A Note on the Bhatia Theory of Liquid NaSn Alloys

A. K. Ray[a]; W. H. Young[bc]

[a] Department of Physics, University of Texas at Arlington, Arlington, TX, USA [b] Physics Department, Sultan Qaboos University, Muscat, Oman [c] School of Mathematics and Physics, University of East Anglia, Norwich, UK

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A. K. RAY

Department of Physics, University of Texas at Arlington, Arlington, TX 76019, USA

and

W. H. YOUNG*

*School of Mathematics and Physics, University of East Anglia, Norwich NR4 7TJ, UK*

1 INTRODUCTION

Currently, there are two competing theories[1,2] of "compound forming" liquid alloys. In the theory proposed by Bhatia *et al.*, a so-called chemical approach is taken in which a mixture of A and B atoms contains also, in equilibrium, complexes of the type $A_\mu B_\nu$ (μ, ν small integers). There may be one or more such complex types and the macroscopic thermodynamic properties of the binary mixture depend on the free energy of formation of the chemical complexes and on the form of the assumed chemical potentials. The present work bears on the liquid $Na_c Sn_{1-c}$ ($0 \le c \le 1$) alloys for which the basic experimental paper, in support of Bhatia theory for NaSn alloys, is by Tamaki *et al.*[3] They interpret their work by strong NaSn complex formation and a small amount of Na_3Sn and provide a binding energy of approximately 8 kcal/mole for addition of liquid to liquid. In this context, a free molecule calculation is of significant interest for two different reasons: such a calculation could contradict the Bhatia theory if no binding is found and secondly, if such complexes do exist in the liquid, they should be found in the vapor and detectable by modern techniques. In the theory proposed by Van der Lugt *et al.*, the basic idea is that each Na atom donates an electron to a Sn atom and $(Sn_4)^{4-}$ tetrahedra form. The Na^+ ions are relatively inactive—perhaps loosely attached to the tetrahedra. The calculations to follow basically bear only on the Bhatia theory.
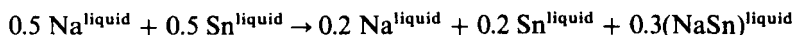
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* Address 1.8.88–31.7.90: Physics Department, Sultan Qaboos University, P.O. Box 32486 Al-Khod, Muscat, Oman.
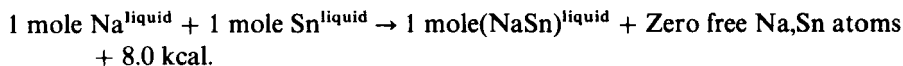
2 COMPUTATIONAL RESULTS AND DISCUSSION

Our calculations are based on accurate all-electron ab initio molecular orbital techniques, specifically Hartree-Fock theory. One of the primary considerations involved in these calculations is determination of the type of basis set to be used. Gaussian-type basis sets used in ab initio molecular orbital computations usually involve some compromise between computational cost and accuracy. For sodium, we have used the so-called 6-31G*[4,5] basis set. This basis consists of six Gaussian functions for inner shells, an inner set of valence s- and p-type functions with three Gaussians, an outer sp set with one Gaussian and a d-function. For Sn, we have used the Basis set provided by Huzinaga.[6] There are five s-type, 4 p-type and two d-type basis functions. Each basis function was in the form of a linear combination with fixed coefficients of primitive gaussian-type orbitals (GTO's). The first s-type function consisted of four s-type primitive GTO's, the other four each consisted of three s-type primitive GTO's. The first p-type function consisted of four p-type primitive GTO's, the other three each consisted of three p-type primitive GTO's. The first d-type function consisted of four d-type primitive GTO's and the second d-type function of three primitive GTO's. The computations were carried out on an IBM 4381 computer, using the program GAMESS, written by Dupuis et al.[7] For the system NaSn, an optimization[8] was carried out to search for the minimum on the potential energy surface. A modified conjugate gradient algorithm, which evaluates and utilizes the gradients each time the energy is computed, has been used. The second derivative matrix is updated employing the gradients. At each step, a one-dimensional minimization using a quartic polynomial is carried out, followed by an n-dimensional search using the second derivative matrix. For NaSn, the optimized bond length has been found to be 3.3120 Å, with a total energy of -6180.289599 atomic units (1 a.u. = 27.2 eV). Since the total energy of Na atom is -161.84144 a.u. and for the Sn atom, the total energy is -6018.33558 a.u., we get a binding energy per atom of 1.53 eV. Now, according to Tamaki et al.[3] if the NaSn alloy is composed of Na and Sn atoms and two types of chemical complexes NaSn and Na_3Sn with finite lifetimes, we have the chemical equation

$$(1 - c)Na + cSn \rightarrow (1 - c - n'c' - 3n''c'')Na + (c - n'c' - n''c'')Sn + c'(NaSn)_{n'}$$
$$+ c''(Na_3Sn)_{n''} \qquad (1)$$
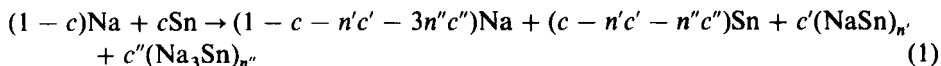
where n' and n'' indicate the magnitudes of the association of complexes. From their Figure 7, we then have, for $c = 0.5$, $c' = 0.3$, $n' = 1$, $n'' = 1$, (the equiatomic case):

$$0.5 \, Na^{liquid} + 0.5 \, Sn^{liquid} \rightarrow 0.2 \, Na^{liquid} + 0.2 \, Sn^{liquid} + 0.3(NaSn)^{liquid}$$

Furthermore, their Table 1 suggests

$$1 \text{ mole } Na^{liquid} + 1 \text{ mole } Sn^{liquid} \rightarrow 1 \text{ mole}(NaSn)^{liquid} + \text{Zero free Na,Sn atoms}$$
$$+ 8.0 \text{ kcal.}$$

This is equivalent to a binding of 0.35 eV per atom (of either Na or Sn) and we have ignored differences between free energy and internal energy. According to our calculation, we can write

$$1 \text{ mole Na}^{\text{vapor}} + 1 \text{ mole Sn}^{\text{vapor}} \rightarrow 1 \text{ mole (NaSn)}^{\text{vapor}} + 1.53 \text{ eV per atom}$$
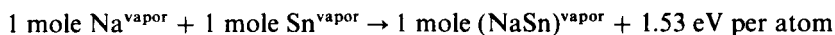
One would expect that binding is less in the liquid than in free space since overlap allows easier escape of the valence electrons doing the binding and so, our calculations basically support the Bhatia theory. It would be worthwhile to detect, therefore, the diatomic system NaSn in vapor.

In summary, we have considered the diatomic system NaSn from ab-initio Hartree–Fock theory point of view and the consequent implications for the Bhatia theory for liquid NaSn alloys.

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