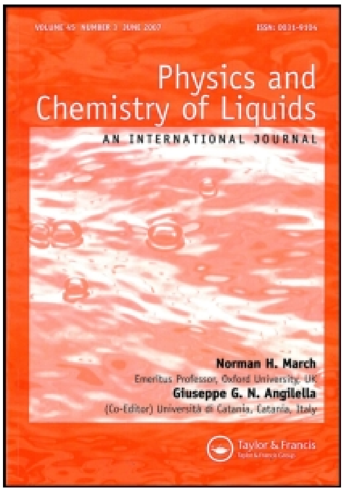

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Thermodynamic Behaviour of Liquid Alloys With Stable Compound of *AB*-Type and Size Distribution of Complexes

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The ideal associated solution model for the thermodynamic mixing functions of the binary liquid alloys with the stable compound is developed. It is suggested that congruently melting compound exists in the form of the arbitrary size complexes in the liquid alloy. For the alloys with stable compound of *AB*-type the distribution of the mole fractions of the complexes of any sizes is found. The thermodynamic mixing functions are expressed by the only energetical parameter (bonding enthalphy of *AB* pair). It is shown that pair enthalpy of *AB* pair can be evaluated from the melting temperature and geometry of the crystal lattice of *AB*-compound in nearest neighbours approach.

Application of the model to liquid alloys of aluminium, gallium and indium with antimony is discussed.

INTRODUCTION

Today extensive experimental data on physical and chemical properties of liquid alloys have been accumulated. Concentration dependence behaviour of thermodynamic properties of such systems can be explained on the basis of various phenomenological theories and in particular the ideal associated solution theory.[1-4] Liquid alloys are usually represented in this model as consisting of single atoms of pure components and associates of a determined composition.[2-4]

However this type of analysis brings up new questions concerning the nature of complexes and their binding with respective intermetallic compounds in solid phase.

Some authors (see recent reviews[2,3]) in characterizing thermodynamic behaviour of liquid alloys choose the composition of complexes rather arbitrarily. For example, in In–Sb alloys having a single compound InSb in solid phase, the presence of two complexes InSb and In_3Sb in liquid is assumed; in Mg–Pb alloys having Mg_2Pb in solid phase, the presence of Mg_2Pb and MgPb in liquid is assumed etc. It has been found for bunary liquid alloys[3] that only a few have stoichiometry of complexes similar to that of respective compound in phase diagrams.

Also the fact is often ignored that many of these alloys do not contain any intermetallic compounds and no difference is made between compounds that decompose during melting and those that do not. Moreover, efforts to minimize the number of parameters often result in reducing consideration to complexes of the smallest size only, which is unfounded in terms of basic theory.

In this paper an attempt is made to relate complexing in liquid alloys to stable intermetallide melting by an example of systems with congruently melting AB-compound. It is assumed here that complexes of random sizes are present in liquid alloys.

Applicability of this approach is discussed for Al-, Ga- and In-Sb alloys.

GENERAL THEORY

Consider a binary A_cB_{1-c} system, in which the following equilibria take place

$$iA + jB = A_iB_j,$$

characterized by a set of formation constants of $A_iB_j - K_{ij}$ complexes dependent on temperature and component nature.

This study does not consider the possibility of pure component association and observed activities a_A and a_B are therefore set equal to respective molar fractions of single atoms A and B.[1] Accordingly to obtain them two independent equations are necessary.

As it is assumed in this model that complexes do not react neither with each other, nor with single atoms, the equation of normalization of all molar fractions of the system will have the form

$$1 - x_{A_1} - x_{B_1} - \psi(x_{A_1}, x_{B_1}) = 0, \tag{1}$$

where

$$\psi(x_{A_1}, x_{B_1}) = \sum_{i,j=1}^{\infty} K_{ij} x_{A_1}^i x_{B_1}^j = \sum_{i,j=1}^{\infty} x_{A_iB_j}$$

The second independent equation will be the balance equation, e.g., with respect to component A.

Since

$$c = \left(N_{A_1} + \sum_{i,j=1}^{\infty} iN_{A_1}B_j\right)\left(N_{A_1} + N_{B_1} + \sum_{i,j=1}^{\infty} (i+j)N_{A_iB_j}\right)^{-1}$$

where N_{A_1} and N_{B_1} are the numbers of single A and B atoms respectively and N is the number of A_iB_j complexes, then multiplying and dividing the right-hand side of the above expression by $N_{A_1} + N_{B_1} + \sum_{i,j=1}^{\infty} N_{A_iB_j}$ we get

$$c = \left(x_{A_1} + x_{B_1}\frac{\partial\psi}{\partial x_{A_1}}\right)\kappa_{AB}^{-1} \tag{2}$$

where $\kappa_{AB} = x_{A_1} + x_{B_1} + x_{A_1}\partial\psi/\partial x_{A_1} + x_{B_1}\partial\psi/\partial x_{B_1}$ is the average number of atoms per complex.[1]

Infinite limits of the sums (1, 2) suggest the possibility of formation of very large complexes beginning from certain temperatures corresponding to liquid solution solidification.

Thus with knowledge of K_{ij} values the summation is made and the resulting set of Eqs (1, 2) allows to evaluate concentration dependences of the activities. Other thermodynamic functions of mixing are obtained from general relationships.

ALLOYS WITH STABLE INTERMETALLIC COMPOUND OF *AB*-TYPE

Alloys with semiconducting $A^{\mathrm{III}}B^{\mathrm{V}}$ compound in solid phase (Al-, Ga- and In-Sb) may serve as characteristic examples of such systems.

In the case of alloys of this type it is natural to believe that melt retains the ordering which leads to formation of stoichiometric AB-compound (at least when slightly overheated above liquidus line). However, while it is a "giant complex" with a characteristic crystalline order in solid phase, in liquid phase we deal with an equilibrium concentration distribution of $(AB)_n$-type complexes ($n = 1, 2, \ldots$) that depends on temperature and the nature of A and B components.

Since the condition of chemical equilibrium

$$nA + nB = (AB)_n \tag{3}$$

has the form

$$n\mu_A + n\mu_B - \mu_{(AB)_n} = 0$$

the complex formation constant is expressed by

$$K(n) = \exp[n\mu_A^0 + n\mu_B^0 - \mu_{(AB)_n}^0/k_B T] \tag{4}$$

where μ_i^0 are standard chemical potentials of reactants. The quantity in parentheses is the variation of standard thermodynamic potential ($-\Delta G^0$) of the reaction (3).

Let the variation of standard enthalpy during (AB)-complex formation be

$$\Delta H^0(n) = H_{(AB)_n} - nH_{A_1} - nH_{B_1} = -\alpha m_n \tag{5}$$

where α-bonding enthalpy of AB pair, m_n—the number of AB pairs in complex containing n—"molecules".

Introducing the effect of electron subsystem (for metallic systems) into the free electron approximation as well as that of phonon subsystem into the harmonical approach allows to obtain terms linearly related to the size, but the parameter α becomes temperature dependent. Contributions to of surface (proportional to $n^{2/3}$) and of complex rotation (assuming free rotation proportional to $\ln n^5$) are not considered in this paper.

Neglecting to the temperature dependent contributions to of phonon and electron subsystems we have

$$K(n) = \exp(\alpha m_n/k_B T) \tag{6}$$

It is known,[6,7] that the short-range order typical for solids usually remains in liquid state that is confirmed with the diffraction investigations. Therefore we restrict ourselves to the considerations of the complexes in which mutual arrangements of the atoms are the same as in solid and the number of AB pairs is maximum.

Thus we can express all the thermodynamic mixing functions in terms of the only energetical parameter α, which can be related with the melting temperature of the corresponding chemical compound. As the thermodynamic potential of mixing in the ideal associated solutions at the point $c = 0.5$ and that in the solid is

$$\Delta G_L^M(0.5) = k_B T \ln a_A(0.5), \Delta G_S^M(0.5) = -\frac{\alpha z}{2}, \tag{7}$$

where z is the coordination number of AB compound, then equating these expressions at the melting temperature (T_m^{AB}) we get

$$a_A(0.5) = a_B(0.5) = e^{-\alpha z/2k_B T} \tag{8}$$

This relation within the equation of normalization (1) of the mole fractions in liquid alloy at $c = 0.5$ allows to get the bonding enthalpy of AB pair and the activities of the components of this temperature.

Thus substituting (6) in the set of Eqs (1 – 2) we get the following set of equations for concentration dependences of the activities of A and B components

$$1 - a_A - a_B - \sum_n \exp(\alpha m_n/k_B T)(a_A a_B)^n = 0$$

$$c = \left[a_A + \sum_n n \exp(\alpha m_n/k_B T)(a_A a_B)^n \right] \times \left[a_A + a_B + 2\sum_n n \exp(\alpha m_n/k_B T)(a_A a_B)^n \right]^{-1} \qquad (9)$$

Enthalpy of mixing H^M is calculated in the following way. By definition we have

$$\Delta H^M = \sum_n H_{(AB)_n} N_{(AB)_n} + N_{A_1} H_{A_1} + N_{B_1} H_{B_1} - N_A H_A - N_B H_B,$$

where H_i are absolute enthalpies of single atoms and complexes, N_A and N_B are total numbers of atoms of A and B types in binary system. Since $H_{A_1} = H_A$ and $H_{B_1} = H_B$, because pure liquids only contain single atoms and since $N_A = N_{A_1} + \sum_n nN_{(AB)_n}$, $N_B = N_{B_1} + \sum_n nN_{(AB)_n}$, we shall have

$$\Delta H^M = \sum_n N_{(AB)_m}(H_{(AB)_n} - nH_A - nH_B).$$

The bracketed quantity is none other than αm_n taken with reversed sign. Therefore the ultimate expression for enthalpy of mixing per atom

$$\Delta H^M = -\alpha \sum_n m_n \exp(\alpha m_n/k_B T)(a_A a_B)^n \times \left[a_A + a_B + 2\sum_n n \exp(\alpha m_n/k_B T)(a_A a_B)^n \right]^{-1} \qquad (10)$$

Thermodynamic potential of mixing per atom is

$$\Delta G^M = k_B T[c \ln a_A + (1 - c) \ln a_B] \qquad (11)$$

Entropy of mixing per atom will be, as usual,

$$\Delta S^M = T^{-1}(\Delta H^M - \Delta G^M) \qquad (12)$$

In the region of concentrations near zero or unity it is easy to obtain asymptotic expressions for thermodynamic quantities. Thus, at $c \to 0$ we get for the activities in the second order in concentration

$$a_A = \frac{c}{1 + K_1} - \frac{K_2 - K_1(1 + K_1)}{(1 + K_1)^3} c^2$$

$$a_B = 1 - c + \frac{K_2 - K_1(1 + K_1)}{(1 + K_1)^2} c^2, \qquad (13)$$

where K_1, K_2-formation constants of AB and $(AB)_2$ complexes respectively. Comparison of the above expressions with the model that only takes into account one complex of the smallest size (AB) indicates that discrepancy begins to reveal itself in the second order in concentration. Similar expressions obtained by expansion (26.67) in [1] give (to the same accuracy)

$$a_A = \frac{c}{1+K_1} + \frac{K_1}{1+K_1} c^2$$

$$a_B = 1 - c.$$

At $c \to 1$ the expressions will be symmetrical with respect to substitution of a_A for a_B and c for $1 - c$.

The expressions for partial enthalpies in the case of infinite dilution will be following: since

$$\bar{h}_A(0) = -k_B T^2 \frac{\partial \ln \gamma_A(0)}{\partial T},$$

where γ_A is an activity coefficient of A using (13), then we get

$$\bar{h}_A(0) = -\frac{\alpha K_1}{(1+K_1)^2} \tag{14}$$

By above-mentioned symmetry, the same expression may be written for $\bar{h}_B$ (1).

RESULTS AND DISCUSSION FOR LIQUID ALUMINIUM-, GALLIUM- AND INDIUM-ANTIMONY ALLOYS

Considering alloys of aluminium, gallium and indium with antimony form the semiconductor compounds of $A^{\mathrm{III}}B^{\mathrm{V}}$-type with the ZnS-type structure (coordination number $z = 4$) in the solid state. Thus to relate the bonding enthalpy of AB pair with the melting temperature of the corresponding compound (in accordance with general remarks of section III), it is necessary at first to solve the geometrical problem (to find the maximum number of bonds of A–B type for given structure in nearest neighbours approach if the number of AB pairs, i.e.—size of complex (n) are given). As it will be shown below it is quite enough to restrict ourselves to the maximum n about ten for our purposes, i.e. for the evaluation of the thermodynamic mixing functions.

The results of this geometrical solution are represented in Table I.

TABLE I

The maximum number of bonds (m_n) in ZnS type structure for fixed size of complex (n)

n	1	2	3	4	5	6	7	8	9	10
m_n	1	3	6	8	11	14	18	20	23	26

Further using the relation (8) with $z = 4$ the equation of normalization at $c = 0.5$ will be

$$1 - t - \sum_n t^{(4n - m_n)/2} = 0$$

where $t = a_A(0.5, T_m^{AB}) = a_B(0.5, T_m^{AB})$.

It easy to solve this equation by numerical methods (we are interested in the physical solution in the region $0 < t < 1$).

So for given structure

$$\alpha = 0.547 k_B T_m^{AB} \quad \text{and} \quad a_A(0.5) = a_B(0.5) = 0.335.$$

The calculation of the bonding entalpies of AB pairs using the melting temperatures of ALSb, GaSb and InSb compounds[8] gives the following values: 6040, 4500 and 3640 (J mol^{-1}), respectively.

The computer calculations were performed to find the concentration dependences of the thermodynamic mixing functions.

The system of non-linear Eqs (9) was solved by Newton method and the solutions of the previous step were used as the initial conditions.

Figures 1-5 show calculated thermodynamic functions and activities of component for these alloys as a function of antimony concentration.

In general the values of activities and thermodynamic potential of mixing are in good agreement with experimental determinations although the accuracy of the experiments on these properties is not high enough. This fact is well illustrated by the values of activities for liquid Ga-Sb alloys collected by the authors of [10] as well as by their own experiment.

The agreement between calculated and experimental enthalpies of mixing, measured with a higher precision is rather of qualitative kind. Similarly, comparison of temperature dependences of enthalpy of mixing, at $c_{Sb} = 0.5$, for In-Sb alloys only shows a qualitative agreement with experimental studies.[13] The behaviour of calculated temperature dependence is more gentle than that of experimental dependence revealing though a weak nonlinear form which is in qualitative agreement with experiment (~ 1.5 J mol^{-1} K^{-1} against ~ 4 J mol^{-1} K^{-1}).

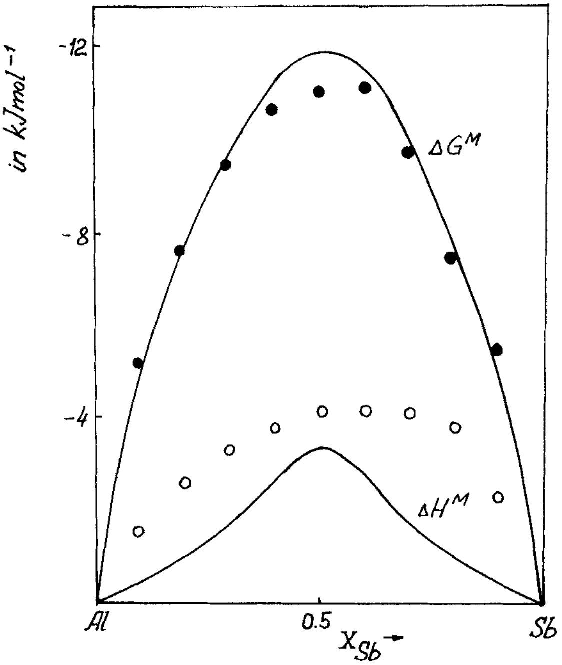

FIGURE 1 Experimental and calculated values of thermodynamic potential (ΔG^M) and enthalpy of mixing in Al-Sb liquid alloys at $T = 1330$ K. ● ● ● experimental ΔG^M [9], ○ ○ ○ experimental ΔH^M [9], ——— calculation.

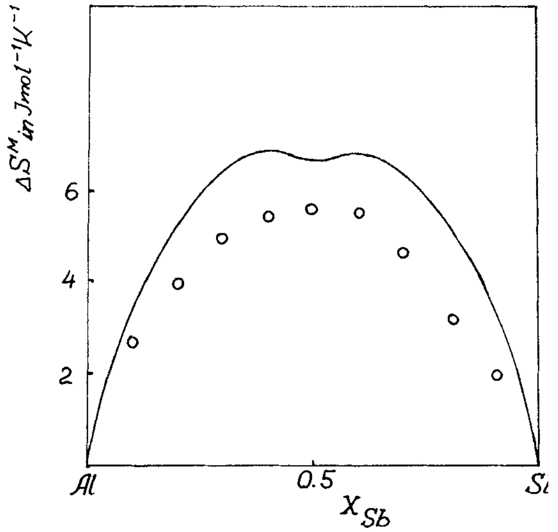

FIGURE 2 Experimental and calculated values of entropy of mixing (ΔS^M) in Al-Sb liquid alloys at $T = 1330$ K. ○ ○ ○ experimental ΔS^M [9], ——— calculation.

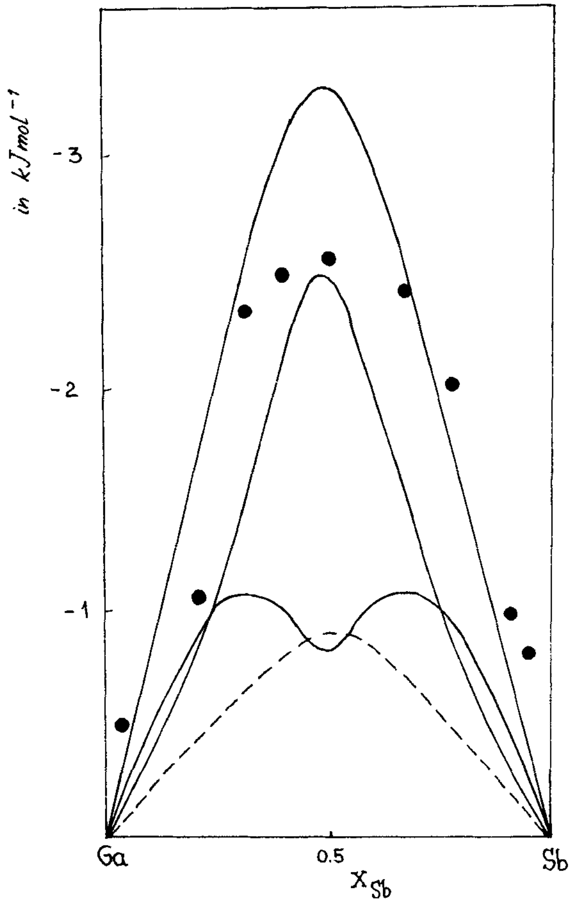

FIGURE 3 Excess thermodynamic functions in Ga-Sb liquid alloys at $T = 1000$ K. ● ● ● experimental ΔG^E [10], ----- experimental $\Delta H^E \equiv \Delta H^M$ [11], ——— calculation.

Discrepancies in enthalpy of mixing and especially in its temperature dependence allow to infer that in order to attain a higher accuracy of determinations model of this type should consider temperature dependence of parameter α. However, the considerations set forth below are rather of evaluative character.

Consider the difference between vibratory motions in a complex and in pure liquids. Assuming validity of the approximation of Einstein-model type, we assign one mean (size-independent) frequency w_{AB} to complexes and do the same with respect to single atoms, designating the vibration frequency for single atom A with w_A and that for atom B with w_B. The number of

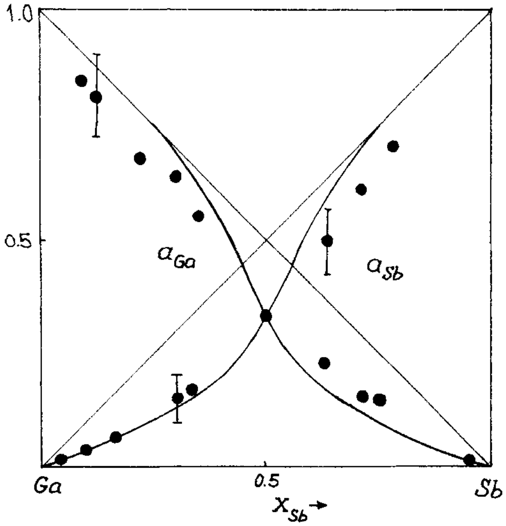

FIGURE 4 Activities of Ga (a_{Ga}) and Sb (a_{Sb}) in Ga-Sb liquid alloys at $T = 1000$ K. ● ● ● experimental[10], ——— calculation.

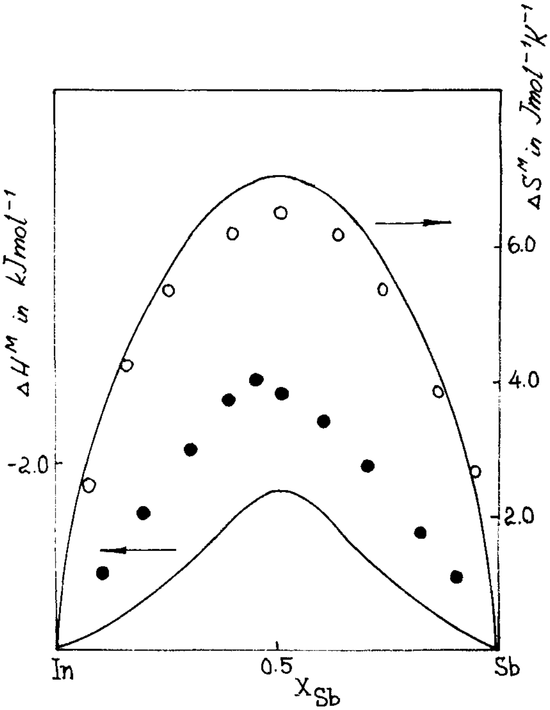

FIGURE 5 Enthalpy and entropy of mixing in In-Sb liquid alloys at $T = 900$ K. ● ● ● experimental ΔH^M ($T = 910$ K)[12], ○ ○ ○ experimental ΔS^M [14], ——— calculation.

vibrational degrees of freedom in a complex is $6n - 6$ (for nonplanar species) and that for single atoms is about $3n$. Now the contribution in thermodynamic potential of the difference between complex vibratory motion and single atom vibrations will be

$$\Delta G_{\text{vib}}(n) = (6n - 6)k_B T \ln \frac{\hbar w_{AB}}{k_B T} - 3nk_B T \ln \frac{\hbar^2 w_A w_B}{(k_B T)^2}$$

$$= f(T) + 3nk_B T \ln \frac{w^2 ab}{w_A w_B}$$

$f(T)$ here does not depend on the size n. This expression is again linearly related to n and the second term can formally be introduced in α, thus endowing α with temperature dependence. At a reasonable $w_{AB} - w_A - w_B$ relation, kilojoule effects can be obtained in ΔH^M and ΔS^M, respectively.

A similar approach may be used in respect of electron energy of the single-atom system. In the free-electron model the expression for chemical potential per electron has the form

$$\mu_{el} = \varepsilon_F[1 - \pi^2/12(k_B T/\varepsilon_F)^2 + \cdots]$$

where ε_F is Fermi energy of respective metal. Assuming that the temperature independent term has been taken into account in α, we get temperature-dependent contribution in ΔG^0 the following form

$$\Delta G_{\text{el}}(n) = -n \frac{\pi^2}{12} k_B T^2 \left(\frac{T_F^A + T_F^B}{T_F^A T_F^B} \right)$$

where T_F^i are Fermi temperatures of respective components. At $T \sim 10^3$ K and $T_F \sim 10^4$ K, we have ΔG_{el} of the order of 10^2 K, i.e. the effect of the order of a kilojoule.

The above considerations allow to qualitatively understand the disagreement between thermodynamic functions of mixing determined experimentally and calculated using Eqs (9 – 12) for these systems. A more detailed examination of vibrational, electronic, etc. contributions in considered thermodynamic parameters is beyond the scope of this paper.

CONCLUSION

1. A method of taking into account sizes of complexes in the ideal associated solution theory is proposed. Within a simple approximation of statistical theory, an equilibrium size distribution of complex concentrations may be obtained in terms of a single energy parameter.

2. The presence of complexes of an arbitrary size in solution allows to consider the stable compound as a complex of infinite size in solid phase and accordingly to relate a model parameter to melting temperature of this compound. With this approach, the ideal associated solution model allows to make nonempirical calculations of thermodynamic functions of mixing of a binary system.

3. Taking into account electronic and vibrational contributions in the variation of thermodynamic potential of complex formation endows the energy parameter of the model with temperature dependence, but also leads to the increase in number of model parameters.

4. The calculation made for aluminium-, gallium- and indium-antimony alloys shows a satisfactory agreement with experimental studies of thermodynamic functions of mixing.

5. The presence of complexes consisting of atoms of one kind seems to account for the assymmetry observed in experimental curves of enthalpy and entropy of mixing of these alloys.

6. The considered model can be generalized and applied to alloys with an arbitary stoichiometry of stable compound.

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