Volume Effects and Associations in Liquid Alloys

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The regular associated solution model for binary systems has been modified by incorporating the size of the complex as an explicit variable. The thermodynamic properties of the liquid alloy and the interactions between the $A_\mu B$ type of complex and the unassociated atoms in an A-B binary have been evaluated as a function of relative size of the complex using the activity coefficients at infinite dilution and activity data at one other composition in the binary. The computational procedure adopted for determining the concentration of clusters and interaction energies in the associated liquid is similar to that proposed by Lele and Rao. The analysis has been applied to the thermodynamic mixing functions of liquid Al-Ca alloys believed to contain Al_2Ca associates. It is found that the size of the cluster significantly affects the interaction energies between the complex and the unassociated atoms, while the equilibrium constant and enthalpy change for the association reaction exhibit only minor variation, when the equations are fitted to experimental data. The interaction energy between unassociated free atoms remains virtually unaltered as the size of the complex is varied between extreme values. Accurate data on free energy, enthalpy, and volume of mixing at the same temperature on alloy systems with compound forming tendency would permit a rigorous test of the proposed model.

I. INTRODUCTION

IN systems which do not exhibit pronounced electronic effects the deviation from regular solution behavior in liquid alloys can be attributed to chemical short range order resulting from strong associations. Negative heats of mixing with a sharp change in slope near a stoichiometric composition and large negative excess entropy of mixing are characteristic of compound forming liquid alloys. Attractive interactions often manifest themselves in the phase diagram through the appearance of intermetallics at lower temperatures. The liquid phase is assumed to contain short range ordered volume elements, termed associates or complexes, having a well defined stoichiometric composition and free unassociated atoms. Besides the thermodynamic properties, many other physical properties of liquid alloys are also found to exhibit anomalous behavior near such compositions.[1] As shown by Bhatia *et al.*,[2] structure factors in the long wave length limit S_{cc} (0) can also be derived from the model parameters of the associated solution model when data from low angle X-ray and neutron diffraction experiments are not available.

The model of an ideally associated solution was used by the early workers[2,3,4] to describe the thermodynamic mixing functions of liquid alloys. In an ideally associated solution it is assumed that the liquid solution consists of an ideal mixture of the free atoms and the complex in equilibrium. Although this model has been applied with partial success to explain a variety of properties,[5,6,7] it ignores the interactions between the different species in the liquid state. In 1970, Jordan[8] proposed a model for associated liquid mixtures taking into consideration the interaction between the different species and derived equations for the thermodynamic properties and the liquidus curve in the Zn-Te and Cd-Te systems, where *AB*-type clusters predominate. As a first approximation, Jordan[8] suggested that departures from ideality in an associated solution due to short-range nearest neighbor interactions should be taken into account by identifying the activity coefficients γ_A, γ_B, and γ_{AB} with those of a strictly regular ternary solution. Jordan[8] named such solutions as regular associated solutions. Jordan, however, assumed that the interactions between both the unassociated atoms and the complex are approximately equal. In liquid mixtures where the complex has a relatively large volume compared to the unassociated atoms, the model of Jordan[8] may be inadequate to represent the experimental thermodynamic mixing properties.

More recently equations for concentration fluctuations and the thermodynamic properties of compound forming binary liquid alloys were derived by Bhatia and Hargrove[9] adopting two different approaches. In the first instance they treat the ternary mixture of the unassociated species and the complex in the conformal solution approximation, which assumes the volume effects to be small. In the second approach they consider the volume effects through Flory's approximation[10,11] for mixtures of monomers and polymers. However, they have assumed that the volume of the associate is stoichiometrically related to the volume of the free atoms and that the volumes of the free atoms are equal. The methodology for solving the resultant equations for determining the interaction coefficients and the concentration of the cluster in Bhatia and Hargrove's[9] treatment is tedious and involves choosing initial values for the unknown parameters and continuous iteration to get a set of values that gives the best fit to the experimental data.

The mathematical procedure for evaluating the interaction energies and concentration of the complex was greatly simplified by Lele and Rao[12] without introducing any simplifying assumptions. The activity coefficients of the components at infinite dilution of the binary liquid alloy and the activity data at one other intermediate composition have been used for determining the pairwise interaction energies and the equilibrium constant for the formation of the complex. The volume effects have, however, been ignored in their treatment of the regular associated solution.

Since the formation of the complex implies strong interactions, it is physically realistic to expect volume effects. The purpose of this paper is to relax the constraint in Bhatia and Hargrove's treatment regarding the volume of the clus-

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ter. Equations for thermodynamic mixing functions have been formulated here using a modified approach in which the volume of the complex can be varied. If the volume of mixing is known, then relative volume of the complex can be estimated accurately.

II. BASIC EQUATIONS

Mass Balance

Consider one mole of the binary solution comprising of x_1 moles of A atoms and x_2 moles of B atoms. The formation of $A_\mu B$ type complex in this solution will reduce the concentration of free atoms of A and B. The liquid mixture is thus composed of three species: free atoms of A and B and the complex $A_\mu B$. It is convenient to operate with two frames of reference, one referring to the gross mole fractions x_1 and x_2 and the other referring to the actual mole fractions of each specie (x_A, x_B, and $x_{A_\mu B}$). Further, it is assumed that per mole of the binary solution there are n_1 moles of species A, n_2 moles of species B, and n_3 moles of species $A_\mu B$. The two reference frames are interrelated through mass balance:

$$n_1 = x_1 - \mu n_3; \qquad n_2 = x_2 - n_3$$
$$\text{and} \quad n = n_1 + n_2 + n_3 = 1 - \mu n_3 \qquad [1a]$$

$$n_1 = x_A/(1 + \mu x_{A_\mu B}); \qquad n_2 = x_B/(1 + \mu x_{A_\mu B});$$
$$n_3 = x_{A_\mu B}/(1 + \mu x_{A_\mu B}) \qquad [1b]$$

$$x_A = x_1[1 + \mu x_{A_\mu B}] - \mu x_{A_\mu B};$$
$$x_B = x_2[1 + \mu x_{A_\mu B}] - x_{A_\mu B} \qquad [2a]$$

$$x_A = n_1/(1 - \mu n_3); \qquad x_B = n_2/(1 - \mu n_3)$$
$$\text{and} \quad x_{A_\mu B} = n_3/(1 - \mu n_3) \qquad [2b]$$

For the sake of convenience one or more of these frames of reference may be used.

III. FREE ENERGY OF MIXING WITH VOLUME OF COMPLEX AS A VARIABLE

The free energy of mixing for the binary alloy with the presence of associates in it can be written as

$$G^m = -n_3 g + G' \qquad [3]$$

where $(-n_3 g)$ represents the reduction of the free energy due to the formation of the chemical complex and G' is the free energy of mixing of a ternary consisting of A, B, and $A_\mu B$, which are assumed to interact relatively weakly with one another—the strong bonding interaction between A and B atoms having been already taken care of *via* the formation of the chemical complex. A simple approximate expression for G' taking into account the differences in sizes between the unassociated free species and the complex is that due to Flory,[10,11] namely

$$G' = \mathrm{R}T \sum n_i \ln \varphi_i + \sum_{i<j} \sum n_i \varphi_j \lambda'_{ij} \qquad [4]$$

where φ_i is the concentration by volume of the ith species in the mixture and λ'_{ij} ($= 0$ if $i = j$) are interaction energies. For simplicity it may be assumed that the volumes of A and B atoms are nearly the same (r) and the volume of $A_\mu B$ complex is p times that of A or B (*i.e.*, pr). Then,

$$\varphi_1 = n_1/V; \qquad \varphi_2 = n_2/V \quad \text{and} \quad \varphi_3 = pn_3/V,$$
$$\text{where} \quad V = (n_1 + n_2 + pn_3) \qquad [5]$$

Combining Eqs. [3] to [5], the free energy of mixing G^m for the complex forming binary alloy is:

$$G^m = -n_3 g + \mathrm{R}T[n_1 \ln(n_1/V) + n_2 \ln(n_2/V) + n_3 \ln(pn_3/V)] + \frac{n_1 n_2}{V} v_{12} + \frac{n_2 n_3}{V} v_{23} + \frac{n_1 n_3}{V} v_{13} \qquad [6]$$

where

$$v_{12} = \lambda'_{12}, \qquad v_{13} = p\lambda'_{13} \quad \text{and} \quad v_{23} = p\lambda'_{23}$$

Following Jordan,[8] the mixture of free atoms and complex is taken to be a strictly regular ternary solution to a first approximation. The activity coefficients γ_A, γ_B, and $\gamma_{A_\mu B}$ of the unassociated species and complex, respectively, can be expressed in terms of pairwise interaction energies through,

$$\mathrm{R}T \ln \gamma_A = \mathrm{R}T(1 + \ln(n/V) - n/V) + \frac{1}{V}(n_3 v_{13} + n_2 v_{12}) - \left(\frac{1}{V^2}\right) \sum_{i<j}^{3} \sum^{3} n_i n_j v_{ij} \qquad [7a]$$

$$\mathrm{R}T \ln \gamma_B = \mathrm{R}T(1 + \ln(n/V) - n/V) + \frac{1}{V}(n_1 v_{12} + n_3 v_{23}) - \left(\frac{1}{V^2}\right) \sum_{i<j}^{3} \sum^{3} n_i n_j v_{ij} \qquad [7b]$$

$$\mathrm{R}T \ln \gamma_{A_\mu B} = \mathrm{R}T(1 + \ln(pn/V) - pn/V) + \frac{1}{V}(n_1 v_{13} + n_2 v_{23}) - (p/V^2) \sum_{i<j}^{3} \sum^{3} n_i n_j v_{ij} \qquad [7c]$$

These equations are obtained from G' using,

$$\mathrm{R}T \ln \gamma_i = \left(\frac{\partial G'}{\partial n_i}\right)_{T,P,n_j,n_k,\ldots} - \mathrm{R}T \ln\left(\frac{n_i}{n}\right)$$

Equations [7] fulfill the Gibbs-Duhem relationship.

The equilibrium number of chemical complexes at a given temperature and pressure is given by the condition of minimization of free energy as

$$\left(\frac{\partial G^m}{\partial n_3}\right)_{T,P,x} = 0 \qquad [8]$$

Applying this requirement to the expression for free energy of mixing, Eq. [6], substituting for the free energy of formation of the complex g in terms of the equilibrium constant for its dissociation according to $A_\mu B \rightarrow \mu A + B$ and rearrangement results in,

$$K_1 = \frac{n_1^\mu n_2}{n_3 V_f} \exp(-Z) \qquad [9]$$

where,

$$K_1 = K \exp(-\mu); \qquad K = \exp(-g/\mathrm{R}T) \qquad [10]$$

$$V_f = pV^\mu \exp\left[\frac{n}{V}(\mu + 1 - p)\right] \qquad [11]$$

and

$$Z = \frac{1}{V\mathrm{R}T}[-(n_1 + \mu n_2)\nu_{12} + (n_2 - n_3)\nu_{23} + (n_1 - \mu n_3)\nu_{13}] + \frac{(\mu + 1 - p)}{V^2\mathrm{R}T} \cdot [n_1 n_2 \nu_{12} + n_2 n_3 \nu_{23} + n_1 n_3 \nu_{13}] \qquad [12]$$

Equation [9] can also be derived from [1] and [7] using the relationship,

$$K = \frac{x_A^\mu x_B}{x_{A_\mu B}} \frac{\gamma_A^\mu \gamma_B}{\gamma_{A_\mu B}} \qquad [13]$$

IV. ESTIMATION OF MODEL PARAMETERS

A knowledge of the pairwise interaction energies, the mole fraction of the complex, and the relative size of the complex with respect to the free atoms are essential for using Eq. [9]. The transcendental nature of the equations have led some investigators to make simplifying assumptions such as equally strong interactions between the free atoms and complex[8] and ideal association.[13] However, Lele and Rao[12] have shown that all the parameters of the model can be estimated without any assumptions from the activity coefficients at infinite dilution and adoption of an iterative procedure. In the present analysis we have a further unknown parameter (p) introduced through the incorporation of the volume effect. We have adopted a procedure similar to that of Lele and Rao[12] to estimate the interaction energies and concentration of the complex for specific values of p. The procedure is outlined separately for the cases $\mu > 1$ and $\mu = 1$, respectively.

A. *Case* $\mu > 1$

The gross activity coefficients γ_1 and γ_2 of the components are given by,[12]

$$\ln \gamma_1 = \ln \gamma_A + \ln\left[1 - \frac{\mu x_2 x_{A_\mu B}}{x_1}\right] \qquad [14]$$

and

$$\ln \gamma_2 = \ln \gamma_B + \ln\left[1 - \frac{(1 - \mu x_2) x_{A_\mu B}}{x_2}\right] \qquad [15]$$

Using Eqs. [1] and [9] and application of the L'Hospital's rule it can be shown that in the limit $x_1 \rightarrow 0$

$$n_1 \rightarrow 0; \quad n_2 \rightarrow 1; \quad n_3 \rightarrow 0; \quad n_3' \rightarrow x_{A_\mu B}' \quad \text{and} \quad \left(\frac{dx_{A_\mu B}}{dx_1}\right) = 0 \qquad [16]$$

and in the limit $x_2 \rightarrow 0$

$$n_1 \rightarrow 1; \quad n_2 \rightarrow 0; \quad n_3 \rightarrow 0; \quad n_3' \rightarrow x_{A_\mu B}';$$
$$V \rightarrow 1; \quad n \rightarrow 1; \quad V_f \rightarrow p \exp(\mu + 1 - p);$$
$$Z \rightarrow \frac{\nu_{13} - \nu_{12}}{\mathrm{R}T} \quad \text{and} \quad \left(\frac{dx_{A_\mu B}}{dx_2}\right)_{x_2 \rightarrow 0} = \left[1 + K_1 p \exp(\mu + 1 - p) \exp\left\{\frac{\nu_{13} - \nu_{12}}{\mathrm{R}T}\right\}\right]^{-1} \qquad [17]$$

where n_3' and $x_{A_\mu B}'$ indicate differentiation with respect to x_2.

The functions $\ln \gamma_A$ and $\ln \gamma_B$ in the limits $x_1 \rightarrow 0$ and $x_2 \rightarrow 0$, respectively, assumes an identical value of $\nu_{12}/\mathrm{R}T$ by virtue of Eq. [7]. Substitution of these limiting values into Eqs. [14] and [15] yields:

$$\ln \gamma_1^\circ = \nu_{12}/\mathrm{R}T \qquad [18]$$

and

$$\frac{\gamma_1^\circ \gamma_2^\circ}{\gamma_1^\circ - \gamma_2^\circ} = K_1 p \exp(\mu + 1 - p) \exp(\nu_{13}/\mathrm{R}T) \qquad [19]$$

With the information obtained from the known properties at infinite dilution using Eqs. [18] and [19], it is possible to determine the specific values of interaction energies and concentration of the complex as functions of relative size of the complex. The expressions for the interaction energies ν_{13} and ν_{23} can be derived in terms of ν_{12}, a term involving the cluster size, and the gross activities, a_1 and a_2, of the two components and the number of moles of the species A, B, and $A_\mu B$ per mole of the total binary solution at any given concentration x_2 of the liquid alloy using Eqs. [7a] and [7b]. These are given by

$$\frac{\nu_{13}}{\mathrm{R}T} = \frac{V\left[(V - n_2)\ln\frac{a_1}{n_1} + n_2 \ln\frac{a_2}{n_2} + V\ln(1 - \mu n_3) - \frac{\nu_{12}}{\mathrm{R}T}\left\{\frac{n_2 V(V - n_2)}{V^2}\right\} - V\left(1 + \ln\frac{n}{V} - \frac{n}{V}\right)\right]}{n_3(V - n_1 - n_2)} \qquad [20a]$$

and

$$\frac{\nu_{23}}{\mathrm{R}T} = \frac{V\left[(V - n_1)\ln\frac{a_2}{n_2} + n_1 \ln\frac{a_1}{n_1} + V\ln(1 - \mu n_3) - \frac{\nu_{12}}{\mathrm{R}T}\left\{\frac{n_1 V(V - n_1)}{V^2}\right\} - V\left(1 + \ln\frac{n}{V} - \frac{n}{V}\right)\right]}{n_3(V - n_1 - n_2)} \qquad [20b]$$

The equilibrium condition [9] can be rewritten in the form:

$$K_1 p \exp(\mu + 1 - p) \exp(v_{13}/\mathrm{R}T) = \left(\frac{n_1^{\mu} n_2}{n_3 V_f}\right) \exp(-Z) \cdot p \exp(\mu + 1 - p) \exp\left(\frac{v_{13}}{\mathrm{R}T}\right) \qquad [21]$$

The left-hand side of the above equation is determined from the known values of activity coefficients at infinite dilution. Expressions for v_{23} and v_{13} from [20] can be substituted into [21]. Since n_1 and n_2 are related to n_3 through x_2 and μ, n_3 and p are the only remaining unknown parameters in Eq. [21]. Thus, using a numerical iterative procedure, the concentration of the complex as a function of relative size of the complex can be determined by solving Eq. [21] with the values of the activity coefficients at infinite dilution, and activity values at any one composition as inputs. Specific values of K_1, v_{13}, and v_{23} can then be obtained as a function of p with the aid of Eqs. [9], [20a], and [20b], respectively.

B. *Case $\mu = 1$*

In the case when μ is unity, the evaluation of the limiting values of $dx_{A_\mu B}/dx_1$ and $dx_{A_\mu B}/dx_2$ at $x_1 \to 0$ and $x_2 \to 0$ by the same procedure as outlined in the earlier case yields:

$$\ln \gamma_1^\circ = \frac{v_{12}}{\mathrm{R}T} + \ln\left[1 - \left\{1 + K_1 p \exp(2 - p) \cdot \exp\left(\frac{v_{23} - v_{12}}{\mathrm{R}T}\right)\right\}^{-1}\right] \qquad [22]$$

and

$$\ln \gamma_2^\circ = \frac{v_{12}}{\mathrm{R}T} + \ln\left[1 - \left\{1 + K_1 p \exp(2 - p) \cdot \exp\left(\frac{v_{13} - v_{12}}{\mathrm{R}T}\right)\right\}^{-1}\right] \qquad [23]$$

In this special case of μ being unity it becomes difficult to estimate the unknown parameters unless the concentration of cluster is determined independently. A procedure to determine $x_{A_\mu B}$ and the interaction energy v_{12} is outlined below.

Once again, following a procedure similar to that of the previous case (*i.e.*, $\mu > 1$) it can be shown that

$$K_1 p \exp(2 - p) \exp\left(\frac{v_{13}}{\mathrm{R}T}\right) = \frac{\exp\left(\frac{v_{12}}{\mathrm{R}T}\right) \gamma_2^\circ}{\exp\left(\frac{v_{12}}{\mathrm{R}T}\right) - \gamma_2^\circ} \qquad [24]$$

and

$$\frac{v_{23} - v_{13}}{\mathrm{R}T} = \frac{V\left[(V - n_1 - n_2) \ln\left(\frac{n_1}{n_2}\right) + (V - n_1 - n_2) \ln\left(\frac{a_2}{a_1}\right) + \frac{v_{12}}{\mathrm{R}T}\left\{\frac{V(n_2 - n_1) - (n_2^2 - n_1^2)}{V}\right\}\right]}{n_3(V - n_1 - n_2)}$$

$$= \ln\left[\frac{\gamma_1^\circ}{\gamma_2^\circ} \cdot \frac{1 - \gamma_2^\circ \exp(-v_{12}/\mathrm{R}T)}{1 - \gamma_1^\circ \exp(-v_{12}/\mathrm{R}T)}\right] \qquad [25]$$

For an alloy of equiatomic composition where $x_1 = x_2$, *i.e.*, $x_A = x_B$ and $n_1 = n_2$,

$$n_3 = \frac{V \ln\left(\frac{a_2}{a_1}\right)_{x_1 = x_2 = 0.5}}{\ln\left[\frac{\gamma_1^\circ}{\gamma_2^\circ} \cdot \frac{1 - \gamma_2^\circ \exp(-v_{12}/\mathrm{R}T)}{1 - \gamma_1^\circ \exp(-v_{12}/\mathrm{R}T)}\right]} \qquad [26]$$

Combination of Eqs. [21] and [24] for $\mu = 1$ gives,

$$\left(\frac{n_1 n_2}{n_3 V_f}\right) \cdot \exp(-Z) \cdot p \exp(2 - p) \exp(v_{13}/\mathrm{R}T) = \frac{\exp\left(\frac{v_{12}}{\mathrm{R}T}\right) \cdot \gamma_2^\circ}{\exp\left(\frac{v_{12}}{\mathrm{R}T}\right) - \gamma_2^\circ} \qquad [27]$$

The parameter $v_{13}/\mathrm{R}T$ and $v_{23}/\mathrm{R}T$ appearing in Eq. [27] can be expressed in terms of $v_{12}/\mathrm{R}T$ using Eqs. [20]. Equations [26] and [27] can then be solved simultaneously for v_{12} and n_3 at any given value of p after substituting for n_1, n_2, V_f, and Z for $\mu = 1$ using Eqs. [1], [11], and [12]. Separate values for K_1, v_{13}, and v_{23} as a function of the size of the complex are estimated through Eqs. [9] and [20], respectively.

V. DISCUSSION

The regular associated solution model incorporating the volume effect has been applied to the analysis of thermodynamic properties of Al-Ca alloys at 1373 K. The activity data required for the analysis have been taken from a recent study.[15]

The Al-Ca binary system exhibits a stable intermetallic compound Al_2Ca which melts at 1352 K. There are strong indications of the presence of Al_2Ca complex in the liquid at temperatures close to its melting point. Though the phase diagram shows the existence of another intermetallic Al_4Ca, melting incongruently at 973 K, the presence of Al_4Ca complexes is not likely at 1373 K. Hence for the present analysis we have considered a liquid mixture of Al, Ca, and Al_2Ca.

The equilibrium constant for the formation of the complex and the interaction energies for the Al-Ca system at 1373 K have been calculated using the modified regular associated solution model as a function of the size of the complex (p). The results are presented in Table I. The free energy of mixing as a function of the relative complex size was determined from Eq. [6] and is tabulated in Table II along with experimental data. It can be seen that the experimental data

Table I. Interaction Energies in the Al-Ca System at 1373 K as a Function of the Size of the Complex

	Interaction Energies (kJ/mol)			H^{diss}	
p	v_{12}	v_{13}	v_{23}	(kJ/mol)	$K \times 10^2$
1.0	−38.587	−16.771	−22.013	94.859	1.4890
1.2	−38.587	−12.498	−19.084	97.205	1.0375
1.4	−38.587	− 9.219	−17.250	98.593	0.8169
1.6	−38.587	− 6.753	−16.111	99.357	0.6990
1.8	−38.587	− 4.500	−15.345	99.779	0.6267
2.0	−38.587	− 2.676	−14.834	100.020	0.5838
2.2	−38.587	− 0.876	−14.447	100.180	0.5556
2.4	−38.587	0.744	−14.123	100.310	0.5382
2.6	−38.587	2.377	−13.811	100.440	0.5269
2.8	−38.587	3.949	−13.477	100.570	0.5202
3.0	−38.587	5.613	−13.104	100.730	0.5160

Table II. Free Energy of Mixing as a Function of Cluster Size and Composition for the Al-Ca System at 1373 K; $-G^m$ (kJ/mol)

p \ X_{Ca}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
1.0	9.855	16.725	20.874	22.312	21.703	19.667	16.547	12.462	7.293
1.2	9.871	16.794	20.981	22.368	21.714	19.667	16.552	12.471	7.298
1.4	9.879	16.849	21.085	22.425	21.726	19.667	16.557	12.480	7.304
1.6	9.892	16.903	21.186	22.480	21.737	19.667	16.562	12.490	7.310
1.8	9.893	16.937	21.271	22.530	21.747	19.667	16.567	12.500	7.316
2.0	9.902	16.974	21.345	22.572	21.756	19.667	16.571	12.570	7.323
2.2	9.904	16.998	21.401	22.606	21.764	19.667	16.575	12.519	7.329
2.4	9.910	17.023	21.445	22.631	21.770	19.667	16.579	12.529	7.336
2.6	9.913	17.041	21.477	22.649	21.774	19.667	16.583	12.537	7.343
2.8	9.918	17.059	21.502	22.661	21.777	19.667	16.586	12.545	7.349
3.0	9.919	17.071	21.518	22.668	21.779	19.667	16.588	12.552	7.356
Expt. (Ref. 15)	9.881	16.850	20.882	21.158	21.681	19.665	16.564	12.389	7.199

for the free energy of mixing can be fitted for values of p ranging from 1 to 3. When the value of $p = 3$, the volume of the complex is an additive sum of the volumes of free atoms and the result is analogous to that given by Bhatia and Hargrove[9] using Flory's formulae.[10,11] When the value of $p = 1$, the size of the Al_2Ca complex is equal to that of a free atom, and the results correspond to Bhatia and Hargrove's[9] conformal solution model or Lele and Rao's[12] treatment.

The expression for the enthalpy of mixing of a regular associated solution can be given by

$$H^m = -n_3H^{\text{diss}} + \sum_{i<j}^{3}\sum^{3} n_i\varphi_j\lambda'_{ij}$$

$$= -n_3H^{\text{diss}} + \frac{1}{V}\sum_{i<j}^{3}\sum^{3} n_in_jv_{ij} \qquad [28]$$

The values of the equilibrium constant at 1157 K and H^{diss} as a function of the size of the complex were computed through a numerical iteration technique using the Van't Hoff equation,

$$\frac{\partial \ln K}{\partial\left(\frac{1}{T}\right)} = \frac{H^{\text{diss}}}{R}$$

combined with a least square fitting of the experimental values for the enthalpy of mixing reported by Sommer *et al.*[14] between 1125 and 1190 K. The values of H^{diss} and the enthalpy of mixing calculated from Eq. [28] for different values of the cluster size have also been summarized in Table III along with experimental data.[14]

It can be seen from Table I that the size of the complex significantly affects the interaction energies between the complex and the unassociated atoms when the modified model is fitted to the experimental data on the Al-Ca system. The equilibrium constant and the enthalpy change for complex formation exhibit minor variations especially as p tends to unity. The interaction energy between unassociated free atoms remains virtually unaltered. Before these results can be generalized, it is prudent to check the model against other alloy systems. Accurate data on volume of mixing would permit an evaluation of the value of p in a binary system. Coordinated attempts are being made to obtain accurate values for G^m, H^m, and V^m for a simple compound forming system at the same temperature to check the equations derived in this paper. If it is assumed that the volume change on mixing is due purely to complex formation, then it can be shown that

$$V^m = \mathrm{N}rx_{A_\mu B}(p - 1)$$

Table III. Enthalpy of Mixing as a Function of Cluster Size and Composition for Liquid Al-Ca Alloys between 1125 and 1190 K; $-H^m$ (kJ/mol)

p \ X_{Ca}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
1.0	10.672	20.134	25.575	25.461	22.484	18.282	13.575	8.742	4.101
1.2	10.528	20.156	26.334	26.019	22.689	18.326	13.564	8.734	4.109
1.4	10.392	20.121	27.081	26.603	22.932	18.399	13.576	8.736	4.117
1.6	10.266	20.061	27.647	27.080	23.137	18.477	13.590	8.735	4.126
1.8	10.132	19.950	28.040	27.464	23.327	18.554	13.617	8.744	4.139
2.0	10.021	19.855	28.282	27.711	23.465	18.625	13.644	8.757	4.148
2.2	9.904	19.752	28.433	27.892	23.583	18.701	13.679	8.771	4.161
2.4	9.809	19.660	28.522	28.010	23.669	18.772	13.723	8.787	4.173
2.6	9.711	19.575	28.586	28.093	23.743	18.835	13.765	8.810	4.186
2.8	9.623	19.501	28.630	28.160	23.798	18.893	13.814	8.829	4.198
3.0	9.535	19.425	28.669	28.217	23.854	18.951	13.864	8.854	4.210
Expt. (Ref. 14)	9.830	18.220	—	—	—	18.360	14.290	9.780	5.010

where N is the Avagadro number and r the volume of A or B atom. If the volume of mixing is significantly influenced by the interactions between the different species in the associated liquid mixture, one needs to introduce volume interaction terms in the expression for the volume of mixing.

A limitation of the present treatment arises from the assumption that the volumes of the two free atoms A and B are identical. In principle this can easily be relaxed and values for the volume of each type can be computed from density. However, the resulting equations are algebraically unwieldy. For metallic systems size mismatch between atoms is not very significant compared to the difference between the volume of the complex and undissociated atoms.

VI. SUMMARY

In regular associated solution model for a binary system, containing one complex in the liquid, five constants — three w_{ij} terms, K, and H^{diss} — have to be evaluated from experimental data. In the modified treatment presented in this paper, another constant p, designating the volume change in forming a complex, has been added. While the addition of the sixth parameter is not necessary for improving the fit between experimental data and the model, it improves the physical basis of the model. The incorporation of the volume parameter is necessary to explain the negative volumes of mixing in systems that form strong complexes in the liquid.

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