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Concentration fluctuations in simple liquid alloys with atomic size mismatch

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Résumé. — L'expression de Flory pour l'énergie libre de mélange dans les alliages liquides binaires constitués d'atomes de dimensions différentes est modifiée par l'introduction de la dépendance en concentration de la chaleur de mélange, donnée par la théorie semi-empirique de Miedema. L'expression résultante est utilisée pour étudier les fluctuations de concentration des alliages liquides Na K et Na Cs.

Abstract. — Flory's expression for the free energy of mixing of binary liquid alloys with atomic size mismatch is modified by introducing the concentration dependency of the heat of mixing given by the semiempirical theory of Miedema. The resulting expression is used to study the concentration fluctuations in liquid Na K and Na Cs alloys.

The concentration fluctuations in binary liquid alloys with a small heat of mixing but with a sizeable atomic volume mismatch between the component metals cannot be explained by the Conformal Solution theory. To overcome this problem, Bhatia and March [1] have used Flory's theory [2, 3]. In this theory, the free energy of mixing $\Delta G_M(c)$ of a liquid $A_c B_{1-c}$ alloy has the following form

$$\Delta G_M(c) = NK_B T [c \ln \alpha + (1 - c) \ln (1 - \alpha)] + NWc(1 - \alpha). \quad (1)$$

The first term is $(-T)$ times the entropy of mixing and the second term is the heat of mixing $\Delta H_M(c)$. N is the number of atoms in the alloy, K_B is the Boltzmann constant, T is the temperature, W is an interchange energy and α is the concentration by volume of species A

$$\alpha = \frac{cV_A}{cV_A + (1 - c)V_B} \quad (2)$$

where V_A and V_B are the partial molar volumes. The expression for the concentration fluctuations results from [4, 5]

$$\langle (\Delta c)^2 \rangle = S_{cc}(0) = K_B T / (\partial^2 G_M(c) / \partial c^2)_{T,P,N} \quad (3)$$

where $S_{cc}(0)$ is the long wavelength limit of the concentration-concentration structure factor $S_{cc}(q)$. Using (1) in (3), Bhatia and March [1] found

$$\langle (\Delta c)^2 \rangle = \frac{c(1-c)}{1 + c(1-c) \delta^2 \left[1 - \frac{2W}{K_B T} \frac{\beta \delta}{(\beta - 1)^3} \right]} \quad (4)$$

where $\beta = V_A/V_B$, and

$$\delta = \frac{V_A - V_B}{cV_A + (1-c)V_B}. \quad (5)$$

This theory was used successfully to study the concentration fluctuations in liquid Na Cs alloys [1]. In this paper we are interested in simple alloys, that is, alloys with a small heat of mixing. In this case the excess volume of formation is generally near zero and we can approximate the partial molar volumes V_A , V_B by the molar volumes V_A^0 , V_B^0 of the pure metals.

We now recall that a semiempirical theory of the heat of mixing proposed by Miedema and coworkers [6, 7, 8] gives the following concentration dependency for ΔH_M

$$\Delta H_M(c) = NW^* c(1 - \alpha^*) \quad (6)$$

where α^* is the atomic surface-area concentration for atoms A, that is

$$\alpha^* = \frac{c(V_A^0)^{2/3}}{c(V_A^0)^{2/3} + (1-c)(V_B^0)^{2/3}}. \quad (7)$$

The interchange energy W^* is also given by the theory. This is in contrast to Flory's theory, where W is a parameter to be fixed by the experiments. W^* is a simple function of $(\phi_A - \phi_B)$ and $(n_A^{1/3} - n_B^{1/3})$, where ϕ is the work function and n is the electron density at the boundary of bulk atomic cells of the pure metal. Extensive tables of W^* have been published [7]. According to Miedema, the heat of mixing is controlled by electronic interactions proportional to the total area of contact between dissimilar atomic cells. As a consequence, the atomic surface area concentration α^* appears in equation (6). In contrast, the atomic volume concentration α (strictly speaking, the partial molar volume concentration) appears in Flory's theory (Eq. (1)). For comparison, one should notice that in the Regular Solution theory

$$\Delta H_M(c) = NWc(1 - c). \quad (8)$$

Since the theory of Miedema has been applied with considerable success during the past years to many problems related to the heat of formation of solid and liquid alloys it seemed worthwhile to study the consequences of an alternative form of the free energy of mixing, namely

$$\Delta G_M(c) = NK_B T [c \ln \alpha + (1 - c) \ln (1 - \alpha)] + NW^* c(1 - \alpha^*) \quad (9)$$

in which Miedema's form for $\Delta H_M(c)$ is combined with Flory's expression for the entropy of mixing. Using (9) in (3) we obtain after some algebra

$$\langle (\Delta c)^2 \rangle = \frac{c(1-c)}{1 + c(1-c) \delta^2 \left[1 - \frac{2W^*}{K_B T} \frac{g(c)}{\delta^2} \right]} \quad (10)$$

where

$$g(c) = \frac{(cR + 1)^2 + R(cR + 1)(1 - 2c) - R^2 c(1 - c)}{(cR + 1)^3} \quad (11)$$

$$R = (V_A^0/V_B^0)^{2/3} - 1. \quad (12)$$

The results of equations (4) and (10) will now be compared for liquid Na K and Na Cs alloys. It has been emphasized by Bhatia and March [1] that Flory's theory is only valid for large volume ratios, say $V_B^0/V_A^0 \geq 2$. In our case $V_K^0/V_{Na}^0 = 1.96$ and $V_{Cs}^0/V_{Na}^0 = 3.03$. The results for these two alloys are compared in figures 1 and 2, using the values of W and W^* giving the best fits

Fig. 1. — Concentration fluctuations in liquid Na_c K_{1-c} alloys. Experimental results are from reference [9]. Flory's results correspond to $W/K_B T = 0.9$. Flory-Miedema curve corresponds to $W^*/K_B T = 0.95$.

to the experimental results for $S_{cc}(0)$. This freedom is needed because the theoretical W^* given by Miedema's theory [7] is usually not accurate enough for the present purposes. The figures show that the Flory-Miedema's theory is more successful than Flory's theory in Na K, whereas the opposite is true for Na Cs. The reason can be understood from the following argument : The heat of solution ΔH_s can be obtained from the heat of mixing $\Delta H_M(c)$ as

$$\Delta H_s(A \text{ in } B) = \lim_{c \rightarrow 0} \frac{\Delta H_M(c)}{c(1-c)} \quad (13)$$

$$\Delta H_s(B \text{ in } A) = \lim_{c \rightarrow 1} \frac{\Delta H_M(c)}{c(1-c)}. \quad (14)$$

Thus, in Miedema's theory

$$\frac{\Delta H_s(B \text{ in } A)}{\Delta H_s(A \text{ in } B)} = \left[\frac{V_B^0}{V_A^0} \right]^{2/3} \quad (15)$$

Fig. 2. — Concentration fluctuations in liquid $\text{Na}_x\text{Cs}_{1-x}$ alloys. Experimental results are from references [10] and [11]. Flory's curve corresponds to $W/K_B T = 1.14$. Flory-Miedema curve corresponds to $W^*/K_B T = 1.49$.

Table I. — Values of (V_B^0/V_A^0) , $(V_B^0/V_A^0)^{2/3}$ and $\Delta H_s(\text{B in A})/\Delta H_s(\text{A in B})$ for solid alloys (from Refs. [14] and [15]), and experimental values of $\Delta H_s(\text{B in A})/\Delta H_s(\text{A in B})$ for liquid alloys (from Ref. [13]).

Alloy (A B)	$(V_B^0/V_A^0)^{2/3}$	(V_B^0/V_A^0)	$\frac{\Delta H_s(\text{B in A})}{\Delta H_s(\text{A in B})}$	$\frac{\Delta H_s(\text{B in A})}{\Delta H_s(\text{A in B})}$ (expt. Liquid)
—	—	—	—	—
Li Na	1.45	1.74	1.56	
Li K	2.18	3.23	2.52	
Li Rb	2.53	4.03	2.96	
Li Cs	3.04	5.31	3.76	
Na K	1.53	1.89	1.66	1.61
Na Rb	1.75	2.31	1.85	2.04
Na Cs	2.08	3.03	2.65	3.57
K Rb	1.14	1.22	1.16	1.0
K Cs	1.32	1.59	1.47	2.27
Rb Cs	1.22	1.35	1.28	1.0
Mg Ba	1.95	2.72	1.99	
Mg Sr	1.80	2.42	1.95	
Mg Ca	1.52	1.87	1.65	
Ca Ba	1.28	1.45	1.53	
Ca Sr	1.19	1.29	1.40	
Sr Ba	1.08	1.13	1.0	

whereas in Flory's theory

$$\frac{\Delta H_s(\text{B in A})}{\Delta H_s(\text{A in B})} = \frac{V_B^0}{V_A^0}. \quad (16)$$

The asymmetry of ΔH_s is then higher in Flory's theory. The experimental values [12, 13] of (V_B^0/V_A^0) , $(V_B^0/V_A^0)^{2/3}$ and $\Delta H_s(\text{B in A})/\Delta H_s(\text{A in B})$ are 1.96, 1.56 and 1.61 respectively in Na K, and 3.03, 2.08 and 3.57 in Na Cs. Then, equation (15) does a better job for Na K whereas equation (16) is more accurate for Na Cs. This is in agreement with the conclusion from figures 1 and 2. A more detailed comparison of equations (15) and (16) is provided in table I, where values of (V_B^0/V_A^0) , $(V_B^0/V_A^0)^{2/3}$ and $\Delta H_s(\text{B in A})/\Delta H_s(\text{A in B})$ are given for several simple homovalent alloys. The theoretical values of $\Delta H_s(\text{B in A})/\Delta H_s(\text{A in B})$ were obtained [14, 15] using the Density Functional formalism [16]. The results of this table seem to favour equation (15). This conclusion is supported by the experimental results given in table 1 of reference [8], which correspond to liquid alloys with a heat of mixing substantially different from zero.

In summary, the combination of the Flory and the Miedema theories embodied in equation (9) can be helpful in studies of the concentration fluctuations in liquid alloys, in cases when atomic size mismatch is important. To close this work we mention that the authors have recently combined the Miedema theory with the Conformal Solution theory to study the concentration fluctuations in liquid alloys with small atomic size mismatch [17, 18].

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