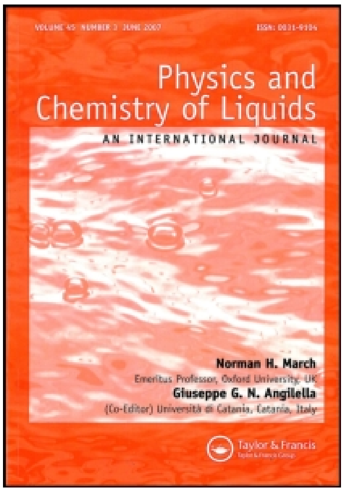

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Structural and energetic asymmetry in liquid Ag-Al alloys

D. Adhikari[a]; B. P. Singh[a]; I. S. Jha[b]
[a] Department of Physics, T.M. Bhagalpur University, Bhagalpur, Bihar, India [b] Deptartment of Physics, M.M.A.M. Campus, Tribhuvan University, Biratnagar, Nepal

To cite this Article Adhikari, D. , Singh, B. P. and Jha, I. S.(2010) 'Structural and energetic asymmetry in liquid Ag-Al alloys', Physics and Chemistry of Liquids, 48: 6, 787 — 796
To link to this Article: DOI: 10.1080/00319101003699008
URL: http://dx.doi.org/10.1080/00319101003699008

Physics and Chemistry of Liquids
Vol. 48, No. 6, December 2010, 787–796

Structural and energetic asymmetry in liquid Ag–Al alloys

D. Adhikari[a]*, B.P. Singh[a] and I.S. Jha[b]

[a]*Department of Physics, T.M. Bhagalpur University, Bhagalpur, Bihar, India;*
[b]*Deptartment of Physics, M.M.A.M. Campus, Tribhuvan University, Biratnagar, Nepal*

(*Received 18 January 2010; final version received 13 February 2010*)

The thermodynamic and microscopic structure of Ag–Al liquid alloy at 1273 K has been studied by using regular associated solution model. This model has been utilised to determine the complex concentration in a regular associated solution of Ag and Al. We have then used the complex concentration to calculate the free energy of mixing, enthalpy of mixing, entropy of mixing, activity and concentration fluctuations in long wavelength limit $S_{CC}(0)$ and the Warren–Cowley short-range parameter α_1. The analysis suggests that heterocoordination leading to the formation of complex Ag_3Al is likely to exist in the liquid but is of a weakly interacting nature. The theoretical analysis reveals that the pairwise interaction energies between the species depend considerably on temperature and the alloy is more ordered towards Ag-rich region. The alloy behaves like a segregating system in Al-rich region.

Keywords: thermodynamic properties; short-range order; complexes

1. Introduction

A large number of binary liquid alloys exhibit interesting behaviour with respect to a function of concentration as regards to thermodynamics properties. The properties of mixing are not symmetrical about equiatomic composition. They deviate maximally from those of ideal alloys. The partial excess free energies and entropies show an S-shaped curvature in their compositional dependence and the heat of mixing and excess free energy of mixing are large negative quantities at one or other concentration [1–3]. Such anomalous behaviour of these liquid alloys have prompted several investigators to propose the existence of 'associations', 'complexes' or 'clusters' [4–10]. Further, the formation of compound in solid state led many theoreticians to believe that 'complexes' or 'pseudomolecules' might exist in the liquid state. Various theoretical models [5,9–11] based on the assumption of complexes in liquid state are being used to investigate alloying behaviour of binary alloys. The relationship of concentration fluctuation in long wavelength limit, $S_{CC}(0)$ with activities [10] and free energy of mixing can also be understood in terms of the presence of complexes. It is proper to mention that $S_{CC}(0)$ has emerged as a powerful microscopic function to visualise the nature of chemical order in the alloy [9,11–13].

Jordan [5] evaluated the thermodynamic equation for liquidus curve of a binary system with congruently melting semiconductors Zn–Te and Cd–Te by assuming

---

*Corresponding author. Email: adksbdev@yahoo.com

ISSN 0031–9104 print/ISSN 1029–0451 online

DOI: 10.1080/00319101003699008
http://www.informaworld.com

complexes or associations in liquid phase to be present. Jordan also derived the approximate activities of the unassociated species and complexes by treating the solution of unassociated species and complexes as regular ternary solution and termed such solution as a regular associated solution. Jordan, however, assumed that both the unassociated species interact equally strongly with the complex. Lele and Rao [14] applied Jordan's analysis with some correction to estimate the complex concentration in a regular associated solution and used it to compute the thermodynamic functions of Mg–Sn and In–Sb system in liquid state. In this study, we have used regular associated solution model to compute thermodynamic functions as well as microscopic functions (concentration fluctuation in long wavelength limit $S_{CC}(0)$ and Warren–Cowley short-range order parameter α_1 [15,16]) for Ag–Al alloy in liquid state, which is known to be associated as Ag_3Al.

Asymmetry in various properties of mixing of Ag–Al alloys in molten state is noticed around equiatomic composition. The size factor ($\Omega_{Ag}/\Omega_{Al} = 1.03$; Ω being the atomic volume) and electronegativity difference ($E_{Ag} - E_{Al} = 0.32$) are not large enough to account for the anomalous behaviour of mixing properties. The phase diagram of Ag–Al alloy from Shunk and Pearson manifests the presence of Ag_3Al and Ag_2Al intermediate phases in the solid state [22]. Several experimental evidences clearly demonstrate that the asymmetric behaviour for a large number of liquid alloys occur at or near the stoichiometric composition where stable intermetallic compound exists in the solid phase. It is, therefore, natural to propose that the 'chemical complexes' or 'psedomolecules' exist in the liquid phase near the melting temperature. An appropriate estimation of the stoichiometry of complexes in the liquid alloy is usually made by an analysis of the physical properties and also from the phase diagram. For simplicity, we assume the Ag_3Al complexes to explain the structural and energetic asymmetry of liquid Ag–Al alloy.

In the next section, the basic expression for the formalism used in the calculation is presented. Section 3 gives the results and discussion of this work and the conclusions are outlined in Section 4.

2. Formalism

Let there be three species in equilibrium in the liquid alloy, namely, monomers A(=Ag), B(=Al) and A_pB(=Ag_3Al) molecules in the respective concentrations n_A, n_B and n_{A_pB} moles. Considering a solution of n_1 atoms of A and n_2 atoms of B, the formation of n_{A_pB} complex requires $n_1 = n_A + pn_{A_pB}$ and $n_2 = n_B + n_{A_pB}$ for conservation of mass in the partially associated solution. When there is association, the thermodynamic behaviour of complexes A and B components is governed by their true mole fractions x_A, x_B and x_{A_pB} rather than their gross mole fraction x_1 and x_2, where

$$x_1 = \frac{n_1}{n_1 + n_2}, \quad x_2 = \frac{n_2}{n_1 + n_2} \tag{1}$$

$$x_A = \frac{n_A}{n_A + n_B + n_{A_pB}}, \quad x_B = \frac{n_B}{n_A + n_B + n_{A_pB}} \quad \text{and} \quad x_{A_pB} = \frac{n_{A_pB}}{n_A + n_B + n_{A_pB}}. \tag{2}$$

Using Equations (1) and (2), the two sets of mole fractions are related to each other by the relations

$$x_{\mathrm{A}} = x_1 - px_2 x_{\mathrm{A}_p\mathrm{B}}, \quad x_{\mathrm{B}} = x_2 - (1 - px_2)x_{\mathrm{A}_p\mathrm{B}}. \tag{3}$$

Prigogine and Defay [17] have shown that in associated solutions, the gross chemical potentials of components 1 and 2 are equal to the chemical potentials of the monomeric species A and B. Following Jordan [5], the activity coefficients γ_{A}, γ_{B} and $\gamma_{\mathrm{A}_p\mathrm{B}}$ of monomers and complex can be expressed in terms of pairwise interaction energies through

$$RT \ln \gamma_{\mathrm{A}} = x_{\mathrm{B}}^2 \omega_{12} + x_{\mathrm{A}_p\mathrm{B}}^2 \omega_{13} + x_{\mathrm{B}} x_{\mathrm{A}_p\mathrm{B}}(\omega_{12} - \omega_{23} + \omega_{13}) \tag{4a}$$

$$RT \ln \gamma_{\mathrm{B}} = x_{\mathrm{A}_p\mathrm{B}}^2 \omega_{23} + x_{\mathrm{A}}^2 \omega_{12} + x_{\mathrm{A}} x_{\mathrm{A}_p\mathrm{B}}(\omega_{23} - \omega_{13} + \omega_{12}) \tag{4b}$$

$$RT \ln \gamma_{\mathrm{A}p\mathrm{B}} = x_{\mathrm{A}}^2 \omega_{13} + x_{\mathrm{B}}^2 \omega_{23} + x_{\mathrm{B}} x_{\mathrm{A}_p\mathrm{B}}(\omega_{13} - \omega_{12} + \omega_{23}), \tag{4c}$$

where ω_{12}, ω_{13} and ω_{23} are the interaction energies for the species A, B; A, $\mathrm{A}_p\mathrm{B}$ and B, $\mathrm{A}_p\mathrm{B}$, respectively, T denotes the temperature and R the universal gas constant.

The equilibrium constant for the reaction $\mathrm{A}_p\mathrm{B} \Longleftrightarrow p\mathrm{A} + \mathrm{B}$ is given

$$k = \frac{x_{\mathrm{A}}^p x_{\mathrm{B}} \gamma_{\mathrm{A}}^p \gamma_{\mathrm{B}}}{x_{\mathrm{A}_p\mathrm{B}} x_{\mathrm{A}_p\mathrm{B}}}. \tag{5}$$

Thus, using Equations (3) to (5), one gets

$$\begin{aligned} \ln k = {} & \ln\left(\frac{x_{\mathrm{A}}^p\, x_{\mathrm{B}}}{x_{\mathrm{A}_p\mathrm{B}}}\right) + \frac{\omega_{12}}{RT}[px_{\mathrm{B}}(1 - x_{\mathrm{B}}) + x_{\mathrm{A}}] \\ & + \frac{\omega_{13}}{RT}\left[px_{\mathrm{A}_p\mathrm{B}}(1 - x_{\mathrm{A}}) - x_{\mathrm{A}}\right] + \frac{\omega_{23}}{RT}\left[x_{\mathrm{A}_p\mathrm{B}}(1 - px_{\mathrm{B}}) - x_{\mathrm{B}}\right]. \end{aligned} \tag{6}$$

Now using the equations listed above, the integral excess free energy ΔG^{xs} is given by

$$\begin{aligned} \Delta G^{\mathrm{xs}} = {} & \frac{1}{(1 + px_{\mathrm{A}_p\mathrm{B}})}(x_{\mathrm{A}} x_{\mathrm{B}} \omega_{12} + x_{\mathrm{A}} x_{\mathrm{A}_p\mathrm{B}} \omega_{13} + x_{\mathrm{B}} x_{\mathrm{A}_p\mathrm{B}} \omega_{23}) + \frac{RT}{(1 + px_{\mathrm{A}_p\mathrm{B}})} \\ & \times (x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}} + x_{\mathrm{A}_p\mathrm{B}} \ln x_{\mathrm{A}_p\mathrm{B}}) - RT(x_1 \ln x_1 + x_2 \ln x_2) \\ & + \frac{x_{\mathrm{A}_p\mathrm{B}}}{(1 + px_{\mathrm{A}_p\mathrm{B}})} RT \ln k. \end{aligned} \tag{7}$$

Once the expressions for $\Delta G (= \Delta G^{\mathrm{xs}} + RT(x_1 \ln x_1 + x_2 \ln x_2))$ is obtained, other thermodynamic and microscopic functions follow readily. Enthalpy of mixing, entropy of mixing and concentration fluctuations in the long wavelength limit are related to ΔG through standard thermodynamic relations

$$\Delta H = \Delta G - T\left(\frac{\partial \Delta G}{\partial T}\right)_{T,P}, \tag{8}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}, \tag{9}$$

$$S_{\mathrm{CC}}(0) = RT\left(\frac{\partial^2 \Delta G}{\partial C^2}\right)^{-1}_{T,P}, \tag{10a}$$

$$S_{\mathrm{CC}}(0) = (1-C)a_1\left(\frac{\partial a_1}{\partial C}\right)^{-1}_{T,P} = Ca_2\left(\frac{\partial a_2}{\partial(1-C)}\right)^{-1}_{T,P}, \tag{10b}$$

where C $(=x_{\mathrm{Ag}})$ is the concentration of A component in the alloy. Using Equation (7) in Equations (8) and (10), we obtained the expressions for ΔH and $S_{\mathrm{CC}}(0)$ as follows:

$$\begin{aligned}\Delta H = {} & \frac{1}{(1+px_{\mathrm{A}_p\mathrm{B}})}(x_{\mathrm{A}}x_{\mathrm{B}}\omega_{12} + x_{\mathrm{A}}x_{\mathrm{A}_p\mathrm{B}}\omega_{13} + x_{\mathrm{B}}x_{\mathrm{A}_p\mathrm{B}}\omega_{23}) - \frac{T}{(1+px_{\mathrm{A}_p\mathrm{B}})} \\ & \times \left(x_{\mathrm{A}}x_{\mathrm{B}}\frac{\partial\omega_{12}}{\partial T} + x_{\mathrm{A}}x_{\mathrm{A}_p\mathrm{B}}\frac{\partial\omega_{13}}{\partial T} + x_{\mathrm{B}}x_{\mathrm{A}_p\mathrm{B}}\frac{\partial\omega_{23}}{\partial T}\right) - \frac{x_{\mathrm{A}_p\mathrm{B}}}{(1+px_{\mathrm{A}_p\mathrm{B}})}RT^2\frac{\mathrm{d}\ln k}{\mathrm{d}T}\end{aligned} \tag{11}$$

$$\begin{aligned}S_{\mathrm{CC}}(0) = {} & \left\{\frac{1}{(1+px_{\mathrm{A}_p\mathrm{B}})}\left[\frac{2}{RT} + (x'_{\mathrm{A}}x'_{\mathrm{B}}\omega_{12} + x'_{\mathrm{A}}x'_{\mathrm{A}_p\mathrm{B}}\omega_{13} + x'_{\mathrm{B}}x'_{\mathrm{A}_p\mathrm{B}}\omega_{23})\right.\right. \\ & \left.\left. + \left(\frac{x'^2_{\mathrm{A}}}{x_{\mathrm{A}}} + \frac{x'^2_{\mathrm{B}}}{x_{\mathrm{B}}} + \frac{x'^2_{\mathrm{A}_p\mathrm{B}}}{x_{\mathrm{A}_p\mathrm{B}}}\right)\right]\right\}^{-1}.\end{aligned} \tag{12}$$

Here, $\partial^2\Delta G/\partial \mathrm{C}^2 > 0$ for $\partial\Delta G/\partial \mathrm{C} = 0$, where prime denotes the differentiations with respect to concentration and x'_{A} and x'_{B} are determined by using Equation (3). $x'_{\mathrm{A}_p\mathrm{B}}$ is determined using Equation (6) and the condition $\mathrm{d}\ln k/\mathrm{d}C = 0$. It may be noted that the factor $(1+px_{\mathrm{A}_p\mathrm{B}})^{-1}$ which appears as a coefficient of all terms containing x_{A}, x_{B} and $x_{\mathrm{A}_p\mathrm{B}}$ in Equations (7), (11) and (12) is a result of the change in the basis for expressing mole fractions of species A, B and $\mathrm{A}_p\mathrm{B}$ from that used for x_1 and x_2.

The experimental determination of $S_{\mathrm{CC}}(0)$ posses more difficulty. It can be determined from measured activity data following Equation (10b) [18]. This is usually considered as the experimental value.

In order to fit the degree of order in the liquid alloy, Warren–Cowley short-range parameter α_1 [15,16] can be estimated from the knowledge of concentration–concentration structure factor $S_{\mathrm{CC}}(q)$ and the number–number structure factor $S_{\mathrm{NN}}(q)$. However, in most diffraction experiments these quantities are not easily measurable for all kinds of binary liquid alloys [19,20]. On the other hand, α_1 can be estimated from the knowledge of $S_{\mathrm{CC}}(0)$ [9,11,21]

$$\alpha_1 = \frac{S-1}{S(Z-1)+1}, \quad S = \frac{S_{\mathrm{CC}}(0)}{S^{\mathrm{id}}_{\mathrm{CC}}(0)}; \quad S^{\mathrm{id}}_{\mathrm{CC}} = C(C-1), \tag{13}$$

where Z is the coordination number and $Z = 10$ is taken for our calculation. We note that varying the value of Z does not have any effect on the position of the minima of α_1; the effect is to vary the depth while the overall feature remains unchanged.

The pairwise interaction energies and equilibrium constant are determined by the following method:

In a regular associated solution, $x_1\gamma_1 = x_A\gamma_A$ and $x_2\gamma_2 = x_B\gamma_B$, where γ_1 and γ_2 are respective gross activity coefficients of components 1 and 2. Thus,

$$\ln\gamma_1 = \ln\gamma_A + \ln\frac{x_A}{x_1} \tag{14a}$$

and

$$\ln\gamma_2 = \ln\gamma_B + \ln\frac{x_B}{x_2}. \tag{14b}$$

Following the technique of Lele and Rao [14] the pairwise interaction energies, the equilibrium constants and the activity coefficients at infinite dilution can be written as follows:

$$\ln\gamma_1^o = \frac{\omega_{12}}{RT} \tag{15a}$$

$$k\exp(\omega_{13}/RT) = \frac{\gamma_1^o\gamma_2^o}{\gamma_1^o - \gamma_2^o}, \tag{15b}$$

where γ_1^o and γ_2^o are activity coefficients of component A and that of B at zero concentrations.

Solving Equations (4a) and (4b), we obtain

$$\frac{\omega_{13}}{RT} = \frac{x_B\ln\left(\frac{a_2}{x_B}\right) + (1-x_B)\ln\left(\frac{a_1}{x_A}\right) - x_B(1-x_B)\frac{\omega_{12}}{RT}}{x_{A_pB}^2} \tag{16}$$

$$\frac{\omega_{23}}{RT} = \frac{x_A\ln\left(\frac{a_1}{x_A}\right) + (1-x_A)\ln\left(\frac{a_2}{x_B}\right) - x_A(1-x_A)\frac{\omega_{12}}{RT}}{x_{A_pB}^2}. \tag{17}$$

Using Equations (6), (16) and (17), we can derive

$$\ln k + \frac{\omega_{13}}{RT} = \left(\frac{1+x_A}{x_{A_pB}}\right)\ln\left(\frac{a_1}{x_A}\right) + \frac{x_B}{x_{A_pB}}\left[\ln\left(\frac{a_2}{x_B}\right) - \frac{\omega_{12}}{RT}\right] + \ln\left(\frac{a_1^p a_2}{x_{A_pB}}\right). \tag{18}$$

3. Results and discussion

The mole fraction x_{Ag_3Al} of complex Ag_3Al is determined by using the experimental data of activity [22] and Equations (15) and (18) employing the iterative procedure. The compositional dependence of various species (Figure 1) shows that the maximum association occurs at 71 at.% of Ag. At this composition and 1273 K, about 31 mol.% of the liquid alloy is associated.

The equilibrium constant and pairwise interaction energies are estimated from the Equations (6), (15a), (16) and (17) and observed data for integral excess free energy of mixing. The equilibrium constant and interaction energies for the alloy Ag_3Al in liquid state at 1273 K are found to be $K = 0.0494$, $\omega_{12} = -11.387\,\text{kJ mol}^{-1}$, $\omega_{13} = -0.617\,\text{kJ mol}^{-1}$ and $\omega_{23} = -28.046\,\text{kJ mol}^{-1}$.

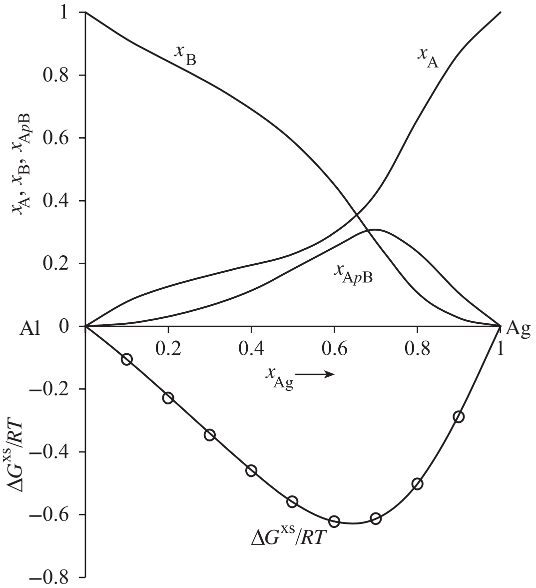

Figure 1. Upper part: compositional dependence of mole fractions x_A (A = Ag), x_B (B = Al) and x_{A_pB} ($A_pB = Ag_3Al$) *vs.* x_{Ag} (concentration of Ag); lower part: integral excess free energy of mixing (ΔG^{xs}/RT) *vs.* x_{Ag} in the liquid Ag–Al solution (1273 K); (——) theory, (○○○) experiment [22].

All the interaction energies are negative and show that Ag and Al atoms are attracted to each other and to the complex.

Theoretical calculation of free energy of mixing for Ag–Al liquid alloy shows that the minimum value of free energy of mixing for Ag–Al is about $-1.22RT$, whereas it is $-3.35RT$ for Hg–K and $-3.13RT$ for Hg–Na [23,24]. This suggests that Ag–Al alloy in liquid state is not as strong an interacting system as liquid amalgams. Figure 1 shows that the agreement between the experimental and calculated integral excess free energies is very good. The agreement between observed and calculated values of activity of Ag and Al is excellent as shown in Figure 2.

If the interaction energies are independent of temperature, i.e., $\partial\omega_{12}/\partial T = 0$ etc., then the heat of formation simply becomes

$$\Delta H = \frac{1}{(1 + px_{A_pB})}(x_A x_B \omega_{12} + x_A x_{A_pB}\omega_{13} + x_B x_{A_pB}\omega_{23}) - \frac{x_{A_pB}}{(1 + px_{A_pB})} RT^2 \frac{\mathrm{d}\ln k}{\mathrm{d}T}.$$

In such situations, ΔH can be obtained from the knowledge of interaction energies between the unassociated atoms and to the complex and $RT^2\,\partial \ln k/\partial T$. We have observed that ΔH and ΔS so obtained are in very poor agreement with experimental data. This simply suggests the importance of the dependence of interaction energies on temperature. On using Equation (11) and observed values of

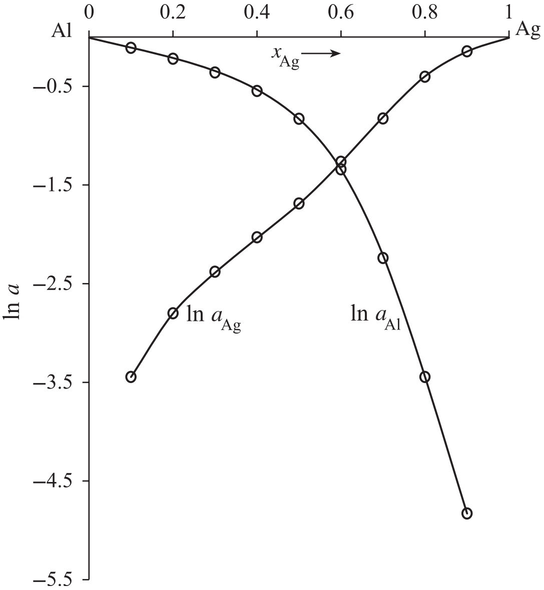

Figure 2. Activity (ln a) of Ag and Al in liquid Ag–Al solution (1273 K) *vs.* x_{Ag}; (——) theory, (○○○) experiment [22].

ΔH [22], we have chosen the following values for the given parameters as the best-fit values for the heat of formation of Ag_3Al complex.

$$\frac{\partial \omega_{12}}{\partial T} = -15.5\,\mathrm{J\,mol\,K^{-1}}, \quad \frac{\partial \omega_{13}}{\partial T} = 0, \quad \frac{\partial \omega_{23}}{\partial T} = -20.5\,\mathrm{J\,mol\,K^{-1}} \text{ and}$$

$$RT^2\frac{\partial \ln k}{\partial T} = 34.4 \pm 0.8\,\mathrm{kJ\,mol^{-1}}.$$

It is found from the analysis that the enthalpy of mixing is negative at all concentration, being minimum around stoichiometric composition ($\Delta H = -0.611\,RT$ at $x_{Ag} = 0.72$). Further, it is observed that the concentration dependence of asymmetry in ΔH can be explained only when one considers the temperature dependence of the pairwise interaction energies. The ΔS^{xs} values are also calculated by using integral excess free energy of mixing and enthalpy of mixing. The calculated values do not always match in sign with experimental values. The discrepancy could be due to errors in enthalpy data or neglect of vibrational and electronic contributions on entropy. The deviations in excess entropy are, however, not significant enough to influence the agreement between calculated and observed thermodynamic functions as shown in Figure 3.

Figure 4 shows the computed and experimental values of $S_{CC}(0)$ as well as ideal values. The calculated values for $S_{CC}(0)$ shows a good agreement with the experimental values. $S_{CC}(0)$ can be used to understand the nature of atomic order in the binary liquid alloys [9,25,26]. At a given composition, if $S_{CC}(0) < S^{id}_{CC}(0)$, ordering in liquid alloy is expected and if $S_{CC}(0) > S^{id}_{CC}(0)$, there is a tendency of segregation, where $S^{id}_{CC}(0)$ (=C(1 − C)) is the ideal value. Our theoretical analysis shows that the order exists for Ag–Al alloy in the liquid state in the region

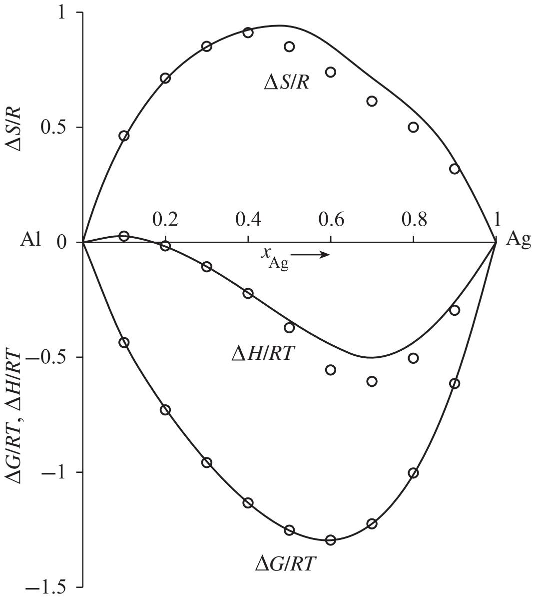

Figure 3. Upper part: entropy of mixing ($\Delta S/R$) *vs.* x_1; lower part: free energy of mixing ($\Delta G/RT$) and heat of mixing ($\Delta H/RT$) *vs.* x_{Ag} of liquid Ag–Al solution (1273 K); (——) theory, (○○○) experiment [1].

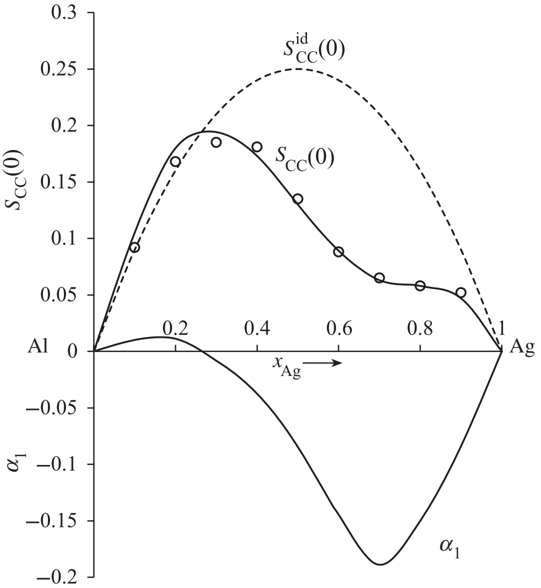

Figure 4. Upper part: concentration fluctuations in long wavelength limit ($S_{CC}(0)$) *vs.* x_{Ag} of liquid Ag–Al solution (1273 K); lower part: short-range ordering parameter (α_1) of liquid Ag–Al solution (1273 K) *vs.* x_{Ag}; (——) theory, (○○○) experiment, (- - - -) ideal values.

$x_{Ag} > 0.25$; the alloy behaves like a slightly segregating system in the region $x_{Ag} \leq 0.25$. $S_{CC}(0)$ is markedly depressed from ideal values near stoichiometric concentration, i.e., around the concentration 0.75 of Ag. Our calculated values of $S_{CC}(0)$ almost matches with the values obtained by Bhatia and Singh [27].

The knowledge of α_1 provides an immediate insight into the nature of the local arrangements of atoms in the mixture. At equiatomic composition, one has $-1 \leq \alpha_1 \leq 1$. The minimum possible value of α_1 is $\alpha_1^{\min} = -1$ and that implies complete ordering of unlike atoms at nearest neighbours. On the other hand, the maximum value of α_1 is $\alpha_1^{\max} = +1$, which implies total segregation leading to the phase separation and $\alpha_1 = 0$ corresponds to a random distribution of atoms. Figure 4 shows that α_1 is negative in the region $x_{Ag} > 0.25$ whereas it is positive in $x_{Ag} \leq 0.25$. This result implies that Ag–Al is an ordering system of unlike atoms in Ag-rich region, whereas it is segregating system in Al-rich concentration. The asymmetry in α_1 is distinctly noticeable.

It is a well-known fact that the size factor and electronegativity difference of the constituent metals play an important role on the alloying behaviour of the binary alloys. The size factor, which has been considered to explain the anomalous behaviour of liquid alloy [28], is very small (= 1.03) and does not seem responsible for asymmetry in such alloys. The electronegativity difference of the constituent metals is also important for making alloys. Many researchers [4,30] have argued that when metals of very different electronegativity are alloyed, a change from metallic behaviour to, at least, partly ionic behaviour is expected. The ionic character ($\mathrm{IC} = 1 - \exp(-0.25d^2)$, d being the electronegativity difference of the constituent metals) of our alloy is also very small (= 0.025). Thus, the anomalous behaviour of our alloys cannot be easily understood at the cost of size factor and electronegativity.

The formation of Ag_3Al complexes in liquid Ag–Al alloys can be discussed on the basis of electron compounds. These compounds are formed at specific electron to atom (e/a) ratio. It is pointed out that the e/a ratio controls certain intermediate phases which are termed as electron compounds. The three e/a ratios that corresponds to the specific structure in alloy systems are 3/2, 21/7 and 7/4. In case of Ag–Al system, the Ag_3Al structure gets three valence electrons from aluminium, one each from silver atoms which give rise to an e/a ratio of six electrons to four atoms. This is same as $e/a = 3/2$.

The observed asymmetry in the free energy of mixing, heat of mixing and entropy of mixing is well explained with our assumed complexes in the liquid Ag–Al alloys. The position of asymmetry seems to be directly linked to the nature of the chemical complexes. The minimum in ΔH has been found to occur close to the compound-forming concentration. We have observed that the computed values of $S_{CC}(0)$, which is useful to understand the microscopic (at atomic level) structure of the liquid alloys, shows a deep minimum in the vicinity of the compound-forming concentration. The variation of α_1 with respect to the concentration of Ag also strengthens the above results.

4. Conclusions

In this work, we have used regular associated solution model to obtain equilibrium constant, pairwise interaction energies of Ag_3Al liquid alloy at 1273 K. The knowledge of nature and extent of interaction energies between the components and complex have been used for the estimation of thermodynamic properties of Ag_3Al alloy in the liquid state. Computed results suggest that Ag–Al is an ordering system of unlike atoms in Ag-rich region, whereas it is slightly a segregating system in Al-rich concentration. The analysis also shows that the Ag–Al system is a weakly interacting heterocoordination system and the pairwise interaction energies of this system depend strongly on temperature. Our theoretical analysis shows that there exist complexes Ag_3Al in Ag–Al alloy in molten state.

Acknowledgements

One of the authors (D. Adhikari) is thankful to University Grant Commission (UGC), Nepal, for providing financial support to pursue the research.

References

[1] P. Chieux and H. Ruppereberg, J. Phys (Les Ulis. Fr.) (Lam 4) **41**, C8-145 (1981).
[2] P. Lamperter, W. Martin, and S. Steeb, J. Non-Cryst. Solids **61**, 279 (1984).
[3] C.N. Wagner, J. Rap. Quen. Met. **BV**, 405 (1982).
[4] J.R. Wilson, Metall. Rev. **10**, 381 (1965).
[5] A.S. Jordan, Metall. Trans. **1**, 239 (1970).
[6] B. Predel and G. Oehime, Z. Metallkd. **67**, 826 (1976).
[7] D. Ahhikari, I.S. Jha, and B.P. Singh, Physica B **405**, 1861 (2010).
[8] B.C. Anusionwu, Pramana J. Phys. **67**, 319 (2006).
[9] R.N. Singh, Can. J. Phys. **65**, 309 (1987).
[10] A.B. Bhatia and W.H. Hargrove, Phys. Rev. B **10**, 316 (1974).
[11] K. Hoshino and W.H. Young, J. Phys. F: Met. Phys. **10**, 1365 (1980).
[12] N.K.P. Singh, R.N. Singh, and R.B. Choudhary, J. Phys. Condens. Matter **3**, 5345 (1991).
[13] R.N. Singh, Phys. Chem. Liq. **25**, 251 (1993).
[14] S. Lele and P. Ramachandra Rao, Metall. Trans. **12B**, 659 (1981).
[15] B.E. Warren, *X-ray Diffraction* (Addison-Wesley, Reading, MA, 1969), p. 227.
[16] J.M. Cowley, Phys. Rev. **77**, 667 (1950).
[17] I. Prigogine and R. Defay, *Chemical Thermodynamics*, (Longmans Green, London, 1974), p. 257.
[18] T.S. Yih and J.C. Thompson, J. Phys. F: Met. Phys. **12**, 1625 (1982).
[19] S. Steeb, F. Falch, and P. Lamparter, Z. Metallkd. **75**, 599 (1984).
[20] C.N.J. Wagner, in *Rapidly Quenched Metals*, edited by S. Steeb and H. Warlemont (North-Holland, Amsterdam, 1985), p. 4095.
[21] R.N. Singh and F. Sommer, Z. Metallkd. **83**, 553 (1992).
[22] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, and K.K. Kelley, *Selected Values of the Thermodynamic Properties of Binary Alloys* (ASM, Metal Park, OH, 1973).
[23] R.N. Singh, I.S. Jha, and D.K. Pandey, J. Condens. Matter **5**, 2469 (1993).
[24] I.S. Jha, R.N. Singh, P.L. Shrivastava, and N.R. Mitra, Philos. Mag. **61**, 15 (1990).
[25] R.N. Singh, I.K. Mishra, and V.N. Singh, J. Phys.: Condens. Matter **2**, 8445 (1990).
[26] L.C. Prasad, S.K. Chattarjee, and V.N. Singh, Physica B **217**, 285 (1996).
[27] A.B. Bhatia and R.N. Singh, Phys. Chem. Liq. **11**, 343 (1982).
[28] A.B. Bhatia and N.H. March, J. Phys. F: Met. Phys. **5**, 1100 (1975).
[29] W.B. Pearson, *The Crystals Chemistry and Physics of Metals* (Wiley Interscience, NY, 1972).
[30] M.L. Saboungi, J. Marr, and M. Blander, J. Chem. Phys. **68**, 1375 (1978).