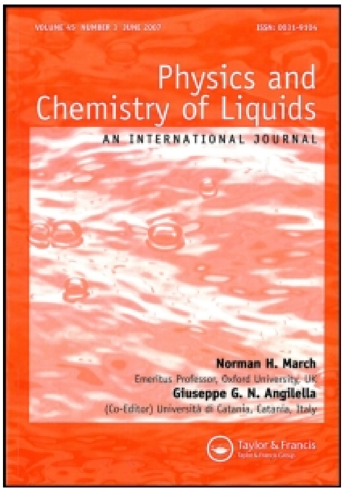

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Karaoglu, B.(1993) 'Effective Atomic Diameter Changes on Mixing Liquid Metals', Physics and Chemistry of Liquids, 26: 3, 179 — 184
To link to this Article: DOI: 10.1080/00319109308030661
URL: http://dx.doi.org/10.1080/00319109308030661

Phys. Chem. Liq., 1993, Vol. 26, pp. 179–184
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EFFECTIVE ATOMIC DIAMETER CHANGES ON MIXING LIQUID METALS

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(Received 9 March 1993)

A simple model based on the variational Gibbs-Bogoliubov method is used to investigate the manner in which the effective hard sphere diameters change on mixing liquid metals. It implies that in general the diameter of the ions with lower pure liquid valence electron density contracts while the other expands, provided the bare pseudopotentials are unaffected by alloying.

KEY WORDS: Hard sphere diameter, liquid metals.

1 INTRODUCTION

In studying the thermodynamic properties of liquid metals, one of the most useful tools is the hard sphere reference system. In interpreting measured thermodynamic quantities, such as entropy, one crucial problem is the effective hard sphere diameter changing pattern on alloying. It is customary to use the Gibbs–Bogoliubov (GB) method to define, at each concentration, the sphere diameters as those which minimize the free energy.

The question of the behaviour of the hard sphere diameters has been addressed by Young[1], whose proposition is that, on mixing at constant volume, the diameter of the ion from the pure metal with higher mean valence electron density should expand while the other should contract.

The argument derives from the facts that, for a one-component case the entropy S decides the diameter σ, while the pressure coefficient

$$\gamma \equiv \left(\frac{\partial P}{\partial T}\right)_\Omega = \left(\frac{\partial S}{\partial \Omega}\right)_T \tag{1}$$

decides its variation with volume Ω, at constant T. The measured data then lead to the conclusion that when the mean valence electron density increases, the core size decreases and vice versa. On alloying, one set of ions see a larger average electron density, while the other set see the average electron density to become smaller, compared to the one-component case. To the extent that the ions respond to the ambient electronic pressure as though they were part of a pure metal, the above proposition follows.

Past tests have, to some extent, confirmed this conclusion. Calculations[2,3] were made using the GB method with actual volumes of the alloys. The results show, rather generally, that one set of ions shrink while the other set expand. Moreover, the ions from the metal of higher valence electron density seem to expand preferentially.

However, this argument is not rigorous since it ignores various aspects of alloying. One is the presence around an ion of unlike neighbours. Another is that a volume change (of the order 1%) also occurs in mixing. If $\Omega(c)$ is the actual volume at a given concentration, then the volume change is defined as

$$\Delta\Omega = \Omega(c) - \Omega_o \quad \text{with} \quad \Omega_0 = c_1\Omega_1 + c_2\Omega_2 \tag{2}$$

where Ω_1,Ω_2 are the pure metal volumes.

The above proposal should be tested using model alloy systems at constant volume, i.e., $\Delta\Omega = 0$ (Vegard's rule). Previous tests were made using data from calculations that used the actual volumes, and a volume change may cloud whatever effect occurs. For example, if we considered a hypothetical cases where $\Delta\Omega$ is very large, we might reasonably expect both ions to swell. Furthermore, those calculations used older forms of the screening, a feature which is known to be crucial in describing the electron-ion interaction.

The purpose of this work is to test Young's proposal more rigorously by considering a wider variety of alloys, by calculating the diameter changes at constant volume ($\Delta\Omega = 0$) and by using a well-established screening function (Ichimaru and Utsumi[4]). Otherwise, the usual tools (Ashcroft pseudopotential, Gibbs-Bogoliubov method) are used.

2 METHOD

A brief description of the GB method[5], as applied to the present binary alloy problem, is in order. Suppose the component ions are present in concentrations $c_1 \equiv c$ and $c_2 \equiv 1 - c_1$ and are modelled by hard spheres of diameter σ_1 and σ_2. Then the free energy F of an alloy accepts an upper bound given by

$$F(\sigma_1, \sigma_2, c) = F_{hs} = F + F_{ps} \tag{3}$$

where F_{hs} is the free energy of the reference hard sphere system and F_{ps} is the perturbation term averaged over the reference system. The latter includes various contributions

$$F_{ps} = F_{eg} + F_1 + F_2 + F_M \tag{4}$$

where F_{eg} is the free energy of the electron gas, F_1 and F_2 are the first and second order perturbations due to the pseudopotential and F_M is the Madelung contribution of the ion-ion interaction.

The quantity (σ_1, σ_2, c) is minimized with respect to σ_1, σ_2 at fixed concentration c. The analytical expressions for F_{hs}, F_{eg}, F_1 and F_M are known. The F_2 term is calculated numerically through the expression

$$F_2 = \frac{1}{16\pi^3}\int_0^\infty \{c_1 v_1^2 S_{11} + 2\sqrt{c_1 c_2}\, v_1 v_2 S_{12} + c_2 v_2^2 S_{22}\}\left[\frac{1}{\varepsilon(q)} - 1\right] q^4\, dq \qquad (5)$$

Here v_q is the bare pseudopotential of the i-th species of ions and $S_{ij}(q)$ are the Percus–Yevick partial structure factors. $\varepsilon(q)$ is the dielectric screening function given as

$$\varepsilon(q) = 1 - \frac{4\pi e^2}{q^2}\,[1 - G(q)]\chi_0(q)$$

$$\chi_0(q) = \frac{m}{\hbar^2}\frac{k_F}{\pi^2}\left[\frac{1}{2} + \frac{1 - x^2}{4x}\ln\left|\frac{1 + x}{1 - x}\right|\right] \qquad (x = q/2k_F) \qquad (6)$$

$G(q)$ is the correlation factor for the exchange and correlated motion of the conduction electrons. Experience has shown that the use of a sufficiently accurate $G(q)$ is essential for obtaining realistic results. The Ichimaru-Utsumi screening factor seems to be well-established for this purpose.

3 RESULTS, DISCUSSION AND CONCLUSION

Table 1 displays our calculations for the same set of binary alloys quoted in reference 1 plus some other alloys. The empty core radii of the pseudopotentials are taken from the same source, but it should be stressed that the choice of these parameters has little or no bearing on the general study of the above proposition for which *any* choice of parameters provides a test.

The change of diameters at 50–50 concentration supports, in the majority of cases, the proposition that one set of ions expands, while the other contracts. The other weak rule is also nearly always observed, i.e., the ions from the metal of higher valence electron density expand preferentially. (For convenience of reference in Table 1, the alloy component with lower mean electron gas comes first so, for the rule to hold, we require $\Delta\sigma_1 < 0$, $\Delta\sigma_2 > 0$). The percent change is of the order of 1–4% and, indeed, this effect could have been easily masked if the volume change were included in the calculations.

The profile of the diameter change against the concentration shows in more detail the gradual change occurring on alloying. A set of thumbnail sketches are given in

Table 1 Hard sphere diameters of the selected alloys calculated with Gibbs-Bogoliubov method. Ashcroft empty core pseudopotential is adopted throughout with empty core radii of reference 1. The first alloy component is always the one with lower valence electron density.

Alloy	T/K	σ_1^0	σ_1	$100 \times \frac{\Delta\sigma_1}{\sigma_1^0}$	σ_2^0	σ_2	$100 \times \frac{\Delta\sigma_2}{\sigma_2^0}$	*Range of* η
Mg–Al	1000	5.35	5.16	−3.7	4.76	4.91	+3.2	0.44–0.47
In–Zn	700	5.06	5.02	−0.8	4.64	4.71	+1.5	0.37–0.47
Cd–In	723	5.04	5.01	−0.4	5.05	5.09	+0.7	0.36–0.42
Cd–Tl	673	5.06	5.02	−0.8	4.94	4.97	+0.5	0.32–0.42
Mg–Zn	923	5.38	5.23	−2.7	4.57	4.65	+1.8	0.44–0.48
Sn–Bi	608	4.93	4.89	−0.7	4.97	4.98	+0.3	0.28–0.32
Pb–Bi	700	4.91	4.87	−0.7	4.96	4.99	+0.6	0.27–0.28
Pb–Sn	773	5.58	5.47	−2.0	5.36	5.45	+1.7	0.41–0.42
K–Na	373	7.57	7.46	−1.4	6.24	6.19	−0.8	0.44–0.47
Cd–Zn	800	5.04	4.93	−1.6	4.61	4.68	+1.5	0.41–0.45
Zn–Sn	750	4.63	4.60	−0.6	4.91	4.91	+0.1	0.32–0.46
In–Bi	900	5.02	4.89	−2.5	4.94	4.98	+0.9	0.26–0.34
Tl–Bi	750	4.93	4.83	−1.9	4.95	5.01	+1.1	0.27–0.30
Cd–Ga	700	5.05	4.93	−2.3	4.78	4.89	+2.4	0.42–0.44
Mg–Ga	923	5.38	5.19	−3.6	4.73	4.86	+2.6	0.41–0.48
Mg–Pb	973	5.37	5.18	−3.6	4.87	4.90	+0.8	0.27–0.47
Mg–In	923	5.38	5.31	−1.4	5.01	5.06	+1.1	0.34–0.48

Figure 1. In the majority of cases, the two diameters change gradually in the opposite sense, in accordance with the hypothesis under investigation.

However, in some cases, this trend is not clear, notably for the cases of K–Na and Zn–Sn alloys. The diameter changes for these ions are not uniform. The fact that, for K–Na alloy, the difference in pure metal diameters is much larger, compared to the other cases, may render the simple proposition under study inapplicable to this case. In the other case, the pair potential profile of the Sn ion exhibits a shoulder near the potential minimum[1] and, the minimisation is affected by this behaviour.

The numerical results were found to be sensitive to the empty-core radii of the Ashcroft pseudopotentials used. Though this is irrelevant for real metals, we nevertheless investigated the effect of varying the empty core radii since such hypothetical systems are also covered by the hypothesis. The resulting diameter changes for In–Zn alloy are presented in Table 2. While the calculated ratios are different, the ion (Zn) with richer valence electron in the pure liquid still expands while the In ion with lesser electron density contracts, and hence the proposition still holds. One could question here a possible interplay between empty-core radii and the hard sphere diameters. However, it would involve a 4-parameter problem that would not be suitable for a simple study such as ours.

Finally, we performed a calculation *with* volume change. Table 3 shows the result of including an artifical volume change (up to 20% of Ω_0) in the In–Zn alloy. In a larger volume, while the Zn expands more, the contraction of the In ion is lessened and, at around 15% volume change, both ions start to expand. It follows that the

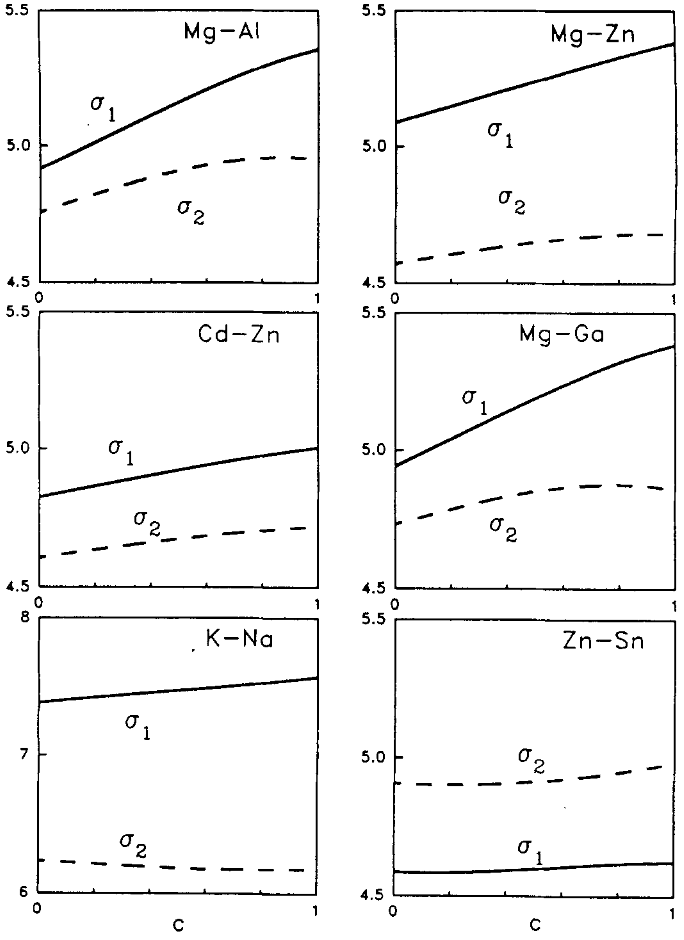

Figure 1 Hard sphere diameter changes against concentration $c \equiv c_1$ for a set of binary alloys; solid lines the first, dashed lines the second alloy component as in Table 1. Because the first component is that with the lower valence electron density, behaviour consistent with the hypothesis corresponds to both diameters increasing as c increases.

Table 2 Effect of the empty core radius change on the hard sphere diameters for In–Zn alloy. The value $r_{c1} = r_{In} = 5.06$ is kept fixed while $r_{c2} = r_{Zn}$ is changed by ±15%. The diameters are calculated at 50–50 concentration.

Change in r_{c2}	σ_1	$100 \times \frac{\Delta\sigma_1}{\sigma_1^0}$	σ_2	$100 \times \frac{\Delta\sigma_2}{\sigma_2^0}$
−15%	4.98	−1.4	4.36	+1.6
−10%	5.00	−1.2	4.48	+1.6
−5%	5.01	−1.0	4.60	+1.6
0%	5.02	−0.8	4.71	+1.5
+5%	5.03	−0.6	4.82	+1.4
+10%	5.04	−0.4	4.93	+1.4
+15%	5.05	−0.2	5.04	+1.4

Table 3 Effect of the volume change on the hard sphere diameters for In–Zn alloy. The diameters are calculated at 50–50 concentration.

$\frac{\Delta\Omega}{\Omega_0}$	$100 \times \frac{\Delta\sigma_1}{\sigma_1^0}$	$100 \times \frac{\Delta\sigma_2}{\sigma_2^0}$
0%	−0.8	+1.5
5%	−0.5	+1.8
10%	−0.2	+2.1
15%	0.0	+2.3
20%	+0.2	+2.4

above proposition cannot be safely tested using actual volumes, and this confirms the need for a test using zero volume change such as presented in this work.

Calculated excess free energies (ΔF^{XS}) and packing fractions (η) are not close to those observed in some cases; however, our calculations were limited, as explained earlier, to examining Young's proposition that the ions from the metal of richer valence electron density expand on alloying and those from the poorer contract. This proposition seems to hold in general for 'Ashcroft alloys" at least, and provides a simple criterion for the behaviour of hard sphere diameters in mixing.

Acknowledgements

I am grateful to Professor W. H. Young for his helpful advice and guidance throughout the completion of the work. I gratefully acknowledge Professor K. Hoshino's help in making his GB program available to me, and Dr S. M. M. Rahman for useful discussions.

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