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Study of thermodynamical properties of liquid binary alloys by a pseudopotential method

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Abstract

On the bases of the Percus-Yevick (PY) hard sphere model as a reference system and the Gibbs–Bogoliubov (GB) inequality, a thermodynamic perturbation method has been applied with use of well known model potential. By applying a variational method the best hard core diameters have been found which correspond to minimum free energy. With this procedure the thermodynamical properties such as internal energy, entropy, Helmholtz free energy, entropy of mixing and heat of mixing have been computed for liquid NaK binary systems. The influence of local field correction function viz; Hartree (HR), Taylor (TY), Ichimaru-Utsumi (IU), Farid *et al*. (FD) and Sarkar *et al*. (SS) is also investigated. The computed excess entropy compares favourably in the case of liquid alloys while the agreement with the experiment is poor in the case of heats of mixing. This may be due to the sensitivity of the heats of mixing, with the potential parameters and the dielectric function.

1. Introduction

The theoretical basis for an understanding of 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 been made possible due to the combination of the pseudopotential with thermodynamic perturbation theories. The pseudopotential theory enables one to formulate the energy in terms of the pseudopotential and of the structure factor [1-13]. On the other side it is possible to write down closed form expressions for the thermodynamic quantities of hard sphere systems, including the structure factor, in the Percus-Yevick (PY) approximation [14]. A link between both theories is provided by a variational technique based on the Gibbs–Bogoliubov (GB) inequality [1-13]. This Gibbs–Bogoliubov (GB) 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 of the hard spheres, and the hard sphere diameters will be chosen to minimize the free energy. Recently, Chekmarev *et al*.

[15] have been reported structural information of alkali metals in liquid-vapor interface using a simple model potential. Also, very recently Ghatee and Bahadori [16] have reported Inter-ionic potential function in liquid alkali metals by thermodynamic regularity approach.

The general theory of thermodynamics of alloys is based on results which arise from three distinct areas of current interest. First there exists theory of pseudopotentials developed by Harrison [17]. This enables one to write down the energy of an alloy in terms of the pseudopotentials and partial structure factors. Except in very special circumstances, however, the latter are not sufficiently well known for most purposes. Also, it is really the free energy that is of prime interest at elevated temperatures [18]. But it has been known for some time [19] that for pure liquid metals, at least, the structure factors resembles closely to those for hard spheres. Faber [2] has also shown that the corresponding entropies can be characterized by hard sphere behaviour. This brings us to our second area of interest, namely, the thermodynamics of hard sphere systems which has been studied by Lebowitz *et al*. [20-22]. As a result, it is now possible to write down, in closed form Percus-Yevick approximation, thermodynamic quantities of interest, including partial structure factors and free energies, for mixtures of hard spheres. There is an indication also that such structure factors might be useful for the interpretation of x-ray and neutron form factors in at least some binary alloy systems [2, 14, 23]. Finally, the precise way of

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linking up the formal hard sphere results with the pseudopotential technique is provided by the Gibbs-Bogoliubov (GB) inequality [24, 25]. This states that if the Hamiltonian for a system is regarded as that for a reference system plus a perturbation, then the Helmholtz free energy for the reference system plus the expectation value of the perturbation averaged over the reference system is greater than or equal to the Helmholtz free energy of the actual system.

Though the theoretical formulation for investigating thermodynamical properties of binary alloys is very straight forward, from the pseudopotential point of view, a few attempts have been found to compute such properties as a function of concentration [1-12]. Hence, we are motivated to compute the thermodynamical properties as a function of concentration like internal energy, entropy, Helmholtz free energy, entropy of mixing and heat of mixing of liquid binary alloys of alkali–alkali component. We have used well known single parametric empty core (EMC) model potential of Ashcroft [26] in the present computation. The modified Hartree dielectric function [17] together with the exchange and correlation effects proposed by Hartree (HR) [17], Taylor (TY) [27], Ichimaru-Utsumi (IU) [28], Farid *et al.* (FD) [29] and Sarkar *et al.* (SS) [30] of the conduction electrons generates good energy wave number characteristics.

2. Computational Methodology

The well known model potential of Ashcroft's empty core (EMC) model potential [26] employed in the present study has the form (in atomic units):

$$W_B(q) = \frac{-8\pi Z}{\Omega_0 q^2} \cos(q r_c), \qquad (1)$$

here Z, Ω_0, q and r_C are the valence, atomic volume, wave vector and parameter of the model potential of the alloy systems, respectively.

We consider an alloy having $(1-x)N$ atoms of type 1 at positions $\{R_1\}$ and xN atoms of type 2 at positions $\{R_2\}$. Also consider $(1-x) + x = 1$ so that N is the total number of atoms. The number densities of the ion species are $n_1 = (1-x)n$ and $n_2 = xn$, here $n = N/\Omega_0$. If Z_1 and Z_2 are the valences, then the free electron Fermi wave vector is given by $k_F^3 = 3\pi^2 \bar{Z} n$, where $\bar{Z} n = Z_1 n_1 + Z_2 n_2$, is the mean average valence electron density [6].

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

$$F_{el}(\{R_1\}, \{R_2\}) = F_{eg} + F_1 + F_2(\{R_1\}, \{R_2\}), \qquad (2)$$

where, F_{eg} is the free energy of the electron gas, F_1 and F_2 are obtained via first and second order pseudopotential theory.

By adding direct Coulomb interaction between ions, one obtains the effective potential energy for the ion system. We need only the expectation value of this effective potential averaged over some reference system, which is given by [6]:

$$F_{ps} = F_{eg} + F_M + F_1 + F_2. \qquad (3)$$

F_{eg} is given by [6],

$$F_{eg} = \left[\frac{3}{10} k_F^3 - \frac{3}{4\pi} k_F + E_{core} - \frac{1}{2}\gamma_{eg} T^2 \right] \bar{Z}, \qquad (4)$$

here $E_{core} = -0.0474 - 0.0155 \ln k_F$ is the correlation energy contribution. The constant $\gamma_{eg} = (\pi k_B/k_F)^2$ is the low temperature specific heat of the electron gas.

The Madelung contribution (F_M) in the closed form can be written as [6]:

$$F_M = c_1^2 Z_1^2 I_{11} + c_2^2 Z_2^2 I_{22} + 2 c_1 c_2 Z_1 Z_2 I_{12}, \qquad (5)$$

where,

$$
\begin{aligned}
I_{11} = [\pi n/(1+2\eta)] \Big[& -\sigma_1^2 \\
& + \frac{1}{5}(1 - \eta/2)(\eta_1 \sigma_1^2 + \eta_2 \sigma_2^2) \\
& + \eta_1 \sigma_1 (\sigma_2 - \sigma_1) \\
& + \frac{1}{2}\eta_1 \eta_2 (\sigma_2 - \sigma_1)^2 \Big]
\end{aligned}
\qquad (6)
$$

$$
\begin{aligned}
I_{12} = [\pi n/(1+2\eta)] \Big[& -\frac{1}{4}(\sigma_2 - \sigma_1)^2 \\
& + \frac{1}{5}(1 - \eta/2)(\eta_1 \sigma_1^2 + \eta_2 \sigma_2^2) \\
& + \frac{1}{2}(\eta_2 \sigma_1 - \eta_1 \sigma_2)(\sigma_2 - \sigma_1) \\
& + \frac{1}{2}\eta_1 \eta_2 (\sigma_2 - \sigma_1)^2 \Big],
\end{aligned}
\qquad (7)
$$

I_{22} is obtained by interchanging η_1, σ_1 with η_2, σ_2 in the expression for I_{11}. The packing fraction, η, of the alloy is expressed as [9]:

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

Using zeroth Fourier component of the bare pseudopotential F_1 is obtained. If we denote the qth components by $W_{Bi}(q), (i = 1,2)$, then [6]:

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

where,

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

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

$$\begin{aligned}
F_2 = \frac{1}{16\pi^3}\int_0^\infty &\{c_1 c_2(W_{B1} - W_{B2})^2 + c_1^2 W_{B1}^2 \alpha_{11} \\
&+ 2(c_1 c_2)^{1/2} W_{B1} W_{B2} \\
&+ c_2^2 W_{B2}^2 \alpha_{22}\}\left(\frac{1}{\varepsilon(q)} - 1\right)dq \\
&- \frac{\overline{Z}}{2}\gamma_2(T)T^2.
\end{aligned}$$

(11)

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

$$\varepsilon(q) = 1 + \left(\varepsilon_H(x) - 1\right)\left(1 - G(x)\right); \; x = \frac{q}{2k_F}, \qquad (12)$$

here $\varepsilon_H(x)$ is the static Hartree dielectric function [12] and is given by:

$$\begin{aligned}
\varepsilon_H(x) = 1 + \frac{me^2}{2\pi k_F \hbar^2 \eta^2}&\left(\frac{1 - x^2}{2x}\ln\left|\frac{1 + x}{1 - x}\right| + 1\right); x \\
&= \frac{q}{2k_F}.
\end{aligned}$$

(13)

While $G(x)$ is the local field correction function. In the present investigation, the local field correction functions due to Hartree (HR) [17], Taylor (TY) [27], Ichimaru-Utsumi (IU) [28], Farid *et al.* (FD) [29] and Sarkar *et al.* (SS) [30] are incorporated to see the impact of exchange and correlation effects. The details of the local field corrections are narrated below.

$\gamma_2(T)$ is the second order correction to the usual γ factor describing the low temperature electronic specific heat and is given by [6]:

$$\begin{aligned}
\gamma_2(T) = \frac{2k_B^2}{2\pi^2 \overline{Z}}\int_0^\infty dy \frac{y^2}{y^2 - 1} f(y)&\{c_1 c_1(W_{B1} \\
&- W_{B2})^2 + c_1^2 W_{B1}^2 \alpha_{11} \\
&+ 2(c_1 c_1)^{1/2} W_{B1} W_{B2} \\
&+ c_2^2 W_{B2}^2 \alpha_{22}\},
\end{aligned}$$

(14)

with,

$$f(y) = \frac{1}{2} + \frac{y^2 - 1}{4y}\ln\left|\frac{1 + y}{1 - y}\right| ; y = \frac{q}{2k_F}. \qquad (15)$$

The free energy per particle F_{hs} of the hard sphere mixture can be written as [6]:

$$F_{hs} = c_1\mu_1 + c_1\mu_1 - \frac{P_{hs}}{n}, \qquad (16)$$

here $\mu_i(i = 1,2)$ and P_{hs} are the chemical potentials of the components and the pressure, respectively.

In PY approximation, these quantities are written by [6]:

$$\begin{aligned}
\frac{\mu_i}{k_B T} = \ln\left(n_i \frac{2\pi\hbar^2}{m_i k_B T}\right)^{3/2} &- \ln(1 - \eta) \\
&+ \ln\left(\frac{3X\sigma_i}{1 - \eta}\right) + \frac{3}{2}\left(\frac{3X^2}{(1 - \eta)^2}\right. \\
&\left. + \frac{2Y}{1 - \eta}\right)\sigma_i^2 + \left(\frac{\pi P_{hs}\sigma_i^3}{6k_B T}\right),
\end{aligned}$$

(17)

and

$$\frac{P_{hs}}{k_B T}$$
$$= \frac{n(1 + \eta + \eta^2) - \frac{1}{2}\pi n_1 n_2(\sigma_1 - \sigma_2)^2(\sigma_1 + \sigma_2 + \sigma_1\sigma_2 X)}{(1 - \eta)^3},$$

(18)

where,

$$X = \frac{1}{6}\pi(n_1\sigma_1^2 + n_2\sigma_2^2)$$
and
$$Y = \frac{1}{6}\pi(n_1\sigma_1 + n_2\sigma_2).$$

(19)

Here, $m_i(i = 1,2)$ denote the masses of the spheres.

Substitution of the equations (17-19) in (16) and use of $S = -(\partial F/\partial T)_{\Omega_0}$, we get:

$$F_{hs} = \frac{3}{2}k_B T - TS_{hs}, \qquad (20)$$

where:

$$S_{hs} = S_{gas} + S_c + S_\eta + S_\sigma, \qquad (21)$$

with:

$$\frac{S_{gas}}{k_B} = \ln\left(\frac{e}{n}\left(\frac{emk_B T}{2\pi\hbar^2}\right)^{3/2}\right); \qquad \left(m = m_1^{c_1}m_2^{c_2}\right),$$

(22)

$$\frac{S_c}{k_B} = -(c_1\ln c_1 + c_2\ln c_2), \qquad (23)$$

$$\frac{S_n}{k_B} = \ln(1 - \eta) + \frac{3}{2}\left(1 - \frac{1}{(1 - \eta)^2}\right), \qquad (24)$$

and

$$\frac{S_\sigma}{k_B}$$
$$= \frac{\pi c_1 c_2 n(\sigma_1 - \sigma_2)^2(12(\sigma_1 + \sigma_2) - \pi n(c_1\sigma_1^4 + c_2\sigma_2^4))^2}{24(1 - \eta)^2}.$$

(25)

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The Helmholtz free energy (*A*) per ion of the alloy is given as:

$$A = F_{ps} + F_{hs}. \qquad (26)$$

Hard sphere diameters σ_i are obtained by minimizing the Helmholtz free energy (*A*) treating η_i as the variation parameter:

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

Now, the total entropy is written in terms of Helmholtz free energy (*A*):

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

and similarly the pressure is given by

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

where *n* is the density. From the use of equations (25-26), the entropy is written as:

$$S = S_{hs} + S_{ps}, \qquad (30)$$

here, S_{hs} is calculated from equation (21), while $S_{ps} = \bar{Z}(\gamma_{eg} + \gamma_2)T$. The term S_{ps} is negligibly small in comparison with the S_{hs}.

Generally, the internal energy (*U*) and Helmholtz energy (*A*) are connected by $A = U - TS$. Hence, the heat of mixing is given by:

$$\Delta H_{mixing} = \Delta A_{mixing} + P\Delta\Omega_{0\,mixing} + T\Delta S_{mixing}, \qquad (31)$$

here, $P\Delta\Omega_{0\,mixing}$ is negligibly small and close to zero, then equation (28) is written by:

$$\Delta H_{mixing} = \Delta A_{mixing} + T\Delta S_{mixing}, \qquad (32)$$

where ΔA_{mixing} and ΔS_{mixing} include all terms 'ps' and 'hs'. Only those values can be compared with the experiment. The heat of mixing is calculated from the equation given below:

$$\Delta A_{mixing} = \Delta F_{eg} + \Delta F_1 + \Delta F_2 + \Delta F_M, \qquad (33)$$

where:

$$\Delta F_i = F_i(alloy) - C_1 F_{1A} - C_2 F_{2B}, \qquad (34)$$

i denotes *eg*, 1, 2 and *M*.

Similarly in the computation of the excess entropy $\Delta S_{ps} = 0$ and $\Delta\Omega_{0\,maxing} = 0$. Hence, the excess entropy is given by

$$\Delta S = \Delta S_{gas} + \Delta S_\eta + \Delta S_\sigma, \qquad (35)$$

here,

$$\Delta S_i = S_i(alloy) - C_1 S_{1A} - C_2 S_{2B}. \qquad (36)$$

In equation (33) *i* corresponds to *gas*, η and σ terms.

3. Results and Discussion

The input parameters and constants used in the present investigation of the thermodynamic properties are tabulated in Table 1. All the input parameters are taken from the literature [6]. The computations are performed at T = 373K.

Table 1. Input parameters and other constants.

Elements	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

The various contributions to the internal energy have been computed at different concentrations for NaK binary alloys are tabulated in Table 2. From Table 2 it is observed that, the values of F_{eg}, F_2 and F_M are negative while F_1 has positive contribution to the internal energy (*E*). The contributions F_1 and F_2 are model potential dependent while other i.e. F_{eg} and F_M contributions are independent from the model potential. Here, we use PY partial structure factor [9] to describe the structural behaviour of alloy systems. It is seen that the local field correction functions affected the term F_2 only, which is the second order band structure energies. The presently computed results of F_2 differ from those of Umar *et al.* [6] because of the different local field correction functions are used in both computations.

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Table 2. Various contributions to the internal energy for NaK binary alloys (in 10^{-3} au).

x	F_{eg} Present	Others [6]	F_1 Present	Others [6]	F_2 Present HR	TY	IU	FD	SS	Others [6]	F_M Present	Others [6]	F_{hs} Present	Others [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

The various contributions to the total entropy S_{hs} for NaK binary alloy is displayed in Fig. 1. Among the four contributions to the total entropy, S_{gas} represents the gas term, S_c is the ideal entropy of mixing, S_η corresponds to packing density η and S_σ arises due to the difference in diameters of the hard sphere of first and second atoms of alloy. It is seen from Figure 1 that, S_η is found negative values while the rest of the contributions are found positive values. The maximum contribution to the
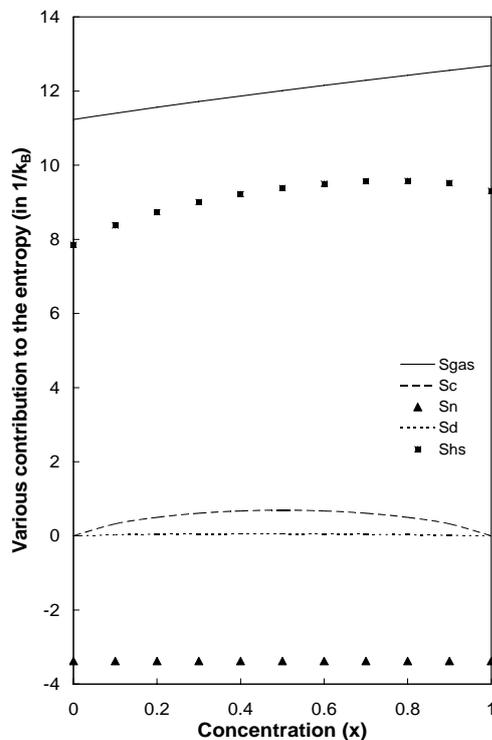

Fig. 1. Various contributions to the entropy for NaK binary alloy.

total entropy comes from the term S_{gas} while minimum comes from S_η which depends only on the numerical values of packing density η. The contribution of S_{gas} increases the absolute value of the total entropy whereas S_η tends to decrease the total entropy of the system. As we have already stated that S_c is the ideal entropy of mixing, its magnitude remains same for NaK binary alloy at every concentration. The natures of $S_c \to x$ curves are parabolic. It is also seen that, as the concentration 'x' increases, the numerical values of the term S_{gas} increases. The natures of $S_{hs} \to x$ curves are non linear. All the contributions of the total entropy are independent of model potential used in the present investigation as well as not influenced by the nature of the local field correction functions.

Finally, the total internal energy (*U*) and Helmholtz free energy (*A*) are calculated as a function of concentration and tabulated in Tables 3 and 4. It is noticed that the major contribution to the total internal energy comes from the structural part of the energy. The magnitude of the Madelung energy $|F_M|$, is quite large, in comparison with other energy terms. Its magnitude decreases with an increase in the atomic fraction of the heavier element of the alloy. The energy of the electron gas F_{eg}, in the mixture varies slightly with respect to temperature of the metallic elements. The negative contribution to the energy comes from the first-order pseudopotential term F_1, which decreases as increase the concentration of the heavier element. The modulus of the band structure energy $|F_2|$ has a maximum in the intermediate range of concentration. However, the aggregate effects of different energy terms are such that the total internal energy (*U*) of the system is found to be almost linear. And hence,

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Table 3. Total internal energy (*U*) for NaK binary alloys (in 10^{-3} au)

x	Present Results					Others	Expt.
	HR	TY	IU	FD	SS	[6]	[6]
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

the Helmholtz free energy (*A*) of the system is also found to be almost a linear nature for most of the alloy concentration. It is seen that, the exchange and correlations affected the numerical values of Helmholtz free energy (*A*). It is also found that, the influence of local field correction functions is found very small. The Helmholtz free energy (*A*) obtained due to the TY, IU and SS-local field correction functions lies between those obtained due to HR and FD-local field correction functions, in general. As the volume of a particular system increases, it decreases the magnitude of the total internal energy (*U*) as well as the Helmholtz free energy (*A*) of the system. The present results of total internal energy (*U*) and Helmholtz free energy (*A*) for pure metallic components as well as equiatomic alloy like Na$_{0.5}$K$_{0.5}$ are found in qualitative agreement with the available theoretical data [6].

The percentile influence of the various local field correction functions with respect to the static HR-screening function on F_2 is observed in the range of 4.74%-26.02%. While those influence on Helmholtz free energy (*z*) is found in the range of 0.14%-0.86%. The percentile influence of the various local field correction functions with respect to

the static HR-screening function on total internal energy (*U*) is noted in the range of 0.15%-0.90%.

Also Ashcroft-Langreth [14] pointed out that, the core radius of the bare ion model pseudopotential was fitted to the experimental data at $q = 2k_F$, and therefore there is uncertainty in the behaviour of $W_B(q)$ at $q = 0$. Therefore, α_i of equation (10) may be viewed as an independent parameter and can be chosen to fit some further property , say, internal energy (*F*) for pure liquid, and then this parameter may be used in the alloy calculation.

The heat of mixing (*ΔE*) for NaK binary alloy calculated from equation (33) is plotted in Figure 2. From Fig. 2 it is seen that, the heat of mixing (*ΔE*) are asymmetrical at *x* = 0.5. Another important noticeable point is that the different forms of the local field correlation functions is much affected in the computations of the heat of mixing (*ΔE*) than those of the total internal energy (*U*) and Helmholtz free energy (*A*). Therefore, the heat of mixing (*ΔE*) of alloys is found very less dependent on the choice of the forms of local field correction functions which enters into the calculation through the dominant second-order potential term F_2. Thus, the form of the model potential used in the computation also plays a vital role to predict such

Table 4. Helmholtz free energy (*A*) for NaK binary alloys (in 10^{-3} au)

x	Present Results					Others
	HR	TY	IU	FD	SS	[6]
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

properties. Moreover it is found from Fig. 2 that, the HR-dielectric function gives the lower value of the heat of mixing (ΔE) whereas the inclusion of the FD-dielectric functions give higher values. Initially, the heat of mixing (ΔE) is found negative up to concentration (x) = 0.2, after that the heat of mixing (ΔE) is found positive. The present results of heat of mixing (ΔE) are found much higher than the experimental data [31]. While experimental data are found positive with respect to present yielding. The large discrepancies are found in the presently computed results and experimental data because of the different criteria used to calculate the thermodynamic properties of the alloying systems.
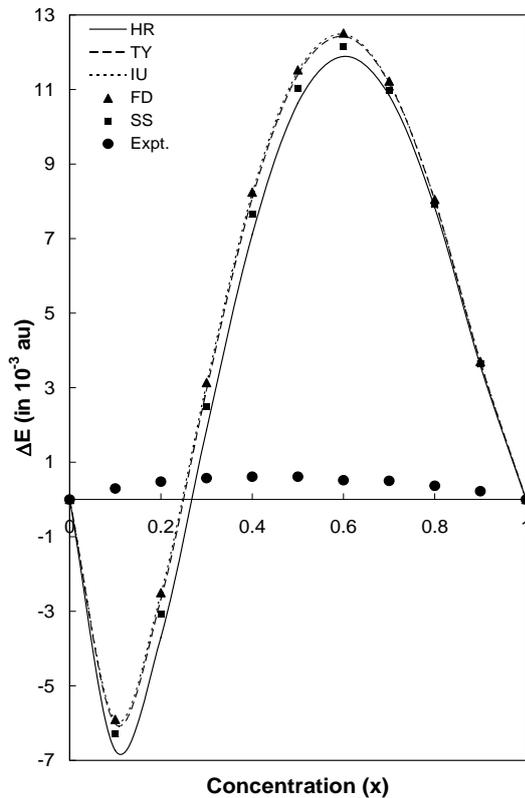
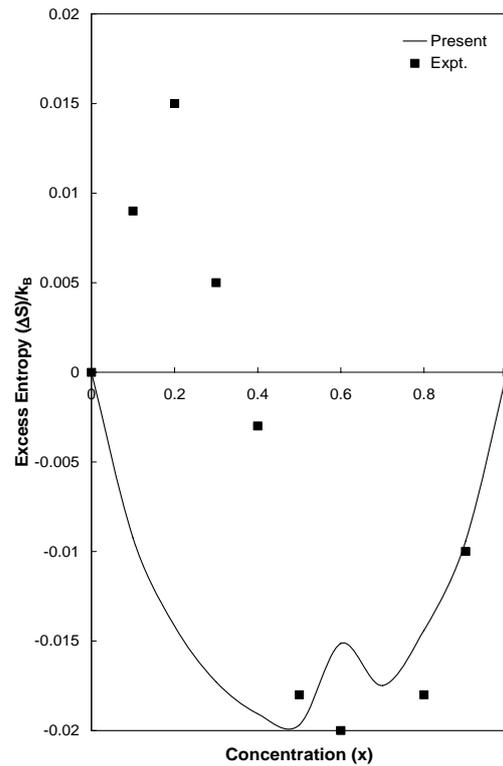cy in its dependence on the composition of the alloy was similar.

Fig. 3. Excess entropy for NaK binary alloys.

While, Umar *et al.* [6] have used the EMC model potential with older local field correction function in their computation. But, in the present study we have used here most recent and well known local field corrections proposed by Hartree (HR) [17], Taylor (TY) [27], Ichimaru-Utsumi (IU) [28], Farid *et al.* (FD) [29] and Sarkar *et al.* (SS) [30]. Therefore, the present results may be differed from the reported results of the Umar *et al.* [6].

Thus, in this work we have shown that a local pseudopotential with an appropriate dielectric screening function can be applied to the liquid metal alloy with reasonable accuracy. The validity of pseudopotential theory for alloys is questionable, particularly with the evidence that the pseudopotential theory becomes less reliable in alloys where the valance difference increases. Thus, this calculation shows an energy separation between non-structural and structural energies expressed as a sum of pairwise interactions between ions. Indeed, the quantitative difference between experimental and reference structure factors which is not very much and not strongly reflected in the thermodynamic properties because of the fact that these properties depended on the integrals of the structure factors [8].

Fig. 2. Heat of mixing for NaK binary alloys.

The excess entropy (ΔS) calculated from equation (32) and is plotted in Fig. 3 as a function of concentration (x). The presently computed is slightly asymmetrical at $x = 0.5$ and also found in qualitative agreement with the available experimental data [31]. Also, the computed data is found negative values throughout whole computation while the experimental data [31] is found initially positive upto some concentration concentration (x) and then turned out to negative. Our present yielding is not showing this type of behaviour. Also, the bump is observed at concentration $x = 0.6$ may be due to the disorder created in the alloy systems. Hence, the experimentally and theoretically observed excess entropy agreed qualitatively well upto some higher concentration (x) and the tenden-

4. Conclusions

Finally, we concluded that, the GB technique is successfully used in the present study of the thermodynamic properties of NaK binary alloys. It is found that, the properties are sensitive to the form of the model potential used, structural part of the energy, the form of the local field correction functions and volume of the mixing. The different forms of the local field correction functions have little affected on the total internal energy, Helmholtz free energy and the heat of mixing. Thus, the proper choice of the model potential along with the local field correction function is very less affected on the thermodynamic properties of binary alloys. This confirms the applicability of the presently adopted EMC model potential in explaining the thermodynamics of liquid binary alloys. Also, we can infer that the EMC model potential with five local field correction functions due to HR, TT, IU, FD and SS gives comparable and qualitative excess entropy and heat of mixing for liquid NaK alloy.

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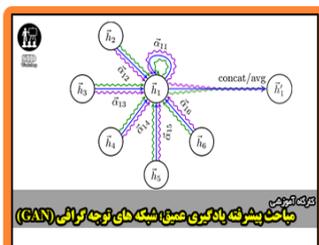آموزشی

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