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ELECTRICAL RESISTIVITY AND THERMODYNAMIC PROPERTIES OF ALKALI-ALKALI LIQUID BINARY ALLOYS

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The pseudopotential perturbation theory (TPT) has been used to compute the concentration dependence of the thermodynamic (entropy of mixing, heat of mixing), structural (static structure factors and interionic pairpotential) and the electrical (electrical resistivity) properties of alkali-alkali alloys viz., Na–K, Na–Rb, Na–Cs, K–Rb and K–Cs. The diameters of the hard sphere reference systems were determined by minimizing the interionic pairpotentials acting between the constituent species of the alloys. It has been found that TPT theory provides a simultaneous interpretation of thermodynamic and electrical properties of alkali-alkali liquid alloys.

KEY WORDS: Pseudopotentials, entropy of mixing, conductivity.

1 INTRODUCTION

The problems of liquid metals and alloys are interesting in many ways. These are dense metallic liquids but are devoid of long range crystalline order. During last few years, considerable efforts have been made to devise a respectable theory^{1,2} to explain the structural disorder in molten metallic systems. The latter also occurs as one of the important ingredients for the evaluation of electrical and thermodynamic properties of liquid metals and alloys.

Over the last two decades considerable progress has been made to explain the structural disorder by blending the pseudopotential and the thermodynamic perturbation theories^{3–7}. The major step in such studies is the selection of the reference system for which there are four important methods: (i) hard sphere and interionic pairpotential⁸, (ii) hard sphere and variational method⁹ (iii) Weeks–Chandler and Anderson method^{10–12} and (iv) one component plasma system¹³.

As regards the choice of reference system, the hard sphere is largely used because these systems have analytical representations in terms of single parameter, which is known as hard sphere diameter (σ). The structure factor and the entropy can be analytically expressed in terms of σ . The latter can be determined either by minimising the Helmholtz free energy of the system^{3,6}, or by minimising the interionic pair-potential⁴. Though considerable progress has been made by using hard sphere and variational method but very little has been done for hard sphere reference system in the frame work of interionic pairpotential¹⁴. The present work intends to bridge such gaps.

The knowledge of interionic pairpotential has been used to evaluate the hard sphere diameters of different concentrations for alkali-alkali alloys (Na-K, Na-Rb, Na-Cs, K-Rb, K-Cs). These, in turn, have been applied to give simultaneous interpretations of thermodynamic (entropy of mixing, heat of mixing), structural (static structure factors) and electrical properties (electrical resistivity) of binary liquid alloys.

2 INTERIONIC PAIRPOTENTIAL AND HARD SPHERE

Within the frame work of pseudopotential theory the total energy may be split up into two parts, say E_0 and E . E_0 is the volume dependent part which is independent of the ionic position. E is the structure dependent part and may be written in the compact form as

$$E = E_{bs} + E_{es} \quad (1)$$

E_{es} is the electrostatic energy of a lattice of point charge Z embedded in a uniform compensating background. E_{bs} is the band structure energy from which the pair wise potentials V_{ij} (i, j refer to constituent element) for binary alloys can readily be obtained¹⁵ as

$$V_{ij} = \frac{Z_i Z_j}{R} \left[1 - \frac{2}{\pi} \int F_{ij}^N(q) \frac{\sin qR}{q} dq \right] \quad [i = 1, 2] \quad (2)$$

where Z_i, Z_j are the valencies of the constituent elements, q is the phonon wave vector, $F_{ij}^N(q)$ are normalized wave number characteristics given by

$$F_{ij}^N(q) = - \left(\frac{q^2 \Omega}{2\pi Z_i Z_j} \right) F_{ij}(q) \quad (3)$$

Here

$$\Omega = \Omega_{ideal} + \Delta\Omega \quad (4)$$

with

$$\Omega_{ideal} = C_i \Omega_i + C_j \Omega_j \quad (5)$$

Ω_i, Ω_j are the atomic volume of the constituent elements of the alloy at required temperature and $\Delta\Omega$ accounts the contraction or expansion on alloying, C_i, C_j are the concentrations.

In the local approximation, $F_{ij}(q)$ is expressed as

$$F_{ij}(q) = -\left(\frac{\Omega q^2}{8\pi}\right) \left[W_i(q)W_j(q) \frac{\varepsilon^*(q) - 1}{\varepsilon^*(q)} \frac{1}{1 - G(q)} \right] \quad (6)$$

$\varepsilon^*(q)$ is the modified Hartree dielectric function given by

$$\varepsilon^*(q) = 1 + (\varepsilon(q) - 1)(1 - G(q)) \quad (7)$$

$\varepsilon(q)$ is the usual dielectric function. $G(q)$ takes into account the correlation among the conduction electrons.

$W(q)$ is the unscreened form factor for which harmonic model potential (HMP)¹⁶ has been considered. The HMP is defined as (in the atomic unit $e = \hbar = m = 1$)

$$\begin{aligned} W(r) &= \sum_l (a_l - b_l \gamma^2) \hat{p}_l \quad \text{for } \gamma \leq \gamma_m \\ &= -\frac{Z}{\gamma} \quad \text{for } \gamma \geq \gamma_m \end{aligned} \quad (8)$$

where a_1, b_1 are the model parameters which are evaluated following the procedure mentioned in the works of Sahay *et al.*⁷, \hat{p}_1 stands for projection operator, 1 is the orbital quantum number. In the local approximation $W_i(q)$ reads as

$$\begin{aligned} W_i(q) &= \frac{Z_i}{Z_i^*} \left(\frac{\gamma_{im}}{\gamma_s}\right)^3 \left\{ -a_{0i}g(x) + \left(\frac{3b_{0i}}{q^2}\right) \left[x^2g(x) - 2g(x) + 2 \cos x \right] \right\} \\ &\quad - \frac{4\pi Z_i \cos x}{q^2 \Omega} + \frac{4\pi \rho_i (1 - \cos x)}{q^2 \Omega} \end{aligned} \quad (9)$$

r_{im} is the model radius and ρ_i is the depletion charge.

$$\begin{aligned} \gamma_s &= \left(\frac{3\Omega}{4\pi}\right)^{1/3} \\ Z_i^* &= Z_i - \rho_i \\ g(x) &= \frac{3(\sin x - x \cos x)}{x^3} \\ x &= q|\gamma_{im}| \end{aligned} \quad (10)$$

The form factors needed to compute the interionic pairpotential [through Eq. (2)] have been calculated through Eq. (9) at required concentration using Fermi wave

vector K_F

$$K_F^3 = 3\pi^2\Omega^{-1} \sum_{i=1}^2 C_i Z_i \quad (11)$$

and the model parameters given in Table 1. The Vashishta and Singwi¹⁸ forms of $G(q)$ have been used for exchange and correlation function. The values of Ω in the present work have been taken from density data of Huijbin *et al.*^{19,20} for Na-K, Na-Cs and K-Rb and for Na-Rb, K-Cs Ω_{ideal} have been used.

The pairpotentials between the constituent atoms in the elemental state and in the alloys have been depicted in Figure 1 [a-d]. It is observed from the Figures that the

Table 1 Values of model parameters (a_0 , b_0 , r_m) depletion charge (ρ) and presently determined diameter (σ) (all in a.u) of alkali-alkali alloys

	a_0	Na 0.370	K 0.281	Rb 0.260	Cs 0.241
Model parameters					
	b_0	0.0075	0.0032	0.0025	0.0020
	ρ	-0.012	-0.007	-0.029	-0.021
	r_m	3.931	4.862	5.197	5.625
Systems	Temp(°C)	C_2	σ_1	σ_2	
Na-K	100	0.0	6.376	—	
		0.2	6.337	7.878	
		0.4	6.299	7.842	
		0.5	6.281	7.823	
		0.6	6.266	7.806	
		0.8	6.235	7.768	
		1.0	—	7.730	
Na-Rb	100	0.2	6.330	8.352	
		0.4	6.265	8.283	
		0.5	6.243	8.256	
		0.6	6.222	8.227	
		0.8	6.186	8.170	
		1.0	—	8.115	
Na-Cs	100	0.2	6.302	8.907	
		0.4	6.241	8.847	
		0.5	6.211	8.801	
		0.6	6.186	8.761	
		0.8	6.148	8.680	
		1.0	—	8.602	
K-Rb	100	0.2	7.713	8.187	
		0.4	7.696	8.169	
		0.5	7.688	8.160	
		0.6	7.682	8.154	
		0.8	7.667	8.136	
		1.0	—	8.136	
K-Cs	100	0.2	7.688	8.751	
		0.4	7.650	8.711	
		0.5	7.631	8.691	
		0.6	7.620	8.679	
		0.8	7.580	8.635	
		1.0	—	8.635	

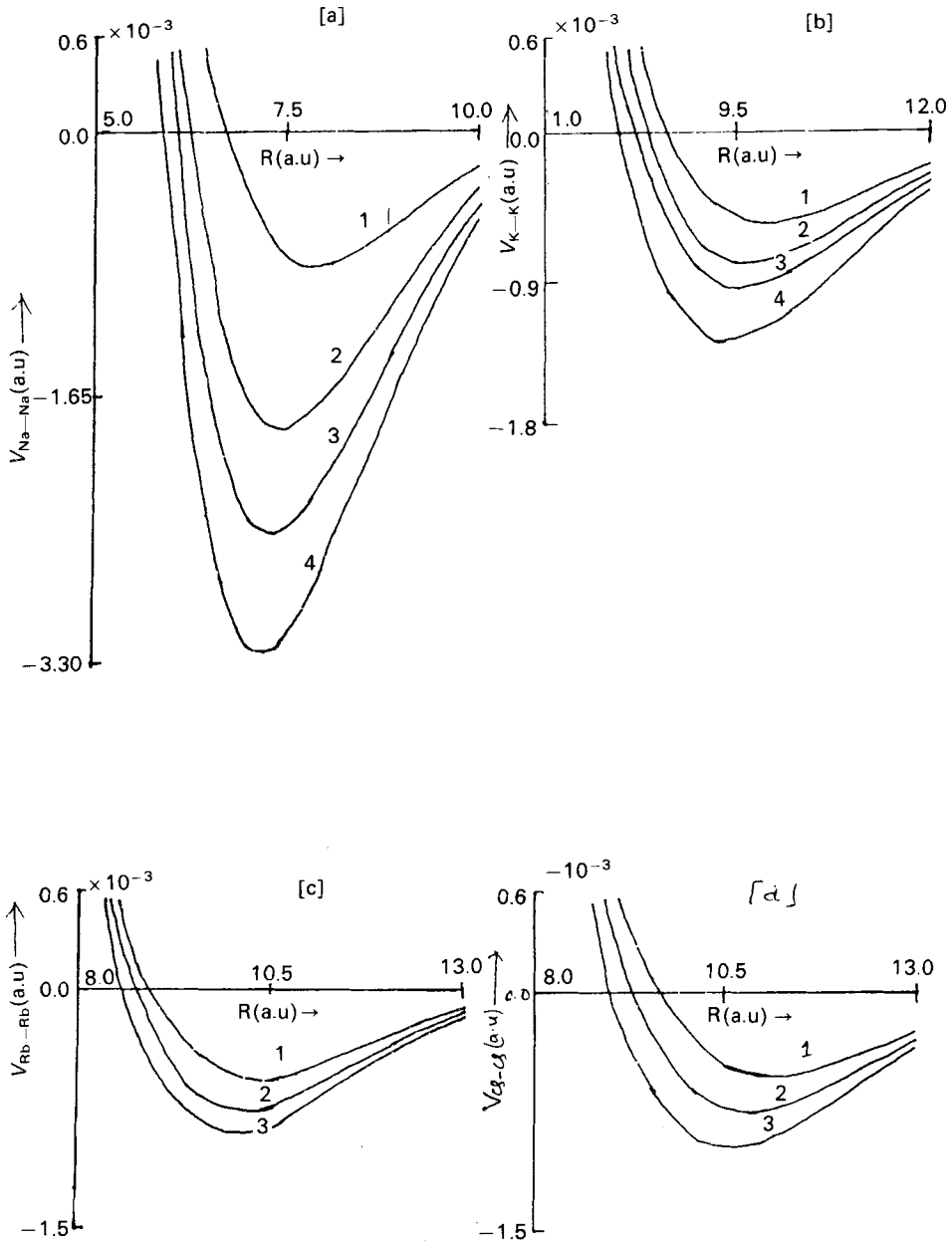


Figure 1 (a) Interionic pairpotential [$V_{\text{Na-Na}}$] of Na-Na atoms: Curves 1, 2, 3, 4 refer respectively to pure Na and equiatomic Na-K, Na-Rb, Na-Cs alloys. (b) Interionic pairpotential [$V_{\text{K-K}}$] of K-K atoms: Curves 1, 3, 4 refer respectively to equiatomic Na-K, K-Rb and K-Cs alloys and Curve 2 is for pure K. (c) Interionic pairpotential [$V_{\text{Rb-Rb}}$] atoms: Curves 1, 2, 3 refer respectively to equiatomic alloys Na-Rb, K-Rb and pure Rb. (d) Interionic pairpotential [$V_{\text{Cs-Cs}}$] of Cs-Cs atoms: Curves 1, 2, 3 refer respectively to equiatomic alloys Na-Cs, K-Cs and pure Cs.

effective interaction between Na–Na atoms increases after alloying it with K, Rb and Cs atoms. $V_{\text{Na–Na}}$ in Na–Cs liquid alloys is smaller than in Na–Rb and Na–K liquid alloys in order. The nearest neighbour distance between Na–Na atoms also decreases after alloying. This decrease is greater in Na–Cs than that of Na–Rb and Na–K liquid alloys.

Similarly the effective interaction between K–K atoms in pure state is greater than that in the alloy Na–K but smaller than that of K–Rb and K–Cs liquid alloys. The nearest neighbour distance between K–K atoms increases in Na–K and decreases in K–Rb and K–Cs alloys. This decrease is greater in K–Cs than that in K–Rb alloys. In Rb based alloys, the effective interaction between Rb–Rb atoms decreases after alloying it with Na and K atoms. The nearest neighbour distance between Rb–Rb atoms increases in Na–Rb and K–Rb alloys. This increase is greater in Na–Rb than that in K–Rb. Finally the effective interaction between Cs–Cs atoms in pure state is greater than that in Na–Cs and K–Cs alloys. The nearest neighbour distance between Cs–Cs atoms increases in Na–Cs and K–Cs liquid alloys. This increase is greater in Na–Cs alloy than that in K–Cs alloy.

The hard sphere diameters have been calculated⁸ using the relation

$$V_{ij}(\sigma_i) = V_{\min} + 3/2K_B T \quad (12)$$

where $\frac{3}{2}K_B T$ is the mean kinetic energy and V_{\min} is the first minimum in the interionic pair potential.

The hard sphere diameters thus evaluated are given in Table 1. It is found that the ratio σ_1/σ_2 remains almost constant for the whole concentration range in the case of all the alloys though the hard spheres of heavier elements expand and lighter elements shrink. The expansion and shrinkage of hard sphere diameters are usually understood at the cost of charge transfer among the constituent species^{4,21–22}.

The diameters (σ_i) can also be determined from the variational thermodynamic sense by minimizing the Helmholtz free energy of the system²³, i.e.,

$$\left(\frac{\partial F}{\partial \sigma_i}\right)_{\Omega, T} = 0 \quad [i = 1, 2] \quad (13)$$

where F is the Helmholtz free energy whose detailed expression is given in Section 4.

For sake of comparison σ_i computed from Eq. (12) and Eq. (13) for Na–Cs liquid alloys are plotted in Figure 2. Figure shows that σ_i resulting from Eq. (13) are opposite in nature to that obtained by minimizing the pairpotential. For earlier case the hard sphere diameters of Cs contract and that of Na expands which are opposite in nature to that obtained from Eq. (12).

In Table 2 we have compared the computed values of hard sphere diameters for equiatomic Na–K and Na–Cs liquid alloys to that obtained by other theoretical methods^{3,4,6}. It is observed from Figure 2 as well as from Table 2 that our values are comparable to the values obtained by Hafner⁴. It may be recalled that he has also used the interionic pairpotential for the selection of hard sphere diameter which

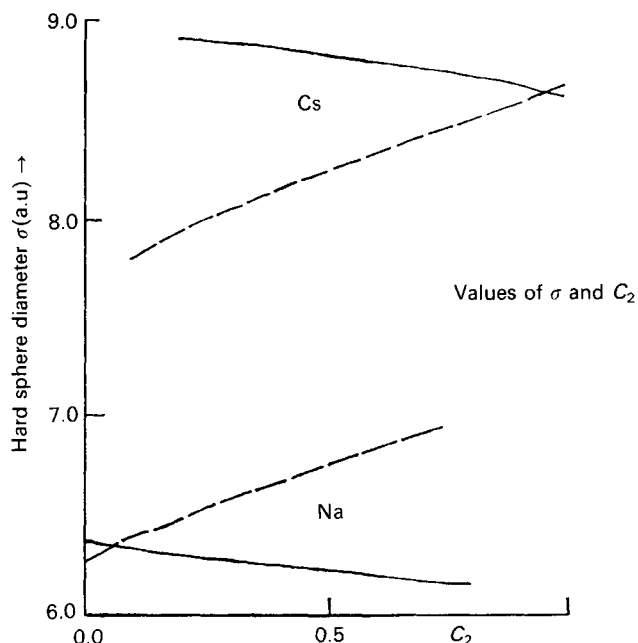


Figure 2 Hard sphere diameters of Na [lower curves] and Cs [upper curves] versus concentration of Cs. — and — — correspond to the values calculated through Eq. (12) and Eq. (13) respectively.

is different to Ref.^{3,6}. In the latter case the Helmholtz free energy has been minimized for the selection of σ .

3 ENTROPY OF MIXING

Let us consider a binary alloy consisting of $N_A (= C_1 N)$ atoms of the element A and $N_B (= C_2 N)$ atoms of the element B so that there are N atoms in all. The entropy of

Table 2 Effective hard sphere diameters (a.u), their change upon alloying of Na-K and Na-Cs at equatomic composition.

Alloy	Reference	σ_{Na}	$[\sigma_{Na}]_{Na-K}$	$\left(\frac{\Delta\sigma}{\sigma_{Na}}\right)\%$	σ_K	$[\sigma_K]_{Na-K}$	$\left(\frac{\Delta\sigma}{\sigma_K}\right)\%$
Na-K	Present	6.376	6.281	-1.4	7.730	7.823	1.2
	Umar <i>et al.</i> ³	6.09	6.24	2.4	7.40	7.35	-0.6
	Singh ⁶	6.21	6.35	2.2	7.53	7.44	-1.2
	Hafner ⁴	6.10	6.04	-1.0	7.51	7.62	1.5
		σ_{Na}	$[\sigma_{Na}]_{Na-Cs}$	$\left(\frac{\Delta\sigma}{\sigma_{Na}}\right)\%$	σ_{Cs}	$[\sigma_{Cs}]_{Na-Cs}$	$\left(\frac{\Delta\sigma}{\sigma_{Cs}}\right)\%$
Na-Cs	Present	6.376	6.211	-2.5	8.602	8.801	2.3
	Singh ⁶	6.21	6.40	3.1	8.57	8.44	-1.4

mixing of such a binary mixture can be expressed as

$$\Delta S = S - C_1 S_A - C_2 S_B \quad (14)$$

where S is the entropy of the alloy and S_A and S_B are the enterprise of the species A and B of the alloy.

$$S = S_{\text{gas}} + S_{\sigma} + S_c + S_{\eta} \quad (15)$$

Here S_{gas} represents the gas term, S_{η} corresponds to packing density η , S_c is the ideal entropy of mixing and S_{σ} arises due to the difference in diameters of the hard spheres of A and B . The expression for the various contributions are^{3,24}

$$\begin{aligned} \frac{S_{\text{gas}}}{k_B} &= 2.5 + \ln \left[\Omega \left(\frac{m_1^c m_2^c k_B T}{2\pi \hbar^2} \right)^{3/2} \right] \\ \frac{S_{\eta}}{k_B} &= -(\beta - 1)(\beta + 3) \\ \frac{S_c}{k_B} &= -(C_1 \ln C_1 + C_2 \ln C_2) \\ \frac{S_{\sigma}}{k_B} &= \frac{3}{2}(\beta^2 - 1)y_1 + \frac{3}{2}(\beta - 1)^2 y_2 - \left[\frac{1}{2}(\beta - 1)(\beta - 3) + \ln \beta \right] (1 - y_3) \end{aligned} \quad (16)$$

With

$$\begin{aligned} y_1 &= C_1 C_2 (\sigma_1 + \sigma_2)(\sigma_1 - \sigma_2)^3 / \sigma^3 \\ y_2 &= C_1 C_2 \sigma_1 \sigma_2 (C_1 \sigma_1^2 + C_2 \sigma_2^2)(\sigma_1 - \sigma_2)^2 / \sigma^6 \\ y_3 &= (C_1 \sigma_1^2 + C_2 \sigma_2^2)^3 / \sigma^6 \\ \sigma^3 &= C_1 \sigma_1^3 + C_2 \sigma_2^3 \\ \beta &= \frac{1}{1 - \eta} \end{aligned}$$

m_1, m_2 are the atomic masses of A and B and η is the packing density given by

$$\eta = \frac{\pi}{6\Omega} \sigma^3 \quad (18)$$

The entropy of mixing has been computed through Eq. (14). The hard sphere diameters are taken from Table 1. The computed entropy of mixing $[\Delta S]$ with concentration has been plotted in Figure 3 alongwith the experimental results for Na-K²⁵ and Na-Cs²⁶. ΔS for the rest of the alloys have not been compared as experimental values for these alloys are not available to the best of our knowledge. The calculated entropy of mixing of all the alkali alloys considered here is symmetrical at $C = \frac{1}{2}$. The experimental ΔS for Na-K and Na-Cs are also symmetrical at $C = \frac{1}{2}$.

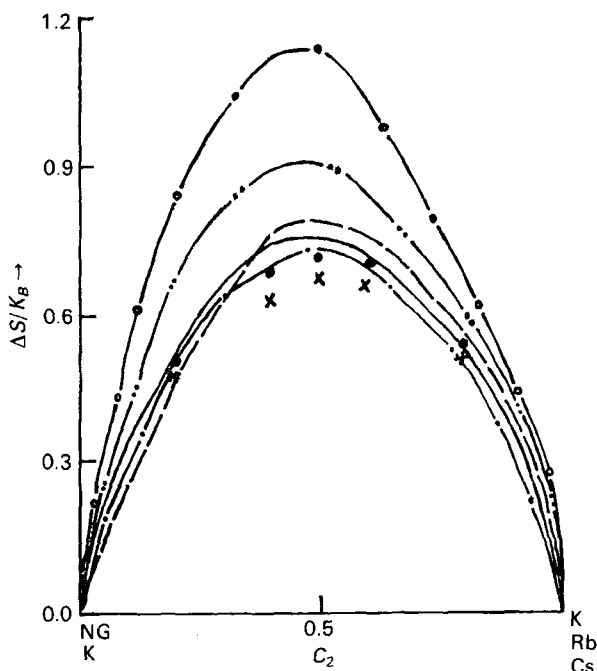


Figure 3 Entropy of mixing versus concentration: Theoretical values [—] Na-K, [—○—] Na-Rb, [—○—] Na-Cs, [—○—] K-Rb, [—○—] K-Cs alloys; ●●● and ××× refer to experimental points for Na-K²⁵ and Na-Cs²⁶ respectively.

and are in reasonable agreement with our values. The computed values of ΔS differ from experiment to a maximum of 7.5% in the case of Na-K and 15% in the case of Na-Cs.

4 ENERGY OF MIXING

Considering the electron-ion interaction within the frame work of second-order perturbation theory, the Helmholtz free energy per ion at a given temperature T and volume Ω can be written as^{3,6}.

$$F = F_{PS} + F_{HS} \quad (19)$$

Here F_{PS} is the effective potential energy and F_{HS} is the Helmholtz free energy of the hard sphere system. In an expanded notation¹⁹ F can be expressed as

$$F = (F_1 + F_2 + F_M + F_{eg}) + (3/2K_B T - TS) \quad (20)$$

The first order pseudopotential energy F_1 is given by

$$F_1 = (C_1\alpha_1 + C_2\alpha_2)Z/\Omega \quad (21)$$

with $Z(= C_1Z_1 + C_2Z_2)$ the mean valence and

$$\alpha_i = \lim_{q \rightarrow 0} \left(W_i(q) + \frac{4\pi Z_i}{q^2} \right) \tag{22}$$

F_2 is the second-order pseudopotential perturbation energy

$$F_2 = \frac{1}{16\pi^3} \int_0^\infty \left[\sum_{i,j}^{1,2} W_i(q)W_j(q)(C_iC_j)^{1/2}S_{ij}(q) \left(\frac{1}{\epsilon^*(q)} - 1 \right) q^4 dq \right] \tag{23}$$

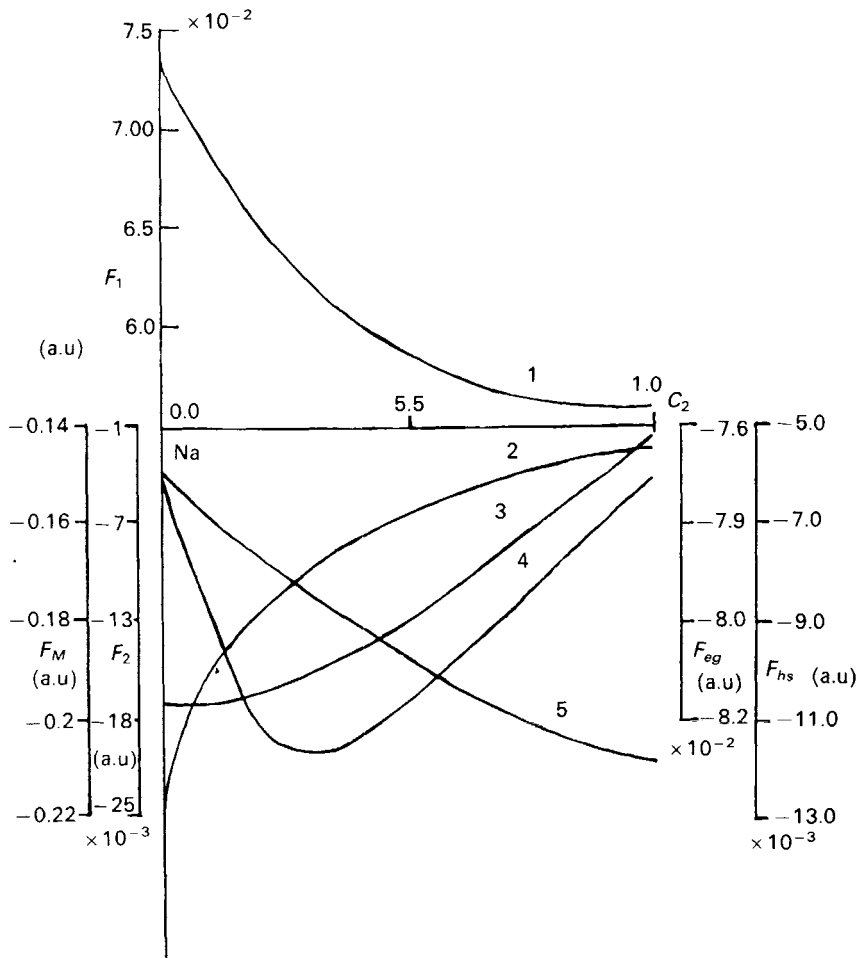


Figure 4 Different contributions to the free energy F for Na-Cs at different composition: Curves 1, 2, 3, 4, 5 refer respectively to F_1 , F_M , F_{eg} , F_2 and F_{hs} .

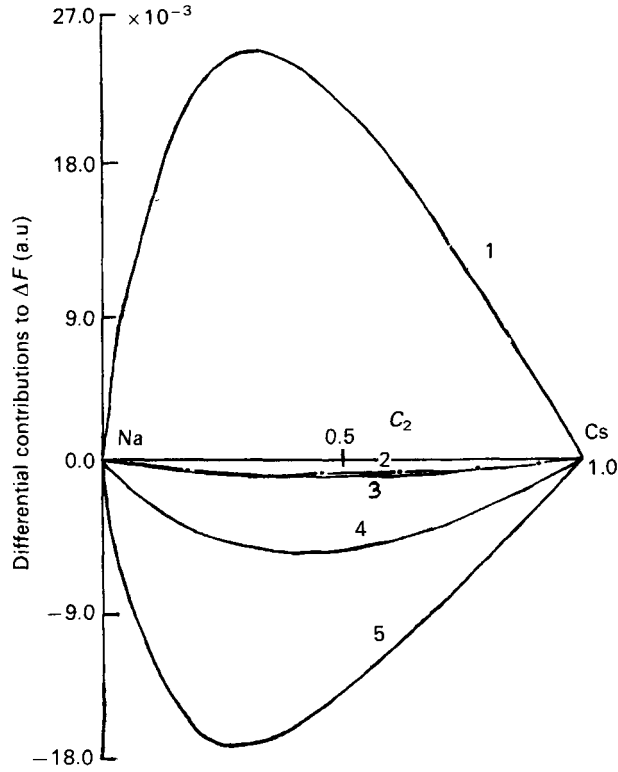


Figure 5 Different contributions to the free energy of mixing ΔF for Na-Cs at different compositions: Curves 1, 2, 3, 4, 5 refer respectively to ΔF_M , ΔF_{hs} , ΔF_{eg} , ΔF_1 and ΔF_2 .

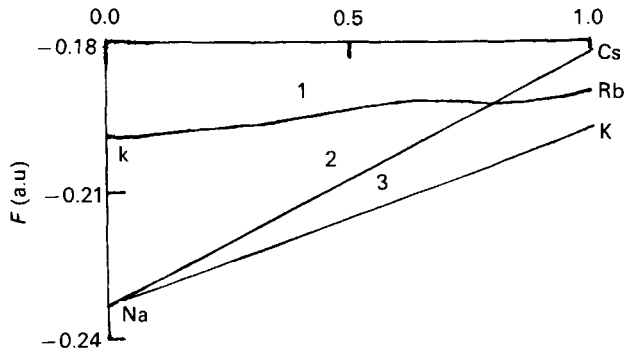


Figure 6 Energy of the systems at different compositions: Curves 1, 2, 3 correspond to K-Rb, Na-Cs and Na-K alloys.

$S_{ij}(q)$ are the partial structure factors which are evaluated in the hard sphere percus-Yevick approximation²⁷. The Madelung energy F_M is

$$\begin{aligned}
 F_M &= C_1^2 Z_1^2 I_{11} + C_2^2 Z_2^2 I_{22} + 2C_1 C_2 Z_1 Z_2 I_{12} \\
 I_{11} &= \left(\frac{\pi N}{1 + 2\eta} \right) \left[-\sigma_1^2 + 0.2(1 - 0.5\eta)(\eta_1 \sigma_1^2 + \eta_2 \sigma_2^2) \right. \\
 &\quad \left. + \eta_2 \sigma_1 (\sigma_2 - \sigma_1) + \frac{1}{2} \eta_1 \eta_2 (\sigma - \sigma_1)^2 \right] \\
 I_{12} &= \left(\frac{\pi N}{1 + 2\eta} \right) \left[-0.25(\sigma_1 + \sigma_2)^2 + 0.2(1 - 0.5\eta)(\eta_1 \sigma_1^2 + \eta_2 \sigma_2^2) \right. \\
 &\quad \left. - \frac{1}{2}(\eta_2 \sigma_1 - \eta_1 \sigma_2) + \frac{1}{2} \eta_1 \eta_2 (\sigma_2 - \sigma_1)^2 \right]
 \end{aligned} \tag{24}$$

I_{22} is evaluated by interchanging 1 and 2 in I_{11} . F_{eg} is the free energy of the electron gas

$$F_{eg} = \left[0.3 K_F^2 - \frac{3}{4\pi} k_F - 0.0474 - 0.155 \ln k_F - 0.5 \left(\frac{\pi K_B T}{k_F} \right)^2 \right] \tag{25}$$

S is the entropy of the system which has already been discussed in the previous section.

The heat of mixing and free energy of mixing are obtained through

$$\text{Heat of mixing } [\Delta H] = \Delta F_1 + \Delta F_2 + \Delta F_M + \Delta F_{eg} \tag{26}$$

Free energy of mixing

$$[\Delta F] = \text{Heat of mixing} - T\Delta S \tag{27}$$

Here $F_i = F_i \text{ alloy} - C_1 F_{iA} - C_2 F_{iB}$; i denotes 1, 2, M , eg and A , B , stand for constituent species.

The form factors needed to compute the second order pseudopotential contribution to free energy have been calculated through Eq. (9). The hard sphere diameters to calculate the partial structure factors and Madelung energy have been taken from Table 1. The heat of mixing ΔH and free energy of mixing ΔF are calculated for Na-K, K-Rb and Na-Cs because experimental results for these systems are available for sake of comparison. The heat of mixing $[\Delta H]$ and free energy of mixing $[\Delta F]$ have been calculated through Eq. (26) and (27) respectively. It has been observed that the magnitude of the band structure energy (F_2) is small [Figure 4] but ΔF_2 becomes dominant [Figure 5] in the calculation of heat of mixing. So the choice of pseudopotential plays a significant role in this calculation. F_M contributes much to the total energy. F_{eg} varies slightly with concentration. Only F_1 gives the positive contribution to the free energy. However, the total energy of the system is found almost linear function of the concentration [Figure 6]. The computed values of heat

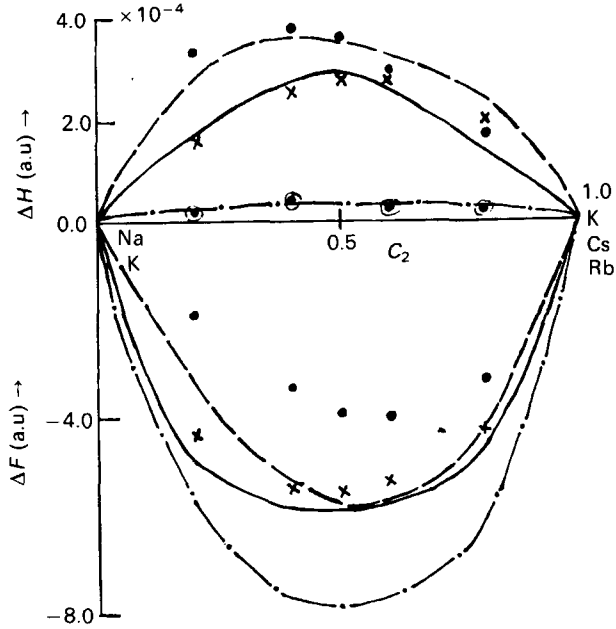


Figure 7 Heat of mixing ΔH [upper part] and free energy of mixing ΔF [lower part] versus concentration: theoretical value [—] Na-K, [---] Na-Cs, [-●-] K-Rb; $\times \times \times$, $\circ \circ \circ$, $\bullet \bullet \bullet$ refer to experimental points for Na-K²⁵, K-Rb²⁵ and Na-Cs²⁹ respectively.

of mixing [ΔH] and free energy of mixing [ΔF] have been shown in Figure 7 along with the experimental values Hultgren *et al.*²⁵ for Na-K and K-Rb and Ichikawa *et al.*²⁸ for Na-Cs. We observe that unlike entropy of mixing, the heat of mixing and free energy of mixing of Na-K, Na-Cs, K-Rb are asymmetrical at $C = \frac{1}{2}$. The deviation from the ideal behaviour is maximum in case of Na-Cs followed by Na-K and K-Rb. The asymmetry in the heat of mixing ΔH is mainly contributed from the asymmetries of ΔF_M , ΔF_2 and ΔF_1 [See Figure 5]. However, the asymmetry in ΔF is not that visible as for ΔH . This happens due to entropy terms of Eq. (27). The latter has a comparatively larger contribution and therefore the asymmetry of ΔH is overcome due to symmetrical nature of ΔS .

5 ELECTRICAL RESISTIVITY

The modified form of Faber-Ziman²⁹ formula for the electrical resistivity of binary alloy can be written as

$$R = \frac{3\pi}{\hbar e^2} \frac{\Omega}{k_F^2} \langle f(q) \rangle \quad (28)$$

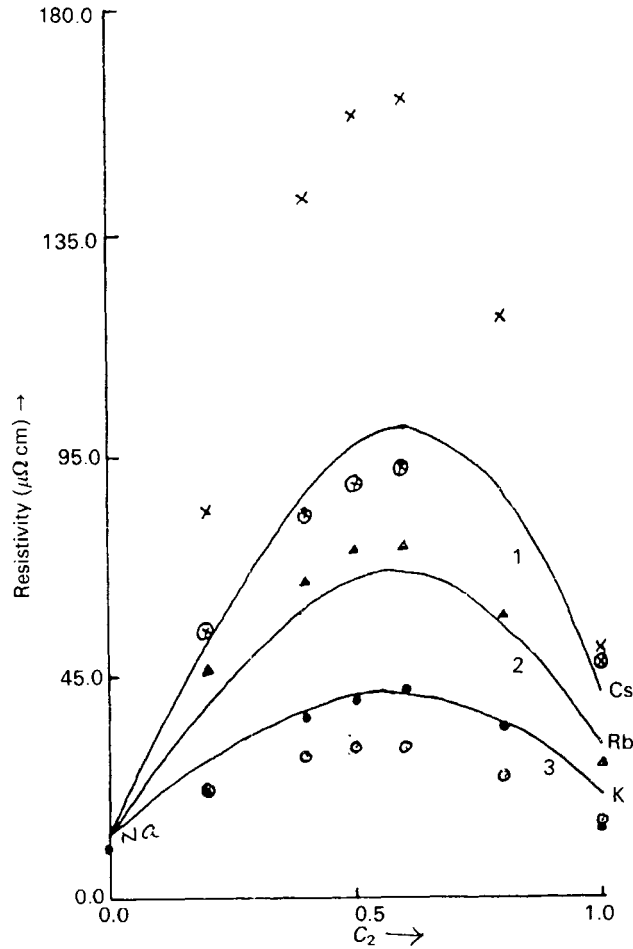


Figure 8 Electrical resistivity with composition: Curves 1, 2, 3 refer present values for Na-Cs, Na-Rb and Na-K alloys respectively; ○○○, ▲▲▲, ××× are experimental points respectively for Na-K³⁰, Na-Rb³² and Na-Cs³⁰; ○○○, ⊗⊗⊗ correspond to theoretical values³⁵ for Na-K, Na-Cs respectively.

Where

$$\langle f(q) \rangle = 4 \int_0^1 [C_1 V_1^2(q) S_{11}(q) + C_2 V_2^2(q) S_{22}(q) + 2(C_1 C_2)^{1/2} V_1(q) V_2(q) S_{12}(q)] (q/2k_F)^3 d(q/2k_F) \quad (29)$$

V_F is the Fermi velocity and $V_i(q) [= W_i(q)/\epsilon^*(q)]$ are the screened form factors.

The electrical resistivity has been calculated through Eq. (28). These have been plotted in Figure 8 and Figure 9 along with the experimental measurements Henephof *et al.*³⁰ for Na-K, Na-Cs; Henephof *et al.*³¹ for K-Rb; Vander Lugt *et al.*³² for Na-Rb and K-Cs. The electrical resistivity for Na-K, Na-Cs, K-Cs and Na-Rb is

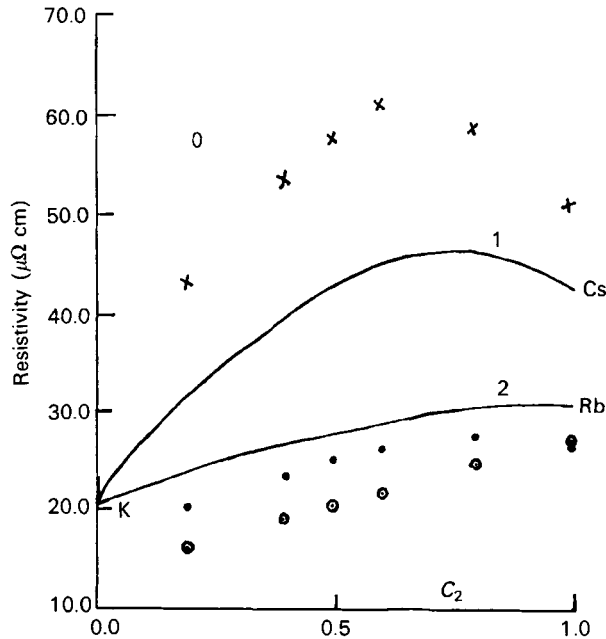


Figure 9 Electrical resistivity with composition: Curves 1, 2 refer present values for K-Cs and K-Rb respectively; $\circ\circ\circ$ correspond to theoretical values for K-Rb³⁵; $\bullet\bullet\bullet$, $\times\times\times$ are experimental points for K-Rb³¹ and K-Cs³² respectively.

asymmetrical about $C = \frac{1}{2}$. The nature of asymmetry from theory and experiments is alike. But unlike other systems the electrical resistivity of K-Rb varies linearly with composition and does not show any maximum around equatomic composition.

The numerical values of electrical resistivity for Na-Cs and K-Cs are in marked disagreement with the experimental observation but their variation with concentration exhibits the same pattern as that observed from the experiment. Among these, Na-Cs liquid alloys are well known^{33,34} for exhibiting anomalous behaviour. The concentration fluctuations differ appreciably from the values of an ideal solution and show a strong peak around $C_{cs} = 0.8$. The large size effect in Na-Cs seems to be responsible for exhibiting the anomalous effect.

The disagreement in case of Cs-alloys can possibly be linked to the presence of 5d band in Cs which lies just above the Fermi level. The presence of *d* electrons makes the system highly non-local. As soon as Cs is mixed with Na- or K, the Fermi level is supposed to approach the *d*-band which gives extra scattering of electrons. The presence of *d*-band also suggests that the pseudopotential should be strongly energy dependent. The inclusion of such effects in the present theory is likely to improve the numerical agreement. Wang *et al.*³⁵ have also calculated the electrical resistivity of Na-K, Na-Cs and K-Rb. Their values are also plotted in Figures 8 and 9 for sake of comparison. The two theoretical values are of similar nature. However, they have suggested that necessary correction for effective mass should be made to Faber-Ziman formula in order to obtain closer agreement with experiment.

6 CONCLUSION

The pseudopotential perturbation theory can successfully be used to provide a simultaneous interpretations of the thermodynamic and electrical properties of alkali-alkali liquid alloys subject to suitable choice for the diameters of the hard sphere reference system. The latter has been achieved here by minimizing the interatomic pairpotentials between the constituent species of the alloys. At one hand the theory explains the symmetry of the entropy of mixing while on the other a slight asymmetry in the heat of mixing and the electrical resistivity is correctly reproduced.

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