THEORETICAL DETERMINATION OF SOME THERMODYNAMIC PROPERTIES OF SELECTED BINARY LIQUID ALLOYS

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THEORETICAL DETERMINATION OF SOME THERMODYNAMIC PROPERTIES OF SELECTED BINARY LIQUID ALLOYS

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CERTIFICATION

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DEDICATION

This work is dedicated to Madam (Mrs) D. O. Ogunsanya (Grandma) and her children.

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LIST OF SYMBOLS

Except otherwise specified the following symbols used in this thesis are as define below:

Symbols	**Quantity**
A, B	Components of a binary A-B alloys
$a_i(i = A, B)$	Activity of component i
$C_i(i = A, B)$	Composition of component i (where $c_A + c_B = 1$)
D_M	Inter-diffusion coefficient of any binary alloy
D_{id}	Intrinsic diffusion coefficient for an ideal mixture
D_i	Self-diffusion coefficient of component i
E	Configurational energy of the bulk
G_M	Gibbs free energy of mixing
G_M^{XS}	Excess Gibbs free energy of mixing
H_M	Enthalpy of mixing
k_B	Boltzmann's conctant
N_A,N_B	Number of atoms of components A and B
N	Total number of atoms
N_A	Avogagro's number
$P_{ij}(i, j = A, B)$	Probability of finding one of the components of the i-j bond as a part of the complex $A_\mu B_\nu$
$q_i^{N_i}(T)(i = A, B)$	Atomic partition function of component i for the bulk
R	Gas constant
S_M	Entropy of mixing
$S_{cc}(0)$	Concentration-concentration fluctuations in long-wavelength limits
$S_{cc}^{id}(0)$	Concentration fluctuations for the ideal mixing condition
$S_{cc}(q)$	Concentration-concentration structure factor
$S_{NN}(q)$	Number-Number structure factor
T	Absolute temperature

$V_i(i = A, B)$	Atomic volume of the component i
Z	Coordination number
α_1	Short-range order parameter
γ	Ratio of activity coefficients of A and B components
$\gamma_i(i = A, B)$	Activity coefficient of component i
η	Viscosity
ϵ_{ij}	Energy of i-j bond for regular solution
$\Delta\epsilon_{ij}$	Difference in the energy of an i-j bond when one of the bond forming component is present in the compound $A_\mu B_\nu$
μ, ν	Stoichiometric coefficients
$\mu_i(i = A, B)$	Chemical potential of component i
$\Omega_i(i = A, B)$	Atomic volume of the component i
ω	Order or interchange energy parameter
Ξ	Grand partition function for the bulk

LIST OF ABBREVIATIONS

CFM	Complex Formation Model
CSRO	Chemical Short Range Order
FACM	Four Atom Cluster Model
FT	Fourier Transform
HOCP	Higher Order Conditional Probability
MIVM	Molecular Interaction Volume Model
RASM	Regular Associated Solution Model
SAM	Self Association Model
TACM	Two Atom Cluster Model
QCM	Quasi Chemical Model
QCAM	Quasi Chemical Approximation Model
QLM	Quasi Lattice Model
QLT	Quasi Lattice Theory
WIAM	Weak Interaction Approximation Model

ABSTRACT

Binary liquid alloys have found wide applications in electronics, communications, automotive and aerospace technologies. The development of new alloys and improvement of existing ones require accurate knowledge of thermodynamic variables of the constituent systems which may not be obtainable experimentally. Hence, there is always the need for theoretical investigation to complement experiment. This study was aimed at theoretical determination of the thermodynamic properties of nine binary liquid alloys.

Nine liquid alloys (Al-Zn, Bi-In, Ga-Zn, Ga-Mg, Al-Ga, Sb-Sn, In-Pb, Ga-Tl and Al-Si) with insufficient theoretical investigation were selected for investigation using three different models. Quasi-lattice theory which connects thermodynamic and dynamical properties was employed to determine the concentration-concentration fluctuation in the long-wavelength limit [$S_{cc}(0)$], chemical short range order parameter (α_1), free energy of mixing (G_M), the concentration dependence of diffusion and viscosity of Al-Zn and Bi-In liquid alloys. Quasi-chemical approximation model for strongly interacting systems was used to investigate ordering and glass formation tendencies in Ga-Zn, Ga-Mg and Al-Ga binary alloys. A statistical thermodynamic theory was used to determine the mixing properties of Sb-Sn, In-Pb, Ga-Tl and Al-Si liquid alloys. The choice of model was influenced by the type of available experimental data.

The $S_{cc}(0)$ and α_1 showed that a reasonable degree of chemical order existed in Bi-In system, while Al-Zn liquid alloys exhibited a liquid miscibility gap or phase separation at all concentrations. The values of free energy of mixing at the equiatomic composition were -0.4986RT and -0.9344RT for Al-Zn and Bi-In alloys respectively. The free energy of mixing of Ga-Zn, Al-Ga and Ga-Mg alloys are almost symmetrical around the equiatomic composition with Ga-Mg being the most interacting, while Al-Ga is more interacting than Ga-Zn alloy. Apart from Ga-Mg alloys with negative enthalpy of mixing, both the enthalpy of mixing and entropy of mixing of the three Ga-based systems are positive and symmetrical about the equiatomic composition. In the concentration range $0 \leq c_{Al} \leq 0.3$ and $0.7 \leq c_{Al} \leq 1$, Al-Ga systems exhibited a glass-forming potential. The free energy of mixing, enthalpy of mixing and entropy of mixing of Sb-Sn and Al-Si liquid alloys exhibited negative deviations from ideality and were symmetric around the equiatomic composition, while In-Pb and Ga-Tl systems exhibited positive deviations with Ga-Tl alloys showing asymmetry behaviour.

The compound formation in liquid phase was weaker in Al-Zn than in Bi-In alloys. The Sb-Sn and Al-Si liquid alloys had tendency for heterocoordination, while In-Pb and Ga-Tl exhibited homocoodination. The Ga-Zn and Al-Ga alloys exhibited homocoordination, whereas Ga-Mg alloys had tendency towards heterocoodination.

Keywords: Binary liquid alloys, Phase separation, Concentration-concentration fluctuations, Short range order

Word Counts: 415

Chapter 1

Introduction

1.1 Background to the research

Understanding the properties of liquid alloys is really a matter of interest in the field of liquid science mainly because most of the binary solid alloys are formed by cooling from their respective liquid state. The properties of liquid alloys provide some unique information that can improve the processing and qualities of materials in the solid state. Recent advancement in the use of liquid alloys and their composites in high temperature applications in many diverse fields call for better understanding of the thermodynamic and dynamical properties of alloys in the liquid state to aid the development of new alloys, improving the existing ones and characterizing the glassy solids (Anusionwu and Adebayo, 2001; M*ü*ller, 2003; Novakovic et al., 2003, 2004) and (Novakovic and Takana, 2006).

Though our daily experience testifies to the classification of three different classical phases of matter: solid, liquid and gas or vapour (other phases of matter include plasma and superfluid). Solids are rigid, and when studied by diffraction experiment give rise to sharp Bragg reflections. This is the hall-mark of crystallinity: an ordered array of the building blocks, be they atoms or groups of atoms. Diffraction experiments have shown that liquids in general and metallic liquids in particular exhibit some kind of short-range order (SRO), that is, absence of long-range order, demonstrating that there is no long-range structural order among the atoms or molecules (Singh and March, 1995; *Müller*, 2003).

However, a very characteristic property of liquids and gases is that they have low viscosity and are thereby endowed with fluidity. In spite of our understanding of solid state of matter, the qualitative distinction drawn from diffraction experiments between solid and liquid does not carry through to distinguish liquid and vapour. The physical principles underlying the solid-liquid or liquid-vapour phase transformations are not fully understood. Due to the non-existence of exact liquid state theory, the understanding of the solid phases have served as guidelines to characterize the structural behaviour of respective liquids and vapour. Their characteristic behaviour is usually ascribed to an outcome of the interplay of the energetic and structural readjustment of the constituent elemental atoms that hold the system together, yet our present knowledge provides no clear-cut message as to the ways the structure and forces are coupled (Singh and March, 1995).

Modelling the thermodynamic, structural and surface properties of liquid binary alloys and liquid metals require the data regarding their structures and the relevant forces that quantify the interatomic interactions (i.e. the energetics of systems). This is why understanding the mixing behaviour of two elemental metals forming a binary alloy has engaged the attention of many physicists, chemists, and metallurgists (Bhatia and March, 1975; Singh, 1987; Alblas et al., 1982; McGreevy and Pusztai, 1988; Singh and March, 1995; Singh and Sommer, 1997; Kaban et al., 2003; Dubinin, 2003; Novakovic et al., 2004; Anusionwu, 2006; Awe et al., 2005).

A number of different theoretical approaches have been proposed and used to study the thermodynamic and structural properties of these systems. Some of these models include the Quasi-lattice approximation (Guggenheim, 1952), the electron theory (Ashcroft and Stroud, 1978), the Bhatia and Hargrove formalism (1974) which was later reformulated in Bhatia and Singh (1984) and the *ab-initio* methods (Jank and Hafner, 1988; Dalgic et al., 1998) which involve the calculations of thermodynamic quantities using the pseudopotential formalism. The first one is based on simple theoretical model that makes it possible to express the energetics of a system in terms of the interaction parameters reproducing its thermodynamic properties as well as to explain the ordering and phase separation phenomena in liquid binary alloys. Consequently, the thermophysical properties, as surface tension, viscosity and chemical diffusion (Bhatia and Hargrove, 1974; Prasad et al., 1998; Jha and Mishra, 2001; Novakovic et al., 2002 and Awe et al., 2006) can then be described.

The mixing behaviour of two metals forming binary alloys is the result of the interplay of energetic and structural readjustment of the constituent atoms. On mixing, A and B atoms can prefer to remain self-coordinated forming A-A or B-B pairs, or can exhibit a strong interactive tendency between unlike atoms forming heterocoordinated A-B pairs. Based on this, all liquid binary alloys can be classified according to deviations of their thermodynamic and thermophysical properties from the additive rule of mixing (Raoult's law) into two main categories: segregation (positive deviation) or short-range ordered (negative deviation) alloys (Bhatia and Hargrove, 1974; Sommer, 1982; Bhatia and Singh, 1984; Singh and Singh,1995; Singh and Sommer, 1997; Prasad et al., 1998).

However, there are some liquid alloys which do not belong exclusively to any of the above two categories. For example, the excess Gibbs energy of mixing G_M^{XS} for Ag-Ge and Cd-Na is negative at certain compositions, while positive at other compositions (Singh and Sommer, 1997). Also in liquid alloys such as Au-Bi, Bi-Cd and Bi-Sb, the enthalpy of mixing (H_M) is a positive quantity but G_M^{XS} is negative (Singh and Sommer, 1997). Bi-Pb has positive H_M and G_M^{XS} in the solid phase as against the negative values of H_M and G_M^{XS} in the liquid phase. In addition, systems such as Au-Ni and Cr-Mo exhibit immiscibility in the solid phase which is not evidently visible in the corresponding liquid phase. While alloys such as Ag-Te show intermetallic phases and large negative H_M values in the liquid phase together with a liquid miscibility gap (Singh and Sommer, 1997).

It is of interest to note that many binary liquid alloys such as Al-Bi, Al-In, Al-Pb, Ga-Pb, Ga-Hg, Pb-Zn and Cu-Pb exhibit characteristic features as function of concentration based on their thermodynamic properties like free energy of mixing, enthalpy of mixing, entropy of mixing (Hultgren et al, 1973) and many other electrical properties (Heine, 1970) and (Busch and Guntnerodt, 1974). They are characterized by liquid miscibility gaps and exhibit large positive H_M (Singh and Sommer, 1997). Their properties in the liquid phase tend to change markedly as a function of composition (c), temperature (T) and pressure (P). The liquidus lines for these systems are complicated and usually S-shaped while their enthalpy of mixing and excess free energy of mixing are large negative quantities at one or more concentrations (Anusionwu, 2006). The understanding of such anomalous behaviour of liquid alloys as functions of concentration is still a great challenge and demands extensive theoretical investigation.

In addition, the development of new alloys and improvement of existing ones require accurate knowledge of thermodynamic variables of the constituent systems due to their scientific and technological applications in electronics, communications, medical science, automotive and aerospace technologies. For instance, for many years the traditional silver solders have been used in joining ceramics and glasses with metallic materials (Eustathopoulos et al., 1999). Other examples are silver based alloys containing the additions of the group IV transition metals, Ti, Zr and Hf. Ti-based alloys are principally used in aircraft, spacecraft, naval ships and medicine as reported by Ratner et al.,(1996) and Novakovic and Zivkovic (2005). Hf and its alloys are constituents or subsystems of complex metallic glasses (Saida and Inoue, 2003), superconducting alloys (Novakovic and Zivkovic, 2005) or are used in nuclear propulsion (Frost, 1981). Many properties of Cu-Zr and Cu-Si liquid alloys have been studied by many researchers (Akinlade et al., 1998; Anusionwu and Adebayo, 2001) due to their manifest behaviours and their potential usefulness in technological applications.

It may therefore be necessary that a detail theoretical and thorough understanding of the structural readjustment and energetic preferences of atoms in binary liquid metallic systems go beyond the knowledge of the empirical metallurgical constructs to explain the characteristic behaviours. Advances in these areas have been made possible due to the combination of a number of simple theoretical approaches or models to discuss the deviations and the anomalies in terms of heterocoordination or self-coordination species that might exist in liquid and vapour.

The foremost task in this work is to put together the various experimental and theoretical information with a view to establishing a respectable understanding between experimental results, theoretical approaches and empirical models via a theoretical determination of some thermodynamic properties of nine binary liquid alloys. Binary liquid Ga-Tl and Al-Si alloys whose experimental data were recently published Ga-Tl (Katayama et al.,(2003) and Al-Si (Kostov et al.,2007) and seven others (Al-Zn, Bi-In, Ga-Zn, Ga-Ma, Al-Ga, Sb-Sn and In-Pb) from Hultgren et al,(1973) with insufficient theoretical investigation, thus forming the basis to evaluate the energetics of the systems and the driving forces behind the anomalous behaviour in binary liquid alloys.

1.2 Aim and Objectives of this work

The aim of this study is to theoretically determine some thermodynamic properties of selected liquid binary alloys while the objectives of the thesis are summarized as follows:

1. determine the thermodynamics and microscopic structural properties of binary liquid Al-Zn, Bi-In, Ga-Zn, Ga-Mg, Al-Ga, Sb-Sn and In-Pb alloys at different temperatures.

2. evaluate the phase separation and compound forming tendencies in the liquid alloys for a proper understanding of the anomalous behaviour in liquid alloys.

3. extract useful microscopic information on the energetics of formation in binary liquid alloys.

4. carry out a theoretical determination of mixing properties and activities of

binary liquid Sb-Sn, In-Pb, Ga-Tl and Al-Si alloys using a statistical thermodynamic theory.

5. evaluate existing thermodynamic data related to the peculiarities of the atomic size.

6. show that thermodynamic data obtained could serve as a basis for comparison with some future critical experimental works.

The properties of some relevant parameters of constituents pure metals which will be used in the present work are listed in table 1.1.

1.3 Outline of Thesis

The thesis is composed of five chapters. The present chapter introduces the main theme of the research. Chapter 2 reviews the relevant literatures on thermodynamics and its consequences. Methodology in chapter 3 along with introductions and the theoretical basis of each of the models used in this study. The Quasi-Lattice Theory of liquid mixtures relating two dynamic properties such as diffusion coefficient and viscosity with thermodynamic properties used in the study of Al-Zn and Bi-In liquid alloys is presented in section 3.1. The theoretical basis of the Quasi-Chemical Approximation Model (QCAM) in determining the probable existence of chemical ordering and glass formation tendencies in binary liquid Ga-Zn, Ga-Mg and Al-Ga alloys is given in section 3.2. The Four Atom Cluster Model (FACM) used to study liquid Sb-Sn and Bi-Pb alloys follows in section 3.3. The theoretical formulation of an approach for determination of the mixing properties and activities of liquid binary Sb-Sn, In-Pb, Ga-Tl and Al-Si alloys using a statistical thermodynamic theory is given section 3.4. While, results and discussion for various thermodynamic models used are given in chapter 4. And finally in chapter 5, conclusions and recommendations on the possible future research prospects realized from this study along with contributions to body of knowledge are given.

Table 1.1: Table showing melting points, boiling points and atomic volume of some elements.

		Melting point*	Boiling point*	Atomic Volume$^+$
Elements	Symbols	T$_m(K)$	T$_b(K)$	V$_m(10^{-6}m^3g.atom^{-1})$
Aluminium	Al	933.35	2333.15	10.00
Antimony	Sb	903.00	1913.15	18.19
Bismuth	Bi	544.05	1833.15	21.31
Cobalt	Co	1768.05	3458.15	6.67
Cadmium	Cd	594.05	1039.15	13.00
Casium	Ca	1124715	1513.15	26.20
Copper	Cu	1356.15	2903.15	7.11
Gallium	Ga	302.93	2573.15	11.80
Iron	Fe	1808.15	3003.15	7.09
Lead	Pb	600.55	2033.15	18.26
Magnesium	Mg	923.15	1380.15	14.00
Mercury	Hg	234.28	629.73	14.09
Nickel	Ni	1728.15	3448.15	6.59
Silicon	Si	1687.15	2608.15	9.80
Sodium	Na	378.05	1150.65	23.78
Tin	Sn	504.79	2548.15	16.29
Thallium	Tl	575.65	1730.15	18.62
Zinc	Zn	692.62	1203.15	9.16

For instance, Liquid range = T_b - T_m (Iida and Guthrie, 1993)

e.g. the liquid range for Al = 1400K, Ga = 2270K

$*$ Iida and Guthrie, (1993); + Singman, (1984)

Chapter 2

Literature Review

2.1 Study techniques for binary liquid alloys

The alloying behaviour of binary liquid alloys can be studied using two distinct theories. The electron theory of mixing and statistical mechanical theory of mixing. According to the first theory a liquid alloy is assumed to consist of a system of ions and electrons. The problem, usually, in this approach is tackled through the use of pseudo-potential theory (Harrison, 1966; Heine, 1970; Busch and Guntnerodt, 1974; Thakur et al., 2005; Kanth and Chakrabarti, 2009) and hard sphere model which had been used by Faber (1972) and Shimoji (1977). The major drawback of the approach is that it cannot be used to obtain information regarding the concentration fluctuations in the long wavelength limit $S_{cc}(0)$, an important thermodynamic function which determines the stability of alloys. The approach is also computationally demanding and has several limitations in situations where there is formation of chemical complexes (Akinlade, 1994).

The second theory also known as thermodynamic model approach is a very useful tool to study the behaviour of liquids and liquid mixtures. It involves the use of analytical solutions of liquid state equations based on some approximations. It has been used to obtain analytical expressions for various thermodynamic functions that are not possible otherwise and proved useful for qualitative description of thermodynamic and microscopic structural properties of binary liquid alloys. The conformal solution model has been used to study $S_{cc}(0)$ of different binary alloys (Bhatia and Hargrove, 1974; Alonso and March, 1990; Thakur et al., 2005). But the model cannot be used to study the short-range order parameters. The Quasi-chemical theory of Guggenheim (1952) is successful in studying the chemical short-range order parameters of binary liquid alloys, but cannot be used to explain the observed asymmetry in the properties of mixing as a function of concentration. In order to overcome the identified shortcomings of the models, a number of theoretical models have been established by theoreticians within the framework of statistical mechanical theory of mixing to explain the energetics of liquid alloys and the various concentration dependence thermodynamic properties based on the deviations from ideality in terms of heterocoordination or homocoordination species that might exist in liquid and vapour phases.

Some of the established thermodynamic models include: the Quasi Lattice Model(QLM), the Quasi-Chemical Approximation Model(QACM); the Self- Association Model(SAM) in demixing liquid alloys and vapour species; the Complex Formation Model (CFM) in liquid binary alloys; the Four-Atom-Cluster Model FACM), the Regular Associated-Solution Model(RASM) and the Weak Interaction Approximation Model (WIAM)(Singh and March, 1995).

Thermodynamic and thermophysical data of alloys play an important role in the present production processes and design of reliable materials for high temperature applications but due to experimental difficulties they have not been successfully measured well above and well below the melting temperature (Novakovic et al., 2005). Experimental investigation of the thermodynamic properties of binary liquid alloys and higher component systems is a rather difficult, time consuming and very expensive endeavour. The main reason for the experimental difficulties are:

1. high investigating temperature required,
2. high melting points and their strong chemical affinity for oxygen, in pure states or alloyed form, and
3. difficulties of making experimental measurements over a wide range of

temperature well above and below the melting temperatures with high precision.

It is anticipated that most of the thermodynamic data on binary and multi-component systems will come from theoretical calculations, rather than from direct experimentation. Therefore, theoretical calculation is an indispensable and effective approach to obtaining thermodynamic data for alloy of interest from some other data available on that system. In this regards, researchers have been motivated to develop different models to solve the difficulties and complexities of obtaining thermodynamic quantities such as activity, free energy of mixing, enthalpy of mixing, entropy of mixing as well as thermophysical quantities like diffusion and viscosity of many binary liquid alloys by experiments. However, these models are rarely valid (Chen et al., 2002) over the whole concentration ranges for real liquid and solid metallic solutions. For instance, extensive description of the hard sphere model to calculate the entropy of mixing of binary liquid alloys have been reported by Hoshino and Young (1981); Visser et al.,(1980) and Alblas et al., (1982), but the model could not explain thermodynamic properties of systems with chemical short-range order (Pettifor, 1993) and (Dalgic et al., 1998). The Melting point depression method (Chou and Wang, 1987) was used for simple eutectic systems based on two approximations: the regular solution model of Hildebrand and Scott, (1950) and the melting enthalpy of component is assumed to be temperature independent. The approximation dealing with regular behaviour was found to cause great errors in calculated activity values. Arising from this, in 1990, Chou developed a new method based on Rao-Belton method (Rao and Belton, 1981) and Richardson assumption (Richardson, 1974) to calculate thermodynamic properties of binary liquid alloys based on their known phase diagram. Sommer and Lee used two different models, an association model(Sommer et al., 1983) and the Miedema model(Godbole et al., 2004) to study thermodynamic properties of aluminum-calcium, aluminum-Strontium, aluminum-nickel and calcium-nickel as well as calculated the liquid phase enthalpy of mixing of liquid copper-magnesium alloys. Takana and Gokcen (1995) derived a statistical thermodynamic solution model based on the free volume theory that each atom moves in a liquid metal within a restricted region in a cell made by its nearest-neighbour atoms. Empirical relation for estimation of entropy of mixing of liquid alloys was proposed by Witusiewicz and Sommer (2000) on the basis of experimental enthalpy of mixing data at constant temperature. The molecular interaction volume model (MIVM) which is a two-parameter model proposed by Tao (2000; 2003) was able to predict some component activities of liquid alloys and solid solution by using only the partial molar mixing enthalpies and the coordination numbers of the constituent elements in liquid alloys. This model has been used (Tao et al., 2002; Yang et al., 2008, 2009) for prediction of the mixing enthalpies of 23 binary liquid alloys. Whereas, Iwata et al.,(2003) predicted thermodynamic properties, including activity coefficients and the interaction parameters of the solute elements in infinite dilute Si solutions, by the use of first-principles calculations based on density functional theory.

In addition, Chen and co-workers (2002) derived a statistical thermodynamic solution model based on the free volume theory. Their main aim was to calculate the excess entropy and excess Gibbs free energy in solid binary alloys through the experimental results of enthalpy of mixing. However, for successful application of the model the experimental results of mixing enthalpy should be known for different concentration ranges, otherwise the calculation cannot be carried out.

Broadly speaking, the main problems associated with all the present models on liquid alloys are as follows: In a general way, the excess entropy was not accounted for or taken into consideration in the models formulations (Chen et al., 2002). The regular solution model proposed by Hildebrand and Scott (1950) and the sub-regular solution model proposed by Hardy (1953), also had not taken the problem of excess entropy $S_{ij}^{E} \neq 0$ into consideration. The S_{ij}^{E} does not equal to zero in some molten solutions. It can be either positive or negative, mainly because the mixing of two components can not be completely random. In order to overcome this problem, Lupis and Elliott (1967) proposed the sub-regular solution model in which S_{ij}^{E} is directly proportional to ΔH. And, Guggenheim (1976) proposed the solution model of standard chemical theory and provided the expression of excess free energy for binary systems. Though these models have physical background in some degree, they still however depend on the experimental data.

It is thus obvious, that each of the proposed thermodynamic model requires inputs from thermodynamic measurements such as order energy or activity coefficients for the determination of the various thermodynamic properties and the models fail to make accurate prediction for liquid alloys over a wide range of concentration and temperature with high precision. Thus underlining the importance of investigations of thermodynamic studies for binary liquid alloys in the framework of theoretical investigation. Therefore, a good, economic and effective method for obtaining thermodynamic data from the theories or from thermodynamic models for binary liquid alloys without experimental values as input becomes a great necessity.

In this study, using a statistical thermodynamic theory within the framework of Flory model (1942), an improved calculation method for obtaining the mixing properties and activities of binary liquid alloys based only on analytical expressions have been introduced (in chapter 3.4) without recourse to experimental data as input. The approach is capable of determining and evaluating the mixing properties and activities of components in binary liquid alloys. It is also a very useful approach to cut down the cost and time for the development of new alloys because the conventional alloy development has been primarily based on experimental approach and is frequently performed by trial and error methods (Liu and Fan, 2002). Such experimental approach to alloy design is cost intensive and time consuming. The thermodynamic data obtained using the analytical expressions are compared with the experimental data and the results obtained are found to be in satisfactory agreement with experimental values. Thus suggesting that the approach is reliable, convenient and economic and has a good physical basis.

2.2 Observable thermodynamic indicators

2.2.1 Structure factors S(q) of Liquid

The structure factor $S(q)$ of liquid is one of the most important properties to study the various electronic, magnetic, static and dynamic properties of a material in liquid states (Thakor et al., 2002). It is a measure of particle correlations in the reciprocal space. The liquid structure factor $S(q)$ is related to $I(q)$ as

$$S(q) = \frac{I(q)}{Nf^2} \tag{2.1}$$

where $I(q)$ is the intensity of the scattered radiation (say neutron or X-ray) is measured as a function of scattering angle, N is the number of scattering points and f is the atomic scattering factor, $q = 4\pi sin\theta/\lambda$, 2θ is the scattering angle and λ is the wavelength of the radiation.

The physical significance of $S(q)$ is defined in terms of the pair distribution function $g(r)$ of a liquid with density ρ (Ganesh and Widom, 2006), which measures the probability of finding an atom at a distance r from the origin (r=0)

$$S(q) = 1 + 4\pi\rho \int_0^\infty [g(r) - 1] \frac{sin(qr)}{qr} r^2 dr \tag{2.2}$$

Evidently, one needs a knowledge of the radial distribution function up to large values of r to get a good $S(q)$. $g(r)$ and $S(q)$ both oscillate between 0 and 1. Besides providing the information regarding the distribution of atoms, $g(r)$ can be utilized to determine the coordination number, z, for the first coordination shell,

$$z = \int 4\pi r^2 \rho g(r) dr \tag{2.3}$$

The limit of integration can be chosen to vary from zero to the distance where $g(r)$ exhibits the first minimum.

According to Bhatia and Thornton (1970), the concentration-concentration fluctuations $S_{cc}(q)$ for a binary mixture at $q = 0$ (long wavelength) may be expressed as

$$S_{cc}(0) = N\langle(\Delta c)^2\rangle \tag{2.4}$$

where $\langle(\Delta c)^2\rangle$ represents the mean square fluctuations in the concentration and are readily derived from statistical mechanics in terms of the Gibbs free energy G, i.e.

$$S_{cc}(0) = \frac{NK_BT}{(\partial^2 G/\partial c_A^2)_{T,P,N}} \tag{2.5}$$

For a binary mixture consisting of $N_A = Nc_A$ and $N_B = Nc_B$)g moles of A and B atoms where $c_A + c_B = 1$, G may be expressed as

$$G = N[c_A G_A^0 + c_B G_B^0] + G_M \tag{2.6}$$

with G_A^0 and G_B^0 being the Gibbs free energies per atom of the species A and B, respectively. G_M is the free energy of mixing. In view of equation (2.6), $S_{cc}(0)$ becomes

$$\begin{aligned} S_{cc}(0) &= \frac{NK_BT}{(\partial^2 G_M/\partial c_A^2)_{T,P,N}} \\ &= \frac{a_A c_B}{(\partial a_A/\partial c_A)_{T,P,N}} \\ &= \frac{c_A a_B}{\partial a_B/\partial c_B}_{T,P,N} \end{aligned} \tag{2.7}$$

where a_A and a_B are the thermodynamic activities of components A and B in the mixture. It should be pointed out the $(\partial^2 G/\partial c_A^2)$ is also known as the stability of the solution, which was originally introduced by Darken (1967) (Singh and March, 1995). Thus, the reciprocal of $S_{cc}(0)$, i.e. $NK_BT/S_{cc}(0)$, is a measure of the stability of the mixture. The $S_{cc}(0)$ is directly related to the excess stability function by the equation

$$E^{xs} = \left(\frac{\partial^2 G_M^{xs}}{\partial c_A)^2}\right) \quad = RT\left(\frac{1}{S_{cc}(0)} - \frac{1}{c_A c_B}\right) \tag{2.8}$$

For ideal solutions, $G_M = RT\sum_i c_i \ln c_i$, and $S_{cc}(0)$ and E^{xs} become

$$S_{cc}^{id}(0) = c_A c_B; \qquad E^{XS} = 0 \tag{2.9}$$

It is obvious from equation (2.7) that $S_{cc}(0)$ can be determined directly from the measured activity data or from the Gibbs free energy of mixing. In the literature, this is usually referred to as an experimental $S_{cc}(0)$. It should pointed out that such a numerical differentiation is very sensitive, in particular around the critical region when activity and G_M start to flatten (Singh and Sommer, 1997). However, a direct measurement of $\partial a_A/\partial c_A$, for instance, with the help of electromotive force (emf) measurements, can be a suitable experimental basis for the calculation of $S_{cc}(0)$ as reported by Singh and Sommer (1997).

2.2.2 Small-angle scattering experiment

In principle, the long wavelength limit of the structural factors $S_{cc}(0)$ can be determined from the small-angle scattering experiments either by using neutron or x-ray as sources of radiation for extracting structural information from liquid metals and liquid alloys, but it poses a much more experimental problem that has never been successfully solved. As such, there is no direct information on $S_{cc}(0)$ from the diffraction experiments, although it can be determined directly from the measured activity data or measured free energy of mixing data as earlier mentioned.

Owning to experimental difficulties, theoretical determination of $S_{cc}(0)$ is of great importance to anyone trying to visualize the nature of atomic interactions in the mixture, particularly if the region of interest is of the order of atomic dimensions. The mixing behaviour of liquid binary alloys can be deduced from the deviation of $S_{cc}(0)$ from the ideal value $S_{cc}^{id}(0)$. If, at a given composition, $S_{cc}(0)>S_{cc}^{id}(0)$, then there is a tendency for segregation (preference for like atoms to pair as nearest neighbours); while $S_{cc}(0)<S_{cc}^{id}(0)$ is an indicator of heterocoordination (preference for unlike atoms to pair as nearest neighbour). The latter is often interpreted as a signature of chemical short-range order or existence of chemical complexes.

For strongly interacting liquid alloys, $G_M \simeq$ - 3RT, $S_{cc}(0)$ is much less than $S_{cc}^{id}(0)$ and exhibits a dip around a particular stoichiometric composition. The position of the dip in the $S_{cc}(0)$-c curve usually yields information on the stoichiometric composition of the probable chemical complexes in liquid binary alloys, and its depth signifies the strength of the interaction (Singh and March, 1995).

Since its inception by Bhatia and Thornton (1970), the long-wavelength limit of concentration fluctuations, $S_{cc}(0)$ has been widely used (Wagner, 1985; Singh, 1987) to study the nature of atomic order in binary liquid alloys. The effect of temperature on $S_{cc}(0)$ is also of particular interest and is visibly dominant in the region of segregation rather than the heterocoodination region where stability is maximum. It decreases fast in the segregation region whereas in the heterocoodination region it increases slightly with increasing temperature (Singh and Sommer, 1992; Singh and March, 1995).

2.2.3 Segregating liquid alloys

From the point of view of interatomic interactions, a binary liquid alloy is either (i) ordered alloy, where unlike atoms are preferred as nearest neighbours over like atoms, or (ii) a segregated alloy, where like atoms are preferred to pair as nearest neighbours over unlike atoms, as earlier classified in section 1. Up till now surprisingly, there is no direct ways of identifying the different components of elemental atoms and, consequently the identification of a nearest-neighbour pair of atoms is a very difficult task. In this circumstance, it is either we resort to the structural data or the observed thermodynamic quantities or other thermophysical properties (like viscosity, chemical diffusion, density, surface tension, electrical resistivity) as possible ways to extract useful thermodynamic information associated with interatomic interactions. Considerable efforts have been made to identify the factors affecting the alloying behaviour of liquid metallic mixtures, such as differences in atomic sizes, electronegativity difference, valence differences, solubility differences, etc. For the sake of a quick understanding, the underlisted identified empirical criteria as well as microscopic parameters are used to classify binary liquid alloys as segregated alloy (Singh and Sommer, 1997):

1. Alloys exhibiting positive deviations from Raoultian behaviour.

2. The heat of formation and the excess Gibbs energy of mixing are positive.

3. The concentration fluctuations in the long-wavelength limit, $S_{cc}(0) > S_{cc}^{id}(0)$.

4. The Warren-Cowley short-range order parameter, $\alpha_1 > 0$.

5. In the framework of regular solution theory, the interchange energy, $\omega > 0$.

For instance, the following liquid alloys Bi-Zn, Cu-Pb, Bi-Cu, Cd-Ga, Ag-Te, Na-Cs, Na-K (Singh and Sommer, 1997), which exhibit liquid immiscibility and comparatively large positive H_M values are typical examples of segregating liquid alloys.

On the other hand, short-range ordered alloys exhibit negative deviations from Raoultian behaviours in contrast to the above highlighted empirical criteria. Examples of short-range ordered alloys are Bi-K, Al-Au, Bi-Mg and Hg-Na (Singh and March, 1995), Bi-Pb (Novakovic et al., 2002) and Cu-Zr (Novakovic et al., 2004). These alloys are usually strongly interacting and their mixing properties such as free energy of mixing, G_M, heat of mixing, H_M and concentration fluctuations $S_{cc}(0)$, etc. are often symmetrical about the equiatomic composition $c_c = 0.5$.

2.3 Short-range order parameter

The Warren-Cowley (Warren, 1969; Cowley, 1950) chemical short-range order (CSRO) parameter α_1 which is frequently used to quantify the degree of order and segregation in the melt, is directly related to the conditional probability, [A/B],

$$[A/B] = c(1 - \alpha_1) \tag{2.10}$$

where $[A/B]$ defines the probability of finding A atom as a nearest neighbour of B atom. The sign of α_1 indicates whether atoms in a given mixture prefer AB ordering ($\alpha_1 < 0$) or segregating ($\alpha_1 > 0$ (Singh,1987). The SRO parameters are normalized such that the limiting values of α_1 lie in the range

$$-\frac{c}{(1-c)} \leq \alpha_1 \leq 1, \quad c \leq \frac{1}{2} \tag{2.11}$$

$$-\frac{1-c}{(c)} \leq \alpha_1 \leq 1, \quad c \leq \frac{1}{2} \tag{2.12}$$

For a perfect random distribution of atoms i.e. an alloy without atomic correlations, $[A/B]$ is simply c and then $\alpha_1 = 0$. If $\alpha_1 < 0$, then A-B pairs of atoms are preferred over A-A or B-B pairs as nearest neighbours, and for the converse case $\alpha_1 > 0$. For c $= 1/2$, one has $-1 \leq \alpha_1 \leq 1$. The minimum possible value, $\alpha_1^{min} = -1$, means complete ordering of A-B pairs in the melt, whereas the maximum value, $\alpha_1^{man} = 1$, suggests that the A-A and B-B pairs in the melt are totally segregated.

However, since α_1 can be determined from diffuse x-ray and neutron diffraction experiments (M$\ddot{u}$ller, 2003), a quantitative comparison between calculation and measurement is possible. Experimentally, α_1 is determined from the concentration-concentration structure factors S_{cc}(q) and the number-number structure factors S_{NN}(q). For mixtures in which the A and B atoms are nearly the same size, (Singh and Sommer, 1997) showed that

$$\int_{r_1-\epsilon}^{r_1+\epsilon} 4\pi r^2 \rho_{cc}(r) dr = \alpha_1 z \tag{2.13}$$

where r_1 is the mean distance of the first neighbour shell from a given atom. The actual distance is, however, taken between $r_1 - \epsilon$ and $r_1 + \epsilon$. z is the number of atoms in the first shell, usually known as the coordination number, and is determined from S_{NN}(q). ρ_{cc}(r) is called the radial concentration-correlation function, which is obtained from the Fourier transform (FT) of concentration-concentration structure factor, S_{cc}(q), i.e.,

$$4\pi r^2 \rho_{cc}(r) = 4\pi r FT\left[\frac{S_{cc}(q)}{c(1-c)} - 1\right] \tag{2.14}$$

However, because of practical difficulties involved in the measurement of S_{cc}(q), experimental data on α_1 are very scarce.

Chapter 3

Methodology

3.1 Quasi Lattice Theory of Liquid Mixtures

Bulk and Dynamic properties in Al-Zn and Bi-In Liquid Alloys Using a Theoretical Model

Keywords: Al-Zn, Bi-In, Entropic, Enthalpic, Dynamic properties, Segregation

3.1.1 Introduction

Different kinds of theoretical models proposed to explain the concentration dependence of the thermodynamic properties of liquid binary alloys and by so doing, extracting useful microscopic information on them has attracted the attention of Physicists, Chemists and Metallurgists for a long time (Bhatia and Hargrove, 1974; Singh, 1987; Akinlade, 1994 and 1995; Singh and Singh, 1995). In this regard, a substantial effort has been directed towards the understanding of the mechanism for the phenomenon of compound formation in liquid binary alloys (Singh, 1987; Singh and March, 1995).

In addition, their energetics are reasonably well understood theoretically. On the contrary, relatively little is known and written on the other class of liquid alloys that exhibit segregation (i.e. preference of like atoms as nearest neighbours) or on the liquid alloys endowed with a miscibility gap. Singh and Sommer (1997) have documented extensively on thermodynamic information (both experimentally and theoretically) on phase separating systems. They have equally mentioned different kinds of theoretical methods that could be used to explain the mechanism for the energetics of liquid alloys.

Singh and Sommer (1992a, 1992b) established an empirical model which provides a possible way of relating two of the dynamics properties, as diffusion coefficient (D) and viscosity (η) with thermodynamic properties like the concentration-concentration fluctuations in the long wavelength limit, $S_{cc}(0)$, and the free energy of mixing, $\frac{G_M}{RT}$, for liquid binary alloys. These quantities can then be connected in terms of entropic and enthalpic contributions to the free energy of mixing. However, no practical application was made to a particular liquid alloy in their work so as to know the limit of suitability of the model.

In this section, an attempt was made in this direction to use the theory by Singh and Sommer (1992a, 1992b) and show that it could be used to model the structure of liquid binary alloys and to facilitate our understanding of the energetics of the liquid alloys.

The model was applied to Al-Zn and Bi-In liquid alloys. The choice of Al-Zn and Bi-In was however influenced by the availability of all the required thermodynamic data for both systems. Moreso, due to the difficulties in performing high temperature surface and viscosity measurements, in the literature only a few reference data for metals (Lucas, 1984) are available. For binary systems they are scarce, and in the case of complex alloys a nearly complete lack of data is evident. Therefore, it is of interest to estimate the missing values of the viscosity data by theoretical models. The dynamic properties of Al-Zn and Bi-In liquid alloys are calculated in the framework of quasi-lattice theory (QLT) with the aim to analyze existing thermodynamic data and use these data as the input for the fitted parameter calculations, and to explain the ordering and phase separating phenomena in liquid binary alloys. In addition, available information on phase diagrams and other thermodynamic properties indicate the existence of liquid miscibility gap in Al-Zn system. Its $S_{cc}(0)$ exhibit a tendency for phase separation over the concentration range, whereas the $S_{cc}(0)$ for Bi-In alloy exhibits compound formation tendency. The above mentioned facts motivated the study of these two systems to widen the theoretical understanding of the energetics in liquid binary alloys.

3.1.2 Basic Theory of Quasi-Lattice Theory

The quasi-lattice theory (QLT) of liquid mixtures is based on the Guggenheim theory (Guggenheim, 1952) which assumes the existence of a binary mixtures consisting of $N_A = Nc_A$ and $N_B = Nc_B$ atoms of elements A and B, respectively. The theory also assume that a small gradient of composition c_A is maintained in an equilibrium condition along the x-direction by the application of a force F_A, such that for dilute alloy, it is possible to write (Akinlade et al., 1998)

$$F_A = -k_B T\Big(d\ln\frac{c_A}{dx}\Big) \tag{3.1}$$

where T is the temperature and k_B, the Boltzmann's constant. Using equation (3.1), Singh and Sommer (1992a, 1992b) have shown that $S_{cc}(0)$ is related to the diffusion coefficient, D_M for liquid alloys (Singh and March, 1995; Singh and Sommer, 1997) by

$$\eta = \frac{k_B T}{D_M}\left(\frac{c_A}{\lambda_2} + \frac{c_B}{\lambda_1}\right)\frac{c_A c_B}{S_{cc}(0)} \tag{3.2}$$

where λ_1 and λ_2 are functions of the size and shape of the constituent particles. Thus, the quantity ϕ is defined as

$$\phi = \frac{c_A c_B}{S_{cc}(0)} \tag{3.3}$$

and the ideal value of $S^{id}_{cc}(0)$ as

$$S^{id}_{cc}(0) = c_A c_B \tag{3.4}$$

Equation (3.3) can be rewritten as

$$\eta = \eta_o \phi \tag{3.5}$$

with

$$\eta_o = \frac{k_BT}{D_M}\left(\frac{c_A}{\lambda_2} + \frac{c_B}{\lambda_1}\right) \tag{3.6}$$

Thermodynamic investigation of ϕ have been performed by Osman and Singh (1995) for the more general case in which one introduces the entropic contribution (i.e. the size ratio $\gamma = \frac{\Omega_A}{\Omega_B}$, $\Omega_B > \Omega_A$), where Ω is the atomic volume and the enthalpic contributions (via the interchange energy, ω). They obtained an expression for ϕ given by

$$\phi = 1 - c_Ac_Bf(\gamma, W) \tag{3.7}$$

where

$$f(\gamma, W) = \frac{2\gamma^2W - (\gamma-1)^2(c_A+\gamma c_B)}{(c_A+\gamma c_B)^3} \tag{3.8}$$

$$W = \Omega_A\Big(\frac{\omega}{K_BT}\Big) \tag{3.9}$$

with

$$w = Z\Big(\epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2\Big) \tag{3.10}$$

Equation (3.10) is known as the interchange energy and it should be stated that ϵ_{AB}, ϵ_{AA}, and ϵ_{BB} are the energies for AB, AA and BB pairs of atoms, respectively and Z is the coordination number of the liquid alloys. Obviously, if $\omega < 0$, there is tendency to form unlike atom pairs, and if $\omega > 0$, like atoms tend to pair together. ω=0, however, shows that atoms in the mixture are perfectly disordered(Singh, 1987). By taking together equations (3.5), (3.7), (3.8) and (3.9), one expresses $\frac{\Delta\eta}{\eta_o}$ as

$$\frac{\Delta\eta}{\eta_o} = -c_Ac_Bf(\gamma, W) \tag{3.11}$$

The factor $f(\gamma, W)$ which introduces both the entropic and enthalpic effects is responsible for the characteristic behaviour of $\Delta\eta$ for a given binary alloy. In the light of the result obtained by Singh and March (1992a, 1992b), it is readily shown that

$$\frac{\Delta\eta}{\eta_o} = -\frac{H_M}{RT} \tag{3.12}$$

R is the universal gas constant. It is important to note that in using the formulae given above, one does not have sufficient information on thermodynamic quantities to relate it to η. In order to do this, the general expression for the Gibb's free energy of mixing G_M is employed

$$G_M = -TS_M + H_M \tag{3.13}$$

where S_M is the entropy of mixing and H_M is the enthalpy of mixing. Using Guggenheim's theory of mixtures (Guggenheim, 1952), QLT makes it possible to write an explicit expression for G_M as

$$\frac{G_M}{RT} = c_B \ln \Psi + c_A \ln(1-\Psi) + c_A \Psi \Big(\Omega_A \frac{\omega}{K_B T} \Big) \tag{3.14}$$

$$= c_B \ln \Psi + c_A \ln(1-\Psi) + c_A \Psi W \tag{3.15}$$

with

$$\Psi = \frac{\gamma c_B}{c_A + \gamma c_B} \tag{3.16}$$

And from G_M as in equation (3.14) or (3.15), $S_{cc}(0)$ can easily be calculated from standard relationship in terms of free energy of mixing,

$$S_{cc}(0) = RT \left(\frac{\partial^2 G_M}{\partial c^2} \right)^{-1}_{T,P,N} \tag{3.17}$$

or in terms of activity, a_A and a_B,

$$S_{cc}(0) = (1-c) a_A \left(\frac{\partial a_A}{\partial c} \right)^{-1}_{T,P,N} = c a_B \left(\frac{\partial a_B}{\partial (1-c)} \right)^{-1}_{T,P,N} \tag{3.18}$$

as

$$S_{cc}(0) = \frac{c_A c_B}{1 - c_A c_B f(\gamma, W)} \tag{3.19}$$

Once $S_{cc}(0)$ is fitted from equation (3.19), then all other parameters can be calculated.

The degree of order and segregation in the melt can be quantified by another important microscopic function, known as Warren-Cowley short range order parameter or simply chemical short-range order (CSRO), α_1, (Cowley, 1950) and (Warren,1969). The parameter α_1 is related to the $S_{cc}(0)$ by

$$\frac{S_{cc}(0)}{c_A c_B} = \frac{1 + \alpha_1}{1 - (Z-1)\alpha_1} \tag{3.20}$$

For equiatomic composition, the CSRO α_1, is found to be in the range $-1 \leq \alpha_1 \leq 1$. The negative values of this parameter indicate the ordering in the melt, and complete ordering is shown by α_1^{min}=-1. On the contrary, the positive values of α_1 indicate segregation, whereas the phase separation takes place if α_1^{max}=1.

In addition,the mixing properties of binary molten metals forming alloys can as well be analyzed at the microscopic scale in terms of the quantity ϕ defined in equation (3.3) known as diffusion. The formalism relation that connects diffusion and $S_{cc}(0)$ (Singh and Sommer, 1992) combines the Darken's thermodynamic equation for diffusion (Darken,1967) with the basic thermodynamic relation in the form (Singh and Sommer, 1992):

$$\frac{D_M}{D_{id}} = \frac{S_{cc}^{id}(0)}{S_{cc}(0)} \tag{3.21}$$

where D_M is the mutual diffusion coefficient and D_{id} is the intrinsic diffusion coefficient for an ideal mixture, given as

$$D_{id} = c_A D_B + c_B D_A \tag{3.22}$$

with D_A and D_B being the self-diffusion coefficients of pure components A and B, respectively. For ideal mixing, $S_{cc}(0) \rightarrow S_{cc}^{id}(0)$, i.e. $D_M \rightarrow D_{id}$; for ordered alloys, $S_{cc}(0) < S_{cc}^{id}(0)$, i.e. $D_M > D_{id}$; and similarly for segregation, $D_M < D_{id}$. The highest peak of $\frac{D_M}{D_{id}}$ as a function of composition indicate the presence of maximum chemical order in molten alloy system as well as the composition of the most likely associates to be formed in the liquid phase (Singh and March, 1995).

3.2 Quasi-Chemical Approximation Model

Thermodynamic properties of some gallium-based liquid alloys

Keywords: Chemical order, Homocoordination, Interaction energy, Raoultian behaviour

3.2.1 Introduction

Many investigations have been reported in literature on liquid binary alloy systems which are of importance from both the scientific and also the technological points of view. An accurate knowledge of the thermodynamic properties and phase diagrams of the alloy systems are essential to establish a respectable understanding between the experimental results, theoretical approaches and empirical models for liquid alloys with a miscibility gap.

The interatomic interactions and the related energies of the bond between the A and B component atoms of a binary alloy play an essential role in understanding the mixing behaviour of two metals. Because of this, the energetically preferred heterocoordination of A-B atoms as nearest neighbours over self-coordination A-A and B-B, or vice versa lead to the classification of all binary alloys into two distinct groups: short-range ordered (Bhatia and Hargrove, 1974; Bhatia and Singh, 1982; Singh and March, 1995; Novakovic et al., 2002; Novakovic et al., 2004) or segregating (demixing) alloys (Singh, 1993; Singh and Sommer, 1997; Prasad and Mikula, 2000a).

The three binary alloys namely Ga-Zn, Ga-Mg and Al-Ga are the alloys of interest. The choice of these alloys arises from the fact that the three alloys have various industrial applications. Alloy systems containing semiconducting components such as gallium which is a group IIIB element like aluminium have been the subject of an increasing attention in the semiconductor production for their important application in the solid-state electronic devices and as a useful thermometric liquid (Awe et al., 2005). Also, magnesium alloys offer lightweight alternatives to conventional metallic alloys and consequently, research on Mg alloys is fuelled nowadays by the need for low-density materials that suit aerospace and automobile industries (Islam and Medraj, 2004) and as a result of which the world consumption of magnesium alloys in the automobile industry has been on the increase in the last decade (Awe et al., 2006). Moreover, aluminium and its alloys are used in many aspects of modern life, from soda cans and household foil to automobiles and aircraft in which we travel. Al-based alloys have also been found useful as additives in various fuel formulations for propellants, explosives, incendiaries or pyrotechnics (Awe et al., 2006). Large quantities of zinc are used to produce die castings. In addition, all the essential experimental data that are required for the calculation of the thermodynamic properties are available.

It has been established in this work that both Ga-Zn and Al-Ga systems are characterized by positive interaction energies indicating segregation in the melts, while Ga-Mg alloy is characterized by a negative interchange energy indicating ordering in the melt. This characteristic behaviour is likely to be a reflection of the interplay of the energetic and structural re-adjustment of the constituent elemental atoms in the alloys.

In this section, the composition dependence of thermodynamic properties of these liquid alloys has been studied using a quasi-chemical approximation model by Singh (1987) for compound forming binary alloys and that for simple regular alloys. The energetics of mixing as well as the positive deviation from Raoultian behaviour was discussed for the various thermodynamic quantities calculated.

3.2.2 Theory of QCAM

The fundamental idea about the quasi chemical model is that the thermodynamic properties of a compound forming A-B alloy can be explained by treating the alloy as pseudo ternary mixture of A atoms, B atoms and $A_\mu B_\nu$ (μ and ν are small integers) complexes. The grand partition function Ξ of a binary molten alloy AB, which consists of $N_A = Nc$ and $N_B = N(1-c)$ atoms of elements A and B, respectively, where the total number of atoms, N, is equal to $N_A + N_B$,can be expressed as

$$\Xi = \sum_E q_A^{N_A}(T) q_B^{N_B}(T) exp[(\mu_A N_A + \mu_B N_B - E)/k_B T] \tag{3.23}$$

where $q_i^N(T)$ and μ_i are atomic partition function and chemical potential of i^{th} components ($i = A, B$), k_B is Boltzmann's constant, T is the absolute temperature and E is the configurational energy of the alloy. The QCM is utilized to determine the probable chemical complexes existing in a liquid binary alloy.

The solution of equation (3.23) in line with (Prasad et al., 1998) is given as the ratio of the activity coefficient γ ($\gamma = \frac{\gamma_A}{\gamma_B}$); ($\gamma_A$ and γ_B are activity coefficients of A and B atoms, respectively) for the compound ($A_\mu B_\nu$) forming alloys as

$$\ln\gamma = \frac{Z(1-c)}{2c}.\frac{(\beta+2c-1)}{(\beta-2c+1)} \tag{3.24}$$

with

$$\gamma_A = \left[\frac{\beta-1+2c}{c(1+\beta)}\right]^{\frac{Z}{2}} \tag{3.25}$$

$$\gamma_B = \left[\frac{\beta+1-2c}{(1-c)(1+\beta)}\right]^{\frac{Z}{2}} \tag{3.26}$$

The excess free energy of mixing G_M^{XS} is related to the free energy of mixing G_M by the expression:

$$G_M^{XS} = G_M - RT\Big\{c\ln c + (1-c)\ln(1-c)\Big\} \tag{3.27}$$

The quasi chemical expression for the excess free energy of mixing G_M^{XS} is given as:

$$\frac{G_M^{XS}}{RT} = Z\int_0^c \Big[\ln\sigma + (2k_BT)^{-1}(P_{AA}\Delta\epsilon_{AA} - P_{BB}\Delta\epsilon_{BB})\Big]dx + \phi \tag{3.28}$$

where Z is the coordination number, c is the concentration of atom A and R is the universal gas constant and

$$\ln\sigma = \frac{1}{2}\ln\frac{(1-c)(\beta+2c-1)}{c(\beta-2c+1)} \tag{3.29}$$

with

$$\beta = \{1+4c(1-c)(\eta^2-1)\}^{1/2} \tag{3.30}$$

and

$$\eta^2 = exp\Big(\frac{2\omega}{zk_BT}\Big)exp\Big(\frac{2P_{AB}\Delta\epsilon_{AB} - P_{AA}\Delta\epsilon_{AA} - P_{BB}\Delta\epsilon_{BB}}{k_BT}\Big) \tag{3.31}$$

For a simple regular alloy, η is given as

$$\eta = exp\Big(\frac{\omega}{zk_BT}\Big) \tag{3.32}$$

ω is the interchange or order energy, expressed as:

$$\omega = Z[\Delta\epsilon_{AB} - \frac{1}{2}(\Delta\epsilon_{AA} + \Delta\epsilon_{BB})] \tag{3.33}$$

$\Delta\epsilon_{AB}$, $\Delta\epsilon_{AA}$, $\Delta\epsilon_{BB}$ are the interaction parameters and $\Delta\epsilon_{ij}$ is the change in the energy of the ij bond in the complex $A_\mu B_\nu$. P_{ij} is the probability that the ij bond is a part of the complex. P_{ij} may be expressed as

$$P_{AB} = c^{\mu-1}(1-c)^{\nu-1}[2 - c^{\mu-1}(1-c)^{\nu-1}] \tag{3.34}$$

$$P_{AA} = c^{\mu-2}(1-c)^{\nu}[2 - c^{\mu-2}(1-c)^{\nu}], \ \mu \geq 2 \tag{3.35}$$

$$P_{BB} = c^{\mu}(1-c)^{\nu-2}[2 - c^{\mu}(1-c)^{\nu-2}], \ \mu \geq 2 \tag{3.36}$$

The constant ϕ in equation (3.28) is determined from the requirement that $G_M^{xs} = 0$ at c=0 and c=1.

The concentration-concentration fluctuations in the long-wavelength limit, $S_{cc}(0)$, has emerged as an important microscopic function to understand the mixing behaviour of liquid alloys in terms of compound formation and phase segregation (Singh, 1987). The $S_{cc}(0)$ can be expressed by G_M, or the activity, $a_i(i = A, B)$, as

$$\begin{aligned} S_{cc}(0) = RT\left(\frac{\partial^2 G_M}{\partial c_A^2}\right)^{-1}_{T,P,N} &= c_B a_A \left(\frac{\partial a_A}{\partial c_A}\right)^{-1}_{T,P,N} \\ &= c_A a_B \left(\frac{\partial a_B}{\partial(1-c_A)}\right)^{-1}_{T,P,N} \end{aligned} \tag{3.37}$$

For ideal mixing the energy parameters, ω, given in equation (3.33) is equal to zero, and equation (3.37) becomes

$$S_{cc}^{id}(0) = c_A c_B \tag{3.38}$$

Substituting equation (3.27) for G_M into equation (3.37), one obtains

$$S_{cc}(0) = \frac{c(1-c)}{1 + \frac{Z}{2}\left(\frac{1}{\beta} - 1\right)} \tag{3.39}$$

Equation (3.37) is usually utilized to obtain the experimental values of $S_{cc}(0)$ from the measured activity or the free energy of mixing data (Akinlade, 1998). The mixing behaviour of liquid binary alloys can be inferred from the deviation of $S_{cc}(0)$ from $S_{cc}^{id}(0)$. The presence of chemical order is indicated by $S_{cc}(0)<S_{cc}^{id}(0)$; on the contrary, if $S_{cc}(0)>S_{cc}^{id}(0)$, the segregation and demixing in liquid alloy take place.

The Warren-Cowley short-range order parameter α_1 for the first nearest neighbours is expressed in term of β-function (Anusionwu, 2006), (equation (3.30)) as:

$$\alpha_1 = \frac{\beta - 1}{\beta + 1} \tag{3.40}$$

The enthalpy of mixing, H_M within the QCM can be obtained from the standard thermodynamic relation (Novakovic and Zivkovic, 2005)

$$H_M = G_M - T\Big(\frac{\partial G_M}{\partial T}\Big)_P \tag{3.41}$$

Making use of G_M in equation (3.27), H_M is expressed as

$$H_M = -\frac{8RTc^2(1-c)^2 exp(\frac{2\omega}{Zk_BT})}{(\beta - 1 + 2c)(1+\beta)(\beta + 1 - 2c)}\Big(\frac{1}{k_B}\frac{d\omega}{dT} - \frac{\omega}{T}\Big) \tag{3.42}$$

and thus the entropy of mixing,

$$S_M = \frac{H_M - G_M}{T} \tag{3.43}$$

3.3 Four Atom Cluster Model

Energetics of Mixing in Bi-Pb and Sb-Sn Liquid Alloys

Keywords: Four atom cluster model; Bi-Pb; Sb-Sn; heterocoordination; Bulk properties

3.3.1 Introduction

Different theoretical models or formalisms have been established with a view to explaining or describing thermodynamic, structural and thermophysical properties of binary molten alloys. Some of these are Bhatia and Hargrove formalism (1974), electron theory (Aschroft and Stroud, 1978), four atom cluster model (FACM)

(Bhatia and Singh, 1982; 1984) and the pseudopotential formalism (Dalgic et al., 1998; Thakur et al., 2005).

FACM is a model established by Singh (1993) as an extension of his earlier work on a two atom cluster model (TACM) (Singh et al., 1988). This model is established to give a more realistic value of the ordering energy ω and the chemical short range order (CSRO) parameter α_1 and hence, a better quantitative approach to the processes of compound formation or phase separation in liquid binary systems (Akinlade, 1997). Essentially, in FACM a simple scheme is used to connect conditional probabilities enumerating the occupation of neighbouring sites by the atoms of the constituent elements in the liquid alloys. One significant advantage of the FACM, over the other available methods of calculating CSRO parameter α_1 is the fact that in obtaining this parameter, the model formulation does not require the assumption of any preferred complexes (Akinlade et al., 2003). The implication of this is that we can obtain information on the properties of liquid alloys without having to necessarily look for information on such features like the phase diagrams, which normally provides information on the possible complexes (Akinlade, 1997).

Furthermore, the calculation of α_1 using the FACM only requires as input data, a knowledge of the activity ratio a_B/a_A, where A and B are the individual components of the alloy AB of interest.

In addition to the aforementioned, FACM makes it possible to obtaining higher order conditional probabilities (HOCPs) encompassing atomic distribution in nearest neighbour shells. Hence, it is possible to define i/iji as the probability of finding i atoms on a given lattice site while the other three neighbours in the cluster are occupied by i, j, and i atoms.

For the present study one has chosen Bi-Pb and Sb-Sn for some reasons. The choice of Bi-Pb for investigation was influenced by the recent work on the surface properties of Bi-Pb liquid alloys which suggested that Bi-Pb system is characterized by short-range ordering in the liquid phase (Novakovic et al., 2002). In addition, bismuth metal is used primarily as an alloy and metallurgical additive. One class of bismuth alloys comprises the low fusible (low-melting-point) alloys-combinations of bismuth and other metals, such as cadmium, lead, gallium, indium and tin. These alloys found applications in fuel tank safety plugs, holders for lens grinding and other articles for machining, solders, and sprinkler triggering mechanisms (Brown, 2000).

Although, not quite much is known about the uses of Sb-Sn, yet one notes that since antimonial lead (Sb-Pb) is primarily used in grid metal for lead acid storage batteries and tin and lead are elements belonging to the same group of the periodic table (meaning that they have similar chemical properties), then, it is not unlikely that Sb-Sn will be relevant in the battery making industries. In addition, the availability of enough data on the two systems makes them good candidates for investigation.

In this section, the FACM has been used to compute the energetics of Bi-Pb and Sb-Sn systems in terms of the ordering energy parameter reproducing their respective activity ratios and two other thermodynamic properties (free energy of mixing and the concentration-concentration fluctuations in the long wavelength limit) as well as CSRO parameter and chemical diffusion.

3.3.2 Theory of FACM

The general expression for the grand partition function Ξ of a binary alloy AB consisting of N atoms, of which N_A = Nc are A atoms and N_B = N(1-c) are B atoms can be expressed as (Cartier and Barriol, 1976; Singh, 1993)

$$\Xi = \sum_E q_A^{N_A}(T) q_B^{N_B}(T) e^{\beta(\mu_A N_A + \mu_B N_B)} e^{-\beta E} \tag{3.44}$$

where $q_i(T)$ are the particle functions of atoms i (A or B) associated with inner and vibrational degrees of freedom, μ_A and μ_B are the chemical potentials and E is the configurational energy. In solving equation (3.44), some simplifying assumptions are essential (Singh, 1993). The first assumption is that the interactions between the atoms should be of short range and effective only between nearest neighbours. The second assumption is that the atoms are located on lattice sites such that each site has Z nearest neighbours. Also, the lattice sites are further subdivided into smaller cluster of just a few lattice sites in domain 1 and the remainder in domain 2.

In view of the above assumptions, one could then write the grand partition function as the product of the partition function of the two domains (i.e $\Xi = \Xi_1 \cdot \Xi_2$). The grand partition function for the cluster can be expressed as (Singh, 1993; Cartier and Barriol, 1976)

$$\Xi_1 = \sum_{E_1} \xi_A^{N_{1A}} \xi_B^{N_{1B}} \phi_A^{Z_A} \phi_B^{Z_B} e^{-\beta E_1} \tag{3.45}$$

where ϕ_A and ϕ_B are constants to be eventually eliminated

$$N_A = N_{1A} + N_{2A} \quad ; \quad N_B = N_{1B} + N_{2B} \quad ; \quad E = E_1 + E_2 + E_{12} \tag{3.46}$$

In equation (3.46), E_1 denotes the configurational energies of domain 1 and E_{12} takes into account the interactions between atoms in cluster and the remainder. The ξ_A and ξ_B in equation (3.45) can be expressed as

$$\xi_A = q_A(T) e^{\beta \mu_A} \qquad ; \quad \xi_B = q_B(T) e^{\beta \mu_B} \tag{3.47}$$

For a cluster of one lattice site, $E_1 = 0$ because there are no AA, AB, or BB atom in the bond. Hence, the single lattice site can be occupied by either an A-atom or a B-atom and $Z_A = Z_B = Z$ (the coordination number), and equation (3.45) becomes

$$\Xi_1^{(1)} = \xi_A \phi_A^Z + \xi_B \phi_B^Z \tag{3.48}$$

The superscripts (1) in equation (3.48) is necessary to show that the expression for Ξ_1 is for a cluster of one atom. For a cluster of four lattice sites in domain 1, taking into consideration, the possible arrangements of atoms that can be obtained statistically, one can then write equation (3.45) as

$$\Xi_1^{(4)} = \xi_A^4 \phi_A^{4ZL} P_{AA}^6 + 4\xi_A^3 \xi_B \phi_A^{3ZL} \phi_B^{ZL} P_{AA}^3 P_{AB}^3 + \xi_B^4 \phi_B^{4ZL} P_{BB}^6$$

$$+6\xi_A^2 \xi_B^2 \phi_A^{2ZL} \phi_B^{2ZL} P_{AA} P_{BB} P_{AB}^4 + 4\xi_A \xi_B^3 \phi_A^{ZL} \phi_B^{3ZL} P_{BB}^3 P_{AB}^3 \tag{3.49}$$

Where $ZL = Z - 3$, $P_{ij} = e^{\beta E_{ij}}$, (i,j = A,B) and the E_{ij}'s are bond energies for ij nearest neighbour bond. Further simplification of equation (3.49) leads to an expression of the form

$$\sigma^{12} - B_1\sigma^9 - B_2\sigma^6 - B_3\sigma^3 - B_4 = 0 \tag{3.50}$$

where

$$\sigma = \frac{\phi_B}{\phi_A}\left(\frac{P_{AA}}{P_{BB}}\right) \tag{3.51}$$

$$B_4 = x^3 \tag{3.52}$$

$$B_3 = 3x^2\frac{(1 - x/3)}{\eta^3} \tag{3.53}$$

$$B_2 = 3x\frac{(1 - x)}{\eta^4} \tag{3.54}$$

$$B_1 = \frac{1 - 3x}{\eta^3} \tag{3.55}$$

$$x = \frac{1 - c}{c} \qquad \mathit{and} \quad \eta = \exp\left(\frac{\beta\omega}{Z}\right) \tag{3.56}$$

$$w = Z\Big(\epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2\Big) \tag{3.57}$$

Equation (3.57) is the interchange energy or order energy for the alloy. With the activity ratio earlier defined $\Big(i.e$ a $= a_B/a_A\Big)$, one recalls the thermodynamic relation for the chemical potentials μ_A and μ_B for the two components elements A and B in the alloy,

$$\mu_A = \mu_o^A + \beta\ln a_A \quad \mathit{and} \quad \mu_B = \mu_o^B + \beta\ln a_B \tag{3.58}$$

where μ_o^A and μ_o^B are the chemical potentials of the pure species A and B. Using the grand partition function and the above equation, one obtains

$$\mu_A^o = -\beta\ln q_A(T) + \frac{1}{2}Z\epsilon_{AA} \tag{3.59}$$

$$\mu_B^o = -\beta\ln q_B(T) + \frac{1}{2}Z\epsilon_{BB} \tag{3.60}$$

Equations (3.47), (3.59) and (3.60) combined to yield

$$a = \frac{a_B}{a_A} = \frac{\xi_B}{\xi_A}\left(\frac{P_{BB}}{P_{AA}}\right)^{Z/2} \tag{3.61}$$

Where a_A and a_B are the activities of component A and B in the alloy. An expression connecting a and σ can be found in (Singh, 1993) as

$$cf_1(a,\sigma) = (1-c)f_2(a,\sigma) \tag{3.62}$$

where $f_1(a,\sigma)$ and $f_2(a,\sigma)$ are defined as

$$f_1(a,\sigma) = a^4\sigma^{4ZL} + \frac{3a^3\sigma^{3ZL}}{\eta^3} + \frac{3a^2\sigma^{2ZL}}{\eta^4} + \frac{a\sigma^{ZL}}{\eta^3} \tag{3.63}$$

and

$$f_2(a,\sigma) = \frac{a^3\sigma^{3ZL}}{\eta^3} + \frac{3a^2\sigma^{2ZL}}{\eta^4} + \frac{3a\sigma^{ZL}}{\eta^3} + 1 \tag{3.64}$$

where ZL in both equations (3.63) and (3.64) has the same meaning as in equation (3.49). The activity ratio for a given binary alloy can be determined by solving equation (3.64) numerically based on the knowledge of σ obtained from the numerical solution of equation (3.50). The value of σ needed in the calculations should be optimized in such a way that it gives a good overall representation of activity at all concentrations as reported by (Akinlade, 1997). The major idea behind the FACM is to express the degree of CSRO in terms of probabilities. Even in the framework of this model, the probability of finding an A atom or B atom on any lattice site still depends on the nature of atoms already existing in the neighbouring sites (Akinlade, 1995). One begins by stating the probability that all four lattice sites occupied by atoms A as (A, A, A, A) and similar probabilities (i, j, k, l) can readily be reduced to HOCPs such that i/iji (the probability of finding i atom on a given lattice site while the other three sites in the cluster are occupied by i, j, and i atoms) and similar others. Having this in mind, one can express the pairwise conditional probability P_{AB} as

$$P_{AB} = (A/B) = \frac{(A/BB)}{(B/AB) + (A/BB)} \tag{3.65}$$

In terms of HOCP, one writes for the terms in equation (3.65)

$$(A/BB) = \frac{(A/BBB)}{(B/ABB) + (A/BBB)} \tag{3.66}$$

$$(B/AB) = \frac{(B/AAB)}{(B/AAB) + (A/ABB)} \tag{3.67}$$

and one further notes that (B/ABB)=1-(A/ABB). However, equations (3.65)-(3.67) are only useful in this context if they can be expressed in terms of a and σ. Hence, the results are

$$(A/BBB) = \frac{1}{1 + a\sigma^{ZL}\exp(3\beta\omega/Z)} \tag{3.68}$$

$$(A/ABB) = \frac{1}{1 + a\sigma^{ZL}\exp(\beta\omega/Z)} \tag{3.69}$$

$$(B/AAB) = \frac{a\sigma^{ZL}\exp(-\beta\omega/Z)}{1 + a\sigma^{ZL}\exp(-\beta\omega/Z)} \tag{3.70}$$

The value of P_{AB} defined by equation (3.65) can then be obtained by solving equations (3.68)-(3.70). A useful quantity which can be obtained from knowledge of P_{AB} is the Cowley-Warren short range order parameter α_1 (Cowley, 1950). For nearest neighbour sites, α_1 can be defined as:

$$\alpha_1 = 1 - \frac{P_{AB}}{c} \tag{3.71}$$

From a simple probabilistic approach the limiting values of α_1 lie in the range

$$-\frac{c}{(1-c)} \leq \alpha_1 \leq 1 \quad c \leq \frac{1}{2} \tag{3.72}$$

$$-\frac{1-c}{(c)} \leq \alpha_1 \leq 1 \quad c \geq \frac{1}{2} \tag{3.73}$$

For $c = \frac{1}{2}$, one has $-1 \leq \alpha_1 \leq 1$. The minimum possible value, α_1^{min}, means complete ordering of A-B pairs in the melts, whereas the maximum value $\alpha_1^{max} = +1$, suggests that the A-A and B-B pairs in the melts are totally segregated (Singh, 1987). A situation in which $\alpha_1 = 0$, implies a random alloy. On the basis of the discussion on the equations written so far, one can say that we have obtained all the essential equations required for FACM.

In order to calculate the bulk thermodynamic properties, the values of ω obtained above have been used; hence, one has computed the excess Gibb's free energy of mixing, G_M^{XS} and the concentration-concentration fluctuations in the long wavelength limit, $S_{cc}(0)$. In obtaining these, one has used

$$G_M = G_M^{id} + G_M^{XS} \tag{3.74}$$

where

$$G_M^{id} = RT\Big\{c + (1-c)\ln(1-c)\Big\} \tag{3.75}$$

and

$$G_M^{XS} = RT\Big\{c\ln\gamma_A + (1-c)\ln\gamma_B\Big\} \tag{3.76}$$

Here γ_A and γ_B are activity coefficients and are related to the activity a by the standard relations:

$$a_A = c\gamma_A \qquad ; \qquad a_B = (1-c)\gamma_B \tag{3.77}$$

$$\gamma_A = \left(\frac{\beta - 1 + 2c}{c(\beta+1)}\right)^{Z/2} \tag{3.78}$$

$$\gamma_B = \left(\frac{\beta + 1 - 2c}{(1-c)(\beta+1)}\right)^{Z/2} \tag{3.79}$$

with

$$\beta = \{1 + 4c(1-c)(\eta^2 - 1)\}^{1/2} \tag{3.80}$$

From equation (3.74), $S_{cc}(0)$ can be determined using thermodynamic relations:

$$\begin{aligned} S_{cc}(0) = RT\left(\frac{\partial^2 G_M}{\partial c^2}\right)^{-1}_{T,P,N} &= (1-c)a_A\left(\frac{\partial a_A}{\partial c}\right)^{-1}_{T,P,N} \\ &= ca_B\left(\frac{\partial a_B}{\partial(1-c)}\right)^{-1}_{T,P,N} \end{aligned} \tag{3.81}$$

Substituting equation (3.74) in equation (3.81), one obtains

$$S_{cc}(0) = \frac{c(1-c)}{1 + \frac{Z}{2}\left(\frac{1}{\beta} - 1\right)} \tag{3.82}$$

Hence, from equations (3.74) and (3.81), it means that once a suitable optimized value of ω is obtained, it can be used to compute $\frac{G_M}{RT}$ and $S_{cc}(0)$ which can then be compared with experiments and deductions made therefrom. One observes that β in equation (3.82) depends on the interchange energy ω through equation (3.56) and brings about the deviation from ideality. As $\omega \to 0$, $\beta \to 1$ and $S_{cc}(0)$ = c(1-c) = $S_{cc}^{id}(0)$, the ideal values.

Equation (3.81) is usually utilized to obtain the experimental values of $S_{cc}(0)$ from the measured activity or the free energy of mixing data (Bhatia and Hargroove, 1974).

The knowledge of $S_{cc}(0)$ has been further used to investigate the nature of chemical diffusion in the two liquid alloys, which is likely to play an important role in many technological and corrosion phenomena. Using the Darken (1948) thermodynamic equation for diffusion, an expression that relates diffusion and $S_{cc}(0)$ can be established (Singh and Sommer, 1992a; Prasad et al., 1998); thus one can write

$$\frac{D_M}{D_{id}} = \frac{S_{cc}^{id}(0)}{S_{cc}(0)} \tag{3.83}$$

where D_M is the mutual diffusion coefficient and D_{id} is the intrinsic diffusion coefficient for an ideal mixture, given as

$$D_{id} = x_A D_B + x_B D_A \tag{3.84}$$

with D_A and D_B being the self-diffusion coefficients of pure components A and B, respectively. For ideal mixing, $S_{cc}(0)$ $\rightarrow$S$_{cc}^{id}(0)$, i.e. $D_M$$\rightarrow$D$_{id}$; for ordered alloys,$S_{cc}(0)$<$S_{cc}^{id}(0)$, i.e. $D_M > D_{id}$; and similarly for segregation, $D_M < D_{id}$. The maximum peak of D_M/D_{id} as a function of composition indicate the presence of maximum chemical order in molten alloy system as well as the composition of the most probable associates to be found in the liquid phase (Prasad et al., 1998; Singh and March, 1995).

3.4 Statistical Thermodynamic Theory

Determination of Mixing Properties and Activities of Binary Liquid Alloys

Keywords: Statistical thermodynamic, size factor, activity, enthalpy of mixing, entropy of mixing

3.4.1 Introduction

A great deal of thermodynamic data on binary liquid alloys have been compiled in monographs such as (Hultgren et al., 1973), but multi-component data is scattered over some journals and quite scarce because the determination of thermodynamic data of these liquid alloys needs not only the consummate skill of a researcher and excellent instruments but also the continuous financial support (Tao, 2000). Although, the development of new and reliable materials requires sometimes the knowledge of thermodynamic and thermophysical data which due to the experimental difficulties, especially high investigation temperatures required have not been successfully measured (Novakovic and Takana, 2006; Kostov et al., 2007; 2008) and coupled with the growing numbers of liquid alloys and numerous multi-component systems in industrial processes. The main reasons for this high scientific attention is certainly due to increasing applications of liquid alloys, especially in aerospace industry, due to their high oxidation resistance, low density and high melting point. It was obviously unrealistic to measure all the data experimentally. At present, several experimental methods, such as calorimetric method, electromotive force (emf) method and Knudsen effusion method, are in use to measure thermodynamic data for liquid binary alloys and for ternary compounds. Although, the experimental method is regarded to be the reliable one, but it is usually costly, laborious and time-consuming.

Studies in both theoretical and computational modelling of liquid alloys have led to rapid increase in the development of advanced high performance materials in industrial world. These high performance liquid and metallic alloys find usage in various segments of materials and chemical industry as catalysts, low weight and high strength structural materials (Liu and Fan, 2002; Tao 2000; 2003; Tao et al., 2002). In this regards, focus is on research areas having direct impact on innovative development of such materials. Thus, the need for timely, cost efficient and environmentally compliant methods for development of such advanced materials. This aroused a genuine interest to carry out a theoretical determination of the mixing properties and activity of the liquid Sb-Sn, In-Pb, Al-Si and Ga-Tl alloy systems based on the recently published experimental data on Al-Si (Kostov et al., 2007) and Ga-Tl (Katayama et al., 2003).

Although, different computational methods have been developed in literature to obtain thermodynamic properties such as free energy of mixing, heat of mixing, etc. Witusiewicz and Sommer, (2000); Islam and Medraj, (2004); Kanth and Chakrabarti, (2009) as well as thermophysical properties such as viscosity and diffusion (Akinlade et al., 1998; Novakovic et al., 2008; Anusionwu et al., 2009; Yong and Chen, 2011) of many binary liquid alloys. But these methods require inputs from thermodynamic measurements such as ordered or interchange energy, activity or activity coefficients for the determination of various thermodynamic properties, otherwise the calculations cannot be done.

In this section, an effective and cost efficient approach to determine the mixing properties like the free energy of mixing, G_M, enthalpy of mixing, H_M, entropy of mixing, S_M and activities of binary liquid alloys at different temperatures within the framework of a statistical thermodynamic theory without the need for input from thermodynamic measurements has been proposed. With this approach limited experiments can then be focused on the most promising alloy compositions identified by thermodynamic calculations, while avoiding the experiments with the less promising ones. This approach is a very useful method to cut down the cost and time for the development of new alloys.

Analytical expressions have been obtained for the various thermodynamic quantities such as G_M, H_M, S_M and a_i using standard thermodynamic relations by incorporating the atomic size mismatch volume. These expressions can be used for determination of the mixing properties and activities of binary liquid alloys at any temperature of interest and, the results obtained can then be compared with the experimental data. The analytical expressions were applied to liquid Sb-Sn at 905K, In-Pb at 673K, Ga-Tl at 973K, 1073K and 1173K and Al-Si at 2000K, 2400K and 2473K, respectively.

The free energy of mixing G_M and activity of liquid alloys play important role in predicting the glass-forming ability of the multi-components metallic alloys to the extent that many multi-component glass forming alloys like Ca- Senkov et al., (2004), Fe- Liu et al.,(2004), Cu- Cai Anhui et al.,(2008), and Mg-based alloys- Jha and Mishra, (2001) and Cai Anhui et al.,(2006) possess excellent glass-forming ability. Mg-Zn is similar in structure to Ca-Mg. Ca-Mg is a good glass former while Mg-Zn glass was reported by Jha and Mishra,(2001) as the first transition metal-free metallic glass. The two quantities G_M and a_i are among the fortunate thermodynamic functions which are obtained directly from experiment. However, there is no universal applicable expression for G_M, though attempts have been made to derive analytical expressions for free energy of mixing of different materials (Cai et al., 2008; Lad Kint et al., 2004).

Besides the factors mentioned above, the alloys or the individual constituent elements of the chosen candidates are known for their industrial relevance and the availability of the required experimental data for the liquid alloys is another important factor. Some of the important uses of these materials are as follows: Aluminum alloyed with tin, indium and zinc is used as sacrificial anodes and corrosion-proof anodic coating for steel (Popescu and Taloi, 2007), while Al-Sn-Zn alloys are used as soldering materials (Prasad and Mikula, 2006). Also, Mg-based alloys with different additives such as Pb, Ga, Al, Zn, Hg and Tl have been widely used as anode materials due to their rapid activation, low density, low electrode potential and high current capacity (Islam and Medraj, 2004; Aljarrah et al., 2007). In addition, various properties of Mg liquid alloys show anomalous behaviour as a function of concentration, with Mg being the lightest structural metal, with a density of $1.741 g/cm^3$, in comparison with the densities of aluminium ($2.70 g/cm^3$) and iron ($7.86 g/cm^3$). This makes magnesium alloys particularly attractive for weight reduction and higher fuel efficiency transportation applications (Islam and Medraj, 2004; Aljarrah and Medraj, 2008). As a result, thermodynamics of liquid alloys are currently engaging attentions of numerous researchers.

Moreover, no systematic thermodynamical study of Ga-Tl and Al-Si liquid alloys has been done or completely reported in literature until very recently, when Katayama et al., (2003) carried out an activity measurement of Ga in liquid Ga-Tl alloys by electromotive force (emf) method and measured the free energy of mixing, G_M and a_A of binary Ga-Tl liquid alloys at 973K, 1073K and 1173K, respectively.

And Kostov et al,(2007) for the first time used a FactSage Thermo-Chemical Softwares and Databases developed in 2001 to make thermodynamic predicting of the free energy of mixing, G_M of Al-Si liquid alloys at different temperatures of 2000K, 2400K and 2473K, respectively.

Thus, the result obtained using the analytical expressions proposed for theoretical calculations of free energy of mixing G_M and activity a_A of Ga-Tl and Al-Si at investigated temperatures for which the data exist were compared with Katayama et al.,(2003) for Ga-Tl and Kostov et al.,(2007) for Al-Si, respectively.

3.4.2 Theoretical formulation

The grand partition function of a binary liquid $A-B$ alloy consisting of $N_A = Nc_A$ and $N_B = Nc_B$ atoms of the element B, respectively, where the total number of atoms, $N = N_A + N_B$, is expressed in terms of the configurational energy, E, as:

$$\Xi = \sum q_A^{N_A}(T) q_B^{N_B}(T) exp((\mu_A N_A + \mu_B N_B - E)/k_B T) \tag{3.85}$$

where q_i(T) are the partition functions of atoms i ($= A$ or B) associated with inner and vibrational degrees of freedom and it is assumed that the partition functions remain unchanged immaterial of whether the atom i is located in the pure state or located in the alloy; μ_1 and μ_2 are the chemical potentials, k_B is Boltzmann's constant and T is the absolute temperature. Equation (3.85) is solved in the framework of the quasi-lattice theory to obtain an expression for the activity. The activity of an element in a binary mixture is given by (Takana and Gokcen,1995) as:

$$\ln a = \frac{-zFE_m}{k_B T} \tag{3.86}$$

where z is the valence of carrier ions of the element, F is the Faraday's constant and E_m is the electromotive force which can be observed directly from experiment.

Using statistical thermodynamic theory, an expression for the Gibbs free energy of mixing is obtained as:

$$\frac{G_M}{RT} = \Big[c_A \ln c_A + (1-c_A)\ln(1-c_A) + c_A \ln(1-\nu) - \ln(1-\nu c_A)\Big] + \omega c \frac{(1-c_A)}{1-\nu c} \tag{3.87}$$

with

$$\nu = 1 - \frac{1}{n} \qquad ; \qquad n = \frac{V_B}{V_A} \tag{3.88}$$

where V_A and V_B are the atomic volume of species A and B, respectively in the binary mixture A-B alloys and ω is the interchange energy. In order to obtain the expression for the activity of components $a_i, (i = A, B)$ in the binary alloy, one makes use of the standard thermodynamic relation:

$$RT \ln a_A = \left(\frac{\partial G_M}{\partial N_A}\right)_{T,P,N_B} = G_M + (1 - c_A)\left(\frac{\partial G_M}{\partial c_A}\right)_{T,P,N} \tag{3.89}$$

Recalling that $N = N_A + N_B$ and $c_A = N_A/N$, and upon differentiating equation (3.87) partially with respect to c_A, one obtains

$$\frac{\partial G_M}{\partial c_A} = RT\left[\ln c_A - \ln(1 - c_A) + \ln(1 - \nu) + \frac{\nu}{\nu c_A}\right] + \omega\left[\frac{1 - 2c_A}{1 - \nu c_A} + \frac{\nu(1 - c_A)c_A)}{(1 - \nu c_A)^2}\right] \tag{3.90}$$

By putting equations (3.87) and (3.90) in equation (3.89) and solving, the activities can be expressed as:

$$\ln a_A = \ln \frac{c_A(1 - \nu)}{1 - \nu c_A} + \frac{\nu(1 - c_A)}{1 - \nu c_A} + \frac{\omega}{RT}\frac{(1 - c_A)^2}{(1 - \nu c_A)^2} \tag{3.91}$$

and

$$\ln a_B = \ln \frac{c_A}{1 - \nu c_A} + \frac{\nu(1 - c_A)c_A}{1 - \nu c_A} + \frac{\omega}{RT}\frac{(1 - c_A)\nu}{(1 - \nu c_A)^2} \tag{3.92}$$

Once the expression for G_M is obtained, other thermodynamic quantities readily follows. Enthalpy of mixing and entropy of mixing are related to G_M through standard thermodynamic relations:

$$H_M = G_M - T\left(\frac{\partial G_M}{\partial T}\right)_{T,P,N} \qquad ; \qquad S_M = \frac{H_M - G_M}{T} \tag{3.93}$$

Differentiating equation (3.87) with respect to T and substituting in equation (3.93), an expression for the enthalpy of mixing is given as

$$\begin{aligned} H_M = \omega\frac{c_A(1 - c_A)}{1 - \nu c_A} - T\frac{c_A(1 - c_A)}{1 - \nu c_A}\frac{\partial \omega}{\partial T} + RT^2\frac{c_A(1 - c_A)}{1 - \nu c_A} \\ \times\left[\frac{\nu}{1 - \nu} - \frac{c_A}{1 - \nu c_A}\frac{\omega}{RT}\right]\frac{\partial \nu}{\partial T} \end{aligned} \tag{3.94}$$

and, the entropy of mixing as:

$$\begin{aligned} S_M = R[c_A \ln c_A + (1 - c_A)\ln(1 - c_A)] &+ R[c_A \ln n - \ln(1 - \nu c_A)] \\ -\frac{c_A(1 - c_A)}{1 - \nu c_A}\frac{\partial \omega}{\partial T} + RT\frac{c_A(1 - c_A)}{1 - \nu c_A}&\left[\frac{\nu}{1 - \nu} - \frac{c_A}{1 - \nu c_A}\frac{\omega}{RT}\right]\frac{\partial \nu}{\partial T} \end{aligned} \tag{3.95}$$

Equations (3.87), (3.91), (3.92), (3.94) and (3.95) are the essential equations for the model calculations.

Chapter 4

Results and Discussion

In this chapter, results and discussion on each of the models used in the previous chapter are presented.

4.1 Quasi-lattice theory

The QLT theory discussed in section 3.1, has been used to investigate the composition dependence of the bulk thermodynamics and dynamic properties such as diffusion and viscosity for the two systems Al-Zn and Bi-In liquid alloys. It is evident from the theory that there are some parameters that need to be fitted in order to perform the calculations. These parameters are the size ratio,γ, the coordination number, Z and the interchange energy, ω. For consistency, the coordination number, Z in the liquid phase was chosen as 10 (Waseda, 1980; Anusionwu and Adebayo, 2001). It was observed in the course of these calculations that the choice of Z does not significantly affect the results obtain. In addition, the size ratio, γ should have been obtained from experimental density measurements but one has chosen to treat it as a free parameter in performing this calculations simply because there are no experimental measurements for the densities at the temperatures for which thermodynamics data are available. Once suitable values of these parameters are chosen, the theory allows to calculate other quantities described above. The values of the fitted interaction parameters obtained are presented in table 4.1.

4.1.1 Concentration Fluctuations in the long-wavelength limit, the Free Energy of Mixing and the Chemical Short-range order parameter

Due to the difficulties associated with diffraction experiments, the theoretical calculation of $S_{cc}(0)$ is of great interest when investigating the nature of interaction as well as the structure of binary liquid alloys(Novakovic et al., 2004). The mixing behaviour of liquid binary alloys can be inferred from the deviation of $S_{cc}(0)$ from the ideal value, $S_{cc}^{id}(0)$. The presence of chemical order is indicated as $S_{cc}(0)<S_{cc}^{id}(0)$, on the contrary, if $S_{cc}(0)>S_{cc}^{id}(0)$, the segregation and demixing in liquid alloys take place.

A perusal of Fig. 4.1, the plot of concentration fluctuations in the long-wavelength limit $S_{cc}(0)$ versus concentration for the systems studied show that the fitted parameters yield a good representation of the experimental data. The experimental values of $S_{cc}(0)$ for the two systems were derived from the experimental free energy of mixing equation (3.17), the theoretical $S_{cc}(0)$ was obtained using equation (3.19) and thermodynamic data were taken from(Hultgren et al., 1973).

The $S_{cc}(0)$ values for the Al-Zn system at T=1000K (fig. 4.1) clearly indicate that $S_{cc}(0)>S_{cc}^{id}(0)$ in the whole concentration range. This implies a tendency for homocoordination, i.e. segregation of preference for like atom Al-Al and Zn-Zn tend to pair as nearest neighbours. The $S_{cc}(0)$ curve exhibits the maximum value of about 0.409 at $C_{Al} = 0.50$. For Bi-In system, the $S_{cc}(0)$ values show that $S_{cc}(0) < S_{cc}^{id}(0)$ over the concentration range. This suggests a tendency of complex formation i.e. preference for unlike atoms pairing as nearest neighbour.

The plot of the concentration dependence of $\frac{G_M}{RT}$ for the two alloys are given in Fig. 4.2. It is interesting to note that the computed values are in quite excellent agreement with experiment. From the result, the Gibbs energies of mixing G_M for Al-Zn and Bi-In liquid alloys, have values of about -0.4986RT and -0.9344RT,

Table 4.1: Values of the parameters for Al-Zn and Bi-In liquid alloys

Alloy	T(K)	Z	$\frac{W}{RT}$	γ
Al-Zn	1000	10	0.800	0.950
Bi-In	900	10	-0.900	1.135

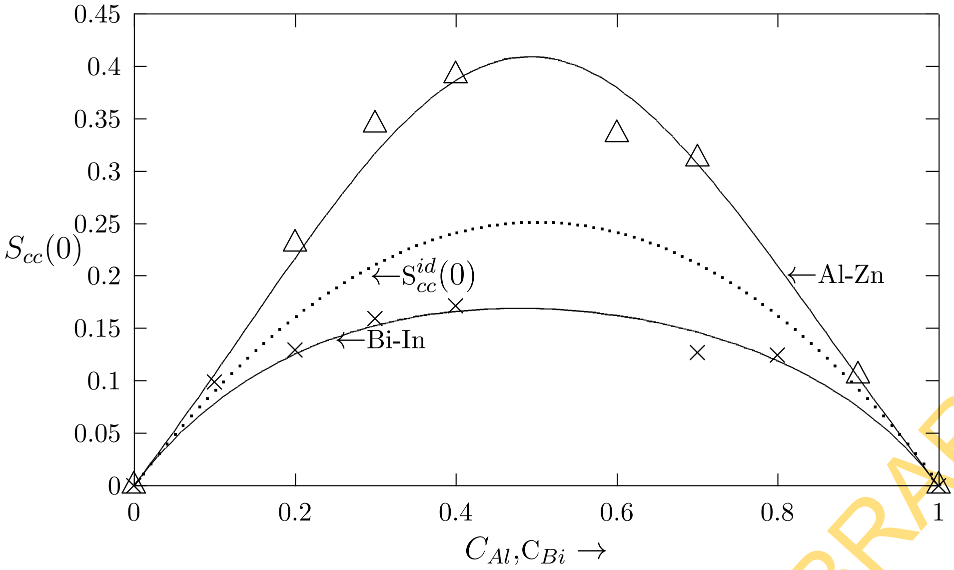

Figure 4.1: Concentration fluctuations in the long-wavelength limit ($S_{cc}(0)$ and $S_{cc}^{id}(0)$) vs. concentration for Al-Zn and Bi-In liquid alloys at 1000K and 900K respectively. The solid line denotes theoretical values while the triangle and the cross denote experimental values for Al-Zn and Bi-In respectively. The dot denotes the ideal values $S_{cc}^{id}(0)$. c_{Al} and c_{Bi} are the Al and Bi concentrations in the alloy.

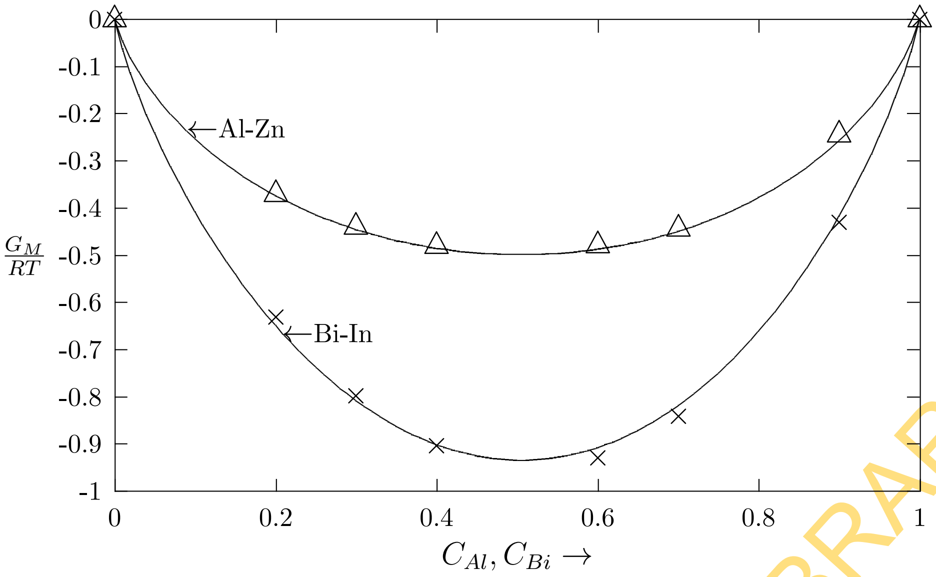

Figure 4.2: Concentration dependence of $\frac{G_M}{RT}$ for Al-Zn and Bi-In liquid alloys at 1000K and 900K, respectively. The solid line denotes theoretical values while the triangles and the crosses denote experimental values for Al-Zn and Bi-In, respectively. c_{Al} and c_{Bi} are the Al and Bi concentrations in the alloy. The experimental data were taken from Hultgren et al., (1973).

respectively. This shows that the tendency of compound formation in the liquid phases is weaker in Al-Zn than in Bi-In alloy.

The same mixing behaviour can be deduced from the values of the Warren-Cowley short-range order parameter, α_1, table 4.2. The positive values of the parameter α_1, for Al-Zn support a tendency towards segregation and the negative values of α_1, for Bi-In system at all concentrations confirm a tendency of complex formation.

4.1.2 Dynamic properties: diffusion and Viscosity

From the ordering point of view, the computed chemical diffusion ratio (equation (3.21)) seems to be a more realistic parameter than the Warren-Cowley short range order parameter, α_1, (Novakovic et al., 2004) since equation (3.21) does not take into consideration the coordination number, Z, as an input and thus the inherent problems related to its estimation are avoided. The relationship between the $S_{cc}(0)$ and diffusion expressed by the ratio of the mutual and self-diffusion coefficient $\frac{D_M}{D_{id}}$, indicates the mixing behaviour of alloys, i.e. phase separation tendency or segregation in Al-Zn, for $\frac{D_M}{D_{id}} < 1$ over the concentration range, table 4.3. The values $\frac{D_M}{D_{id}} > 1$ for Bi-In liquid phase at all concentrations suggest a tendency for compound formation in the melt.

As to the other aspect of the calculations which is to investigate how well the theoretical formulation in equations (3.11) and (3.12) compare with experiment, Fig. 4.3 shows the results obtained for $\frac{\Delta\eta}{\eta_o}$ and $-\frac{H_M}{RT}$, but due to the lack of experimental data for viscosity at temperatures of interest, it was not possible to compare the results from this work for viscosity with experimental values. However, examination of Fig. 4.3 reveals that the computed $\frac{\Delta\eta}{\eta_o}$ for Al-Zn show a negative deviation while its $-\frac{H_M}{RT}$ is characterized by liquid miscibility gaps and exhibit large positive heat of mixing, H_M. This fact is substantiated by the earlier hypothesis of the existence of a liquid miscibility gap in Al-Zn liquid alloy.

On the other hand, the computed $\frac{\Delta\eta}{\eta_o}$ for Bi-In exhibit positive deviation and

Table 4.2: Computed chemical short range order parameter (α_1) for Al-Zn and Bi-In alloys at T = 1000K and 900K, respectively.

$C_{Al,Bi}$	$(\alpha_1)_{Al-Zn}$	$(\alpha_1)_{Bi-In}$
0.1	0.0697	-0.0696
0.2	0.0625	-0.0614
0.3	0.0551	-0.0534
0.4	0.0476	-0.0453
0.5	0.0399	-0.0375
0.6	0.0322	-0.0298
0.7	0.0244	-0.0222
0.8	0.0164	-0.0145
0.9	0.0083	-0.0073

Table 4.3: Concentration dependence of $\frac{D_M}{D_{id}}$ for Al-Zn and Bi-In alloys at T = 1000K and 900K, respectively.

$C_{Al,Bi}$	$\frac{D_M}{D_{id}}_{Al-Zn}$	$\frac{D_M}{D_{id}}_{Bi-In}$
0.1	0.8510	1.1493
0.2	0.7393	1.2751
0.3	0.6631	1.3746
0.4	0.6209	1.4443
0.5	0.6112	1.4805
0.6	0.6324	1.4792
0.7	0.6824	1.4358
0.8	0.7623	1.3334
0.9	0.8683	1.2021

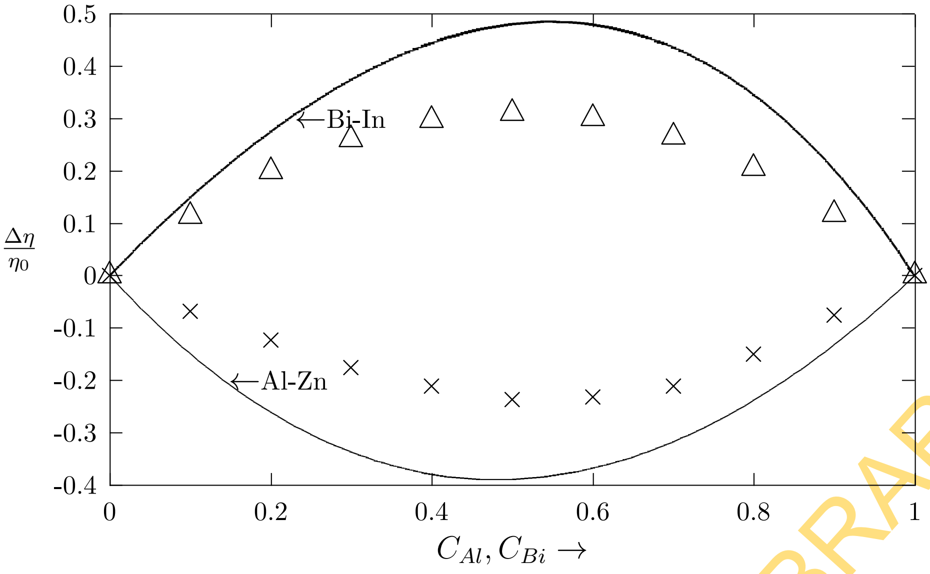

Figure 4.3: Concentration dependence of viscosity $\frac{\Delta\eta}{\eta_o}$ eqns.(3.11) and (3.12) for Al-Zn and Bi-In at 1000K and 900K respectively. The solid line are for calculated $\frac{\Delta\eta}{\eta_o}$. The triangles and the crosses denote experimental values for $\frac{-H_M}{RT}$ for Al-Zn and Bi-In respectively. c_{Al} and c_{Bi} are the Al and Bi concentrations in the alloy. The experimental data were taken from Hultgren et al., (1973).

its $\frac{-H_M}{RT}$ shows negative deviation which confirm that Bi-In liquid alloy is an ordered alloy. In order to discuss the disagreement between the calculated values of $\frac{\Delta\eta}{\eta_o}$ and $\frac{-H_M}{RT}$ for the two systems, it is important one looks at the parameters used to fit $S_{cc}(0)$ and hence to carry out the calculations. It is observed that the fitted value of γ for Bi-In is 1.135 and 0.950 for Al-Zn, (table 4.1). The calculated values of γ for Bi-In is closer to that determined at the melting point than that of Al-Zn. One reasonably inference from this is that the size effect plays a prominent role in the energetics of Bi-In than it plays in Al-Zn alloy and thus pulling the system from segregation to order phase.

4.1.3 Summary

A Quasi-Lattice Theory has been utilized to obtain the fitted parameters, that are assumed to be invariant in all calculations. The bulk and dynamic properties in Al-Zn and Bi-In liquid alloys have been investigated using a theoretical approach with special interest on their bulk thermodynamic properties such as free energy of mixing, Concentration fluctuations in long-wavelength limit, chemical short range order parameter and the concentration dependence of diffusion and viscosity. The theoretical investigation of bulk properties of Al-Zn liquid alloy is substantiated by the experimental data, obtained at 1000K (Hultgren et al., 1973). The ordering in Al-Zn liquid phase has been analyzed in terms of the microscopic functions, $S_{cc}(0)$, and CSRO (α_1). The calculated values of these functions indicate the existence of liquid miscibility gap or segregation in the melt. On the contrary, the presence of chemical order was observed for Bi-In at 900K. The bulk thermodynamic and dynamic properties of the two liquid alloys have been explained to a reasonable extent and the role of size effects notwithstanding the non-availability of the experimental viscosity data. The results obtained in this work establish or confirm the applicability of this theoretical approach for a proper description of mixing properties of binary liquid alloys.

4.2 Quasi Chemical Approximation Model

The mixing properties of Ga-Zn, Ga-Mg and Al-Ga binary liquid alloys have been discussed based on the model formulation described in section 3.2. The values of the relevant parameters used to obtain various thermodynamic quantities are presented in table 4.4.

Keeping these fitted parameters which gives the best representation of the observed Gibbs free energy of mixing G_M data unchanged in all calculations, one then proceeded using these fixed values to compute properties such as the $S_{cc}(0)$, α_1, H_M and S_M and thus, forming a basis for discussing the energetics of the liquid alloys.

The free energy of mixing for these liquid alloys has been computed using equation (3.27). The experimental data given as symbols in figure 4.4 were taken from (Hultgren et al., 1973). Examination of figure 4.4 shows that the interaction parameters give a good reproduction of the experimental values of the free energy of mixing for the alloys Ga-Zn, Ga-Mg and Al-Ga at temperatures of 700K, 923K, and 1073K, respectively. The good agreement obtained for G_M as shown in the figure for the three systems investigated, allow the use of the fitted energy parameters to study the nature of ordering in the liquid alloys. A comparison of the figure for the three liquid alloys reveal that the free energy of mixing are almost symmetric around the equiatomic composition ($c_{Ga,Al} = 0.5$), with Ga-Mg $[(\frac{G_M}{RT})_{c_c} = 2.08]$ exhibiting a higher tendency for compound formation and is the most interacting of the three alloys; Al-Ga $[(\frac{G_M}{RT})_{c_c} = 0.652]$ is more interacting than Ga-Zn alloy $[(\frac{G_M}{RT})_{c_c} = 0.569]$.

For proper analysis of the nature of ordering in the melts, it is important to critically consider the results for the structure related quantities. From this point of view the first quantity considered is the concentration fluctuations $S_{cc}(0)$. The deviation of $S_{cc}(0)$ from ideal value $S_{cc}^{id}(0)$=$c_A c_B$ is an essential parameter in order to visualize the nature of atomic interactions in the mixture. If, at a given composition $S_{cc}(0)$>$S_{cc}^{id}(0)$, then there is a tendency for segregation and vice versa

Table 4.4: Fitted interaction parameters for the systems.

System	T(K)	Z	$\omega(eV)$	$\frac{d\omega}{dT} \times 10^{-3}$	μ	ν
Ga-Zn	700	10	0.0323	-1.240	1	1
Ga-Mg	923	10	-0.3932	9.215	1	1
Al-Ga	1073	10	0.0150	-0.250	1	1

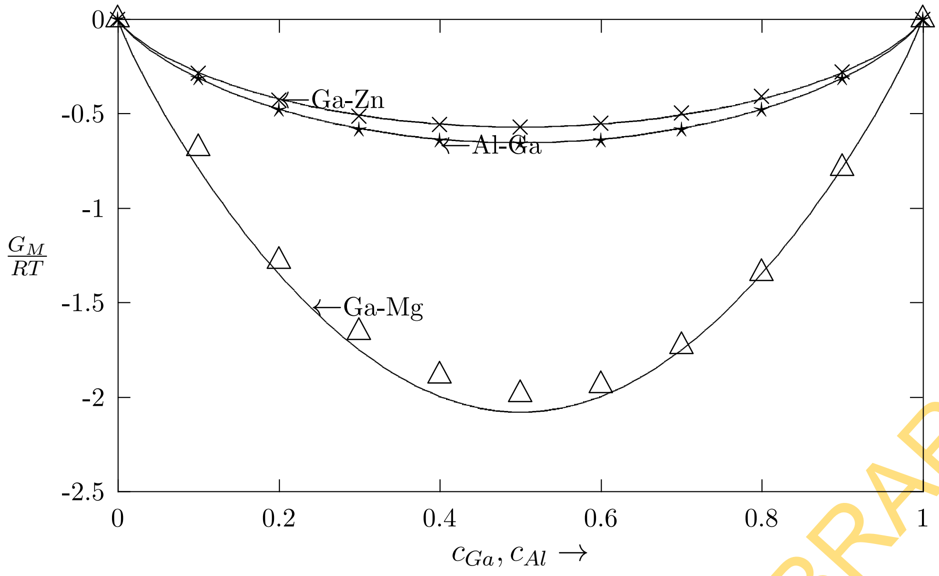

Figure 4.4: Free energy of mixing, $\frac{G_M}{RT}$ versus concentration for Ga-Zn, Ga-Mg and Al-Ga liquid alloys at 700K, 923K and 1073K, respectively. The solid line denotes theoretical values while the crosses, triangles and the stars denote experimental values for Ga-Zn, Ga-Mg and Al-Ga respectively. c_{Ga} and c_{Al} are the Ga and Al concentrations in the alloy. The experimental data were taken from Hultgren et al., (1973).

for heterocoordination. It is obvious from equation (3.37) that $S_{cc}(0)$ can be obtained directly from the experimental Gibbs energy of mixing or from the activity data. This is usually referred to as an experimental $S_{cc}(0)$ in literature. Equation (3.39) was used to determine the computed $S_{cc}(0)$ for these liquid alloys, while their measured $S_{cc}(0)$ were obtained by numerical differentiation of the Gibbs free energy of mixing data taken from (Hultgren et al., 1973). It is important to add that equation (3.38) was used to obtain $S_{cc}^{id}(0)$. The results for the concentration fluctuations as a function of composition for the three systems are as shown in figure 4.5. From the figure, it is clear that the calculated $S_{cc}(0)>S_{cc}^{id}(0)$ for Ga-Zn and Al-Ga, while calculated $S_{cc}(0)<S_{cc}^{id}(0)$ for Ga-Mg. This implies a tendency for homocoordination in Ga-Zn and Al-Ga alloys i.e. like atoms Ga-Ga, Zn-Zn or Al-Al tend to pair as nearest neighbours and a presence of heterocoordination in Ga-Mg i.e. unlike atoms Ga-Mg tend to pair as nearest neighbours. A look at figure 4.5 shows that in the region of $0 \leq c_{Al} \leq 0.30$ and $0.7 \leq c_{Al} \leq 1$, it is noted that the calculated $S_{cc}(0)$ values for Al-Ga liquid alloy almost attain ideal values. This indicates that Al-Ga alloy has tendency to exhibit ideal behaviour for these concentrations.

For a better knowledge of the local arrangement of atoms in the molten alloys, equation (3.40) is used to obtain the Warren-Cowley short-range order parameter α_1. The positive values of α_1 (figure 4.6) in the whole concentration range for both Ga-Zn and Al-Ga alloys are sufficient indicators of the presence of homocoordination (Segregation) in the liquid alloys, while negative values of α_1 for Ga-Mg indicates chemical order in this concentration range. In addition, α_1 is much less than unity for both Ga-Zn and Al-Ga alloys and a pointer that the alloys are weakly segregating alloys. It must be noted that varying the value of Z does not have any significant effect on $\alpha_1 - c$ curves, its only effect is to vary the position of the maxima while the overall features remain unchanged.

From equation (3.42) it is seen that in order to obtain a good fit to H_M,there is need to incorporate the temperature dependence of the interaction parameters.

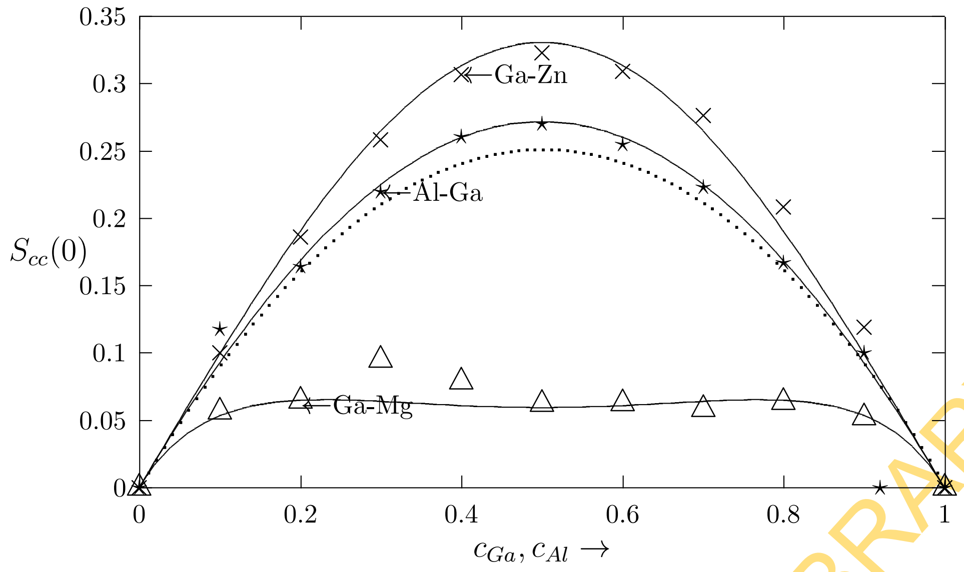

Figure 4.5: Concentration-concentration fluctuations $S_{cc}(0)$ versus concentration for Ga-Zn, Ga-Mg and Al-Ga liquid alloys at 700K, 923K and 1073K, respectively. The solid line denotes theoretical values while the crosses, triangles and the stars denote experimental values for Ga-Zn, Ga-Mg and Al-Ga respectively. The dot denotes the ideal values. c_{Ga} and c_{Al} are the Ga and Al concentrations in the alloy.

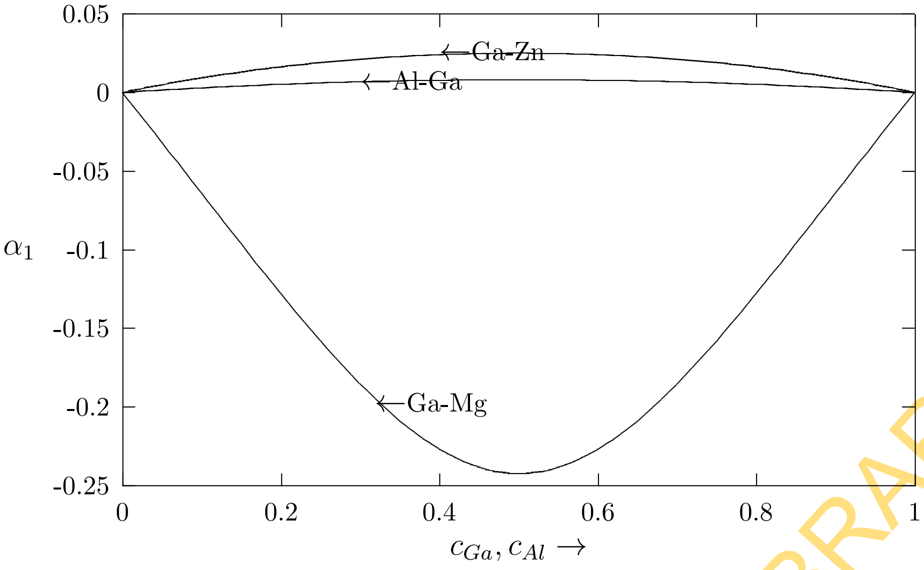

Figure 4.6: Calculated Warren-Cowley short range order parameter α_1 versus concentration for Ga-Zn, Ga-Mg and Al-Ga liquid alloys at 700K, 923K and 1073K, respectively. c_{Ga} and c_{Al} are the Ga and Al concentrations in the alloy.

Using equations (3.42) and (3.43), one ascertained the variation in temperature parameters from the measured values of H_M and S_M, the results are shown in table 4.4. From the fitted enthalpy of mixing and entropy of mixing in Figures 4.7 and 4.8, respectively, it is noted that the fits obtained for the three alloys compared quite well with the experimental data. The values obtained (table 4.4) show that the temperature dependence of the energy parameters are quite small. Also, it is seen that the enthalpy of mixing for Ga-Zn and Al-Ga alloys are symmetric and positive (typical of segregating systems) in agreement with the work of Novakovic and Zivkovic,(2005) on Ga-Zn and Singh et al., (1997) on gallium-based alloys, although their Gibbs free energy of mixing are indicative of a very weakly interacting system. On the contrary, both the free energy of mixing, G_M and the enthalpy of mixing, H_M exhibit negative deviations from Raoultian behaviour for Ga-Mg alloy. In addition, the entropy of mixing (figure 4.8) for the three alloys investigated are almost symmetric and positive around the equiatomic composition. Generally, one observes that both the reported literature data and theoretical values obtained using the interaction parameters and their temperature dependence are in very good agreement.

4.2.1 Summary

The thermodynamic properties of the three binary liquid alloys, namely Ga-Zn, Ga-Mg and Al-Ga have been discussed in terms of the free energy of mixing, $\frac{G_M}{RT}$, the concentration fluctuations in the long-wavelength limit, $S_{cc}(0)$, the chemical short-range order parameter, α_1, as a functions of compositions on the basis of the theory discussed in section 4.2. Positive deviations from Raoultian behaviour was observed in the thermodynamic properties of Al-Ga and Ga-Zn which agrees with the result of Awe et al,(2005) using four-atom -cluster model (FACM), while Ga-Mg exhibits negative deviation. An indication that both Ga-Zn and Al-Ga are segregating systems, while a reasonable degree of chemical order exists in Ga-Mg alloy across the whole concentration range. The enthalpy of mixing and entropy of mixing for the three alloys investigated are positive and symmetric around equiatomic composition, except for the enthalpy of mixing, H_M of Ga-Mg alloy that shows a negative deviation from Raoultian behaviour. It is established that in the glass-forming composition range which usually lies far away from the stoichiometric composition, computed $S_{cc}(0)$ almost attain ideal values for Al-Ga: i.e. Al-Ga exhibits ideal behaviuor for the composition $0 \leq c_{Al} \leq 0.30$ and $0.7 \leq c_{Al} \leq 1$.

4.3 Four Atom Cluster Model

The theory discussed in section 3.3 has been used to compute the concentration dependence of the activity ratio of the individual systems, the concentration-concentration fluctuations in the long wavelength limit, the free energy of mixing, the CSRO parameter and the chemical diffusion. For consistency, the coordination number Z was chosen as 10 for the two systems investigated. It is, however, noted that the choice of Z does not have significant effect on the results obtained. The experimental $S_{cc}(0)$ were obtained from experimental free energy of mixing using equation (5.38). The experimental data used for the thermodynamic calculations were taken from Hultgren et al., (1973) for the alloys.

One observes that the only parameter that needs to be fitted in order to perform the present calculation is the interchange energy ω. Table 4.5 shows the appropriate values of this parameter for the two alloys obtained, via FACM. A close perusal of Tables 4.6 and 4.7 confirms that the two alloys investigated are ideal candidates for the FACM. The theoretical and observed values of the activity ratios are in reasonable agreements. Although some minor discrepancies exist for smaller contents of Bi and Sb in the alloys, as these concentrations increase the agreement improves significantly. Table 4.5 shows the values of the parameters used for the calculations of bulk properties of Bi-Pb and Sb-Sn liquid alloys. In general, it is known that if $\omega < 0$, there is a tendency for the two different atoms in an alloy to form unlike-atom pairs; otherwise, like atoms tend to pair together. However, $\omega = 0$, indicates that atoms in the mixtures are perfectly disordered (Singh and

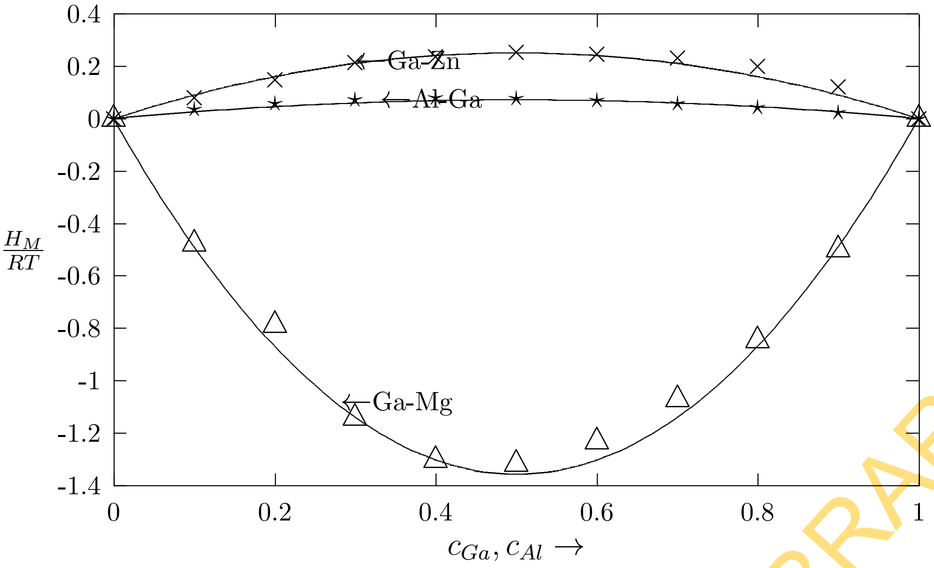

Figure 4.7: Enthalpy of mixing, $\frac{H_M}{RT}$ versus concentration for Ga-Zn, Ga-Mg and Al-Ga liquid alloys at 700K, 923K and 1073K, respectively. The solid line denotes theoretical values while the crosses, triangles and the stars denote experimental values for Ga-Zn, Ga-Mg and Al-Ga respectively. c_{Ga} and c_{Al} are the Ga and Al concentrations in the alloy. The experimental data were taken from Hultgren et al.,(1973).

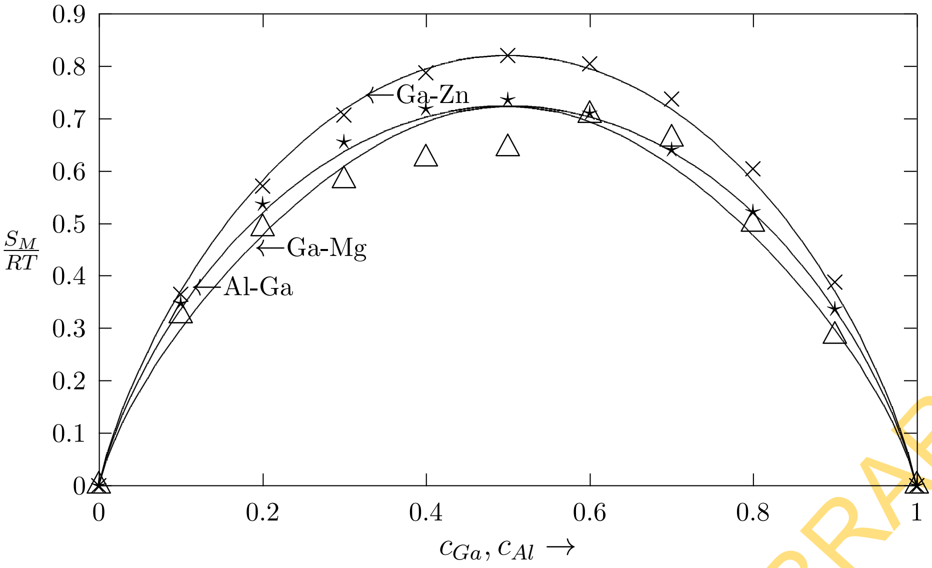

Figure 4.8: Entropy of mixing, $\frac{S_M}{R}$ versus concentration for Ga-Zn, Ga-Mg and Al-Ga liquid alloys at 700K, 923K and 1073K, respectively. The solid line denotes theoretical values while the crosses, triangles and the stars denote experimental values for Ga-Zn, Ga-Mg and Al-Ga, respectively. c_{Ga} and c_{Al} are the Ga and Al concentrations in the alloy. The experimental data were taken from Hultgren et al.,(1973).

Sommer, 1987; Singh and March, 1995). Hence, that the values of $\omega < 0$ for both Bi-Pb and Sb-Sn show that there is higher tendency for unlike atoms to pair in the two alloys which implies heterocoordination. Also, the value of ω for Sb-Sn is lower than that for Bi-Pb. This is an indication that the degree of chemical order in Sb-Sn is higher than in Bi-Pb.

Fig. 4.9 shows the results obtained for $\frac{G_M}{RT}$ for the two alloys, using equation (3.74). The qualitative agreement between the experimental and calculated values is a confirmation that the chosen values of ω for each of the two alloys is okay. One interesting characteristic exhibited by the two alloys investigated is the concentration dependence of their free energy of mixing which exhibits a regular solution behaviour. It is observed that the two alloys are weakly interacting in view of the fact that their respective plots of G_M/RT are quite less than 3.0 throughout the entire compositions. Also, it is noticed that the chemical interaction in Sb-Sn at 905k is not as weak as that in Bi-Pb at 700K as the plot of the former is below the latter which is in harmony with one's expectations for the two alloys (the ordering parameter of Sb-Sn of value -0.0695 is lower than that of Bi-Pb of value -0.0497 by as much as 0.0198).

Equation (3.82) has been used for the computation of the $S_{cc}(0)$ for Bi-Pb and Sb-Sn. The plot of $S_{cc}(0)$ as a function of concentration obtained are shown in Fig 4.10. The agreement between the computed and experimental values for each of the two alloys is quite good. That the $S_{cc}(0)$ for both alloys is less than $S_{cc}^{id}(0)$ is an indication that there is chemical order over the whole concentration range in the two alloys. Also, that the deviation of $S_{cc}(0)$ from ideality of Sb-Sn is greater than that of Bi-Pb is a corroborating evidence that although the two alloys are both weak chemically interacting alloys yet, Bi-Pb is weaker than Sb-Sn. Fig. 4.11 shows the plot of α_1 against chemical composition, obtained from equation (3.71) for Bi-Pb and Sb-Sn at 700K and 905K, respectively. It is observed that the two plots are symmetrical about equiatomic composition and negative throughout the concentration range. The negative values of α_1 in the two alloys are signatures

Table 4.5: Interchange energy $\omega(eV)$ for the systems.

System	T(K)	Z	$\omega(eV)$
Bi-Pb	700	10	-0.0497
Sb-Sn	905	10	-0.0695

Table 4.6: Computed and experimental activity ratio for Bi-Pb alloy.

c_{Bi}	Theory	Experimental*
0.1	10.373	7.611
0.2	4.455	3.435
0.3	2.509	2.041
0.4	1.556	1.337
0.5	1.000	1.000
0.6	0.643	0.906
0.7	0.399	0.403
0.8	0.224	0.239
0.9	0.096	0.108

*Hulgren et al,(1973)

Table 4.7: Computed and experimental activity ratio for Sb-Sn alloy.

c_{Sb}	Theory	Experimental*
0.1	10.287	9.000
0.2	4.427	3.088
0.3	2.498	2.351
0.4	1.552	1.494
0.5	1.000	0.996
0.6	0.644	0.703
0.7	0.400	0.429
0.8	0.226	0.251
0.9	0.097	0.111

*Hulgren et al,(1973)

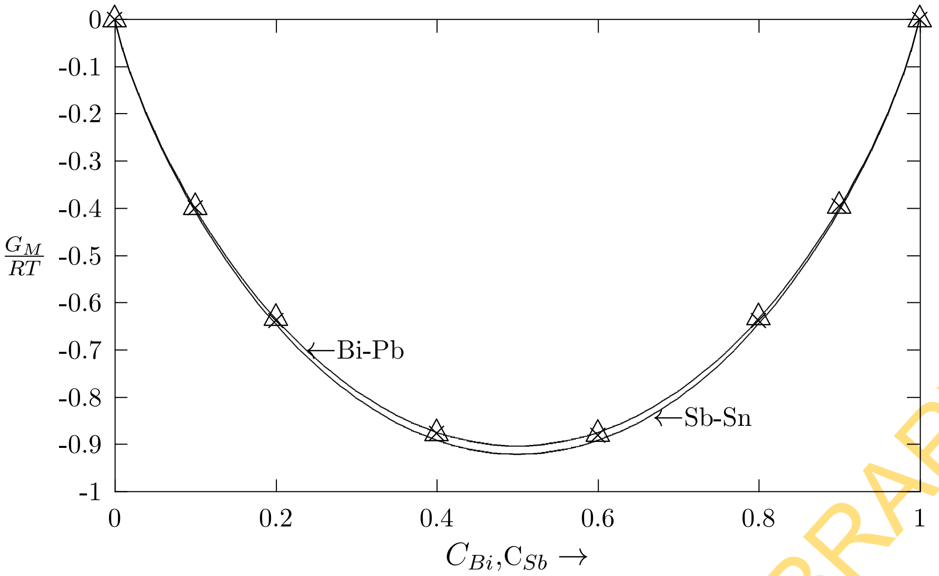

Figure 4.9: Free energy of mixing, $\frac{G_M}{RT}$ versus concentration for Bi-Pb and Sb-Sn liquid alloys at 700K and 905K respectively. The solid line represents theoretical values using Eqn. (3.74) while the triangle and the cross represent experimental values for Bi-Pb and Sb-Sn respectively. c_{Bi} and c_{Sb} are the Bi and Sb concentrations in their respective alloys. The experimental data were taken from Hultgren et al., (1973).

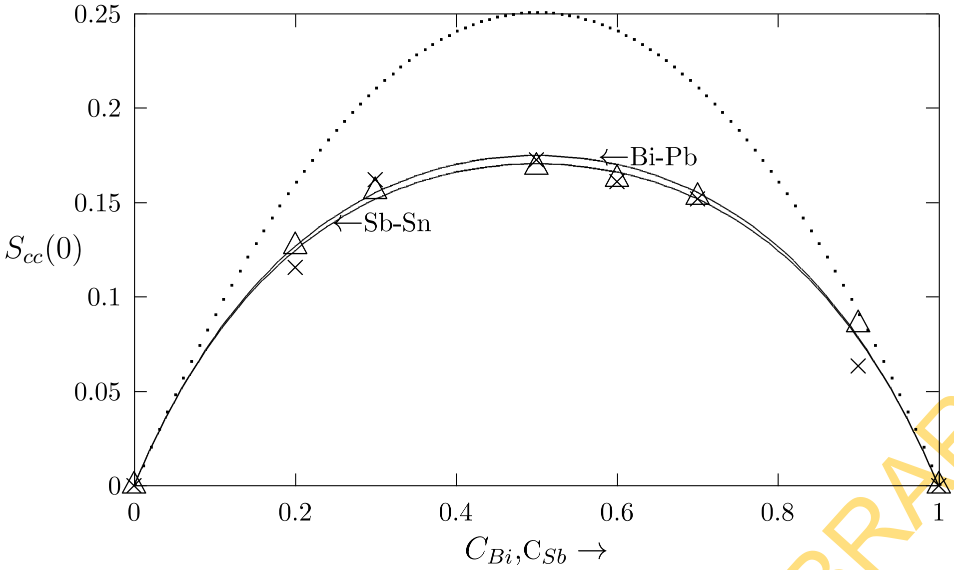

Figure 4.10: Concentration-concentration fluctuations $S_{cc}(0)$ versus concentration for Bi-Pb and Sb-Sn liquid alloys at 700K and 905K respectively. The solid line represents theoretical values obtained from Eqn. (3.82) while the triangle and the cross represent experimental values for Bi-Pb and Sb-Sn respectively. c_{Bi} and c_{Sb} are the Bi and Sb concentrations in their respective alloys.

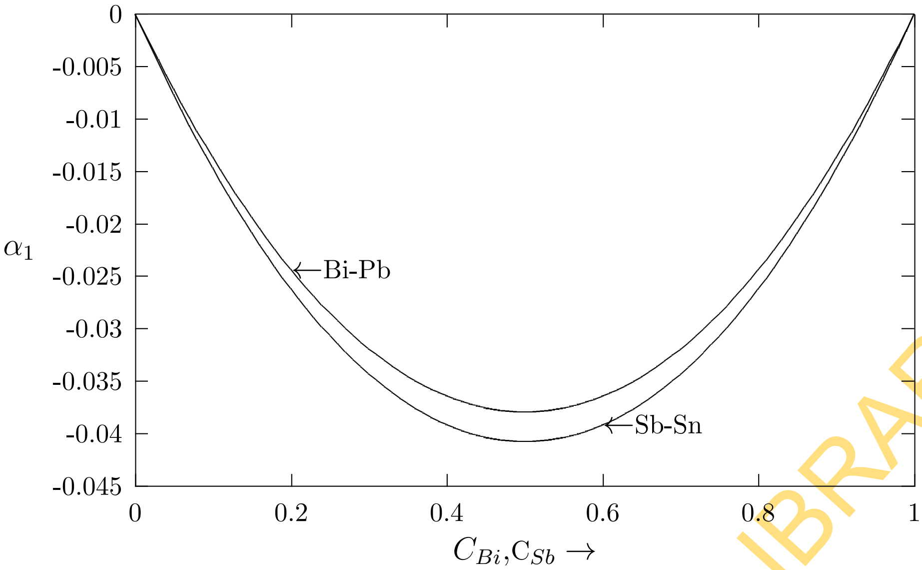

Figure 4.11: Calculated Cowley-Warren short range order parameter, α_1 versus concentration, using Eqn. (3.71) for Bi-Pb and Sb-Sn liquid alloys at 700K and 905K, respectively. C_{Bi} and C_{Sb} are the Bi and Sb concentrations in the alloys.

of heterocoordination in the Bi-Pb and Sb-Sn systems, as earlier evident in the calculations of $\frac{G_M}{RT}$ and $S_{cc}(0)$ and in the values of obtained for ω. Furthermore, that the plot of Sb-Sn is lower than that of Bi-Pb reinforce earlier submission that the degree of order in the latter is not as high as in the former.

The computed values of $S_{cc}(0)$ have been used in equation (3.83) to evaluate D_M/D_{id} as a function of composition. These are presented in Fig. 4.12. It is observed that D_M/D_{id} is greater than 1 in the entire concentration range for these alloys. This is indicative of the presence of chemical order in the alloys, and further shows that the degree of order in Sb-Sn is higher than in Pb-Bi alloy.

4.3.1 Summary

Although the FACM employed in the study of thermodynamic functions of Bi-Pb and Sb-Sn has been reported to have some shortcomings when applied to alloys where size effect or/and electronegativity difference are significant (Akinlade, 1997); yet the model as used here has successfully explained some thermodynamics properties of Bi-Pb and Sb-Sn. This might perhaps be connected with the fact that their size ratios (Bi-Pb is $\Omega_{Bi}/\Omega_{Pb} \approx 1.07$, while Sb-Sn is $\Omega_{Sb}/\Omega_{Sn} \approx 1.11$)) and electronegativity differences (0.18 for Bi-Pb and 0.09 for Sb-Sn) are quite ignorable.

The bulk property calculations reveal that both Bi-Pb and Sb-Sn at temperatures of 700 and 905K in that order are heterocoordinated liquid alloys with degree of chemical order in the latter being more than the former.

For both systems, in view of the fact that the size ratios are quite less than 2.0 and their electronegativity differences are ignorable, one thus infers that the characteristic behaviour of each of the alloy is dependent on the energetics of the respective system.

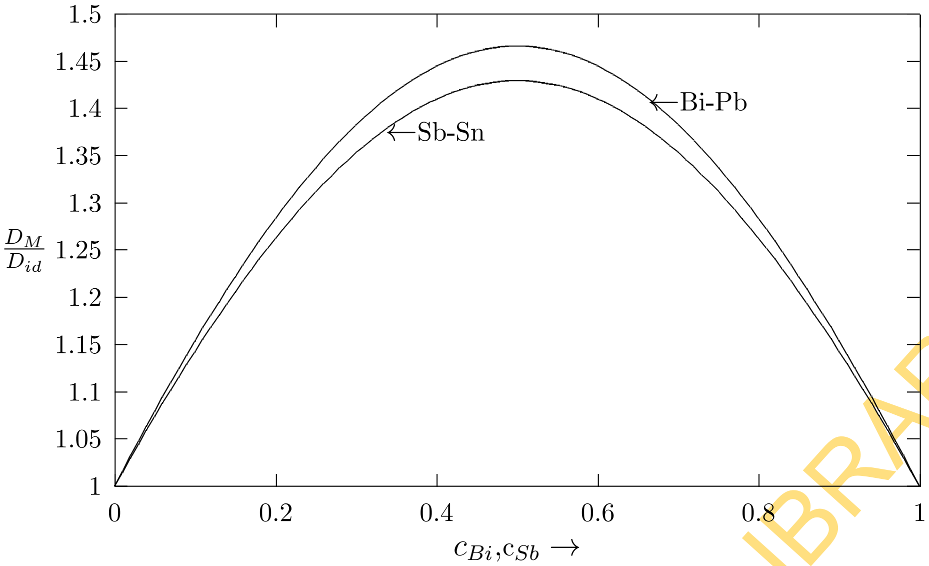

Figure 4.12: Calculated ratio of mutual diffusion and self-diffusion coefficients, D_M/D_{id} versus concentration, using Eqn. (3.83) for Bi-Pb and Sb-Sn liquid alloys at 700K and 905K, respectively. c_{Bi} and c_{Sb} are the Bi and Sb concentrations in the alloys.

4.4 Statistical thermodynamic theory

The formulation described in section 3.4 has been utilized to compute the various mixing properties such as G_M, H_M, S_M and activities a_A for binary liquid Sb-Sn, In-Pb, Ga-Tl and Al-Si alloys at different temperatures. Table 4.8 shows the values of model parameters used in the calculations for Sb-Sn and In-Pb, while Table 4.9 shows the values of model parameters used in the calculations for Ga-Tl and Al-Si liquid alloys, respectively.

Keeping the values of the interaction energy parameters which give the best representation of the experimental free energy of mixing unchanged in all calculations, one has incorporated the temperature dependence of the interaction energy parameters to obtain the enthalpy of mixing and the entropy of mixing for the liquid alloys.

It is important to say that equation (3.87) was used to obtain the calculated free energy of mixing, $\frac{G_M}{RT}$, equation (3.91) for the calculated activity, a_A, while equations (3.94) and (3.95) were used to obtain the enthalpy of mixing, H_M and entropy of mixing, S_M, respectively, for the liquid binary alloys.

4.4.1 Sb-Sn liquid alloys at 905K

The calculated activity of Sb in liquid Sb-Sn alloys at 905K is obtained via Equation (3.91). The values are given in Table 4.10 together with the experimental values from Hultgren et al.,(1973). The computed and experimental values are in good agreement.

The computed values of free energy of mixing, $\frac{G_M}{RT}$ through equation (3.87) are plotted in Figure 4.13 with the experimental data for Sb-Sn at 905K, as a function of concentration. The qualitative agreement between the computed and experimental values as seen from the figure is a confirmation that the value of the fitted interaction energy parameter ω for Sb-Sn is okay. The negative value of this parameter for Sb-Sn as given in Table 4.8, clearly indicates the tendency for unlike atoms to pair as nearest-neighbour (i.e Sb-Sn pairs) in the alloys. It may be noted

Table 4.8: Parameters used in the model calculations for Sb-Sn and In-Pb.

Systems	T(K)	ν	ω	$\frac{\partial\omega}{\partial T}$	$\frac{\partial\nu}{\partial T}$
Sb-Sn	905	0.0957	-0.85	-0.20	-0.15
In-Pb	673	0.1607	0.45	-0.10	-0.20

Table 4.9: Parameters used in the model calculations for Ga-Tl and Al-Si.

Systems	T(K)	ν	ω
Ga-Tl	973	0.3140	1.55
Ga-Tl	1073	0.3140	1.30
Ga-Tl	1173	0.3140	1.12
Al-Si	2000	0.0177	-0.82
Al-Si	2400	0.0177	-0.70
Al-Si	2473	0.0177	-0.67

Table 4.10: Activity of Sb in Sb-Sn liquid binary alloys at 905K.

c_{Sb}	Theory	Experimental*
0.1	0.049	0.049
0.2	0.113	0.113
0.3	0.192	0.194
0.4	0.287	0.290
0.5	0.495	0.497
0.6	0.514	0.520
0.7	0.641	0.646
0.8	0.769	0.772
0.9	0.891	0.892

* Hultgren et al.,(1973)

that the $\frac{G_M}{RT}$ of Sb-Sn liquid alloys is symmetrical around equiatomic composition with the minimum value of $\frac{G_M}{RT}$ = -0.929393 at about $c_{Sb} = 0.5$.

The enthalpy of mixing and entropy of mixing of Sb-Sn liquid alloys at 905K have been evaluated as a function of concentration through equations (3.94) and (3.94), respectively, on taking the values of interaction parameters given in table 4.8 and their temperature derivatives as used for the calculation of G_M. The computed values of enthalpy of mixing are plotted in Figure 4.14 together with its experimental values. It is observed from figure 4.14 that the calculated results are in good agreement with experimental values across the concentration range. The minimum value of H_M (-0.185879RT) is observed around $c_{Sb} = 0.526$ which is the compound forming concentration. Figure 4.14 is also symmetric around the equiatomic concentration. It is also evident from the figure that Sb-Sn liquid alloys deviate negatively from the ideal values, and thus Sb-Sn liquid alloys belong to the class of liquid alloys that exhibit a tendency towards compound formation.

As shown in Figure 4.15, the calculated entropy of mixing, $\frac{S_M}{R}$ of Sb-Sn at 905K agrees well with the experimental data . The values are positive at all concentrations, which shows atomic order. The S_M Vs. c_{Sb} is found symmetric at equiatomic concentration, $c_{Sb} = 0.5$. The effects of the size ratio $\frac{V_{Sn}}{V_{Sb}} \approx 0.895$ on the mixing properties can be neglected.

4.4.2 In-Pb liquid alloys at 673K

The computed values of activity of In in In-Pb liquid alloys at 673K are presented in Table 4.11 along with the experimental values. The computed In activity values compare reasonably well with the experimental values across the concentration range.

Figure 4.16 shows the plot of the $\frac{G_M}{RT}$ versus c_{In} for In-Pb liquid alloys at 673K. It is seen from the figure that there is a close agreement between the computed and experimental values of G_M across the whole concentration range. The values are negative at all concentrations, symmetric around the equiatomic composition

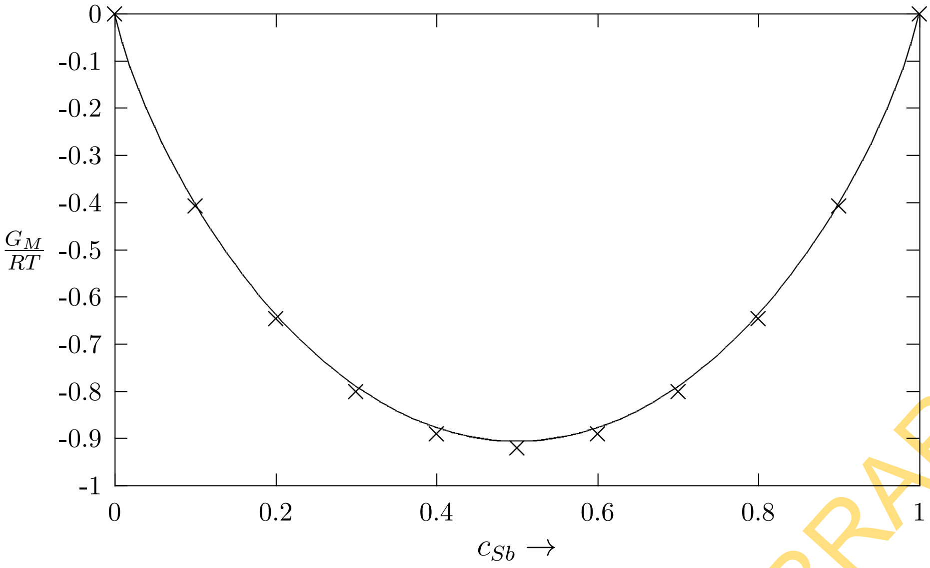

Figure 4.13: Concentration dependence of $\frac{G_M}{RT}$ for Sb-Sn liquid binary alloy at 905K. The solid line denotes theoretical values while the times denote experimental values respectively. c_{Sb} is Sb concentrations in the alloy. The experimental data were taken from Hultgren et al., (1973).

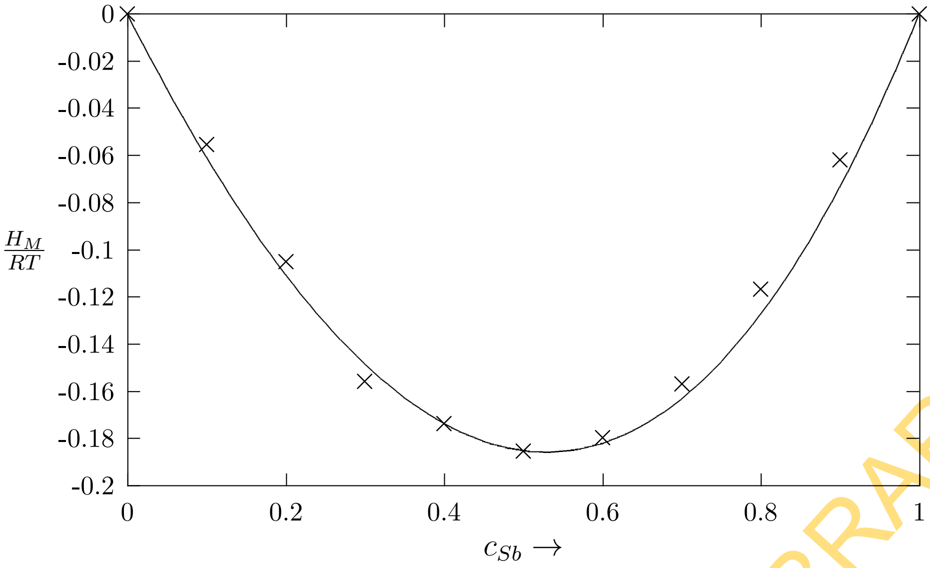

Figure 4.14: Concentration dependence of $\frac{H_M}{RT}$ for Sb-Sn liquid binary alloy at 905K. The solid line denotes theoretical values while the times denote experimental values respectively. c_{Sb} is Sb concentrations in the alloy. The experimental data were taken from Hultgren et al.,(1973).

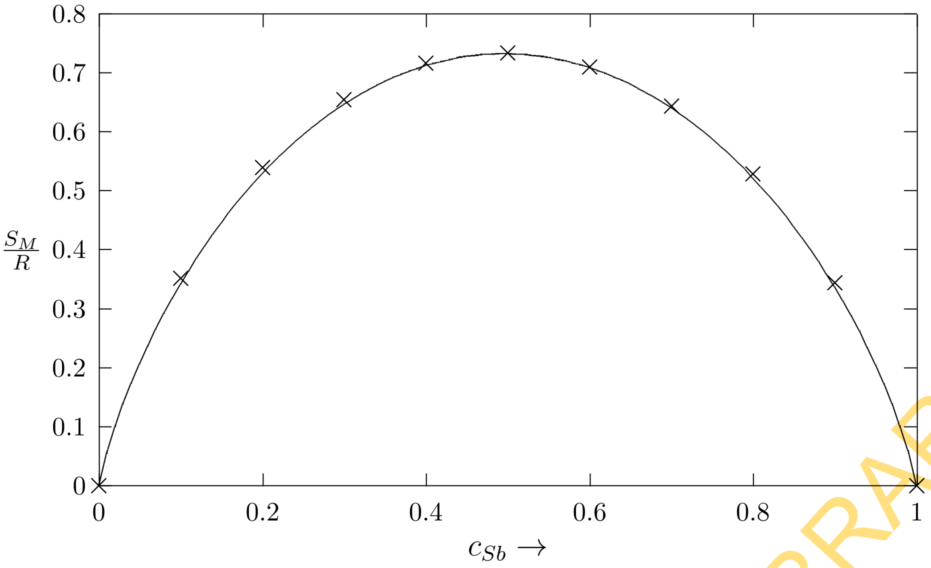

Figure 4.15: Concentration dependence of $\frac{S_M}{R}$ for Sb-Sn liquid binary alloy at 905K. The solid line denotes theoretical values while the times denote experimental values respectively. c_{Sb} is Sb concentrations in the alloy. The experimental data were taken from Hultgren et al.,(1973).

Table 4.11: Activity of In in In-Pb liquid binary alloy at 673K

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c_{In}	Theory	Experimental*
0.1	0.138	0.133
0.2	0.260	0.259
0.3	0.370	0.375
0.4	0.469	0.480
0.5	0.560	0.576
0.6	0.647	0.662
0.7	0.731	0.745
0.8	0.816	0.825
0.9	0.905	0.908

* Hultgren et al., (1973)

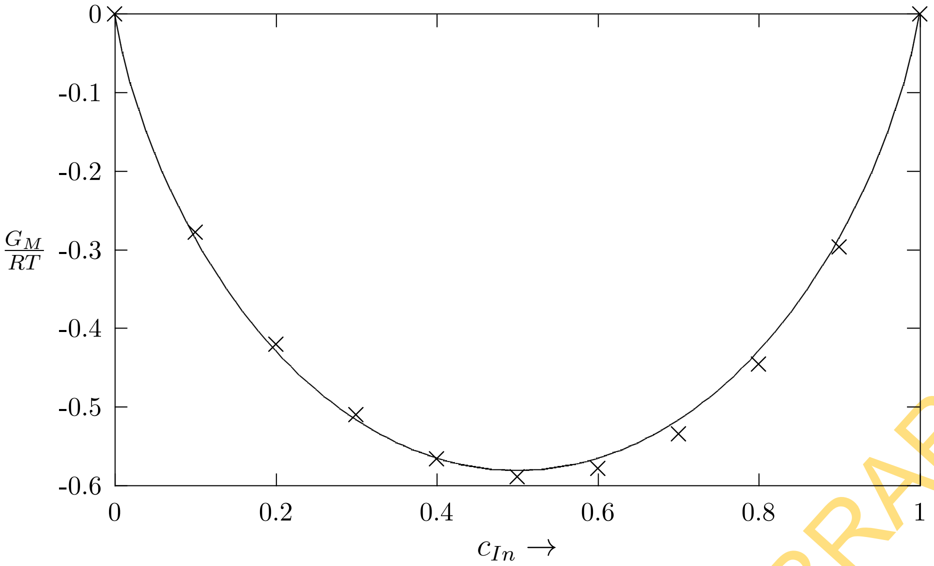

Figure 4.16: Concentration dependence of $\frac{G_M}{RT}$ for In-Pb liquid binary alloy at 673K. The solid line denotes theoretical values while the times denote experimental values respectively. c_{In} is In concentrations in the alloy. The experimental data were taken from Hultgren et al.,(1973).

and being minimum at G_M = -0.586657RT with c_{In} = 0.5. The positive value of the interaction energy parameter ω shows that the preference for like atoms to pair as nearest-neighbour is higher in the liquid alloys i.e. In-In or Pb-Pb pairs.

The plot of concentration dependence of H_M for In-Pb liquid alloys at 673K is shown in Figure 4.17. It is obvious from the figure that the calculated values of H_M reproduced fairly well the experimental values at 673K. The curve is symmetric around the equiatomic composition with minimum value of H_M = 0.152522RT at about c = 0.55. It is clear from the figure that the H_M values deviate positively from the ideal values, and thus In-Pb alloys belong to the class of liquid alloys that exhibit a tendency towards segregation.

Figure 4.18 shows the plot of S_M versus c_{In} for In-Pb liquid alloys at 673K. The calculated S_M values compare well with the experimental values across the concentration range. The curve is also symmetric around the equiatomic composition. The effects of size ratio on the mixing properties can be ignored in In-Pb liquid alloys due to the fact that the ratio $\frac{V_{Pb}}{V_{In}} \approx 1.17$, is small.

4.4.3 Al-Si liquid alloys at 2000K, 2400K and 2473K, respectively.

The consistency obtained between the calculated and experimental values for both the mixing properties and activities of Sb-Sn and In-Pb alloys at respective temperatures gave us the confidence to use the analytical expressions to determine the properties of mixing and activities of both Al-Si and Ga-Tl liquid alloys at three different temperatures each, for which experimental data exist.

Activity is a very important thermodynamic function because it can be obtained directly from experiment and used to obtain other thermodynamic functions. The calculated activities obtained using equation (3.91) for Al-Si liquid alloys at temperatures of 2000K, 2400K and 2473K, are given in tabular form in Table 4.12. The calculated activities show a relatively negative deviation from ideal behaviour for the liquid alloys. However, due to the non availability of thermodynamic data

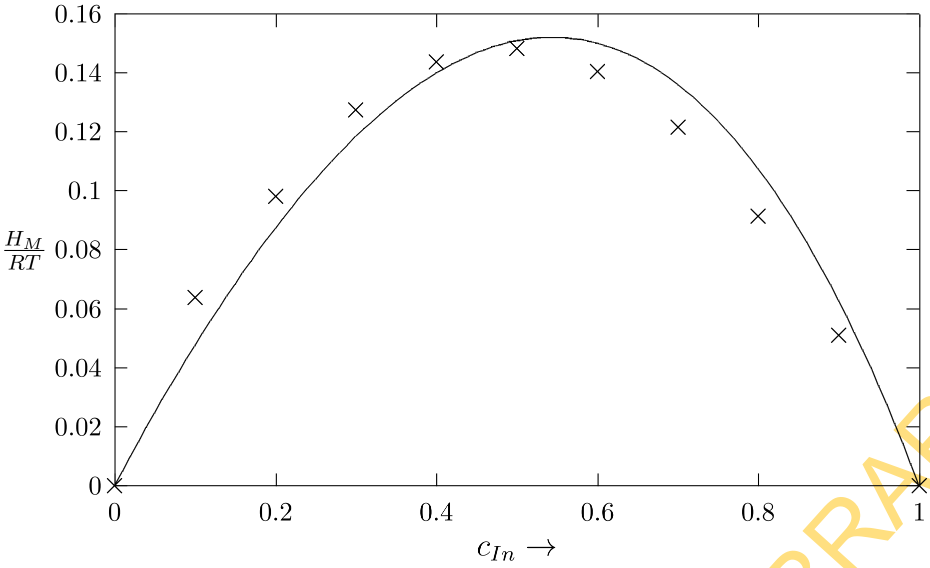

Figure 4.17: Concentration dependence of $\frac{H_M}{RT}$ for In-Pb liquid binary alloy at 673K. The solid line denotes theoretical values while the times denote experimental values respectively. c_{In} is In concentrations in the alloy. The experimental data were taken from Hultgren et al.,(1973).

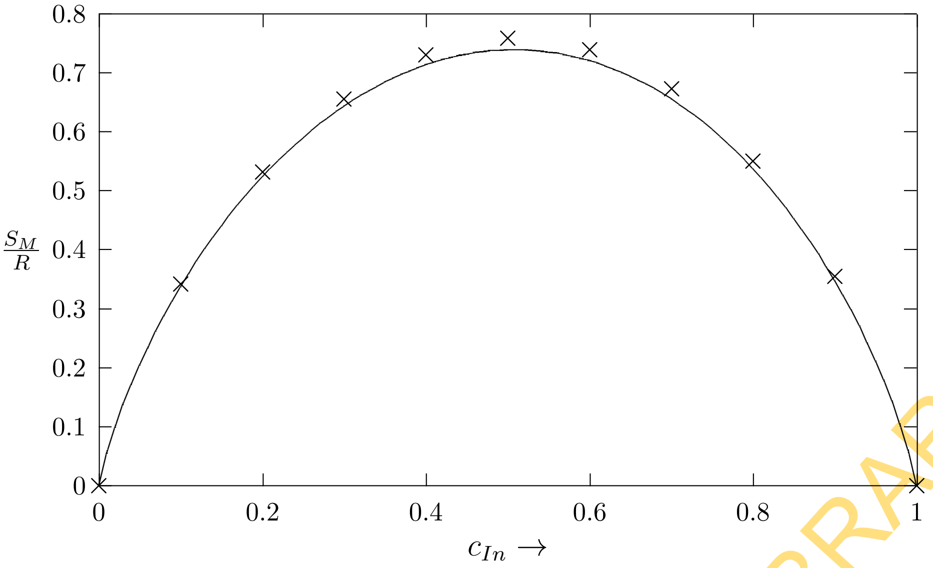

Figure 4.18: Concentration dependence of $\frac{S_M}{R}$ for In-Pb liquid binary alloy at 673K. The solid line denotes theoretical values while the times denote experimental values respectively. c_{In} is In concentrations in the alloy. The experimental data were taken from Hultgren et al.,(1973).

Table 4.12: Computed activities of Al in Al-Si liquid binary alloy at 2000K, 2400K and 2473K, respectively

c_{Al}	2000K	2400K	2473K
0.1	0.051	0.058	0.059
0.2	0.118	0.129	0.130
0.3	0.201	0.214	0.215
0.4	0.295	0.312	0.313
0.5	0.407	0.420	0.422
0.6	0.526	0.536	0.538
0.7	0.650	0.657	0.658
0.8	0.774	0.777	0.776
0.9	0.893	0.894	0.894

on activities of the components in the alloys at the investigated temperatures, there is no possibility for comparison between experimental and calculated data. It was however noticed that the increase in temperature do not significantly affect the change in activity values in the temperature interval 2000-2473K.

Figures 4.19 - 4.21 give the plots of the calculated free energy of mixing for Al-Si liquid alloys at temperatures of 2000K, 2400K and 2473K, respectively, as functions of concentration along with the respective experimental data for the alloys. The calculated free energies of mixing at each temperature show good agreement with the results of Kostov et al., (2007). The G_M are symmetrical around the equiatomic composition with G_M^{min} = -0.900283RT, -0.871280RT and -0.859690RT at 2000K, 2400K and 2473K, respectively. The effects of size ratio on the mixing properties of Al-Si can be neglected because the ratio, $\frac{V_{Si}}{V_{Al}} \approx 0.98$, is very close to 1 and too small to cause anomalous behaviour in Al-Si alloys. The magnitudes of G_M are found to decrease with increasing temperature. An indication that liquid Al-Si alloys at 2000K is the most interacting of the alloys, that is, the interaction increases as temperature decreases. The negative values of ω for the liquid Al-Si Alloys at the investigated temperatures further support the existence of chemical order leading to compound formation in the liquid alloys.

Both the results for the H_M and S_M are presented in Figure 4.22 and Tables 4.13, respectively, but the results could not be compared due to lack of experimental data at the investigated temperatures. The calculated enthalpy of mixing are negative and symmetrical around the equiatomic composition for Al-Si alloys. The magnitudes of H_M are found to decrease with increasing temperature. The effect of temperature is more distinct around the stoichiometric composition and the positions of the minima in H_M shift with increasing temperature.

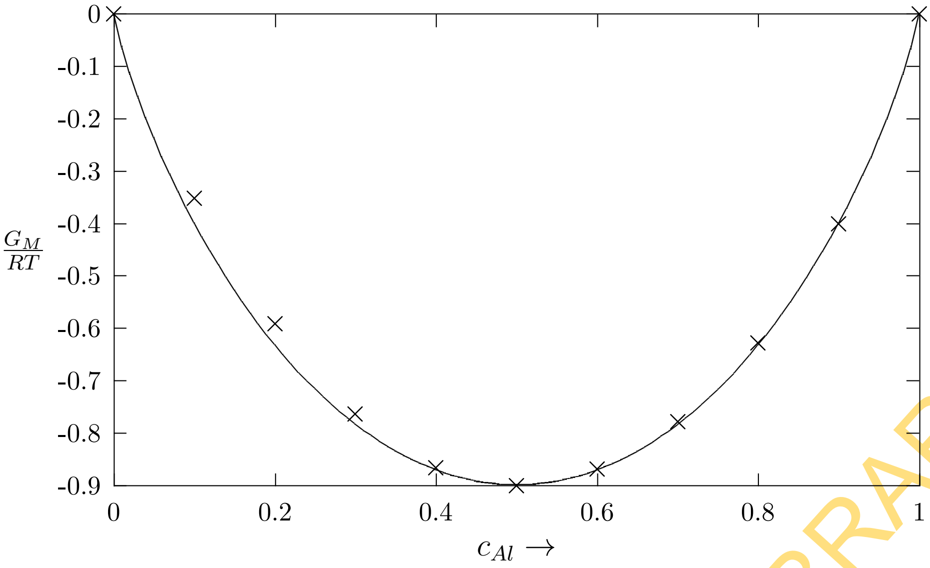

Figure 4.19: Concentration dependence of $\frac{G_M}{RT}$ for Al-Si liquid binary alloy at 2000K. The solid line denotes theoretical values while the times denote experimental values respectively. c_{Al} is Al concentrations in the alloy. The experimental data were taken from Kostov et al.,(2007)

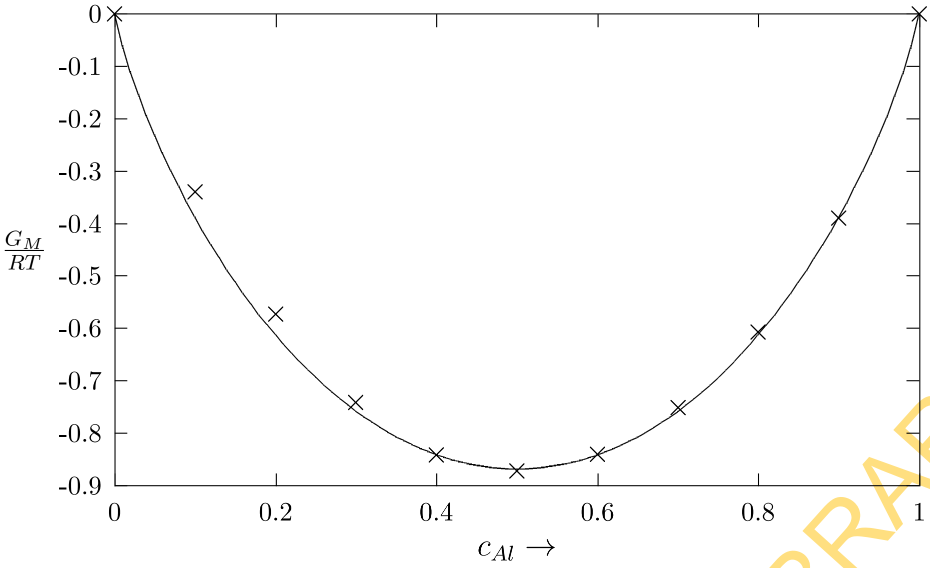

Figure 4.20: Concentration dependence of $\frac{G_M}{RT}$ for Al-Si liquid binary alloy at 2400K. The solid line denotes theoretical values while the times denote experimental values respectively. c_{Al} is Al concentrations in the alloy. The experimental data were taken from Kostov et al.,(2007).

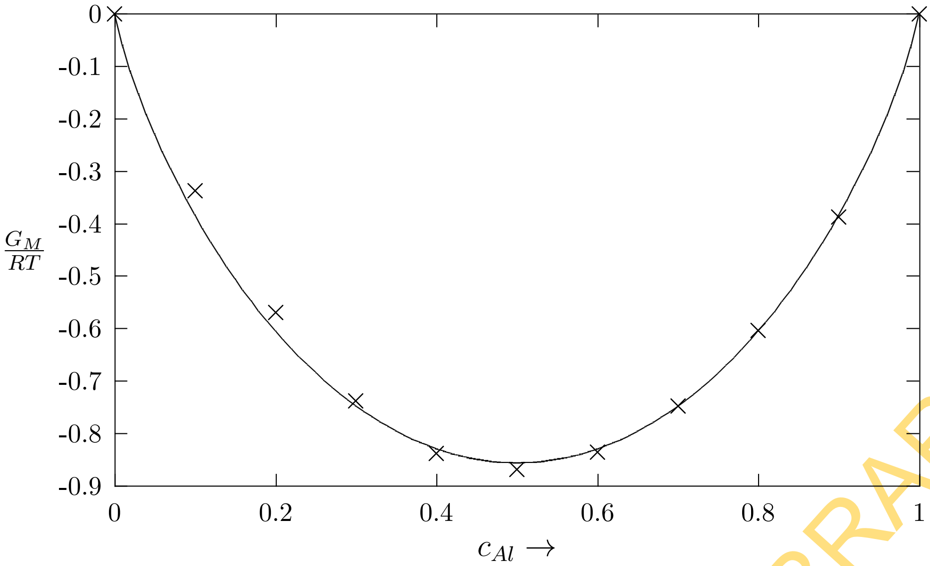

Figure 4.21: Concentration dependence of $\frac{G_M}{RT}$ for Al-Si liquid binary alloy at 2473K. The solid line denotes theoretical values while the times denote experimental values respectively. c_{Al} is Al concentrations in the alloy. The experimental data were taken from Kostov et al.,(2007).

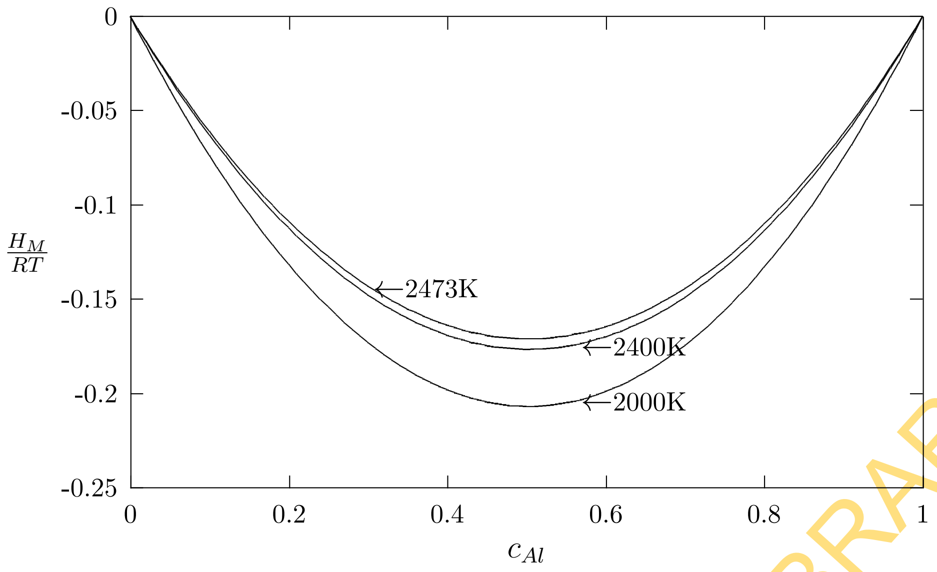

Figure 4.22: Computed enthalpy of mixing, $\frac{H_M}{RT}$, of Al-Si liquid binary alloy at 2000K, 2400K and 2473K, respectively. The solid line denotes theoretical values. c_{Al} is Al concentrations in the alloy.

Table 4.13: Computed entropy of mixing for Al-Si liquid binary alloy at 2000K, 2400K and 2473K, respectively

c_{Al}	2000K	2400K	2473K
0.1	0.325	0.058	0.059
0.2	0.500	0.129	0.130
0.3	0.611	0.214	0.215
0.4	0.673	0.312	0.313
0.5	0.693	0.420	0.422
0.6	0.673	0.536	0.538
0.7	0.611	0.657	0.658
0.8	0.500	0.777	0.776
0.9	0.325	0.894	0.894

4.4.4 Ga-Tl liquid alloys at 973K, 1073K and 1173K, respectively.

Tables 4.14 - 4.16 show the results of the calculated activities with the respective experimental data of Ga in Ga-Tl liquid alloys. The activity of Ga shows large positive deviations from ideal behaviour at each temperature, indicating some demixing tendencies between constituent components of Ga-Tl binary systems, while the temperature dependence of the activity is not so large. As a whole, the calculated activities of Ga in this study followed the same trend as the experimental results obtained by Katayama et al.,(2003).

For Ga-Tl liquid alloys at each temperature, figures 4.23 - 4.25 show the plot of the calculated free energy of mixing against concentration with the experimental data given as symbols. The calculated free energies of mixing are found to be in satisfactory agreement with the experimental data obtained by Katayama et al,(2003) at respective temperatures. The curves are asymmetric and it is most evident at the point where the free energy of mixing at 973K, 1073K and 1173K have values of G_M = -0.265287RT, -0.294290RT and -0.316273RT at about c_{Ga} = 0.288, 0.324 and 0.350, respectively. The asymmetry behaviour observed in G_M curves of Ga-Tl alloys can be ascribed to the size ratio values, $\frac{V_{Tl}}{V_{Ga}} \approx 1.578$ (which is close to 2) because for size ratio >> 1, the entropic effects become dominant over the enthalpic effect and tend to pull the system from the segregation to order phase. Thus suggesting a limited solubility in the solid state of the liquid alloys. The magnitudes of G_M are found to increase with increasing temperature. An indication that Ga-Tl liquid alloy is such a weakly interacting system like Al-Ca, Al-Mg, Hg-Sn, Ag-Al, Cu-Sn and Mg-Zn liquid binary alloys (Prasad and Mikula, 2006; Jha nd Mishra, 2001) with Ga-Tl alloys at 1173K being the most interacting of the three Ga-Tl liquid alloys.

The results of the H_M and S_M computed at three different temperatures, T = 973K, 1073K and 1173K, are presented as functions of concentration in Figure 4.26 and Tables 4.17, respectively. A comparison between calculated theoretical

Table 4.14: Activity of Ga in Ga-Tl liquid binary alloy at 973K.

c_{Ga}	Theory	Experimental*
0.050	0.200	0.232
0.079	0.298	0.299
0.098	0.356	0.366
0.151	0.493	0.517
0.203	0.597	0.586
0.276	0.704	0.649
0.397	0.805	0.751
0.502	0.846	0.779
0.588	0.861	0.824
0.697	0.873	0.865
0.800	0.890	0.910

* Katayama et al.,(2003)

Table 4.15: Activity of Ga in Ga-Tl liquid binary alloy at 1073K.

c_{Ga}	Theory	Experimental*
0.050	0.158	0.206
0.079	0.238	0.270
0.098	0.286	0.339
0.151	0.404	0.492
0.203	0.498	0.553
0.276	0.601	0.612
0.397	0.716	0.720
0.502	0.775	0.757
0.588	0.807	0.803
0.697	0.841	0.840
0.800	0.874	0.891

* Katayama et al.,(2003)

Table 4.16: Activity of Ga in Ga-Tl liquid binary alloy at 1173K.

c_{Ga}	Theory	Experimental*
0.050	0.134	0.187
0.079	0.203	0.247
0.098	0.245	0.318
0.151	0.350	0.473
0.203	0.438	0.528
0.276	0.537	0.583
0.397	0.657	0.695
0.502	0.728	0.738
0.588	0.771	0.785
0.697	0.818	0.824
0.800	0.863	0.876

* Katayama et al.,(2003)

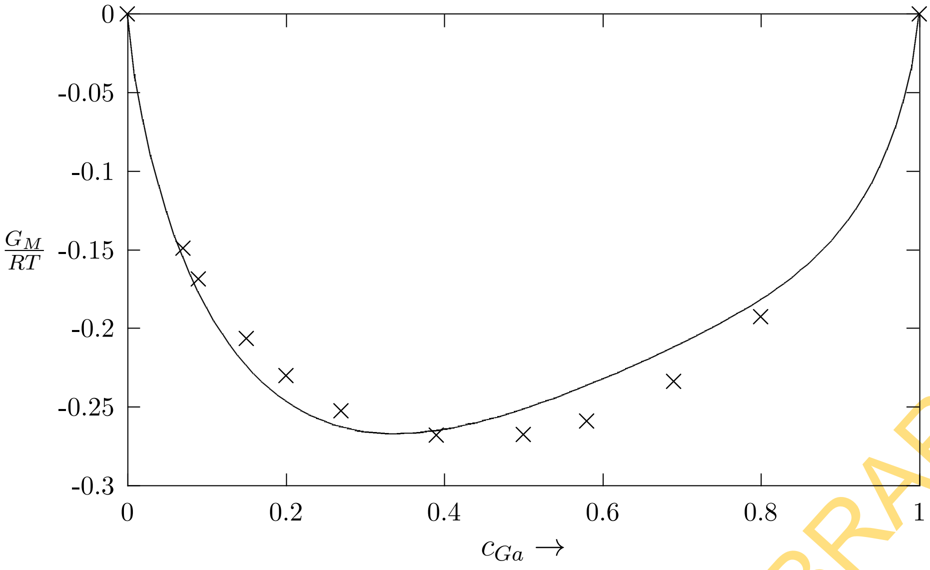

Figure 4.23: Concentration dependence of $\frac{G_M}{RT}$ for Ga-Tl liquid binary alloy at 973K. The solid line denotes theoretical values while the times denote experimental values respectively. c_{Ga} is Ga concentrations in the alloy. The experimental data were taken from Katayama et al.,(2003).

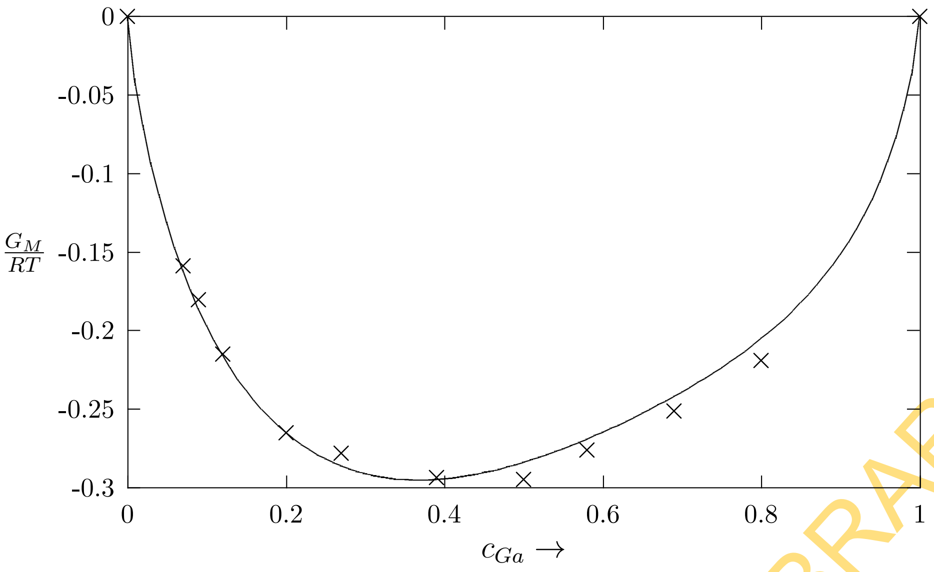

Figure 4.24: Concentration dependence of $\frac{G_M}{RT}$ for Ga-Tl liquid binary alloy at 1073K. The solid line denotes theoretical values while the times denote experimental values respectively. c_{Ga} is Ga concentrations in the alloy. The experimental data were taken from Katayama et al.,(2003).

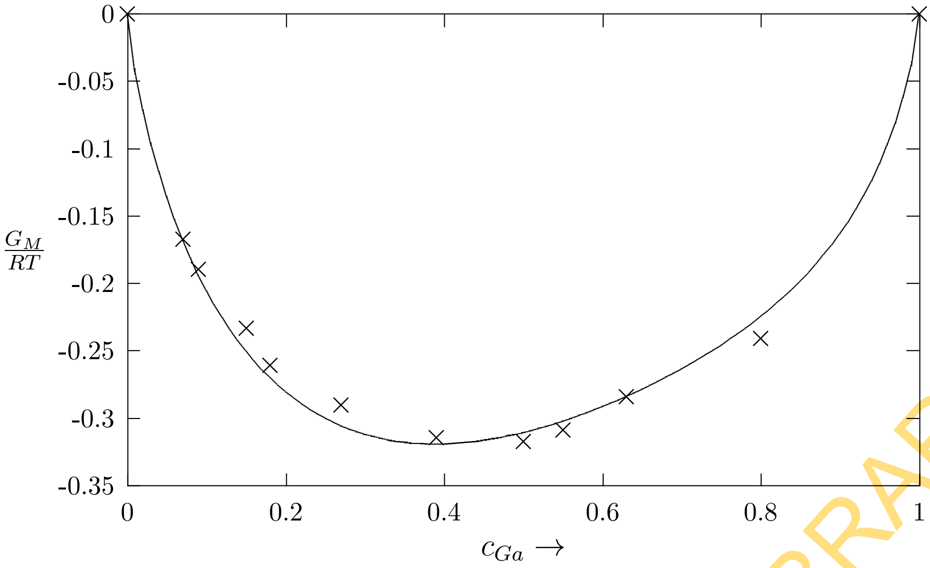

Figure 4.25: Concentration dependence of $\frac{G_M}{RT}$ for Ga-Tl liquid binary alloy at 1173K. The solid line denotes theoretical values while the times denote experimental values respectively. c_{Ga} is Ga concentrations in the alloy. The experimental data were taken from Katayama et al.,(2003).

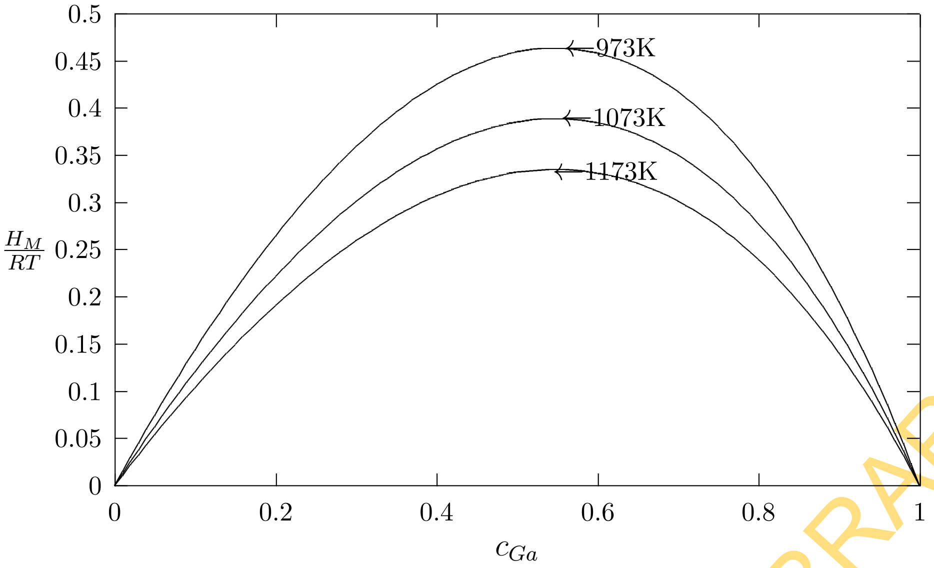

Figure 4.26: Computed enthalpy of mixing, $\frac{H_M}{RT}$, of Ga-Tl liquid alloy at 973K, 1073K and 1173K, respectively. The solid line denotes theoretical values. c_{Ga} is Ga concentrations in the alloy.

Table 4.17: Computed entropy of mixing of Ga-Tl liquid alloy at 973K, 1073K and 1173K, respectively

c_{Ga}	973K	1073K	1173K
0.1	0.281	0.331	0.331
0.2	0.326	0.511	0.511
0.3	0.432	0.625	0.625
0.4	0.515	0.690	0.690
0.5	0.602	0.711	0.711
0.6	0.688	0.690	0.690
0.7	0.710	0.626	0.626
0.8	0.695	0.512	0.512
0.9	0.629	0.332	0.332

values at the investigated temperatures and the experimental data cannot be made due to lack of experimental data. Nonetheless, the calculated enthalpy of mixing are positive and exhibited slight asymmetrical behaviour near the equiatomic composition for Ga-Tl liquid alloys. The magnitudes of H_M are found to increase with decreasing temperature. The effect of temperature is more distinct around the stoichiometric composition and the positions of the maxima in H_M shift with decreasing temperature.

4.4.5 Summary

The concentration dependence of the properties of mixing and activities of binary liquid Sb-Sn, In-Pb, Al-Si and Ga-Tl systems at respective temperatures were determined using analytical expressions only. This has made it possible to extract a consistent interpretation of the temperature and concentration dependence of the mixing properties. Bearing in mind that thermodynamical study of Al-Si and Ga-Tl systems have not been completely reported in the literature. Both Sb-Sn and Al-Si alloys exhibited negative deviations from ideal behaviour, while In-Pb and Ga-Tl systems exhibited positive deviations from ideality.

For segregating alloys, such as In-Pb, having the size ratio value close to 1, the effects of size on their mixing properties can be neglected. On the contrary, for the segregating systems such as Ga-Tl, with the size ratio of 1.5 or higher, the size effects on the mixing behaviour becomes significant. The anomalous behaviour observed in the mixing properties of binary alloys in molten state as observed in Ga-Tl alloy as functions of concentration may then be attributed to the size difference of the constituent species. The size effect plays a significant role in the energetics of In-Pb and Ga-Tl which are segregating systems than it plays in both Sb-Sn and Al-Si liquid alloys. The effect of temperature on the thermodynamic functions is more visible around the stoichiometric composition. The theoretical results obtained are in good agreement with the corresponding experimental data for Sb-Sn, In-Pb, Al-Si and Ga-Tl liquid alloys at the investigated temperatures. At this stage, it is still not possible to single out any particular elemental properties which might be held responsible for the observed anomalous behaviours of liquid alloys. However, the empirical investigations suggest that quantities such as atomic size, heat of vapourization and electronegativity together hold the key to the understanding of the segregation or order in a liquid alloy.

Hence, the approach discussed in this chapter, represent an effective and cost efficient method for obtaining the mixing properties like G_M, H_M, S_M and activities of binary liquid alloys at desire temperatures without the need for input from thermodynamic measurements. The approach is a very useful method to cut down the cost and time for the development of new alloys, and obtained thermodynamic data may as well be useful for comparison with some future critical experimental results and in developing new alloys.

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

Theoretical approaches have been used in this study to determine some thermodynamic properties of selected binary liquid alloys at different concentration temperatures, because good understanding of thermodynamic and microscopic structural properties of liquid alloys is an important prerequisite in the design and development of reliable materials for high temperature applications and also the need to find cost effective substitutes to obtain thermodynamic data as against the present conventional alloy development which is primarily based on experimental approach motivated this study. The energetics of alloy formations in Al-Zn (at 1000K), Bi-In (at 900K), Ga-Zn (at 700K), Ga-Mg (at 923K), Al-Ga (at 1073K), Sb-Sn (at 905K), In-Pb (at 900K), Al-Si (at 2000K, 2400K and 2473K) and Ga-Tl (at 973K, 1073K and 1173K) liquid alloys have been evaluated with special focus on their bulk thermodynamic and dynamical properties. From the results obtained, the following conclusions are made:

The liquid binary alloys studied have been classified into two main groups: segregating (demixing) or short-range ordered based on the deviations of their thermodynamic properties from Raoultian behaviour.

The study of microscopic functions of Al-Zn at 1000K indicates that Al-Zn is a segregated alloy while its heat of mixing $\frac{-H_M}{RT}$ is characterized by liquid miscibility gaps and exhibits large positive heat of mixing values. On the other hand, Bi-In at 900K exhibits positive deviation and its $\frac{-H_M}{RT}$ shows negative deviation which confirmed that Bi-In liquid alloy is an ordered alloy. In addition, the concentration dependence of the dynamic properties of both systems have been analyzed through the study of diffusion coefficient and viscosity within the framework of the Quasi-Lattice Theory (QLT). The size effect plays a prominent role in the energetics of Bi-In than it plays in Al-Zn alloy and thus pulling the system from segregation to order phase. The study has shown the suitability of the formalism which relates the dynamic properties with thermodynamic properties for a proper description of the alloying behaviours of binary liquid alloy.

The mixing properties of binary alloys, namely Ga-Zn at 700K, Ga-Mg at 923K and Al-Ga at 1073K have been described in terms of the $\frac{G_M}{RT}$, $S_{cc}(0)$, α_1, enthalpy of mixing, $\frac{H_M}{RT}$ and entropy of mixing, $\frac{S_M}{RT}$ as a function of composition using the Quasi-Chemical Approximation Model (QACM). Both Al-Ga and Ga-Zn alloys were observed to exhibit positive deviations from ideal mixture behaviour. The positive deviation supports a tendency of both systems towards segregation. The results obtained for Ga-Zn agrees with the results of Awe et al., (2005) using four-atom-cluster-model (FACM). On the contrary, Ga-Mg exhibits negative deviation, an indication that a reasonable degree of chemical order exists in Ga-Mg alloy across the entire composition range. It is noted that the enthalpy of mixing and entropy of mixing for the three alloys are positive and symmetrical about the equiatomic composition in accord with the result obtained by Novakovic et al.,(2005) and Singh et al., (1997) on Ga-based alloys, except for Ga-Mg alloy whose enthalpy of mixing is negative. Furthermore, it was established that in the concentration range $\leq c_{Al} \leq 0.30$ and $0.7 \leq c_{Al} \leq 1$, the calculated $S_{cc}(0)$ almost equal to the ideal $S_{cc}^{id}(0)$ values for Al-Ga systems. An indication that Al-Ga liquid alloy exhibited the highest glass-forming potential among the three Ga-based alloys investigated in these concentration ranges.

The FACM which was successfully used in the study of thermodynamic functions of Bi-Pb and Sb-Sn has been reported to have some shortcomings when applied to alloys where size effect or/and electronegativity difference are significant (Akinlade, 1997); yet one is still of the opinion that the use of the FACM which is an extension of Singh earlier work on a two atom cluster model(Singh et al., 1988) and reformulated to give a more realistic value of the ordering energy ω and the chemical short range order (CSRO) parameter α_1 and hence, to explain the energetics of mixing in liquid alloys in terms of compound formation or phase separation is still justified. For both systems, in view of the fact that the size ratios are quite less than 2.0 and their electronegativity differences are ignorable, one thus infers that the characteristic behaviour of each of the alloy is dependent on the energetics of the respective system.

In addition, evaluation of the atomic size mismatch in each of the alloys Al-Zn, Bi-In, Sb-Sn, In-Pb, Al-Si and Ga-Tl shows that size factor is less than 2.0 and thus, the observed anomalies in the thermodynamic properties of the liquid alloys is perhaps a function of the energetics of the respective alloys. However, in this study, the anomalous behaviour observed in the mixing properties of Ga-Tl alloys as functions of concentration has been ascribed to the size factor. Several experimental evidences clearly demonstrate that the asymmetric behaviour for a large number of liquid alloys occur at or near the stoichiometric composition where stable intermetallic compound exists in the solid phase. It is, therefore, natural to propose that the chemical complexes or pseudomolecules exist in the liquid phase near the melting temperature. An appropriate estimation of the stoichiometry of complexes in the liquid alloy is usually made by an analysis of the physical properties and also from the phase diagram. For segregating systems, the size effects have an appreciable influence on their mixing properties. The magnitude of these effects increases together with a tendency of a system to phase separation

(Novakovic et al., 2005). It was established in this study that size effect plays a prominent role in the energetics of Bi-In, Sb-Sn and Al-Si than it plays in Al-Zn, In-Pb and Ga-Tl liquid alloys and tends to pull the systems from segregation to order phase. The observed characteristic behaviour of Ga-Tl alloys as a function of concentration was attributed to the effect of the size ratio which is about 1.57 or higher.

Furthermore, it is necessary to acknowledge the fact that the experimental values of $S_{cc}(0)$ can be obtained theoretically from the observed free energy of mixing or activity data, respectively and such $S_{cc}(0)$ are usually termed experimental values. The experimental values of $S_{cc}(0)$ used in all aspects of calculations in this study were obtained from the free energy of mixing. It was shown in this study that $S_{cc}(0)$ obtained via free energy of mixing compares well with the theoretical $S_{cc}(0)$ values. One generally notes that both the reported literature data and calculated theoretical values were in general good agreement. However, since theoretical determination of $S_{cc}(0)$ is of considerable interest to anyone trying to visualize the nature of atomic interactions in the mixtures, it would therefore be of high interest to obtain $S_{cc}(0)$ using the two approaches to be able to ascertain which of the two give consistent agreement with the theoretical $S_{cc}(0)$ values.

A theoretical approach to determine the mixing properties and activities of liquid binary alloys using analytical expressions based on a statistical thermodynamic theory has been presented without recourse to input from thermodynamic measurements. The potential of the approach has been verified to be quite convenient and reliable based on the fact that theoretical results obtained conveniently reproduced the experimental results obtained by Hultgren et al.,(1973), Katayama et al.,(2003) and Kostov et al.,(2007). The approach can be adopted for determining thermodynamic properties of liquid alloys, which might not be available in the literature. For instance, the Gibbs free energies of mixing of liquid Al-Si and Ga-Tl alloys determined by the current approach agree with the experimental data, while all the mixing properties and activities of both In-Pb and Sb-Sn calculated compare well with the experiment. Thus the approach is a good and very useful method to cut down the cost and time for obtaining thermodynamic data (mixing properties and activities) of binary liquid alloys from theoretical calculations, rather than from experiment and thereby enhancing the development of new alloys.

5.2 Limitations to this study

The major hindrance which tends to limit the scope of this study was non-availability or complete lack of recent and sufficient experimental data which would have facilitated comparison of the calculated theoretical results with experiment at investigated temperatures. Another challenge faced was lack of enough fund or support to get experimental data on high temperature liquid alloys. It should however be noted that the main drawback of the theoretical approach presented in section 3.4 to obtaining thermodynamic data of binary liquid alloys is that it still depends on availability of experimental data to validate the theoretical results obtain using the method.

5.3 Recommendations

In the light of these limitations and the experience acquired during this study, the following suggestions are recommended for further studies:

1. From technological point of view, binary liquid alloys are of practical importance in the present production practice. Therefore, an important task for the present scientific investigations should be a good theoretical understanding of the energetics of the interrelationship between thermodynamic and structural behaviour of these materials due to complications and difficulty associated with the high-temperature experiments.

2. Adequate fund and technical assistance is required and future work should be geared towards identifying binary liquid alloys for which no thermody-

namic data presently exist in the literature with a view to determine their thermodynamic data as calculation of thermodynamic properties of ternary and quaternary systems relies heavily on their constituent binary systems (Zivkovic et al., 2011) and could thus serve as a guide towards predicting thermodynamic data for ternary and higher components liquid alloys.

3. It would also be highly desirable to extend the present understanding of concentration-concentration fluctuations in the long-wavelength limits, $S_{cc}(0)$ and the chemical short-range order parameter, α_1 in explaining the energetics of mixing of liquid binary alloy in terms of chemical ordering and phase separation to ternary and quaternary liquid alloys in future studies. As increasing attention is recently being shifted towards higher components liquid alloys due to their potential usefulness in industrial applications (Gomidzelovic et al., 2007; Zivkovic et al., 2011).

4. It is believed that with a significant increase in activity in this emerging area of research, our understanding of the electronic, structural and thermodynamic properties of ternary and quaternary liquid alloys still at the early stages will continue to evolve in years to come.

5.4 Contributions

The contributions that this work has made in the area of high temperature applications of liquid alloys are many. The study identified the inadequacies of many of the models in the literature used for studying thermodynamic properties of liquid systems. The suitability of a formalism which relates both the thermodynamic and dynamical properties within the frame of the Quasi-Lattice theory has been established in this thesis for a proper description of the alloying behaviours of liquid binary alloys. This was presented in section 4.1 of this thesis. The quasi-chemical approximation model for strongly interacting systems used to investigate ordering and glass formation tendencies in Ga-Zn, Ga-Mg and Al-Ga binary alloys at different temperatures through the study of their thermodynamic functions was reported in section 4.2 of this thesis. In spite of some shortcomings of the FACM as reported by Akinlade (1997), yet the model as used here has successfully explained the thermodynamics properties of Bi-Pb and Sb-Sn alloys. This might perhaps be connected with the fact that their size ratios are just close to 1, which can be neglected. This was given in section 4.3 of this thesis. It has also been shown through this study that the experimental $S_{cc}(0)$ obtained via free energy of mixing compare well with the theoretical $S_{cc}(0)$ values as all the experimental values of $S_{cc}(0)$ used in all aspects of the calculations were obtained from the free energy of mixing. This can be found in chapters 3, 4 and 5 of the thesis. Finally, I have presented and tested an approach for determining the mixing properties and activities data of liquid binary systems. The approach is economic, cost effective, environmentally friendly and thus, the data obtained using this approach could as well be adopted as a basis for comparison with some future critical experimental results and aid in developing new alloys. It is these contributions that one hopes will go to further the understanding of the thermodynamic properties and the energetics of alloy formations in binary liquid alloys.

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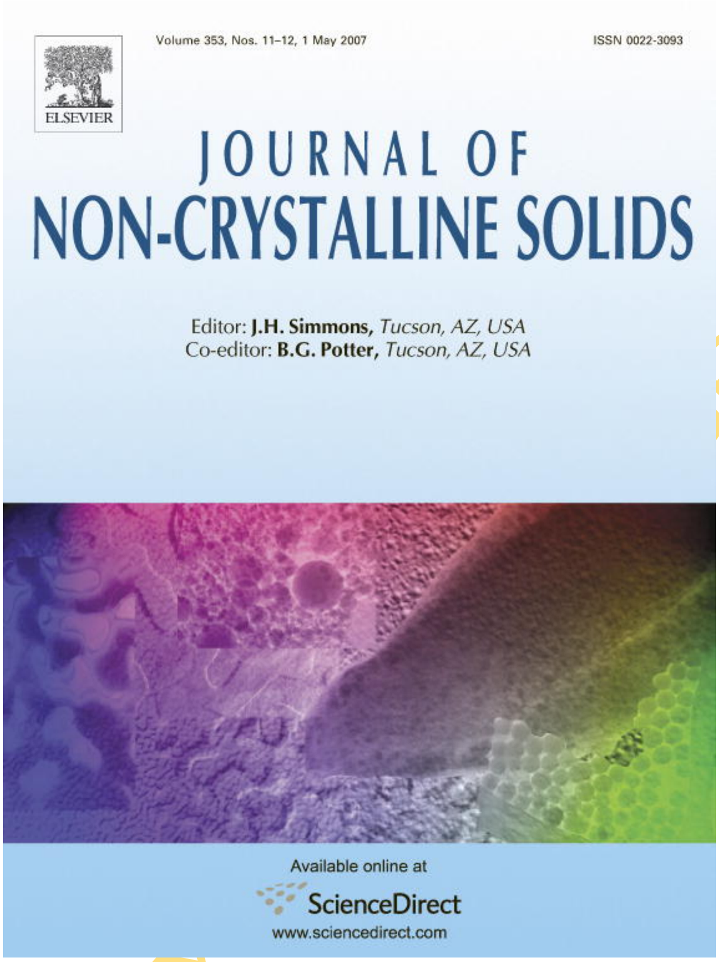
APPENDIX A

PUBLISHED WORK



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Bulk and dynamic properties in Al–Zn and Bi–In liquid alloys using a theoretical model

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Abstract

A formalism that connects thermodynamic and dynamic properties such as viscosity and diffusion coefficient has been used to calculate the concentration dependence of the free energy of mixing, concentration–concentration fluctuations in the long-wavelength limit and the concentration dependence of diffusion as well as viscosity in Al–Zn and Bi–In binary liquid alloys at various temperatures. Our calculations show that a reasonable degree of chemical order exists in Bi–In system, while Al–Zn liquid alloy was observed to exhibit a liquid miscibilty gap or phase separation over the concentration range. It can be concluded that size effect plays a more prominent role in the energetics of Bi–In than it plays in Al–Zn alloy. This fact is substantiated by predicted dynamic properties of both systems.

Keywords: Alloys; Liquid alloys and liquid metals

1. Introduction

Different kinds of theoretical models proposed to explain the concentration dependence of the thermodynamic properties of liquid binary alloys and by so doing, extracting useful microscopic information on them has attracted the attention of physicists, chemists and metallurgists for a long time [1–5]. In this regard, a substantial effort has been directed towards the understanding of the mechanism for the phenomenon of compound formation in liquid binary alloys [1,6].

In addition, their energetics are reasonably well understood theoretically. On the contrary, relatively little is known and written on the other class of liquid alloys that exhibit segregation (i.e. preference of like atoms as nearest neighbours) or on the liquid alloys endowed with a miscibility gap. Singh and Sommer [7] have documented extensively on thermodynamic information (both experimentally and theoretically) on phase separating systems. They have equally mentioned different kinds of theoretical methods that could be used to explain the mechanism for the energetics of liquid alloys.

Modelling of thermodynamic, structural and surface properties of liquid alloys usually requires data regarding their structures and the relevant forces that describes the interatomic interactions, i.e. the energetics of the system. This can be done by different theoretical approaches such as the electron theory [8] and the Bhatia and Hargrove [2] formalism put in a more tractable form by [1].

Singh and Sommer [9,10] established an empirical model which provides a possible way of relating two of the dynamics properties, as diffusion coefficient (D) and viscosity (η) with thermodynamic properties like the concentration–concentration fluctuations in the long wavelength limit, $S_{cc}(0)$ and the free energy of mixing, $\frac{G_M}{RT}$ for liquid binary alloys. These quantities can then be connected in terms of entropic and enthalpic contributions to the free energy of mixing. However, no practical application was made

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to a particular liquid alloy in their paper so as to know the limit of suitability of the model.

In this paper, an attempt is made to apply the theory in [9,10] and show that it could be used to model the structure of liquid binary alloys and to facilitate our understanding of the energetics of the liquid alloys that have been investigated.

Here, we apply the model to Al–Zn and Bi–In liquid alloys. Our choice of Al–Zn and Bi–In was however influenced by the availability of all the required thermodynamic data for both systems. Moreso, due to the difficulties in performing high temperature surface and viscosity measurements, in the literature only a few reference data for metals [11,12] are available. For binary systems they are scarce, and in the case of complex alloys a nearly complete lack of data is evident. Therefore, it is necessary to estimate the missing values of the viscosity data by theoretical models. The dynamic properties of Al–Zn and Bi–In liquid alloys are calculated in the framework of Quasi-Lattice Theory (QLT) with the aim to analyse existing thermodynamic data and use these data as the input for the fitted parameter calculations, and to explain the ordering and phase separating phenomena in liquid binary alloys. In addition, available information on phase diagrams and other thermodynamic properties indicate the existence of liquid miscibility gap in Al–Zn system. Its $S_{cc}(0)$ exhibit a tendency for phase separation over the concentration range, whereas the $S_{cc}(0)$ for Bi–In alloy exhibits compound formation tendency. Based on the above mentioned facts, we deemed it fit to investigate these two systems to widen our theoretical understanding of liquid binary alloys.

The layout of the paper is as follows: In Section 2, we discuss the basic theory used for the calculations. In the next section, we present our results and discussion and finally, we make our conclusions.

2. Basic theory

We propose to apply the Quasi-Lattice Theory (QLT) of liquid mixtures which is based on the ideas underlying the Guggenheim theory [13] in which one assumes the existence of a binary mixtures consisting of $N_A = Nc_A$ and $N_B = Nc_B$ atoms of elements A and B respectively. We assume also that a small gradient of composition c_A is maintained in an equilibrium condition along the x-direction by the application of a force F_A, such that for dilute alloy, it is possible to write [14]:

$$F_A = -K_{\mathrm{B}}T\left(d\ln\frac{c_A}{\mathrm{d}x}\right), \tag{1}$$

where T is the temperature and K_{B}, the Boltzmann's constant. In the framework of the compound formation model the stoichiometry of associates can be ascertained by the viscosity, η. By using Eq. (1), it has been shown [9,10] that we can relate $S_{cc}(0)$ and diffusion coefficient, D_{m} for liquid alloys [6,7] by

$$\eta = \frac{K_{\mathrm{B}}T}{D_{\mathrm{m}}}\left(\frac{c_A}{\lambda_2}+\frac{c_B}{\lambda_1}\right)\frac{c_Ac_B}{S_{cc}(0)}, \tag{2}$$

where λ_1 and λ_2 are functions of the size and shape of the constituent particles. Thus, we define the quantity ϕ as

$$\phi = \frac{c_Ac_B}{S_{cc}(0)} \tag{3}$$

and the ideal value of $S_{cc}^{\mathrm{id}}(0)$ as

$$S_{cc}^{\mathrm{id}}(0) = c_Ac_B \tag{4}$$

Eq. (3) can be rewritten as

$$\eta = \eta_o\phi, \tag{5}$$

with

$$\eta_o = \frac{K_{\mathrm{B}}T}{D_{\mathrm{m}}}\left(\frac{c_A}{\lambda_2}+\frac{c_B}{\lambda_1}\right). \tag{6}$$

Ordinarily, one would expect that η_o be linear in c_A, so that the deviation of $\eta - c_A$ isotherm from the additive rule of mixing can be attributed to the factor ϕ (i.e. $\eta = \sum_i c_i\eta_i$). This factor has been extensively reported in the literature for a number of binary liquid alloys [6,7].

Thermodynamic investigation of ϕ have been performed [15] for the more general case in which one then introduces the entropic contribution (i.e. the size ratio $\gamma = \frac{\Omega_A}{\Omega_B}$, $\Omega_B > \Omega_A$), where Ω is the atomic volume and the enthalpic contributions (via the interchange energy, ω). They obtained an expression for ϕ given by

$$\phi = 1 - c_Ac_Bf(\gamma, W), \tag{7}$$

where

$$f(\gamma, W) = \frac{2\gamma^2W - (\gamma-1)^2(c_A+\gamma c_B)}{(c_A+\gamma c_B)^3}, \tag{8}$$

$$W = \Omega_A\left(\frac{\omega}{K_{\mathrm{B}}T}\right), \tag{9}$$

with

$$w = Z(\epsilon_{AB} - (\epsilon_{AA}+\epsilon_{BB})/2). \tag{10}$$

Eq. (10) is known as the interchange energy, here we remind ourselves that ϵ_{AB}, ϵ_{AA}, and ϵ_{BB} are the energies for AB, AA and BB pairs of atoms respectively and Z is the coordination number of the liquid alloys. Obviously, if $\omega < 0$, there is tendency to form unlike atom pairs, and if $\omega > 0$, like atoms tend to pair together. $\omega = 0$, however, shows that atoms in the mixture are perfectly disordered [1]. By taking together Eqs. (5), (7)–(9), we express $\frac{\Delta\eta}{\eta_o}$ as

$$\frac{\Delta\eta}{\eta_o} = -c_Ac_Bf(\gamma, W). \tag{11}$$

The factor $f(\gamma, W)$ which introduces both the entropic and enthalpic effects is responsible for the characteristic behaviour of $\Delta\eta$ for a given binary alloy. In the light of the result obtained in [9,10], it is readily shown that

$$\frac{\Delta\eta}{\eta_o} = -\frac{H_{\mathrm{M}}}{RT}, \tag{12}$$

R is the universal gas constant. It is observed that using the formulae given above, we do not have sufficient information on thermodynamic quantities to relate it to η. In order to achieve this, we make use of the general expression for the Gibb's free energy of mixing G_{M}

$$G_{\mathrm{M}} = -TS_{\mathrm{M}} + H_{\mathrm{M}}, \tag{13}$$

where S_{M} is the entropy of mixing and H_{M} is the enthalpy of mixing. Using Guggenheim's theory of mixtures [13], QLT makes it possible for one to write an explicit expression for G_{M} as

$$\frac{G_{\mathrm{M}}}{RT} = c_B \ln \Psi + c_A \ln(1-\Psi) + c_A \Psi\left(\Omega_A \frac{\omega}{K_{\mathrm{B}}T}\right), \tag{14}$$

$$= c_B \ln \Psi + c_A \ln(1-\Psi) + c_A \Psi W, \tag{15}$$

with

$$\Psi = \frac{\gamma c_B}{c_A + \gamma c_B}. \tag{16}$$

And from G_{M} as in Eq. (14) or (15), $S_{\mathrm{cc}}(0)$ can easily be calculated from standard relationship in terms of free energy of mixing,

$$S_{\mathrm{cc}}(0) = RT\left(\frac{\partial^2 G_{\mathrm{M}}}{\partial c^2}\right)^{-1}_{T,P,N}, \tag{17}$$

or in terms of activity, a_A and a_B,

$$S_{\mathrm{cc}}(0) = (1-c)a_A\left(\frac{\partial a_A}{\partial c}\right)^{-1}_{T,P,N} = c a_B\left(\frac{\partial a_B}{\partial(1-c)}\right)^{-1}_{T,P,N} \tag{18}$$

as

$$S_{\mathrm{cc}}(0) = \frac{c_A c_B}{1 - c_A c_B f(\gamma, W)}. \tag{19}$$

Once $S_{\mathrm{cc}}(0)$ is fitted from Eq. (19), then all other parameters could be calculated.

The degree of order and segregation in the melt can be quantified by another important microscopic function, known as Warren–Cowley short range order parameter (CSRO), α_1, [16,17]. The parameter α_1 is related to the $S_{\mathrm{cc}}(0)$ by

$$\frac{S_{\mathrm{cc}}(0)}{c_A c_B} = \frac{1+\alpha_1}{1-(Z-1)\alpha_1}. \tag{20}$$

For equiatomic composition, the chemical short range order (CSRO) parameter, α_1, is found to be $-1 \leqslant \alpha_1 \leqslant 1$. The negative values of this parameter indicate the ordering in the melt, and complete ordering is showed by $\alpha_1^{\min} = -1$. On the contrary, the positive values of α_1 indicate segregation, whereas the phase separation takes place if $\alpha_1^{\max} = 1$.

In addition,the mixing properties of binary molten metals forming alloys can as well be analysed at the microscopic scale in terms of the quantity ϕ defined in Eq. (3) known as diffusion. The formalism relation that connects diffusion and $S_{\mathrm{cc}}(0)$ [9] combines the Darken's thermodynamic equation for diffusion [18] with the basic thermodynamic relation in the form [10]:

$$\frac{D_{\mathrm{m}}}{D_{\mathrm{id}}} = \frac{S_{\mathrm{cc}}^{\mathrm{id}}(0)}{S_{\mathrm{cc}}(0)}, \tag{21}$$

where D_{m} is the mutual diffusion coefficient and D_{id} is the intrinsic diffusion coefficient for an ideal mixture, given as

$$D_{\mathrm{id}} = c_A D_B + c_B D_A, \tag{22}$$

with D_A and D_B being the self-diffusion coefficients of pure components A and B, respectively. For ideal mixing, $S_{\mathrm{cc}}(0) \rightarrow S_{\mathrm{cc}}^{\mathrm{id}}(0)$, i.e. $D_{\mathrm{m}} \rightarrow D_{\mathrm{id}}$; for ordered alloys, $S_{\mathrm{cc}}(0) < S_{\mathrm{cc}}^{\mathrm{id}}(0)$, i.e. $D_{\mathrm{m}} > D_{\mathrm{id}}$; and similarly for segregation, $D_{\mathrm{m}} < D_{\mathrm{id}}$. The highest peak of $\frac{D_{\mathrm{m}}}{D_{\mathrm{id}}}$ as a function of composition indicate the presence of maximum chemical order in molten alloy system as well as the composition of the most likely associates to be formed in the liquid phase [6].

3. Results and discussion

The basic theory explained in Section 2, have been used to investigate the composition dependence of the bulk thermodynamics and dynamic properties such as diffusion and viscosity for the two systems Al–Zn and Bi–In liquid alloys. It is understood from the theory that there are some parameters that need to be fitted in order to carry out the present calculations. These parameters are the size ratio, γ, the coordination number, Z and the interchange energy, ω. For uniformity, the coordination number, Z in the liquid phase was chosen as 10 [19,20]. We observed that the choice of Z does not significantly affect our results. In addition, the size ratio, γ should have been obtained from experimental density measurements but we chose to treat it as a free parameter in our calculations simply because there are no experimental measurements for the densities at the temperatures for which thermodynamics data are available. Once suitable values of these parameters are chosen, the theory allows to calculate other quantities mentioned above. The values of the fitted parameters are presented in Table 1.

3.1. Concentration fluctuations in the long-wavelength limit, the free energy of mixing and the chemical short-range order parameter

Due to the difficulties associated with diffraction experiments, the theoretical calculation of $S_{\mathrm{cc}}(0)$ is of great interest when investigating the nature of interaction as well as the structure of binary liquid alloys [21]. The mixing behaviour of liquid binary alloys can be inferred from the deviation of $S_{\mathrm{cc}}(0)$ from the ideal value, $S_{\mathrm{cc}}^{\mathrm{id}}(0)$. The presence of chemical order is indicated as $S_{\mathrm{cc}}(0) < S_{\mathrm{cc}}^{\mathrm{id}}(0)$, on the con-

Table 1
Values of the parameters for Al–Zn and Bi–In liquid alloys

Alloy	T (K)	Z	$\frac{W}{RT}$	γ
Al–Zn	1000	10	0.800	0.950
Bi–In	900	10	−0.900	1.135

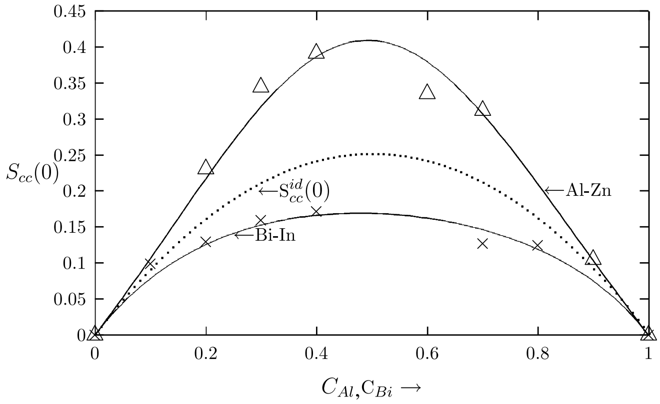

Fig. 1. Concentration fluctuations in the long-wavelength limit ($S_{cc}(0)$ and $S^{id}_{cc}(0)$) vs. concentration for Al–Zn and Bi–In liquid alloys at 1000 K and 900 K respectively. The solid line denotes theoretical values while the triangle and the cross denote experimental values for Al–Zn and Bi–In respectively. The dot denotes the ideal values $S^{id}_{cc}(0)$. C_{Al} and C_{Bi} are the Al and Bi concentrations in the alloy.

trary, if $S_{cc}(0) > S^{id}_{cc}(0)$, the segregation and demixing in liquid alloys take place.

A perusal of Fig. 1, the plot of concentration fluctuations in the long-wavelength limit $S_{cc}(0)$ versus concentration for the systems studied show that the fitted parameters yield a good representation of the experimental data. The experimental values of $S_{cc}(0)$ for the two systems were derived from the experimental free energy of mixing Eq. (17), the theoretical $S_{cc}(0)$ was obtained using Eq. (19) and thermodynamic data were taken from [22].

The $S_{cc}(0)$ values for the Al–Zn system at $T = 1000$ K (Fig. 1) clearly indicate that $S_{cc}(0) > S^{id}_{cc}(0)$ in the whole concentration range. This implies a tendency for homocoordination, i.e segregation of preference for like atom Al–Al and Zn–Zn tend to pair as nearest neighbours. The $S_{cc}(0)$ curve exhibits the maximum value of about 0.409 at $C_{Al} = 0.50$. For Bi–In system, the $S_{cc}(0)$ values show that $S_{cc}(0) < S^{id}_{cc}(0)$ over the concentration range. This suggests a tendency of complex formation i.e. preference for unlike atoms pairing as nearest neighbour.

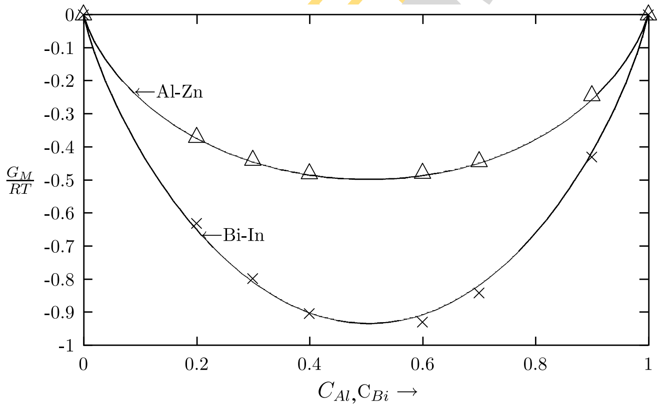

Fig. 2. Concentration dependence of $\frac{G_m}{RT}$ for Al–Zn and Bi–In liquid alloys at 1000 K and 900 K respectively. The solid line denotes theoretical values while the triangle and the cross denote experimental values for Al–Zn and Bi–In respectively. C_{Al} and C_{Bi} are the Al and Bi concentrations in the alloy. The experimental data are from [22].

Table 2
Computed chemical short range order parameter (α_1) for Al–Zn and Bi–In alloys at $T = 1000$ K and 900 K respectively

$C_{Al,Bi}$	$(\alpha_1)_{Al–Zn}$	$(\alpha_1)_{Bi–In}$
0.1	0.0697	−0.0696
0.2	0.0625	−0.0614
0.3	0.0551	−0.0534
0.4	0.0476	−0.0453
0.5	0.0399	−0.0375
0.6	0.0322	−0.0298
0.7	0.0244	−0.0222
0.8	0.0164	−0.0145
0.9	0.0083	−0.0073

The plot of the concentration dependence of $\frac{G_M}{RT}$ for the two alloys are given in Fig. 2. It is interesting to observe that the computed values are in quite excellent agreement with experiment. From the result, the Gibbs energies of mixing G_M for Al–Zn and Bi–In liquid alloys, have values of about $-0.4986RT$ and $-0.9344RT$ respectively. This shows that the tendency of compound formation in the liquid phases is weaker in Al–Zn than in Bi–In alloy.

The same mixing behaviour can be deduced from the values of Warren–Cowley short-range order parameter, α_1, Table 2. The positive values of the parameter α_1, for Al–Zn support a tendency towards segregation and the negative values of α_1, for Bi–In system at all concentrations confirm a tendency of complex formation.

3.2. Dynamic properties: diffusion and viscosity

From the ordering point of view, the computed chemical diffusion ratio (Eq. (21)) seems to be a more realistic parameter than the Warren–Cowley short range order parameter, α_1, [21] since Eq. (21) does not take into consideration the coordination number as an input and thus the inherent problems related to its estimation are avoided. The relationship between the $S_{cc}(0)$ and diffusion expressed by the ratio of the mutual and self-diffusion coefficient $\frac{D_m}{D_{id}}$, indicates the mixing behaviour of alloys, i.e. phase separation tendency or segregation in Al–Zn, for $\frac{D_m}{D_{id}} < 1$ over the concentration range, Table 3. The values $\frac{D_m}{D_{id}} > 1$ for Bi–In

Table 3
Concentration dependence of $\frac{D_m}{D_{id}}$ for Al–Zn and Bi–In alloys at $T = 1000$ K and 900 K respectively

$C_{Al,Bi}$	$\frac{D_m}{D_{id_{Al--Zn}}}$	$\frac{D_m}{D_{id_{Bi--In}}}$
0.1	0.8510	1.1493
0.2	0.7393	1.2751
0.3	0.6631	1.3746
0.4	0.6209	1.4443
0.5	0.6112	1.4805
0.6	0.6324	1.4792
0.7	0.6824	1.4358
0.8	0.7623	1.3334
0.9	0.8683	1.2021

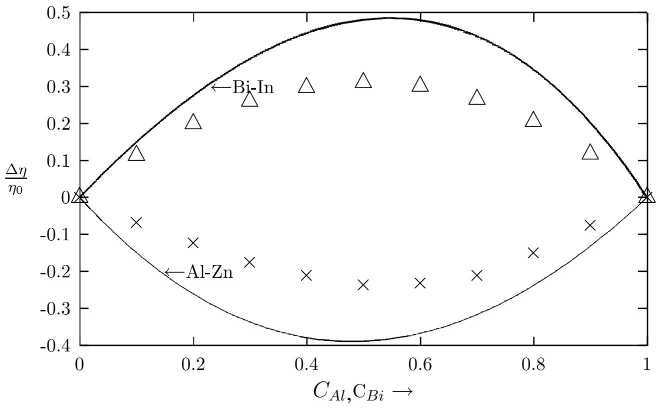

Fig. 3. Concentration dependence of viscosity $\frac{\Delta\eta}{\eta_o}$ Eqs. (11) and (12) for Al–Zn and Bi–In at 1000 K and 900 K respectively. The solid line are for calculated $\frac{\Delta\eta}{\eta_o}$. The triangle and the cross denote experimental values for $-\frac{H_M}{RT}$ for Al–Zn and Bi–In respectively. C_{Al} and C_{Bi} are the Al and Bi concentrations in the alloy. The experimental data for heat of mixing are taken from [22].

liquid phase at all concentrations suggest a tendency for compound formation in the melt.

As to the other aspect of our calculations which is to investigate how well the theoretical formulation in Eqs. (11) and (12) compare with experiment, we show in Fig. 3, our results for $\frac{\Delta\eta}{\eta_q}$ and $-\frac{H_M}{RT}$, but due to the lack of experimental data for viscosity at temperatures of interest it was not possible to compare our calculated results for viscosity with experimental values. However, a perusal of Fig. 3, reveals that computed $\frac{\Delta\eta}{\eta_o}$ for Al–Zn show a negative deviation while its $-\frac{H_M}{RT}$ is characterized by liquid miscibility gaps and exhibit large positive heat of mixing, H_M. This fact is substantiated by our earlier submission of the existence of a liquid miscibility gap in Al–Zn liquid alloy.

On the other hand, the computed $\frac{\Delta\eta}{\eta_o}$ for Bi–In exhibit positive deviation and its $-\frac{H_M}{RT}$ shows negative deviation which confirm that Bi–In liquid alloy is an ordered alloy. In order to discuss the disagreement between the calculated values of $\frac{\Delta\eta}{\eta_o}$ and $-\frac{H_M}{RT}$ for the two systems, it is important one looks at the parameters used to fit $S_{cc}(0)$ and hence to carry out the calculations. It is observed that the fitted value of γ for Bi–In is 1.135 and 0.950 for Al–Zn (Table 1). The calculated values of γ for Bi–In is closer to that determined at the melting point than that of Al–Zn. One reasonable conclusion drawn from this is that the size effect plays a prominent role in the energetics of Bi–In than it plays in Al–Zn alloy and thus pulling the system from segregation to order phase.

4. Conclusions

A Quasi-Lattice Theory has been utilised to obtain the fitted parameters, that are assumed to be invariant in all calculations. We investigated the bulk and dynamic properties in Al–Zn and Bi–In liquid alloys using a theoretical approach with special interest on their bulk thermodynamic properties such as free energy of mixing, concentration fluctuations in long-wavelength limit, chemical short range order parameter and the concentration dependence of diffusion and viscosity. Our theoretical investigation of bulk properties of Al–Zn liquid alloy is substantiated by the experimental data, obtained at 1000 K [22]. The ordering in Al–Zn liquid phase has been analysed in terms of the microscopic functions, $S_{cc}(0)$, and CSRO (α_1). The calculated values of these functions indicate the existence of liquid miscibility gap or segregation in the melt, on the contrary, the presence of chemical order was observed for Bi–In at 900 K. The bulk thermodynamic and dynamic properties of the two liquid alloys have been explained to a reasonable extent and the role of size effects notwithstanding the non-availability of the experimental viscosity data. The results obtained in this work further confirm the applicability of this theoretical approach for a proper description of mixing properties of binary liquid alloys.

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Thermodynamic properties of some gallium-based binary alloys

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Abstract

We have studied the concentration dependence of the free energy of mixing, concentration–concentration fluctuations in the long-wavelength limit, the chemical short-range order parameter, the enthalpy and entropy of mixing of Ga–Zn, Ga–Mg and Al–Ga binary alloys at different temperatures using a quasi-chemical approximation for compound forming binary alloys and that for simple regular alloys. From the study of the thermodynamic quantities, we observed that thermodynamic properties of Ga–Zn and Al–Ga exhibit positive deviations from Raoultian behaviour, while Ga–Mg exhibits negative deviation. Hence, this study reveals that both Ga–Zn and Al–Ga are segregating systems, while chemical order exists in Ga–Mg alloy in the whole concentration range. Furthermore, our investigation indicate that Al–Ga binary alloy have a tendency to exhibit ideal mixture behaviour in the concentration range $0 \leqslant c_{\mathrm{Al}} \leqslant 0.30$ and $0.7 \leqslant c_{\mathrm{Al}} \leqslant 1$.

Keywords: Chemical order; Homocoordination; Interaction energy; Raoultian behaviour

1. Introduction

Many investigations have been reported in literature on liquid binary alloy systems which are of importance from both the scientific and also the technological points of view. An accurate knowledge of the thermodynamic properties and phase diagrams of the alloy systems are essential to establish a respectable understanding between the experimental results, theoretical approaches and empirical models for liquid alloys with a miscibility gap.

The interatomic interactions and the related energies of the bond between the A and B component atoms of a binary alloy play an essential role in understanding the mixing behaviour of two metals. Because of this, the energetically preferred heterocoordination of A–B atoms as nearest neighbours over self-coordination A–A and B–B, or vice versa lead to the classification of all binary alloys into two distinct groups: short-range ordered [1–5] or segregating (demixing) alloys [6–9].

In this study, Ga–Zn, Ga–Mg and Al–Ga binary alloys are the alloys of interest. Our choice of these alloys arises from the fact that the three alloys have various industrial applications. Alloy systems containing semiconducting components such as gallium which is a group IIIB element like aluminium have been the subject of an increasing attention in the semiconductor production for their important application in the solid-state electronic devices and as a useful thermometric liquid [10]. Also, magnesium alloys offer lightweight alternatives to conventional metallic alloys and consequently, research on Mg alloys is fuelled nowadays by the need for low-density materials that suit aerospace and automobile industries [11] and as a result of which the world consumption of magnesium alloys in the automobile industry has been on the increase in the last decade [12]. Moreover, aluminium and its alloys are used in many aspects of modern life, from soda cans and household foil to automobiles and aircraft in which we travel. Al-based alloys have also been found useful as additives in various fuel formulations for propellants, explosives,

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incendiaries or pyrotechnics [13]. Large quantities of zinc are used to produce die castings. In addition, all the essential experimental data that are required for the calculation of the thermodynamic properties are available.

We observed that both Ga–Zn and Al–Ga systems are characterized by positive interaction energies indicating segregation in the melts, while Ga–Mg alloy is characterized by a negative interchange energy indicating ordering in the melt. This characteristic behaviour is likely to be a reflection of the interplay of the energetic and structural re-adjustment of the constituent elemental atoms.

The long-wavelength limit of the concentration fluctuations, $S_{cc}(0)$, the Warren–Cowley chemical short-range order parameter (CSRO), α_1, the enthalpy of mixing, H_{M} and the entropy of mixing, S_{M} of Ga–Zn and Al–Ga molten alloys deviate positively from the ideality and thus both alloys belong to the class of liquid alloys that exhibits a preference towards homocoordination (segregation), while Ga–Mg deviate negatively from ideality suggesting a preference towards heterocoordination.

In this work, we study the composition dependence of thermodynamic properties of these binary alloys by using a quasi-chemical approximation model [14] for compound forming binary alloys and that for simple regular alloys. The energetics of mixing as well as the positive deviation from Raoultian behaviour was discussed for the various thermodynamic quantities calculated.

The structure of this paper is as follows. In Section 2, we present the model descriptions for calculating the thermodynamic properties of the alloys. This is followed by results and discussion in Section 3 and our conclusions at the end of the paper.

2. Model descriptions

The general mathematical expression treats an alloy as a pseudoternary mixture of A atoms, B atoms and $A_\mu B_\nu$ (μ and ν are small integers) group of atoms or clusters with the stoichiometry of intermetallics present in the solid state, all in chemical equilibrium with one another. The absence of clusters in the melt reduces the model to the quasi-chemical approximation for regular solutions. The grand partition function Ξ of a binary molten alloy AB, which consists of $N_A = Nc$ and $N_B = N(1-c)$ atoms of elements A and B, respectively, where the total number of atoms, N, is equal to $N_A + N_B$, can be expressed as

$$\Xi = \sum_E q_A^{N_A}(T) q_B^{N_B}(T) \exp[(\mu_A N_A + \mu_B N_B - E)/k_{\mathrm{B}}T], \tag{1}$$

where $q_i^N(T)$ and μ_i are atomic partition function and chemical potential of ith components ($i = A, B$), k_{B} is Boltzmann's constant, T is the absolute temperature and E is the configurational energy of the alloy. The quasi-chemical model (QCM) is utilized to determine the probable chemical complexes existing in a liquid binary alloy. Detailed discussion of the model are given in Ref. [14].

After doing some algebra [15], the solution of Eq. (1) is given as the ratio of the activity coefficient γ ($\gamma = \gamma_A/\gamma_B$); γ_A and γ_B are activity coefficients of A and B atoms, respectively) for the compound ($A_\mu B_\nu$) forming alloys as

$$\ln\gamma = \frac{Z(1-c)}{2c}\cdot\frac{(\beta+2c-1)}{(\beta-2c+1)} \tag{2}$$

with

$$\beta = \{1 + 4c(1-c)(\eta^2-1)\}^{1/2}, \tag{3}$$

where

$$\eta^2 = \exp\left(\frac{2\omega}{zk_{\mathrm{B}}T}\right)\exp\left(\frac{2P_{AB}\Delta\varepsilon_{AB} - P_{AA}\Delta\varepsilon_{AA} - P_{BB}\Delta\varepsilon_{BB}}{k_{\mathrm{B}}T}\right) \tag{4}$$

and the interchange or ordered energy, ω is expressed as

$$\omega = Z[\Delta\varepsilon_{AB} - \tfrac{1}{2}(\Delta\varepsilon_{AA} + \Delta\varepsilon_{BB})]. \tag{5}$$

$\Delta\varepsilon_{AB}$, $\Delta\varepsilon_{AA}$, $\Delta\varepsilon_{BB}$ are the interaction parameters and $\Delta\varepsilon_{ij}$ is the change in the energy of the ij bond in the complex $A_\mu B_\nu$. P_{ij} is the probability that the ij bond is a part of the complex. P_{ij} may be expressed as

$$P_{AB} = c^{\mu-1}(1-c)^{\nu-1}[2 - c^{\mu-1}(1-c)^{\nu-1}], \tag{6}$$

$$P_{AA} = c^{\mu-2}(1-c)^{\nu}[2 - c^{\mu-2}(1-c)^{\nu}], \quad \mu \geqslant 2, \tag{7}$$

$$P_{BB} = c^{\mu}(1-c)^{\nu-2}[2 - c^{\mu}(1-c)^{\nu-2}], \quad \mu \geqslant 2. \tag{8}$$

We now try to obtain an expression for the excess Gibbs free energy of mixing G_{M}^{xs} defined by

$$G_{\mathrm{M}}^{xs} = G_{\mathrm{M}} - RT\{c\ln c + (1-c)\ln(1-c)\}. \tag{9}$$

G_{M} being the free energy of mixing. G_{M}^{xs} can be obtained from Eq. (2) by using the thermodynamic relationship [3]

$$\frac{G_{\mathrm{M}}^{xs}}{RT} = Z\int_0^c [\ln\sigma + (2k_{\mathrm{B}}T)^{-1}(P_{AA}\Delta\varepsilon_{AA} - P_{BB}\Delta\varepsilon_{BB})]\,\mathrm{d}x + \phi. \tag{10}$$

Here Z is the coordination number, c is the concentration of atom A and R is the universal gas constant and

$$\ln\sigma = \frac{1}{2}\ln\frac{(1-c)(\beta+2c-1)}{c(\beta-2c+1)}. \tag{11}$$

The constant ϕ in Eq. (10) is determined from the requirement that $G_{\mathrm{M}}^{xs} = 0$ at $c = 0$ and 1. One observes that for $\Delta\varepsilon_{ij} = 0$, the expression reduces to the regular solution expression [16].

The concentration–concentration fluctuations in the long-wavelength limit, $S_{cc}(0)$, has emerged as an important microscopic function to understand the mixing behaviour of liquid alloys in terms of compound formation and phase segregation [14]. The $S_{cc}(0)$ can be expressed by G_{M}, or the activity, a_i $(i = A, B)$, as

$$S_{cc}(0) = RT\left(\frac{\partial^2 G_{\mathrm{M}}}{\partial c_A^2}\right)^{-1}_{T,P,N} = c_B a_A \left(\frac{\partial a_A}{\partial c_A}\right)^{-1}_{T,P,N} = c_A a_B \left(\frac{\partial a_B}{\partial(1-c_A)}\right)^{-1}_{T,P,N}. \tag{12}$$

For ideal mixing the energy parameters, ω, given in Eq. (5) is equal to zero, and Eq. (12) becomes

$$S_{cc}^{id}(0) = c_A c_B. \tag{13}$$

Substituting Eq. (9) for G_{M} into Eq. (12), we obtain

$$S_{cc}(0) = \frac{c(1-c)}{1 + Z/2(1/\beta - 1)}. \tag{14}$$

Eq. (12) is usually utilized to obtain the experimental values of $S_{cc}(0)$ from the measured activity or the free energy of mixing data [17]. The mixing behaviour of liquid binary alloys can be inferred from the deviation of $S_{cc}(0)$ from $S_{cc}^{id}(0)$. The presence of chemical order is indicated by $S_{cc}(0) < S_{cc}^{id}(0)$; on the contrary, if $S_{cc}(0) > S_{cc}^{id}(0)$, the segregation and demixing in liquid alloys take place.

The Warren–Cowley short-range order parameter, α_1 [18,19] can further be used to gain insight into the local arrangement of atoms in the molten alloys. This parameter α_1 is expressed in term of β-function (Eq. (5)), as

$$\alpha_1 = \frac{\beta - 1}{\beta + 1}. \tag{15}$$

The enthalpy of mixing, H_{M} within the QCM can be obtained from the standard thermodynamic relation [20]

$$H_{\mathrm{M}} = G_{\mathrm{M}} - T\left(\frac{\partial G_{\mathrm{M}}}{\partial T}\right)_P. \tag{16}$$

From the expression for G_{M} in Eq. (9), we obtain

$$H_{\mathrm{M}} = -\frac{8RTc^2(1-c)^2 \exp\left(\dfrac{2\omega}{Zk_{\mathrm{B}}T}\right)}{(\beta - 1 + 2c)(1+\beta)(\beta + 1 - 2c)}\left(\frac{1}{k_{\mathrm{B}}}\frac{\mathrm{d}\omega}{\mathrm{d}T} - \frac{\omega}{T}\right) \tag{17}$$

and thus the entropy of mixing,

$$S_{\mathrm{M}} = \frac{H_{\mathrm{M}} - G_{\mathrm{M}}}{T}. \tag{18}$$

3. Results and discussion

Based on the model descriptions in Section 2, the mixing behaviour of Ga–Zn, Ga–Mg and Al–Ga binary alloys have been defined. The values of the relevant parameters used to obtain our results are presented in Table 1. It is important to add that keeping these fitted parameters, which gives the best representation of the observed Gibbs free energy of mixing G_{M} data unchanged in our calculations, one can then proceed using these fixed values to compute such properties as the $S_{cc}(0)$, α_1, the enthalpy of mixing, H_{M} and the entropy of mixing, S_{M} and thus, forming a basis to elucidate the energetics of the alloys.

Using Eq. (9), we have calculated the free energy of mixing for these alloys. The experimental data given as symbols in Fig. 1 were obtained from Ref. [21]. A perusal of Fig. 1 shows that our interaction parameters give a good representation of the experimental values of the free energy of mixing for the alloys Ga–Zn, Ga–Mg and Al–Ga at temperatures of 700, 923 and 1073 K, respectively. The good agreement obtained for G_{M} as shown in the figure for the three systems we have worked on, gives us the confidence to use the fitted energy parameters to study the nature of ordering in the liquid alloys. A comparison of the figure for the three binary alloys reveal that the Gibbs free energy of mixing are almost symmetric around the equiatomic composition ($c_{\mathrm{Ga,Al}} = 0.5$), with Ga–Mg $[(G_{\mathrm{M}}/RT)_{c_c} = -2.08]$ exhibiting a higher tendency for compound formation and is the most interacting of the three alloys; Al–Ga $[(G_{\mathrm{M}}/RT)_{c_c} = -0.652]$ is more interacting than Ga–Zn alloy $[(G_{\mathrm{M}}/RT)_{c_c} = -0.569]$.

For proper analysis of the nature of ordering in the melts, it is important to critically consider the results for the structure related quantities. From this point of view the first quantity investigated is the concentration fluctuations $S_{cc}(0)$. The deviation of $S_{cc}(0)$ from ideal value $S_{cc}^{id}(0) = c_A c_B$ is an essential parameter in order to visualize the nature of atomic interactions in the mixture. If, at a given composition $S_{cc}(0) \gg S_{cc}^{id}(0)$, then there is a tendency for segregation and vice versa for heterocoordination.

Table 1
Fitted interaction parameters for the systems

System	T (K)	Z	ω (eV)	$\mathrm{d}\omega/\mathrm{d}T \times 10^{-3}$
Ga–Zn	700	10	0.0323	−1.240
Ga–Mg	923	10	−0.3932	9.215
Al–Ga	1073	10	0.0150	−0.250

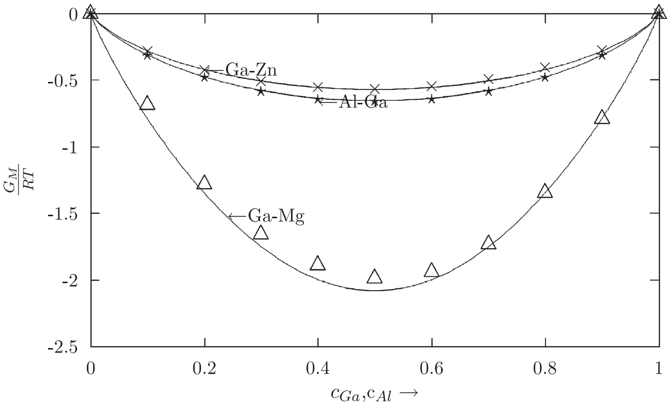

Fig. 1. Free energy of mixing, G_{M}/RT versus concentration for Ga–Zn, Ga–Mg and Al–Ga liquid alloys at 700, 923 and 1073 K, respectively. The solid line denotes theoretical values while the cross, triangle and star denote experimental values for Ga–Zn, Ga–Mg and Al–Ga, respectively. c_{Ga} and c_{Al} are the Ga and Al concentrations in the alloy. The experimental data are from Ref. [21].

It is obvious from Eq. (12) that $S_{cc}(0)$ can be obtained directly from the experimental Gibbs energy of mixing or from the activity data. This is usually referred to as an experimental $S_{cc}(0)$ in literature. We have used Eq. (14) to determine the computed $S_{cc}(0)$ for these liquid alloys, while their measured $S_{cc}(0)$ were obtained by numerical differentiation of the Gibbs free energy of mixing data taken from Ref. [21]. It is important to add that Eq. (13) was used to calculate $S_{cc}^{id}(0)$. Our results for the concentration fluctuations as a function of composition for the three systems are as shown in Fig. 2. From the figure, it is clear that the calculated $S_{cc}(0) > S_{cc}^{id}(0)$ for Ga–Zn and Al–Ga, while calculated $S_{cc}(0) < S_{cc}^{id}(0)$ for Ga–Mg. This implies a tendency for homocoordination in Ga–Zn and Al–Ga alloys, i.e. like atoms Ga–Ga, Zn–Zn or Al–Al tend to pair as nearest neighbours and a presence of heterocoordination in Ga–Mg, i.e. unlike atoms Ga–Mg tend to pair as nearest neighbours. A close look at Fig. 2 shows that in the region of $0 \leqslant c_{\mathrm{Al}} \leqslant 0.30$ and $0.7 \leqslant c_{\mathrm{Al}} \leqslant 1$, it is observed that the calculated $S_{cc}(0)$ values for Al–Ga liquid alloy almost attain ideal values. This indicates that Al–Ga alloy have tendency to exhibit ideal behaviour for these concentrations.

To have a clear understanding into the local arrangement of atoms in the molten alloys. We have used Eq. (15) to obtain the Warren–Cowley short-range order parameter α_1. The positive values of α_1 (Fig. 3) in the whole concentration range for both Ga–Zn and Al–Ga alloys are sufficient indicators of the presence of homocoordination (segregation) in the liquid alloys, while negative values of α_1 for Ga–Mg indicates chemical order in this concentration range. In addition, α_1 is much less than unity for both Ga–Zn and Al–Ga alloys and a pointer that the alloys are weakly segregating alloys. It is noted that varying the value of Z does not have any significant effect on $\alpha_1 - c$ curves, the only effect is to vary the position of the maxima while the overall features remain unchanged.

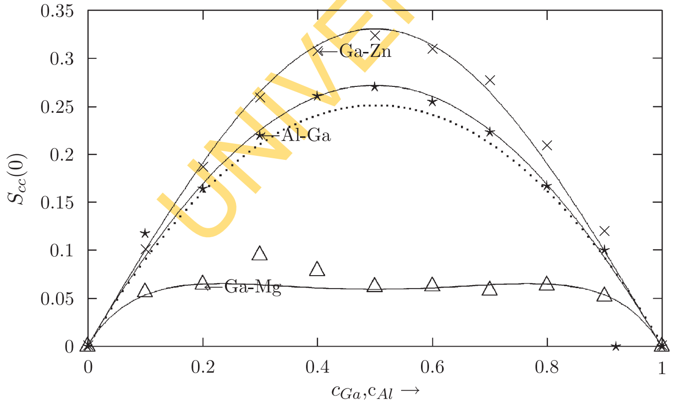

Fig. 2. Concentration–concentration fluctuations $S_{cc}(0)$ versus concentration for Ga–Zn, Ga–Mg and Al–Ga liquid alloys at 700, 923 and 1073 K, respectively. The solid line denotes theoretical values while the cross, triangle and star denote experimental values for Ga–Zn, Ga–Mg and Al–Ga, respectively. The dot denotes the ideal values. c_{Ga} and c_{Al} are the Ga and Al concentrations in the alloy.

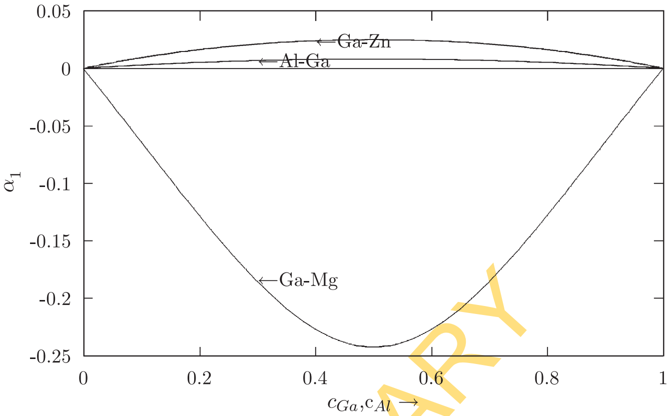

Fig. 3. Calculated Warren–Cowley short-range order parameter α_1 versus concentration for Ga–Zn, Ga–Mg and Al–Ga liquid alloys at 700, 923 and 1073 K, respectively. c_{Ga} and c_{Al} are the Ga and Al concentrations in the alloy.

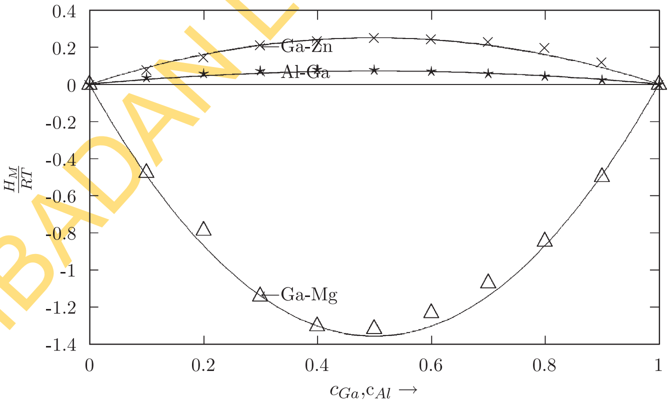

Fig. 4. Enthalpy of mixing, H_{M}/RT versus concentration for Ga–Zn, Ga–Mg and Al–Ga liquid alloys at 700, 923 and 1073 K, respectively. The solid line denotes theoretical values while the cross, triangle and star denote experimental values for Ga–Zn, Ga–Mg and Al–Ga, respectively. c_{Ga} and c_{Al} are the Ga and Al concentrations in the alloy. The experimental data are from Ref. [21].

It is seen from Eq. (16) for H_{M} that in order to obtain a good fit to this parameter, we need to incorporate the temperature dependence of the interaction parameters; any other approximation would be invalid. Using Eqs. (17) and (18), we have ascertained the variation in temperature parameters from the measured values of H_{M} and S_{M}, the results are shown in Table 1. From the fitted enthalpy of mixing and entropy of mixing in Figs. 4 and 5, respectively, we note that the fits obtained for the three alloys compared quite well with the experimental data. The values obtained (Table 1) show that the temperature dependence of the energy parameters are quite small. Also, one notes that the enthaply of mixing for Ga–Zn and Al–Ga alloys are symmetric and positive (typical of segregating systems) in agreement with the work of Novakovic et al. [20] on Ga–Zn and Singh et al. [6] on gallium-based alloys, although their Gibbs free energy of mixing are indicative of a very weakly interacting system. On the contrary, both the free energy of mixing, G_{M} and the enthalpy of mixing,

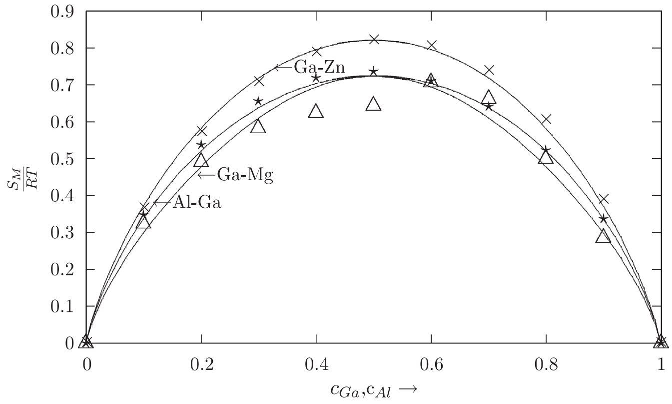

Fig. 5. Entropy of mixing, S_M/R versus concentration for Ga–Zn, Ga–Mg and Al–Ga liquid alloys at 700, 923 and 1073 K, respectively. The solid line denotes theoretical values while the cross, triangle and star denote experimental values for Ga–Zn, Ga–Mg and Al–Ga, respectively. c_{Ga} and c_{Al} are the Ga and Al concentrations in the alloy. The experimental data are from Ref. [21].

H_M exhibit negative deviations from Raoultian behaviour for Ga–Mg alloy. In addition, the entropy of mixing (Fig. 5) for the three alloys investigated is almost symmetric and positive around the equiatomic composition. Generally, one observes that both the reported literature data and theoretical values obtained using the interaction parameters and their temperature dependence are in very good agreement.

4. Conclusions

The thermodynamic properties of the three binary alloys, namely Ga–Zn, Ga–Mg and Al–Ga have been discussed in terms of the free energy of mixing, G_M/RT, the concentration fluctuations in the long-wavelength limit, $S_{cc}(0)$, chemical short-range order parameter, α_1, as a function of compositions on the basis of the theory in Section 2. Positive deviations from Raoultian behaviour was observed in the thermodynamic properties of Al–Ga and Ga–Zn which agrees with the result of Awe et al. [10] using four-atom-cluster-model (FACM), while Ga–Mg exhibits negative deviation. An indication that both Ga–Zn and Al–Ga are segregating systems, while a reasonable degree of chemical order exists in Ga–Mg alloy across the whole concentration range. The enthalpy of mixing and entropy of mixing for the three alloys studied are positive and symmetric around equiatomic composition, except for the enthalpy of mixing, H_M of Ga–Mg alloy that shows a negative deviation from Raoultian behaviour. We conclude that in the glass-forming composition range which usually lies far away from the stoichiometric composition, computed $S_{cc}(0)$ almost attain ideal values for Al–Ga: i.e. Al–Ga exhibits ideal behaviour for the composition $0 \leqslant c_{Al} \leqslant 0.30$ and $0.7 \leqslant c_{Al} \leqslant 1$.

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