Computational Study of the Thermodynamic Properties of Some Lead-free Solder Alloys

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Abstract

Activities of the components of the binary lead-free solder alloys Cu-Sn, and Ag-Cu were computed using the molecular interaction volume model (MIVM). The theoretical data have been compared with the corresponding experimental values. For the validity of the model parameters, the excess Gibbs free energy of mixing of Cu-Sn, and Ag-Cu liquid alloys have been determined and compared with the corresponding experimental data available in the literature. Similarly, the activities of Sn in ternary liquid alloys Sn-Ag-Cu were computed and examined with the available experimental data at 1000 K. It has been observed that the calculated activities of the components of the binary and ternary solder alloys have nearly the same tendency as the experimental data.

Keywords Activity, Molecular Interaction Volume Model, Excess Gibbs free energy, Binary liquid alloys, Ternary liquid alloys.

1. Introduction

Lead systems are mainly used for soldering purposes due to their low cost. However, the use of lead has environmental and health issues (Abtew & Selvaduray, 2000; Moelans et al., 2003). Today, the use of lead is banned worldwide. One of the main reasons to replace lead in the soldering process is when we dispose of electronic devices such as TVs, mobile phones, computers, etc. on land, it pollutes the groundwater and affects human health. It will be cheaper to replace lead in soldering technology instead of washing the electronic waste. So, the evolution of lead-free soldiers has become the main subject in the electronic field. Unless sudden development of adhesive fixing technology, soldering will remain the main technology (Knott & Mikula, 2002). In the periodic table, in the group of lead Pb, there are a few elements that can replace Pb. The new alloys should have a similar melting point and other criteria for substitute alloys i.e. wetting properties, fatigue resistance, corrosion resistance, non-toxicity, low cost, etc. Nowadays, much research work is being done on the replacement of Pb in solder alloys by others (Knott & Mikula, 2002).

Tin is a soft silvery-white metal that adds shine to materials. It has a lower melting point i.e. 505.15 K and a higher boiling point i.e. 2875 K. Tin alloys are corrosion-

resistant. The combination of copper and tin alloy also called bronze is mostly used in various utensils. Cu-Sn alloys are conductive, soft, non-ferrous, ductile, and have corrosive resistance. Similarly, there are some special characteristics of silver-copper alloys. The other use of such alloys is making good electrical contacts. The combination of less silver and more copper creates new metals such as sterling silver which increases malleability and working capacity. For these reasons, we chose copper-tin and silver-copper alloys for the study of their thermodynamic properties.

The invention of lead-free solder will be a better alternative to the classic Sn-Pb alloys (Official, 2003). Many binaries, ternary, and higher alloy systems have been invented, among which most of them are Sn-based (Amore et al., 2008; Lee et al., 2004). John P. Hager et al. studied the activities of Cu and Sn in Cu-Sn liquid system at 1593 K by Knudsen Cell Mass Spectrometry in1970 (Hager et al., 1970). Activities of the components of Ag-Cu liquid alloys have been investigated based on a simple statistical model by I.S. Jha et al. in 2014 (Jha et al., 2014). The activities in liquid Ag-Cu at 1416 K have been also determined by E. Oktay using mass-spectrometric analysis of effusates (Oktay, 1993). The thermodynamic properties of liquid Sn-Ag-Cu alloys were determined by the electromotive force measurement method by Marek Kopyto et al. at different cross sections of Ag/Cu and for the tin composition ranging from 0.1 up to 0.8 (Kopyto et al., 2010). But its theoretical study based on MIVM hasn't been done yet. Therefore, we decided to measure the activities of the components of binary alloys Cu-Sn and Ag-Cu at 1400 K and 1423 K respectively and the excess Gibbs free energy of mixing for each binary alloy, and also the activities of the component Sn in Sn-Ag-Cu ternary liquid alloys at 1000 K at the three cross-sections keeping Ag to Cu ratios constant as 1:3, 1:1, and 3:1 by applying the MIVM.

MIVM model states that "the liquid molecules are not like gas molecules and they are different from the solid molecules in which they oscillate continuously and remains always in motion from one molecular cell to another and also the central molecules and their nearest molecules are interchangeable, cells movable and identical" (Tao, 2000).

2. Methodology

By the molecular interaction volume model, for a liquid binary alloy, the molar excess Gibbs energy of the liquid mixture i-j, ΔG^{XS} can be given by (Tao, 2000),

$$\Delta G^{XS} = RT \left\{ x_i \ln\left(\frac{V_{mi}}{x_i V_{mi} + x_j V_{mj} A_{ji}}\right) + x_j \ln\left(\frac{V_{mj}}{x_j V_{mj} + x_i V_{mi} A_{ij}}\right) - \frac{x_i x_j}{2}\left(\frac{Z_i A_{ji} \ln A_{ji}}{x_i + x_j A_{ji}} + \frac{Z_j A_{ij} \ln A_{ij}}{x_j + x_i A_{ij}}\right) \right\} \quad (1)$$

For binary alloys, the coefficients of activity of their components are (Tao, 2000),

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

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

For the system of alloys of higher orders i.e. for a multicomponent mixture, Eq. (1) becomes (Tao, 2000),

$$\frac{\Delta G^{XS}}{RT} = \sum_{i=1}^{N} x_i \ln \frac{V_{mi}}{\sum_{j=1}^{N} x_j V_{mj} A_{ji}} - \frac{1}{2} \sum_{i=1}^{N} Z_i x_i \left(\frac{\sum_{j=1}^{N} x_j A_{ji} \ln A_{ji}}{\sum_{j=1}^{N} x_j A_{ji}} \right) \tag{4}$$

For any i^{th} component, the expression of the activity coefficient is given by (Tao, 2008),

$$\ln \gamma_i = 1 + \ln \frac{V_{mi}}{\sum_{j=1}^{N} x_j V_{mj} A_{ji}} - \sum_{j=1}^{N} \frac{x_j V_{mi} A_{ij}}{\sum_{l=1}^{N} x_l V_{ml} A_{lj}} - \frac{1}{2} \left\{ \frac{Z_i \sum_{j=1}^{N} x_j A_{ji} \ln A_{ji}}{\sum_{l=1}^{N} x_l A_{li}} + \sum_{j=1}^{N} \left(\frac{x_j Z_j A_{ij}}{\sum_{l=1}^{N} x_l A_{lj}} \right) \times \left(\ln A_{ij} - \frac{\sum_{l=1}^{N} x_l A_{lj} \ln A_{lj}}{\sum_{l=1}^{N} x_l A_{lj}} \right) \right\} \tag{5}$$

Here the first coordination numbers are denoted by Z_i and Z_j. The expression for Z_i is given by (Tao, 2008),

$$Z_i = \frac{4\sqrt{2\pi}}{3} \left(\frac{r_{mi}^3 - r_{oi}^3}{r_{mi} - r_{oi}} \right) \rho_i r_{mi} \exp\left(\frac{\Delta H_{mi}(T_{mi} - T)}{Z_c RT T_{mi}} \right) \tag{6}$$

Here, the value of molecular number density can be found by the relation $\rho_i = \frac{0.6022}{V_{mi}}$, where $N_i = 0.66022$ is the molecular number, and V_{mi} is the molar volume of the ith component of the alloys. The melting enthalpy and melting temperature have been denoted by ΔH_{mi} and T_{mi} respectively. Z_c is a close-packed coordination, its value is equal to 12 for those liquid metals. R is the gas constant and T is the absolute temperature.

The first peak value of the radial distribution function, r_{oi} is related to the atomic covalent diameter, d_{covi} as (Tao, 2008),

$$r_{oi} = 0.918 d_{covi} \tag{7}$$

And the initial value of the radial distribution function, r_{mi} is related to the atomic diameter, σ_i as (Tao, 2008),

$$r_{mi} = \sigma_i \tag{8}$$

A_{ji} and A_{ij} are the interaction parameters of pair potential energy, which are given by (Odusote et al., 2017),

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

Where, $\varepsilon_{ij}, \varepsilon_{ii}$ and ε_{jj} are the i-j, i-i, and j-j pair potential energies respectively, K is the Boltzmann constant.

Now, infinite dilute activity coefficients are given by (Odusote et al., 2017),

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

and

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

The values of A_{ji} and A_{ij} can be determined by solving Eqs. (10) and (11) by the Newton-Raphson method. Once the proper values of A_{ji} and A_{ij} at a given temperature are obtained on solving, their corresponding values at other temperatures also can be determined (Odusote et al., 2017). For example, for the binary system Ag-Sn at 1000 K; (You et al., 2021)

$$-\frac{\varepsilon_{ji} - \varepsilon_{ii}}{k} = T\ln A_{ji} = 1250\ln(1.3801) = 402.6949$$

$$A_{ji} = \exp\left(\frac{402.6949}{1000}\right) = 1.4958 \text{ at } 1000 \text{ K}$$

and

$$-\frac{\varepsilon_{ij} - \varepsilon_{jj}}{k} = T\ln A_{ij} = 1250\ln(0.7633) = -337.6301$$

$$A_{ij} = \exp\left(\frac{-337.6301}{1000}\right) = 0.7134 \text{ at } 1000 \text{ K}$$

Now, treating Sn-Ag-Cu ternary liquid alloy to be the 1-2-3 system, the activity coefficient of the constituent metal 1 of the system can be obtained from Eq. (5) as (Odusote et al., 2017),

$$\ln\gamma_1 = 1 + \ln\left(\frac{V_{m1}}{x_1V_{m1} + x_2V_{m2}A_{21} + x_3V_{m3}A_{31}}\right) - \frac{x_1V_{m1}}{x_1V_{m1} + x_2V_{m2}A_{21} + x_3V_{m3}A_{31}} - \frac{x_2V_{m1}A_{12}}{x_1V_{m1}A_{12} + x_2V_{m2} + x_3V_{m3}A_{32}} - \frac{x_3V_{m1}A_{13}}{x_1V_{m1}A_{13} + x_2V_{m2}A_{23} + x_3V_{m3}} -$$
$$\frac{1}{2}\left\{\frac{Z_1(x_2A_{21} + x_3A_{31})(x_2A_{21}\ln A_{21} + x_3A_{31}\ln A_{31})}{(x_1 + x_2A_{21} + x_3A_{31})^2} + \frac{Z_2 x_2A_{12}[(x_2 + x_3A_{32})\ln A_{12} - x_3A_{32}\ln A_{32})]}{(x_1A_{12} + x_2 + x_3A_{32})^2} + \frac{Z_3 x_3A_{13}[(x_2A_{23} + x_3)\ln A_{13} - x_2A_{23}\ln A_{23}]}{(x_1A_{13} + x_2A_{23} + x_3)^2}\right\} \tag{12}$$

3. Results and discussion

The necessary input parameters have been taken from Table 1. The values of interaction parameters of pair-potential energy A_{ji}, A_{ij}, and first coordination numbers Z_i, Z_j of the components of the binary system are presented in Table 2. Calculation of coordination numbers can be obtained from Eq. (6). By substituting the values of A_{ji} and A_{ij} in Eqs. (2) and (3), the activities of the components in the system Cu-Sn and Ag-Cu systems at 1400 K and 1423 K can be found which are depicted in Table 3 and Table 4 and they are shown through the graphs in Fig. 1 and Fig. 3 respectively along with the corresponding experimental values. The excess Gibbs free energy of mixing, ΔG^{XS} of those binary alloys can be obtained by Eq. (1), which are also presented in Table 3 and Table 4 respectively.

Table 1. Some Input parameters (Iida T., 1988).

Metal, i	ΔH_{mi} [KJ/mol]	r_{mi} [x10^{-8}cm]	r_{oi} [x10^{-8}cm]	V_{mi} [cm^3/mol]
Cu	13.00	2.50	2.06	7.94[1+1.00x10^{-4}(T-1357)]
Sn	7.07	3.14	2.68	17.00[1+0.87x10^{-4}(T-505)]
Ag	11.30	2.28	2.46	11.64[1+0.98x10^{-4}(T-1234)]

**Table 2.** Calculated values of A_{ji}, A_{ij}, Z_i, and Z_j, of different binary alloys at different temperatures.

i-j	T[K]	A_{ji}	A_{ij}	Z_i	Z_j
Cu-Sn	1400	1.4596	0.7996	9.8401	8.0246
Ag-Cu	1423	0.8653	0.9157	9.5015	9.8019
Ag-Cu	1000	0.8549	0.8951	10.2085	10.6370
Cu-Sn	1000	1.5439	0.6604	10.6370	8.4615
Ag-Sn	1000	1.4958	0.7134	10.2085	8.4615

Table 3. Excess Gibbs free energy of mixing, ΔG^{XS} for Cu-Sn liquid alloys, and the activities of Cu and Sn in Cu-Sn liquid alloy at 1400 K.

x_{Cu}	x_{Sn}	ΔG^{XS}, Th. [Cal/mol]	ΔG^{XS}, Exp* [Cal/mol]	$a_{Cu, Th.}$	$a_{Cu, Exp*}$	$a_{Sn, Th.}$	$a_{Sn, Exp*}$
0.000	1.000	0.0	0.0	0.000	0.000	1.000	1.000
0.100	0.900	-445.2	-291.0	0.022	0.038	0.890	0.892
0.200	0.800	-829.3	-545.0	0.054	0.082	0.763	0.784
0.300	0.700	-1143.1	-784.0	0.099	0.125	0.624	0.681
0.400	0.600	-1376.0	-1017.0	0.162	0.169	0.479	0.580
0.500	0.500	-1514.5	-1238.0±300	0.248	0.220±0.025	0.338	0.467±0.05
0.600	0.400	-1542.3	-1427.0	0.361	0.284	0.213	0.340
0.700	0.300	-1438.4	-1495.0	0.505	0.389	0.114	0.197
0.800	0.200	-1175.1	-1442.0	0.676	0.539	0.047	0.072
0.900	0.100	-714.3	-1018.0	0.856	0.802	0.011	0.007
1.000	0.000	0.0	0.0	1.000	1.000	0.000	0.000

*Experimental (Hultgren, 1973)

From Table 1, it is clear that the theoretical and experimental values of activities of Cu and Sn in Cu-Sn alloys at 1400 K are in reasonable agreement with some discrepancies.
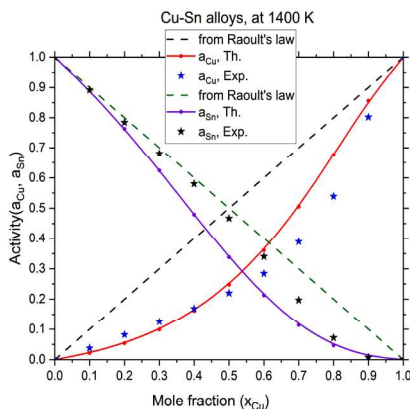
Fig. 1. Theoretical and Experimental variation of Cu and Sn vs. concentration of Cu in Cu-Sn liquid alloys at 1400 K (Hultgren, 1973).

From Fig. 1, it is clear that there is a small deviation between the theoretical and experimental values of activities of Cu in the range of $0.6 < x_{Cu} < 0.8$. In the case of Sn, there is a small deviation between the theoretical and experimental values in the range of $0.3 < x_{Cu} < 0.7$. The negative deviation from Raoult's law shows that the partial vapor pressures of both the components in Cu-Sn at 1400 K are less than their corresponding vapor pressures in the case of an ideal mixture.
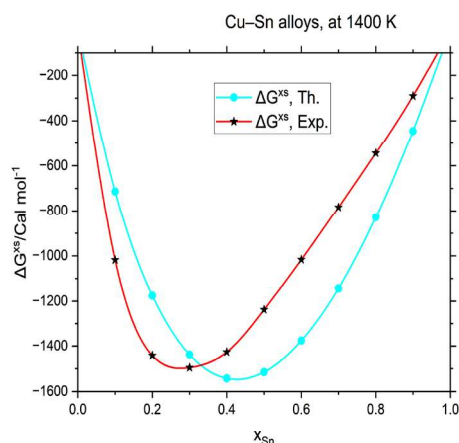

Fig. 2. Excess free energy of mixing, ΔG^{XS} for the liquid alloys in Cu-Sn system at 1400 K from this study compared with literature data (Hultgren, 1973).

The graphical plot for the excess Gibbs free energy of the mixing, ΔG^{XS} of Cu-Sn liquid binary alloys at 1400 K is shown in Fig. 2. Here we can see both the theoretical and the experimental curves have the same trend with some discrepancies. In the entire concentration range, the excess free energy of mixing, ΔG^{XS} has negative values with minimum values i.e. -1542.3 Cal/mol at the concentration $x_{Sn}=0.4$ (Theoretical) and -1495 Cal/mol at the concentration $x_{Sn}=0.3$ (Experimental). The negative values of ΔG^{XS} indicate that after mixing the alloys, the average distance between the molecules of the two liquid metals becomes closer i.e. the volume of the mixture contracts relative to the ideal mixture.

Table 4. Excess Gibbs free energy of mixing for Ag-Cu liquid alloys, and the activities of Ag and Cu in Ag-Cu liquid alloy at 1423 K.

x_{Ag}	x_{Cu}	ΔG^{XS}, Th. [Cal/mol]	ΔG^{XS}, Exp.* [Cal/mol]	$a_{Ag, Th.}$	$a_{Ag, Exp.*}$	$a_{Cu, Th.}$	$a_{Cu, Exp.*}$
0.000	1.000	0.0	0.0	0.000	0.000	1.000	1.000
0.100	0.900	317.3	309.0	0.270	0.266	0.912	0.912
0.200	0.800	556.8	546.0	0.431	0.431	0.844	0.841
0.300	0.700	722.0	714.0	0.533	0.537	0.788	0.782
0.400	0.600	815.8	812.0	0.604	0.610	0.736	0.731
0.500	0.500	840.0	841.0±50	0.662	0.667±0.01	0.683	0.679±0.01
0.600	0.400	799.1	803.0	0.716	0.722	0.621	0.616
0.700	0.300	692.7	701.0	0.772	0.779	0.539	0.535

0.800	0.200	523.2	536.0	0.835	0.841	0.424	0.422
0.900	0.100	291.0	305.0	0.909	0.912	0.255	0.260
1.000	0.000	0.0	0.0	1.000	1.000	0.000	0.000

*Experimental (Hultgren, 1973)

The theoretical values of activities of Ag and Cu in Ag-Cu binary alloy at 1423 K are compared with the experimental values. It has been found that the theoretical values of activities of Ag and Cu mostly concur with their experimental values provided by Hultgren et. al (Hultgren et. al, 1973).
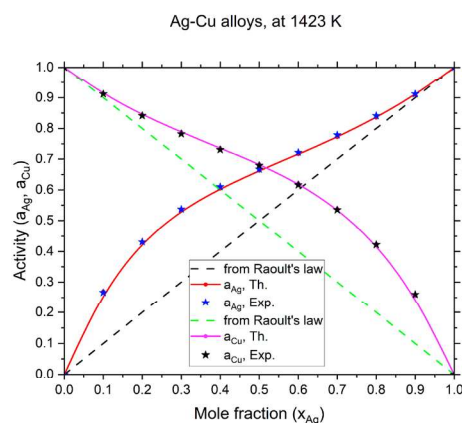

Fig. 3. Theoretical and Experimental variation of Ag and Cu vs. concentration of Ag in Ag-Cu liquid alloys at 1423 K (Hultgren, 1973).

From Fig. 3, it is clear that the activities of both Ag and Cu have the same trend as that of the experimental values provided by the literature. The positive deviation of each component from Raoult's law shows that their partial vapor pressure in the mixture is more than their corresponding partial vapor pressure in the case of an ideal mixture.
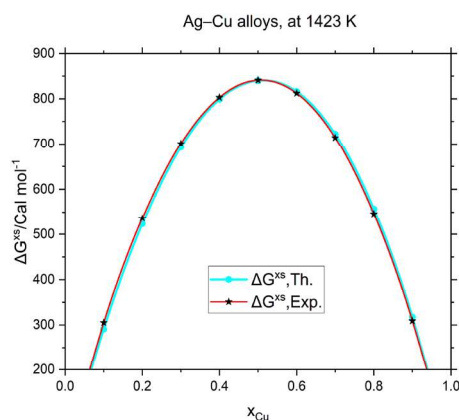

Fig. 4. Excess free energy of mixing, ΔG^{XS} for the liquid alloys in the Ag-Cu system at 1423 K from this study compared with literature data (Hultgren, 1973).

The graphical plot for ΔG^{XS} of Ag-Cu liquid binary alloys at 1423 K is shown in Fig. 4.

Here we can see both the theoretical and the experimental curves have the same trend. In the entire concentration range, ΔG^{XS} has positive values with maximum values i.e. 840 Cal/mol (Theoretical) and 841 Cal/mol (Experimental) both at the same concentration $x_{Cu}=0.5$. The positive values of ΔG^{XS} indicate that after mixing, the average distance between the molecules of the two liquid metals increases i.e. the volume of the mixture expands relative to the ideal mixture.

Table 5. Theoretical and experimental values of activities of Sn in Sn-Ag-Cu ternary alloys at 1000 K at the three cross-sections.

| Ag: Cu=1:3 | | | | | |
x_{Sn}	x_{Ag}	x_{Cu}	$a_{Sn, Th.}$	$a_{Sn, Exp.*}$	$\lvert a_{Sn, Th.} - a_{Sn, Exp.*} \rvert$
0.0000	-------	-------	0.0000	-------	-------
0.1000	0.2250	0.6750	0.0089	0.0036	0.0053
0.2000	0.2000	0.6000	0.0391	0.0474	0.0083
0.3000	0.1750	0.5250	0.1014	0.1982	0.0968
0.4000	0.1500	0.4500	0.1986	0.3493	0.1507
0.5000	0.1250	0.3750	0.3248	0.4695	0.1397
0.6000	0.1000	0.3000	0.4687	0.5809	0.1122
0.7000	0.0750	0.2250	0.6177	0.6740	0.0563
0.8000	0.0500	0.1500	0.7607	0.8141	0.0756
0.9000	0.0250	0.0750	0.8897	-------	-------
1.0000	-------	-------	1.0000	-------	-------
Ag: Cu=1:1					
0.0000	-------	-------	0.0000	-------	-------
0.1000	0.4500	0. 4500	0.0090	0.0061	0.0029
0.2000	0.4000	0.4000	0.0392	0.0567	0.0175
0.3000	0.3500	0.3500	0.1014	0.1909	0.0895
0.4000	0.3000	0.3000	0.1985	0.3630	0.1645
0.5000	0.2500	0.2500	0.3248	0.5166	0.1918
0.6000	0.2000	0.2000	0.4689	0.6287	0.1598
0.7000	0.1500	0.1500	0.6180	0.7472	0.1292
0.8000	0.1000	0.1000	0.7609	0.8588	0.0979
0.9000	0.0500	0.0500	0.8898	-------	-------
1.0000	-------	-------	1.0000	-------	-------
Ag: Cu =3:1					
0.0000	-------	-------	0.0000	-------	-------
0.1000	0.6750	0.2250	0.0121	0.0048	0.0073
0.2000	0.6000	0.2000	0.0470	0.0553	0.0083
0.3000	0.5250	0.1750	0.1133	0.2061	0.0928
0.4000	0.4500	0.1500	0.2124	0.3797	0.1673
0.5000	0.3750	0.1250	0.3378	0.5080	0.1702
0.6000	0.3000	0.1000	0.4790	0.6634	0.1844
0.7000	0.2250	0.0750	0.6243	0.7418	0.1175
0.8000	0.1500	0.0500	0.7639	0.8527	0.0888
0.9000	0.0750	0.0250	0.8905	-------	-------
1.0000	-------	-------	1.0000	--------	-------

*Experimental (Kopyto et al., 2010)

The calculated activities of Sn in the Sn-Ag-Cu system at a temperature of 1000 K are presented in Table 5 and the results are compared with the experimental data of the reference (Kopyto et al., 2010). The agreement between our calculated activities and

experimentally measured ones is almost good in all three cross-sections Ag: Cu = 1:3, 1:1, and 3:1. Here the concentrations of the first component i.e. Sn is varying between 0 and 1.
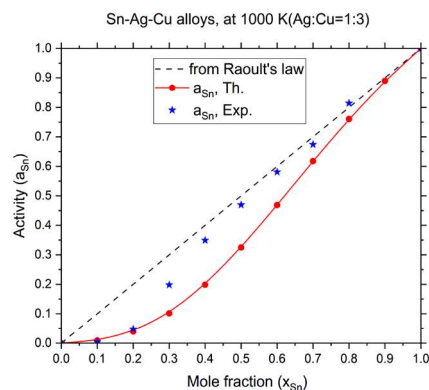

Fig. 5. Variation of activity of Sn vs. concentration of Sn in Sn-Ag-Cu alloy at 1000 K for the cross-section Ag: Cu= 1:3 (Kopyto et al., 2010).
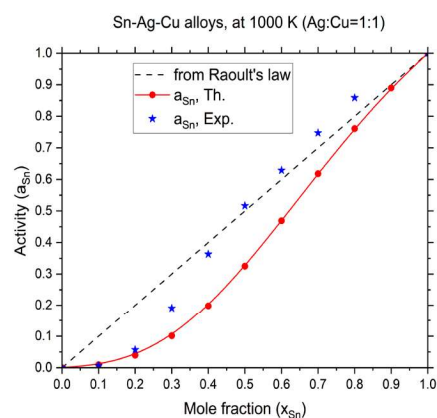

Fig. 6. Variation of activity of Sn vs. concentration of Sn in Sn-Ag-Cu alloy at 1000 K for the cross-section Ag: Cu= 1:1 (Kopyto et al., 2010).
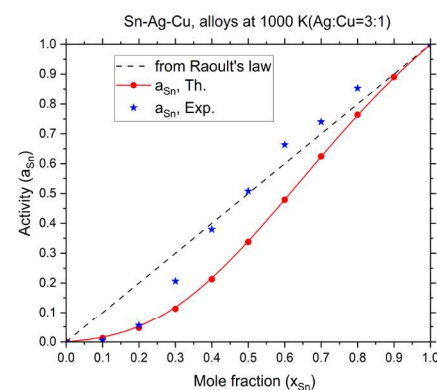

Fig. 7. Variation of activity of Sn vs. concentration of Sn in Sn-Ag-Cu alloy at 1000 K for the cross-section Ag: Cu=3:1 (Kopyto et al., 2010).

From Fig. 5, Fig. 6, and Fig. 7, it is evident that there are the same trends of theoretical activity of Sn in Sn-Ag-Cu alloys at 1000 K as that of the experimental at all three cross-sections of Ag/Cu with some discrepancies. The negative deviation from Raoult's law shows that the partial vapor pressures of the component Sn in Sn-Ag-Cu alloys at 1000 K are less than their corresponding vapor pressures in the case of an ideal mixture. For the cross-section Ag: Cu=1:3, the activities of Sn slightly deviate from the experimental values in the concentration range of 0.3 $<x_{Sn}<$0.6 while for the cross-sections of Ag: Cu=1:1, and 3:1, the activities of Sn slightly deviate from the experimental values in the concentration range of 0.3 $<x_{Sn}<$0.8, otherwise the same tendency has been found with the experimental values. Here also it is to be noticeable that the activity curves in Fig. 5, Fig. 6, and Fig. 7 for all three cross-sections are approaching the ideal behavior line at the higher concentration of Sn. The activity curves for the experimental data in Fig. 6 and Fig. 7 show negative deviation from the ideal Raoult's law for lower concentrations of tin and slightly positive for the higher one.

4. Conclusion

The present study reveals that the molecular interaction volume model is an appropriate model to explain the thermodynamic functions like the excess free energy of mixing and activity of the components of the binary lead-free liquid alloys. The approximate similarities between the experimental & theoretical results (MIVM) for the binaries system promote us for the further study of the ternary and quaternary systems. A negative deviation of the activity of the component metal Cu and Sn from ideal behavior is found to exist in evaluated thermodynamic properties in alloys Cu-Sn and while a positive deviation of the component metal Ag and Cu from ideal behavior is found to exist in Ag-Cu alloys. The observed negative deviation of the activity of Sn in the Sn-Ag-Cu system from ideal mixing has been explained successfully by the present theoretical model. The satisfactory agreement of the theoretical results with corresponding experimental values should be a supplement base for the further development of new lead-free solder alloys.

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