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Computation of infinite dilute activity coefficients of binary liquid alloys using complex formation model

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ABSTRACT

A new method for calculating Infinite Dilute Activity Coefficients ($\gamma^{\infty}s$) of binary liquid alloys has been developed. This method is basically computing $\gamma^{\infty}s$ from experimental thermodynamic integral free energy of mixing data using Complex formation model. The new method was first used to theoretically compute the $\gamma^{\infty}s$ of 10 binary alloys whose $\gamma^{\infty}s$ have been determined by experiments. The significant agreement between the computed values and the available experimental values served as impetus for applying the new method to 22 selected binary liquid alloys whose $\gamma^{\infty}s$ are either nonexistent or incomplete. In order to verify the reliability of the computed $\gamma^{\infty}s$ of the 22 selected alloys, we recomputed the $\gamma^{\infty}s$ using three other existing methods of computing or estimating $\gamma^{\infty}s$ and then used the $\gamma^{\infty}s$ obtained from each of the four methods (the new method inclusive) to compute thermodynamic activities of components of each of the binary systems. The computed activities were compared with available experimental activities. It is observed that the results from the method being proposed, in most of the selected alloys, showed better agreement with experimental activity data. Thus, the new method is an alternative and in certain instances, more reliable approach of computing $\gamma^{\infty}s$ of binary liquid alloys.

1. Introduction

Since the last century, much effort has been made by theoreticians and experimentalists to study the properties of binary alloys due to their scientific and technological importance [1]. In the recent times, attention has shifted to studying various thermodynamic properties of multicomponent alloy systems [2–4]. Two of the notable reasons for the interest in multicomponent alloys are (i) they are known to exhibit lower liquidus temperature and critical quenching rates required for glass formation than their binary sub-systems [4]; (ii) the growing demand for materials with more specific properties has led to the increased relevance of multicomponent alloy systems.

In the study of multicomponent alloys, a number of models have been established and one of these models which appear to be more popular by the day is the Molecular Interaction Volume model (MIVM) [3,5–12]. The interest in MIVM is due to its reliability, its statistical thermodynamic origin and the fact that its application requires few parameters [10,13]. However, a successful use of MIVM depends on among other things, complete values of Infinite Dilute Activity Coefficient ($\gamma^{\infty}s$) of all binary alloys components of a multicomponent system of interest, and in many binary alloys $\gamma^{\infty}s$ values are either non-existence or incomplete.

Also, $\gamma^{\infty}s$ of binary liquid alloys, which reflect the behaviour of a single atom of one of the two species of atoms being completely surrounded by infinite atoms of the second specie, have been known to be very useful for both scientific and engineering applications [14,15].These include $\gamma^{\infty}s$ relevance in the characterization of liquid mixture and estimation of solubility [16] and in models like Wilson equation (known for its relevance to the study of totally miscible systems) [17], Non-random two-liquid model (NRTL) (useful for studying a variety of mixtures, including those of relatively low miscibility) [18], and Margules model (useful in the study of ionic solutions) [19]. In addition, $\gamma^{\infty}s$ found relevance in the design of processes involving the separation of dilute contaminants (or hazardous substances) from water and or waste stream [15].

Despite the above relevancies of $\gamma^{\infty}s$, and the fact that calculating $\gamma^{\infty}s$ has been a subject of interest for about a century, unfortunately, due to what appears to be experimental difficulties, there are many binary alloys (including alloys with known industrial relevancies such as Ag, Au, Cu and Zn based binary systems) [20–25] whose $\gamma^{\infty}s$ are neither available nor complete [20–26]. Hence, the need to consider an alternative to experimental method of obtaining $\gamma^{\infty}s$.

In order to theoretically determine $\gamma^{\infty}s$ for a binary liquid alloy of interest, we observed that various methods have been introduced [10,15,27],and each method, has been known to have one

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constraint or the other that either limit the degree of its successful application or make it completely unsuitable for certain category of alloys whose $\gamma^{\infty}s$ are unknown. These constraints may be in the form of what it takes to successfully carry out an extrapolation which will eventually lead to $\gamma^{\infty}s$ (as in the case in Refs. [15,27–29]) or lack of important parameters a method require for its application (as in Electron affinity approach which require that one of the pair values of $\gamma^{\infty}s$ be known [10]).

In this paper, we have attempted to present a new method of computing $\gamma^{\infty}s$ which has the merits of (i) requires only experimental integral free energy of mixing data and stoichiometric compositions of a binary alloy of interest, (ii) does not require the knowledge of one of the $\gamma^{\infty}s$ for the binary alloy of interest and (iii) has better agreement with experimental data when applied in thermodynamic studies of binary and multicomponent alloy systems. This method, to the best of our knowledge is being presented for the first time. The proposed method is applied to 22 binary alloys selected on the basis that they (i.) do not have complete $\gamma^{\infty}s$ and (ii.) have significant industrial importance (for example, Ag–Bi alloy can function like a narrow gap semiconductor in electronics [30,31], Au–In is relevant in microelectronics [32], Cu–Zn alloy is used in marine engineering due to its resistance to marine corrosion [33], Hg–In is used in dental surgery [34], and Sb–Zn alloy which exhibits low thermal conductivity is used in thermoelectricity [35]).

The detail of the proposed method is presented in Section 2. Results of our computation of $\gamma^{\infty}s$ from the proposed method, and a comparison of these results with results from three of the existing methods are presented with discussion in Section 3.The paper is concluded in Section 4.

2. Theoretical formalism

The estimation of $\gamma^{\infty}s$ being proposed in this work is obtained by mathematically computing $\ln\gamma_i$ and $\ln\gamma_j$ for a binary alloy using the Complex formation model (CFM) [36–38]. In order to do this, there is need for an appropriate expression for integral free energy of mixing. In this regard, the following expression for integral free energy of mixing in the Flory's approximation of the complex formation becomes relevant [36]:

$$G_M = -n_3 g + RT\left[n_1 \ln\frac{n_1}{N} + n_2 \ln\frac{n_2}{N} + n_3 \ln\frac{n_3(\mu+\nu)}{N}\right] + \sum\sum_{p<q}\frac{n_p n_q}{N}\nu_{pq} \quad (1)$$

where $p=\{1, 2\}$ and $q=\{2, 3\}$; g is the formation energy of the complex; ν_{12}, ν_{13} and ν_{23} are interaction parameters that are independent of composition but depends on temperature; μ and ν are the respective number of i and j atoms that makes up a mole of $i_\mu j_\nu$ complex (or integers obtained from the stochiometry of energetically favoured compound); n_1, n_2 and n_3 are respectively the mole numbers of individual i atoms, j atoms and $i_\mu j_\nu$ complexes in the binary alloy system.

CFM cannot be successfully employed without obtaining n_1, n_2 and n_3 that will satisfy the conservation equations: $n_1 = N_i - \mu n_3$, $n_2 = N_j - \nu n_3$, $n = n_1 + n_2 + n_3$ (taken n is the total mole) and the equilibrium condition $\frac{\partial G_M}{\partial n_3}=0$.

In order to relate Eq. (1) to $\gamma^{\infty}s$, the thermodynamic relations (obtained from Ref. [39]), the following Eqs. (2)–(5) become relevant:

$$\hat{g}_i^{real} = \left(\frac{\partial G_M}{\partial N_i}\right)_{T,P,N_j} \quad (2)$$

$$\hat{g}_i^{E} = RT\ln\gamma_i \quad (3)$$

$$\hat{g}_i^{ideal} = RT\ln\frac{N_i}{N} \quad (4)$$

$$\hat{g}_i^{E} = \hat{g}_i^{real} - \hat{g}_i^{ideal} \quad (5)$$

Where $\hat{g}_i^{real}$, $\hat{g}_i^{E}$ and $\hat{g}_i^{ideal}$ are partial Gibbs, partial excess Gibbs and ideal Gibbs energies of component i respectively; N_i and N_j are the mole numbers of i and j atoms of the i–j binary system respectively.

Hence, if Eqs. (2)–(4) are substituted in Eq. (5), the following equations will be obtained:

$$\ln\gamma_i = \frac{1}{RT}\left(\frac{\partial G_M}{\partial N_i}\right)_{T,P,N_j} - \ln\left(\frac{N_i}{N}\right) \quad (6)$$

$$\ln\gamma_j = \frac{1}{RT}\left(\frac{\partial G_M}{\partial N_j}\right)_{T,P,N_i} - \ln\left(\frac{N_j}{N}\right) \quad (7)$$

Where $N = N_i + N_j$; $N_i = Nc$; $N_j = N(1-c)$; c is the concentration of component i in the binary mixture; $(1-c)$ is the concentration of component j in the binary mixture; R and T are the molar gas constant and the system temperature respectively.

Mathematically, it is understood that the negative exponential of the second term on the right hand side of Eq. (6) simply represents the concentration of component i in the binary alloy while the negative exponential of the second term on the right hand side of Eq. (7) equally represents the concentration of component j in the binary alloy. Simplification of Eqs. (6) and (7) after Eq. (1) has been appropriately introduced will lead to the following respective equations involving $\ln\gamma_i$ and $\ln\gamma_j$:

$$\ln\gamma_i = \ln\frac{n_1}{N_i} + \frac{N-n}{N} + \frac{1}{NRT}\left(n_2\nu_{12} + n_3\nu_{13} - \frac{n_1 n_2 \nu_{12}}{N} - \frac{n_1 n_3 \nu_{13}}{N} - \frac{n_2 n_3 \nu_{23}}{N}\right) \quad (8)$$

$$\ln\gamma_j = \ln\frac{n_2}{N_j} + \frac{N-n}{N} + \frac{1}{NRT}\left(n_1\nu_{12} + n_3\nu_{23} - \frac{n_1 n_2 \nu_{12}}{N} - \frac{n_1 n_3 \nu_{13}}{N} - \frac{n_2 n_3 \nu_{23}}{N}\right) \quad (9)$$

The formation energy (g), and the interaction parameters (ν_{ij}s) including corresponding values of n_1, n_2 and n_3 (all obtained from using experimental integral free energy of mixing to fit Eq. (1)) are substituted in Eqs. (8) and (9) to obtain $\ln\gamma_i$ and $\ln\gamma_j$ at various compositions. A graph of $\ln\gamma_i$ against concentration of i (i.e. c_i) and a graph of $\ln\gamma_j$ against concentration j (i.e. c_j) are then plotted. From the lines of best fit (using appropriate polynomial order), γ_i^{∞} is deduced from the value of $\ln\gamma_i$ when $c_i=0$, while γ_j^{∞} is deduced from the value of $\ln\gamma_j$ when $c_j=0$.

3. Results and discussion

In order to test the reliability of the proposed method outlined in Section 2, we used the method to predict the $\gamma^{\infty}s$ for 10 binary liquid alloys whose $\gamma^{\infty}s$ are known [26]. The result obtained is shown in Table 1a while the parameters needed to obtain the