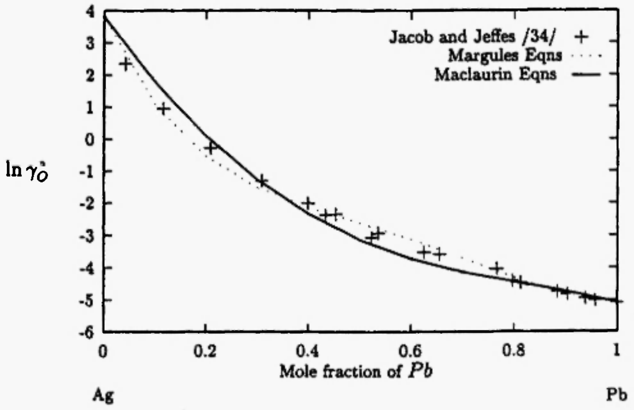

Fig. 8: Calculated and experimental values of oxygen infinite dilute value in Ag-Pb melts at 1273 K.

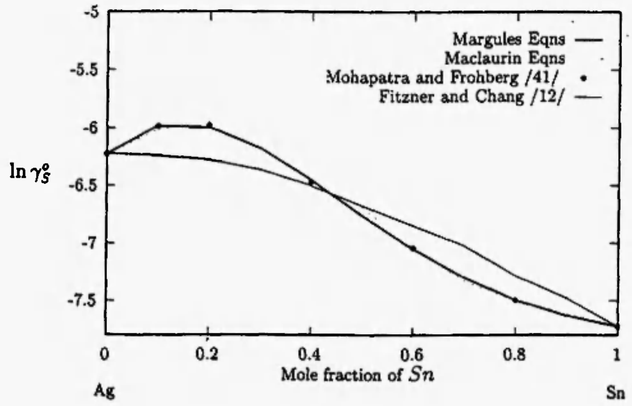

Fig. 9: Calculated and experimental values of sulphu infinite dilute value in Ag-Sn melts at 1223 K.

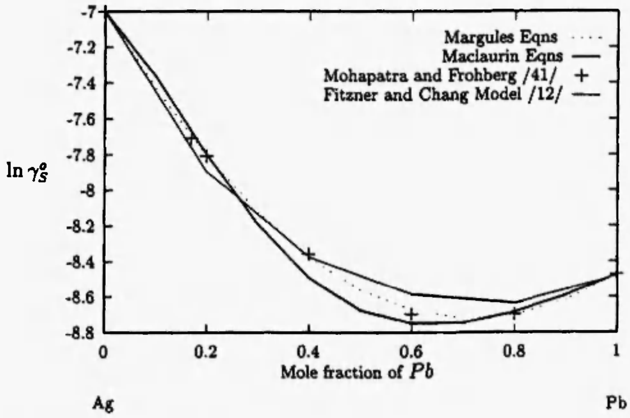

Fig. 10: Calculated and experimental values of sulphur infinite dilute value in Ag-Pb melts at 1100 K.

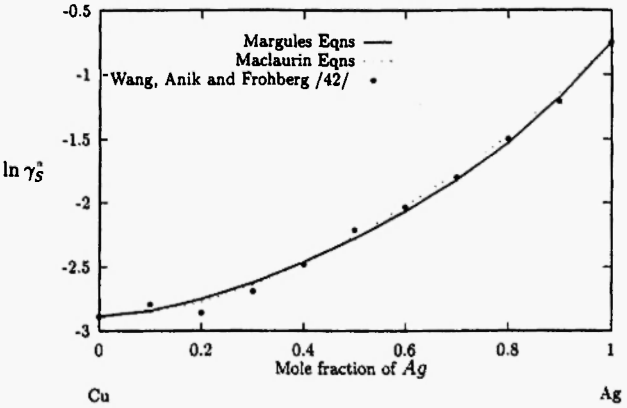

Fig. 11: Calculated and experimental values of sulphur infinite dilute value in Cu-Ag melts at 1473 K.

of other researchers for the sake of comparison. The infinite dilution data of solutes oxygen and sulfur in the respective solvent systems were taken from the experimental data, in both the models, from the following systems: Cu-S-Ag /42/, Ag-S-Sn /41/, Ag-S-Pb [41], Pb-O-Bi /31/, and Pb-O-Cu /32/. But for all other oxide systems the values are taken from Chiang and Chang /10/ whose calculations are based on thermodynamic properties of dilute binary metal-oxygen liquid solutions.

Figures 12 and 13 depict the comparison between calculated and experimental values of self-interaction parameter of oxygen as a function of alloy composition for the systems Pb-O-Cu at 1473 K and Pb-O-Bi at 1173 K respectively. In the Pb-O-Cu system at 1473 K shown in Figure (1), the activity coefficient of oxygen is compared with Jacob and Alcock's /3/ model, and Holcomb and St. Pierre's /17/ exponential model. In the exponential model values of parameters are ln $f_O^{\bullet}$ = -2.14 and $k = 3.39 \times 10^{-03}$ and they are calculated from experimental values /32/. Calculated values from exponential model deviate significantly from experimental data and also from our predicted values using Maclaurin and Margules equations. As seen from Figure (1), an excellent agreement can be seen between our model predicted values and the experimental values /32/.

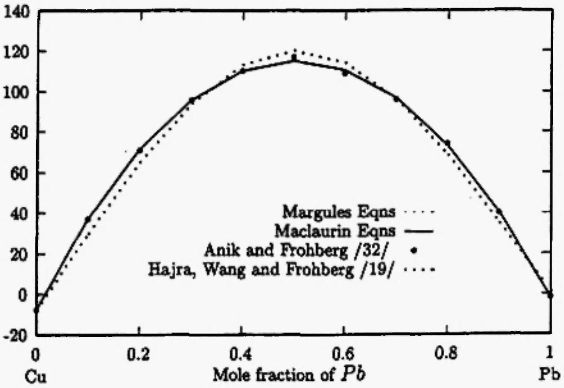

Fig. 12: Calculated and experimental values of the self-interaction parameters of oxygen in Pb-Cu binary solvent melts at 1473 K.

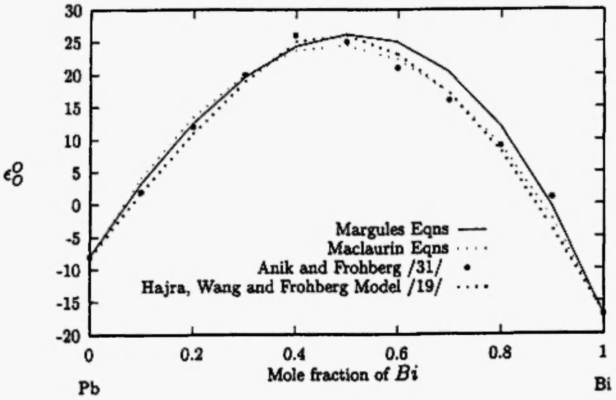

Fig. 13: Calculated and experimental values of the self-interaction parameters of oxygen in Pb-Bi binary solvent melts at 1173 K.

In the sulfur containing ternary systems, our predicted values are in an excellent agreement with the experimental data. The predicted values for sulfur systems are in better agreement with the experimental data than that of the oxide systems. This may be because of lower interaction energies in the sulfur systems and also oxides form more stable phases compared to the sulfides in the solutions. Calculated data of sulfur activity coefficient in Ag-Sn at 1223 K and Ag-Pb at 1100 K in binary melts are compared with the data of Fitzer and Chang /12/. They calculated using Wagner's model /4/ with an adjustable energy parameter value 560 J/g-atom in Ag-S-Sn system and 940 J/g-atom in Ag-S-Pb system and are shown in Figures 8 and 9. The ln γ_S^0 values predicted by our model are in excellent agreement with the experimental data. In Figures 12 and 13, the predicted self-interaction parameter of oxygen data using Maclaurin and Margules Equations are given for Pb-O-Cu and Pb-O-Bi systems respectively, along with the predictions by Hajra *et al.* /19/. The calculated data are in excellent agreement with the experimental data. In Table 1, detailed comparisons between the infinite series thermodynamic models of Margules and Maclaurin are presented.

CONCLUSIONS

The fourth-order Margules equation was used to derive activity coefficients of solutes in ternary systems. In the present model, ln $\gamma_2^0(1)$. ln $\gamma_2^0(3)$ and Margules coefficients were used to evaluate the logarithmic activity coefficients of oxygen and sulfur in ternary systems. The self-interaction parameters of solutes were derived using partial property of excess Gibbs functions. The self-interaction parameters $\varepsilon_2^2(1)$, $\varepsilon_2^2(3)$, and Margules coefficients were used to calculate the self-interaction parameter of oxygen in Pb-O-Cu and Pb-O-Bi ternary systems. The calculated data using our model were found to be in excellent agreement with the experimental values. In the present study, using Maclaurin equations, solubilities of solute in solvents, first order interaction of solute in solvents and phase equilibria between the binaries were considered to evaluate the activity coefficient of solutes in binary melts. In the case of self-interaction parameter calculations, the coefficients were evaluated based on experimental data. The logarithmic activity coefficient values of the oxygen in seven metallic systems and that of sulfur in three metallic system and also self-interaction parameter of oxygen in two systems were calculated. The interaction parameters values predicted by using Maclaurin infinite series model were more accurate and consistent with the experimental data than those of the other models. For the systems considered here, the activity coefficients and self-interaction parameter data predicted by Maclaurin infinite series and Margules equation models were in excellent agreement with the experimental data.

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