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STUDY OF THERMODYNAMIC PROPERTIES OF LIQUID BINARY ALLOYS BY A PSEUDOPOTENTIAL METHOD

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On the basis of the Percus–Yevick hard-sphere model as a reference system and the Gibbs–Bogoliubov inequality, a thermodynamic perturbation method is applied with the use of the well-known model potential. By applying a variational method, the hard-core diameters are found which correspond to a minimum free energy. With this procedure, the thermodynamic properties such as the internal energy, entropy, Helmholtz free energy, entropy of mixing, and heat of mixing are computed for liquid NaK binary systems. The influence of the local-field correction functions of Hartree, Taylor, Ichimaru–Utsumi, Farid–Heine–Engel–Robertson, and Sarkar–Sen–Haldar–Roy is also investigated. The computed excess entropy is in agreement with available experimental data in the case of liquid alloys, whereas the agreement for the heat of mixing is poor. This may be due to the sensitivity of the latter to the potential parameters and dielectric function.

Keywords: *pseudopotential method, liquid NaK alloys, Percus–Yevick (PY) hard-sphere model, local-field correction functions, thermodynamic properties.*

Introduction. The theoretical basis for understanding the thermodynamics of simple liquid metals has been forged in recent years to a point where it can be used to calculate the thermodynamic properties with some success. This advance has become possible due to the combination of the pseudopotential and thermodynamic perturbation theories. The pseudopotential theory enables one to formulate the energy in terms of the pseudopotential and structure factor [1–13]. On the other hand, it is possible to write closed-form expressions for the thermodynamic quantities of hard-sphere systems, including the structure factor, in the Percus–Yevick (PY) approximation [14, 15]. A link between both theories is provided by a variational technique based on the Gibbs–Bogoliubov (GB) inequality [1–13]. This inequality states that, when the Hamiltonian of a given system is regarded as the Hamiltonian of a reference system plus a perturbation, the free energy of the system will always be smaller than that of the reference system plus the expectation values of the perturbation (calculated with the structure factors of the reference system). In our case, the reference system is one consisting of hard spheres, and their diameters will be chosen so as to minimize the free energy. Recently, Chekmarev et al. [16] reported structural information for alkali metals in the liquid–vapor interface using a simple model potential. Moreover, very recently Ghatee and Bahadori [17] described the interionic potential function in liquid alkali metals by the thermodynamic regularity approach.

The general theory of the thermodynamics of alloys is based on the results obtained from three distinct areas of current interest. First, there exists the theory of pseudopotentials developed by Harrison [18]. This enables one to write the energy of an alloy in terms of the pseudopotentials and partial structure factors. However, except for very special circumstances, they are not sufficiently well known for most purposes. Moreover, it is precisely the free energy that is of primary interest at elevated temperatures [19]. The structure factors closely resemble the free energy of pure liquid metals for hard spheres [20]. Faber [2] also showed that the corresponding entropies can be characterized by the behavior of hard spheres. This leads us to the second area of interest, namely, the thermodynamics of hard-sphere systems which was studied by Lebowitz et al. [21–23]. As a result, now it is possible to write the thermodynamic quantities of interest for mixtures of hard spheres, including the partial structure factors and free energies, in the closed form of the Percus–Yevick approximation. It is also known that such structure factors might be useful for interpreta-

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tion of x-ray and neutron form factors in at least some binary alloy systems [2, 14, 15, 24]. Finally, the precise way of linking up the formal hard-sphere results with those obtained by the pseudopotential technique is provided by the GB inequality [25, 26]. This states that, if the Hamiltonian for a system is regarded as that for a reference system plus a perturbation, the Helmholtz free energy for the reference system plus the expectation value of the perturbation averaged over the system is greater than or equal to the Helmholtz free energy of the actual system.

Although the theoretical formulation in investigating the thermodynamic properties of binary alloys is very straightforward from the pseudopotential point of view, a few attempts have been made to compute such properties as functions of concentration [1–12]. Therefore, we are motivated to compute the thermodynamic properties of liquid binary alloys of alkali-alkali components, like the internal energy, entropy, Helmholtz free energy, entropy of mixing, and heat of mixing, as functions of concentration. We use the well-known single parametric empty core (EMC) model potential of Ashcroft [27]. The modified Hartree dielectric function [18], together with the exchange and correlation effects proposed by Hartree (HR) [18], Taylor (TY) [28], Ichimaru–Utsumi (IU) [29], Farid et al. (FD) [30], and Sarkar et al. (SS) [31] for the conduction electrons, generates satisfactory values of the energy wave number characteristics.

Computational Methodology. The well-known empty core model potential of Ashcroft [27] employed in the present study has the form (in atomic units)

$$W_{\mathrm{B}}(q) = -\frac{8\pi Z}{\Omega_0 q^2}\cos(q r_{\mathrm{c}})\,. \tag{1}$$

We consider an alloy with c_1N atoms of type 1 at positions $\{R_1\}$ and c_2N atoms of type 2 at positions $\{R_2\}$ $(c_1 + c_2 = 1)$. The number densities of the ion species are $n_1 = c_1n$ and $n_2 = c_2n$, where $n = N/\Omega_0$. If Z_1 and Z_2 are the valences, the free electron Fermi wave vector is given by $k_{\mathrm{F}}^3 = 3\pi^2\overline{Z}n$, where $\overline{Z}n = Z_1n_1 + Z_2n_2$ is the average valence electron density [6].

The electronic free energy of an alloy for some fixed configuration is given by [6]:

$$F_{\mathrm{el}}\big(\{R_1\}, \{R_2\}\big) = F_{\mathrm{e.g}} + F_1 + F_2\big(\{R_1\}, \{R_2\}\big)\,, \tag{2}$$

where F_1 and F_2 are obtained via the first- and second-order pseudopotential theory.

Adding the direct Coulomb interaction between ions, we can obtain the effective potential energy for an ion system. We need only the expectation value of this effective potential averaged over some reference system, which is given as [6]

$$F_{\mathrm{p.s}} = F_{\mathrm{e.g}} + F_{\mathrm{M}} + F_1 + F_2\,. \tag{3}$$

Here, according to [6],

$$F_{\mathrm{e.g}} = \left[\frac{3}{10}k_{\mathrm{F}}^3 - \frac{3}{4\pi}k_{\mathrm{F}} + E_{\mathrm{cor}} - \frac{1}{2}\gamma_{\mathrm{e.g}}T^2\right]\overline{Z}\,, \tag{4}$$

where E_{cor} = –0.0474–0.0155 ln k_{F} is the correlation energy contribution and the constant $\gamma_{\mathrm{e.g}} = (\pi k_{\mathrm{B}}/k_{\mathrm{F}})^2$ is the low-temperature specific heat of an electron gas.

The Madelung contribution in closed form can be written as [6]

$$F_{\mathrm{M}} = c_1^2Z_1^2I_{11} + c_2^2Z_2^2I_{22} + 2c_1c_2Z_1Z_2I_{12}\,, \tag{5}$$

$$I_{11} = \frac{\pi n}{1+2\eta}\left[-\sigma_1^2 + \frac{1}{5}\left(1-\frac{\eta}{2}\right)\big(\eta_1\sigma_1^2 + \eta_2\sigma_2^2\big) + \eta_1\sigma_1(\sigma_2-\sigma_1) + \frac{1}{2}\eta_1\eta_2(\sigma_2-\sigma_1)^2\right], \tag{6}$$

$$I_{12} = \frac{\pi n}{1+2\eta}\left[-\frac{1}{4}(\sigma_1+\sigma_2)^2 + \frac{1}{5}\left(1-\frac{\eta}{2}\right)\big(\eta_1\sigma_1^2 + \eta_2\sigma_2^2\big) + \frac{1}{2}(\eta_2\sigma_1 - \eta_1\sigma_2)(\sigma_2-\sigma_1)\right.$$

$$+\frac{1}{2}\eta_1\eta_2(\sigma_2-\sigma_1)^2\Bigg], \tag{7}$$

I_{22} is obtained by interchanging η_1, σ_1 and η_2, σ_2 in Eq. (6). The total packing fraction of the alloy is expressed as [9]

$$\eta=\frac{1}{6}\left(n_1\sigma_1^2+n_2\sigma_2^2\right). \tag{8}$$

With the use of the zeroth Fourier component of the bare pseudopotential, F_1 is obtained. We denote the components of **q** as $W_{Bi}(q)$ (i = 1, 2), which gives [6]

$$F_1=(c_1\alpha_1+c_2\alpha_2)\,\bar{Z}n, \tag{9}$$

where

$$\alpha_i=\lim_{q\to 0}\left[W_{Bi}(q)+\frac{4\pi Z_i e^2}{q^2}\right]. \tag{10}$$

The second order or the band-structure energy $F_2\left(\{R_1\},\{R_2\}\right)$ is given by

$$F_2=\frac{1}{16\pi^3}\times$$

$$\times\int_0^\infty\left[c_1c_2(W_{B1}-W_{B2})^2+c_1^2W_{B1}^2a_{11}+2(c_1c_2)^{1/2}W_{B1}W_{B2}+c_2^2W_{B2}^2a_{22}\right]\left(\frac{1}{\varepsilon(q)}-1\right)dq-\frac{\bar{Z}}{2}\gamma_2(T)\,T^2. \tag{11}$$

The function $\varepsilon(q)$ is the modified Hartree dielectric screening function, which is often written as [12]

$$\varepsilon(q)=1+(\varepsilon_{HR}(x)-1)(1-G(x)),\quad x=\frac{q}{2k_F}. \tag{12}$$

Here $\varepsilon_{HR}(x)$ is the static Hartree dielectric function [12], which is given by

$$\varepsilon_{HR}(x)=1+\frac{me^2}{2\pi k_F\hbar^2\eta^2}\left(\frac{1-x^2}{2x}\ln\left|\frac{1+x}{1-x}\right|+1\right) \tag{13}$$

and $G(x)$ is the local-field correction function. In the present investigation, the local-field correction functions due to Hartree (HR) [18], Taylor (TY) [28], Ichimaru–Utsumi (IU) [29], Farid et al. (FD) [30], and Sarkar et al. (SS) [31] are incorporated to reflect the impact of the exchange and correlation effects.

The second-order correction to the usual γ factor $\gamma_2(T)$ which describes the low-temperature electronic specific heat is given by [6]

$$\gamma_2(T)=\frac{2k_B^2}{3\pi^2\bar{Z}}$$

$$\times\int_0^\infty f(x)\frac{x^2}{x^2-1}\left[c_1c_2(W_{B1}-W_{B2})^2+c_1^2W_{B1}^2a_{11}+2(c_1c_2)^{1/2}W_{B1}W_{B2}+c_2^2W_{B2}^2a_{22}\right]dx, \tag{14}$$

where

$$f(x) = \frac{1}{2} + \frac{x^2 - 1}{4x} \ln \left| \frac{1 + x}{1 - x} \right| . \tag{15}$$

The free energy per particle $F_{\text{h.s}}$ of the hard-sphere mixture can be written as [6]

$$F_{\text{h.s}} = c_1 \mu_1 + c_2 \mu_2 - \frac{P_{\text{h.s}}}{n} . \tag{16}$$

In the PY approximation, the quantities appearing in Eq. (16) are written as [6]

$$\frac{\mu_i}{k_{\text{B}} T} = \ln \left(n_i \frac{2\pi\hbar^2}{m_i k_{\text{B}} T} \right)^{\frac{3}{2}} - \ln (1 - \eta) + \ln \left(\frac{3X\sigma_i}{1 - \eta} \right) + \frac{3}{2} \left(\frac{3X^2}{(1 - \eta)^2} + \frac{2Y}{1 - \eta} \right) \sigma_i^2 + \frac{\pi P_{\text{h.s}} \sigma_i^3}{6 k_{\text{B}} T} , \tag{17}$$

$$\frac{P_{\text{h.s}}}{k_{\text{B}} T} = \frac{n (1 + \eta + \eta^2) - \frac{1}{2} \pi n_1 n_2 (\sigma_1 - \sigma_2)^2 (\sigma_1 + \sigma_2 + \sigma_1 \sigma_2 X)}{(1 - \eta)^3} , \tag{18}$$

where

$$X = \frac{1}{6} \pi \left(n_1 \sigma_1^2 + n_2 \sigma_2^2 \right) , \quad Y = \frac{1}{6} \pi (n_1 \sigma_1 + n_2 \sigma_2) . \tag{19}$$

Substituting Eqs. (17)–(19) into Eq. (16) and using the relation $S = -(\partial F / \partial T)_{\Omega_0}$, we get

$$F_{\text{h.s}} = \frac{3}{2} k_{\text{B}} T - T S_{\text{h.s}} , \tag{20}$$

where

$$S_{\text{h.s}} = S_{\text{gas}} + S_c + S_\eta + S_\sigma , \tag{21}$$

$$\frac{S_{\text{gas}}}{k_{\text{B}}} = \ln \left(\frac{e}{n} \left(\frac{e m' k_{\text{B}} T}{2\pi\hbar^2} \right)^{\frac{3}{2}} \right) , \quad m' = m_1^{c_1} m_2^{c_2} , \tag{22}$$

$$\frac{S_c}{k_{\text{B}}} = - (c_1 \ln c_1 + c_2 \ln c_2) , \tag{23}$$

$$\frac{S_\eta}{k_{\text{B}}} = \ln (1 - \eta) + \frac{3}{2} \left(1 - \frac{1}{(1 - \eta)^2} \right) , \tag{24}$$

$$\frac{S_\sigma}{k_{\text{B}}} = \frac{\pi c_1 c_2 n (\sigma_1 - \sigma_2)^2 \left(12 (\sigma_1 + \sigma_2) - \pi n \left(c_1 \sigma_1^4 + c_2 \sigma_2^4 \right)^2 \right)}{24 (1 - \eta)^2} . \tag{25}$$

The Helmholtz free energy per ion of an alloy A is given by

$$A = F_{\text{p.s}} + F_{\text{h.s}} . \tag{26}$$

The hard-sphere diameters σ_i are obtained by minimizing the Helmholtz free energy by treating η_i as the variation parameter:

$$\left(\frac{\partial A}{\partial \sigma_i}\right)_{\Omega_0, T} = 0\,, \quad i = 1, 2\,. \tag{27}$$

Now, the total entropy is written in terms of the Helmholtz free energy:

$$S = -\left(\frac{\partial A}{\partial T}\right)_{\Omega_0} \tag{28}$$

and, similarly, the pressure is given by

$$P = n^2 \left(\frac{\partial A}{\partial n}\right)_T . \tag{29}$$

On the basis of Eqs. (25) and (26), the entropy is written as

$$S = S_{\text{h.s}} + S_{\text{p.s}}\,. \tag{30}$$

Here, $S_{\text{h.s}}$ is calculated from Eq. (21), whereas $S_{\text{p.s}} = \overline{Z}(\gamma_{\text{e.g}} + \gamma_2)T$. The term $S_{\text{p.s}}$ is negligibly small in comparison with $S_{\text{h.s}}$.

Generally, the internal energy U and Helmholtz energy A are connected by the relation $A = U - TS$. Therefore, the enthalpy of mixing is given by

$$\Delta H_{\text{mix}} = \Delta E_{\text{mix}} + P\Delta\Omega_{0\text{mix}} + T\Delta S_{\text{mix}}\,. \tag{31}$$

Here, $P\Delta\Omega_{0\,\text{mix}}$ is negligibly small and close to zero, so that Eq. (28) is written as

$$\Delta H_{\text{mix}} = \Delta E_{\text{mix}} + T\Delta S_{\text{mix}}\,, \tag{32}$$

where ΔE_{mix} and ΔS_{mix} include all the terms with the subscripts p.s and h.s (only such values can be compared with the experiment). The heat of mixing is calculated from the following equation:

$$\Delta E_{\text{mix}} = \Delta F_{\text{e.g}} + \Delta F_1 + \Delta F_2 + \Delta F_{\text{M}}\,, \tag{33}$$

where

$$\Delta F_j = F_{\text{al}j} - c_1 F_{1\text{A}} - c_2 F_{2\text{B}}\,, \tag{34}$$

the subscript j takes the values e.g, 1, 2, and M, and the subscripts A and B are related to two metallic components. Similarly, in the computation of the excess entropy $\Delta S_{\text{p.s}} = 0$ and $\Delta\Omega_{0\,\text{mix}} = 0$. Therefore, the excess entropy is given by

$$\Delta S = \Delta S_{\text{gas}} + \Delta S_{\eta} + \Delta S_{\sigma}\,, \tag{35}$$

where

$$\Delta S_j = S_{\text{al}j} - c_1 S_{1\text{A}} - c_2 S_{2\text{B}} \tag{36}$$

and j corresponds to gas, η, and σ.

TABLE 1. Input Parameters and Constants

Element	Z	M, amu	Ω_0, au	r_C, au
Na	1	22.98	280.50	1.67
K	1	39.10	541.73	2.12

TABLE 2. Various Contributions to the Internal Energy (au)

c_2	$-F_{e.g}\cdot 10^3$		$F_1\cdot 10^3$		$-F_2\cdot 10^3$						$-F_M\cdot 10^3$		$-F_{h.s}\cdot 10^3$	
	Present	[6]	Present	[6]	HR	TY	IU	FD	SS	[6]	Present	[6]	Present	[6]
0.0	81.63	81.59	–62.45	–62.46	6.57	5.91	5.78	5.77	6.14	13.69	212.43	210.17	7.51	7.34
0.1	81.74	–	–60.63	–	18.16	16.81	16.58	16.55	17.30	–	201.37	–	8.12	–
0.2	81.72	–	–59.09	–	18.55	16.91	16.64	16.60	17.53	–	192.15	–	8.54	–
0.3	81.62	–	–57.78	–	15.10	13.42	13.15	13.10	14.08	–	184.55	–	8.87	–
0.4	81.45	–	–56.64	–	10.80	9.26	9.02	8.96	9.89	–	178.36	–	9.12	–
0.5	81.24	81.23	–55.65	–56.32	7.17	5.85	5.66	5.61	6.41	19.20	173.40	181.70	9.32	9.29
0.6	81.00	–	–54.78	–	4.88	3.81	3.66	3.61	4.27	–	169.53	–	9.45	–
0.7	80.73	–	–54.00	–	4.07	3.23	3.10	3.07	3.59	–	166.61	–	9.53	–
0.8	80.44	–	–53.31	–	4.47	3.79	3.69	3.67	4.07	–	164.54	–	9.55	–
0.9	80.13	–	–52.69	–	5.45	4.88	4.79	4.77	5.10	–	163.20	–	9.48	–
1.0	79.82	79.76	–52.13	–52.12	5.19	4.74	4.65	4.65	4.90	–14.50	162.53	166.74	9.23	9.62

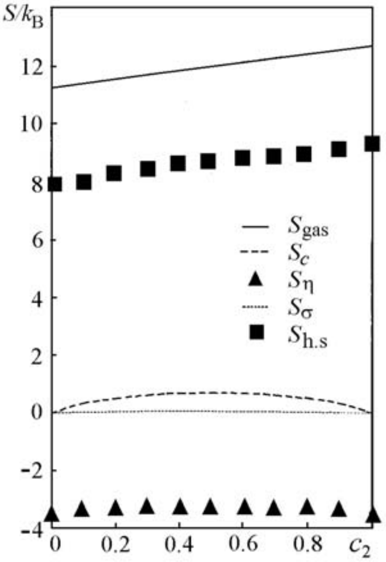


Fig. 1. Various contributions to the entropy for the NaK binary alloy.

Results and Discussion. The input parameters and constants which are used in the present investigation of the thermodynamic properties were taken from [6] and are given in Table 1. The computations are performed for the NaK binary alloys at $T = 373$ K.

Various contributions to the internal energy have been computed at different alloy concentrations. It is seen from Table 2 that the values of $F_{e.g}$, F_2, and F_M are negative, while F_1 makes a positive contribution to the internal energy E. The contributions F_1 and F_2 are dependent on the model potential, while other ones, i.e., $F_{e.g}$ and F_M, are independent of it. Here, we use the PY partial structure factor [9] to describe the structural behavior of alloy systems. It is seen that the local-field correction functions affect only the term F_2, which corresponds to the second-order band-

TABLE 3. Values of the Internal Energy $-U \cdot 10^3$ (au)

c_2	Present results					Theor. [6]	Exp. [6]
	HR	TY	IU	FD	SS		
0.0	236.41	235.75	235.62	235.61	235.98	241.00	226.00
0.1	238.87	237.52	237.29	237.26	238.01	–	–
0.2	231.56	229.92	229.65	229.61	230.54	–	–
0.3	221.71	220.04	219.77	219.72	220.70	–	–
0.4	212.19	210.65	210.41	210.36	211.28	–	–
0.5	204.39	203.07	202.88	202.83	203.63	–	–
0.6	198.86	197.79	197.63	197.59	198.25	–	–
0.7	195.63	194.79	194.67	194.63	195.15	–	–
0.8	194.36	193.68	193.58	193.55	193.96	–	–
0.9	194.33	193.76	193.66	193.65	193.98	–	–
1.0	193.64	193.19	193.11	193.10	193.35	207.00	190.00

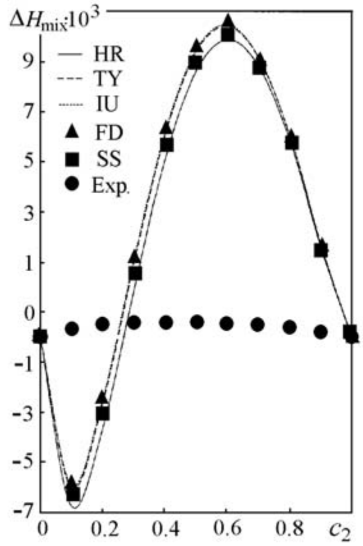
TABLE 4. Values of the Helmholtz Free Energy $-A \cdot 10^3$ (au)

c_2	Present results					[6]
	HR	TY	IU	FD	SS	
0.0	243.92	243.26	243.13	243.12	243.49	250.33
0.1	246.99	245.64	245.41	245.38	246.13	–
0.2	240.10	238.46	238.19	238.15	239.08	–
0.3	230.58	228.90	228.64	228.59	229.56	–
0.4	221.32	219.77	219.54	219.48	220.40	–
0.5	213.71	212.39	212.19	212.14	212.95	235.09
0.6	208.31	207.24	207.09	207.04	207.70	–
0.7	205.16	204.32	204.20	204.16	204.68	–
0.8	203.90	203.23	203.12	203.10	203.51	–
0.9	203.80	203.23	203.14	203.12	203.45	–
1.0	202.87	202.42	202.33	202.33	202.58	218.51

structure energy. Presently computed results for F_2 differ from those of Umar et al. [6] because different local-field correction functions are used in both computations.

The various contributions to the total entropy $S_{h.s}$ are presented in Fig. 1. Among the four contributions, S_{gas} represents the gas term, S_c is the ideal entropy of mixing, S_η corresponds to the packing density η, and S_σ arises due to the difference in the hard-sphere diameters of Na and K atoms. It is seen from Fig. 1 that S_η is negative, while other contributions are positive. The maximum contribution to the total entropy is made by the term S_{gas}. The value of S_η depends only on the packing density η. The contribution S_{gas} increases the absolute value of the total entropy, whereas S_η tends to decrease it. The quantity S_c, as the ideal entropy of mixing, remains the same for all the concentrations. The curve $S_c(c_2)$ is parabolic, S_{gas} increases with concentration, and the dependence $S_{h.s}(c_2)$ is nonlinear. All the contributions to the total entropy are independent of the local-field correction function.

The total internal energy U and the Helmholtz free energy A, which are calculated as functions of the concentration, are presented in Tables 3 and 4. It can be noted that the major contribution to the total internal energy comes from its structural part. The magnitude of the Madelung energy $|F_M|$ is quite large in comparison with other energy terms. This magnitude decreases with an increase in the atomic fraction of the heavier element of the alloy. The energy of an electron gas $F_{e.g}$ in the mixture varies slightly with temperature of the metallic elements. The negative contribution to the energy is due to the first-order pseudopotential term F_1, which decreases with increase in the



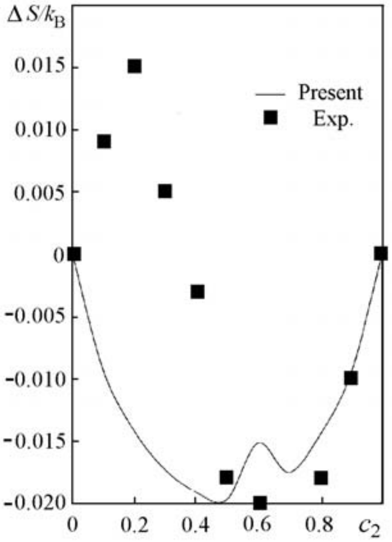


Fig. 2. Heat of mixing for NaK binary alloys. ΔH_{mix}, au.

Fig. 3. Excess entropy for NaK binary alloys.

concentration of the heavier element. The modulus of the band-structure energy $|F_2|$ has a maximum in the intermediate concentration range. However, the aggregate effects of different energy terms are such that the total internal energy of the system is found to be almost linear. Therefore, its Helmholtz free energy is also almost linear for most of the alloy concentrations. The influence of the local-field correction function is found to be very slight. Generally, the Helmholtz free energy *A* obtained due to the TY, IU, and SS local-field correction functions lies between those for the HR and FD functions. As the volume of a particular system increases, the magnitude of both the total internal energy and the Helmholtz free energy of the system decrease. The present values of these characteristics for pure metallic components, as well as for an equiatomic alloy like $Na_{0.5}K_{0.5}$, are found to be in qualitative agreement with the available theoretical data [6].

The percentile influence of various local-field correction functions, namely, TY, IU, FD, and SS, on the values of F_2, the Helmholtz free energy, and the total internal energy has been found, with respect to the static HR screening function, to lie in the ranges 4.74–26.02, 0.14–0.86, and 0.15–0.90, respectively.

Ashcroft and Langreth [14, 15] pointed out that the core radius of the bare-ion model pseudopotential fit the experimental data at $q = 2k_F$, and thus there is an uncertainty in the behavior of $W_B(q)$ at $q = 0$. Therefore, α_i in Eq. (10) may be considered as an independent parameter which can be chosen to give a good fit to some property, say, the internal energy *F* for a pure liquid; then this parameter may be used in alloy calculations.

The heat of mixing ΔH for the NaK binary alloy calculated from Eq. (33) is plotted in Fig. 2. It is seen from this figure that the values of ΔH are asymmetrical about $c_2 = 0.5$. Of great importance is the fact that different forms of the local-field correlation function affect the heat of mixing to a greater extent than the values of the total internal energy and Helmholtz free energy. The heat of mixing is found to have only a weak dependence on the choice of the form of the local-field correction function which enters into the calculation through the dominant second-order potential term F_2. However, the form of the model potential used in the computation plays a vital role in predicting the properties mentioned. It is evident from Fig. 2 that the HR dielectric function gives lower values of the heat of mixing, whereas the FD function results in higher values. Initially, the heat of mixing is negative up to the concentration $c_2 = 0.2$, then ΔH becomes positive. The present results for the heat of mixing are found to be much higher than the experimental data of [32]. The large discrepancy is due to the different criteria used to calculate the thermodynamic properties of alloy systems.

The excess entropy ΔS calculated from Eq. (32) is plotted in Fig. 3. It is slightly asymmetrical about $c_2 = 0.5$ and is found to be in qualitative agreement with the available experimental data [32]. Here the computed data are negative throughout the whole range, whereas the experimental data [32] are initially positive up to some concentration and then become negative. Moreover, the bump which is observed at the concentration $c_2 = 0.6$ may be due to the disorder created in the alloy system. Hence, the experimental and theoretical values of the excess entropy agree qualitatively up to some higher concentration, and their tendencies in the dependences on the alloy composition are similar.

While Umar et al. [6] used the EMC model potential with an older local-field correction function, in the present study we used the most recent and well-known local-field corrections proposed by Hartree [18], Taylor [28], Ichimaru–Utsumi [29], Farid et al. [30], and Sarkar et al. [31]. Therefore, the present results may differ from those reported in [6].

Hence we have shown that the local pseudopotential with an appropriate dielectric screening function can be applied to a liquid metal alloy with reasonable accuracy. The validity of the pseudopotential theory for alloys is questionable, particularly with the evidence that this theory becomes less reliable in alloys where the valence difference increases. Therefore, this calculation reveals energy separation between nonstructural and structural energies expressed as a sum of pairwise interactions between ions. Indeed, a quantitative difference between the experimental and reference structure factors which is moderately large has a slight effect on the thermodynamic properties because of the fact that they depend on integrals of the structure factors [8].

Conclusions. The GB technique has been used successfully to study the thermodynamic properties of NaK binary alloys. It is found that these properties are sensitive to the form of the model potential, the structural part of the energy, the form of the local-field correction function, and the volume of mixing. However, when the proper model potential is chosen, different forms of the local-field correction functions have slight effect on the total internal energy, Helmholtz free energy, and the heat of mixing. This confirms the applicability of the presently adopted EMC model potential in explaining the thermodynamics of liquid binary alloys. We can infer that the EMC model potential with five local-field correction functions (HR, TY, IU, FD, and SS) gives comparable and qualitative values of the excess entropy and heat of mixing for liquid NaK alloys.

NOTATION

A, Helmholtz free energy; a_{11}, a_{12}, a_{22}, partial structure factors; c_i, concentration; E_{cor}, correlation energy contribution; e, charge of electron; F, free energy per particle; F_1 and F_2 correspond to the first- and second-order pseudopotential theory; F_{M}, Madelung contribution; f, correction factor; G, local-field correction function; $\hbar$, Planck constant; k_{B}, Boltzmann constant; k_{F}, Fermi wave vector; M_i, atomic mass; m, electron mass; m_i, sphere mass; N, total number of atoms; n, number density; n_i, number density of the ith metallic element; P, pressure; $\mathbf{q}$, wave vector; r_{c}, parameter of the model potential; S, entropy; S_c, S_η, and S_σ, entropies related to the concentration, packing fraction, and hard sphere, respectively; T, temperature; U, internal energy; V^0, bare ion pseudopotential; W_{B}, EMC model potential of Ashcroft; Z_i, valence; $\gamma_{\text{e.g}}$, low-temperature specific heat of an electron gas; $\gamma_2(T)$, second-order correction; ΔH, heat of mixing; ε and ε_{HR}, modified and static Hartree dielectric functions; η, total packing fraction of an alloy; η_i, packing fraction of the ith metallic element; μ_i, chemical potential; σ_i, sphere diameter; Ω_0, atomic volume. Subscripts: al, alloy; cor, correlation; el, electron; e.g, electron gas; gas, gas; HR, TY, IU, FR, and SS relate to the correction functions of Hartree, Taylor, Ichimaru–Utsumi, Farid et al., and Sarkar et al.; h.s, hard sphere; mix, mixing; p.s, potential for the ion system; subscript i corresponds to metallic elements of the alloy ($i = 1, 2$).

REFERENCES

1. Y. Waseda, *The Structure of Non-Crystalline Materials*, McGraw-Hill, New York (1980).
2. T. E. Faber, *Introduction to the Theory of Liquid Metals*, Cambridge Univ. Press, Cambridge (1972).
3. M. Shimoji, *Liquid Metals*, Academic Press, London (1977).
4. J. Hafner, Structure and thermodynamics of liquid metals and alloys, *Phys. Rev. A*, **16**, 351–364 (1977).
5. R. N. Singh and F. Sommer, Segregation and immiscibility in liquid binary alloys, *Rep. Prog. Phys.*, **60**, 57–150 (1997).
6. I. H. Umar, A. Mayer, M. Watabe, and W. H. Young, Thermodynamic calculations for liquid alloys with an application to sodium-potassium, *J. Phys. F: Met. Phys.*, **4**, 1691–1706 (1974).
7. N. E. Dubinin, A. A. Yuryev, and N. A. Vatolin, Thermodynamics of alkali-alkali liquid alloys. Calculation by pseudopotential method and thermodynamic theory, *Thermochimica Acta*, **316**, 123–129 (1998).

8. R. N. Jordar, S. Palchaudhari, and R. V. Gopala Rao, Thermodynamics of liquid noble-metal alloys through a pseudopotential approach, *Phys. Rev. B*, **30**, 4417–4421 (1984).
9. R. N. Singh, Heat of mixing of equiatomic alkali-alkali alloys, *J. Phys. F: Met. Phys.*, **10**, 1411–1417 (1980).
10. S. C. Mishra and P. L. Srivastava, Thermodynamic properties of liquid alkali metals and their equiatomic alloys, *Phys. Stat. Sol. (b)*, **109**, 457–461 (1982).
11. R. N. Singh, Free energy and heat of mixing of alloys, *J. Phys. F: Met. Phys.*, **11**, 389–396 (1981).
12. A. K. Mishra, R. N. Singh, and B. B. Sahay, Thermodynamic properties of alkali-alkali liquid binary alloys, *Phys. Chem. Liq.*, **25**, 153–168 (1992).
13. Z. Badirkhan, O. Akinlade, G. Pastore, and M. P. Tosi, Thermodynamics and structure of liquid metals: A critical assessment of the charged-hard-sphere reference system, *J. Phys. Condens. Matt.*, **4**, 6173–6188 (1992).
14. N. W. Ashcroft and D. C. Langreth, Structure of binary liquid mixtures, *Phys. Rev.*, **156**, 685–692 (1967).
15. N. W. Ashcroft and D. C. Langreth, Resistivity of alloys and the ion-ion interaction, *Phys. Rev.*, **159**, 500–510 (1967).
16. D. Chekmarev, M. Zhao, and S. Rice, Structure of the liquid–vapor interface of a metal from a simple model potential: Corresponding states of the alkali metals, *J. Chem. Phys.*, **109**, 768–778 (1998).
17. M. H. Ghatee and M. Bahadori, Inter-ionic potential function in liquid alkali metals by thermodynamic regularity approach, *Chem. Phys.*, **335**, 215–220 (2007).
18. W. A. Harrison, *Pseudopotentials in the Theory of Metals*, W. A. Benjamin, New York (1966).
19. M. Hasegawa and M. Watabe, in: S. Takeuchi (Ed.), *The Properties of Liquid Metals*, Taylor and Francis, London (1973).
20. N. W. Ashcroft and J. Lekner, Structure and resistivity of liquid metals, *Phys. Rev.*, **165**, 83–90 (1966).
21. J. L. Lebowitz, Exact solution of generalized Percus–Yevick equation for a mixture of hard spheres, *Phys. Rev. A*, **133**, 895–899 (1964).
22. H. L. Frisch and J. L. Lebowitz, *The Equilibrium Theory of Classical Fluids*, W. A. Benjamin, New York (1964).
23. J. L. Lebowitz and J. S. Rowlinson, Thermodynamic properties of mixtures of hard spheres, *J. Chem. Phys.*, **41**, 133–138 (1964).
24. J. E. Enderby and D. M. North, Percus–Yevick structure factors for liquid alloys, *Phys. Chem. Liq.*, **1**, 1–11 (1968).
25. A. Isihara, The Gibbs–Bogoliubov inequality dagger, *J. Phys. A*, **1**, 539–548 (1968).
26. T. Lukes and R. Jones, Inequalities and variational methods in classical statistical mechanics, *J. Phys. A*, **1**, 29–33 (1968).
27. N. W. Ashcroft, Electron–ion pseudopotentials in the alkali metals, *J. Phys. C*, **1**, 232–243 (1968).
28. R. Taylor, A simple, useful analytical form of the static electron gas dielectric function, *J. Phys. F: Metal Phys.*, **8**, 1699–1702 (1978).
29. S. Ichimaru and K. Utsumi, Dielectric formulation of strongly coupled electron liquids at metallic densities. IV. Static properties in the low-density domain and the Wigner crystallization, *Phys. Rev. B*, **24**, 3220–3225 (1981).
30. B. Farid, V. Heine, G. E. Engel, and I. J. Robertson, Extremal properties of the Harris–Foulkes functional and an improved screening calculation for the electron gas, *Phys. Rev. B*, **48**, 11602–11621 (1993).
31. A. Sarkar, D. S. Sen, S. Haldar, and D. Roy, Static local field factor for dielectric screening function of electron gas at metallic and lower densities, *Mod. Phys. Lett. B*, **12**, 639–648 (1998).
32. R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley, and D. D. Wagman, *Selected Values of the Thermodynamic Properties of Elements and Alloys*, Am. Soc. Metals, Metal Park, Ohio (1973).