Correlation between Bulk and Surface Properties of AgSn Liquid Alloys

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Received: March 24, 1997; In Final Form: September 17, 1997[⊗]

The energetics and its effect on the alloying behavior of AgSn liquid alloys have been theoretically investigated with the clear aim to correlate bulk phenomenon with surface as well as physical properties. The grand partition function for the bulk and the surface have been solved in the framework of compound formation model with the application of quasi-lattice approximations to obtain analytical expressions for various thermodynamic, structural, physical, and surface parameters. An attempt has also been made to link surface phenomena with the bulk through surface tension and concentration fluctuations in the long-wavelength limit ($S_{CC}(O)$). The little explored area of viscosity and diffusion has also been discussed in the light of compound formation model. Our study reveals that the surface is quite enriched with Sn atoms at all bulk compositions.

1. Introduction

In order to draw a complete picture of mixing in binary liquid alloys it is necessary to evolve a clear understanding[1] about the microscopic structure and the energetics of the bulk as well as surface phenomena. Both bulk[2−7] and surface[8−13] effects are being investigated separately by the application of various theoretical models. It is almost clear[1−3] that interactions among the constituent atoms of the alloy play an important role in the stability of liquid alloys. Besides bulk, much emphasis is being laid to understand the surface phenomenon,[8−10] which is important from metallurgical and catalytic point of view, and establish a link with the bulk properties. Surface segregation,[10−12] which manifests itself as enrichment of the surface by the atoms of a particular component element is influenced not only by the interaction among the atoms but also by surface tension effect. So far as bulk segregation is concerned, much work has been done in this direction. But the existence of intermetallic compounds in liquid alloys at stoichiometric compositions—a phenomenon opposite to bulk segregation—is still little explored. It is interesting to observe that in compound-forming (CF) alloys there is a compound formation in the bulk while the surface is quite enriched with a particular component element causing surface segregation. Two opposite phenomena occur in different parts of the alloy. So the main question to be answered is whether the energetics of the surface causing segregation is same as the bulk or not?

AgSn liquid alloys, which we have chosen, is unique in the sense that its excess free energy of mixing,[14] though negative, is not very large. Despite this, its phase diagram[14] indicates the existence of intermetallic compound (Ag_3Sn) at stoichiometric composition in the solid phase. Since the size mismatch effect in the system is not so prominent, the asymmetric behavior of various observed mixing properties might be due to short-range order. So heterocoordination leading to the formation of clusters pseudomolecules, compounds etc. in AgSn melt cannot be ruled out.

Here an attempt has been made to correlate the bulk phenomenon of AgSn liquid alloys with its surface properties through the study of the concentration dependence of various

thermodynamic, structural, physical, and surface properties. The grand partition function for the system has been solved under the framework of compound formation model to obtain analytical expressions for various parameters. Surface segregation has been discussed in terms of the energetics of the bulk as well as that of the surface part.

The theoretical formalism for various thermodynamic and microscopic structural functions in the framework of compound formation model is presented in section 2. Section 3 deals with viscosity and diffusion while surface properties are presented in section 4. We have concluded in section 5.

2. Thermodynamic and Microscopic Functions for the Bulk

2.1. Excess Free Energy of Mixing and Activity. It may be assumed that the component elements A and B of the binary alloy, AB, might arrange preferentially to form chemical complex, $A_\mu B_\nu$ (μ and ν being integers) in the liquid state, i.e.

$$\mu A + \nu B \rightleftharpoons A_\mu B_\nu$$
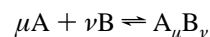
The grand partition function, Ξ, of the alloy, consisting of N_A number of A atoms and N_B number of B atoms, respectively, may be expressed in terms of configurational energy, E, as

$$\Xi = \sum_E (q_A(T))^{N_A} (q_B(T))^{N_B} \exp[(\mu_A N_A + \mu_B N_B - E)/K_B T] \tag{1}$$

$q_i(T)$ and μ_i are atomic partition function and chemical potential of ith ($i = $ A, B) species, respectively. After doing some algebra,[16] one may obtain a relation for the ratio of activity coefficient γ ($\gamma = \gamma_A/\gamma_B$; γ_A and γ_B are activity coefficients of A and B atoms, respectively) for the compound ($A_\mu B_\nu$) forming alloys as

$$\ln \gamma = Z \ln \phi + (Z/2K_B T)(P_{AA}\Delta\epsilon_{AA} - P_{BB}\Delta\epsilon_{BB}) + \mathcal{T} \tag{2}$$

Z is the coordination number and $\mathcal{T}$ is a constant independent of concentration but may depend upon temperature and pressure. ϵ_{ij} is the energy of $i−j$ bond when it is free and $[\epsilon_{ij} + P_{ij}\Delta\epsilon_{ij}]$ denotes its energy when $i−j$ bond is one of the bonds in the complex $A_\mu B_\nu$. P_{ij} denotes the probability of finding the $i−j$ bond as a part of the complex. P_{ij} may be given as

$$P_{AB} = C_A^{u-1}C_B^{v-1}[2 - C_A^{u-1}C_B^{v-1}]$$

$$P_{AA} = C_A^{u-2}C_B^{v}[2 - C_A^{u-2}C_B^{v}]; \quad \mu \geq 2$$

$$P_{BB} = C_A^{u}C_B^{v-2}[2 - C_A^{u}C_B^{v-2}]; \quad \nu \geq 2 \tag{3}$$

and $\ln \phi$ is given as

$$\ln \phi = \frac{1}{2}Z \ln \frac{C_B(\beta + C_A - C_B)}{C_A(\beta + C_B - C_A)} \tag{4}$$

with

$$\beta^2 = 1 + 4C_A C_B(\eta_1^2 - 1) \tag{5}$$

η_1 as been set as follows

$$\eta_1^2 = \exp(Y_1) \tag{6}$$

where

$$Y_1 = \frac{1}{ZK_BT}[2W + 2P_{AB}\Delta W_{AB} - P_{AA}\Delta W_{AA} - P_{BB}\Delta W_{BB}] \tag{7}$$

with

$$\Delta W_{ij} = Z\Delta\epsilon_{ij} \tag{7a}$$

$W [=Z\{\epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2\}]$ is the typical combination of interatomic interaction energies, generally termed as order energy in regular solution theory.

The above expression for $\ln \gamma$ corresponds to strong interacting systems in which the tendency of compound formation is very strong. But there are many alloys in which intermetallic compounds are formed with weak type of interaction; i.e., the interaction energy should be smaller compared to strong interacting systems. With this aim, eq 6 has been reduced in the framework of weak interaction approximation; i.e., energy parameters [(W/ZK_BT) and $(\Delta W_{ij}/ZK_BT)$] should be sufficiently less than unity. This may be achieved by retaining only linear terms in the expansion of $\exp Y_1$ of eq 6, i.e

$$\eta_1^2 \simeq 1 + Y_1 \tag{8}$$

The expressions for β (eq 5) and $\ln \phi$ (eq 4) change into

$$\beta = 1 + 2C_A C_B Y_1 \tag{9}$$

$$\ln \phi = \frac{1}{2}Y_1(C_B - C_A) \tag{10}$$

Application of eqs 9 and 10 in eq 2 provides the expression of $\ln \gamma$ for CF alloys in weak interaction approximation as

$$\ln \gamma = (K_BT)^{-1}[(C_B - C_A)(W + \Delta W_{AB}P_{AB}) + C_A\Delta W_{AA}P_{AA} - C_B\Delta W_{BB}P_{BB}] + \mathscr{T} \tag{11}$$

The value of $\mathscr{T}$ is determined by setting $\int_0^1 \ln \gamma \, dC = 0$. For $\mu = 3$ and $\nu = 1$, it has been found to be

$$\mathscr{T} = \frac{1}{5}\frac{\Delta W_{AB}}{K_BT} - \frac{3}{20}\frac{\Delta W_{AA}}{K_BT} \tag{12}$$

$\ln \gamma$ is related to excess free energy of mixing, G_M^{XS}, through standard thermodynamic relation

$$G_M^{XS} = N\int_0^C \ln \gamma \, dC \tag{13}$$

Equations 11, 12, and 13 give G_M^{XS} for $\mu = 3$ and $\nu = 1$ with $C_A \equiv C$ and $C_B \equiv (1 - C)$ as

$$G_M^{XS} = N\Big[WC(1 - C) + \Delta W_{AB}C\Big(\frac{1}{5} + \frac{2}{3}C^2 - C^3 - \frac{1}{5}C^4 + \frac{1}{3}C^5\Big) + \Delta W_{AA}C\Big(-\frac{3}{20} + \frac{2}{3}C^2 - \frac{3}{4}C^3 + \frac{2}{5}C^4 - \frac{1}{6}C^5\Big)\Big] \tag{14}$$

The expressions for activity coefficients (γ_A and γ_B) for $\mu = 3$, $\nu = 1$ can easily be obtained from eqs 11 and 12 in conjunction with standard thermodynamic relations. These are as

$$\ln \gamma_A = (K_BT)^{-1}\Big[W(1 - C)^2 + \Delta W_{AB}\Big(\frac{1}{5} + 2C^2 - \frac{16}{3}C^3 + 2C^4 + \frac{14}{5}C^5 - \frac{5}{3}C^6\Big) + \Delta W_{AA}\Big(-\frac{3}{20} + 2C^2 - \frac{13}{3}C^3 + \frac{17}{4}C^4 - \frac{13}{5}C^5 + \frac{5}{6}C^6\Big)\Big] \tag{15a}$$

$$\ln \gamma_B = (K_BT)^{-1}\Big[WC^2 + \Delta W_{AB}\Big(-\frac{4}{3}C^3 + 3C^4 + \frac{4}{5}C^5 - \frac{5}{3}C^6\Big) + \Delta W_{AA}\Big(-\frac{4}{3}C^3 + \frac{9}{4}C^4 - \frac{8}{5}C^5 + \frac{5}{6}C^6\Big)\Big] \tag{15b}$$

2.2. Concentration Fluctuations in the Long-Wavelength Limit and Chemical Short-Range Order (CSRO) Parameter. Recently, concentration fluctuations[16] in the long-wavelength limit [$S_{CC}(0)$] has emerged as an important microscopic function to understand the alloying behavior in terms of compound formation and phase segregation. $S_{CC}(0)$ is thermodynamically related to $G_M(G_M^{XS} + RT\sum C_i \ln C_i)$ and activity (a_i). It is given as

$$S_{CC}(0) = NK_BT\Big(\frac{\partial^2 G_M}{\partial C_A^2}\Big)_{T,P,N}^{-1} \tag{16}$$

$$= C_B a_A(\partial a_A/\partial C_A)_{T,P,N}^{-1} \tag{17a}$$

$$= C_A a_B(\partial a_B/\partial C_B)_{T,P,N}^{-1} \tag{17b}$$

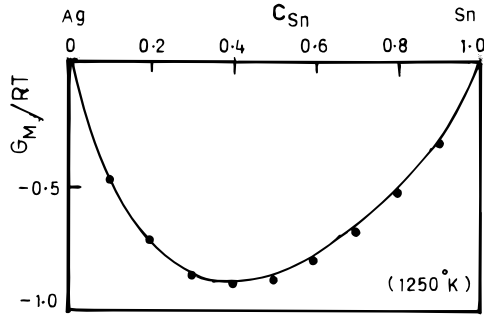Equations 14 and 16 give $S_{CC}(0)$ for $\mu = 3$ and $\nu = 1$ as

$$S_{CC}(0) = C(1 - C)\Big[1 + C(1 - C)(K_BT)^{-1}\Big\{-2W + \Delta W_{AB}\cdot4C\Big(1 - 3C - C^2 + \frac{5}{2}C^3\Big) + \Delta W_{AA}(4 - 9C + 8C^2 - 5C^3)\Big\}\Big]^{-1} \tag{18}$$

The Warren–Cowley[17,18] short-range order (SRO) parameter (α_1) is being frequently used to develop insight into local arrangement of atoms in the molten alloys. α_1 is related to the general probability term X_{ij} (probability of occupation of two lattice sites by i and j atoms) as
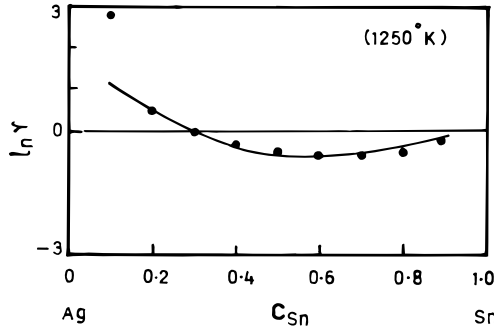
$$X_{ij} = C_iC_j(1 - \alpha_1) \tag{19}$$

The solution of eq 1 connects X_{ij} with the energy parameter η_1 through the relation

$$\frac{(C_i - X_{ij})(C_j - X_{ij})}{X_{ij}^2} = \eta_1^2 \tag{20}$$

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Figure 1. G_M/RT vs C_{Sn} for AgSn liquid alloys: (—) theory, (···) experiment.[14]

Figure 2. $\ln \gamma$ vs C_{Sn} for AgSn liquids alloys: (—) theory, (···) experiment.[14]

Equations 19 and 20 provide an expression for SRO parameter, α_1, as

$$\alpha_1 = \frac{\beta - 1}{\beta + 1} \tag{21}$$

β in weak interaction approximation is already defined by eq 9. For equiatomic composition, α_1 is found to be $-1 \leq \alpha_1 \leq 1$. $\alpha_1^{min} = -1$ means complete ordering of AB pair in the melt, leading to compound formation whereas segregation is indicated by maximum value, $\alpha_1^{max} = 1$.

2.3. Results and Discussion. Since AgSn system is not a very strong interacting system, the expressions derived under weak interaction approximation (for $\mu = 3$ and $\nu = 1$) have been utilized to compute G_M (eq 14), $\ln \gamma$ (eq 11), $S_{CC}(0)$ (eq 18), and α_1 (eq 21) as a function of concentration.

The basic inputs for the computation of above functions are interaction energy parameter (W and ΔW_{ij}). The reasonable choice for W and ΔW_{ij} was made from experimental values of G_M^{XS} at a couple of concentrations. For AgSn liquid alloys at $T = 1250$ K, these are found to be

$$W/K_B T = 7.98; \quad \Delta W_{AB}/K_B T = -3; \quad \Delta W_{AA}/K_B T = 0 \tag{22}$$

The computed values of G_M (Figure 1) and $\ln \gamma$ (Figure 2) are in good agreement with experimental[14] values. G_M vs C is asymmetric around equiatomic composition. G_M is negative at all concentrations. The computed values of $S_{CC}(0)$ and α_1 are presented in Figures 3 and 4, respectively. As regards experimental determination of $S_{CC}(0)$, it is very difficult due to complexities involved in the experiment. However, $S_{CC}(0)$ obtained from observed activity[14] data via eq 17 are taken as experimental values. These values are presented in Figure 3 for comparison. Our computed values of α_1 could not be compared for want of experimental values. it is clear from Figure 3 that $S_{CC}(0)$ deviates considerably from ideal values, $S_{CC}(0,id)$ ($\equiv C_A C_B$). The deviation of $S_{CC}(0)$ from $S_{CC}(0,id)$ is
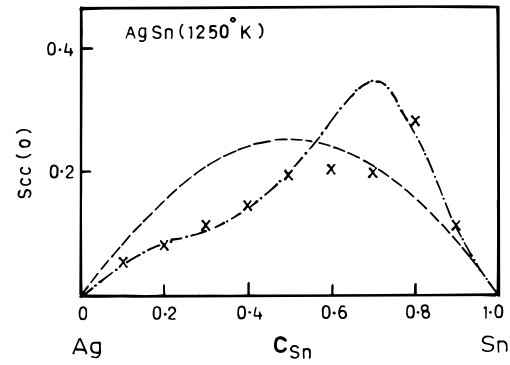
Figure 3. $S_{CC}(0)$ vs C_{Sn} for AgSn liquid alloys: (—·—) theory, ($\times \times \times$) experiment,[14] (- - -) ideal values.
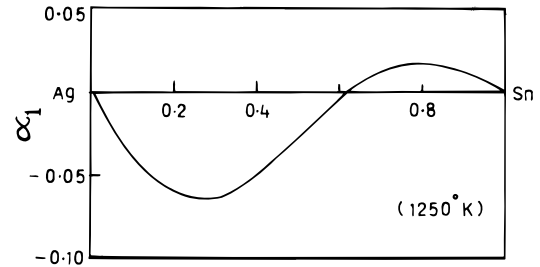
Figure 4. Chemical short-range order parameter α_1 for AgSn liquid alloys.

used to gauge the alloying behavior in liquid alloys. $S_{CC}(0) > S_{CC}(0,id)$ indicates self-coordination which leads to phase segregation whereas heterocoordination causing compound formation is described by $S_{CC}(0) < S_{CC}(0,id)$. In AgSn alloys $S_{CC}(0)$ is smaller than $S_{CC}(0,id)$ in the concentration range, $0 < C_{Sn} < 0.56$ and become greater beyond this range. These values indicate the presence of chemical order in the concentration range $0 < C_{Sn} < 0.55$ and like atoms pairing (self-coordination) beyond this range. Maximum deviation $[S_{CC}(0) - S_{CC}(0,id)]$ in the above range has been noticed around CF concentration $C_{Sn} = 0.25$. The negative values of α_1 (Figure 4) in the concentration range $0 < C_{Sn} < 0.6$ are sufficient to indicate the presence of chemical order in this range. The maximum negative value of α_1 has been found at $C_{Sn} = 0.25$, indicating the existence of Ag₃Sn complex in the alloys. A crossover in α_1 (Figure 4) has been observed around $C_{Sn} = 0.6$.

3. Viscosity and Diffusion Coefficient

Viscosity and chemical diffusion are utilized by theoreticians as well as experimentalists to extract informations about alloying in liquid alloys.

3.1. Expressions for Viscosity and Diffusion Coefficients. One may find various expressions for the viscosity (η) of binary system in the literature.[19-22] For the investigation of viscosity of AgSn liquid alloys as a function of concentration, we have used the following expression[22]

$$\eta = C_A \frac{V_A}{V_M}\left(\frac{v_A}{v}\right)^2 \gamma_A^\alpha \eta_A + C_B \frac{V_B}{V_M}\left(\frac{v_B}{v}\right)^2 \gamma_B^\alpha \eta_B \tag{23a}$$

$$v_A = C_A V_A^{1/3} + \frac{C_B V_B^{4/3}}{V_A} \tag{23b}$$

$$v_B = C_B V_B^{1/3} + \frac{C_A V_A^{4/3}}{V_B} \tag{23c}$$

$$v = C_A V_A^{1/3} + C_B V_B^{1/3} \tag{23d}$$

where V_i ($i =$ A, B) and γ_i ($i =$ A, B) are partial molar volumes and activity coefficient of the ith component, respectively. V_M is the molar volume and η_i is the viscosity of the pure component i. α is a fitted parameter.

The interdiffusion coefficient (D_M) of binary alloy can be expressed[23] in terms of activity (a_i) and self-diffusion coefficient (D_i) of pure component with the help of Darken's equation[24]

$$D_M = D_S \frac{d \ln a_A}{d C_A} \tag{24}$$

with

$$D_S = \sum C_i D_i \tag{25}$$

If we apply eq 17a in eq 24, we obtain an expression for D_M in terms of $S_{CC}(0)$, i.e.

$$D_M = D_S \left[\frac{C_A C_B}{S_{CC}(0)} \right] \tag{26}$$

or

$$\frac{D_M}{D_S} = \frac{C_A C_B}{S_{CC}(0)} \tag{26a}$$

In the case of ideal mixing $S_{CC}(0) \rightarrow C_A C_B$, i.e., $D_M \rightarrow D_S$-[$D_M/D_S \rightarrow 1$] whereas chemical order in the alloy is manifested by

$$D_M/D_S > 1$$

i.e., $D_M > D_S$ since $S_{CC}(0) < C_A C_B$. Similarly for the segregation

$$D_M/D_S < 1$$

i.e., $D_M < D_S$ since $S_{CC}(0) > C_A C_B$.

3.2. Results and Discussion. For the computation of viscosity of AgSn liquid alloy, η, we have used eq 23. Experimental values of activity coefficient[14] and viscosity[25] of pure components (Ag and Sn) are taken. Though experimental values of molar volumes (V_M) are available at $T = 1475$ K, we have used linear volume[26] at $T = 1250$ K. It is observed that experimental values do not deviate considerably from linear values at that temperature. α has been treated as a parameter. So for as this information goes, η for AgSn alloys has not yet experimentally been determined. In order to see the effect of α on viscosity we have calculated η for different values of α. It is interesting to observe (see Figure 5) that α affects considerably the viscosity of AgSn liquid alloys. With positive values of α, a distinct minima is observed. The depth of minima increases with the increasing value of positive α. So far as the negative value of α is concerned, maxima is obtained at a particular concentration. It is proper to mention that compound forming alloys are apt to show maxima[25] in their isothermal viscosity in those composition range where compounds are formed in the solid state. In the case of AgSn system, maxima at CF concentration, $C_{Ag} = 0.75$, has been obtained with $\alpha = -0.8$. The maxima shifts toward the Sn-rich end with the increasing negative value whereas a larger positive α causes displacement of minima toward the Ag-rich end.

The computed values of $S_{CC}(0)$ have been used in eq 26 to evaluate D_M/D_S as a function of concentration. These are presented in Figure 6. It is observed that in the concentration
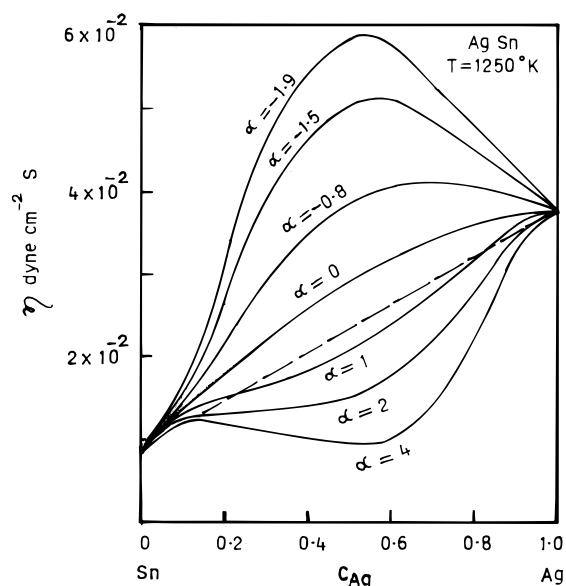

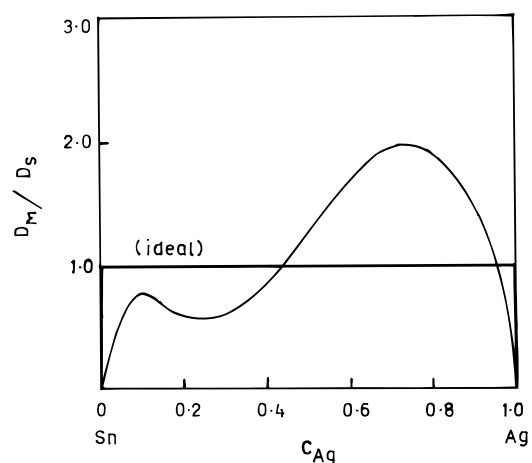**Figure 5.** Viscosity (η) vs C_{Ag} for AgSn liquid alloys at different α.

Figure 6. D_M/D_S vs C_{Ag} for AgSn liquid alloys.

range $0.4 < C_{Ag} < 0.94$, it is greater than 1. This is indicative of the presence of chemical order in this region. Maximum deviation of D_M/D_S from ideal values ($D_M/D_S = 1$) has been noticed around CF concentration, $C_{Ag} = 0.75$. Self-coordination occurs beyond this concentration range because $D_M/D_S < 1$.

4. Surface Properties

4.1. Surface Tension and Surface Composition for Binary Liquid Alloys. Prasad and Singh[10−12] developed an expression for the surface tension of binary liquid alloys by constructing a grand partition function for the surface and solving it in the framework of quasi-lattice theory as

$$\sigma = \sigma_A + \frac{K_B T}{A} \ln \frac{C_A^S}{C_A} + \frac{K_B T}{A} \ln \frac{\gamma_A^S}{\gamma_A}$$

$$= \sigma_B + \frac{K_B T}{A} \ln \frac{C_B^S}{C_B} + \frac{K_B T}{A} \ln \frac{\gamma_B^S}{\gamma_B} \tag{27}$$

where σ_i ($i =$ A or B) is the surface tension of the pure component and A is the mean atomic surface area. C_i^S and γ_i^S refer to the concentration and activity coefficient of the ith ($i =$ A or B) component at the surface, respectively.

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In above model γ_i and γ_i^S are assumed to be related through

$$\ln \gamma_i^S = n(\ln \gamma_i \text{ containing } C_i^S \text{ in place of } C_i) + q \ln \gamma_i \quad (28a)$$

where n and q, usually termed as surface coordination fractions, are fractions of total number of nearest neighbors made by an atom within the layer in which it lies and that in the adjoining layer respectively, so that $n + 2q = 1$.

If one has the proper analytical expression for γ_i, it becomes simple to obtain expression for γ_i^S and subsequently surface tension of binary mixture σ.

Under the framework of the CF model, surface tension of binary liquid alloys, σ, for $\mu = 3$ and $\nu = 1$ may be obtained by using eqs 15, 27, and 28.

$$\sigma = \sigma_A + \frac{K_B T}{A} \ln \frac{C^S}{C} + \frac{W}{A}(n(\phi'-\phi) - q\phi) +$$
$$\frac{\Delta W_{AB}}{A}(n(\phi'_{AB} - \phi_{AB}) - q\phi_{AB}) +$$
$$\frac{\Delta W_{AA}}{A}(n(\phi'_{AA} - \phi_{AA}) - q\phi_{AA}) \quad (29a)$$

$$\sigma = \sigma_B + \frac{K_B T}{A} \ln \frac{1 - C^S}{1 - C} + \frac{W}{A}(n(f' - f) - qf) +$$
$$\frac{\Delta W_{AB}}{A}(n(f'_{AB} - f_{AB}) - qf_{AB}) +$$
$$\frac{\Delta W_{AA}}{A}(n(f'_{AA} - f_{AA}) - qf_{AA}) \quad (29b)$$

where ϕ and f terms are functions of bulk concentration [$C_A \equiv C$; $C_B \equiv (1 - C)$] and ϕ' and f' are functions of surface concentration [$C_A^S \equiv C^S$; $C_B^S \equiv (1 - C^S)$]. These for $\mu = 3$ and $\nu = 1$ are found to be

$$\phi = (1 - C)^2$$
$$\phi_{AB} = \frac{1}{5} + 2C^2 - \frac{16}{3}C^3 + 2C^4 - \frac{14}{5}C^5 - \frac{5}{3}C^6$$
$$\phi_{AA} = -\frac{3}{20} + 2C^2 - \frac{13}{3}C^3 + \frac{17}{4}C^4 - \frac{13}{5}C^5 + \frac{5}{6}C^6 \quad (30a)$$

$$f = C^2$$
$$f_{AB} = -\frac{4}{3}C^3 + 3C^4 + \frac{4}{5}C^5 - \frac{5}{3}C^6$$
$$f_{AA} = -\frac{4}{3}C^3 + \frac{9}{4}C^4 - \frac{8}{5}C^5 + \frac{5}{6}C^6 \quad (30b)$$

$$\phi' = (1 - C^S)^2$$
$$\phi'_{AB} = \frac{1}{5} + 2(C^S)^2 - \frac{16}{3}(C^S)^3 + 2(C^S)^2 - \frac{14}{5}(C^S)^5 - \frac{5}{3}(C^S)^6$$
$$\phi'_{AA} = -\frac{3}{20} + 2(C^S)^2 - \frac{13}{3}(C^S)^3 + \frac{17}{4}(C^S)^4 - \frac{13}{5}(C^S)^5 + \frac{5}{6}(C^S)^6 \quad (30c)$$

$$f' = (C^S)^2$$
$$f'_{AB} = -\frac{4}{3}(C^S)^3 + 3(C^S)^4 + \frac{4}{5}(C^S)^5 - \frac{5}{3}(C^S)^6$$
$$f'_{AA} = -\frac{4}{3}(C^S)^3 + \frac{9}{4}(C^S)^4 - \frac{8}{5}(C^S)^5 + \frac{5}{6}(C^S)^6 \quad (30d)$$

4.2. Surface Tension and Bulk Parameters. Since the inception[16] of structure factors in the long-wavelength limit, particularly $S_{CC}(0)$, it has become clear that fluctuations either in number (ΔN) or in concentration (ΔC) contributes considerably to various anomalous behavior of liquid alloy. One can obtain an expression for σ by extending[27] Cahn−Hillard phenomenological model[28] for pure liquids to binary mixture in terms of fluctuations (ΔN and ΔC) as

$$\sigma \sim ((2\mathcal{A}\, l)/(\varkappa_T N^2)) \left[\{\Delta N + N(\Delta C)\delta\}^2 + \frac{\varkappa_T N^2}{V}\left(\frac{\partial^2 G}{\partial C^2}\right)_{T,P,N}(\Delta C^2) \right] \quad (31)$$

where l is the effective thickness of the liquid interface, $\mathcal{A}_T$ is isothermal compressibility, and δ, termed as dilatation factor, are given as

$$\delta = \frac{1}{V}\left(\frac{\partial V}{\partial C}\right)_{T,P,N} \quad (32)$$

$$\varkappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,P,N,C} \quad (33)$$

$\mathcal{A}$ is accidental fluctuation. The fluctuations in concentration, ΔC, can be determined by minimizing σ with respect to ΔC, i.e., $\partial\sigma/\partial(\Delta C) = 0$. We find

$$\Delta C = [-(\delta/\varkappa_T)\{(1/V)(\partial^2 G/\partial C^2) + (\delta^2/\varkappa_T)\}^{-1}](\Delta N/N) \quad (34)$$

Using eqs 16, 31, and 34 with the conditions

$$\Delta N \sim N$$
$$\Delta N_i \sim N_i$$
$$\Delta C \sim \ll 1$$
$$\mathcal{A} \sim 1/2 \quad (35)$$

we get σ in terms of $S_{CC}(0)$ and $\varkappa_T$ as

$$\sigma \sim (l/\varkappa_T)[1 + \{\delta^2 S_{CC}(0)/NK_B T\varkappa_T\}]^{-1} \quad (36)$$

l appearing in the above equation can be determined by minimizing σ with respect to l, i.e. $d\sigma/dl = 0$.

4.3. Results and Discussion. Equation 29 has been solved numerically to compute surface tension (σ) and surface concentration C_i^S) of AgSn system at $T = 1250$ K. n and q have been treated as parameters and taken as equal to $^1/_2$ and $^1/_4$, respectively. The energy parameters required for the computation are the same (eq 22) as used for bulk parameters. Experimental values[29] for the surface tension of pure components (σ_{Ag} and σ_{Sn}) have been taken. The mean atomic surface area, A, has been calculated from the relation[30]

$$A = 1.12 N^{-2/3} V_M^{2/3}$$

The computed values of σ are presented in Figure 7 along with experimental values.[31] A good agreement between the theory and the experiment[31] is observed. σ is always lower than the ideal values, $\sum C_i \sigma_i$. C_{Sn}^S vs C_{Sn} is depicted in Figure 8. It is observed that Sn atoms segregate to the surface at all alloy compositions. The surface is enriched with Sn atoms even at bulk concentration, $C_{Sn} \simeq 0.25$, where Ag_3Sn complexes are found to be present.
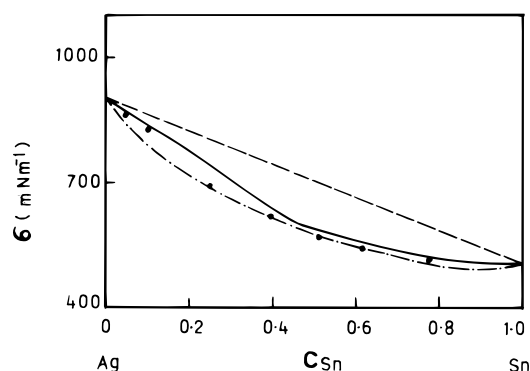
Figure 7. Surface tension (σ) vs bulk concentration (C_{Sn}) for AgSn liquid alloys: (—) theory, eq 29; (—·—) theory, eq 36; (···) experiment;[31] (- - -) ideal values.
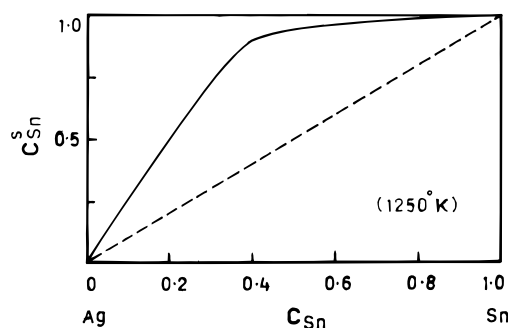
Figure 8. Surface concentration (C_{Sn}^S) vs bulk concentration (C_{Sn}) for AgSn liquid alloys: (—) theory, (- - -) ideal values.

The required input parameters for the computation of σ from eq 36 are $S_{CC}(0)$, $\varkappa_T$, and l. The theoretical values of $S_{CC}(0)$ have been taken and l has been treated as parameter. The experimental values[32] of $\varkappa_T$ are taken. It is interesting to observe (see Figure 7) that despite the fact that eq 36 involves very sensitive parameter, $S_{CC}(0)$, the theory agrees well with the experiment.

5. Conclusion

The phenomenon of compound formation (Ag$_3$Sn) in AgSn liquid alloys at $T = 1250$ K and its effect on mixing properties have been theoretically investigated through the study of concentration dependence of various thermodynamic, structural, physical, and surface properties. The large negative value of G_M, minimum in $S_{CC}(0)$ and α_1, peak in viscosity, and maximum value of D_M/D_S at $C_{Ag} \approx 0.25$ are sufficient to indicate that intermetallic compounds (Ag$_3$Sn) exist in the system at that concentration. The same energy parameters as used for the computation of thermodynamic and structural properties have been used to compute physical as well as surface properties. The surface tension of AgSn liquid alloys, always being smaller than ideal values, decreases with the increase of Sn components.

Sn atoms segregate to the surface at all bulk concentrations. The surface is even quite enriched with Sn atoms at CF concentration, $C_{Sn} \simeq 0.25$. This might be due to surface tension effect. An attempt has also been made to correlate surface tension with bulk properties through $S_{CC}(0)$ and $\varkappa_T$. It is interesting to observe that the despite the involvement of very sensitive bulk parameter, $S_{CC}(0)$, our expressions are giving very good results for AgSn system.

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