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Thermodynamic properties of Al in ternary lead-free solder Al-Sn-Zn alloys

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Thermodynamic properties of Al were calculated using the molecular interaction volume model (MIVM) by analyzing the activities of components in the constitutive binary Al-Sn, Al-Zn and Sn-Zn subsystems of the ternary lead-free solder Al-Sn-Zn systems. The activities of Al content in the ternary system at three cross-sections with constant molar ratios of Sn:Zn = 2:1, 1:1 and 1:2, respectively, were calculated and compared with available experimental data at 973 K. Based on the agreement between the calculated activity values and corresponding literature data for Al-Sn-Zn alloys and their subsystems, the activity of Al content in the ternary Al-Sn-Zn system was estimated at the same cross-sections and mole ratios in the temperature range of 1073 K to 1373 K, respectively. It has been observed through the computed activity values of Al that the thermodynamic properties of the ternary Al-Sn-Zn systems do not change appreciably with temperature across the molar sections.

Keywords: *molecular interaction volume model; activity; ternary Al-Sn-Zn system; lead-free solder*

1. Introduction

Alloy systems containing lead (Pb) have been used extensively as solders in electronics due to their low cost, excellent mechanical, physical and chemical performances. In the last two decades however, the development of lead-free solder materials have attracted much attention of researchers due to environmental and health issues associated with some materials including lead [1–7]. The use of lead and lead containing materials has been restricted by legislation worldwide, hence, the development of alternative lead-free solders with the same or possibly better characteristics than those of traditional Pb-Sn alloys is an important task that needs to be undertaken [8]. In addition, the development of alternative lead-free solders can lead to improved properties and thus extend the current range of application of the soldering technology. In this regard, the new lead-free solder substitute being sought, have to meet some requirements, such as possession of excellent electrical conductivity, suitable melting temperature as well as good substrate wettability resulting in the formation of thin intermetallic layers at the solder/substrate interface [9]. Additional properties, such as high strength, good resistance to mechanical and thermal fatigue, corrosion resistance, environmental friendliness and relatively less expensive material have to be considered in the development of the new solders [2, 6, 8, 10].

In order to design lead-free solders, both the binary and higher alloy systems (ternary, quaternary, etc.) have already been investigated [1, 2, 5, 11–14]. Majority of investigated alloy systems are Sn-based, having Al, In, Sb, Zn, Bi, Au, Tl and Ag as a part of the alloy constituents. In particular, the studies have indicated Sn to be the major component in binary solders and that Sn-based multi-component alloys, such as ternary (Al-Sn-Zn, In-Sn-Zn, Sn-Ag-Cu) and/or quaternary (Sn-Ag-Cu-Sb, Sn-Ag-Cu-Zn) systems are more favored as a primary high-temperature alternative for lead-free solder [1, 6, 8]. Accordingly, the ternary Al-Sn-Zn alloy which is considered as an important system in lead-free soldering together with its binary subsystems, i.e. Al-Sn, Al-Zn and Sn-Zn, has been selected for theoretical investigation. The two other principal reasons considered alongside the ones above are: (i) there seems

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to be a general consensus among researchers that the composition of new lead-free solders would be based on low-melting metals, and Sn and Zn seem to be the most promising ones, and (ii) the potential of Al-Sn-Zn for developing an alternative for lead-free solder [6, 10] and/or its viability as a subsystem for developing complex alloy systems, such as the Al-Sn-Zn-Ag, have been reported in the literature [10, 15].

Moreover, thermodynamic activity of Al measured using the electromotive force method [6] and the enthalpy of mixing determined by calorimetric method [16] are the only experimental thermodynamic datasets for liquid Al-Sn-Zn alloys available in literature to the best of authors' knowledge. Thus, Al-Sn-Zn system is worth thorough investigation. Nonetheless, the binary constituents of Al-Sn-Zn system have been investigated, for instance Al-Zn [17–21], Sn-Zn [22–24] and Al-Sn [9, 25]. Extensive experimental studies of the ternary phase diagrams of the Al-Sn-Zn systems have been already reported [26, 27]. The microstructure of the systems was experimentally determined by Lin et al. [28]. In addition, the oxidation resistance of 91Sn-8.55Zn-0.45Al (wt.%) alongside that of other systems have been measured [29], and a detailed assessment of the system has also been given by Fries et al. [30]. Using theoretical approach, the surface segregation and surface tension in Al-Sn-Zn liquid alloys have been investigated by Prasad et al. [31]. Thus, in complementing previous experimental investigations, the knowledge of thermodynamic activity of multi-component alloys and their subsystems must be well understood both from the theoretical and metallurgical point of view, as this can provide the alloy designers with specific data which meet certain criteria in the production of alloys and aid in understanding how a lead-free solder can be developed based on ternary Al-Sn-Zn system.

A number of geometric models, such as Kohler, Muggianu, Collinet, Chou etc. [32], are widely used to predict the thermodynamic properties of ternary and other higher order systems by combining the corresponding property values of constitutive binaries or of binaries and other subsystems, respectively. The models are classified into two distinct groups: symmetrical and asymmetrical by Hillert [33]. Recently, the aforementioned models have also been applied to predict the thermophysical properties of liquid Ag-Bi-Sn [34] and surface tension [35]. In this work, the molecular interaction volume model (MIVM) which has proved to be reliable [36–39] is used to predict the activities of the three constitutive binaries (Al-Sn, Al-Zn and Sn-Zn) subsystems, and the activity of Al content in Al-Sn-Zn systems at three different cross-sections with constant molar ratios of 2:1, 1:1 and 1:2 in the temperature range of 973 K to 1373 K. This model is based on the physical perception that liquid molecules or atoms are different from gas molecules, which are continuously in random motion, and also differ from the solid ones, which vibrate constantly at lattice sites but are moving regularly from one molecular cell to another. The implication is that the cell molecules are unstable and the molecules may move freely into an adjacent hole as a central molecule. It is assumed that liquid molecules can move freely unhindered through a cell space and the molecular interaction separation tends towards the cell diameter at a certain temperature [38]. Hence, the so-called central molecules and their closest molecules are relative and exchangeable, and the cells are movable and indistinguishable. On the basis of this physical perspective of molecular or atomic movements of liquid, the MIVM was proposed [37].

This article is organized into sections, with the MIVM formulation presented in section 2. This is followed by results and discussion in section 3 and the conclusion is given in the last section.

2. Theoretical formulation of MIVM

Within the frame of the molecular interaction volume model, the molar excess Gibbs energy G_M^E of a liquid binary alloy i-j is given [36] by:

$$G_M^E = x_i \ln\left(\frac{V_{mi}}{x_i V_{mi} + x_j V_{mj} A_{ji}}\right) + x_j \ln\left(\frac{V_{mj}}{x_j V_{mj} + x_i V_{mi} A i_j}\right) - \frac{x_i x_j}{2}\left(\frac{Z_i A_{ji} \ln A_{ji}}{x_i + x_j A_{ji}} + \frac{Z_j A_{ij} \ln A_{ij}}{x_j + x_i A i_j}\right) \quad (1)$$

where x_i and x_j are the molar fractions, V_{mi} and V_{mj} are the molar volumes of component i and j, respectively.

Using the standard thermodynamic relation under the condition that when $i \neq N$, $\delta = 1$ and $i = N$, $\delta = 0$, an expression relating the partial molar and molar excess Gibbs energies can be written as:

$$\overline{G_j}^E = RT \ln \gamma_i = G_m^E + \delta\left(\frac{\partial G_m^E}{\partial x_i}\right)_{T,P,x[i,N]} - \sum_{j=1}^{N-1} x_j \left(\frac{\partial G_m^E}{\partial x_j}\right)_{T,P,x[j,N]} \quad (2)$$

The subscript symbol x[i,N] in equation 2 denotes that x_j and x_N are two variables for the partial differentiation and $x_N = 1 - \sum_{j=1}^{N-1} x_j$ is a subordinate variable. Thus, the activity coefficients of components i and j in a binary system are given as:

$$\ln \gamma_i = \ln\left(\frac{V_{mi}}{x_i V_{mi} + x_j V_{mj} A_{ji}}\right) + x_j\left(\frac{V_{mj} A_{ji}}{x_i V_{mi} + x_j V_{mj} A_{ji}} - \frac{V_{mi} A_{ij}}{x_j V_{mj} + x_i V_{mi} A_{ij}}\right) - \frac{x_j^2}{2}\left[\frac{Z_i A_{ji}^2 \ln A_{ji}}{(x_i + x_j A_{ji})^2} + \frac{Z_j A_{ij} \ln A_{ij}}{(x_j + x_i A_{ij})^2)}\right] \quad (3)$$

$$\ln \gamma_j = \ln\left(\frac{v_{mj}}{x_j V_{mj} + x_i V_{mi} A_{ij}}\right) + x_i\left(\frac{V_{mj} A_{ji}}{x_i V_{mi} + x_j V_{mj} A_{ji}} - \frac{V_{mi} A_{ij}}{x_j V_{mj} + x_i V_{mi} A_{ij}}\right) - \frac{x_i^2}{2}\left[\frac{Z_j A_{ij}^2 ln A_{ij}}{(x_j + x_i A_{ij})^2} + \frac{Z_i A_{ji} ln A_{ji}}{(x_i + x_j A_{ji})^2)}\right] \quad (4)$$

Upon applying equation 1 to a higher order alloy system, its molar excess Gibbs energy is generalized as:

$$\frac{G_m^E}{RT} = \sum_{i=1}^{N} x_i \ln \frac{V_{mi}}{\sum_{j=1}^{N} x_j V_{mj} A_{ji}} - \frac{1}{2}\sum_{i=1}^{N} Z_i x_i \left(\frac{\sum_{j=1}^{N} x_j A_{ji} \ln A_{ji}}{\sum_{j=1}^{N} x_j A_{ji}}\right) \quad (5)$$

and, the expression of activity coefficient of any component i in the frame of MIVM is [37]:

$$\ln \gamma_i = l + \ln \frac{V_{mi}}{\sum_{j=1}^{N} x_j V_{mj} A_{ji}} - \sum_{j=1}^{N} \frac{x_j V_{mi} A_{ij}}{\sum_{l=1}^{N} x_l V_{ml} A_{lj}} - \frac{1}{2}\left(\frac{Z_i \sum_{j=1}^{N} x_j A_{ji} \ln A_{ji}}{\sum_{l=1}^{N} x_l A_{li}} + \sum_{j=1}^{N} \frac{Z_j X_j A_{ij}}{\sum_{l=1}^{N} x_1 A_{lj}} \times \left(\ln A_{ij} - \frac{\sum_{l=1}^{N} x_l A_{lj} \ln A_{ij}}{\sum_{l=1}^{N} x_l A_{lj}}\right)\right) \quad (6)$$

where Z_i and Z_j in equation 1 and equation 6 are the nearest neighbors molecules or first coordination numbers and Z_i can be determined using the relation [37]:

$$Z_i = \frac{4\sqrt{2\pi}}{3}\left(\frac{r_{mi}^3 - r_{0i}^3}{r_{mi} - r_{0i}}\right) \rho_i r_{mi} \exp\left(\frac{\Delta H_{mi}(T_{mi} - T)}{Z_c R T T_{mi}}\right) \quad (7)$$

here $\rho_i = N_i/V_i = 0.6022/V_{mi}$ is the molecular number density, ΔH_{mi} and T_{mi} are the melting enthalpy and the melting temperature, respectively, $Z_c = 12$ is a close-packed coordination, R is the gas constant, r_{mi} and r_{0i} are the initial and first peak values of radial distribution function g(r) of the liquid metal i near its melting point, respectively. The radial distances are connected to the atomic covalent diameter, d_{coni} and the atomic diameter, σ_i, through the following relations [37]:

$$r_{0i} = 0.918 d_{covi}; \quad r_{mi} = \sigma_i \quad (8)$$

The pair-potential energy interaction parameters A_{ji} and A_{ij} in equation 3 to equation 6 are defined as:

$$A_{ji} = \exp\left[-\frac{\varepsilon_{ji} - \varepsilon_{ii}}{kT}\right]; \quad A_{ij} = \exp\left[-\frac{\varepsilon_{ij} - \varepsilon_{jj}}{kT}\right] \quad (9)$$

where ϵ_{ii}, ϵ_{jj} and ϵ_{ji} are the i-i, j-j and i-j pair-potential energies, respectively. $\epsilon_{ji} = \epsilon_{ij}$, k and T

are the Boltzmann constant and the absolute temperature of the liquid metal. For a binary system i-j, the expression of infinite dilute activity coefficients γ_i^{∞} and γ_j^{∞} can be obtained from equation 6 when x_i or x_j tends to zero, respectively as:

$$\ln\gamma_i^{\infty} = 1 - \ln\left(\frac{V_{mj}A_{ji}}{V_{mi}}\right) - \frac{V_{mi}A_{ij}}{V_{mj}} - \frac{1}{2}(Z_i \ln A_{ji} + Z_j A_{ij} \ln A_{ij}) \quad (10)$$

and:

$$\ln\gamma_j^{\infty} = 1 - \ln\left(\frac{V_{mi}A_{ij}}{V_{mj}}\right) - \frac{V_{mj}A_{ji}}{V_{mi}} - \frac{1}{2}(Z_j \ln A_{ij} + Z_i A_{ji} \ln A_{ji}) \quad (11)$$

In order to determine the values of A_{ji} and A_{ij}, equation 10 and equation 11 are solved by using the Newton-Raphson method. Once the appropriate values of A_{ji} and A_{ij} at a given temperature are obtained upon solving equation 10 and equation 11 simultaneously, their respective values at any other temperature of interest can be found by assuming that the pair-potential energy parameters given by equation 9, $-(\epsilon_{ji} - \epsilon_{ii})/kB$ and $-(\epsilon_{ij} - \epsilon_{jj})/k_B$ are independent of temperature [37]. For instance, in the binary system Sn–Zn:

$$-\frac{\varepsilon_{ji} - \varepsilon_{ii}}{kT} = T \ln A_{ji} = 750 \ln(0.6123) = 367.9$$
$$A_{ji} = \exp\left(-\frac{367.9}{1000}\right) = 0.6922 \text{ at } 1000\ K \quad (12)$$

and:

$$-\frac{\varepsilon_{ij} - \varepsilon_{jj}}{kT} = T \ln A_{ij} = 750 \ln(1.1326) = 93.4$$
$$A_{ij} = \exp\left(\frac{93.4}{1000}\right) = 1.0979 \text{ at } 1000\ K \quad (13)$$

Now, allowing the investigated Al–Sn–Zn ternary alloy to be the 1–2–3 system, the activity coefficient of the component 1 of this system can be obtained from equation 6 as:

$$\ln\gamma_1 = 1 + \ln\left(\frac{V_{m1}}{x_1V_{m1} + x_2V_{m2}A_{21} + x_3V_{m3}A_{31}}\right) - \frac{x_1V_{m1}}{x_1V_{m1} + x_2V_{m2}A_{21} + x_3V_{m3}A_{31}} - \frac{x_2V_{m1}A_{12}}{x_1V_{m1}A_{12} + x_2V_{m2} + x_3V_{m3}A_{32}} - \frac{x_3V_{m1}A_{13}}{x_1V_{m1}A_{13} + x_2V_{m2}A_{23} + x_3V_{m3}} - \frac{1}{2}\left(\frac{Z_1(x_2A_{21} + x_3A_{31})(x_2A_{21}\ln A_{21} + x_3A_{31}\ln A_{31})}{(x_1 + x_2A_{21} + x_3A_{31})^2} + \frac{Z_2x_2A_{12}[(x_2 + x_3A_{32})\ln A_{12} - x_3A_{32}\ln A_{32}]}{(x_1A_{12} + x_2 + x_3A_{32})^2} + \frac{Z_3x_3A_{13}[(x_2A_{23} + x_3)\ln A_{13} - x_2A_{23}\ln A_{23}]}{(x_1A_{13} + x_2A_{23} + x_3)^2}\right) \quad (14)$$

3. Results and discussion

3.1. Activities of components in the liquid binary Al-Sn, Al-Zn and Sn-Zn systems

On the basis of the theoretical formulation presented in section 2, the activities of components in liquid binary systems of Al-Sn, Al-Zn and Sn-Zn at 973 K, 1000 K and 750 K, respectively, were calculated in order to establish the validity of the calculated activities results using the MIVM with the available experimental values. Some essential physical parameters of the pure metals required were taken from the literature [40] and these parameters are listed in Table 1. The coordination numbers Z_i's of the metals in the liquid phase were estimated using equation 7. The required binary parameters A_{ji} and A_{ij} were calculated via equation 9 and simultaneous solution of equation 10 and equation 11. The infinite dilute activity coefficients γ_i^{∞} and γ_j^{∞} for the binary phases were obtained from the literature [41] and are listed in Table 2.

The activities of components in the liquid binary systems of Al–Sn, Al–Zn and Sn–Zn at 750 K, 973 K and 1000 K were obtained upon substituting the corresponding values of parameters A_{ji} and A_{ij} into equation 3 and equation 4. The results are presented in Fig. 1 to Fig. 3, respectively. It is evident from the figures that a reasonable agreement exists between the MIVM-based theoretical calculated results and the respective experimental data

Table 1. Some essential parameters of the pure metals [40].

Metal, i	ΔH_{mi} [kJ/mol]	σ_i [$\times 10^{-8}$ cm]	r_{oi} [$\times 10^{-8}$ cm]	V_{mi} [cm^3/mol]
Al	10.46	2.78	2.28	$11.30[1 + 1.50 \times 10^{-4} (T - 933)]$
Sn	7.07	3.14	2.68	$17.00[1 + 0.87 \times 10^{-4} (T - 505)]$
Zn	7.28	2.66	2.16	$9.94[1 + 1.50 \times 10^{-4} (T - 693)]$

Table 2. Computed values of A_{ji}, A_{ij}, Z_i and Z_j with γ_i^{∞} and γ_j^{∞} for the constituents of binary liquid alloys at the required temperatures.

i-j	T [K]	A_{ji}	A_{ij}	Z_i	Z_j	γ_i^{∞}	γ_j^{∞}
Al–Sn	973	1.0718	0.6199	9.48	9.09	2.705	6.637
	1073	1.0649	0.6482	9.34	9.02	2.289	5.007
	1173	1.0592	0.6726	9.21	8.94	1.992	3.964
	1273	1.0544	0.6938	9.08	8.87	1.772	3.255
	1373	1.0504	0.7126	8.95	8.80	1.604	2.751
Al–Zn	973	0.7678	1.0723	9.09	9.48	2.681	2.160
	1073	0.7869	1.0654	9.02	9.34	2.447	1.980
	1173	0.8032	1.0596	8.94	9.21	2.201	1.789
	1273	0.8171	1.0548	8.87	9.08	2.012	1.643
	1373	0.8292	1.0507	8.80	8.95	1.864	1.528
Sn–Zn	973	0.6852	1.1007	9.04	9.09	1.981	1.422
	1073	0.7097	1.0909	8.91	9.02	1.524	1.287
	1173	0.7308	1.0829	8.79	8.94	1.226	1.185
	1273	0.7490	1.0761	8.67	8.87	1.021	1.105
	1373	0.7649	1.0704	8.55	8.80	0.873	1.041

*Experimental γ_i^{∞} and γ_j^{∞} [41]

obtained from the literature [41]. As observed from Fig. 2, the calculated and experimental activities of components in Al-Zn liquid alloys follow the same trend but a slight variation exists between the calculated and experimental Zn activity a_{Zn} in the concentration range of $0.3 < a_{Al} < 0.7$. Experimental data are shown as symbols in figures.

The closeness between the two results (experimental and MIVM obtained results) gave us the confidence to extend the calculation to ternary Al-Sn-Zn systems.

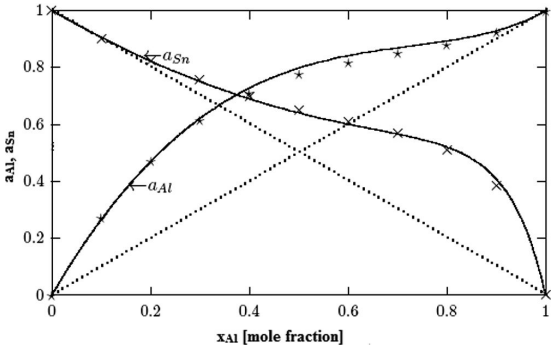

Fig. 1. Concentration dependence of a_{Al} and a_{Sn} activities for liquid Al alloys at 973 K calculated by equation 3 and equation 4, respectively, together with the experimental data [41] (the Raoult law).

3.2. Activity of Al content in ternary Al-Sn-Zn systems

The activity of Al content in Al-Sn-Zn ternary melts were calculated by inserting the corresponding values of the parameters A_{ji} and A_{ij} into equation 16 and subsequently compared with experimental data for Al activity determined

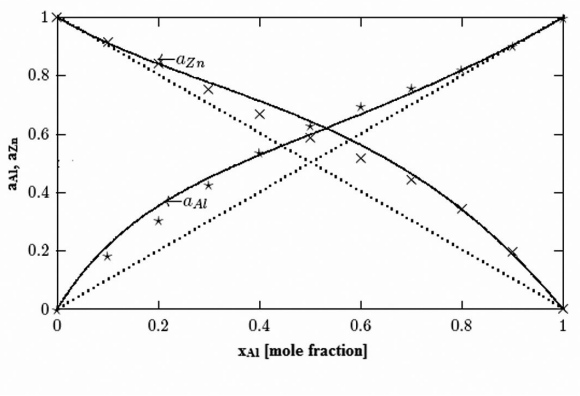

Fig. 2. Concentration dependence of a_{Al} and a_{Zn} activities for liquid Al-Zn alloys at 1000 K calculated by equation 3 and equation 4, respectively, together with the experimental data [41] (the Raoult law).

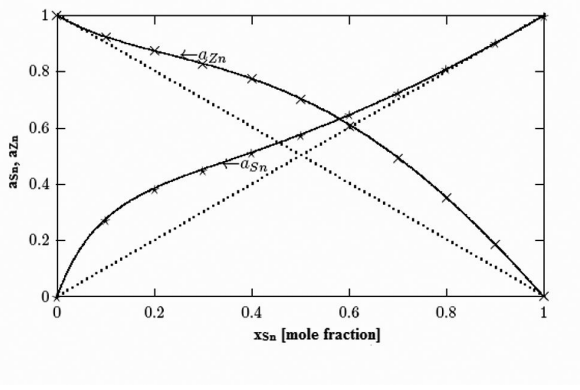

Fig. 3. Concentration dependence of a_{Sn} and a_{Zn} activities for liquid Sn-Zn alloys at 750 K calculated by equation 3 and equation 4, respectively, together with the experimental data [41] (the Raoult law).

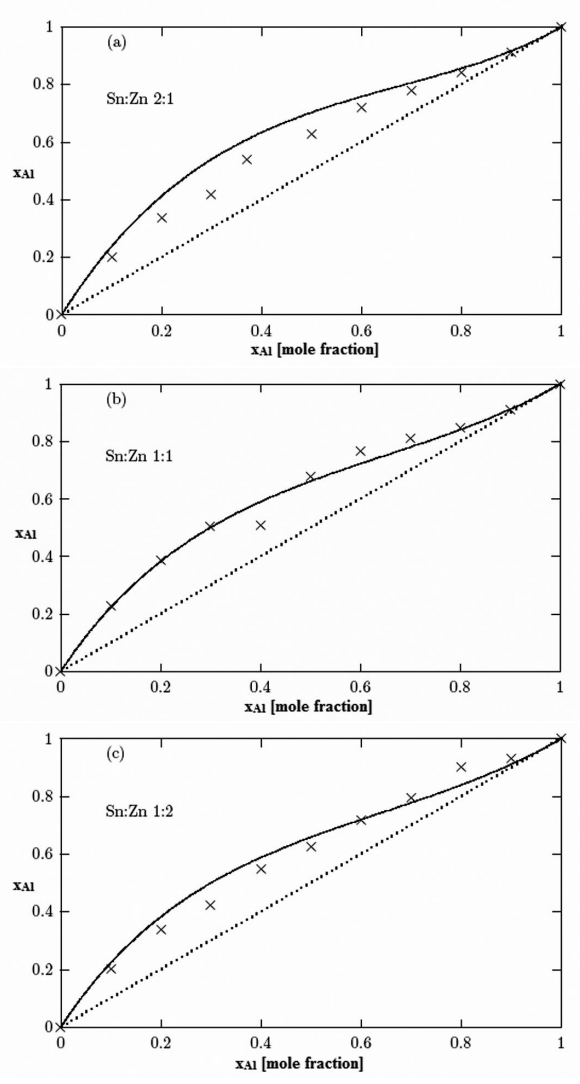

Fig. 4. Concentration dependence of Al activity in ternary Al-Sn-Zn systems calculated using equation 16 at 973 K together with the experimental data [6]. The solid and dotted lines denote theoretical values and the Raoult law, respectively; (a) for Sn:Zn 2:1 cross-section, (b) for Sn:Zn 1:1 cross-section, (c) for Sn:Zn 1:2 cross-section.

at 973 K by Knott et al. [6]. The activities of Al in ternary Al-Sn-Zn system calculated for the three cross sections with constant molar ratios of Sn:Zn = 2:1, 1:1 and 1:2 with Al content varying between 0 and 1 are shown in Fig. 4. Similar results obtained at 973 K were reported in the literature [37].

From the figures, it is noticeable that the activity of Al exhibits positive deviation from Raoult law in the whole concentration range except around $0.8 \leqslant x_{Al} \leqslant 1.0$. This positive deviation indicates the tendency of clustering of Sn and Zn as second nearest neighborhood. The agreement between the predicted activities and the experimental data is quite reasonable, particularly at the cross-sections with Sb:Zn = 1:1 and 1:2. On the contrary, for the constant molar ratio at Sn:Zn = 2:1 cross-section, the agreement is not too impressive. A careful

Table 3. Predicted values of Al activity content in ternary Al-Sn-Zn alloys at 973 K across three sections.

Sn:Zn = 2:1			MIVM a_{Al}	EXPT [6] a_{Al}	$\lvert a_{Al,EXPT} - a_{Al,MIVM} \rvert$
x_{Al}	x_{Sn}	x_{Zn}			
0.0500	0.6333	0.3167	0.1272	0.1460	0.0188
0.1000	0.6000	0.3000	0.2382	0.2010	0.0372
0.2000	0.5333	0.2667	0.4151	0.3370	0.0781
0.3000	0.4667	0.2333	0.5450	0.4180	0.1270
0.4000	0.4000	0.2000	0.6399	0.5380	0.1019
0.5000	0.3333	0.1667	0.7099	0.6270	0.0829
0.6000	0.2667	0.1333	0.7642	0.7190	0.0452
0.7000	0.2000	0.1000	0.8110	0.7800	0.0310
0.8000	0.13 33	0.0667	0.8589	0.8400	0.0189
0.9000	0.0667	0.0333	0.9176	0.9100	0.0086
Sn:Zn = 1:1					
0.0500	0.4750	0.4750	0.1211	0.1140	0.0071
0.1000	0.4500	0.4500	0.2248	0.2290	0.0042
0.2000	0.4000	0.4000	0.3883	0.3880	0.0003
0.3000	0.3500	0.3500	0.5086	0.5060	0.0026
0.4000	0.3000	0.3000	0.5992	0.5080	0.0912
0.5000	0.2500	0.2500	0.6703	0.6800	0.0097
0.6000	0.2000	0.2000	0.7303	0.7670	0.0367
0.7000	0.1500	0.1500	0.7862	0.8100	0.0238
0.8000	0.1000	0.1000	0.8447	0.8480	0.0033
0.9000	0.0500	0.0500	0.9130	0.9100	0.0030
Sn:Zn = 1:2					
0.0500	0.3167	0.6333	0.1223	0.1480	0.0257
0.1000	0.3000	0.6000	0.2262	0.2020	0.0242
0.2000	0.2667	0.5333	0.3890	0.3370	0.0520
0.3000	0.2333	0.4667	0.5079	0.4240	0.0839
0.4000	0.2000	0.4000	0.5972	0.5500	0.0472
0.5000	0.1667	0.3333	0.6675	0.6250	0.0425
0.6000	0.1333	0.2667	0.7274	0.7190	0.0084
0.7000	0.1000	0.2000	0.7837	0.7960	0.0123
0.8000	0.0667	0.1333	0.8431	0.9020	0.0589
0.9000	0.0333	0.0667	0.9125	0.9340	0.0215

$S_{Al} = \pm 8.05\ \%$, $S^*_{Al} = \pm 0.0486\ \%$.

examination of $\lvert a_{Al,EXPT} - a_{Al,MIVM} \rvert$ in Table 3 shows the positive difference between the calculated activity of Al and experimental values. Also, in Table 3, the average relative error, S_i and standard error, S_i^* were respectively computed using the equations [37]:

$$S_i = \pm \frac{100}{n} \sum_{i=1}^{n} \left| \frac{a_i, \exp - a_i, pre}{a_i, \exp} \right| \tag{15}$$

$$S_i^* = \pm \left[\frac{1}{n} \sum_{i=1}^{n} (a_i, \exp - a_i, pre)^2 \right]^{\frac{1}{2}} \tag{16}$$

Table 4. Predicted and experimental values of Al activity content in ternary Al-Sn-Zn alloys at 1073 K and 1173 K across the three sections.

			MIVM	EXPT [6]	MIVM	EXPT [6]
Sn:Zn = 2:1				1073 K	1173 K	
x_{Al}	x_{Sn}	x_{Zn}	a_{Al}		a_{Al}	
0.0500	0.6333	0.3167	0.1175	0.1137	0.1120	0.0924
0.1000	0.6000	0.3000	0.2232	0.1863	0.2109	0.1743
0.2000	0.5333	0.2667	0.3918	0.3193	0.3726	0.3047
0.3000	0.4667	0.2333	0.5183	0.4220	0.4964	0.4253
0.4000	0.4000	0.2000	0.6135	0.5210	0.5920	0.5068
0.5000	0.3333	0.1667	0.6866	0.6116	0.6676	0.5977
0.6000	0.2667	0.1333	0.7457	0.7036	0.7307	0.6901
0.7000	0.2000	0.1000	0.7982	0.7312	0.7879	0.6924
0.8000	0.1333	0.0667	0.8519	0.8179	0.8463	0.8006
0.9000	0.0667	0.0333	0.9154	0.8877	0.9137	0.8690
Sn:Zn = 1:1						
0.0500	0.4750	0.4750	0.1130	0.1101	0.1092	0.0898
0.1000	0.4500	0.4500	0.2105	0.2064	0.1988	0.1896
0.2000	0.4000	0.4000	0.3673	0.3635	0.3501	0.3437
0.3000	0.3500	0.3500	0.4858	0.4802	0.4671	0.4585
0.4000	0.3000	0.3000	0.5776	0.4817	0.5600	0.4594
0.5000	0.2500	0.2500	0.6520	0.6006	0.6371	0.5667
0.6000	0.2000	0.2000	0.7163	0.7322	0.7049	0.7048
0.7000	0.1500	0.1500	0.7769	0.7758	0.7692	0.7480
0.8000	0.1000	0.1000	0.8398	0.8256	0.8358	0.8072
0.9000	0.0500	0.0500	0.9115	0.8886	0.9103	0.8706
Sn:Zn = 1:2						
0.0500	0.3167	0.6333	0.1142	0.1186	0.1071	0.0989
0.1000	0.3000	0.6000	0.2117	0.1858	0.1999	0.1737
0.2000	0.2667	0.5333	0.3679	0.3182	0.3507	0.3035
0.3000	0.2333	0.4667	0.4852	0.4190	0.4666	0.4147
0.4000	0.2000	0.4000	0.5760	0.5288	0.5587	0.5115
0.5000	0.1667	0.3333	0.6497	0.6098	0.6351	0.5975
0.6000	0.1333	0.2667	0.7138	0.7029	0.7027	0.6901
0.7000	0.1000	0.2000	0.7747	0.7747	0.7674	0.7575
0.8000	0.0667	0.1333	0.8384	0.8762	0.8346	0.8553
0.9000	0.0333	0.0667	0.9110	0.9250	0.9099	0.9175

$S_{Al} = \pm 7.82$ %, $S_{Al} = \pm 7.96$ %, $S_{Al}^{*} = \pm 0.0462$ %, $S_{Al}^{*} = \pm 0.0472$ %.

where in equation 15 and equation 16, a_i,exp and a_i,pre and are the experimental data and the predicted values of component activity in the liquid alloys, respectively, and n is the number of experimental data (in the present study, n = 30). Both the average relative error and the standard deviation are ± 8.05 % and ± 0.0486 %, respectively.

The basis for predicting the activity of Al content in the Al-Sn-Zn ternary system at different working temperatures using the molecular interaction volume model stems from the reasonable agreement obtained between the predicted activity values of Al in Al-Sn-Zn system and its experimental data at 973 K. The results are presented

Table 5. Predicted and experimental values of Al activity content in ternary Al-Sn-Zn alloys at 1273 K and 1373 K across the three sections.

			MIVM	EXPT [6]	MIVM	EXPT [6]
Sn:Zn = 2:1				1273 K	1373 K	
x_{Al}	x_{Sn}	x_{Zn}		a_{Al}		a_{Al}
0.0500	0.6333	0.3167	0.1075	0.0776	0.1020	0.0668
0.1000	0.6000	0.3000	0.2005	0.1648	0.1916	0.1572
0.2000	0.5333	0.2667	0.3565	0.2929	0.3426	0.2833
0.3000	0.4667	0.2333	0.4781	0.4282	0.4624	0.4307
0.4000	0.4000	0.2000	0.5741	0.4952	0.5588	0.4855
0.5000	0.3333	0.1667	0.6519	0.5862	0.6385	0.5765
0.6000	0.2667	0.1333	0.7183	0.6789	0.7078	0.6696
0.7000	0.2000	0.1000	0.7795	0.6614	0.7723	0.6360
0.8000	0.1333	0.0667	0.8418	0.7862	0.8379	0.7742
0.9000	0.0667	0.0333	0.9123	0.8535	0.9111	0.8405
Sn:Zn = 1:1						
0.0500	0.4750	0.4750	0.1013	0.0820	0.0965	0.0759
0.1000	0.4500	0.4500	0.1892	0.1765	0.1810	0.1661
0.2000	0.4000	0.4000	0.3358	0.3277	0.3236	0.3148
0.3000	0.3500	0.3500	0.4515	0.4411	0.4382	0.4267
0.4000	0.3000	0.3000	0.5454	0.4415	0.5328	0.4267
0.5000	0.2500	0.2500	0.6246	0.5396	0.6140	0.5176
0.6000	0.2000	0.2000	0.6954	0.6825	0.6872	0.6640
0.7000	0.1500	0.1500	0.7629	0.7253	0.7575	0.7065
0.8000	0.1000	0.1000	0.8324	0.7919	0.8296	0.7792
0.9000	0.0500	0.0500	0.9093	0.8557	0.9085	0.8431
Sn:Zn = 1:2						
0.0500	0.3167	0.6333	0.1012	0.0848	0.0965	0.0743
0.1000	0.3000	0.6000	0.1901	0.1641	0.1818	0.1563
0.2000	0.2667	0.5333	0.3363	0.2917	0.3241	0.2818
0.3000	0.2333	0.4667	0.4512	0.4110	0.4380	0.4079
0.4000	0.2000	0.4000	0.5442	0.4973	0.5318	0.4856
0.5000	0.1667	0.3333	0.6229	0.5872	0.6125	0.5786
0.6000	0.1333	0.2667	0.6935	0.6795	0.6856	0.6706
0.7000	0.1000	0.2000	0.7614	0.7434	0.7562	0.7313
0.8000	0.0667	0.1333	0.8314	0.8382	0.8287	0.8238
0.9000	0.0333	0.0667	0.9090	0.9112	0.9082	0.9058

$S_{Al} = \pm 8.23$ %, $S_{Al} = \pm 8.64$ %, $S_{Al}^{*} = \pm 0.0498$ %, $S_{Al}^{*} = \pm 0.0530$ %.

in Table 3 for the three cross-sections with mole ratios of other two components maintained as 2:1, 1:1 and 1:2 at a temperature of 973 K alongside with the concentrations of Sn and Zn, respectively. This is coupled with the fact that the alloy is considered an important lead-free soldering material for industrial application [23].

Similarly, using the parameters V_{mi}, A_{ji}, A_{ij}, Z_i and Z_j provided in Table 1 and Table 2, the activity values of Al content in the ternary Al-Sn-Zn

systems at different temperatures ranging from 1073 K to 1373 K were predicted using equation 16.

The predictions were made in the ternary systems at each of the three different cross-sections with constant molar ratios of the other two components remaining as 2:1, 1:1 and 1:2, respectively. The results are presented in Table 4 and Table 5, respectively, along with the measured activity of aluminum obtained using the relation [6, 42]:

$$RT \ln a_i(c) = -zFE(c) \tag{17}$$

where F is the Faraday constant, z = 3, is the valence of the ion in the liquid or solid electrolyte, and E is the measured emf of the cell whose values were taken from the literature [6].

Comparison of the calculated activities of aluminum with the respective measured data of the ternary Al-Sn-Zn systems shows good agreement as evident in Table 4 and Table 5, respectively. The predicted activities of Al in the ternary Al-Sn-Zn systems are observed to be less than unity across the three molar sections investigated and also exhibit positive deviation with respect to Raoult's law except around $0.8 \leqslant x_{Al} \leqslant 1.0$. In addition, it is further noticed from Table 4 and Table 5 that the activity decreases with an increase in temperature from 1073 K to 1373 K, which indicates that the system tends towards ideality with the increase in temperature, particularly as regards the existence of deviation (positive) exhibited by the Al-Sn-Zn system. Hence, the results of this study make a contribution to a more complete thermodynamic description of the ternary Al-Sn-Zn systems towards the development of new lead-free solder. The predicted activity results may be useful for further thermodynamic assessment of Al-Sn-Zn system as well as serve as a basis for comparison with some future critical experimental results.

4. Conclusions

Based on the knowledge of molecular or atomic movement of liquid, the effectiveness of the MIVM to predict the activity of Al in a lead-free ternary Al-Sn-Zn system has been examined at different temperatures. The calculated thermodynamic properties exhibit a positive deviation from ideality. The results of the calculated activities of three constituents of binary subsystems of ternary Al-Sn-Zn alloys at the respective temperatures have been compared with corresponding experimental values, showing satisfactory agreement. Bearing in mind that experimental data on multicomponent systems such as a lead-free ternary Al-Sn-Zn systems are still limited in the literature, the theoretical results presented in this study should complement whatever is available and/or serve as a base for further thermodynamic analysis and development of new lead-free solders database.

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