Concentration Fluctuations in Liquid Sodium-Caesium Alloys

L. J. Gallego*
Departamento de Física Fundamental, Universidad de Santiago de Compostela,
La Coruña, Spain

J. A. Alonso
Departamento de Física Teórica, Universidad de Valladolid, Valladolid, Spain

Z. Naturforsch. **39 a**, 596–599 (1984); received February 11, 1984

The non-random two-liquid (NRTL) theory developed by Renon and Prausnitz has been used to calculate the concentration fluctuations in liquid Na-Cs alloys. The agreement with experiment is better than with other theories used previously.

The applicability of the theory of regular solutions (in the zeroth approximation [1]) or of conformal solutions [2] to a binary liquid alloy requires the size difference between the component atoms to be not too large. For example, this theory has been used successfully by Bhatia et al. [3] to study the concentration fluctuations in liquid Na-K alloys, but in the system under consideration here, the liquid Na-Cs alloy, the atomic volumes of the two components differ to much (the Cs/Na volume ratio is approximately 3), and other theories of mixtures have to be invoked. Thus Bhatia and March [4] have employed the well-known Flory model [5], originally developed for polymer solutions. The Flory formula for the molar Gibbs free energy of mixing, g_M, of a liquid alloy A_cB_{1-c} is given by

$$g_M = RT[c \ln \varphi + (1-c)\ln(1-\varphi) + c(1-\varphi)W], \quad (1)$$

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

$$\varphi = \frac{c V_A}{c V_A + (1-c) V_B}, \quad (2)$$

V_A and V_B being the molar volumes of the pure metals. In (1), W is the interchange energy parameter, which is adjusted by experiment. Using the Flory formula, Bhatia and March found the following expression for the long-wavelength limit of the concentration fluctuation structure factor $S_{cc}(0)$ (defined by Bhatia and Thornton [6]):

$$S_{cc}(0) = \frac{RT}{(\partial^2 g_M/\partial c^2)_{T,P}} \quad (3)$$
$$= \frac{c(1-c)}{1 + c(1-c)\delta^2\{1 - [2\beta\delta W/(\beta-1)^3]\}},$$

where $\beta = V_A/V_B$ and

$$\delta = \frac{V_A - V_B}{c V_A + (1-c) V_B}. \quad (4)$$

With $W = 1.14$, Bhatia and March obtained fairly good overall agreement with the experimental results of Ichikawa et al. [7] for $S_{cc}(0)$ in Na-Cs alloys. However, the agreement with the more recent experimental data of Neale and Cusack [8] is less good, and the latter authors modified Flory's model in order to reproduce the peak position of $S_{cc}(0)$ found in their experiments.

A rather different expression for g_M has recently been used by Alonso et al. [9] to study concentration fluctuations in liquid alloys with atomic size mismatch. The new expression is a combination of the Flory formula for the entropy of mixing with the expression for the heat of mixing given by the semi-empirical theory of Miedema and coworkers [10]:

$$g_M = RT[c \ln \varphi + (1-c)\ln(1-\varphi) + c(1-\xi)W^*], \quad (5)$$

where ξ is the atomic cell surface area concentration of metal A in the alloy A_cB_{1-c} and is defined by

$$\xi = \frac{c V_A^{2/3}}{c V_A^{2/3} + (1-c) V_B^{2/3}}. \quad (6)$$

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* Reprint requests to L. J. Gallego, Departamento de Física Fundamental, Universidad de Santiago de Compostela, La Coruña, Spain.

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According to Miedema, the heat of mixing is controlled by electron interactions proportional to the total area of the contact surface between dissimilar Wigner-Seitz atomic cells. As a consequence, (5) differs from Flory's formula in that a surface area concentration appears in the enthalpy term. Using (5), Alonso et al. obtained the following expression for the concentration fluctuations:

$$S_{cc}(0) = \frac{c\,(1-c)}{1 + c\,(1-c)\,\delta^2 \{1 - [2\,W^*\,\gamma/\delta^2]\}}, \tag{7}$$

where

$$\gamma = \frac{R+1}{(c\,R+1)^3}, \quad R = (V_A/V_B)^{2/3} - 1\,. \tag{8}$$

Fitting (3) and (7) to the experimental data for some liquid alloys, they found that for the Na-Cs system the Flory-Miedema theory does a reasonable but less successful job than the Flory theory. The best fit of (7) to the experimental data of Ichikawa et al. was obtained with the value $W^* = 1.49$.

Although both the Flory and the Flory-Miedema models take size differences into account, they assume a random distribution of atoms, just as the theory of regular solutions in the zeroth approximation does, and it may be this which leads to the discrepancies between experimental results for the Na-Cs system and the theoretical predictions of Bhatia and March, and Alonso et al. If a more accurate description is to be achieved, it may therefore be necessary to consider non-randomness effects in addition to the difference in size between the two types of atoms. The use of Flory's theory for Na-Cs has also been criticised by Visser et al. [11] and by Tanaka et al. [12].

The simplest theory of non-random mixtures is perhaps the quasichemical lattice model developed by Guggenheim [1], which can also be formulated in terms of contact surface interactions [13] (for an application of the latter version to liquid metal alloys see Gallego et al. [14, 15]). However, in Guggenheim's treatment this theory underestimates the effect of non-randomness, giving in general only small corrections to the random mixing approximation. In the present paper we consider a semi-empirical theory which has proved to be very useful in the interpretation of the thermodynamic properties of a large variety of liquid mixtures. The theory in question, the non-random two-liquid (NRTL) theory, has been developed by Renon and Prausnitz [16] by applying Wilson's concept of local composition [17] to Scott's two-liquid model [18]. The NRTL theory has been used by Vrestal and Velisek [19] to model the composition dependence of the excess Gibbs free energy in binary alloys. Without going into the details of the NRTL theory in this short communication, we shall show that this model is more in accord with experimental $S_{cc}(0)$ data for liquid Na-Cs alloys than the other theories used previously.

Like any theory of mixtures, the aim of the NRTL model is to provide an analytical expression for the Gibbs free energy of mixing g_M or, alternatively, for the excess Gibbs free energy g_E of a binary mixture A_cB_{1-c}. These two quantities are related by the equation

$$g_M = g_E + RT[c \ln c + (1-c)\ln(1-c)]\,. \tag{9}$$

The expression obtained by Renon and Prausnitz [16] for g_E is

$$g_E = RT\,c\,(1-c)\left[\frac{\tau_1\,e^{-\tau_1\alpha}}{c + (1-c)\,e^{-\tau_1\alpha}} + \frac{\tau_2\,e^{-\tau_2\alpha}}{(1-c) + c\,e^{-\tau_2\alpha}}\right], \tag{10}$$

which contains two energy parameters, τ_1 and τ_2, and the non-randomness parameter α. The parameters τ_1 and τ_2 are defined by $\tau_1 = (g_{AB} - g_{AA})/RT$ and $\tau_2 = (g_{AB} - g_{BB})/RT$, where the g's are (Gibbs) energy parameters characterizing the interaction between the components denoted by the subscripts. By applying (10) to a large number of organic mixtures, Renon and Prausnitz have established rules of thumb for the a priori determination of α. The values of α so established range from about 0.20 to 0.50, depending on the chemical nature of the system under study. In the present paper, however, we shall consider all three parameters in (10) as free.

By substituting (10) in (9) and differentiating twice with respect to c, the following expression is obtained after some algebraic manipulation:

$$S_{cc}(0) = \frac{c\,(1-c)}{1 - 2c\,(1-c)\left[\dfrac{\tau_1\,e^{-2\tau_1\alpha}}{(c + (1-c)\,e^{-\tau_1\alpha})^3} + \dfrac{\tau_2\,e^{-2\tau_2\alpha}}{((1-c) + c\,e^{-\tau_2\alpha})^3}\right]}. \tag{11}$$

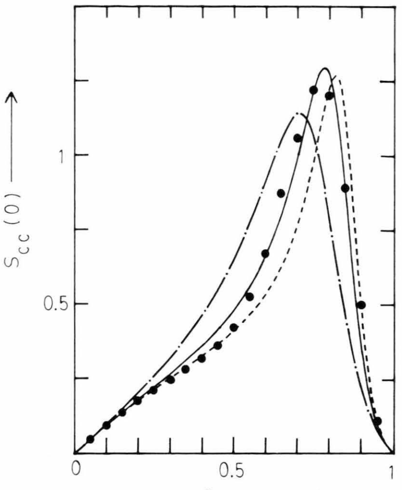

Fig. 1. $S_{cc}(O)$ of the Na-Cs liquid alloy system as a function of Na concentration. (●) experimental data at $T = 110\,°C$, $P = 1$ bar, taken from Neale and Cusack [8]; (---) Flory's model; (-·-·) Flory-Miedema model; (—) non-random two-liquid model.

In order to test the adequacy of the above equation for the Na-Cs system, we have used Marquardt's nonlinear optimization procedure [20] to fit it to the experimental data recently published by Neale and Cusack [8], whose $S_{cc}(0)$ values differ slightly form those of Ichikawa et al. [7]. The same algorithm has also been used to obtain the parameters W and W^* of equations (3) and (7) from Neale and Cusack's data, and so allow a meaningful comparison of the three models. The optimal values of the parameters and the standard deviations of the corresponding fits (in parentheses) are $W = 1.14$ ($\sigma = 0.13$); $W^* = 1.46$ ($\sigma = 0.20$); and $\tau_1 = -0.18$, $\tau_2 = 2.60$, $\alpha = 0.37$ ($\sigma = 0.06$). The values of W and W^* are close to those obtained by Bhatia and March and by Alonso et al. using the experimental data of Ichikawa et al. This is reflected in Fig. 1, which bears out Alonso et al.'s finding that Flory's theory is rather more successful for Na-Cs alloys than the Flory-Miedema model, though the qualitative difference between the two models is less than originally estimated by Alonso et al. since the peak value of $S_{cc}(0)$ occurs at $c_{Na} = 0.77$ in Neale and Cusack's experiments, a value some 0.05 lower than that reported by Ichikawa et al. Figure 1 also shows that of the three methods tested here, the best agreement with experiment is provided by the NRTL model.

Assuming that the range of values of α obtained by Renon and Prausnitz is valid for non-organic mixtures too, then the value of 0.37 obtained for the Na-Cs system appears to indicate rather a moderate degree of non-randomness. This is a reasonable result, since the divergence of the random distribution models' predictions from experimental results is not large. In general, however, reliable appreciation of the significance of the value of α for systems like the one discussed here will require a comprehensive study to be undertaken for liquid metal alloys. It should also be noted that on substituting the fitted values of the parameters τ_1 and τ_2 into the equations defining these parameters it is found that $g_{NaCs} \simeq g_{NaNa}$, and that these two Gibbs energy parameters are very different from g_{CsCs}. Thus the deviation from ideal behaviour of the Na-Cs alloy is due not only to size difference effects but also to a marked difference between one of the three possible pair interactions and the other two. The fact that this particular pair interaction (g_{CsCs}) involves like atoms appears to agree with Ichikawa et al.'s suggestion [7, 21] that there is a tendency to phase separation rather than molecular complex formation in the liquid.

Acknowledgement

This work was supported in part by a Grant from the Spanish Comisión Asesora de Investigación Científica y Técnica.

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