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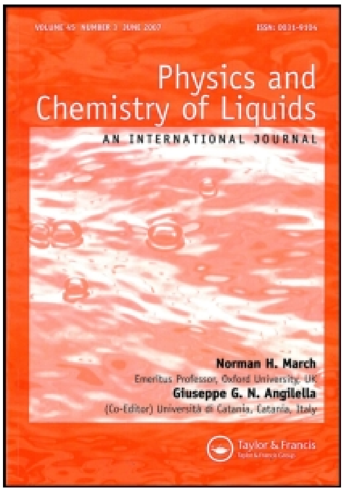

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Letter

Entropy of Mixing of Liquid LiPb Alloy

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A semi-empirical model, based on the theory of hard spheres mixture, has been used to calculate the entropy of mixing of the compound forming liquid alloy LiPb. The volume of mixing across the whole composition range is evaluated by fitting the entropy of mixing to its experimental value at equiatomic concentration. It is shown that the simple theory of pseudobinary mixture of hardspheres successfully describes the behaviour of the entropy of mixing of this alloy with the composition.

In a recent paper[1] a semi-empirical model, based on hard sphere reference system, was proposed for the calculation of the entropy of mixing of liquid mixture across the whole composition diagram. The method provides a way to calculate the separate contribution of each component to entropy of mixing by fitting the excess entropy to its experimental value at the equiatomic concentration of the constituent elements. For several simple liquid mixtures, the method yielded good results. To explore the limits of the model, we now apply the method to the alloy system LiPb, an almost classic example of a compound forming system. Liquid binary alloy systems, containing lithium as one of the components, exhibit strongly varying thermodynamic properties and several alloys such as LiNa[2], LiIn,[3] LiPb[4] exhibit strong indication for compound formation. Recently, Hoshino and Young[5] proposed a theory for the entropy of mixing of compound forming liquid alloys, which assumes the formation of a chemical complex or molecule. They applied the theory to LiPb[5] and later to NaPb,[6] evaluating the contributions to the entropy of mixing over the entire range of Composition. In these alloys the associative tendency between the unlike atoms is strong and there exists a large volume contraction at concentrations far from the equiatomic concentration.[7] However, the experimental information regarding such alloys is very meagre and scattered.

We consider a liquid binary mixture with components of atomic concentrations C_1 and C_2 comprising C_1N hard sphere with diameter σ_1 each and C_2N with diameter σ_2 each. Following Visser *et al.*[8] the expression for the entropy in the hard sphere reference system is given by

$$S_{\text{hs}} = S_{\text{gas}} + S_\eta + S_c + S_\sigma \tag{1}$$

where S_{gas} represents the ideal gas entropy, S_c is the ideal entropy of mixture, S_η is the contribution due to packing density η, and finally S_σ corresponds to the mismatch term between the hard spheres due to different diameters σ_1 and σ_2. The theory has been described elsewhere[1,9] and we write directly its results.

The hard sphere formula for the entropy of mixing is given by

$$\Delta S_{\text{hs}} = S_{\text{hs}} - C_1 S_1 - C_2 S_2 \tag{2}$$

where

$$S_i = S_{\text{gas},i} + S_{\eta,i} \qquad (i = 1, 2)$$

Equation (2) can be rewritten as

$$\Delta S_{\text{hs}} = \Delta S_{\text{gas}} + \Delta S_\eta + S_c + S_\sigma \tag{3}$$

where

$$\Delta S_{\text{gas}} = S_{\text{gas}} - C_1 S_{\text{gas},1} - C_2 S_{\text{gas},2}$$

and

$$\Delta S_\eta = S_\eta - C_1 S_{\eta_1} - C_2 S_{\eta_2}$$

The actual volume Ω of an alloy is considered concentration dependent in the manner described as

$$\Omega = \Omega_{\text{ideal}} + C_1 C_2 \Delta\Omega_0 \tag{4}$$

where

$$\Omega_{\text{ideal}} = C_1\Omega_1 + C_2\Omega_2$$

and $\Delta\Omega_0$ is a constant for the given system. The fractional change in volume on mixing is defined through

$$\Delta\Omega = \frac{(\Omega - \Omega_{\text{ideal}})}{\Omega} = \frac{C_1 C_2 \Delta\Omega_0}{\Omega}$$

The same volume has been used to determine the packing fraction as used to determine ΔS_η and S_σ for the binary mixture. Viz,

$$\eta = \frac{\pi}{6\Omega}(C_1\sigma_1^3 + C_2\sigma_2^3) = C_1\eta_1\frac{\Omega_1}{\Omega} + C_2\eta_2\frac{\Omega_2}{\Omega} \tag{5}$$

Using the packing fraction for the separate liquids as

$$\eta_i = \frac{\pi\sigma_i^3}{6\Omega_i}, \qquad (i = 1, 2) \tag{5a}$$

In the present work, the atomic volume Ω of the liquid mixture at equiatomic concentration is so fitted as to satisfy Eq. (3) with the experimental value of entropy of mixing. That leads to evaluation of $\Delta\Omega_0$ from Eq. (4) and the same value of $\Delta\Omega_0$ is then used to evaluate the volume formation at various concentrations and thereby to evaluate the different contributions of entropy of mixing at different concentrations. Two sets of the hard sphere parameters σ(Li) and σ(Pb) are available[10] to evaluate the entropy of mixing. We shall call parameters I the hard sphere diameters $\sigma(\mathrm{Li}) = 2.87$A° and $\sigma(\mathrm{Pb}) = 2.92$A° that resulted from a fit of the hard sphere model to the long wavelength limit, S(o), of the neutron diffraction data,[4] and parameters II the values $\sigma(\mathrm{Li}) = 2.68$A° and $\sigma(\mathrm{Pb}) = 2.74$A° that are determined by fitting the experimental values of the entropy[11] at 800°K for the pure liquid metals. The corresponding packing fractions are deduced by using formula (5a). The calculated entropy of mixing for varying C_1 is compared in Figure 1 with the experimental data of Demidov *et al.*[12] and Saboungi *et al.*[13] It is

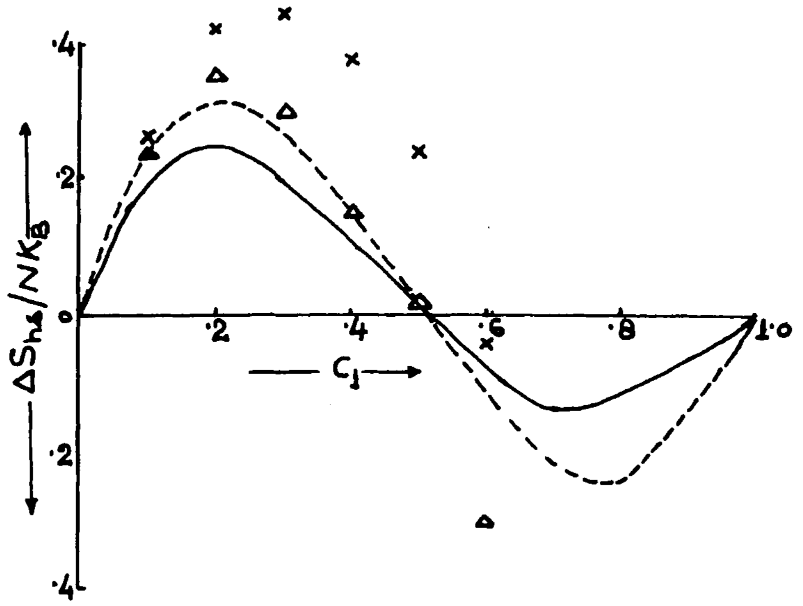

FIGURE 1 Concentration dependence of the entropy of mixing ΔS_{hs} of LiPb alloy. Parameter I: dotted line; Parameter II: full line (for all figures). Experimental results are shown by crosses (Demidov *et al.*) and by triangles (Saboungi *et al.*).

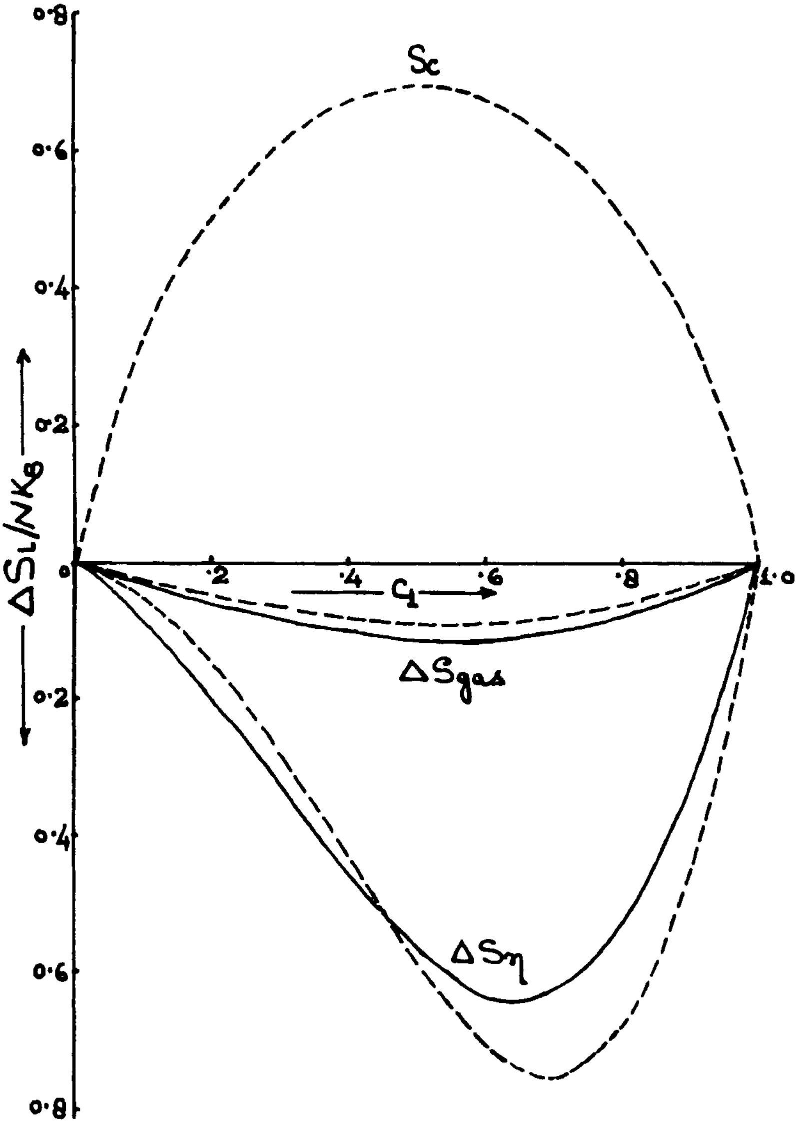

FIGURE 2 Concentration dependence of ΔS_{gas} and ΔS_η. S_σ is too small for the scale.

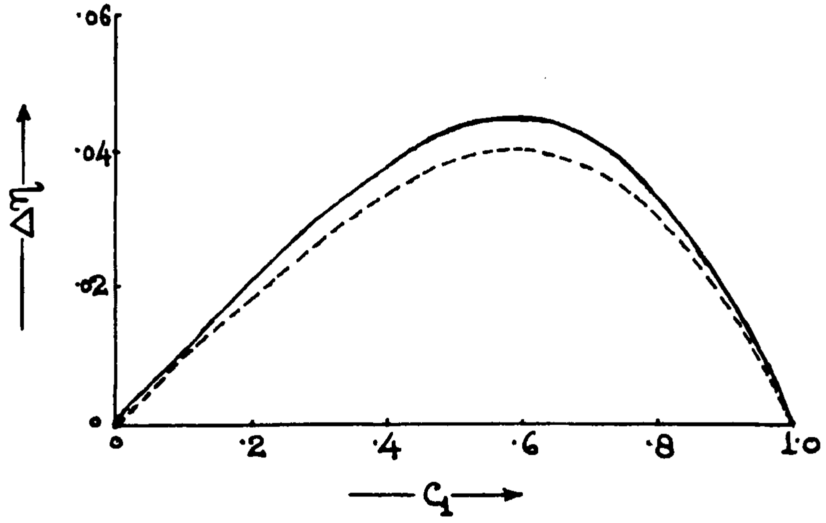

FIGURE 3 Concentration dependence of $\Delta\eta$ of LiPb liquid alloy.

to be noted that the main experimental features of the entropy of mixing curves are explained by the model using either set of the values of hard sphere parameters. Quantitatively, the curve using parameter I shows a close agreement with the experimental values of Saboungi *et al.*[13] for $C_{\mathrm{Li}} < 0.5$. For $C_{\mathrm{Li}} > 0.5$ either curve lies in between the two experimental values. The main feature of the second halves of the curves is that the dip is not so deep as calculated by Alblas *et al.*[10] Figure 2 shows the separate contributions to ΔS_{hs}. It is clear that the plots of ΔS_{gas} and ΔS_η with respect to concentration are asymmetric about 0.5 concentration value. This shifting is as much as 28 % in ΔS_η curve for parameter I. This phenomenon is closely associated with the volume ratio of the constituent elements as described earlier.[1] The mismatch term is negligibly small due to small difference in hard sphere diameters in the present case. The values of $\Delta\eta$ as shown in Figure 3 are found to be positive, which means that the packing fraction increases on alloying the constituent elements which is very well described by the following equation.[1]

$$\eta - (C_1\eta_1 + C_2\eta_2) = \frac{C_1C_2[(\eta_2 - \eta_1)(\Omega_2 - \Omega_1) - \eta_{\mathrm{ideal}}\Delta\Omega_0]}{\Omega} \qquad (6)$$

The shifting in $\Delta\eta$ curve about the mean concentration is also quite noticeable, similarly, a large volume contraction with a shifting far from the mean concentration is the characteristic feature of LiPb alloy. From the shifting in these curves we may infer that the associative tenency to form a stable compound is strong at the particular concentration. On mixing, the

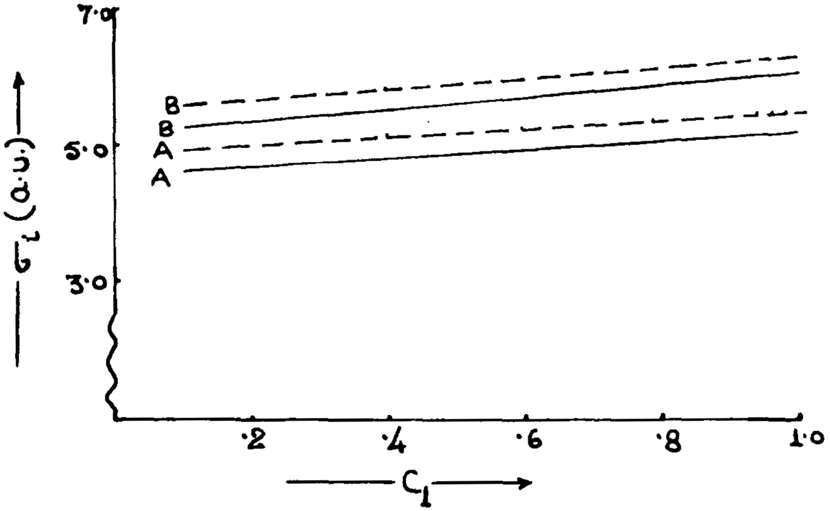

FIGURE 4 Concentration dependence of hard sphere diameters of liquid LiPb alloy. A and B respresent Li and Pb diameters respectively.

sizes of hard spheres of the constituent elements change. The hard sphere of a more electronegative element (Pb) expands while that of the less electronegative (Li) shrinks as observed in other alloys.[1,14] Moreover, the ratio of the hard sphere diameters remains almost constant throughout the whole concentration range. The Figure 4 explains the change in hard sphere diameters with concentration. The negative value of ΔS_{hs} near $C = 0.8$ in Figure 1 may infer the formation of molecule Li_4Pb, as the formation of molecule is essentially responsible for the negative value of ΔS i.e. for the decrease of the degree of disorder. It is also important to note that a large negative value far from mean concentration of ΔS_η curve as revealed in Figure 2 is mainly responsible for the formation of Li_4Pb molecule.

From the present study we conclude that the usual theory of hard sphere mixture is able to explain reasonably the entropy of mixing of compound forming alloys which was considered as a failure.[6] A more suitable choice of the hard sphere diameters may reproduce the entropy of mixing exactly coinciding with experimental values.

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References

1. K. N. Khanna and P. Singh, *Physica* (*B*), Netherlands **114B**, 174 (1982).
2. P. D. Feitsma, J. J. Hallers, F. Van der Werff, and W. Van der Lugt, *Physica*, **B79**, 35 (1975).
3. C. Van der Marel, E. P. Brandenburg, and W. Van der Lugt, *J. Phys.*, **F8**, L273 (1978).
4. H. Ruppersberg and H. Egger, *J. Chem. Phys.*, **63**, 4095 (1975).
5. K. Hoshino and W. H. Young, *J. Phys.*, **F10**, 1365 (1980).
6. K. Hoshino and W. H. Young, *J. Phys.*, **F11**, L7-9 (1981).
7. A. B. Bhatia and R. N. Singh, *Phys. Lett.*, **78A**, 460 (1980).
8. E. G. Visser, W. Van der Lugt, and J. Th. Me De Hosson, *J. Phys.*, **F10**, 1681 (1980).
9. K. N. Khanna and D. P. Khandelwal, *Phys. Stat. Sol.*, **(b)106**, 715 (1981).
10. B. P. Alblas, W. Van der Lugt, E. G. Visser, and J. Th. M. De Hosson, *Physica*, **114B**, 59 (1982).
11. R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelly, and D. D. Wagman. Selected values of the thermodynamic properties of the elements. (Metals Park, Ohio; American Society of Metals).
12. A. I. Demidov, A. G. Morachevskii, and L. N. Gerasimenko, *Sov. Phys. Electrochem.*, **9**, 813 (1973).
13. M. L. Saboungi, J. Marr, and M. Blander. *J. Chem. Phys.*, **68**, 1375 (1978).
14. R. N. Singh and R. B. Choudhary, *J. Phys.*, **F11**, 1577 (1981).