

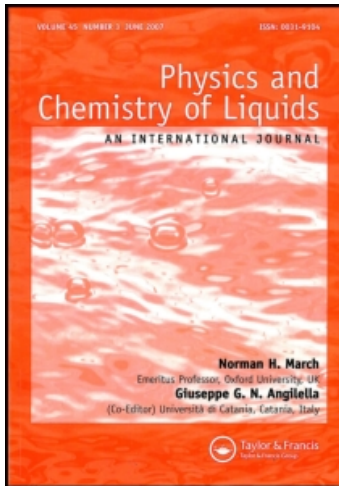
This article was downloaded by:

On: 28 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

A Note on the Bhatia Theory of Liquid NaSn Alloys

A. K. Ray^a; W. H. Young^{b,c}

^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

To cite this Article Ray, A. K. and Young, W. H.(1989) 'A Note on the Bhatia Theory of Liquid NaSn Alloys', *Physics and Chemistry of Liquids*, 19: 1, 7 – 9

To link to this Article: DOI: 10.1080/00319108908028402

URL: <http://dx.doi.org/10.1080/00319108908028402>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

A NOTE ON THE BHATIA THEORY OF LIQUID NaSn ALLOYS

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*

(Received 5 July 1988)

KEY WORDS: Diatomic system NaSn, bond length, Hartree-Fock theory.

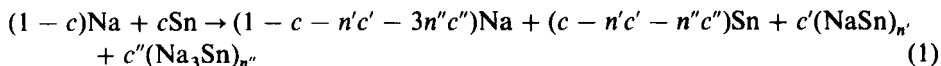
1 INTRODUCTION

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 $\text{Na}_c\text{Sn}_{1-c}$ ($0 \leq c \leq 1$) 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 $(\text{Sn}_4)^{4-}$ 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.

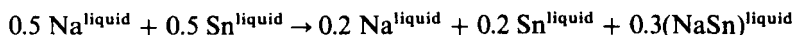
* Address 1.8.88-31.7.90: Physics Department, Sultan Qaboos University, P.O. Box 32486 Al-Khod, Muscat, Oman.

2 COMPUTATIONAL RESULTS AND DISCUSSION

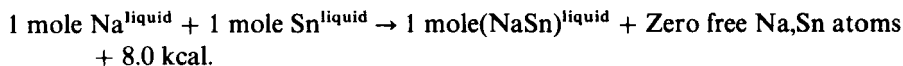
Our calculations are based on accurate all-electron ab initio molecular orbital techniques, specifically Hartree-Fock theory. One of the primary considerations involved in these calculations is determination of the type of basis set to be used. Gaussian-type basis sets used in ab initio molecular orbital 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 optimization⁸ 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 Na₃Sn with finite lifetimes, we have the chemical equation



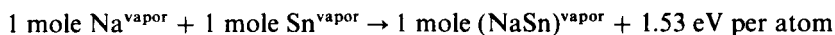
where *n'* and *n''* indicate the magnitudes of the association of complexes. From their Figure 7, we then have, for *c* = 0.5, *c'* = 0.3, *n'* = 1, *n''* = 1, (the equiatomic case):



Furthermore, their Table 1 suggests



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



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.

Acknowledgements

One of us (A.K.R.) would like to acknowledge partial support from the Welch Foundation, Houston, Texas (Grant No. Y-1092). Financial support and kind hospitality from the members of the physics department at the University of East Anglia, are also gratefully acknowledged.

References

1. A. B. Bhatia, W. H. Hargrove and D. E. Thorton, *Phys. Rev.*, **B9**, 435 (1974); A. B. Bhatia and W. H. Hargrove, *Phys. Rev.*, **B10**, 3186 (1974).
2. W. Van Der Lugt and W. Geertsma, *Can. J. Phys.*, **65**, 326 (1987).
3. S. Tamaki, T. Ishiguro and S. Takeda, *J. Phys.*, **F12**, 1613 (1982).
4. M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, **77**, 3654 (1982).
5. W. J. Hehre, L. Radom, P. V. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory* (John Wiley and Sons, 1986), p. 82.
6. J. Andzelm, M. Ktobukowski, E. Radzio-Andzelm, Y. Sakai and H. Tatewaki and S. Huzinaga (editor), *Gaussian Basis Sets for Molecular Calculations* (Elsevier, New York, 1984), pp. 284-285.
7. M. Dupuis, D. Spangler and J. J. Wendoloski, 1979, NRCC Report.
8. H. B. Schlegel, *J. Comp. Chem.*, **3**, 214 (1982).