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Thermodynamics of alkali–alkali liquid alloys. Calculation by pseudopotential method and thermodynamic perturbation theory[1]

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Abstract

The pseudopotential theory in conjunction with the thermodynamic perturbation theory is applied to the calculation of the thermodynamic properties of Na–K, Na–Cs and Na–Rb liquid alloys. Two methods of the thermodynamic perturbation theory are used: variational and Weeks–Chandler–Andersen (WCA). The accuracy of the different pseudopotential models in the framework of the variational method is investigated. The most accurate pseudopotential model is used for calculations by the WCA method. The results obtained by the WCA method are in better agreement with the experimental data as compared with the results of the variational method. © 1998 Elsevier Science B.V.

Keywords: Pseudopotential method; Thermodynamic perturbation theory; Thermodynamic properties; Variational method; WCA approach

1. Introduction

The variational method based on the Gibbs–Bogolyubov inequality in conjunction with the pseudopotential theory had been successfully used to calculate some thermodynamic properties of liquid metal alloys [1–5]. However, only a few attempts to compare the accuracy of different pseudopotential models had been made [3,4]. The first purpose of our work is to determine the best local pseudopotential model for describing the thermodynamics of liquid alkali–alkali alloys in the framework of the variational method. We use two forms of model potentials (Animalu–Heine (AH) [6], Krasco–Gurskiy (KG) [7]) and three forms of exchange-correlation functions (Geldart–Vosko (GV) [8], Toigo–Woodruff (TW) [9], Vashishta–Singwi (VS) [10]). Here, the very simple Ashcroft potential and Heine–Abarenkov potential, which is the predecessor of the AH one, are not under consideration. We investigate such sensitive properties as the heat of mixing, ΔE, and the excess entropy of mixing, ΔS_{ex}. Other properties (internal energy, entropy, isothermal compressibility, thermal expansion coefficient, etc.) have already been investigated earlier [11].

The variational method with the hard-sphere (HS) model as a reference system is the simplest variety of thermodynamic perturbation theory. A more reliable reference system is used in the Weeks–Chandler–Andersen (WCA) method [12]. Earlier, the WCA theory had successfully been used to describe the thermodynamics of pure liquid metals [13] and of

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the structure of binary metal alloys [14,15]. Thus, the second purpose of the present work is to use the WCA method for the investigation of the thermodynamics of alloys and to compare the obtained results with those calculated by the variational method.

2. Theory

The idea to use the perturbation theory for a description of the thermodynamics of simple fluids had been proposed by Zwanzig [16] who had suggested to consider the attractive forces as perturbations on the repulsive ones. Then the potential energy U may by separated into two parts:

$$U = U_0 + U_1 \tag{1}$$

where U_0 is the potential energy of a reference system and U_1 the perturbation.

For binary system in analogy to Eq. (1), the interatomic pair potential $\varphi_{ij}(r)$ and the radial distribution function $g_{ij}(r)$ are split into two parts:

$$\varphi_{ij}(r) = \varphi_{ij}^0(r) + \varphi_{ij}^1(r) \tag{2}$$

$$g_{ij}(r) = g_{ij}^0(r) + g_{ij}^1(r) \tag{3}$$

As it had been shown in Ref. [16], the Helmholtz free energy F per ion can be appeared as

$$F = F_0 + \langle U_1 \rangle_0 \tag{4}$$

where

$$\langle U_1 \rangle_0 = 2\pi\rho \sum_{i,j=1}^{2} c_i c_j \int_0^\infty \mathrm{d}r r^2 g_{ij}^0(r) \varphi_{ij}^1(r) \tag{5}$$

where ρ is the atomic density and c_i the concentration of the ith component.

Mansoori and Canfield [17] had argued that it is true to pass from equality (4) to the following inequality:

$$F \le F_0 + \langle U_1 \rangle_0 \tag{6}$$

Thus, the authors of Ref. [17] connected the thermodynamic perturbation theory with the Gibbs–Bogolyubov inequality [18,19]. They used the additive HS model as a reference system. For binary mixture, the values of the HS diameters σ_{ij} are determined by minimizing the right side of Eq. (6) at each concentration and temperature with respect to σ_{11} and σ_{22}. This procedure is called the variational method, and hereafter we will denote the right side of the Eq. (6) as F_{var}. For not to use the experimental input data, we also fulfill the minimization of the F_{var} with respect to the atomic volume Ω.

If $\varphi_{ij}^0(r) = \varphi_{ij}^{\mathrm{HS}}(r)$, then $\varphi_{ij}^1(r) = \varphi_{ij}(r)$ at $r>\sigma_{ij}$. Besides, in the Percus–Yevick approximation [20], $g_{ij}^{\mathrm{HS}}(r) = 0$ at $r \le \sigma_{ij}$. Therefore,

$$F_{\mathrm{var}} = F_{\mathrm{HS}} + 2\pi\rho \sum_{i,j=1}^{2} c_i c_j \int_{\sigma_{ij}}^\infty \mathrm{d}r r^2 g_{ij}^{\mathrm{HS}}(r) \varphi_{ij}(r) \tag{7}$$

The final expression for the F_{var} obtained for binary metal alloys in the framework of the second-order perturbation theory in the pseudopotential is

$$F_{\mathrm{var}} = 3kT/2 + E_{\mathrm{eg}} + E_{\mathrm{f}} + E_{\mathrm{bs}} + E_{\mathrm{M}} - T(S_{\mathrm{HS}} + S_{\mathrm{eg}}) \tag{8}$$

where k is the Boltzmann's constant; T the temperature; E_{eg} the free energy of the electron gas; E_{f} the first-order pseudopotential perturbation term; E_{bs} the band-structure energy; E_{M} the Madelung energy; S_{HS} and S_{eg} the entropies of the HS mixture and the electron gas, respectively.

In the variational method, the internal energy E_{var} and the entropy S_{var} are obtained as $3kT/2+E_{\mathrm{eg}}+E_{\mathrm{f}}+E_{\mathrm{bs}}+E_{\mathrm{M}}$ and $S_{\mathrm{HS}}+S_{\mathrm{eg}}$, respectively.

The WCA theory gives another form of the $\varphi_{ij}^0(r)$ as compared with the variational method:

$$\varphi_{ij}^0(r) = \begin{cases} \varphi_{ij}(r) - \varphi_{ij}(\lambda_{ij}), & r \le \lambda_{ij} \\ 0, & r > \lambda_{ij} \end{cases} \tag{9}$$

where λ_{ij} is the position of the first minimum in $\varphi_{ij}(r)$.

Two approximate equations are used within the framework of the WCA method:

$$F_0 = F_{\mathrm{HS}} \tag{10}$$

$$g_{ij}^0(r) = y_{ij}^{\mathrm{HS}}(r) \exp(-\varphi_{ij}^0(r)/kT) \tag{11}$$

where

$$y_{ij}^{\mathrm{HS}}(r) = g_{ij}^{\mathrm{HS}}(r) \exp(\varphi_{ij}^{\mathrm{HS}}(r)/kT) \tag{12}$$

The next condition is used in the WCA method to determine the values of the HS diameters:

$$\sum_{i,j=1}^{2} c_i c_j I_{ij} = 0; \quad I_{ij} = \int_0^\infty B_{ij}(r) r^2 \mathrm{d}r \tag{13}$$

where $B_{ij}(r)$ is the blip-function:

$$B_{ij}(r) = g_{ij}^{0}(r) - g_{ij}^{\mathrm{HS}}(r) \tag{14}$$

To take into account Eqs. (9)–(14), the expression for the free energy in the WCA method, F_{WCA}, may be written as follows:

$$F_{\mathrm{WCA}} = F_{\mathrm{var}} - 2\pi\rho \sum_{i,j=1}^{2} c_i c_j \int_{\sigma_{ij}}^{\lambda_{ij}} \mathrm{d}r r^2 g_{ij}^{\mathrm{HS}}(r)\varphi_{ij}^{0}(r) \tag{15}$$

We calculate the second term at the right side of Eq. (15) numerically using the analytical expressions by Leonard et al. [21] for the $g_{ij}^{\mathrm{HS}}(r)$.

It is not possible to satisfy condition (13) when the additive HS model is used. That is why we use the condition $I_{11}=I_{22}=0$. In this case, the additional contribution $2\pi\rho c_1 c_2 \varphi_{12}(\lambda_{12}) I_{12}$ arises at the right side of Eq. (15).

Notice that we use the minimization of the F_{WSA} with respect to Ω as an additional condition of the calculations.

In contrast to the variational method, in the WCA method we calculate the entropy S_{WCA} numerically as $-(\partial F_{\mathrm{WCA}}/\partial T)_{\Omega}$, and as a result the internal energy E_{WCA} is defined to be equal to $F_{\mathrm{WCA}}+TS_{\mathrm{WCA}}$.

For the present work, the KG form of the model potential and the local version of the AH form are used. The form-factors of these potentials for non-screened ion are given as follows:

$$w_{\mathrm{KG}}^{0}(q) = (4\pi z/\Omega q^2)[((2a-1)q^2 r_c^2 - 1)/(1+q^2 r_c^2)^2] \tag{16}$$

$$w_{\mathrm{AH}}^{0}(q) = -\frac{4\pi}{\Omega q^2}[(z - A_0 R_{\mathrm{M}})\cos(qR_{\mathrm{M}}) + A_0 R_{\mathrm{M}}\sin(qR_{\mathrm{M}})/qR_{\mathrm{M}}]\xi(q) \tag{17}$$

where r_c, a, R_{M} and A_0 are the parameters; $\xi(q)=\exp[-0.03(q/2\kappa_{\mathrm{F}})^4/16]$; κ_{F} the free electron Fermi wave index; $z=c_1z_1+c_2z_2$ the mean average valence; and z_i the valence of the ith component.

We use the values of the parameters obtained by Vaks and Trefilov [22] for pure solid metals at $T=0$ K.

3. Results

We take into consideration the concentration dependencies of the heat of mixing and of the excess entropy

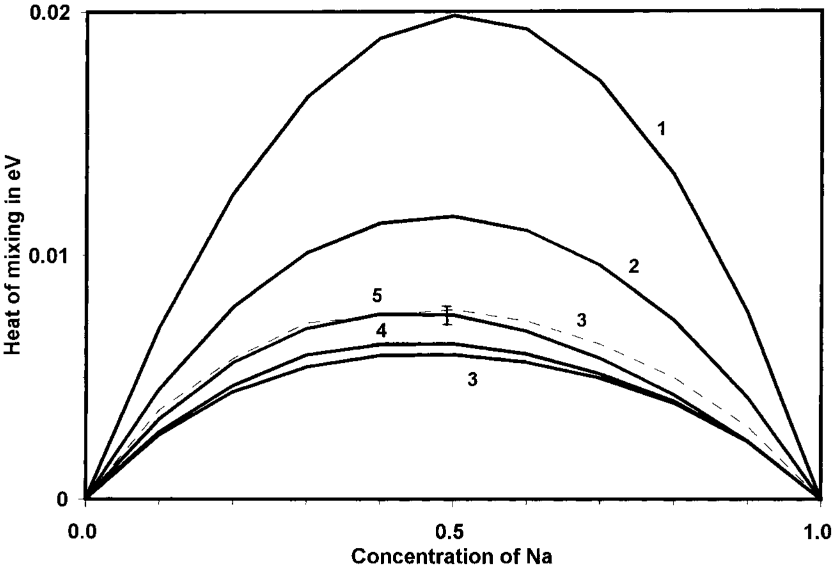

Fig. 1. Concentration dependence of the ΔE of Na–K at $T=373$ K. 1, AH–GV; 2, KG–GV; 3, AH–TW (- - -, with experimental Ω); 4, AH–VS; 5, experimental data [23].

of mixing of some alkali–alkali alloys at T=373 K. These properties are calculated as follows:

$$\Delta E = E_{\text{alloy}} - c_1 E_1 - c_2 E_2 \tag{18}$$

$$\Delta S_{\text{ex}} = S_{\text{alloy}} - c_1 S_1 - c_2 S_2 - S_{id} \tag{19}$$

where E_{alloy} and S_{alloy} are the internal energy and the entropy of the alloy under consideration, respectively; E_i and S_i, respectively, are the internal energy and the entropy of the ith pure component at the same temperature; and $S_{id}=-k(c_1\ln c_1+c_2\ln c_2)$.

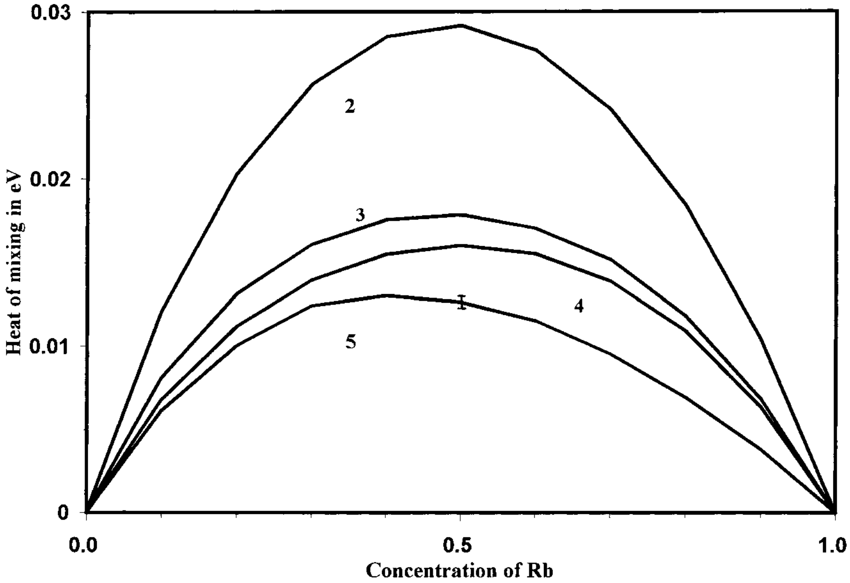

Fig. 2. Concentration dependence of the ΔE of Na–Rb at T=373 K. 2, KG–GV; 3, AH–TW; 4, AH–VS; 5, experimental data [23].

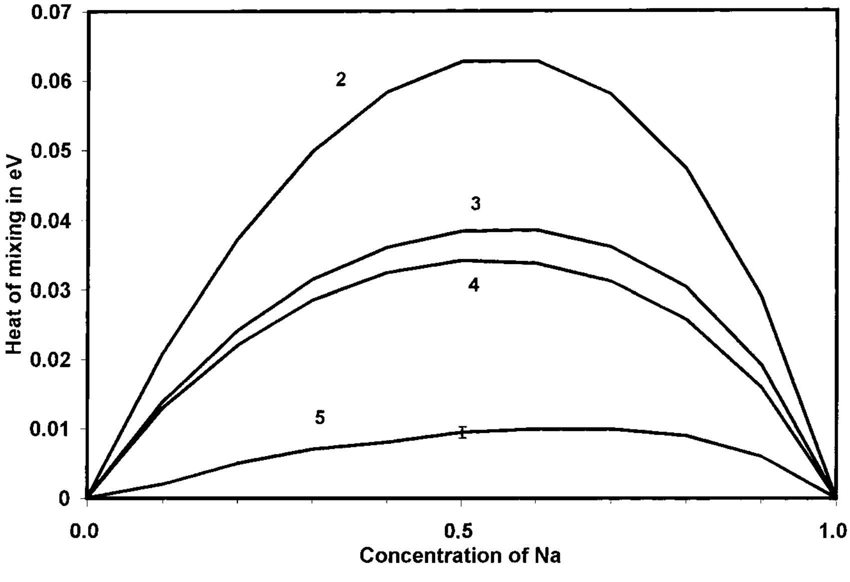

Fig. 3. Concentration dependence of the ΔE of Na–Cs at T=373 K. 2, KG–GV; 3, AH–TW; 4, AH–VS; 5, experimental data [23].

In the framework of the variational method, we use four combinations of the model potential with the exchange-correlation function *f*(*q*): AH–VS; AH–TW; AH–GV; KG–GV. Our results are shown in Figs. 1–5 in comparison with the experimental data [23–25]. The best agreement with the experiment for ΔE is achieved when AH–VS combination is used. For ΔS_{ex} good agreement is also observed when KG–GV combination is used. The results obtained by using the experimental values of the Ω [26] but not from the

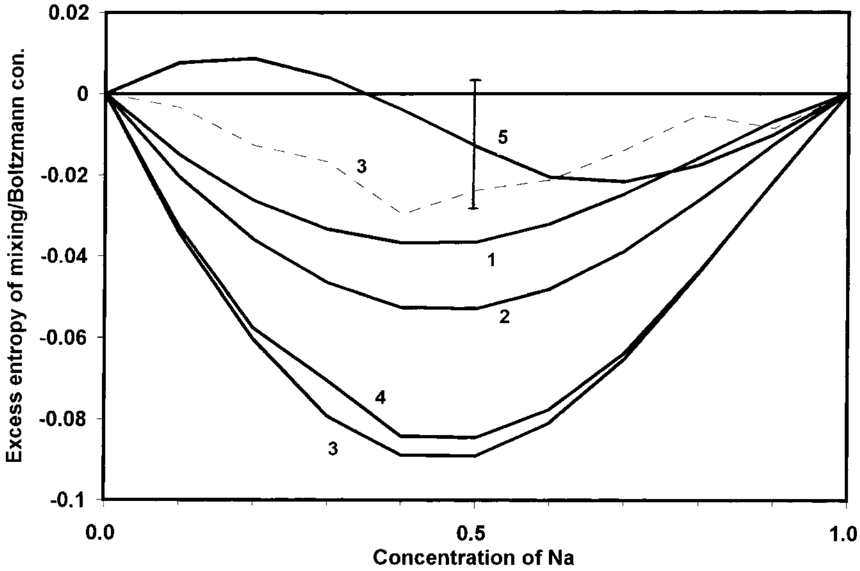

Fig. 4. Concentration dependence of the $\Delta S_{ex}/k$ of Na–K at T=373 K. 1, AH–GV; 2, KG–GV; 3, AH–TW (- - -, with experimental Ω); 4, AH–VS; 5, experimental data [23].

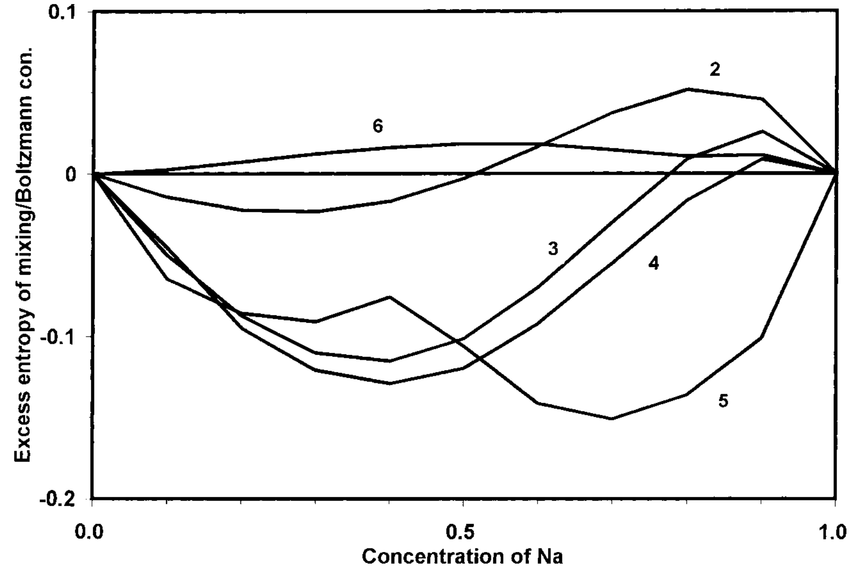

Fig. 5. Concentration dependence of the $\Delta S_{ex}/k$ of Na–Cs at T=373 K. 2, KG–GV; 3, AH–TW; 4, AH–VS; 5, 6, experimental data [24,25].

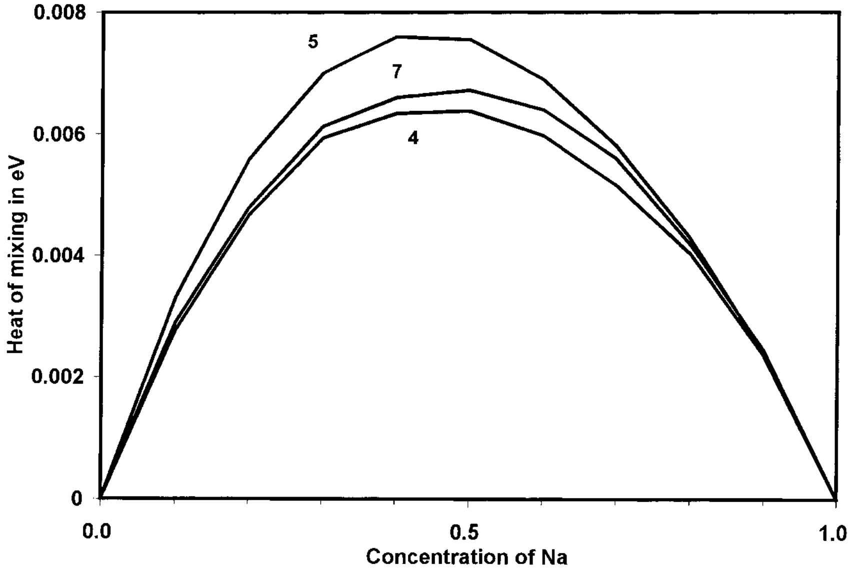

Fig. 6. Concentration dependence of the ΔE of Na–K at T=373 K. 4, variational method (AH–VS); 7, WCA (AH–VS); 5, experimental data [23].

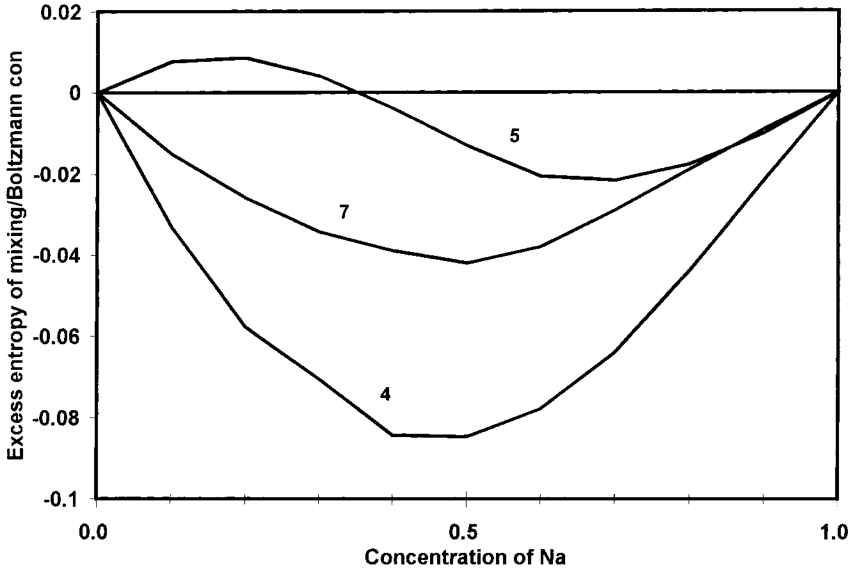

Fig. 7. Concentration dependence of the $\Delta S_{ex}/k$ of Na–K at T=373 K. 4, variational method (AH–VS); 7, WCA (AH–VS); 5, experimental data [23].

calculated ones are more close to the experiment, but the concentration dependence of ΔS_{ex} in this case demonstrates the non-smooth behavior (Figs. 1 and 4).

We take the AH–VS pseudopotential model for calculations by the WCA method. Obtained results for Na–K system are presented in Figs. 6 and 7. It is clear that the WCA method provides better accuracy than the variational one.

4. Discussion

As it follows from Section 3 and our early work [11], worse theoretical results are obtained for Cs-containing alloys (for e.g. in the case of AH–VS combination, the difference between calculated and experimental values of ΔE is ca. 15–20% for equiatomic Na–K and Na–Rb alloys; this disagreement is as low as 3% for equiatomic Na–K alloy when using experimental values of Ω, but it exceeds 300% for equiatomic Na–Cs system). Obviously, it can be explained by large difference between ion sizes of the components in these alloys.

The comparison of the different curves in Figs. 1–5 shows that the replacement of one $f(q)$ with another at the constant model potential often gives more significant change of the results than the replacement of the model potential at the constant $f(q)$.

It follows from consideration of the Figs. 6 and 7 that the replacement of the variational method with the WCA one leads to more drastic change of ΔS_{ex} than of ΔE. This fact seems to be reasonable since ΔS_{ex} is more dependent on structure and is more sensitive to the method of calculation than ΔE.

5. Conclusions

We conclude from our investigations that the pseudopotential theory in conjunction with the thermodynamic perturbation theory can be successfully applied to quantitative study of thermodynamic properties of alkali–alkali liquid alloys. The further progress in this field of research may be achieved by introducing more advanced versions of the thermodynamic perturbation theory, such as the optimized random phase approximation [27] in which the reference system interatomic potential includes attractive effects.

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