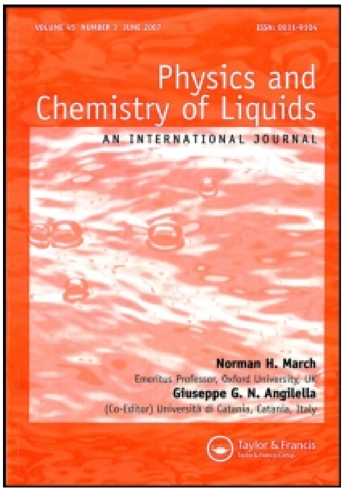

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Effect of Core-Ion Potentials on Thermodynamic Properties of Liquid Alkali Metals and Alloys

Sudhir Singh[a]; R. N. Singh[b]
[a] Deptt. of Physics, R D College, Sheikhpura (Munger) Bhagalpur University, Bhagalpur, India [b] Physics Department, College of Science, Sultan Qaboos University, Al-Khod, Oman

To cite this Article Singh, Sudhir and Singh, R. N.(1994) 'Effect of Core-Ion Potentials on Thermodynamic Properties of Liquid Alkali Metals and Alloys', Physics and Chemistry of Liquids, 27: 4, 203 — 214

To link to this Article: DOI: 10.1080/00319109408029528

URL: http://dx.doi.org/10.1080/00319109408029528

Phys. Chem. Liq., 1994, Vol. 27, pp. 203–214
Reprints available directly from the publisher
Photocopying permitted by license only

EFFECT OF CORE-ION POTENTIALS ON THERMODYNAMIC PROPERTIES OF LIQUID ALKALI METALS AND ALLOYS

SUDHIR SINGH

*Deptt. of Physics, R D College, Sheikhpura (Munger) Bhagalpur University,
Bhagalpur - 7 India*

R. N. SINGH

*Physics Department, College of Science, Sultan Qaboos University,
P.O. Box 32486, Al-Khod, Oman*

(Received 8 August 1993)

A pseudopotential perturbation scheme based on Gibbs-Bogoliubov variational technique is considered to investigate the structure and volume dependent contributions to the internal energies of liquid alkali metals. This has paved the way to analyse the effect of core-ion potentials on Helmholtz free energy, enthalpy, pairwise interactions and on entropy of liquids Na, K, Rb and Cs. Excess entropy of mixing for Na–K, Na–Cs and K–Rb are also calculated and are found very sensitive to the core-ion potentials.

KEY WORDS: Enthalpy, pairwise interaction, excess entropy of mixing.

1. INTRODUCTION

In recent years the variational technique has been extensively utilised to study the thermodynamic properties (for review see Ashcroft and Stroud[1], Young[2]) of liquid metals. The major task in such studies concerns to choose an appropriate reference system for structure and the pseudopotential for electron-ion interactions. Among the numerous existing methods, the use of hard-sphere reference system is largely justified because it provides analytical representation in term of single parameter, σ, known as hard sphere diameter. Also it is convenient to optimise σ in variational sense that ensures the thermodynamic stability of the metallic system; i.e.

$$\left(\frac{\partial F}{\partial \sigma}\right)_{T,\Omega} = 0 \tag{1}$$

Where F is the Helmoltz free energy at a given temperature T and the volume Ω of the system.

In the present work we intend to investigate the second point i.e. the effect of electron-ion interactions on thermodynamic properties under pseudopotential perturbation scheme. It enters into the calculation through the form factors which are Fourier transforms in q-space of the model potentials mapping the electron-ion interactions in real space. The potential seen by conduction electron in the presence of ions is usually written as consists of (i) the ion-core potential (for the region $r < r_m$, r_m is a chosen model radius) and (ii) the potential outside the core-region r_m which is Coulombic ($= -z/r$) in nature. In past, a great effort has been made to model the core-ion potential. Presently we consider three different forms of core-ion potentials (for schematic plot see Figure 1) which have been found very useful for the electronic transport properties of liquid metals. In real space, these are (*a.u*, $e = \hbar = m = 1$ is used)

$$\left.\begin{aligned} V(r) &= 0, \quad \text{Ashcroft potential}^3 \\ V(r) &= -A, \quad \text{Heine-Abarenkov potential}^4. \\ V(r) &= -(a - br^2), \quad \text{Harmonic Model Potential}^5. \end{aligned}\right\} \qquad (2)$$

A, a and b are model parameters which are obtained quantum mechanically[5-6] by matching the wave functions at the chosen model radius $r = r_m$. Such an approach is useful because none of the model potential parameter is fitted to the observed properties and hence the applicability of the pseudopotential perturbation scheme to investigate the thermodynamic properties can be critically analysed.

Application is made to liquid alkali metals Na, K, Rb and Cs and their homovalent liquid alloys (Na–K, Na–Cs and K–Rb). The basic steps which connect the pseudopotential perturbation scheme to thermodynamic functions are outlined in section 2. The results for enthalpy, pairwise interaction and entropy of pure liquid metals are included in section 3. The problem of excess entropy of mixing of binary molten alloys has been considered in section 4, followed by few concluding remarks in section 5.

2. FORMALISM

The Helmboltz free energy, F, lies at the heart of the pseudopotential perturbation scheme to calculate the thermodynamic properties of liquid metals,

$$F = E - TS \qquad (3)$$

where, E is the internal energy and S is the entropy at temperature T. The liquid metals can be assumed to consist of systems of ions and electrons. By ion we mean a nucleus plus the closed shell or core electrons, whereas the electrons in usual sense refer to valence electrons. Thus the internal energy E can be expressed as

$$E = E_{ion} + E_{elec} + E_{elec-ion} \qquad (4)$$

E_{ion} consists of $K.E(= \frac{3}{2}k_B T)$ of ions plus the contribution due to ion–ion interactions. The latter is usually known as Madelung contribution and has been treated in detail by Jones[7]. Thus we write

$$E_{ion} = \frac{3}{2}k_B T + \frac{z^2}{\pi}\int_0^\infty \{a(q) - 1\}\, dq \qquad (5)$$

Z is the valency and $a(q)$ is the structure factor. The term E_{elec} in equation (4) is the energy of the homogeneous electron gas which is the sum of kinetic energy of electrons, exchange energy, correlation energy, and the low temperature specific heat contribution for the electron gas. By adding them together, one writes

$$E_{elec} = Nz\left\{\frac{3}{10}K_F^2 - \frac{3}{4\pi}K_F - 0.0474 - 0.0155\ln K_F - \frac{1}{2}\left(\frac{\pi K_B}{K_F}\right)^2 T^2\right\} \tag{6}$$

K_F is the Fermi wave vactor ($K_F^3 = 3\pi^2 z/\Omega$). Now we turn our attention to the electron–ion contribution i.e. $E_{elec-ion}$ of Eq. (4) which has been obtained here in the framework of pseudopotential perturbation theory[8]. We utilise the perturbation expansion up to second order, which enables us to express,

$$E_{elec-ion} = \lim_{q\to 0}\left\{V^0(q) + \frac{4\pi z}{q^2}\right\}\frac{z}{\Omega} + \frac{1}{16\pi^3}\int_0^\infty \{V^0(q)\}^2 a(q)\left(\frac{1}{\varepsilon^*(q)} - 1\right)q^4\,dq \tag{7}$$

where the first term on right hand side is the first order energy and second is the band structure energy. $V^0(q)$ is the unscreened form factor and is obtained by taking the Fourier transform of the r-space pseudopotential. $V^0(q)$ explicitly depends on the core-ion pseudopotentials and hence allows us to investigate its effect on the thermodynamic functions. For three different forms of potentials (See Eq. 2), one writes

$$V^0(q)\,(\text{Ashcroft}) = -\frac{4\pi z}{q^2\Omega}\cos qr_m \tag{8}$$

$$V^0(q)\,(\text{Heine-Abarenkov}) = -\frac{4\pi z}{q^2\Omega}\cos qr_m - \frac{4\pi A}{q^3\Omega}[\text{Sin}\,qr_m - qr_m\,\text{Cos}\,qr_m] \tag{9}$$

$$V^0(q)\,(\text{Harmonic model potential}) = -\frac{4\pi z}{q^2\Omega}\text{Cos}\,qr_m - \left(\frac{r_m}{r_s}\right)^3\left\{a_0 g(x) - \left(\frac{3b_0}{q^2}\right)(x^2 g(x) - 2g(x) + 2\,\text{Cos}\,x)\right\} \tag{10}$$

with

$$g(x) = \frac{3(\text{Sin}\,x - x\,\text{Cos}\,x)}{x^3}, \quad x = |q|r_m \tag{11}$$

r_s here stands for Wigner-Seitz radius. $\varepsilon^*(q)$ in Eq. (7) is the modified Hartree dielectric screening function which takes into account of the conduction electrons interaction,

$$\varepsilon^*(q) = 1 + \{\varepsilon(q) - 1\}\{1 - G(q)\} \tag{12}$$

$\varepsilon(q)$ is the Hartree dielectric function and $G(q)$ is the correction factor for the exchange and correlated motion of the conduction electrons. Presently we consider $G(q)$ prescribed by Hubbard[9] and Sham[10]

$$G(q) = \tfrac{1}{2}q^2/\{q^2 + [2\pi K_F^3/(0.153 + \pi K_F)]\} \tag{13}$$

$G(q)$, as above, is prefered by virtue of its simplicity and also because it satisfies the compressibility sum rule almost exactly while giving a physically acceptable pair correlation function (see section 3).

The structure factor, $a(q)$, for liquid metals appearing in Eq. (7) can be calculated from the Percus-Yevick solution for hard sphere fluids which is characterised by the hard sphere diameter (σ) or, equivalently, by the packing fraction $\eta(=\pi\sigma^3/6\Omega)$. In order to maintain consistancy, the Perues-Yevick approximation can also be used (for example see Young[2]) to calculate the entropy S, i.e.

$$S = S_{gas} + S_\eta \tag{14}$$

with

$$S_{gas} = \tfrac{5}{2}K_B + K_B \ln\left\{\Omega\left(\frac{mK_BT}{2\pi\hbar^2}\right)^{3/2}\right\} \tag{15}$$

$$S_\eta = K_B \ln(1-\eta) + \tfrac{3}{2}K_B\{1-(1-\eta^{-2})\} \tag{16}$$

It may be noted that the Carnahan and Starling[12] expression of entropy which was obtained through analytical fit to the computer-determined equation of state can readily be procured from Eq. (16) by expanding $\ln(1-\eta)$ and retaining only the terms up to η^2.

Equation (14) has further been improved by adding an electronic term (S_{elec}) which appears due to low temperature specific heat contribution of the electron gas (see last term of the Eq. 6). Thus one writes

$$S = S_{gas} + S_\eta + S_{elec} \tag{17}$$

with

$$S_{elec} = \frac{\pi^2 K_B^2}{K_F^2} T \tag{18}$$

3. EFFECT OF CORE-ION POTENTIALS

3.1 *Enthalpy and Pairwise interactions*

The three different types of core-ion pseudopotentials (see Eq. 2 and Figure 1) are used to calculate the Helmholtz free energy from Eq. (3) which in turn was subjected to condition (1) to yield equilibrium value of hard sphere diameter (σ) and hence the packing fraction (η). The only model parameter r_m needed in the Ashcroft[3] potential has been taken from Cohen and Heine[13] where it has been fixed to reproduce the observed electrical resistivity. The well depth A for $l=0$ required in the Heine-Abarenkov (HA) potential has been taken from the work by Ese and Reissland[6]. The model parameters a and b occurring in the harmonic model potential (HMP) have been opted from the work by Srivastava and Singh[5]. It may be mentioned that the

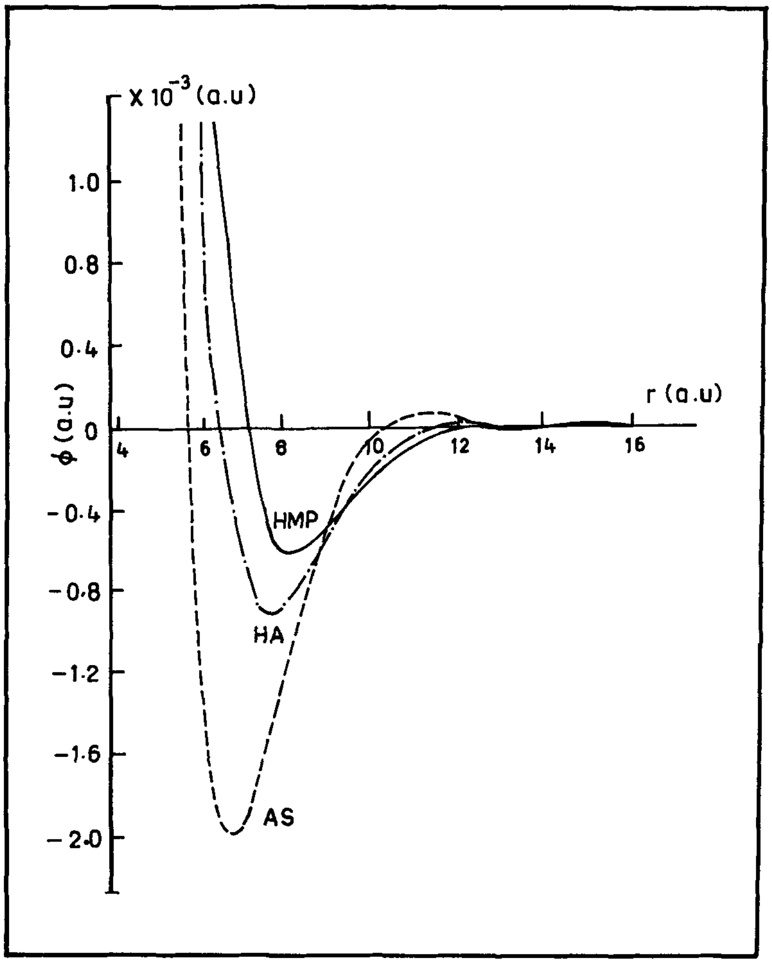

Figure 1 Core-ion potentials in *r* space for liquid Na – – – (Ashcroft, AS), –·–·– (Heine-Aborenkov, HA), ——— (Harmonic Model Potential, HMP).

parameters occurring in HA and HMP potentials have not been fixed with reference to any observed properties rather have been evaluated independently by matching the wave-functions. The atomic volume Ω, appropriate to pure liquid metals at relevant temperatures have been calculated from the densities measured experimetally[14].

The computed values of σ for Na, K, Rb and Cs which ensure minimun Helmholtz free energy are tabulated in Table 1. The various contributions to the internal energy computed for different forms of core-ion potentials are also tabulated in Table 1. E_{elec} and E_{ion} are negative while $E_{elec-ion}$ has positive contribution to the internal energy. The magnitude of the ionic contribution E_{ion} is much larger than E_{elec} and $E_{elec-ion}$.

It is clear from the Table 1 that the core-ion potentials affect the internal energy through E_{ion} and $E_{elec-ion}$. The effect is more visible on $E_{elec-ion}$ which involves the first and second order band structure energies. The value of $E_{elec-ion}$ computed with

Table 1 Various contributions to the internal energy (E) for liquid Na, K, Rb and Cs at 373 °K.

Liquids	*Cere-ion Potentials*	σ (a. u.)	η	*E*			*Enthalpy*	
				E_{elec} (10^{-3}au)	E_{ion} (10^{-3}au)	$E_{elec-ion}$ (10^{-3}au)	*Theory* (10^{-3}au)	*Expt.* (10^{-3}au)
Na	HMP	6.272	0.465	−81.61	−212.19	76.50	−217.31	
	HA	6.252	0.460	−81.61	−211.92	72.57	−220.96	−226.0
	AS	6.130	0.434	−81.61	−210.16	50.00	−241.77	
K	HMP	7.674	0.442	−79.89	−169.03	66.49	−182.43	
	HA	7.609	0.431	−79.89	−168.39	58.47	−189.81	−190.0
	AS	7.426	0.401	−79.89	−166.41	38.29	−208.01	
Rb	HMP	8.092	0.423	−78.41	−156.77	58.54	−176.64	
	HA	8.062	0.418	−78.41	−156.49	53.37	−181.53	−180.0
	AS	7.600	0.350	−78.41	−151.45	26.98	−202.88	
Cs	HMP	8.601	0.401	−76.31	−143.53	56.33	−163.51	
	HA	8.680	0.412	−76.31	−144.19	50.84	−169.66	−170.0
	AS	7.762	0.295	−76.31	−134.38	14.97	−195.72	

HMP: Harmonic model potential, HA: Heine-A baenkev potential, As: Ashcroft potential.

Ashcroft zero-core potential is much lower than that computed with finite core potentials (i.e. HMP or HA).

This can further be understood by calculating the pairwise-interaction potential, which is given by (see Harrison[8])

$$\phi(r)=\frac{z^2e^2}{r}+\frac{\Omega}{\pi^2 r}\int_0^\infty F(q)q\,\mathrm{Sin}(qr)\,dg \tag{19}$$

with

$$F(q)=-\frac{\Omega q^2}{8\pi}\left[\{V^0(q)\}^2\left(1-\frac{1}{\varepsilon^*(q)}\right)\right] \tag{20}$$

Obviously, the pairwise interaction $\phi(r)$ depends on $V^0(q)$ and hence on core-ion potentials through equations (8) to (10). As an example, $\phi(r)$ Calculated for Na is depicted in Figure 2. $\phi(r)$ exhibits an oscillatory behaviour, characteristic of metals, but becomes negligibly small ($\sim 10^{-6}$a.u.) after first minimum. The position of first minimum as well as the amplitude of oscillations are found to be sensitive to the choice of the core-ion potentials. It may be noted that the core-ion potential affect $\phi(r)$ and $E_{elec-ion}$ directly through, $V^0(q)$. The Ashcroft zero-core potential leads to strong pairwise interaction ($\phi(r)$ has large well-depth around the nearest neighbour distance) which corresponds to minimum positive contribution ($E_{elec-ion}$) to the internal energy. The other two finite core potentials (i.e. HMP and HA) are quite closer as regards to the values of $\phi(r)$ and $E_{elec-ion}$.

The theoretical internal energies are compared with the experimental values of the enthalpy functions as tabulated by Hultgren *et al.*[15] The later is obtained by applying third decimal place corrections to the OK values quoted by Heine[16]. There is a

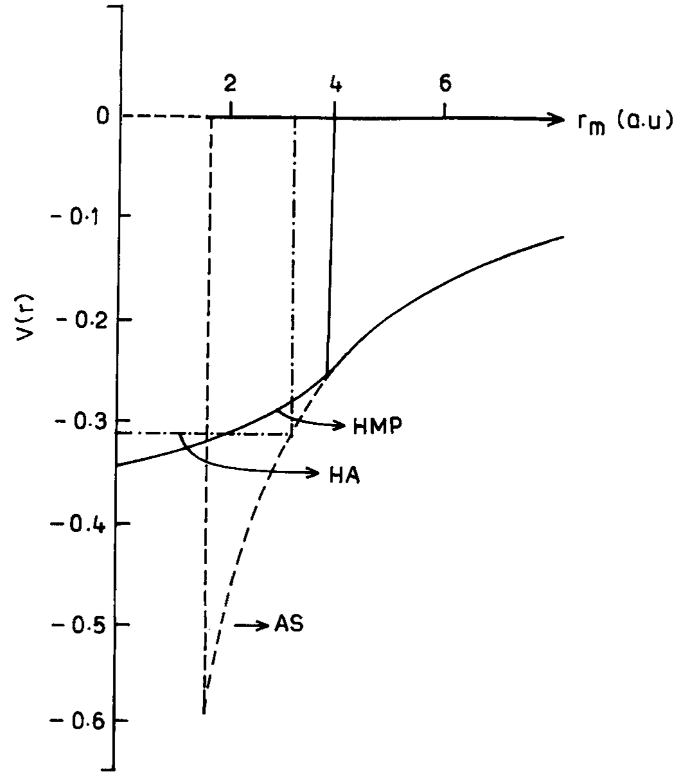

Figure 2 Effect of core-ion potentials on pairwise interaction of liquid Na – – – (due to AS Pot.), –·–·–(due to HA Pot.), ——— (due to HMP).

reasonable degree of agreement between the theoretically calculated internal energy and the enthalpy functions. The values calculated with finite-core potentials (i.e. HMP and HA) are closer to experimental values than that due to AS potential.

3.2 Entropy

The optimised values of σ and hence of η which are obtained through equation (1) and tabulated in Table 1 are used to determine S_η from equation (16). S_{gas} and S_{elec} are evaluated from equations (15) and (18) respectively. The resuts for Na, K, Rb and Cs are tabulated in Table 2. Among the three contributions, only S_η is structure and hence the potential dependent contribution to the entropy. The other two terms i.e. S_{gas} and S_{elec} depend only upon the density and are thus independent of potential. The magnitude of

Table 2 Various contributions to the entropy of liquid alkali metals (Na, K, Rb and Cs) at 373°K.

Liquids	*Cere-ion Potentials*	*Entropy (S)*				*Experimental Values (Hultgren et al., 1973)*
		$\frac{S_{gas}}{K_B}$	$-\frac{S_\eta}{K_B}$	$\frac{S_{elec}}{K_B}$	$\frac{S}{K_B}$	$\left(\frac{S}{K_B}\right)$
Na	HMP	11.22380	4.22847	0.05188	7.047	
	HA	11.22380	4.14008	0.05188	7.136	(7.79)
	AS	11.22380	3.65233	0.05188	7.623	
K	HMP	12.67564	3.79685	0.08031	8.959	
	HA	12.67564	3.60372	0.08031	9.152	(9.45)
	AS	12.67564	3.12111	0.08031	9.635	
Rb	HMP	14.05223	3.46924	0.09198	10.675	
	HA	14.05223	3.39299	0.09198	10.751	(10.35)
	AS	14.05223	2.44727	0.09198	11.697	
Cs	HMP	14.95013	3.12832	0.10763	11.929	
	HA	14.95013	3.29836	0.10763	11.755	(12.12)
	AS	14.95013	1.84738	0.10763	13.210	

S_{gas} is much larger than S_η. The former increases the absolute value of the entropy whereas the later tends to decrease the total entropy of the system. The magnitude of S_η computed with Ashcroft zero-Core potential is much lower than the corresponding values obtained through HMP and HA potentials.

The computed values of the entropy of liquid alkali metals can be seen in very good agreement with the experimental observation (Hultgren *et al.*, 1973). HMP and HA potentials provide consistently good results for Na, K, Rb and Cs, but the entropy computed with Ashcroft potential yield slightly higher values than the experimental observations for K, Rb and Cs. Disagreement with AS potential is quite noticeable in case of Cs.

4. EXCESS ENTROPY OF MIXING OF LIQUID ALKALI ALLOYS

In the present section we shall consider the generalisation of the various expressions as discussed in previous section to evaluate the impact of the core-ion potentials on the entropy of mixing of liquid alkali alloys (Na–K, Na–Cs and K–Rb). Let the alloy consists of C_1N atoms of type 1 and C_2 N atoms of type 2 with a constraint that $C_1 + C_2 = 1$ and N is the total number of atoms. The volume of the alloy is taken that the number densities of the ion species are $n_1 = c_1 n$ and $n_2 = c_2 n$ where $n = N/\Omega$. If Z_1 and Z_2 are valencies of the constituent species then $K_F = (\pi^2 \bar{z}n)^{1/3}$, where $\bar{Z}n = Z_1 n_1 + Z_2 n_2$ represents the mean average valence electron density. Equation (17) can readily be generalised to obtain the expression for entropy of liquid binary alloys[17–19]

$$S_{alloy} = S_{id} + S_{gas} + S_\eta + S_\sigma + S_{elec} \tag{21}$$

with

$$\frac{Sid}{K_B} = -\sum_{i=1,2} C_i \ln C_i \tag{22}$$

$$\frac{S_{gas}}{K_B} = \frac{5}{2} + \ln\left\{\Omega\left(\frac{m_1^{c_1} m_2^{c_2} K_B T}{2\pi\hbar^2}\right)^{3/2}\right\} \tag{23}$$

$$\frac{S_\eta}{K_B} = \ln\alpha + 1.5(1-\alpha^2) \tag{24}$$

$$\frac{S_\sigma}{K_B} = \pi C_1 C_2 (\sigma_1 - \sigma_2)^2 \alpha^2 \left\{\frac{\sigma_1 + \sigma_2}{2} - \pi \frac{(C_1 \sigma_1^4 + C_2 \sigma_2^4)}{24\Omega^2}\right\} \tag{25}$$

where

$$\alpha = (1-\eta)^{-1}$$

and

$$\eta = \pi(C_1 \sigma_1^3 + C_2 \sigma_2^3)/6\Omega,$$

m_1 and m_2 are atomic masses, σ_1 and σ_2 are hard sphere diameters of the constituent species. S_{id}, and S_{elec} are structure independent and hence do not depend on ion-core potentials. The potential affects the entropy of the alloy through S_η and S_σ, because σ in our formalism is potential dependent via Eq. (1). This is achieved by minimising the Helmholtz function (F) of the alloy with respect to σ_1 and σ_2. The expression for internal energy (E) for the alloy to be used in Eq. (3) can now be expressed as (See for example Ashcroft and Stroud[1], Hafner[20], Singh[21-22]).

$$E_{alloy} = E_{ion}^{alloy} + E_{elec}^{alloy} + E_{elec-ion}^{alloy} \tag{26}$$

with

$$E_{ion}^{alloy} = \frac{3}{2} K_B T + \frac{1}{\Pi} \sum_{i,j}^{1,2} Z_i Z_j (C_i C_j)^{1/2} \int_0^\infty (a_{ij}(q) - \delta_{ij})\, dq \tag{27}$$

$$E_{elec}^{alloy} = \bar{Z}\left[\frac{3}{10} K_F^2 - \frac{3}{4\Pi} K_F - 0.0474 - 0.0155 \ln K_F - 0.5\left(\frac{\pi K_B^2}{K_F^2}\right) T^2\right] \tag{28}$$

$$E_{elec-ion}^{alloy} = \lim_{q\to 0} \bar{z} n \left[\sum_i C_i V_i^0(q) + \frac{4\pi\bar{z}}{q^2}\right] + \frac{1}{16\pi^3} \int_0^\infty q^4\, dq$$

$$\cdot \sum_{ij} V_i^0(q) V_j^0(q) (C_i C_j)^{1/2} a_{ij}(q) \left(\frac{1}{\varepsilon^*(q)} - 1\right) \tag{29}$$

The quantities like K_F and n refer to the alloy, $a_{ij}(q)$ are the partial structure factors and are computed following the work of Ashcroft and Langreth[23]. This includes the detailed arrangement of ions in the system and requires the knowledge of the hard sphere diameters σ_1 and σ_2 which have been determined in the variational thermodynamic sense ensuring minimum free energy for the system via Eq. (1).

The values of σ_1 and σ_2 are computed for Na–K, Na–Cs, K–Rb equi-atomic liquid alloys by undergoing repeated optimisation of the Helmholtz free energy through Eq. (1) and (3) where E and S are now suitably replaced by E^{alloy} and S^{alloy}. Having determined σ_2, Eq. (21) can readily be used to calculate excess entropy of mixing (ΔS^{xs}) i.e.

$$\Delta S^{xs} = \Delta S_{gas} + \Delta S_{\eta} + \Delta S_{\sigma} + \Delta S_{elec}$$

where

$$\Delta S_i = S_i^{alloy} - C_1 S_i^{(1)} - C_2 S_i^{(2)}.$$

The computed values of σ_i and ΔS_i are tabulated in Table 3. σ_i suggest that the sizes of the hard spheres of pure constituent elements readjust to attain an equilibrium value on alloying. This is more pronounced in Na–Cs than in K–Rb and Na–K. The heavier elements contract while lighter ones expand. This has also been observed for divalent and trivalent liquid alloys[19,24]. The contraction and expansion of hard spheres can qualitatively be understood by considering the redistribution of the electronic charges at the Fermi surface on alloying. The Fermi wave vector of K ($K_F^{K} = 0.381$ au) is smaller than Na ($K_F^{Na} = 0.474$ au). If Na and K are mixed together then the flow of electrons takes place from K to Na as the later has lower Fermi energy. This leads to the expansion of Na-atoms and the contraction of K-atoms. This can also be understood from the electronegativity values. The hard spheres of more electronegative element expand. The difference in the electronegativity value leads to an accumulation of the electronic charges around the electronegative atomic site giving rise to its effective diameter and, on the other hand, reducing the effective size of the other constituent atom.

Table 3 Excess entropies of mixing of Na–K, Na–Cs and Na–Rb liquid alloys at 373° K.

Alloys (1–2)	$\frac{\Delta S_{gas}}{K_B}$	*Cere-ion Potentials*	σ_1 (au)	σ_2 (au)	$\frac{\Delta S_{\eta}}{K_B}$	$\frac{S_{\sigma}}{K_B}$	$\frac{\Delta S^{xs}}{K_B}$	
							Theory	*Expt*
Na–K	0.0388	HMP	6.525	7.473	−0.0033	0.0054	0.041	0.05(15)
		HA	6.488	7.426	0.0078	0.0049	0.051	
		AS	6.299	7.305	0.0019	0.0046	0.045	
Na–Cs	0.086	HMP	6.741	8.218	0.073	0.009	0.168	0.018(25)
		HA	6.635	8.380	−0.054	0.014	0.046	
		AS	6.435	7.677	0.188	0.004	0.278	
K–Rb	0.0031	HMP	7.790	7.984	0.0077	0.00015	0.011	
		HA	7.684	7.993	0.0014	0.00036	0.005	
		AS	7.514	7.539	0.0176	0.0	0.021	

The various contributions to excess entropy i.e. ΔS_{gas}, ΔS_{η} and S_{σ} are also given in Table 3. ΔS_{elec} happens to be negligibly small and hence are not given. The magnitude of the ideal gas contribution is maximum in Na–Cs followed by Na–K and K–Rb. The magnitude of ΔS_{η} for Na–K and K–Rb are much smaller than Na–Cs. S_{σ} for K–Rb is negligibly small but quite significant for Na–Cs.

The core-ion potential affects the excess entropy of mixing through ΔS_{η} and S_{σ}. The effect of potential is distinctively visible on the value of ΔS_{η}. Though $\Delta S^{xs}/K_B$ is a small number, the agreement between the theory and the experiment is quite satisfactory. The value of ΔS^{xs} calculated for Na–K with HMP potential is close to the experimental value[15] while HA potential yield better agreement for Na–Cs[25] system. From the point of view of the entropy of mixing $(\Delta S_M/K_B) = (\Delta S^{xs}/K_B + \sum_i C_i \ln C_i)$, the agreement between theory and experiment is very good. The values of K–Rb could not be compared for want of experimental result.

The ion-core potentials affects ΔS^{xs} considerably but the same potential could not provide consistently good result for all the systems considered here.

5. CONCLUSION

In the framework of pseudopotential perturbation scheme it has become possible to investigate the effect of core-ion potentials on thermodynamic properties of liquid alkali metals. The internal energy, pair-wise interaction and entropy of pure liquid alkali metals (Na, K, Rb & Cs) are very sensitive to the detail of potential that is considered in core-region of the ion. It is also found to play significant role on the alloying behaviour of binary liquid alkali alloys.

Acknowledgement

One of us (RNS) is thankful to Professor W. H. Young for his constant encouragement and help. The financial support from UGC, New Delhi is being gratefully acknowledged.

References

1. N. W. Ashcroft and D. Stroud, *S. S. P* Vol. **33** (Academic Press, New York, 1978).
2. W. H. Young, *Rep. Prog. Phys.* **55**, 1769 (1992).
3. N. W. Ashcroft, *Phys. Lett.* **23**, 48 (1966).
4. V. Heine and I. V. Abarenkov, *Phil. Mag.* **9**, 41 (1964).
5. P. L. Srivastava and R. N. Singh, *J. Phys. F: Metal. Phys.* **6**, 1819 (1976).
6. O. Ese and I. A. Reissland, *J. Phys. F: Metal. Phys.* **3**, 2066 (1973).
7. H. Jones, *J. Chem. Phys.* **55**, 2640 (1971).
8. W. A. Harrison, Pseudopotential in the theory of metals (Benzamin, New York, 1966).
9. J. Hubbard, *Proc. R. Soc.* **A 240**, 539 (1957).
10. L. J. Sham, *Proc. R. Soc.* **A 283**, 33 (1965).
11. N. W. Ashcroft and J. Lekner, *Phys. Rev.* **145**, 83 (1966).
12. N. F. Carnahan and N. E. Starling, *J. Chem. Phys.* **51**, 635 (1969).
13. M. L. Cohen and V. Heine, *S. S. P* Vol. **24** (Academic Press, 1970).
14. M. J. Huijben (1978). Ph. D. Thesis, University of Groningen, The Netherland.
15. R. Hultgren, P. D. Desai, D. T. Howking, M. Gleiser, K. K. Kelly and D. D. Wagman, Selected values of the thermodynamic properties of the element and alloys (Am Soc Metals, Metal Park, Ohio, 1973).
16. V. Heine (1969) The Physics of Metals 1 Electrons ed J. M. Ziman (Cambridge, Cambridge University Press).

17. G. A. Mansoori, N. F. Carnahan, K. E. Starling and T. W. Leland, *J. Chem. Phys.* **55**, 1523 (1971).
18. I. H. Umar, A. Meyer, W. Watabe and W. H. Young, *J. Phys. F: Metal. Phys.* **4**, 1691 (1974).
19. R. N. Singh and R. B. Chaudhary, *J. Phys. F: Mel. Phys.* **11**, 1577 (1981).
20. J. Jafner, *Phys. Rev.* **A 16**, 351 (1977).
21. R. N. Singh, *J. Phys F: Met., Phys.* **10**, 1411 (1980).
22. R. N. Singh, *J. Phys. F: Metal. Phys.* **11**, 389 (1981).
23. N. W. Ashcroft and D. C. Langreth, *Phys. Rev.* **159**, 500 (1967).
24. D. K. Pandye, R. N. Singh and P. L. Srivastava, *Phys. Chem. Liq.* **18**, 151 (1988).
25. F. E. Neale and N. E. Cusack, *J. Phys. F: Mel. Phys.* **12**, 2839 (1982).