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A Generalized Technique on the Estimation of Entropy of Mixing of Liquid Cs-Pb Alloy

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Abstract

In this article the author proposes an alternative theory for computing the entropy of mixing for structurally inhomogeneous binary liquid alloys composed of alkali metals and group-IV elements, and successfully applies this theoretical model to liquid Cs–Pb alloy. These alloys in the liquid state exhibit Chemical Short-Range Ordering (CSRO) and a tendency to form compounds. Here the binary alloy has been supposed as a system consisting of charged hard spheres where partial charge transfer occurs depending upon the difference of electro-negativities between the two constituent atoms. The model is generalized, being formulated for hard spheres of arbitrary sizes and charges. It is applied here to calculate the entropy of mixing of liquid Cs–Pb alloy, and the theoretical results agree satisfactorily with experimental data.

Keywords: Chemical short range ordering; Partial charge transfer; Hard-sphere model; Stoichiometric composition; Zintl ions.

Introduction

In alloys and liquid metals there exists a universal short range ordering in atomic configuration which leads to structural homogeneity in them [1]. But in some specific liquid alloys there is certain deviance from completely random mixing behaviors. The distribution of constituent atoms around the atom of each component expectedly deviate from the average value. Structural homogeneity is manifested in these liquid alloys as a result of this deviation. When the liquids are made up of two or more atoms with different physio-chemical properties [1,2] then the structural, electric and thermodynamic properties differ significantly from the ideal mixing properties where no interaction among atoms is assumed

The liquid metal alloys those exhibit some unusual characteristics can be divided into two categories [3,4]. One category of atoms shows a tendency of isolation, viz, Al-In, Al-Sn, Na-Li, Cu-Bi [4] and the othe category shows some kind of chemical short-range ordering, viz, Li-Pb, Mg-Sn, Na-Pb, Na-Sn, K-Pb, K-Sn, Na-Sn Cs-Pb etc. [5–8]. For the past four decades, the second group has been in the focus of extensive structural, electrical, and thermodynamic studies worldwide [5-28]. On the thermodynamic, structural and electrical properties of these samples, a significant number of theoretical, simulation-based, and experimental studies have been published [6-21]. Among the reported works major portion are related with liquid alloys consisting of alkali group and group IV elements like liquid Cs-Pb, K-Pb, Li-Sn, Li-Pb, Na-Pb and Na-Sn etc. Though these alloys consist of two different metals but it has been observed that mixing of the constituent atoms in these systems is far different from ideal mixing i. e. mixing without any form of interaction. Measured quantities like resistivities [10,25], structure factor

[5,6,12,13,28], thermodynamic quantities [14–16,24,29,30] and knight shifts [26], all exhibit extreme values at concentrations near stoichiometric composition [18] and show a clear deviation from those of ideal mixing. These binary alloys exhibit properties which are also termed as partial salt like characteristics [18,25,26,31,32].

In recent works Khairulin et al. [24] measured the enthalpy of Cs–Pb system alloys containing 40, 50, 60, and 66.67 at.% Pb and heat capacity using high-temperature drop calorimetry method over a temperature range 430–1075 K covering solid and liquid phases. They have determined temperature dependences of the thermo-dynamical properties heat capacity and enthalpy and the enthalpy changes on phase transitions and the liquidus temperature. The concentration dependence of the heat capacity of Cs–Pb liquid alloys at different temperatures has been constructed, at which the pronounced maximum is observed at a content of 50 at.% Pb by Khairulin et al. H. T. Reijers et al. [8] carried out a molecular-dynamics study on equiatomic Cs-Pb liquid alloy. Among these binary alloys liquid Cs-Pb is an important as well as well studied fluid. Several articles have been published related to liquid Cs-Pb alloy for last few decades [24,]. In recent works Agazhanov et al. [24] measured the the increase of enthalpy of Cs–Pb alloys with the increase of Pb concentration (40.00, 50.00, 60.00 and 66.67 at. %) using laser flash technique. They found that transport and caloric properties of the Cs-Pb system depends on concentration of Pb and exhibits important deviations from computations according to simple additive rule. Density measurements are made on a series of caesium–lead liquid alloys containing 20 to 70 at.% Pb, in a temperature range from the liquidus line to ~1000 K by Khairulin et al. [42] and they carried out experiments using the gamma-ray attenuation technique. They described the concentration dependences of the molar volume, relative excess molar volume and volumetric coefficient of thermal expansion of the caesium–lead liquid system and shown that these dependences strongly deviate from the corresponding dependences for ideal solutions, which confirms a tendency for compound formation in Cs–Pb melts

J A Meijer *et al* [19] measured the resistivity of liquid Rb-Pb and Cs-Pb alloys as a function of composition and temperature and they found that around the equiatomic composition, the resistivity reaches non-metallic values in both systems; equiatomic Cs-Pb (rho =7000 mu Omega cm at T=620 degrees C). They also found that the resistivity of these systems decreases rapidly with rising temperatures since Pb ions presumably join in covalently bound clusters and disintegrate with rising temperatures.

Lugt et al. examined the presence of polyanions [18] in a specific category of liquid ionic alloys. These alloys consist of alkali metals combined with elements from groups 13, 14, 15, and 16 of the periodic table (post-transition-metal groups 3, 4, 5 and 6). Their research revealed significant similarities between these liquid alloys and their corresponding crystalline phases. The crystalline phases have long been known to contain polyanions, often referred to as 'Zintl ions', such as (Pb4)4−, (Sb−)∞, and (Te2)2−. In their study of alloys combining Tl with K, Rb, and Cs, they discovered very long-range superstructures. These structures are analogous to the large, compact, polyhedral clusters frequently observed in many crystalline phases of these materials. D.L. Price et al. performed neutron diffraction measurements [28] on liquid Cs-Pb alloy at the Intense Pulsed Neutron Source with equal atomic proportions. They have studied equiatomic CsPb alloy and found it to be a Zintl alloy with well-defined Cs_4Pb_4 structural units and explained the anomalously high electrical resistivity and specific heat observed in the molten state. They also studied $Cs_{80}Pb_{20}$ and $Cs_{25}Pb_{75}$ alloy systems. They show that structure of liquid $Cs_{25}Pb_{75}$ resembles that of solid KPb_2.

One line of approach for theoretical formalism is assuming the existence of chemical compound called polyions. By assuming the existence of polyanions, it has been attempted to present theoretical model or simulate in various ways to match the experimentally observed properties in these systems [8,12,19,22,23,27]. The hypothesis of chemical compounds with tetrahedral structural units termed as Zintl ions have been developed [8,12,15,16,18,19,22,23,27,28,32]. In systems like liquid Cs-Pb, researchers have proposed the presence of Zintl structural units [B] in the crystalline phase. However, the interpretation of certain features observed in the high-temperature liquid phase remains contentious. Specifically, the explanation for the prepeak, also known as the first sharp diffraction peak (FSDP), in structural data, as well as other observed properties, is still up for debated. The controversy centers around whether these features can be attributed to the persistence of rigid tetrahedral structural [11,18,19,20–23,29,30,33]. units in the liquid state. The Zintl principle fundamentally relies on the complete transfer of valence electrons to more electronegative atoms. However, early electronic structure calculations have challenged this concept. These calculations, which determine the actual charge transfer by spatially integrating charge density over atomic spheres, suggest that the real transfer is minimal. This discrepancy between the principle's assumption and computational findings has led to frequent criticism of the Zintl principle [34-36] .

Given the absence of direct experimental evidence [20-22,11,29,30] and the fact that many authors [18, 19] have described it as a paradox, it can be said that the presence of rigid Zintl chemical complexes as structural units in the liquid state remains unconfirmed in these samples. Conclusive evidence for their presence is still lacking. On the other hand, a number of experiments [5 -7, 10,12] and simulation studies [18,20-23] reveals that there is transfer of significant amount of charge from potassium atoms to lead atoms near the stoichiometric compositions of the alloys. Therefore, it follows that a realistic statistical mechanical model is required to explain these anomalous behaviors. In this regard, Pauling [37] has provided a thorough discussion of partial ionicity caused by effective charge transfer between atoms with substantial differences in electronegativities.

Therefore, taking into account the aforementioned experimental observations as well as the idea of partial ionicity, we have applied the alternative theoretical model to liquid Cs-Pb sample. This study proposes an alternative approach, departing from previous models. It introduces a generalized model of charged hard spheres with variable shape, size and charge. The model incorporates a realistic representation of Coulombic interactions, accounting for effective partial charge transfer between atoms. This framework has already been applied in thermodynamic calculations and structural analyses[11,29,02,38].

Other researchers have also applied the hard sphere mixture concept for calculation of thermodynamic quantities. Meroni et al. [39] calculated the entropy of mixing for a binary hard sphere mixture under constant pressure conditions. They used the Mansoori-Carnahan-Starling equation of state to determine how this entropy varies with the ratio of sphere diameters. Their research demonstrated that the Flory-Huggins formulation for the entropy of mixing provides an inadequate approximation. Furthermore, they found that this approximation becomes increasingly inaccurate as the diameter ratio between the spheres increases. Mansoori et al. [40] developed an equation of state for hard sphere mixtures. Their approach was based on averaging two distinct solutions derived from the Percus-Yevick integral equation, specifically applied to hard sphere mixtures. Mansoori et al. calculated various equilibrium properties of binary hard sphere mixtures, including compressibility. They then compared their results with data obtained from computational methods, specifically Monte Carlo simulations and molecular dynamics.

Their analysis revealed a strong correlation between the predictions of their proposed equation of state and the computationally generated data.

Some practical applications of Cs-Pb alloys in the industry which are i) Optoelectronic Devices (Perovskite Precursors). ii) Used to construct stable, high-efficiency Perovskite Solar Cells (PSCs) with power conversion efficiencies above 20%. iii) Cs-Pb based nanocrystals are used for next-generation displays and lighting. iii)Used in high-sensitivity photodetectors and ultra-stable lasers. iv) Liquid Cs-Pb alloys are primary subjects in the study of Zintl phases and chemical short-range ordering. v) Used in Nuclear and Energy Research vi) Used in Plastic Crystals and Phase Engineering.

2. Formalism

In our current approach, we present a theoretical framework for calculating the entropy of mixing of liquid alloys that exhibit chemical short-range ordering (CSRO). These alloys show partially salt like propertics [18,26] with dominance near the stoichiometric composition. This characteristics is exhibited due to transfer of charge from alkali metal elements to group IV metal elements [15, 17, 18, 20-22]. In this work, it is shown with the help of Cs–Pb system, where transfer of charge takes place from potassium atoms to lead atoms. Here, in conformism of the previous method [11,36], we can assume that the thermodynamic properties and structural properties of a mixture of charged hard sphere is due to two independent components. The first part is the contribution of neutral hard sphere mixtures and the second one is the contribution of Coulombic interaction between different atoms of the mixture due to their effective charges (ΔZi). Satpathy et al. [29, 30] has shown that the additional thermodynamic quantities of the liquid metal alloys can be confined to the size and charge of hard spheres using an expression for generalized Debye inverse screening length parameter 'Γ' [38,41].

2.1. Mathematical formalism

The thermodynamic properties of liquid metal alloys are the contributions of neutral hard sphere mixtures and coulomb interaction. Thus, we can express the total entropy of an ionic liquid alloy as [29,30,38] :

$$S_{total} = S_{hs} + S_{ch} \quad (1)$$

Here S_{hs} is the contribution to entropy from neutral hard spheres and S_{ch} is the entropy due to Coulomb interactions between the different kinds of atoms due to their collected effective charges (ΔZi s). Under Percus–Yevic (PY) compressibility approximations S_{hs} can be written as

$$S_{hs} = S_{id} + S_{mix} + S_{\eta} + S_{mismatch} \quad (2)$$

Here S_{id} is the entropy of the perfect gas term and this quantity S_{id} may be written as

$$S_{id} = S_{id}^{A} + S_{id}^{B} \quad (3)$$

First term :

Here S_{id}^{A} is the entropy of the perfect gas term when A is alone in the volume V_1 and S_{id}^{B} is the entropy of the perfect gas term when B is alone in the volume V_2.

Now S_{id}^{A} and S_{id}^{B} can be calculated [22] from well known Sakur-Tetrode relation:

$$\frac{S_{id}^{j}}{Nk_B} = \frac{5}{2} + ln\left[\Omega_j \left(\frac{m_j k_B T}{2\pi\hbar^2}\right)^{3/2}\right] \quad (4)$$

Here m_j is the mass of one atom of the j-th type and Ω_j is the volume per atom of the j-th type.

Obviously from Eqn. (4) we can write

$$\frac{S_{id}^{A}}{Nk_B} = \frac{5}{2} + ln\left[\Omega_A \left(\frac{m_A k_B T}{2\pi\hbar^2}\right)^{3/2}\right] \quad (5)$$

$$\frac{S_{id}^{B}}{Nk_B} = \frac{5}{2} + ln\left[\Omega_B \left(\frac{m_B k_B T}{2\pi\hbar^2}\right)^{3/2}\right] \quad (6)$$

Ω_A is the volume per atom of A and Ω_B is that corresponding to B.

Here we are considering a binary solution where n(1−c) atoms of A and nc atoms of B are present, n represents the total number of atoms. Here we write

$n_1 = (1-c)n$ (7)

and $n_2 = cn$ (8)

Now we assume mole fraction or the fractional concentration of particles in the binary mixture as follows :

$x_1 = \frac{n_1}{n}$ (9)

and $x_2 = \frac{n_2}{n}$ (10)

Where $x_1 + x_2 = 1$ (11)

From Eqns. (7) and (9) we obtain,

$x_1 = 1 - c$ (12)

and from Eqns. (8) and (10) we obtain,

$x_2 = c$ (13)

So entropy of the ideal gas term may be written as

$$\frac{S_{id}}{Nk_B} = (1-c)\frac{S_{id}^{A}}{Nk_B} + c\frac{S_{id}^{B}}{Nk_B} \quad (14)$$

Second term :

Now we assume the virtual partition between A and B is removed. So the contribution from ideal mixture of entropy arises which is given by

$$\frac{S_{mix}}{Nk_B} = -n \sum_{j=1}^{2} x_j \, ln\, x_j$$

or $\frac{S_{mix}}{Nk_B} = -(x_1 \, ln\, x_1 + x_2 \, ln\, x_2)n$ (15)

Now if we denote '1' by A and '2' by B,

Then Eqn. (15) can be written as

$\frac{S_{mix}}{Nk_B} = -n(x_A \, ln\, x_A + x_B \, ln\, x_B)$ (16)

Here from Eqn. (9) we can write, $x_A = \frac{n_A}{n} = \frac{n_A}{n_A + n_B}$ (17)

and from Eqn. (10) we can write,

$x_B = \frac{n_B}{n} = \frac{n_B}{n_A + n_B}$ (18)

Third term : Here the third term i.e., S_η is called the total packing term (i.e., entropy contribution from the packing density) and this is given by

$$\frac{S_\eta}{Nk_B} = ln(1-\eta) + \frac{3}{2}\left[1 - \frac{1}{(1-\eta)^2}\right] \quad (19)$$

Here η is called the total packing fraction and is expressed as

$$\eta = \sum_{j=1}^{2} \eta_j \quad (20)$$

η_j is the packing fraction from the j-th kind and is expressed as

$$\eta_j = \frac{\pi}{6}\,\rho_j\,\sigma_j^3 \tag{21}$$

ρ_j is called the number density of the j-th kind and this is given by

$$\rho_j = \frac{\eta_j}{V}$$

$$\Rightarrow \rho_j = \frac{\eta_j}{n}\frac{n}{V}$$

$$\Rightarrow\ \rho_j = \frac{x_j}{V/n} \tag{22}$$

Let Ω denotes the volume associated per particle (i.e., per atom) then,

$$\Omega = \frac{V}{n} \tag{23}$$

So from Eqns. (22) and (23) we can write

$$\rho_j = \frac{x_j}{\Omega} \tag{24}$$

So from Eqns. (21) and (24) we can write

$$\eta_j = \frac{\pi}{6}\left(\frac{x_j}{\Omega}\right)\sigma_j^3$$

$$\Rightarrow\quad \eta_j = \frac{\pi}{6\Omega}\ \ x_j\ \ \sigma_j^3 \tag{25}$$

So from Eqn. (20) and (25) we can write the total packing fraction as follows :

$$\eta = \frac{\pi}{6\Omega}\ \ (x_1\ \ \sigma_1^3 + \ x_2\ \ \sigma_2^3) \tag{26}$$

As before replacing '1' by A and replacing '2' by B

Eqn. (26) can be written as

$$\eta = \frac{\pi}{6\Omega}\ \ (x_A\ \ \sigma_A^3 + \ x_B\ \ \sigma_B^3) \tag{27}$$

Fourth term : Here $S_{mismatch}$ represents the entropy due to mismatch of the diameters σ_1 (= σ_A) and σ_2 (= σ_B) of the hard spheres and this is written as

$$\frac{S_{mismatch}}{Nk_B} = \left(\pi x_i x_j \rho_T\right)\left(\left|\sigma_i - \sigma_j\right|\right)^2[24(1-\eta)^2]^{-1}\left[12\left(\sigma_i + \sigma_j\right) - \pi\rho_T\left(x_i\ \ \sigma_i^4 + \ x_j\ \ \sigma_j^4\right)\right] \tag{28}$$

Obviously as before we can write the above Eqn. as

$$\frac{S_{mismatch}}{Nk_B} = (\pi x_A x_B \rho_T)(|\sigma_A - \sigma_B|)^2[24(1-\eta)^2]^{-1}[12(\sigma_A + \sigma_B) - \pi\rho_T(x_A\ \ \sigma_A^4 + \ x_B\ \ \sigma_B^4)] \tag{29}$$

Here ρ_T represents total number density and this is given by

$$\rho_T = \frac{n}{V}$$

$$\Rightarrow\ \rho_T = \frac{n_1+n_2}{V}$$

$$\Rightarrow\ \ \rho_T = \frac{n_1}{V} + \frac{n_2}{V}$$

$$\Rightarrow \quad \rho_T = \rho_1 + \rho_2$$

$$\Rightarrow \quad \rho_T = \rho_A + \rho_B \tag{30}$$

Here $\rho_A = \frac{n_A}{V}$

$$\Rightarrow \quad \rho_A = \frac{n_A}{n}\frac{n}{V}$$

$$\Rightarrow \quad \rho_A = x_A \rho_T \tag{31}$$

Similarly, we can prove,

$$\rho_B = x_B\, \rho_T \tag{32}$$

For a uni-univalent salt we have, $\rho_A = \rho_B = \frac{\rho_T}{2}$ (33)

$$\because \quad x_A = \frac{1}{2} = x_B$$

So we obtain S_{hs} from Eqns. (14), (16), (19), (20) and (29).

2.2 Charge sharing entropy changes

Blum solved the Mean Spherical Model Approximation (MSMA) for the primitive model of electrolytic solutions of arbitrary size and charge. The excess thermodynamic properties, influenced by charge and size effects, can be represented using a rational expression with the generalized inverse Debye screening length parameter Γ, as demonstrated by Blum. Blum's approach builds upon the method developed by Baxter. Blum derived an expression for (Γ) by solving an algebraic equation, which can be represented as follows:

$$4\Gamma^2 = \mathrm{k}^2 \sum_i \rho_i \left(\frac{1}{1+\Gamma\sigma_i}\right)\left(\mathrm{Z_i} - \frac{\pi\sigma_i \mathrm{P_n}}{2\Delta}\right)^2 \;/\; \sum_i \rho_i \mathrm{Z_i^2} \tag{34}$$

$$\text{Where} \quad \mathrm{P_n} = \frac{1}{\Omega}\left(\sum_k \frac{\sigma_k \rho_k Z_k}{1+\sigma_k \Gamma}\right) \tag{35}$$

$$\Omega = 1 + \frac{\pi}{2\Delta}\left(\sum_k \frac{\rho_k \sigma_k^3}{1+\sigma_k \Gamma}\right) \tag{36}$$

$$\text{and } \Delta = \quad 1 - \frac{\pi}{6}\sum_k \rho_k \sigma_k^2 \tag{37}$$

Here obviously l = 1, 2 also k = 1, 2.

From Eqn. (35) it is clear that $\mathrm{P_n}$ is of the order

$$\sum_k \sigma_k\, \rho_k\, Z_k\,.$$

(Here ρ_k represents number density of the charged hard spheres of the kth type of ions and Z_k is the valency of the kth species). Eqn. (34) vanishes for equal size of cations and anions and is small even for appreciable concentrations of different sizes of ionic mixtures.

It can be shown that

$$2\Gamma = k\left[\left(\sum_i \rho_i Z_i^2\right) / \left\{(1+\sigma_i\Gamma)^2 \left(\sum_j \rho_j Z_j^2\right)^2\right\}\right]^{1/2} \tag{38}$$

The rational expression involving the parameter Γ can be written in a convenient form :

$$\Gamma^2 = \frac{\pi c^2}{\epsilon_0 k_B T} \sum_{i=1}^{n} \rho_i \chi_i^2 \tag{39}$$

Obviously in this case n=2.

Above equation may be expressed as,

$\Gamma^2 = C\,D(\Gamma)$ (40)

Where $C = \frac{\pi e^2}{\epsilon_0 k_B T}$ (41)

$$D(\Gamma) = \sum_{i=1}^{n} \rho_i \chi_i^2 \quad (42)$$

Here e represents the charge of electron, ρ_i is the number density of the charged hard sphere of the ith type of ions, ϵ_0 is the dielectric constant of the medium where the ions are placed. χ_i is presented as:

$$\chi_i = \frac{Z_i}{1+\Gamma\sigma_i} - \left(\frac{\nu\sigma_i^2}{1+\Gamma\sigma_i}\right) \sum_{j=1}^{n} \rho_j \sigma_j Z_j (1+\sigma_j)^{-1} \Big/ \left[1 + \nu \sum_{j=1}^{n} \rho_j \sigma_j^3 Z_j (1+\sigma_j)^{-1}\right] \quad (43)$$

Here for binary mixture n=2.

σ_i is the diameter of the ith species and Z_i is its valancy.

The entropy due to Coulomb interaction by MSMA can be obtained as follows :

$$\frac{S_{ch}}{Nk_B} = \frac{\Gamma^3}{3\pi\rho_T} \quad (44)$$

Now we consider the binary liquid. The general procedure to find generalised Debye inverse screening parameter (Γ) is as follows :

We know from previous discussion that the rational expression involving the parameter Γ may be written as,

$\Gamma^2 = CD(\Gamma)$ (45)

Here $C = \frac{\pi e^2}{\epsilon_0 k_B T}$ (46)

$$\text{Where} \quad D(\Gamma) = \sum_{i=1}^{2} \rho_i \chi_i^2 \quad (47)$$

$$D(\Gamma) = \rho_1 \chi_1^2 + \rho_2 \chi_2^2$$

Here $\rho_1 = \rho_T x_1$ (48)

and $\rho_2 = \rho_T x_2$ (49)

Now χ_i is given by the following formula :

$$\chi_i = \frac{Z_i}{1+\Gamma\sigma_i} - \frac{\nu\sigma_i^2 \sum_{j=1}^{n} \rho_j \sigma_j Z_j (1+\Gamma\sigma_j)^{-1}}{(1+\Gamma\sigma_i)\left[1+\nu\sum_{j=1}^{n} \rho_j \sigma_j^3 (1+\Gamma\sigma_j)^{-1}\right]} \quad (50)$$

Now for a binary mixture n = 2.

Here ν is given by $\nu = \frac{\pi}{2}\left[1 - \frac{\pi}{6}\sum_{i=1}^{n} \rho_i \sigma_i^3\right]^{-1}$ (51)

Here Z_i represents the valency of the ith species and σ_i is the diameter of the ith species. It is important to note that in this formalism we assume that partial charge transfer of electrons is possible. So Z_1 and Z_2 can take fractional values. But macroscopically liquid is neutral.

So $\rho_1 Z_1 + \rho_2 Z_2 = 0$

or $x_1 Z_1 + x_2 Z_2 = 0$ (52)

From Eqs. (45) – (48), (51) and (52) it becomes clear that algebraically it is extremely difficult to find a solution of Γ. We have solved the equations numerically to find value of Γ as well as S_{ch} [29,30,38].

2.3 Entropy of mixing

The expression for theoretical entropy of mixing is as follows,

$S_{mix}^{th} = S_{total}^{th} - (C_1 S_1^{th} + C_2 S_2^{th})$. (53)

The total entropy S_{tot}^{th} is theoretically calculatedg Eqs. (1)–(51). Here S_1^{th} and S_2^{th} represent the entropies for pure metals '1' and '2' respectively and S_1^{th} , S_2^{th} can be computed using above relations by setting either $C_1 = 0$ or $C_2 = 0$ and $Z_1 = Z_2 = 0$.

Hence expression for entropy for pure metals can be expressed as:

$$S_j^{th} = S_{id}^j + S_\eta^j \quad \text{(where j = 1, 2)} \qquad (54)$$

Here, S_η^1 and S_η^2 are the entropies due to packing of hard sphere diameters in pure liquid metals '1' and '2'.

3. Results and discussion

There is no investigational instance confirming the presence of zintl ions/ polyanions, i.e. or chemical complexes formed in the liquid Caesium-lead alloy [11,20-23], although there is a strong tendency towards ionicity at concentrations adjacent to the stoichiometric composition. A net amount of charge is transferred even if the valence electronic charge distribution around the component atoms is not uniform [20, 21]. Therefore, we are proposing an alternative method of evaluating the entropy of mixing which is different from the others [14-16]. This article deals with a liquid alloy of alkali - group IV system, specifically the liquid Cs-Pb alloy. Here we have realistically assumed that there is some effective transfer of charge from the caesium atom to the lead atom, resulting in a change in the environment of the atom's nearest neighbour due to some type of overlying of the atomic orbitals but without the formation of stable compounds or complexes of ions in the atom unlike others [8,9,13,19]. Hence, we propose that due to the electronegativity difference, there is a partial transfer of charge from the caesium atom to the lead atom, resulting in a unique local charge structure dissimilar from that of a completely molten ionic salt. Here number densities of both atoms and the partial charges present simultaneously satisfy the condition of electro-neutrality given by Eq. (52). The results for Cs-Pb are presented below.

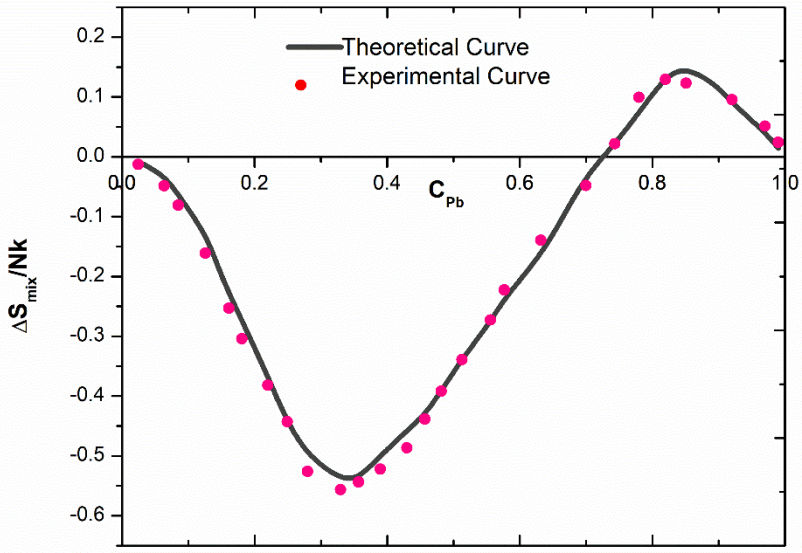

Fig.-1. Entropy of mixing of molten Cs-Pb alloy at 950 K. Continuous line — is the Theoretical Curve and dot points ● are the Experimental results.

The Eqs. (1)–(51) are used to calculate theoretical entropies of Cs-Pb alloys for various Pb concentrations, while the entropies of the pure metals Pb and Cs are calculated from Eq. (54). The alloy atomic volumes for various Cs concentrations in the Cs-Pb system are derived from experimental density data [42] reported in previous studies. Experimental pure atomic volumes $\Omega_{Cs} = 15.026 \times 10^{-23}$ cm^3 for Cs and $\Omega_{Pb} = 3.268 \times 10^{-23}$ cm^3 for Pb at 950 K are obtained from the literature [42]. The entropies of mixing for the Cs-Pb alloy system are calculated theoretically across various Cs concentrations using the Eqs. (1)–(54) and these calculated values are illustrated in Figure 1.

Liquid binary alloys Cs-Pb have been extensively studied by Khairulin et al. [24]. Figure 1 demonstrates that the theoretically calculated entropy of mixing ΔS_{mix}^{th} shows good overall agreement with the experimental results. The theoretical values align well with the experimental data across the entire range of Pb concentrations in the Cs-Pb alloy system. This close correspondence between theory and experiment validates the accuracy of the theoretical model used to predict the thermodynamic properties of the Cs-Pb liquid alloy. We calculated ΔS_{mix}^{th} for the whole range of concentration and this theoretical values are compared with the experimental values [24]. Figure 1 shows that the theoretical entropy of mixing ΔS_{mix}^{th} is a very reliable result showing a minimum at $C_{Pb} = 0.33$. , and this result is also found by another author [45]. Therefore, a strong partial salt like characteristics also occurs near the stoichiometric composition ($C_{Pb} = 0.51$). Our calculations also indicates that the maximum effective charge transfer from the Cs atom to the Pb atom is at the Cs_2Pb composition. The most suitable data is determined as follows:

$\sigma_{Cs} = 4.62$Å, $\sigma_{Pb} = 2.92$Å while $\Delta Z_{Cs} = +0.251e$;

and $\Delta Z_{Pb} = -2\ \Delta Z_{Cs} = -0.502e$ near the stoichiometric composition (Cs_2Pb). For other concentrations of lead, the numerical values of ΔZ_i are calculated by satisfying eletroneutrality condition, $C_{CS}\Delta Z_{Cs} + C_{Pb}\Delta Z_{Pb} = 0$.

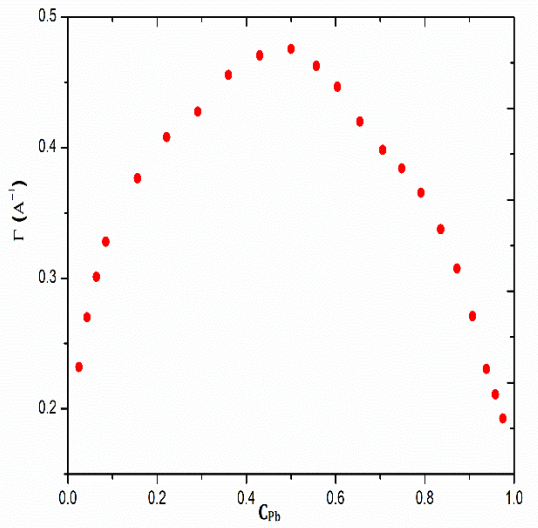

Fig. 2: Variation of Γ with concentration of Pb for molten Cs-Pb alloy at 950 K.

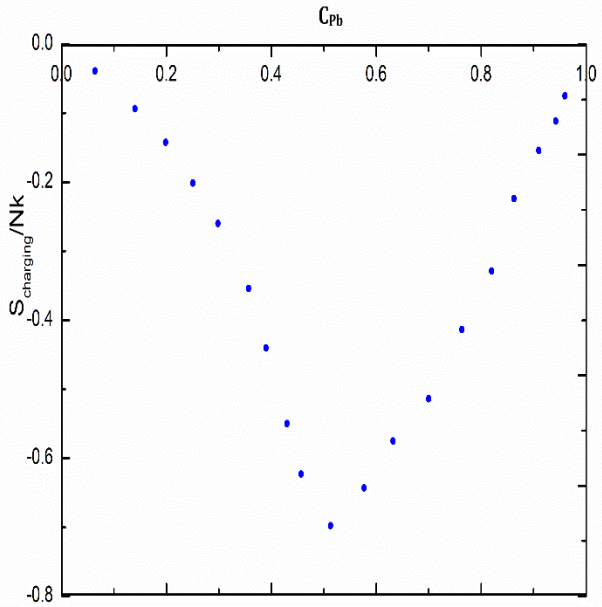

Fig. 3: Variation of entropy due to charging ($S_{charging}$ / Nk) with concentration. of Pb for molten Cs-Pb binary alloy at 950 K.

At this juncture, it is noteworthy that the effective transfer of charge at very low and very high concentrations of Pb atom and Cs atom is insignificant. The generalized screening length parameter Γ is calculated for various concentrations using a previously described method [11,29,30]. We determine Γ values for different lead (Pb) concentrations in the Cs-Pb system. Fig. 2 illustrates how Γ varies with Pb concentration (C_{Pb}). Additionally, Fig. 3 shows the relationship between the entropy per particle due to charging (Sch/NkB) and Pb concentration (C_{Pb}). Fig. 4 illustrates the distortion of the valence electron cloud surrounding caesium (Cs) atoms.

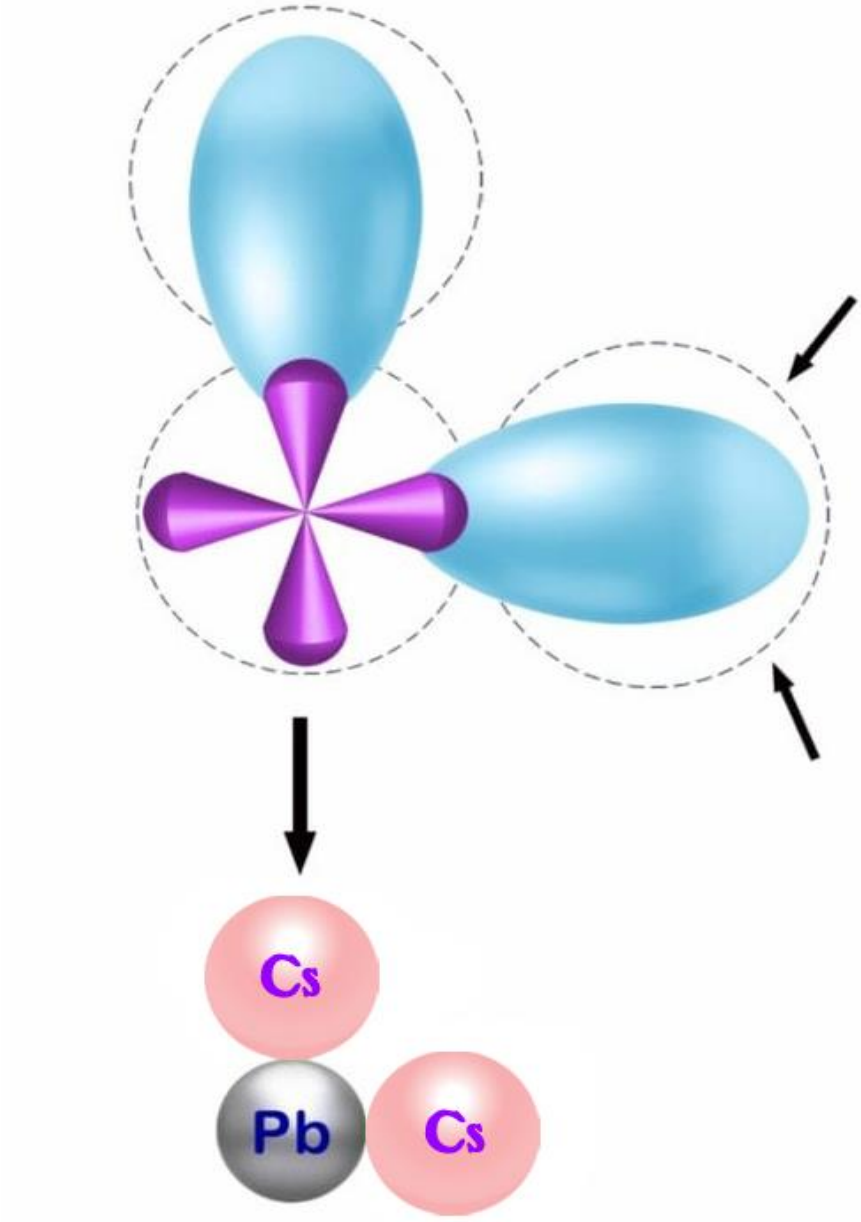

Fig. 4a Distortion of valance electron cloud of Cs atom in contact with Pb atom (electron affinity; $E_a^{Pb} > E_a^{Cs}$) and showing loose s-p overlapping at Cs_2Pb composition.

Fig. 4b partially charged hard spheres of Pb and Cs species are sticked together. Here, ΔZ^{Pb} = -0.51e and ΔZ^{K} = +0.255e.

This distortion occurs in the direction of lead (Pb) atoms due to the electronegativity difference between Cs and Pb. Fig. 5 shows how the total entropy per particle in the binary mixture changes as a function of lead concentration (C_{Pb}). Fig. 2 clearly shows that Γ reaches its peak value of 0.4812 $Å^{-1}$ near the stoichiometric composition where C_{Pb} = 0.50. In contrast, Fig. 3 demonstrates that S_{ch}/NkB exhibits a sharp minimum of (-0.7054) at approximately the same stoichiometric composition (C_{Pb} = 0.50). The analysis reveals that the physical quantity 'Γ' serves as a scaling parameter and functions as an indicator of the charge ordering process.

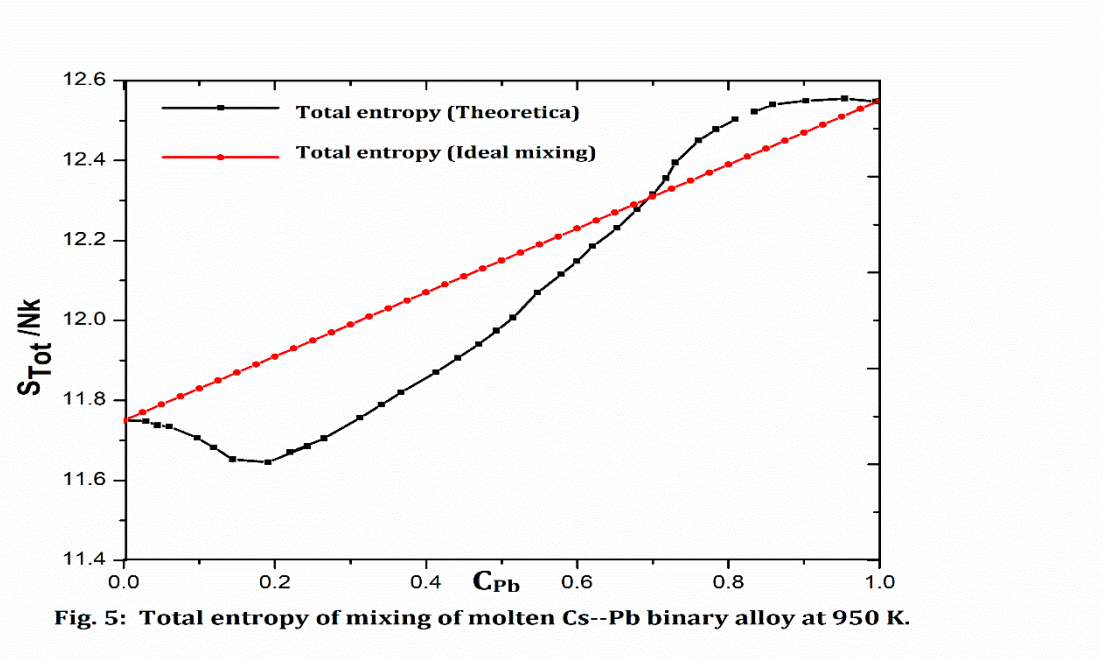

Fig. 5: Total entropy of mixing of molten Cs--Pb binary alloy at 950 K.

Eq. (1) is used to theoretically calculate the total entropy. Fig. 5 illustrates how the calculated total entropy per particle S_{tot}/Nk_B changes with the lead concentration (C_{Pb}) The graph reveals that the total entropy reaches its lowest point at C_{Pb} = 0.249, where it has a value of 11.65. It is noteworthy that the theoretically calculated entropies for pure liquid potassium and lead show excellent agreement with available experimental data. For Cs, the calculated value is $\frac{S_{Cs}^{Th}}{Nk_B}$ = 24.005, closely matching the experimental value $\frac{S_{Cs}^{Ex}}{Nk_B}$ = 24.3 [24] . Similarly, for Pb, the calculated value is $\frac{S_{Pb}^{Th}}{Nk_B}$ = 11.75, which aligns well with the experimental measurement $\frac{S_{Pb}^{Ex}}{Nk_B}$ = 11.77 [14]. Using the atomic volume graph of Cs-Pb alloys provided by Khairulin et al. [42], we have calculated the molar volumes of Cs-Pb liquid alloys at various lead concentrations. From these molar volumes, we have also derived the corresponding number densities of the liquid alloys. Figure 1 displays the theoretically computed entropy of mixing. The graph also includes a comparison between these theoretical calculations and the experimentally determined values [24]. The theoretical entropy of mixing ΔS_{mix}^{th} closely aligns with the experimental results [24] shown in Figure 1. The maximum average charge transfer per bond from potassium to lead atoms occurs at the Cs_2Pb composition (C_{Pb} = 0.50). The Cs–Pb melt achieves maximum stability and order at the stoichiometric (Cs_2Pb) composition, likely due to charge ordering. This is evidenced by a sharp decrease in entropy, resulting from efficient charge transfer between the different atomic species.

A significant excess of the heat capacity of the studied melts over additive values is revealed. It is shown that the results obtained are consistent with the assumptions in the literature about the formation of structural units with a partially ionic character of interatomic interaction in melts of the Cs–Pb system.
Note that the graphs display entropies per particle as dimensionless quantities. Similarly, lead concentrations (C_{Pb}) are expressed as dimensionless mole fractions.

4. Conclusion

This presented model is capable of generate the entropies of mixing and entropies for the liquid Cs-Pb alloy for complete range of concentrations of Pb from $C_{Pb} = 0$ to 1, which is significantly different from the perfect mixing character. This model accurately captures the sharp peaks observed near the stoichiometric composition ($C_{Pb} \approx 0.50$) in the sample. However, it can be concluded that this liquid sample reach a relatively more stable state than perfectly mixed mixtures due to the transfer of the effective partial charge from the potassium atom to the lead atom. The computed charge transfer data for actual calculations show 25.1% ionicity for the Cs- Pb bond at approximately its stoichiometric composition. These calculated data are also apparently supported by the opinion of Pauling [37] that about 15–20% of the ionic nature is due to a single bond around two atoms with an electronegativity difference of 0.8–1.00, as in the current sample. The generalized inverse Debye screening length "Γ" proves to be a crucial physical quantity in this system. It acts as a scaling parameter, providing quantitative insights into both the charge ordering process and the entropic contributions from charging. This model is considered generalized because it can be applied to ionic mixtures with the hard spheres of unequal diameters and species with arbitrary charges. It allows for the calculation of both overall entropy and entropy of mixing in such systems.

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