

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

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Abstract:

Here the authors have proposed an alternative mechanical theory for the computation of entropy of mixing for structurally inhomogeneous binary liquid alloys consisting of alkali metals and group-IV elements and this theoretical model is successfully applied to liquid K-Pb alloy. This type of alloys demonstrates chemical short range ordering (CSRO) and also a compound forming tendency is also displayed by the alloys in liquid state. Here the binary alloy has been presumed as a system consisting of charged hard spheres where partial charge transfer occurs depending upon the difference of electronegativities between the two constituent atoms. The model is generalized as it has been framed on the basis of existence of hard spheres with arbitrary size and charges. Here this model is applied for the calculation of entropy of mixing of liquid K-Pb alloy. The theoretical results match satisfactorily with the experimental results.

Keywords: Partial charge transfer; Hard-sphere model; stoichiometric composition; Zintl ions.

Introduction

In liquid metals and alloys there exists a universal short range ordering in atomic configuration which lead to structural homogeneity in them [1]. But in some specific liquid alloys there are certain deviance from completely random mixing behaviours. Distribution of constituent atoms around the atom of each component expectedly deviate from the average value. Structural inhomogeneity 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 are 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 other category shows some kind of chemical short-range ordering, viz, Li-Pb, Mg-Sn, Na-Pb, Na-Sn, K-Pb, K-Sn, Na-Sn etc. [5–8]. For the past four decades, the second group has been in the focus of extensive structural, electrical, and thermodynamic studies worldwide [5–30]. 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 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 [14–16,24,31,32] 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 [18,25,26,33,34].

Among these binary alloys liquid K-Pb is an important as well as well studied fluid. Several articles have been published related to liquid K-Pb alloy for last few decades [6,14,19,28,30]. In recent works Agazhanov et al. [24] measured the increase of enthalpy of K–Pb alloys with the increase of Pb concentration (50.00 and 66.67 at. %) using laser flash technique. They found that transport and caloric properties of the K-Pb system depends on concentration of Pb and exhibits important deviations from computations according to simple additive rule. Nath et al. studied the irregular structure of liquid K-Pb alloy and related characteristics are presented via an *ab initio* Ljmt method and determined variation of ordering potential with concentration [9]. They shown that ordering occurs and it becomes maximum at the stoichiometric composition ($c_K \sim 0.5$). Arai et al. developed new models [19] of the structure of liquid K-Pb alloy at 873 K, 1473 K and 1873 K.

Hafner et al. demonstrated that in K-Pb alloys [30], alloying effects within the effective interatomic potentials result in a strong preferential interaction among Pb ions. This interaction leads to the formation of polyanionic clusters, which occur not only in the crystalline state but also in the liquid alloy. Ljmt 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 $(Pb_4)^{4-}$, $(Sb)_\infty$, and $(Te_2)^{2-}$. 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. Saboungi et al. performed neutron diffraction measurements [28] on liquid K-Pb alloy with equal atomic proportions at temperatures of 870, 900, and 930 K to explore temperature-dependent structural changes. Their analysis of the total structure factors $S(Q)$ revealed a prominent first sharp diffraction peak (FSDP) at $Q = 0.96 \text{ \AA}^{-1}$ across all three temperatures, reminiscent of patterns observed in glassy substances. Based on these findings, they suggested a structural model involving the random arrangement of K_4Pb_4 units.

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 [8,12,19,22,23,27,30]. The hypothesis of chemical compounds with tetrahedral structural units termed as Zintl ions have been developed [8,12,15,16,18,19,22,23,27,28,30,34]. In systems like liquid K-Pb, researchers have proposed the presence of Zintl structural units 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 [11,18,19,20–23,31,32,35]. 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 [36-38].

Given the absence of direct experimental evidence [20-22,11,31,32] 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 [39] 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 K-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[11,31,32,40].

Other researchers have also applied the hard sphere mixture concept for calculation of thermodynamic quantities. Meroni et al. [41] 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. [42] 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.

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 properties [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 K-Pb system, where transfer of charge takes place from potassium atoms to lead atoms. Here, in conformism of the previous method [11,31,32,40], 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 (ΔZ_i). Satpathy et al. [31, 32] 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 'T' [40,43].

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 [31,32,40] :

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

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 (ΔZ_i 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 cn atoms of B are present, n represents the total number of atoms. Here we write

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

$$\text{and} \quad n_2 = cn \quad (8)$$

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

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

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

$$\text{Where} \quad x_1 + x_2 = 1 \quad (11)$$

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

$$x_1 = 1 - c \quad (12)$$

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

$$x_2 = c \quad (13)$$

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

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

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

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

Then Eqn. (15) can be written as

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

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

and from Eqn. (10) we can write,

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

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

$$\eta_j = \frac{\pi}{6} \rho_j \sigma_j^3 \quad (21)$$

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

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

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

$$\Rightarrow \rho_j = \frac{x_j}{V/n} \quad (22)$$

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

$$\Omega = \frac{V}{n} \quad (23)$$

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

$$\rho_j = \frac{x_j}{\Omega} \quad (24)$$

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

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

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

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

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

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

Eqn. (26) can be written as

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

Fourth term : Here S_{mismatch} represents the entropy due to mismatch of the diameters $\sigma_1 (= \sigma_A)$ and $\sigma_2 (= \sigma_B)$ of the hard spheres and this is written as

$$\begin{aligned} & \frac{S_{\text{mismatch}}}{Nk_B} \\ &= (\pi x_i x_j \rho_T) (|\sigma_i - \sigma_j|)^2 [24(1 - \eta)^2]^{-1} [12(\sigma_i + \sigma_j) \\ & - \pi \rho_T (x_i \sigma_i^4 + x_j \sigma_j^4)] \end{aligned} \quad (28)$$

Obviously as before we can write the above Eqn. as

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

Here ρ_T represents total number density and this is given by

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

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

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

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

$$\Rightarrow \rho_T = \rho_A + \rho_B \quad (30)$$

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

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

$$\Rightarrow \rho_A = x_A \rho_T \quad (31)$$

Similarly, we can prove,

$$\rho_B = x_B \rho_T \quad (32)$$

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

$$\therefore x_A = \frac{1}{2} = x_B$$

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:

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

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

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

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

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

From Eqn. (35) it is clear that 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 k th type of ions and Z_k is the valency of the k th 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

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

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

$$\Gamma^2 = \frac{\pi e^2}{\epsilon_0 k_B T} \sum_{i=1}^n \rho_i \chi_i^2 \quad (39)$$

Obviously in this case $n=2$.

Above equation may be expressed as,

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

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

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

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

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

Here for binary mixture $n=2$.

σ_i is the diameter of the i th species and Z_i is its valency.

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,

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

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

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

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

$$\text{Here } \rho_1 = \rho_T x_1 \quad (48)$$

$$\text{and } \rho_2 = \rho_T x_2 \quad (49)$$

Now χ_i is given by the following formula :

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

Now for a binary mixture $n = 2$.

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

Here Z_i represents the valency of the i th species and σ_i is the diameter of the i th 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.

$$\text{So } \rho_1 Z_1 + \rho_2 Z_2 = 0$$

$$\text{or } x_1 Z_1 + x_2 Z_2 = 0 \quad (52)$$

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} [31,32,40].

2.3 Entropy of mixing

The expression for theoretical entropy of mixing is as follows,

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

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:

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

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 potassium-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 K-Pb alloy. Here we have realistically assumed that there is some effective transfer of charge from the potassium 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 potassium 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 electroneutrality given by Eq. (52). The results for K-Pb are presented below.

The Eqs. (1)–(51) are used to calculate theoretical entropies of K-Pb alloys for various Pb concentrations, while the entropies of the pure metals Pb and K are calculated from Eq. (54). The alloy atomic volumes for various Pb concentrations in the K-Pb system are derived from experimental density data [44] reported in previous studies. Experimental pure atomic volumes $\Omega_K = 9.248 \times 10^{-23} \text{ cm}^3$ for K and $\Omega_{Pb} = 3.268 \times 10^{-23} \text{ cm}^3$ for Pb at 880 K are obtained from the literature [44]. The entropies of mixing for the K-Pb alloy system are calculated theoretically across various Pb concentrations using the Eqs. (1)–(54). These calculated values are then compared with experimental results [45], as illustrated in Figure 1.

Liquid binary alloys K-Pb have been extensively studied by Hultgren et al. [46]. Figure 1 demonstrates that the theoretically calculated entropy of mixing ΔS_{mix}^{th} shows good overall agreement with the experimental results reported by Hultgren et al. [46]. The theoretical values align well with the experimental data across the entire range of Pb concentrations in the K-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 K-Pb liquid alloy. We calculated ΔS_{mix}^{th} for the whole range of concentration and this theoretical values are compared with the experimental values [45,46]. 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 ($C_{Pb} = 0.33$). Our calculations also indicates that the maximum effective charge transfer from the K atom to the Pb atom is at the K_2Pb composition. The most suitable data is determined as follows:

$$\sigma_K = 3.61\text{\AA}, \sigma_{Pb} = 2.89\text{\AA} \quad \text{while } \Delta Z_K = +0.255e;$$

and $\Delta Z_{Pb} = -2 \Delta Z_K = -0.51e$ near the stoichiometric composition (K_2Pb). For other concentrations of lead, the numerical values of ΔZ_i are calculated by satisfying electroneutrality condition, $C_K \Delta Z_K + C_{Pb} \Delta Z_{Pb} = 0$.

At this juncture, it is noteworthy that the effective transfer of charge at very low and very high concentrations of Pb atom and K atom is insignificant. The generalized screening length parameter Γ is calculated for various concentrations using a previously described method [11,31,32]. We determine Γ values for different lead (Pb) concentrations in the K-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 potassium (K) atoms. This distortion occurs in the direction of lead (Pb) atoms due to the electronegativity difference between K 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 $0.4755 \text{ \AA}^{-1}$ near the stoichiometric composition where $C_{Pb} = 0.33$. In contrast, Fig. 3 demonstrates that Sch/NkB exhibits a sharp minimum of (-0.7054) at approximately the same stoichiometric composition ($C_{Pb} = 0.33$). The analysis reveals that the physical quantity ' Γ ' serves as a scaling parameter and functions as an indicator of the charge ordering process. 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 K, the calculated value is $\frac{S_K^{Th}}{Nk_B} = 12.52$, closely matching the experimental value $\frac{S_K^{Ex}}{Nk_B} = 12.5$ [46]. 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, 46]. Using the atomic volume graph of K-Pb alloys provided by Khairulin et al. [44], we have calculated the molar volumes of K-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 [45]. The theoretical entropy of mixing ΔS_{mix}^{Th} closely aligns with the experimental results [45,46] shown in Figure 1. The maximum average charge transfer per bond from potassium to lead atoms occurs at the K_2Pb composition ($C_{Pb} = 0.33$). The K–Pb melt achieves maximum stability and order at the stoichiometric (K_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. 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 and entropies of mixing for the liquid K-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 ($C_{Pb} \approx 0.33$) 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 25.5% ionicity for the K- Pb bond at approximately its stoichiometric composition. These calculated data are also apparently supported by the opinion of Pauling [29] 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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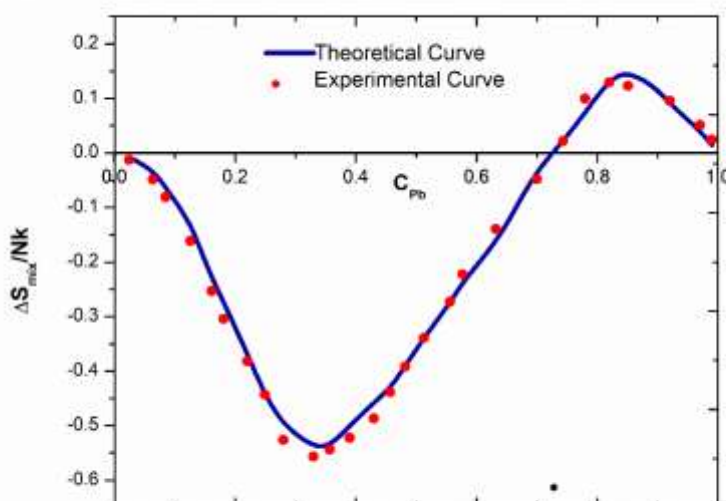


Fig. 1

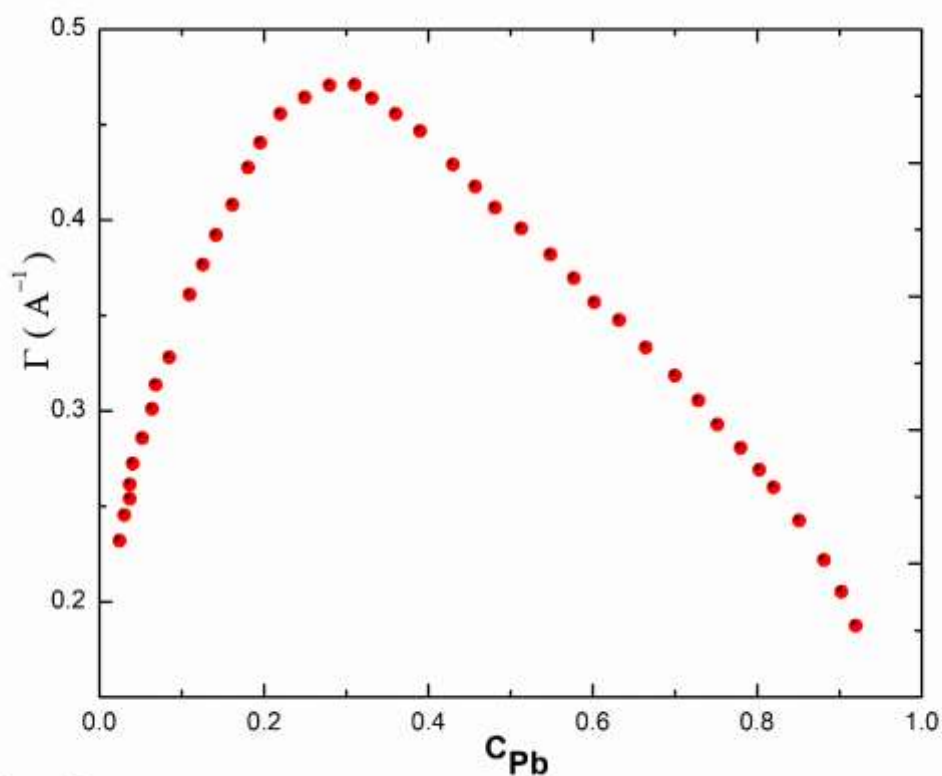


Fig. 2

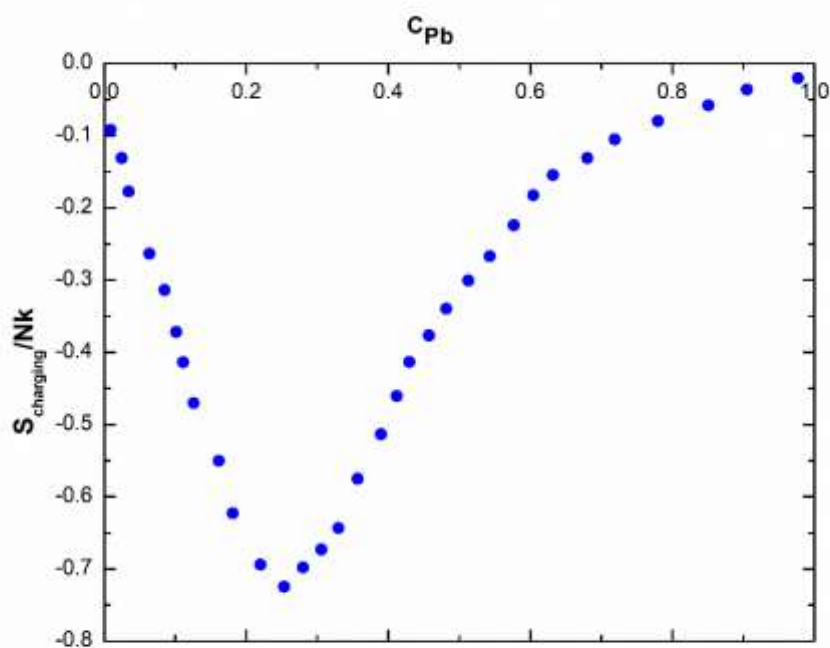


Fig. 3

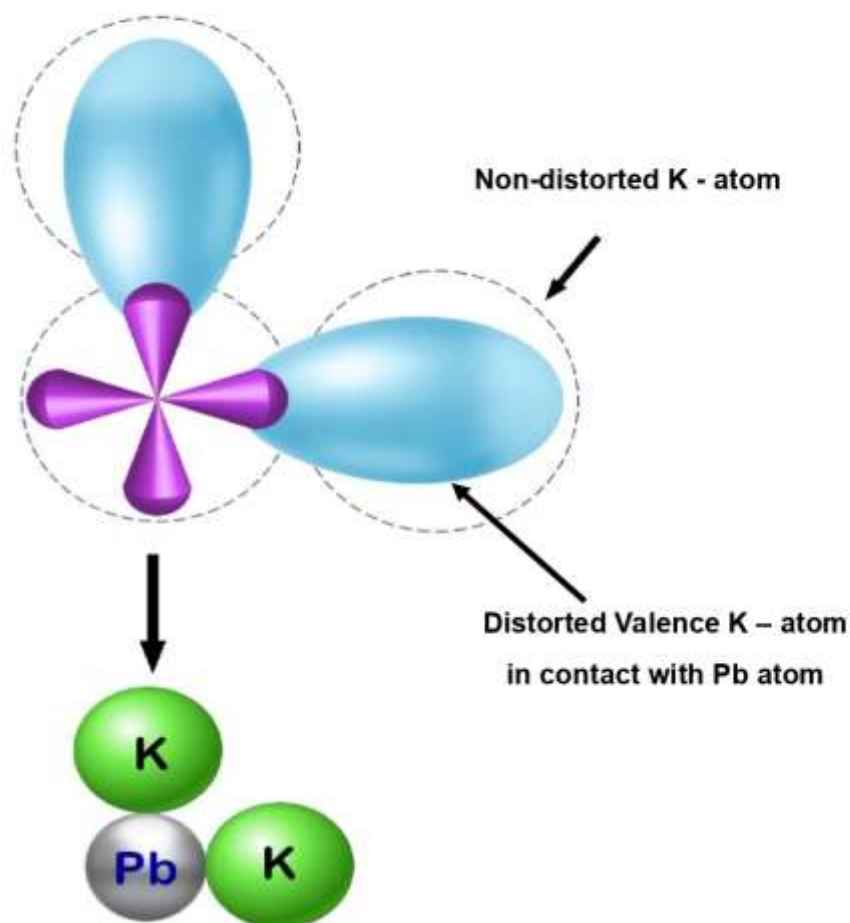


Fig. 4a

Fig. 4b

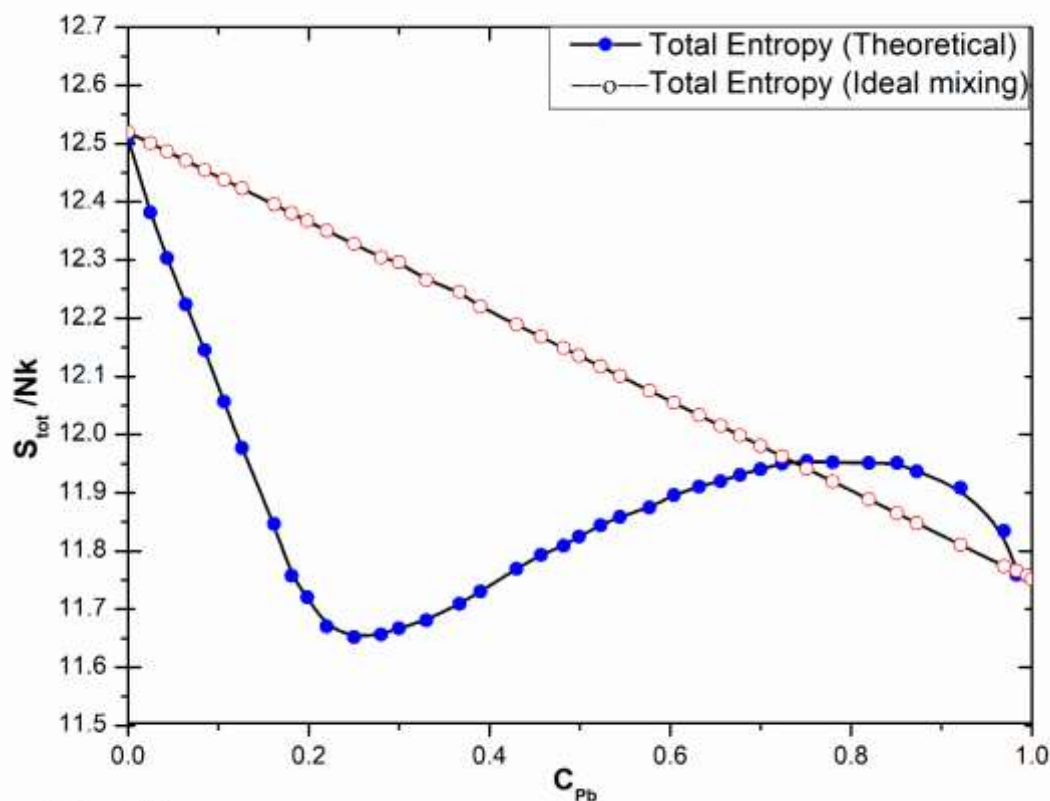


Fig. 5

Figure Caption:

1. Fig. 1: Entropy of mixing of molten K-Pb alloy at 880 K.
2. Fig. 2: Variation of Γ with concentration of Pb for molten K-Pb alloy at 880 K.
3. Fig. 3: Variation of entropy due to charging (S_{ch} / NK) with concentration. of Pb for molten K-Pb binary alloy at 880 K.
4. Fig. 4a: Distortion of valence electron cloud of K atom in contact with Pb atom (electron affinity $E_a^{Pb} > E_a^K$) and showing loose s-p overlapping at K_2Pb composition.
5. Fig. 4b: Partially charged hard spheres of Pb and K Species are stucked together. Here $\Delta Z_{Pb} = -0.51e$ and $\Delta Z_K = +0.255e$
6. Fig. 5: Total entropy of mixing of molten K-Pb binary alloy at 880 K.