

THERMODYNAMICS OF ALKALI METALS MELTS

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The local Animalu-Heine model pseudopotential modified by us earlier in the way that the well depth parameter for each component becomes non-empirically changed with an alloy composition is applied to thermodynamic studies of liquid Na-K-Cs, K-Rb-Cs, and Na-Rb-Cs systems. The atomic structure is described in the framework of the variational method with the hard-sphere pair potential as a reference one. Exchange-correlation effects are approximated by the Vashishta-Singwi function. The Nozieres-Pines interpolation formula is used to estimate the electron gas correlation energy. A number of mixing properties is computed for different concentrations of components in alloys at 373K. For lack of experimental information on investigated alloys our theoretical results may be considered as prognosed.

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1. Introduction

At the last time, the interest of researchers to alkali metals melts is significant in connection with their use as coolants in nuclear reactors. Some efforts to create the coolants with controlled properties lead to increasing in attention to multicomponent liquid alloys of alkali metals.

The pseudopotential theory is widely and successfully used for a quantitative description of simple metals and their alloys. For the liquid state thermodynamics of such substances, the model pseudopotential (MP) technique in conjunction with the thermodynamic perturbation theory (TPT) [1] is the most applicable theoretical approach [2]. The variational method of the TPT [3] is used mainly for these aims. A good agreement with experimental data of many thermodynamic properties has been achieved for a great number of binary liquid metal alloys in the framework of the approach named above [4-6]. However, a sufficiently large discrepancy of theoretical results on mixing characteristics with experiments is observed for alloys containing cesium in most cases.

Recently, we suggested a new version [7] of the local Animalu-Heine (AH) MP [8] (modified local AHMP - MLAHMP) taking into account the well depth dependency on the alloy composition. This approach enables us to improve significantly calculating results on thermodynamic properties of liquid Na-Cs, K-Cs and Rb-Cs alloys in the framework of the variational method [7].

Since our formalism is independent on a number of components in an alloy, it can be applied to ternary systems. On the other hand, earlier we generalized the variational method to n -component metal mixtures [9]. On this basis, we recently investigated the liquid eutectic Na-K-Cs alloy at different temperatures and obtained a good agreement of our results with available experimental information on some thermodynamic properties [10]. The results of refs. [7] and [10] show that the MLAHMP is more accurate method than LAHMP one.

In the present work, we apply the approach mentioned above to the thermodynamic study of liquid Na-K-Cs, K-Rb-Cs, and Na-Rb-Cs alloys at different component concentrations near a melting temperature. Unfortunately, experimental data for the alloys under consideration are unknown.

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However, a good agreement of our results with experiments for binary alkali-Cs alloys and eutectic Na-K-Cs system allows us to hope that our results for alloys under question are sufficiently accurate too.

2. Theory

The expansion of the variational technique in conjunction with the model pseudopotential approach to three-component mixtures is described in details in our previous work [9]. Let us especially emphasize that the description of a structure and interatomic interactions in ternary liquids is limited by pair functions as in cases of pure and binary fluids.

If the hard-sphere (HS) reference system is used, the main expression of the variational method for ternary liquid metal alloys (per atom) is

$$F \leq \frac{3}{2}kT - T(S_{HS} + S_{eg}) + U_e + 2\pi\rho \sum_{i,j=1}^3 c_i c_j \int_{\sigma_{ij}}^{\infty} dr r^2 g_{ij}^{HS}(r) \phi_{ij}(r) \quad (1)$$

where F is the free energy; T the temperature; k the Boltzmann's constant; S_{HS} the entropy of the HS mixture; S_{eg} the electron gas entropy; U_e the structure-independent contribution to the potential energy including the electron gas correlation energy term which is taken in the Nozieres-Pines form [11] in the present study; ρ the number density; c_i the concentration of the i -th component; σ_{ij} are the HS diameters; $g_{ij}(r)$ the pair correlation functions; $\phi_{ij}(r)$ the effective interatomic pair potentials determined as (in a.u.)

$$\phi_{ij}(r) = \frac{z_i z_j}{r} + \frac{1}{\pi^2 \rho} \int_0^{\infty} dq q^2 F_{ij}(q) \sin(qr) / qr \quad (2)$$

Here z_i is the valence of the i -th component and $F_{ij}(q)$ are the energy wave-number characteristics:

$$F_{ij}(q) = -(q^2 / 8\pi\rho) w_i(q) w_j(q) [(\chi_H(q) - 1) / \chi(q)] \quad (3)$$

where $\chi_H(q)$ is the Hartree dielectric function; $\chi(q)$ the dielectric function with an exchange-correlation correction approximated here in accordance with Vashishta and Singwi [12]; $w_i(q)$ the formfactor of the i -th kind bare ion expressed in LAHMP approach as follows:

$$w_i(q) = -4\pi\rho [(z - A_i R_{M_i}) \cos(q R_{M_i}) + A_i R_{M_i} \sin(q R_{M_i}) / q R_{M_i}] \xi(q) / q^2 \quad (4)$$

where z is the mean average valence; $\xi(q) = \exp[-0.03(q/2k_F)^4/16]$; k_F the free electron Fermi wave index; R_{M_i} and A_i are the parameters having the sense of the ion radius and the well depth of the effective ion-electron interaction for the ion of the i -th component. They are called the model radius and well depth, respectively.

Usually, the values of parameters mentioned above are independent on the kind of alloy but they are taken as in the case of pure metals or adjust to some experimental data for an alloy under interest. Below we represent the dependency of A_i on alloy composition introduced in ref. [7].

The well depth of the effective ion-electron interaction depends on electron energy, ε , within the AH approximation in a general case [8]:

$$A_i(\varepsilon) = A_i(\varepsilon_F) + (\varepsilon - \varepsilon_F)(\partial A_i(\varepsilon) / \partial \varepsilon) \quad (5)$$

where ε_F is the Fermi energy.

Supposing that $A_i(\varepsilon)$ for the pure metal is equal to $A_i(\varepsilon)$ for any alloy at the same ε , eq.(5) can be rewritten for both the cases as follows:

$$A_i(\varepsilon) = A_i(\varepsilon_{F_i}^0) + (\varepsilon - \varepsilon_{F_i}^0)(\partial A_i(\varepsilon)/\partial \varepsilon) \quad (6)$$

$$A_i(\varepsilon) = A_i(\varepsilon_F') + (\varepsilon - \varepsilon_F')(\partial A_i(\varepsilon)/\partial \varepsilon) \quad (7)$$

Here $\varepsilon_{F_i}^0$, ε_F' are the Fermi energies for pure metal of the i -th kind and alloy, respectively.

Subtracting eq.(7) from eq.(6) and taking into account that $A_i = A_i(\varepsilon_F')$ within the local pseudopotential approach we obtain the final MLAHMP expression for calculation of the well depth parameter of the i -th component in an alloy, A_i' , from the same one in a pure metal, A_i^0 :

$$A_i' = A_i^0 + (\varepsilon_F' - \varepsilon_{F_i}^0)(\partial A_i(\varepsilon)/\partial \varepsilon) \quad (8)$$

If we use the expression $A_i' = A_i^0$ instead of eq. (8), MLAHMP becomes LAHMP.

Values of A_i^0 and R_{M_i} for each component are taken from ref.[13] where they have been fitted for pure solid metals at $T=0$ K. Fermi energies $\varepsilon_{F_i}^0$ and ε_F' are calculated in accordance with ref.[8]. The values of $\partial A_i(\varepsilon)/\partial \varepsilon$ obtained by Cowly [14] are used.

We use the HS characteristics in analytical form: the Ashcroft-Langreth partial structure factors [15] generalized by Hoshino [16] and the entropy [9] obtained from the compressibility equation closely related to them.

In order to satisfy inequality (1), the minimization of its right hand side with respect to $\sigma_{11}, \sigma_{22}, \sigma_{33}$ and ρ is fulfilled. Due to this operation, our calculations are free from input experimental data for alloy under consideration. The combination of eq.(8) together with the minimization leads to the self-consistent computing procedure.

3. Results and discussion

The internal energies of mixing for liquid X-Y-Cs (X,Y = Na,K,Rb) alloys at different concentrations of components at $T=373$ K are calculated in the present work. Since the minimization of the right hand side of inequality (1) with respect to ρ leads to condition $p=0$, the internal energy of mixing becomes identical to the heat of mixing.

The results obtained are summarized in Table 1. Our previous results [7] on heats of mixing for equiatomic binary alloys (the latter ones are boundary cases of ternary alloys under consideration) are listed in Table 2.

The theoretical results given in Tables 1 and 2 show that the heat of mixing for any of the ternary alloys under consideration is far from additivity with respect to the boundary binary alloys.

Table 1. Heats of mixing of ternary liquid alloys calculated at $T = 373$ K.

Alloy	Composition of Alloy	Heat of Mixing, eV
Na-K-Cs	0.5 Na – 0.25 K – 0.25 Cs	0.0092
	0.25 Na – 0.5 K – 0.25 Cs	0.0041
	0.25 Na – 0.25 K – 0.5 Cs	0.0075
Na-Rb-Cs	0.5 Na – 0.25 Rb – 0.25 Cs	0.0085
	0.25 Na – 0.5 Rb – 0.25 Cs	- 0.0031
	0.25 Na – 0.25 Rb – 0.5 Cs	0.0091
K-Rb-Cs	0.5 K – 0.25 Rb – 0.25 Cs	0.0001
	0.25 K – 0.5 Rb – 0.25 Cs	0.0019
	0.25 K – 0.25 Rb – 0.5 Cs	0.0013

Table 2. Heats of mixing (eV) of binary equiatomic liquid alloys at $T = 373$ K in comparison with experiments [17].

Alloy	Theory	Experiment
Na - Cs	0.0093	0.0095
K - Cs	0.0005	0.0012
Rb - Cs	0.0004	- 0.0014
Na - K	0.0023	0.0076
Na - Rb	0.0050	0.0126
K - Rb	0.0002	0.0013

4. Conclusion

Since experimental data for the ternary alloys are absent our results could be considered as pioneering ones for the quantitative description of the systems under question. Some improvements in accuracy of results may be achieved if the temperature dependency of the well depth parameter will be introduced.

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References

- [1] R. W. Zwanzig, J. Chem. Phys. **22**, 1420 (1954).
- [2] J. Hafner, From Hamiltonians to Phase Diagrams, Springer, Berlin (1987).
- [3] G. A. Mansoori, F. B. Canfield, J. Chem. Phys. **51**, 4958 (1969).
- [4] R. N. Singh, R. B. Choudhary, J. Phys. F: Met. Phys. **11**, 1577 (1981).
- [5] S. C. Mishra, P. L. Srivastava, Phys. Stat. Sol. (b) **109**, 457 (1982).
- [6] N. E. Dubinin, A. A. Yuryev, N. A. Vatolin, Thermochim. Acta **316**, 123 (1998).
- [7] N. E. Dubinin, T. V. Trefilova, A. A. Yuryev, N. A. Vatolin, Int. J. Fluid Mech. Research **27**, 306 (2000).
- [8] A. O. E. Animalu, V. Heine, Phil. Mag. **12**, 1249 (1965).
- [9] N. E. Dubinin, A. A. Yuryev, N. A. Vatolin, High Temp. Mat. Proc. **14**, 285 (1995).
- [10] N. E. Dubinin, T. V. Trefilova, A. A. Yuryev, N. A. Vatolin, Proc. 1-st Intern. Conf. Math. Model. Comp. Simul. Met. Techn., College of Judea and Samaria, Ariel, Israel, 2000, p. 265.
- [11] D. Pines, P. Nozieres, The theory of quantum liquids, Benjamin, New York (1966).
- [12] P. Vashishta, K. S. Singwi, Phys. Rev. B. **6**, 875 (1972).
- [13] V. G. Vaks, A. V. Trefilov, FTT (Russia) **19**, 244 (1977).
- [14] E. R. Cowley, Can. J. Phys. **54**, 2348 (1976).
- [15] N. W. Ashcroft, D. C. Langreth, Phys. Rev. **156**, 685 (1967).
- [16] K. Hoshino, J. Phys. F.: Met. Phys. **13**, 1981 (1983).
- [17] R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelly, D. D. Wagman, Selected Values of the Thermodynamic Properties of the Elements and Binary Alloys, Amer. Soc. Met., Ohio (1973).