

# Thermodynamic, Structural and Transport Properties of Molten Copper-Thallium Alloys

D. Adhikari, R. P. Koirala, and B.P. Singh

**Abstract**—A self-association model has been used to understand the concentration dependence of free energy of mixing ( $G_M$ ), heat of mixing ( $H_M$ ), entropy of mixing ( $S_M$ ), activity ( $a$ ) and microscopic structures, such as concentration fluctuation in long wavelength limit ( $S_{cc}(0)$ ) and Warren-Cowley short range order parameter ( $\alpha_1$ ) for Cu-Tl molten alloys at 1573K. A comparative study of surface tension of the alloys in the liquid state at that temperature has also been carried out theoretically as function of composition in the light of Butler's model, Prasad's model and quasi-chemical approach. Most of the computed thermodynamic properties have been found in agreement with the experimental values. The analysis reveals that the Cu-Tl molten alloys at 1573K represent a segregating system at all concentrations with moderate interaction. Surface tensions computed from different approaches have been found to be comparable to each other showing increment with the composition of copper.

**Keywords**—Concentration fluctuations, surface tension, thermodynamic properties, Quasi-chemical approximation.

## I. INTRODUCTION

THE mixing behavior of binary liquid alloys is described as ordering or segregating depending on the nature of arrangement of atoms of the constituent metals in the alloys. Segregating alloys have pairing of like atoms at equivalent sites. Many of such alloys possess good embedding and antifricition characteristic. They are used as contact material and also as self lubricating advanced bearing material for automotive application. A fine dispersion of phase in binary alloys contributes to the significant increase in mechanical strength of materials especially for high operation temperature.

In the present paper we have studied various properties of copper-thallium molten alloy at 1573K, which shows segregating tendency.

In order to understand the alloying behavior of binary liquid alloys, theoreticians have employed several models [1]-

[8]. In this work, we have computed thermodynamic properties (free energy of mixing, heat of mixing, entropy of mixing and activity), structural properties (concentration fluctuation in long wavelength limit and Warren-Cowley chemical short range order parameter), transport properties (ratio of mutual and intrinsic diffusion coefficients) using a statistical model in the framework of quasi-chemical approximation [9] and surface properties (surface concentration and surface tension) using the approach of Prasad et al. [10]. The concentration fluctuation in long wavelength limit computed directly from observed activity data [11] indicates that self associations of atoms are energetically favored in the Cu-Tl alloy in molten state.

The layout of the present work is as follows: Basic formalism of Quasi-chemical approximation is given in section II. Section III deals with the results and discussions and conclusions are outlined in section IV.

## II. FORMALISM

Let there be  $Nx_A$  atoms of element A and  $N(1 - x_A)$  are atoms of element B in the alloy where  $x_A$  represents the concentration of element A as the mole fraction. On the basis of this assumption expressions for thermodynamic and microscopic functions have been derived for binary liquid alloys [9] as given below.

The free energy of mixing,  $G_M$  for binary liquid alloys in quasi-chemical approximation can be obtained using the expression [9]

$$G_M = RT [x_A \ln \phi + x_B \ln (1 - \phi)] + \phi(1 - \phi)(x_A + \gamma x_B) W \quad (1)$$

where

$$\phi = \frac{x_A}{x_A + \gamma x_B}; \gamma = \frac{j}{i} \text{ and } W = i\omega \quad (2)$$

Here R: universal gas constant, T: the temperature,  $x_A$ ,  $x_B$ : concentrations of species A and B respectively, W: ordering energy parameter, and  $\omega$  is the interchange energy.

In order to obtain the expression for the chemical activity of constituent element in binary liquid alloys we recall the following standard thermodynamic relations which relate activities,  $a_A$  and  $a_B$  of the components A and B respectively to the free energy of mixing,  $G_M$ :

D. Adhikari is with Department of Physics, Mahendra Morang Adarsha Multiple Campus (Tribhuvan University) Biratnagar, Nepal (e-mail: adksbdev@yahoo.com). D. Adhikari is grateful to International Network for the Availability of Scientific Publications (INASP) for providing AuthorAID travel grant. He is also grateful to University Grants Commission (UGC), Nepal and Nepal Academy of Science and Technology (NAST) for financial support to pursue the research work.

R.P. Koirala is with Department of Physics, Mahendra Morang Adarsha Multiple Campus (Tribhuvan University) Biratnagar, Nepal (e-mail: rpphysics@yahoo.com).

B.P. Singh is with University Department of Physics, T.M. Bhag. University, Bhagalpur, India (e-mail: bhrigunandansingh@yahoo.com).

$$RT \ln a_A = \left( \frac{\partial G_M}{\partial N_1} \right)_{T,P,N_2}; RT \ln a_B = \left( \frac{\partial G_M}{\partial N_2} \right)_{T,P,N_1} \quad (3)$$

Using (1) and (3), the working expressions for the activities are obtained as:

$$\ln a_A = 1 + \ln \phi - \frac{\phi}{x_A} + (1 - \phi)^2 \frac{W}{RT} \quad (4)$$

$$\ln a_B = \ln(1 - \phi) + \phi(1 - \gamma) + \gamma \phi^2 \frac{W}{RT} \quad (5)$$

The standard thermodynamic relation for entropy of mixing ( $S_M$ ) is given by:

$$S_M = - \left( \frac{\partial G_M}{\partial T} \right)_P \quad (6)$$

Using (1),  $S_M$  can be expressed as:

$$S_M = -R [x_A \ln \phi + x_B \ln(1 - \phi)] - \phi(1 - \phi)(x_A + \gamma x_B) \frac{\partial W}{\partial T} \quad (7)$$

Once the free energy of mixing,  $G_M$  and entropy of mixing,  $S_M$  are obtained, the heat of mixing,  $H_M$  can be readily calculated using the standard thermodynamic relation:

$$H_M = G_M + TS_M \quad (8a)$$

$$= \phi(1 - \phi)(x_A + \gamma x_B) \left[ W - T \frac{\partial W}{\partial T} \right] \quad (8b)$$

The microscopic functions such as concentration fluctuation in long wavelength limit ( $S_{cc}(0)$ ) and Warren-Cowley [12]-[13] short-range order parameter ( $\alpha_1$ ) are useful properties to obtain valuable information about structure of molten alloys.  $S_{cc}(0)$  indicates nature of local ordering of atoms and  $\alpha_1$  represents the degree of ordering in the melt.

The standard relation for concentration fluctuation in long wavelength limit ( $S_{cc}(0)$ ) for binary liquid alloys is given as:

$$S_{cc}(0) = RT \left( \partial^2 G_M / \partial x_A^2 \right)_{T,P}^{-1} \quad (9)$$

Equations (1) and (9) yield:

$$S_{cc}(0) = \frac{x_A x_B}{1 - x_A x_B f(i, j, \omega)} \quad (10)$$

where

$$f(i, j, \omega) = \frac{2 \frac{W}{RT} \gamma^2 - (\gamma - 1)^2 (x_A + \gamma x_B)}{(x_A + \gamma x_B)^3} \quad (11)$$

The value of ( $S_{cc}(0)$ ) can also be determined using activity data in the following thermodynamic equations:

$$S_{cc}(0) = x_B a_A (\partial a_A / \partial x_A)_{T,P}^{-1} = x_A a_B (\partial a_B / \partial x_B)_{T,P}^{-1} \quad (12)$$

which are usually considered as the experimental values.

In order to quantify the degree of atomic order in the alloy, Warren-Cowley short range order parameter ( $\alpha_1$ ) [12]-[13] can be estimated from the knowledge of concentration-concentration structure factor ( $S_{cc}(q)$ ) and the number-number structure factor ( $S_{NN}(q)$ ). However in most diffraction experiments these quantities cannot be measured easily for all binary liquid alloys. On the other hand the value of  $\alpha_1$  for the first nearest neighbours can be estimated from the relation

$$\alpha_1 = \frac{\beta - 1}{\beta + 1} \quad (13)$$

where  $\beta$  is an auxiliary variable given by:

$$\beta = [1 + 4x_A(1 - x_A)(\eta^2 - 1)]^{1/2} \quad (14)$$

with

$$\eta = \exp(W / ZkT) \quad (15)$$

Here  $Z$  represents the number of nearest neighbors of an atom in the bulk and is called co-ordination number.

In terms of the variable  $\beta$ , an expression for  $S_{cc}(0)$  is expressed as:

$$S_{cc}(0) = \frac{c(1 - c)}{1 + 1/2Z(1/\beta - 1)} \quad (16)$$

By taking together (13) and (16), an expression for  $\alpha_1$  can be derived in the following form:

$$\alpha_1 = \frac{(S - 1)}{S(Z - 1) + 1} \text{ with } S = \frac{S_{cc}(0)}{S_{cc}^{id}(0)} \quad (17)$$

where  $S_{cc}^{id}(0) = x_1 x_2$ . The value of  $\alpha_1$  can be computed from the knowledge of  $S_{cc}(0)$  using the expression (17). In our calculation we have taken  $Z = 10$ . We note that varying the value of  $Z$  does not have any effect on the position of minima of  $\alpha_1$ ; the effect is to vary the depth while the overall feature remains unchanged.

The mixing behavior of the alloys forming molten metals can also be studied at the microscopic level in terms of the diffusion coefficients. The  $S_{cc}(0)$  and diffusion coefficients can be related using Darken thermodynamic equation for diffusion as [14]-[15]

$$\frac{D_M}{D_{id}} = \frac{S_{cc}^{id}(0)}{S_{cc}(0)} \quad (18a)$$

where  $D_M$  is the mutual diffusion coefficient and  $D_{id}$  is the intrinsic diffusion coefficient for an ideal mixture given as [14]-[15]:

$$D_M = x_A D_B + x_B D_A \quad (18b)$$

where  $D_A$  and  $D_B$  are the self-diffusivities of pure components A and B respectively.

The ratio  $D_M/D_{id}$  indicates the mixing behavior of alloy;  $D_M/D_{id} > 1$  indicates the tendency for compound formation and  $D_M/D_{id} < 1$  indicates tendency of segregation. For random mixing, the ratio  $D_M/D_{id}$  approaches 1.

The miscibility phenomenon poses problems during solidification. The surface tension effects play vital role in the formation of solid alloys by solidification process of the melts. Several metallurgical phenomena such as, crystal growth, welding, gas absorption, nucleation of gas bubbles are closely associated with the surface tension phenomena. The surface tension is very sensitive to physical and chemical contamination, particularly at high temperatures. Therefore, for understanding, description and metallurgical modeling as well as prediction of structure development during solidification in the binary system surface properties need to be known. The experimental determination of surface tension involves several difficulties in many cases. Because of this, several theoretical models [10], [16]-[17] have long been developed to determine surface tension data of metals and alloys. We employ the formulation of Prasad et al. for the computation of surface tension of Cu-Tl alloys in molten state at 1573K which is given as

$$\sigma = \sigma_A + \frac{k_B T}{\alpha_A} \ln \frac{x_A^s}{\gamma_A x_A} + [p(x_B^s)^2 + q(x_B)^2] \frac{W}{\alpha_A} \quad (19a)$$

$$\sigma = \sigma_B + \frac{k_B T}{\alpha_B} \ln \frac{x_B^s}{\gamma_B x_B} + [p(x_A^s)^2 + q(x_A)^2] \frac{W}{\alpha_B} \quad (19b)$$

where  $\sigma$ ,  $\sigma_A$  and  $\sigma_B$  are surface tension of alloy and that of pure components A and B respectively;  $k_B$  stands for Boltzmann constant;  $p$  and  $q$  are surface coordination fractions which are taken as  $p = 0.5$  and  $q = 0.25$  for closed packed structure;  $x_A^s$  and  $x_B^s$  are surface concentration of A and B species.  $\alpha_i$  ( $i = A, B$ ) is atomic area of hypothetical surface given by

$$\alpha_i = 1.102 \left( \frac{v_i}{N} \right)^{2/3} \quad (20)$$

where  $v_i$  is the atomic volume of species  $i$  and  $N$  stands for Avogadro's number.

We have used Butler's approach [19], quasi-chemical approach [20] and Guggenheim approach [21] to compute the surface tension of Cu-Tl alloys in liquid state at 1573K.

### III. RESULTS AND DISCUSSION

In quasi-chemical approximation ratio of self associates  $\gamma$  and interchange energy  $\omega$  are the parameters required for the computation of the thermodynamic properties of the binary liquid alloys. The interaction energy parameter  $W$  in this model is considered to be temperature dependent. These input parameters have been estimated by simultaneously fitting the experimental data of free energy of mixing and activity throughout whole concentrations. The best fit values of these parameters for the Cu-Tl molten alloys at 1573K are found to be  $\gamma = 1.6$  and  $W = +1.42 RT$ . These parameters remain constant throughout the calculations. The positive value of  $W$  ensures that the attraction between unlike atoms (A-B) is less than that of like atoms (A-A or B-B), indicating that there is a tendency of segregation in the Cu-Tl alloys in molten state. Theoretical calculation of free energy of mixing for the Cu-Tl liquid alloy shows that there is reasonably good agreement between the experimental and calculated free energies (Fig. 1). Small deviation from this may originate from the term arising from the entropy of mixing.

Heat of mixing and entropy of mixing are two important thermodynamic functions that compete each other to dictate the degree of segregation in the binary system. We have computed these functions by assuming  $\frac{\partial W}{\partial T} = -0.43R$ . Both

the heat of mixing and entropy of mixing for the Cu-Tl liquid alloys are found to be positive at all concentrations. The positive value of heat of mixing indicates the segregating nature of the Cu-Tl alloy which is in agreement with the sign of  $W$ . The computed values show a good agreement with the observed values [11] (Figs. 1 and 2).

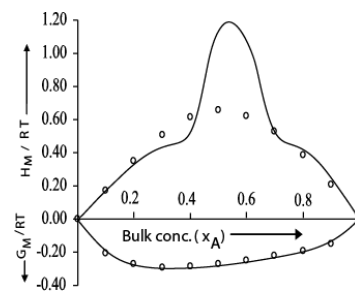


Fig. 1 Free energy of mixing ( $G_M$ ) Vs bulk concentration of Cu ( $c_{Cu}$ ) and Heat of mixing ( $H_M$ ) Vs concentration of Cu ( $c_{Cu}$ ) in liquid Cu-Tl alloy at 1573K; solid lines for theoretical values and circles for experimental values [11]

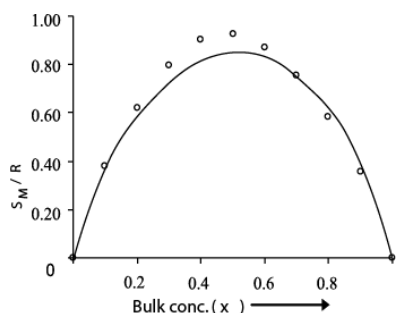


Fig. 2 Entropy of mixing ( $S_M$ ) Vs bulk concentration of Cu ( $c_{Cu}$ ) in liquid Cu-Tl alloy at 1573K; solid line for theoretical values and circles for experimental values [11]

Activity is very important quantity which can be obtained directly from the experiment. The magnitudes of activities are assumed to be determined by the interactions among the constituent species of the system, which in turn determine the bond energies. Thus measurement of activities within a class of similar system can be expected to provide, at least, a basis for correlation of the behavior, which can then be used for extrapolation of the behavior of more complex system. The activity of a component in a solution also provides a measure of tendency to leave the solution. We have calculated the activities of Cu and Tl in the liquid Cu-Tl using (4) and (5). A plot of the activities (Fig. 3) shows a correlation between the computed and observed values [11].

The values of  $S_{cc}(0)$  and  $\alpha_1$  represent the nature and degree of segregation in binary liquid alloys. The value of  $S_{cc}(0) > S_{cc}^{id}(0)$  represents segregating tendency of the alloys while  $S_{cc}(0) < S_{cc}^{id}(0)$  indicates ordering tendency. The knowledge of  $\alpha_1$  provides an immediate insight into the nature of the local arrangements of atoms in the mixture. The normalized values of this parameter provide the strength of the local order of atoms.  $\alpha_1^{\min} = -1$  implies complete ordering of unlike atoms at nearest neighbors,  $\alpha_1^{\max} = +1$  implies total segregation leading to the phase separation and  $\alpha_1 = 0$  corresponds to a random distribution of atoms.

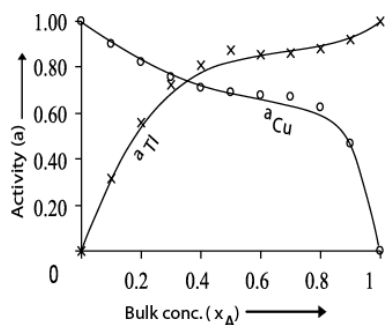


Fig. 3 Chemical activity ( $a_i$ ) Vs bulk concentration of Cu ( $c_{Cu}$ ) in liquid Cu-Tl alloy at 1573K; solid lines for theoretical values and circles for experimental values [11]

The computed and experimental values of  $S_{cc}(0)$  as well as ideal values are depicted in fig. 4. Both the computed and experimental values of  $S_{cc}(0)$  are found to be greater than the ideal values over the full range of concentration. The values of  $\alpha_1$  have been found all positive for all compositions (Fig. 5). Computed values of both  $S_{cc}(0)$  and  $\alpha_1$  imply that the Cu-Tl alloy in liquid state at 1573K is a segregating system.

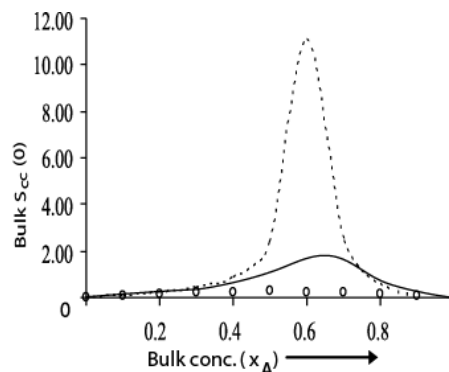


Fig. 4 Concentration fluctuation at long wavelength limit ( $S_{cc}(0)$ ) Vs bulk concentration of Cu ( $c_{Cu}$ ) in liquid Cu-Tl alloy at 1573K; solid line for theoretical values, broken line for experimental values [11] and circles for ideal values

The calculated values of  $S_{cc}(0)$  are used in (13) to evaluate the ratio of the mutual and self-diffusion coefficients,  $D_M/D_{id}$ . The value of  $D_M/D_{id}$  is found less than 1 for all concentrations. This also indicates the segregating feature of the Cu-Tl alloy as observed in  $S_{cc}(0)$  and  $\alpha_1$ . Since  $D_M/D_{id}$  is seen smaller in the region around  $c = 0.7$ , where it is found minimum, the phase separating tendency of the Cu-Tl liquid alloy at 1573K is maximum at intermediate composition (Fig. 6).

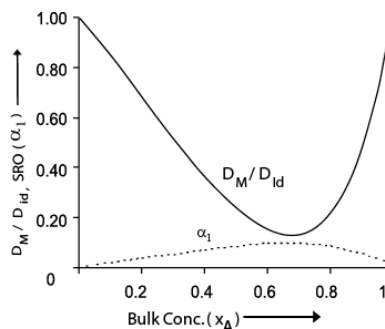


Fig. 5 Short range order parameter ( $\alpha_1$ ) Vs bulk concentration of Al ( $c_{Cu}$ ) and ratio of diffusion coefficients Vs concentration of Cu ( $c_{Cu}$ ) in liquid Cu-Tl alloy at 1573K

The surface concentration of Cu has been computed by simultaneously solving (15). These surface concentrations are used to evaluate the surface tension of Cu-Tl alloy at 1573K. For the computation of surface concentration and surface tension using (15) we have taken the experimental data of surface tension, density and their temperature coefficients of pure Cu and Tl components from the ref. [18]. The density and

surface tension of the pure components at the temperature of investigation have been calculated using the relations

$$\rho(T) = \rho_m + \frac{\partial \rho}{\partial T}(T - T_m) \quad (18)$$

$$\sigma(T) = \sigma_m + \frac{\partial \sigma}{\partial T}(T - T_m) \quad (19)$$

where  $\frac{\partial \rho}{\partial T}$ ,  $\frac{\partial \sigma}{\partial T}$ ,  $T$ ,  $T_m$  are temperature coefficient of density,

temperature coefficient of surface tension, temperature of investigation and melting temperature respectively.

The theoretical investigation shows that there is segregation of Tl atoms to the surface (Fig. 7) at all concentrations. It indicates that the element with lower surface tension tends to segregate on the surface while the element with higher surface tension tends to segregate in the bulk of Cu-Tl molten alloy. When there is a larger difference in surface tension between the solvent and solute, the segregating behavior of the component is more significant.

The computed values of surface tension for the alloy at 1573K with ideal values ( $\sigma = x_A \sigma_A + x_B \sigma_B$ ) is depicted in Fig. 7. We do not have experimental values to compare our computed values of surface tension. However, it is mentioned that the model which we have used in the present work has been successfully used by several workers to compute the surface tension of metallic solutions. It is found from the analysis that the surface tension values for Cu-Tl system at 1573K computed by (15) show some variations from the ideal values for compositions above  $x_A = 0.2$ . This represents the departure of the alloy from the ideal behavior. The surface tension of this alloy is found to increase with increase in the concentration of Cu-component.

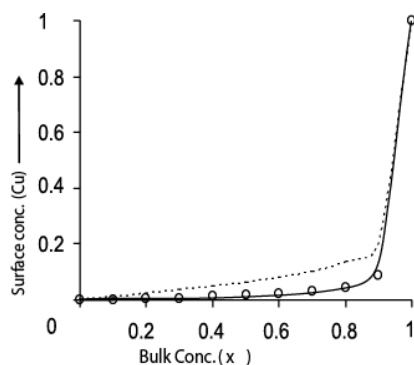


Fig. 6 Surface concentration ( $C^s$ ) Vs bulk concentration of Cu ( $C_{Cu}$ ) in liquid Cu-Tl alloy at 1573K. Solid line – Quasi-chemical model, Broken line – Butler's Model, Circles– Prasad approach

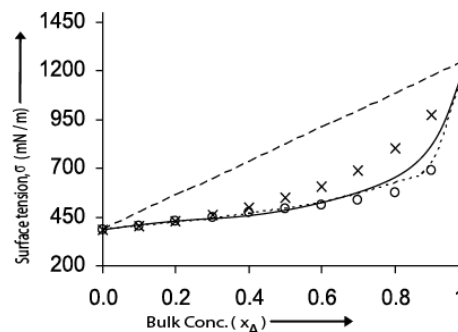


Fig. 7 Surface tension ( $\sigma$ ) Vs bulk concentration of Cu ( $C_{Cu}$ ) in liquid Cu-Tl alloy at 1573K: Solid line – Quasi-chemical model, Short broken line – Butler's model, Circles – Prasad's model, Crosses – March and Alonso approach, Long broken line – Ideal value

#### IV. CONCLUSIONS

The theoretical analysis reveals that the molten Cu-Tl alloy is moderately interacting system showing a significant tendency of formation of homo-pairs or phase separation (preference of like atoms pairing: Cu-Cu and Tl-Tl) at all compositions. The interaction energy parameter in the alloy is temperature dependent. It is found that the surface tension of Cu-Tl alloy increases with increase in the concentration of Cu-component. Moreover, the component with lower surface tension tends to segregate on the surface of molten alloy while that with higher surface tension tends to segregate in the bulk.

#### REFERENCES

- [1] R.N. Singh and F. Sommer, "Temperature dependence of the thermodynamic functions of strongly interacting liquid alloys", *J. Phys. Condens. Matter*, vol.4, p. 5345, 1992.
- [2] F. Sommer, "Thermodynamic properties of compound-forming liquid alloys", *J. Non-Cryst. Solids*, vol. 117, pp. 505–512, 1990.
- [3] D. Adhikari, "Disorder in liquid Cu-Pd alloy", *Phase Transitions*, vol. 84, pp. 308-314, 2011.
- [4] K. Hoshino, "On the temperature dependence of the structure factor of the liquid Li-Pb alloy", *J. Phys. F: Met. Phys.*, vol. 13, p. L189, 1983.
- [5] W.H. Young, "Structural and thermodynamic properties of NFE liquid metals and binary alloys", *Rep. Prog. Phys.* Vol. 55, p. 1769, 1992.
- [6] P.J. Flory, "Thermodynamics of high polymer solutions", *J. Chem. Phys.* Vol. 10, pp. 51–61, 1942.
- [7] D. Adhikari, I.S. Jha, and B.P. Singh, "Structural asymmetry in liquid Fe-Si alloys", *Philos. Mag.*, vol.90, pp. 2687–2694, 2010.
- [8] A.B. Bhatia and R.N. Singh, "A quasi-lattice theory compound forming molten alloys", *Phys. Chem. Liq.* Vol. 13, pp. 177–190, 1984.
- [9] R. Singh and F. Sommer, "Segregation and immiscibility in liquid binary alloys", *Rep. Prog. Phys.*, vol. 60, pp.57-150, 1997.
- [10] L.C. Prasad, R.N. Singh, and G.P. Singh, "The role of size effects on surface properties", *Physics and Chemistry of Liquids*, vol. 27, pp. 179-185, 1994.
- [11] R. Hultgren, P. D. Desai, D.T. Hawkins, M. Gleiser, and K.K. Kelley, *Selected values of the thermodynamic properties of binary alloys*, ASM, Metal Park, OH, 1973.
- [12] B.E. Warren, *X-ray Diffraction*, Addison-Wesley, Reading, MA, 1969.
- [13] J.M. Cowley, "An Appropriate Theory of Order in Alloys", *Phys. Rev.*, Vol. 77, pp.669, 1950.
- [14] L. S. Darken, R.W. Gurry, *Physical chemistry of metals*, McGraw Hill, New York, p.53, 1953.
- [15] R.N. Singh and F. Sommer, "Thermodynamic Investigations of Viscosity and Diffusion of binary Molten alloys", *Phys. Chem. Liq.* Vol. 36, p. 17, 1998.

- [16] R. Novakovic, "Thermodynamics, surface properties and microscopic functions of liquid Al-Nb and Nb-Ti alloys". *Journal of Non-Crystalline Solids*, vol. 356, pp. 1593-1598, 2010.
- [17] B.C. Anusionwu and C.A. Madu, "Theoretical studies of mutual diffusivities and surface properties of Cd-Ga liquid alloys", *PRAMANA-J. Physics*, vol.72, pp. 951-967, 2009.
- [18] H.M. Lu and Q. Jiang "Surface Tension and Its Temperature Coefficient for Liquid Metals" *J. Phys. Chem. B* , **vol. 109**, pp. 15463-15468, 2005.
- [19] J. A.V. Butler, "The thermodynamics of the surface of solutions" *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, vol.135, pp. 348-375, 1932.
- [20] R. Novakovic, " Thermodynamics, surface properties and microscopic functions of liquid Al-Nb and Nb-Tl alloys", *J. Non-Crystalline Solids*, vol. 356, pp. 1593-1598, 2010.
- [21] N.H March and J.A. Alonso, "Non-monotonic behaviour with concentration of the surface tension of certain binary liquid alloys", *Phys. Chem. Liq.* vol. 46, pp.522-526, 2008.