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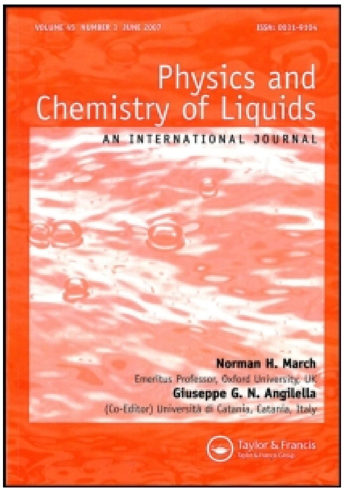

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On the free energy of mixing of a binary liquid alloy

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On the Free Energy of Mixing of a Binary Liquid Alloy

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It is pointed out that Flory–Miedema formula for the free energy of mixing, proposed recently by Alonso, López and March to study the concentration fluctuations in a binary liquid alloy, appears in a natural way within the framework of a general theory of mixtures. The theory in question is that of Kehiaian, which is a version of Guggenheim's quasi-lattice theory in terms of contact surface interactions.

1 INTRODUCTION

In recent years, a number of workers have discussed the characteristic features of the concentration fluctuations of a binary liquid alloy A_cB_{1-c} on the basis of different theoretical expressions for the free energy of mixing G_M[1-11]. The expression for the concentration fluctuations results from[1,2]

$$\langle(\Delta c)^2\rangle = S_{cc}(0) = \frac{KT}{(\partial^2 G_M/\partial c^2)_{T,P,N}}, \tag{1}$$

where $S_{cc}(0)$ is the long wavelength limit of the concentration-concentration structure factor $S_{cc}(q)$. K is the Boltzmann constant and T is the temperature. One of the simplest expressions for G_M arises from the conformal solution theory[12] (or the theory of regular solutions in the zeroth approximation[13]), namely

$$G_M = NKT[c\ln c + (1-c)\ln(1-c)] + NWc(1-c). \tag{2}$$

where the first term is $(-T)$ times the entropy of mixing S_M and the second term is the heat of mixing H_M. W is the interchange energy, a parameter adjusted to agree with experiment. If $W = 0$, we have the "ideal" solution. For expression (2) for G_M to be valid two conditions are necessary. First, the size difference between the two types of atoms must be small, roughly[13]

$$1 < \frac{V_A}{V_B} < 2, \tag{3}$$

where V_A and V_B are the volumes, per atom, of the two pure species. Secondly, W should be small; strictly,

$$\frac{W}{KT} \rightarrow 0, \tag{4}$$

since otherwise the assumption of a random distribution of atoms used in obtaining (2) is not valid. Bhatia[2] has shown that expression (2) works well for Na_cK_{1-c} alloys using the value $W/KT = 1.10$.

When the atomic volumes V_A and V_B differ considerably from each other, a simple approximate expression for G_M is that due to Flory[14], namely,

$$G_M = NKT[c \ln \phi + (1 - c)\ln(1 - \phi)] + NWc(1 - \phi), \tag{5}$$

where ϕ is the concentration by volume of species A, that is,

$$\phi = \frac{cV_A}{cV_A + (1 + c)V_B}. \tag{6}$$

If $V_A = V_B$, then $\phi = c$ and expression (5) becomes identical with Eq. (2). Flory's formula has been used successfully by Bhatia and March[3] to explain the observed results for $S_{cc}(0)$ in liquid NaCs alloys.

The consequences of an alternative form of expression (5) have recently been studied by Alonso *et al.*[11] The expression is a combination of Flory's formula for the entropy of mixing with the form for H_M given by the semi-empirical theory of Miedema and coworkers,[15] that is,

$$G_M = NKT[c \ln \phi + (1 - c)\ln(1 - \phi)] + NW^*c(1 - \xi), \tag{7}$$

where ξ is the atomic surface-area concentration for atoms A defined as

$$\xi = \frac{cV_A^{2/3}}{cV_A^{2/3} + (1 - c)V_B^{2/3}} \tag{8}$$

and W^* is an interchange energy, which is given in Miedema's theory in terms of the electronegativity difference and the boundary electron densities of pure metals A and B. Expression (7) thus appears as a suggestive link between Flory's theory of solutions and the electron theory of metals. The question naturally arises whether expression (7) for G_M is simply a fortunate ad hoc combination or whether there exists, in the same way as for Eqs. (2) and (5), a concrete theoretical model which leads to it in a natural way. The aim of the present paper is to point out that such a theory does in fact exist.

The theory in question, which is essentially a version of Guggenheim's quasi-lattice theory in terms of contact surface interactions, has been developed by Kehiaian *et al.*[16] and applied successfully to organic mixtures. In the next section we shall apply the results of that theory to a binary liquid alloy A_cB_{1-c} in order to find the whole expression (7). For this purpose we shall make use of Kehiaian's theory in the zeroth approximation. A higher approximation to G_M than (7) is possible (the quasi-chemical approximation), but it will not be pursued here.

2 FLORY-MIEDEMA'S FORMULA OBTAINED FROM KEHIAIAN'S THEORY

The structural model in Kehiaian's theory is that of a mixture whose molecules are ensembles of distinct "functional groups" consisting of a few atoms situated in a given intramolecular environment. By treating the energy effects in terms of contact surface interactions between the different groups, he applies arguments similar to those of Guggenheim in order to find the expression for the combinational factor of the configurational partition function and then the concrete form of the different thermodynamic functions. In the zeroth approximation, that is, when the coordination number z is large (formally, when $z \to \infty$), Kehiaian's theory gives the following expression for the molar excess Gibbs free energy

$$g_E = RT \sum_i c_i \ln \frac{\phi_i}{c_i} + N_0 \left(\sum_i q_i c_i \right) \sum_{i<j} \sum \xi_i \xi_j g_{ij} \tag{9}$$

with

$$g_{ij} = - \sum_{s<t} \sum (\alpha_{si} - \alpha_{sj})(\alpha_{ti} - \alpha_{tj}) W_{st}, \tag{10}$$

where c_i, ϕ_i and ξ_i are respectively the concentration, the concentration by volume and the surface concentration of the ith component in the mixture; q_i is the characteristic surface-area of each molecule of component i, α_{si} is the ratio q_{si}/q_i, where q_{si} is the surface-area of the group s on a molecule of type i; the W_{st} are the interchange energies between the different groups, which are defined per unit of contact surface, and N_0 is Avogadro's number.

If the above expression is applied to a binary mixture A_cB_{1-c} in which each type of molecule consists of just a single group, we have

$$g_E = RT\left[c\ln\frac{\phi}{c} + (1-c)\ln\frac{1-\phi}{1-c}\right] + N_0[q_Ac + q_B(1-c)]\xi(1-\xi)W \tag{11}$$

or, in terms of the molar free energy of mixing,

$$g_M = RT[c\ln\phi + (1-c)\ln(1-\phi)] + N_0[q_Ac + q_B(1-c)]\xi(1-\xi)W \tag{12}$$

The expression for $G_M = Ng_M/N_0$ will then be

$$G_M = NKT[c\ln\phi + (1-c)\ln(1-\phi)] + N[q_Ac + q_B(1-c)]\xi(1-\xi)W, \tag{13}$$

and since $\xi = q_Ac/[q_Ac + q_B(1-c)]$,

$$G_M = NKT[c\ln\phi + (1-c)\ln(1-\phi)] + NW^*c(1-\xi), \tag{14}$$

where we have written $Wq_A = W^*$.

Expression (14) for G_M is just Flory-Miedema's formula used by Alonso *et al.*, which can therefore be deduced within the framework of a general theory of mixtures. This is the important point we wish to stress here. This derivation of Eq. (14) permits a rational use of Miedema's theory to develop the link between a theory of mixtures and the electron theory of metals.

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