
BIBECHANA

A Multidisciplinary Journal of Science, Technology and Mathematics

ISSN 2091-0762 (online)

Journal homepage: <http://nepjol.info/index.php/BIBECHANA>

Surface tension of two weakly interacting liquid alloys

R. P. Koirala^{1,2}, D. Adhikari², B. P. Singh^{1*}

¹University Department of Physics, T.M. Bhagalpur University, Bhagalpur, India

²Department of Physics, M.M.A.M. Campus Biratnagar, Tribhuvan University, Nepal

*Corresponding author: E-mail : bhrigunandansingh@yahoo.com

Article history: Received 22 October, 2012; Accepted 14 November, 2012

Abstract

We report surface tension of two weakly segregating alloys Al-Ga and Cd-In in molten state at temperatures of 1023 K and 800 K respectively using different approaches. Our analysis based on different assumptions reveal that the metal with lower surface tension tends to segregate on the surface of molten alloy and the metal with higher surface tension tends to segregate in the bulk. Different approaches predict consistency in the values of the surface tension of Al-Ga liquid alloy that increases with increase in bulk concentration of aluminium in the alloy with all values smaller than the ideal values. In Cd-In alloy the models reveal no such regularity in the surface tension; it varies slightly from the ideality.

Keywords: Concentration; Surface tension; Surface segregation; Order energy parameter; Activity coefficients

1. Introduction

The surface tension is one of the important thermo-physical properties of mixing of liquid metallic alloys. A good knowledge of surface tension is required in many fields of engineering and metallurgical science. The processing of materials and the production in metallurgical industry are very important aspects of modern technology. In many phenomena such as, heterogeneous catalysis, welding, corrosion, gas absorption, nucleation of gas bubbles, nucleation and growth of nonmetallic inclusions and slag/metal reaction and kinetics of phase transformation, the role of surface tension is crucial [1]. The motivation of study of surface properties of liquid alloys thus stems from such importance of the surface tension. The study in general leads to expansion of knowledge in the field of material science and engineering for producing construction materials of enhanced properties such as increased mechanical strength, heat and chemical resistance, a wider range of colour not found naturally and even economic from the point of view of production costs. In this context, we have chosen two weakly interacting binary molten alloys,

one of aluminium and the other of cadmium namely Al-Ga and Cd-In for investigation of their surface properties. Al-Ga alloy is reported to split up water spontaneously to generate hydrogen in large scale on demand which can keep away unnecessary storage of hydrogen [2]. Cd-In alloys are common used in applications which include bearing assembly, ballast, casting and radiation shielding. Eutectic Cd-In alloy (Composition 25% Cd and 75% In by weight) is known to be a desirable solder in electro-deposition for obtaining superior strength joints in delicate electrical fabrication of transistor electrodes in electronic circuits [3].

The surface tension is very important in physical and chemical contamination, particularly at high temperatures. But the experimental determination of surface tension at different temperatures involves several difficulties in many cases. Thus there is a strong need of theoretical studies and for this reason theoreticians have employed several models [4-15] for the study of thermodynamic and surface properties of binary liquid alloys. We have employed the formulations mentioned in the papers of Prasad et al. [4], Novakovic [5], March and Alonso [6], and Butler [7-8] for the comparative study of concentration dependence of surface properties for Al-Ga liquid alloy at 1023 K and the first three formulations for the Cd-In alloy at 800 K. Most of the theoretical models for determining the surface tension require the inputs from the thermodynamic data. The statistical formulations of Prasad et al. and Novakovic require order energy input, estimated from thermodynamic data, for the computation of surface concentration and surface tension. The value of the thermodynamic order energy parameter can be obtained from consideration of different theoretical models. As the values of concentration fluctuation, $S_{cc}(0)$ computed directly from activity data [16] for the liquid alloys Al-Ga and Cd-In at temperatures of 1023 K and 800 K respectively are all slightly greater than the ideal values, the alloys are weakly segregating; and hence we have used quasi-chemical approximation (QCA) for regular alloys [13] to estimate the required thermodynamic parameters for the alloys. The thermodynamical treatment of Guggenheim is generally applied to determine the surface tension of the binary liquid alloys in which the surface tension varies with concentration in a monotonic way between the values of the surface tension of two pure metals forming the alloys [6]. In Butler's monolayer model [7], excess free energy of mixing is used to calculate both surface concentration and surface tension.

In the next section, the basic expressions for the formalism used in calculations are outlined. Section 3 gives the result and discussions of the work and conclusions are presented in section 4.

2. Formalism

For comparative study of surface properties such as surface concentration and surface tension of Al-Ga and Cd-In alloys in molten state respectively at temperatures of 1023 K and 800 K, we have employed the following treatments.

2.1. Consider one mole of a binary liquid alloy A-B consisting of $N_A (= x_A N)$ atoms of A-component and $N_B (= x_B N)$ atoms of B-component in the bulk phase, N being the total number atoms, and x_A and x_B are the concentrations expressed in mole fractions such that $x_A + x_B = 1$.

In the statistical formulation of Prasad et al. [4], a binary liquid alloy is considered to have a layered structure near the surface with a thermodynamic equilibrium existing between the species at the surface

and in the bulk. There is direct influence of bulk thermodynamic properties of liquid alloys on their surface properties. The expressions that connect the surface properties namely surface tension, Γ of a binary liquid alloy and surface concentrations of the alloy component metal with the thermodynamic properties such as chemical activity, γ_i ($i = A, B$) and interaction energy parameter, W at a given temperature, T have been derived in this model [4] in the following form:

$$\Gamma = \Gamma_A + \frac{k_B T}{\alpha} \ln \frac{x_A^S}{\gamma_A x_A} + [p(x_B^S)^2 + q(x_A^S)^2] \frac{W}{\alpha} \quad (1a)$$

$$\Gamma = \Gamma_B + \frac{k_B T}{\alpha} \ln \frac{x_B^S}{\gamma_B x_B} + [p(x_B^S)^2 + q(x_A^S)^2] \frac{W}{\alpha} \quad (1b)$$

where Γ_A and Γ_B are surface tensions of pure components A and B respectively; k_B stands for Boltzmann constant; x_A and x_B are bulk concentrations; x_A^S and x_B^S are surface concentrations; and γ_A and γ_B are the bulk activity coefficients of the alloy components A and B respectively. The mean atomic surface area, α is given as

$$\alpha = \sum x_i \alpha_i \quad (i = A, B) \quad (2)$$

where the atomic area of hypothetical surface for each component is given as [4]:

$$\alpha_i = 1.102 (\Omega_i / N_A)^{2/3} \quad (3)$$

where Ω_i is the molar volume of species i and N_A stands for Avogadro's number.

p and q are surface coordination fractions which are defined as the fractions of the total number of nearest neighbours made by atom within its own layer and that in the adjoining layer. For p and q the following relation is available [4, 9]:

$$p + 2q = 1 \quad (4)$$

For closed packed structures the values of these parameters are taken as 0.5 and 0.25 respectively.

The ordering energy term W is a temperature dependent quantity and for an alloy at a given temperature, it can be estimated as a model fit parameter in QCA [13]. QCA for regular binary liquid alloys assumes the homo-coordination of like atoms at equivalent sites that results in the formation of self-associates of types μA and νB . In QCA, the following standard thermodynamic expressions for the free energy of mixing for the binary system, G_M and chemical activities of the components, a_A and a_B are used to estimate the best fit value for W :

$$\frac{G_M}{RT} = [x_A \ln \phi + x_B \ln (1 - \phi)] + \phi(1 - \phi)(x_A + n x_B) \frac{W}{RT} \quad (5)$$

$$\ln a_A = 1 + \ln \varphi - \frac{\varphi}{x_A} + (1 - \varphi)^2 \frac{W}{RT} \quad (6)$$

$$\ln a_B = \ln(1 - \varphi) + \varphi(1 - n) + n\varphi^2 \frac{W}{RT} \quad (7)$$

Here, R is molar gas constant; $\varphi = \frac{x_A}{x_A + n x_B}$ with $n = \frac{v}{\mu}$ = ratio of self-associates.

2.2. The surface tension of regular binary liquid alloys in which no complexes are formed can be examined by the application of quasi-lattice theory [5,17]. The following pair of equations are available for the theoretical investigation of the surface tension of the binary liquid alloys :

$$\Gamma = \Gamma_A + \frac{k_B T (2 - pZ)}{2\alpha} \ln \frac{x_A^s}{x_A} + \frac{Z k_B T}{2\alpha} \left[p \ln \frac{(1 + \lambda)(\lambda^s + x_A^s - x_B^s)}{(1 + \lambda^s)(\lambda + x_A - x_B)} - q \ln \frac{(\lambda + x_A - x_B)}{(1 + \lambda)x_A} \right] \quad (8a)$$

$$\Gamma = \Gamma_B + \frac{k_B T (2 - pZ)}{2\alpha} \ln \frac{x_B^s}{x_B} + \frac{Z k_B T}{2\alpha} \left[p \ln \frac{(1 + \lambda)(\lambda^s + x_B^s - x_A^s)}{(1 + \lambda^s)(\lambda + x_B - x_A)} - q \ln \frac{(\lambda + x_B - x_A)}{(1 + \lambda)x_B} \right] \quad (8b)$$

Here Z is co-ordination number in the bulk and all the other notations have the same meaning as those in Eqs. (1a-1b), with λ as the concentration dependent auxiliary variable defined in terms of the order energy parameter, W through the following equation [5]

$$\lambda = [1 + 4 x_A x_B \{ \exp(2W / Zk_B T) - 1 \}^2]^{1/2} \quad (9)$$

The function λ^s for surface is obtained from Eq. (9) by substituting the bulk concentration x_A by the surface concentration x_A^s and the coordination number Z by coordination number of the surface atoms, Z^s . The value of Z^s is calculated from its relation with Z given by [1]

$$Z^s = (p + q) Z \quad (10)$$

2.3. In third approach the standard expression for obtaining the surface tension, Γ of a binary liquid alloy which usually varies with concentration x in a smooth way between the surface tension of the two pure metals of the alloy, is expressed as follows [6]:

$$\exp(-\beta\alpha\Gamma) = (1 - x) \exp(-\beta\alpha\Gamma_A) + x \exp(-\beta\alpha\Gamma_B) \quad (11)$$

Here x represents the concentration of the component B with smaller surface tension; Γ_A and Γ_B are the surface tensions of the components A and B respectively at the temperature of investigation, T; and the

term $\beta = 1/k_B T$, k_B being Boltzmann constant. The symbol α denotes the mean atomic surface area of the alloy, which can be calculated as function of bulk concentration from Eq. (2).

2.4. Butler's formulation [7] is based on the assumption of monatomic surface layer which is considered as a separate phase that is in thermodynamic equilibrium with the bulk. The surface tension, Γ of a binary liquid solution in this model can be expressed as:

$$\Gamma = \frac{\mu_A^s - \mu_A^b}{\alpha_1} = \frac{\mu_B^s - \mu_B^b}{\alpha_2} = \dots = \frac{\mu_i^s - \mu_i^b}{\alpha_i} \quad (12)$$

where μ_i^s , μ_i^b and α_i denote respectively the chemical potential in the hypothetical surface, and that in the bulk, and the molar surface area of pure component i . From equation (12), the expressions for the surface tension has been derived in terms of partial excess free energy of mixing, $G_i^{E,b}$ in the bulk and $G_i^{E,s}$ at the surface, and surface concentrations, x_i^b in the bulk and x_i^s at the surface ($i = A, B$), in the following forms [8,18]:

$$\Gamma = \Gamma_A + \frac{1}{\alpha_A} [G_A^{E,s} - G_A^{E,b} + RT \ln \frac{x_A^s}{x_A^b}] \quad (13a)$$

$$\Gamma = \Gamma_B + \frac{1}{\alpha_B} [G_B^{E,s} - G_B^{E,b} + RT \ln \frac{x_B^s}{x_B^b}] \quad (13b)$$

where Γ_A and Γ_B are surface tension of pure metals A and B respectively.

The partial excess free energy of mixing of component i at the surface and that in the bulk are related to each other through a parameter β as [8]:

$$\beta = \frac{G_i^{E,s}}{G_i^{E,b}} \quad (14)$$

The value of β is assumed a constant number in the calculations. The area of monatomic surface layer for the component i is commonly calculated from the following relation [19]

$$\alpha_i = L N_A^{1/3} \Omega_i^{2/3} \quad (15)$$

where $L = 1.091$ is called geometrical factor for the closed packed atoms of the surface monolayer, N_A is Avogadro's constant and Ω_i stands for the molar volume of the component i . The molar volume of a component can be calculated from its molar mass and density.

Solving Eqs. (13a) and (13b) together for the surface concentration using the partial excess free energy of mixing in the bulk, one can work out the surface tension of a binary liquid solution.

3. Results and Discussion

3. 1. For the computation of surface properties namely surface concentration, surface tension of the binary liquid alloys using the equations (1a) and (1b), we need experimental data of density, surface tension and partial excess free energies of mixing of the components at the working temperature. We calculated the

density and surface tension for each of the components Al, Ga, Cd and In at the respective working temperature by using their temperature coefficients and the values at their respective melting temperatures in the following equations [20]:

$$\rho(T) = \rho_m + \frac{\partial \rho}{\partial T} (T - T_m) \quad (16)$$

$$\sigma(T) = \sigma_m + \frac{\partial \sigma}{\partial T} (T - T_m) \quad (17)$$

where T and T_m are respectively the temperature of investigation and melting temperature; and $\frac{\partial \rho}{\partial T}$ and $\frac{\partial \sigma}{\partial T}$ represent the temperature coefficient of density and temperature coefficient of surface tension for each component metal of the alloys.

The other parameter that is required for calculating surface tension is the interaction energy parameter, W. We have estimated the values of W separately for Al-Ga and Cd-In alloys by simultaneously fitting equations (5), (6) and (7) to the experimental data of free energy of mixing and chemical activities [16] of respective alloy throughout whole concentration range. Thus having numerical values of all the terms, surface concentrations of aluminium in Al-Ga alloy and cadmium in Cd-In alloy have been obtained separately as function of bulk concentration by concurrently solving the equations (1a) and (1b). In both cases surface concentrations of A-component of the Al-Ga and Cd-In alloys are found to increase with the increase in their bulk concentrations (Fig. 1 & Fig. 3). Due to a significant difference in the values of surface tension of component metals in the Al-Ga liquid alloy at 1023 K, the mixing shows strong segregation of the component with smaller surface tension at the surface and the other in the bulk. On the other hand, with very comparable values of the surface tension of the metals in Cd-In liquid alloy at 800 K, surface concentrations of components do not differ much from the bulk concentrations.

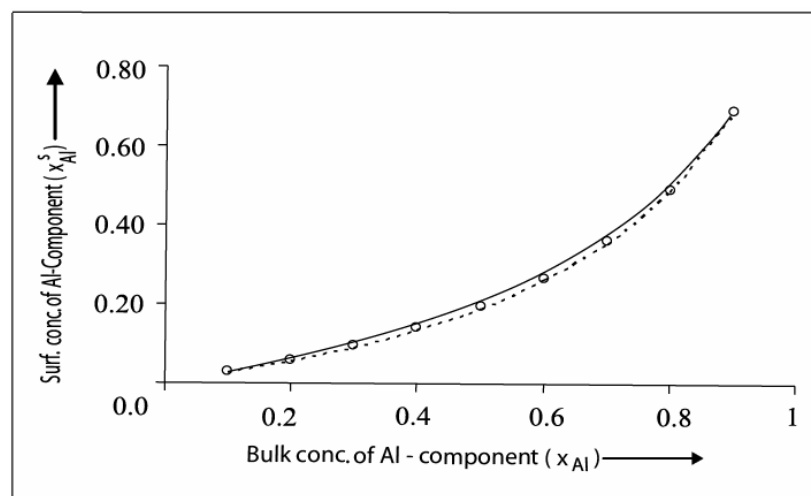


Fig. 1: Surface concentration versus bulk concentration of Al-component in Al-Ga alloy at 1023 K: Broken line -approach 1; Circles-approach 2; Solid line-approach 4.

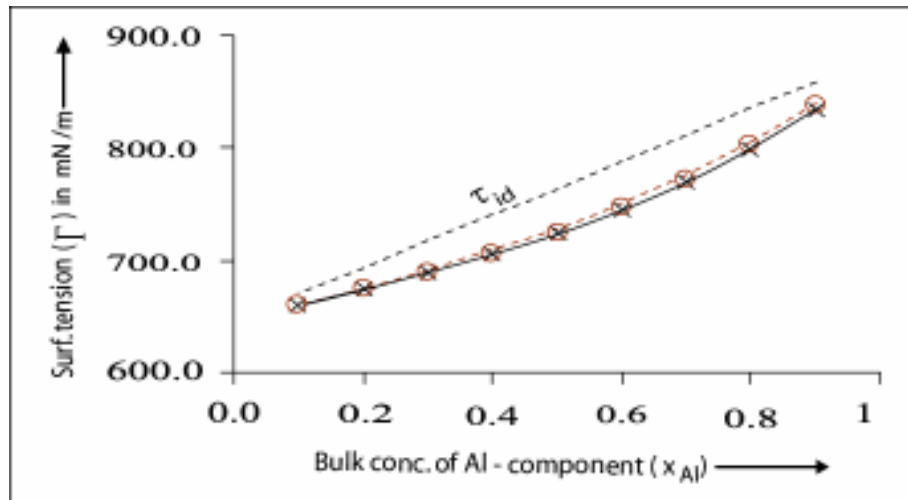


Fig. 2: Surface tension of Al-Ga alloy at 1023 K versus bulk concentration of Al-component: Crosses -approach 1; Circles-approach 2; Broken curve(Lower)-approach 3; Solid line-approach 4; Broken line (Upper)- Ideal.

Using the obtained values of surface concentrations, we computed the surface tensions of the Al-Ga and Cd-In liquid alloys at temperatures of 1023 K and 800 K respectively for whole concentration range. This approach predicts that the surface tension of Al-Ga alloy increases with increase in bulk concentration of aluminium part in the alloy (Fig. 2). In contrast, very small variation is noticed in the surface tension of the Cd-In alloy with the bulk concentration, through a flat peak around the equiatomic composition (Fig. 4). Further, it is noted that the computed values are found to be all smaller than the corresponding ideal values ($\Gamma_{id} = \Gamma_A x_A + \Gamma_B x_B$) in Al-Ga alloy but greater in Cd-In alloy (from first approach) even though both alloys are weakly segregating. However, the surface tension of the Cd-In alloy liquid alloy at 800 K is found to be less than the ideal values computed from the second approach. The sign and size of difference in the surface tension of alloy components A and B and the interaction energy parameter W together thus decide the concentration dependence of surface tension of the alloy.

3.2. Eqs. (8a) and (8b) were solved together for the surface concentration of component-A of both the alloys at all bulk concentrations by using their interaction energies obtained from the application of quasi-chemical approximation to the alloys separately. Surface tension and densities of the components calculated above from Eqs. (16) and (17) were used in solving the equations for surface concentrations. The surface concentration of Al in Al-Ga alloy at 1023 K have been found to be very nearly equal to those obtained from the above approach at the corresponding concentrations with nonlinear variation with bulk composition of Al-component. (Fig.1). However, in Cd-In alloy at 800 K surface concentration is found to vary almost linearly with bulk composition (Fig. 3). This approach predicts extremely matching result for the surface tension of Al-Ga system with the result of first approach, and for Cd-In system, the result shows very small variation in surface tension values (Fig. 2 & Fig. 4).

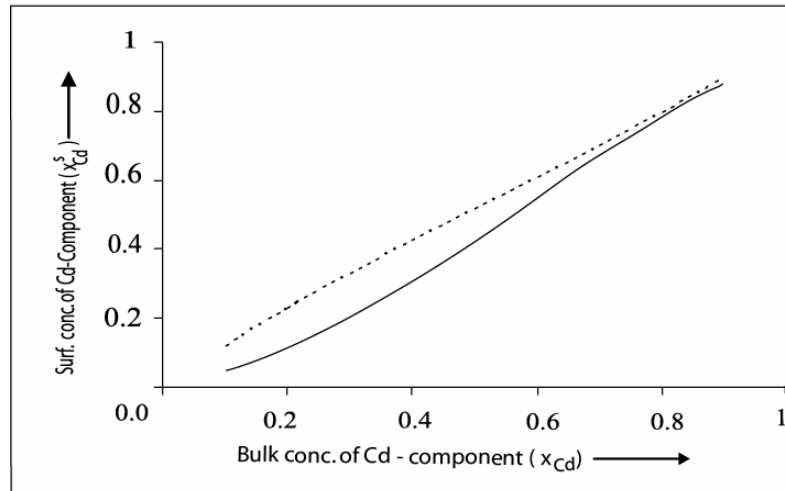


Fig. 3: Surface concentration of Cd-component versus bulk concentration in Cd-In alloy at 800 K : Solid curve -approach 1; Broken line-approach 2.

3.3. The concentration dependence of surface tension is studied by computing surface tensions for the alloys from Eq. (11). The surface tensions of Al-Ga are in extremely good agreement with the results of above mentioned approaches. The values of surface tension of Cd-In alloy calculated from this approach are found to lie between the results of the above two sections (3.1. & 3.2.) for whole concentration range; and are almost equal to the ideal values (Fig. 2 & Fig. 4).

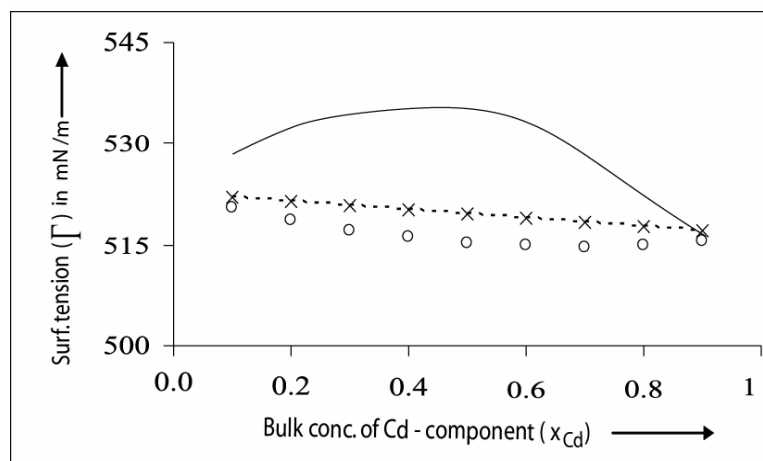


Fig. 4: Surface tension of Cd-In alloy at 800K versus bulk concentration of Cd-component: Solid curve - approach 1; Circles-approach 2; Crosses-approach 3; Broken line - Ideal.

It is to be noted that for alloys with component metals having large difference in their surface tension values, the theoretical models we are using, give well matching result for the surface properties. For alloys with metals having very comparable surface tensions, the values of surface tension predicted by different approaches are not matching so exactly.

3.4. Finally we employed Butler's model for the computation of surface concentration and surface tension of the Al-Ga alloy. The partial excess free energies of mixing of the pure components of the alloys at the temperature of investigation were taken from the ref. [16]. Both the surface concentration of A-component and the surface tension of the alloy are found to have nonlinear increment with the increasing bulk concentration (Fig. 1 & Fig. 2) as observed in the first two approaches.

We do not have experimental values of surface tension to compare our result. However, it is mentioned that the models which we have used in present work have been successfully used by several workers to compute the surface tension of metallic solution.

4. Conclusion

This theoretical study shows that the metal with lower surface tension tends to segregate on the surface of molten alloy while the metal with higher surface tension tends to segregate in the bulk. When there is a larger difference in surface tension between the solvent and solute, the segregating behaviour of the component is more significant. In Al-Ga system at 1023 K, there is consistency in the values of surface tension obtained from different approaches, with small negative deviations from ideality whereas in Cd-In system at 800 K, such consistency is not observed in the computed values of the surface tension.

Acknowledgements

We are grateful to Prof. Dr. L.N. Jha (Head, Central Department of Physics, T.U., Nepal), Prof. Dr. Pradeep Raj Pradhan and Dr. I.S. Jha (Post-Graduate Department of Physics, M.M.A.M. Campus, Biratnagar, Nepal) for fruitful suggestions and inspiring discussions.

References

- [1] B.C. Anusionwu, C. A. Madhu, C. E. Orji, *Physics*, 72 (2009) 951.
- [2] Woodall Jerry, M.; Ziebach, Jeffrey; Allen Charles R., *The science and technology of Al-Ga alloys as a material for energy storage, transport and splitting water*, Proc. of 2nd Energy Nanotechnology International Conference, ENIC, (2007) 45014.
- [3] George L. Schnable, John G. Javes, *J. Electrochem. Soc.*, 105 (1958) 84.
- [4] L.C. Prasad, R.N. Singh, G.P. Singh, *Phys. Chem. Liq.*, 27 (1994) 179.
- [5] R. Novakovic, *J. Non-Cryst. Solids*, 356 (2010) 1593.
- [6] N.H. March and J.A. Alonso, *Phys. Chem. of Liq.*, 46 (2008) 522.
- [7] J.A. Butler, *Proc. Roy. Soc. A*, 135 (1932) 348.
- [8] D. Adhikari, I.S. Jha, B.P. Singh, *Adv. Mat. Lett.*, 3 (2012) 226.
- [9] R. Novakovic, E. Ricci, D. Giuranno, F. Gnecco, *Surface Science*, 515 (2002) 377.
- [10] B.P. Singh, D. Adhikari, I.S. Jha, B.C. Kumar, S.K. Chaudhary, S.K. Jayaswal, R.P. Koirala, *BIBECHANA*, 8 (2012) 81.
- [11] D. Adhikari, B.P. Singh, I.S. Jha, *J. Molecular Liquids*, 167C (2012) 52.
- [12] B. P. Singh, D. Adhikari, I.S. Jha, J. Kumar, R. P. Koirala, *Materials Sciences and Applications*, 2 (2011) 1139.
- [13] R.N. Singh, F. Sommer, *Rep. Prog. Phys.*, 60 (1997) 57.
- [14] B.P. Singh, D. Adhikari, I.S. Jha, B.K. Singh, *BIBECHANA*, 7 (2011) 1.
- [15] D. Adhikari, *Physica B*, 406 (2011) 445.
- [16] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, and K.K. Kelly, *Selected Values of the Thermodynamic Properties of Binary Alloys*, ASM, Metal Park (1973).

- [17] E.A. Guggenheim, *Mixtures*, Oxford University Press, London (1952).
- [18] J. Lee, W. Shimoda, T. Tanaka, *Materials Transactions*, 45 (2004) 2864.
- [19] T.P. Hoar, D.A. Melford, *Trans. Faraday Soc.*, 53 (1957) 315.
- [20] Brandes, *Smithells Metals Reference Book*, Sixth Edition, (1983), Sec. 14-6.