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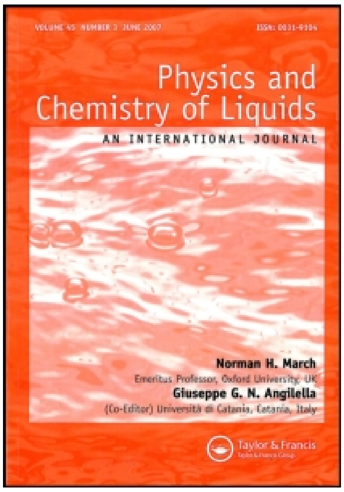

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Thermodynamical properties of RbCs liquid binary alloys

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Thermodynamical properties of RbCs liquid binary alloys

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Our well established model potential is applied to compute the thermodynamical properties like internal energy (E), entropy (S_{hs}), Helmholtz free energy (F), heat of mixing (ΔE) and entropy of mixing(ΔS) of $Rb_{c1}Cs_{c2}$ liquid binary alloys as a function of concentration at constant temperature and pressure. To introduce exchange and correlation effects, the local field correction functions due to Hartree, Taylor and Sarkar *et al*. are used. It is found that thermodynamical properties of $Rb_{c1}Cs_{c2}$ liquid binary alloys are sensitive to the form of the model potential used, structural part of the energy, form of the local field correction function and volume of the mixing. The theory explains the symmetry of heat of mixing and entropy of mixing. Thus, the proper choice of the model potential along with the local field correction function plays an important role in the study of the thermodynamical properties of $Rb_{c1}Cs_{c2}$ liquid binary alloys. This confirms the applicability of our model potential in explaining the thermodynamics of liquid $Rb_{c1}Cs_{c2}$ liquid binary alloys.

Keywords: pseudopotential; thermodynamical properties; internal energy; entropy; Helmholtz free energy; heat of mixing; entropy of mixing

1. Introduction

A well established technique based on the Gibbs–Bogoliubov (GB) inequality was effectively used in the past [1–7] to investigate the thermodynamical properties of liquid binary alloys using pseudopotential theory. In these studies [1–7], it was found that thermodynamical properties of liquid binary alloys are sensitive to the form of the model potential used, structural part of the energy, form of the local field correction function and volume of the mixing.

The general theory is based on results which are pertaining to three distinct areas of current interest. First, there exists a theory of pseudopotentials developed by Harrison [8]. This enables one to write down the energy of an alloy in terms of the pseudopotentials and partial structure factors. Except for 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 high temperatures [9]. It has been known for some time [10] that for pure liquid metals, at least the structure factors

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resemble closely those of hard spheres. Faber [11] has shown that the corresponding entropies can be characterised 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 [12], Frisch and Lebowitz [13] and Lebowitz and Rowlinson [14]. As a result, it is now possible to write down in closed form Percus–Yevick (PY) approximation the thermodynamic quantities of interest including partial structure factors and free energies for mixtures of hard spheres. There is an indication that such structure factors might be useful for the interpretation of X-ray and neutron form factors in some binary alloy systems [11,15,16]. Finally, the precise way of linking up the formal hard sphere results with the pseudopotential technique is provided by the Gibbs–Bogoliubov (GB) inequality [17,18]. 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.

Hence, we considered it worthwhile to compute the thermodynamical properties of liquid binary alloys using our own model potential [19–24]. In the present article our well established model potential [19–24] is applied to compute the thermodynamical properties like internal energy (E), entropy (S_{hs}), Helmholtz free energy (F), heat of mixing (ΔE) and entropy of mixing (ΔS) of $\mathrm{Rb}_{c1}\mathrm{Cs}_{c2}$ liquid binary alloys as a function of concentration at constant temperature and pressure. To introduce the exchange and correlation effects, the local field correction functions due to Hartree [8], Taylor [25] and Sarkar *et al.* [26] are used.

The present form of the model potential in real space [19–24] is:

$$\begin{aligned} W_B(r) &= 0; & r < r_c, \\ &= -\left(\frac{Ze^2}{r}\right)\left[1-\exp\left(\frac{-r}{r_c}\right)\right]; & r \geq r_c. \end{aligned} \tag{1}$$

The corresponding bare-ion form factor in the reciprocal space [19–24] is given by:

$$W_B(q) = \left(\frac{-4\pi Ze^2}{\Omega q^2}\right)\left[\cos(qr_c) - \left\{\frac{(qr_c)\exp(-1)}{1+q^2r_c^2}\right\}\left\{\sin(qr_c) + (qr_c)\cos(qr_c)\right\}\right]. \tag{2}$$

Here Z, e, Ω, q and r_c are the valence, electronic charge, atomic volume, wave vector and the parameter of the potential, respectively. The potential contains only single parameter $r_{c.}$ In the present investigation the potential parameter is estimated by employing the values of the wave vector, q_0, for which the form factor takes a first zero value, i.e. $W_B(q) = 0$ for $q = q_0$. For the present model, the condition is $q_0 r_c = 1.3439$ [21–24]. This model potential is continuous in **r**-space and it is a modified version of the Ashcroft's empty core model. Compared with the Ashcroft empty core model potential, we have introduced $(Ze^2/r)\exp(-r/r_c)$ as a repulsive part outside the core, which vanishes faster only than Coulomb potential $-(Ze^2/r)$ as $r \to \infty$.

2. Theory

An alloy having c_1N atoms of type 1 at positions $\{R_1\}$ and c_2N atoms of type 2 at positions $\{R_2\}$ is considered. We restrict $c_1 + c_2 = 1$ so that N is the total number of atoms. The number densities of the ion species are $n_1 = c_1 n$ and $n_2 = c_2 n$, where $n = (N/\Omega)$ and Ω is the total volume of the alloy. Here m_1 and m_2 are the masses of the spheres c_1N and c_2N, respectively. Supposing σ_1 and σ_2 are the diameters of c_1N and c_2N spheres, respectively, the packing fraction is given by:

$$\eta = \frac{1}{6}\pi\left(n_1\sigma_1^3 + n_2\sigma_2^3\right), \tag{3}$$

where

$$\sigma_i = \left(\frac{6\Omega\eta_i}{\pi}\right)^{1/3} (i = 1, 2).$$

The Fermi wave vector in the present formulation is defined as:

$$k_F^3 = 3\pi^2\overline{Z}n, \tag{4}$$

where $\overline{Z}n = Z_1n_1 + Z_2n_2$ is the mean average valence electron density and Z_1 and Z_2 are the valencies.

The electronic free energy of the alloy for some fixed configuration is obtained by [1–6].

$$F_{\mathrm{el}}\{R_1, R_2\} = F_{\mathrm{eg}} + F_1 + F_2\{R_1, R_2\}, \tag{5}$$

where F_{eg} is the free energy of the electron gas, and F_1, F_2 are obtained via first- and second-order pseudopotential perturbation 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 [1–6]:

$$F_{\mathrm{ps}} = F_{\mathrm{eg}} + F_M + F_1 + F_2. \tag{6}$$

F_{eg} is represented as:

$$F_{\mathrm{eg}} = \left[\frac{3}{10}k_F^2 - \frac{3}{4\pi}k_F + E_{\mathrm{core}} - \frac{1}{2}\gamma_{\mathrm{eg}}T^2\right]\overline{Z}. \tag{7}$$

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

The Madelung contribution F_M is given by:

$$F_M = \frac{1}{\pi}\int_0^\infty \left\{c_1^2Z_1^2(S_{11} - 1) + 2c_1c_2Z_1Z_2(S_{12} - 1) + c_2^2Z_2^2(S_{22} - 1)\right\}\mathrm{d}q, \tag{8}$$

where S_{ij} is the partial structure factor [27].

Using the zeroth Fourier component of the bare pseudopotential, F_1 is obtained. If we denote the *q-th* components by $W_{Bi}(q)$, $(i=1,2)$, then

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

where

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

The second-order (band structure) energy is given by:

$$F_2=\frac{1}{16\pi^3}\int_0^\infty\left\{\begin{matrix} c_1c_2\left(W_{B_1}-W_{B_2}\right)^2+c_1^2W_{B_1}^2S_{11} \\ +2c_1c_2W_{B_1}W_{B_2}S_{12}+c_2^2W_{B_2}^2S_{22}\end{matrix}\right\}\left\{\frac{1}{\varepsilon(q)}-1\right\}q^4\mathrm{d}q-\frac{\overline{Z}}{2}\gamma_2(T)T^2. \tag{11}$$

Here $\varepsilon(q)$ is the dielectric screening function. $\gamma_2(T)$ is the second-order correction to the usual γ factor describing the low temperature electronic specific heat and is given by:

$$\gamma_2(T)=\frac{2k_B^2}{3\pi^2\overline{Z}}\int_0^\infty\mathrm{d}x\frac{x^2}{x^2-1}f(x)\left\{\begin{matrix} c_1c_2(W_1-W_2)^2+c_1^2W_1^2S_{11} \\ +2c_1c_2W_1W_2S_{12}+c_2^2W_2^2S_{22}\end{matrix}\right\}. \tag{12}$$

Here, W_i,$(i=1,2)$ is the screened form factor [19–24] and $f(x)$ is given by:

$$f(x)=\frac{1}{2}+\frac{x^2-1}{4x}\ln\left|\frac{1+x}{1-x}\right|;\ x=\frac{q}{2k_F}. \tag{13}$$

The free energy per particle of the mixture can be written as [1–6]:

$$F_{\mathrm{hs}}=c_1\mu_1+c_2\mu_2-\frac{P_{\mathrm{hs}}}{n}. \tag{14}$$

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

In the PY approximation, these are given by:

$$\begin{aligned}\frac{\mu_i}{k_BT}=\ln\left[n_i\frac{2\pi\hbar^2}{m_ik_BT}\right]^{3/2}-\ln(1-\eta)+\ln\left[\frac{3X\sigma_i}{1-\eta}\right] \\ +\frac{3}{2}\left[\frac{3X^2}{(1-\eta)^2}+\frac{2Y}{1-\eta}\right]\sigma_i^2+\left[\frac{\pi P_{hs}\sigma_i^3}{6k_BT}\right]\end{aligned} \tag{15}$$

and

$$\frac{P_{\mathrm{hs}}}{k_BT}=\frac{n\left(1+\eta+\eta^2\right)-\frac{1}{2}\pi n_1n_2(\sigma_1-\sigma_2)^2(\sigma_1+\sigma_2+\sigma_1\sigma_2X)}{(1-\eta)^3}, \tag{16}$$

where

$$X=\frac{1}{6}\pi\left(n_1\sigma_1^2+n_2\sigma_2^2\right) \tag{17}$$

and

$$Y = \frac{1}{6}\pi(n_1\sigma_1 + n_2\sigma_2). \tag{18}$$

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

The internal energy is given by:

$$E = \frac{3}{2}k_B T + F_{\mathrm{eg}} + F_M + F_1 + F_2. \tag{19}$$

Substituting Equations (15)–(18) in (14) and using $S = -(\partial F/\partial T)_\Omega$, we get

$$F_{\mathrm{hs}} = \frac{3}{2}k_B T - TS_{\mathrm{hs}}, \tag{20}$$

where S_{hs} is the entropy of the alloy of form [1–6].

$$S_{\mathrm{hs}} = S_{\mathrm{gas}} + S_c + S_\eta + S_\sigma. \tag{21}$$

Here 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.

The expressions for the various contributions are [1–6]:

$$\frac{S_{\mathrm{gas}}}{k_B} = \ln\left[\frac{e}{n}\left(\frac{emk_B T}{2\pi\hbar^2}\right)^{3/2}\right]; \quad \left(m = m_1^{c_1} m_2^{c_2}\right), \tag{22}$$

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

$$\frac{S_\eta}{k_B} = \ln(1-\eta) + \frac{3}{2}\left[1 - \frac{1}{(1-\eta)^2}\right], \tag{24}$$

and

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

Finally, using Equations (6) and (25), the Helmholtz free energy per ion of the alloy is given as [1–6]:

$$F = F_{\mathrm{ps}} + F_{\mathrm{hs}}. \tag{26}$$

The heat of mixing of the binary alloy has been calculated as follows [1–6]:

$$\Delta E = \Delta F_{\mathrm{eg}} + \Delta F_M + \Delta F_1 + \Delta F_2, \tag{27}$$

where $\Delta F_i = F_i(\mathrm{alloy}) - c_1 F_{i1} - c_2 F_{i2}$; $(i = \mathrm{eg}, M, 1, 2)$ and c_1 and c_2 refer to the pure components.

Also the entropy of mixing is given by [1–6]:

$$\Delta S = S_{\mathrm{hs}} - c_1 S_1 - c_2 S_2, \tag{28}$$

where S_{hs} is the entropy of the alloy and S_1 and S_2 are the entropies of the first and second atoms.

3. Results and discussion

The present article deals with the study of thermodynamical properties like internal energy (E), entropy (S_{hs}), Helmholtz free energy (F), heat of mixing (ΔE) and entropy of mixing(ΔS) of $\mathrm{Rb}_{c1}\mathrm{Cs}_{c2}$ liquid binary alloys as a function of concentration at constant temperature and pressure. The input parameters [27,28] used in the present computations are tabulated in Table 1. The various contributions to the internal energy as a function of concentrations for $\mathrm{Rb}_{c1}\mathrm{Cs}_{c2}$ liquid binary alloys are tabulated in Table 2.

From Table 2, it is observed that the value of F_{eg}, F_2 and F_M are negative while F_1 has a positive contribution to the internal energy (E). The contributions F_1 and F_2 are potential dependent while the other contributions, i.e. F_{eg} and F_M are independent of the potential. It is seen that the local field correction functions affect the term F_2 only, which is the second-order band structure energies. The various contributions to the entropy and the total entropy S_{hs} for $\mathrm{Rb}_{c1}\mathrm{Cs}_{c2}$ liquid binary alloys is plotted in Figure 1.

Among the four contributions to the 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. It is seen from Figure 1 that S_η is negative while rest of the contributions are positive. The maximum contribution to the total entropy comes from the term S_{gas} and the minimum contribution from S_η which depends only on the value of packing density η.

Table 1. Input parameters.

Metal	$T(K)$	$\frac{q_0}{2k_F}$ [28]	r_c (au)	Ω(au)[27]	k_F (au)[27]	η [27]
Rb	313	1.00	1.8802	648.6826	0.3574	0.4313
Cs	303	1.07	1.8923	810.0596	0.3319	0.4311

Table 2. Various contributions to the internal energy for $\mathrm{Rb}_{c1}\mathrm{Cs}_{c2}$ liquid binary alloys at melting temperature.

	Various contributions to the internal energy in au x 10^{-3}					
			F_2			
c_1	F_{eg}	F_1	H	T	SS	F_M
0.1	−78.2885	82.6545	−3.6629	−3.3774	−3.4587	−193.9419
0.2	−78.0890	80.7998	−3.7802	−3.4785	−3.5657	−192.1422
0.3	−77.8901	79.0309	−3.9120	−3.5947	−3.6878	−190.4340
0.4	−77.6922	77.3421	−3.9829	−3.6504	−3.7494	−188.8837
0.5	−77.4952	75.7281	−4.2671	−3.9198	−4.0248	−187.2081
0.6	−77.2993	74.1838	−4.0227	−3.6612	−3.7721	−186.1431
0.7	−77.1045	72.7051	−3.9691	−3.5939	−3.7107	−184.9608
0.8	−76.9111	71.2877	−2.6716	−2.2834	−2.4060	−185.0923
0.9	−76.7190	69.9279	−3.7551	−3.3543	−3.4827	−182.9024

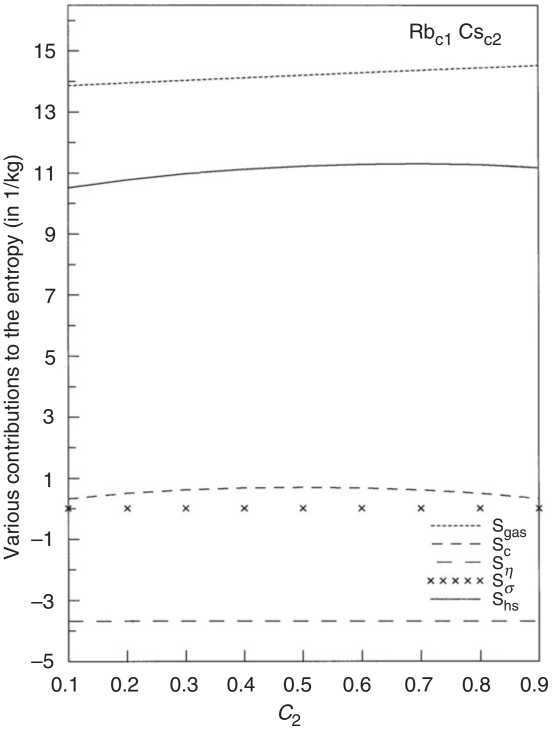

Figure 1. Various contributions to the entropy for $Rb_{c1}Cs_{c2}$ liquid binary alloys.

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, S_c is the ideal entropy of mixing and its magnitude remains same at every concentration. The nature of $S_c \rightarrow c_2$ curve is parabolic. It is also seen that as the concentration c_2 increases the term S_{gas} increases. The nature of $S_{hs} \rightarrow c_2$ curve is non-linear. All the contributions to the entropy are independent of the model potential used in the present investigation as well as not influenced by the nature of exchange and correlation functions. Finally, the total internal energy (E) and Helmholtz free energy (F) are calculated as a function of concentration and are tabulated in Table 3.

It is noticed that the major contribution to the internal energy comes from the structural part of the energy. The magnitude of the Madelung energy, $|F_M|$ is quite large throughout the concentration range in comparison with other energy terms. Its magnitude decreases with an increase in the atomic fraction of the heavier element. The modulus of the band structure energy, $|F_2|$, has a maximum in the intermediate range of concentration. The energy of the electron gas, F_{eg} in the mixture varies slightly with respect to concentration. The only positive contribution to the energy comes from the first-order pseudopotential term, F_1 which decreases as we increase the concentration of the heavier element. However, the aggregate effects of different energy terms are such that the total internal energy (E) of the system is found to be almost a linear function of the concentration. Hence, the Helmholtz free energy (F) of the system is also found to be almost a linear function of the concentration.

Table 3. Internal energy (*E*) and Helmholtz free energy (*F*) for $Rb_{c1}Cs_{c2}$ liquid binary alloys at melting temperature.

	Internal energy $E \times 10^{-3}$au			Helmholtz free energy $F \times 10^{-3}$au		
c_1	*H*	*T*	SS	*H*	*T*	SS
0.1	−191.7565	−191.4710	−191.5523	−212.5321	−212.2465	−212.3279
0.2	−191.7340	−191.4324	−191.5196	−212.9620	−212.6604	−212.7476
0.3	−191.7324	−191.4151	−191.5082	−213.2793	−212.9620	−213.0550
0.4	−191.7486	−191.4161	−191.5150	−213.5144	−213.1819	−213.2808
0.5	−191.7790	−191.4318	−191.5367	−213.6773	−213.3301	−213.4350
0.6	−191.8226	−191.4612	−191.5720	−213.7714	−213.4099	−213.5208
0.7	−191.8755	−191.5004	−191.6172	−213.7902	−213.4150	−213.5318
0.8	−191.9383	−191.5500	−191.6726	−213.7231	−213.3348	−213.4574
0.9	−192.0043	−191.6035	−191.7319	−213.5326	−213.1319	−213.2602

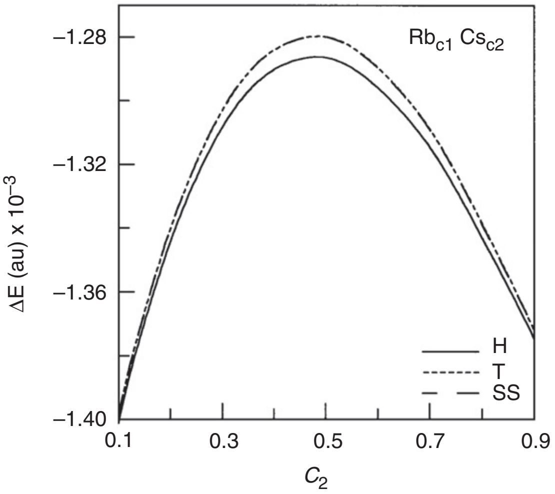

Figure 2. Heat of mixing for $Rb_{c1}Cs_{c2}$ liquid binary alloys as a function of concentration.

It is seen that the exchange and correlations affect the numerical values of internal energy (*E*) and Helmholtz free energy (*F*) in the order of 10^{-3}au. Thus, the influence of local field correction functions on the numerical values of internal energy (*E*) and Helmholtz free energy (*F*) is very small. The internal energy (*E*) and Helmholtz free energy (*F*) obtained due to the SS [26] local field correction function lies between those obtained due to *H* [8] and T [25] local field correction functions, in general. As the concentration in a particular system increases, it decreases the magnitude of the internal energy (*E*) as well as the Helmholtz free energy (*F*) of the system. The heat of mixing (ΔE) and entropy of mixing (ΔS) for $Rb_{c1}Cs_{c2}$ liquid binary alloys as a function of concentration are plotted in Figures 2 and 3, respectively.

From Figure 2 it is seen that the heat of mixing (ΔE) is symmetrical at $c_2 = 0.5$. Another important noticeable point is that the different forms of the exchange and correlation functions have more influence on the calculation of the heat of mixing (ΔE)

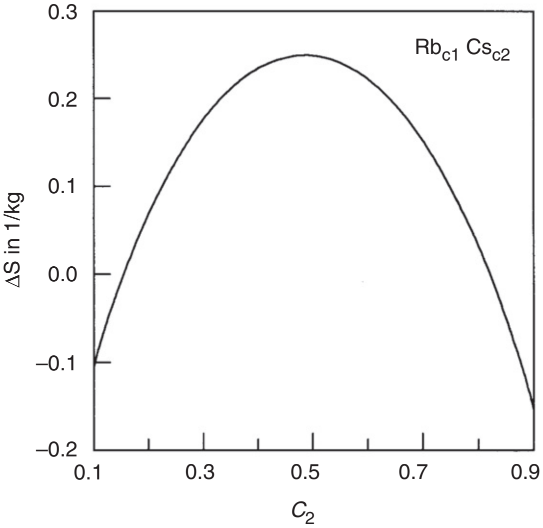

Figure 3. Entropy of mixing for $Rb_{c1}Cs_{c2}$ liquid binary alloys as a function of concentration.

Table 4. Heat of mixing (ΔE) and entropy of mixing (ΔS) of equiatomic $Rb_{c1}Cs_{c2}$ liquid binary alloys at melting temperature.

	Present			Others [3]				Expt. [29]
				Ashcroft model		Shaw model		
Properties	*H*	*T*	SS	VS	Shaw	VS	Shaw	
Heat of mixing $\Delta E \times 10^{-3}$au	−1.286	−1.280	−1.279	−1.727	−2.647	−0.003	−0.11	−0.054
Entropy of mixing (ΔS) in ($1/k_B$)		0.2491		−0.05051				–

than those of the internal energy (E) and Helmholtz free energy (F). Therefore, the heat of mixing (ΔE) of alloys is very much dependent on the choice of the forms of local field correction function 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 type of properties. Moreover, it is found that the *H* [8] dielectric function gives the lower value of the heat of mixing (ΔE) whereas the inclusion of the other dielectric functions, i.e. *T* [25] and SS [26] give higher values and their contributions are negative. The heat of mixing (ΔE) are obtained due to the *T* [25] and SS [26] local field correction functions having nearly the same values. The calculated entropy of mixing (ΔS) is symmetrical at $c_2 = 0.5$. The heat of mixing (ΔE) and entropy of mixing (ΔS) of equiatomic alloys have been presented in Table 4 along with the available experimental values [29] and other theoretical values [3].

From Table 4 it is seen that the heat of mixing (ΔE) is in good agreement with experimental values [29] and are also better than those of the other theoretical values [3]. In the case of entropy of mixing (ΔS), it is found that the other result [3] gives negative sign while the present results do not produce any negative sign. Thus, present result is far better in comparison to other [3] and it produces correct sign.

Finally, we conclude that:

1. The GB technique can be successfully used to study the thermodynamical properties of $\mathrm{Rb}_{c1}\mathrm{Cs}_{c2}$ liquid binary alloys.
2. It is found that thermodynamical properties of $\mathrm{Rb}_{c1}\mathrm{Cs}_{c2}$ liquid binary alloys are sensitive to the form of the model potential used, structural part of the energy, form of the local field correction function and volume of the mixing.
3. The different forms of the local field correction functions have little effect on the internal energy and Helmholtz free energy, whereas they significantly affect the heat of mixing.
4. The theory explains the symmetry of heat of mixing and entropy of mixing.
5. The partial structure factor due to PY reference system [27] is also capable of predicting the thermodynamical properties of $\mathrm{Rb}_{c1}\mathrm{Cs}_{c2}$ liquid binary alloys.

Thus, the proper choice of the model potential along with the local field correction function plays an important role in the study of the thermodynamical properties of $\mathrm{Rb}_{c1}\mathrm{Cs}_{c2}$ liquid binary alloys. This confirms the applicability of our model potential [19–24] in explaining the thermodynamics of $\mathrm{Rb}_{c1}\mathrm{Cs}_{c2}$ liquid binary alloys.

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