Thermodynamic Prediction of the Free Energy of Mixing and Activities of some Gold-based Binary Liquid Alloys

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Abstract: The free energy of mixing and activities of gold in selected six Au-based binary liquid Au-Cu, Au-Zn, Au-Pb, Au-Ni, Au-Sn and Al-Au alloys at different working temperatures have been studied using the quasi-chemical approximation model (QCAM). The predicted free energy of mixing and activities results were compared with available experimental values. The predicted results are in reasonable agreement with reported experimental data and confirms that the model is reliable and, thus should serve as an alternative for the prediction of thermodynamic properties of binary liquid alloys.

Keywords: free energy of mixing, activities, Au, Binary liquid alloys, concentration

1. INTRODUCTION

Lack of sufficient thermodynamic data especially on the free energy of mixing and activity data has been identified as a great challenge in the field of liquid alloy developments. Although some

experimental investigations have been carried out [1-7]. Still, there exists quantitative data gaps for the multi-component liquid alloys due to the difficulties associated with high-temperature experiments. More so that evidences have shown that the binary and other multi-component systems may have better properties for industrial processes, it is therefore obviously unrealistic to rely solely on the experiments for all relevant data. To compliment experimental efforts and fill the needed data gaps, the scientific community has over the years relied on modelling [8-12].

For this purpose, many theories or thermodynamic models that attempts to explain reasonably the change of activity coefficient with concentration for binary and multi-component liquid alloys have been proposed [8-9, 13-15]. Despite the success of these models, it is however, limited in most cases for estimating large quantities of thermodynamic data directly. The heat of formation model for binary alloys by Miedema and co-workers [16-17] is a very important achievement in this regard. The model allows the calculation of heat of formation of almost all binary alloys on the basis of properties such as molar volume V, electronegativity Ø, and electron density, n_{ws}, of elements in the systems. The quasi-chemical approximation model (QCAM) [18] or any of the other numerous available models have been employed by researchers [19-23] to explain the concentration dependent thermodynamic properties of binary liquid alloys. In the model formulations, the deviation of the properties of an alloy from the ideal mixing behaviour is gauged in terms of the

interatomic interactions and the energy of the bonds between the constituent species. The information on the energetic and the structure of melts as well as the ways they are coupled are important factors in understanding the alloying behaviour in binary liquid alloys.

From the viewpoint of theoretical modelling, all binary liquid alloys may be broadly grouped into two major categories: short-range ordered or segregating alloys. The categorization is based on the deviation of the mixing properties from ideal mixture behaviour. In terms of energetic and structure, the first group is characterized by a strong interactive tendency between unlike atoms and by the formation of hetero-paired atoms. On the other hand, the second category is one in which the attractive force between like atoms is much greater than between unlike atoms, and the formation of homo-paired atoms takes place [18, 24-25].

The purpose of this work is to apply the QCAM to predict the thermodynamic properties i.e. the free energy of mixing and activity of some selected gold-based binary alloys. These two thermodynamic properties are cardinal in understanding the separation mechanism in metallurgical process [26]. It is important to note that existence of reliable and consistent thermodynamic databases on binary liquid systems is crucial for the reliable modelling of thermodynamic properties of higher component systems such as ternary Au-Sb-Sn and quaternary Au-Sb-Sn-Cu, which relies on accurate data of their constitutive binary systems. In order to further establish the reliability of the QACM in predicting thermodynamic properties, the free energy of mixing of binary liquid Ti-Si alloys at 2000 K, 2400 K and 2473 K, respectively were also calculated and compared with the experimental data of Kostov et al. [10].

The motivation for selecting gold-based binary liquid Au-Cu, Au-Zn, Au-Pb, Au-Ni, Au-Sn and Al-Au alloys for investigation are borne out of the fact that gold and its

constituent alloying elements have attracted a lot of attention in recent times due to their diverse commercial and industrial values [27-28]. For instance, gold is particularly relevant for both fundamental and applied research. In the bulk form, gold is the most inert and softest metal [29]. Apart from its commercial value, the unique chemical and physical properties offered by gold are increasingly being investigated in a growing number of applications. These include uses within the fields of nanotechnology and medicine for products such as smartcards, automotive electronics, sensors, medical implants and drug delivery systems.

The rest of the manuscript is organized as follows: the theoretical formulation of the QCAM is given in the next section, followed by results and discussion. Finally, the conclusions are provided in the last section.

2. QUASI-CHEMICAL APPROXIMATION MODEL (QCAM) FORMULATION

If the grand partition function Ξ of a binary liquid A-B alloy containing $N_A = Nc$ and $N_B = N(1-c)$ atoms of elements A and B, respectively, is expressed as:

$$\Xi = \sum_E q_A^{N_A}(T) q_B^{N_B}(T) \, exp[\,\mu_A N_A - \mu_B N_B - E)/k_B T$$
(1)

where the total number of atoms, $N = N_A + N_B$. k_B is the Boltzmann's constant, T is the absolute temperature and E is the configurational energy of the alloy. The quantities $q_i^N(T)$ and μ_i are atomic partition function and chemical potential of ith components $(i = A,B)$, respectively.

The solution of Eqn. (1) is given as the ratio of the activity coefficient of alloy components, γ, ($\gamma = \gamma_A/\gamma_B$), after some algebraic simplifications [30-31]:

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

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

$$\eta^2 = exp\left(\frac{2\omega}{zk_BT}\right) \quad ;$$

$$\omega = Z[\Delta\epsilon_{AB} - \frac{1}{2}(\Delta\epsilon_{AA} + \Delta\epsilon_{BB})]$$
(4)

The quantity ω in Eqn. (4) is the interchange or ordered energy, while $\Delta\epsilon_{AB}$, $\Delta\epsilon_{AA}$, $\Delta\epsilon_{BB}$ are the interaction energy parameters. $\Delta\epsilon_{ij}$ is the change in the energy of the ij bond in the complex $A_\mu B_v$, Z is the coordination number, c is the concentration of atom A and R is the universal gas constant. Using standard thermodynamic relations [32], the Gibbs free energy of mixing G_M is obtained from Eqn. (2) as:

$$G_M = RT\{c\,ln\,c + c(1-c)\,ln(1-c) + c\,ln\,\gamma_A + (1-c)\,ln\,\gamma_B\}$$
(5)

with

$$\gamma_A = \left\{\frac{\beta-1+2c}{c(1+\beta)}\right\}^{z/2} \quad ;$$

$$\gamma_B = \left\{\frac{\beta+1-2c}{(1-c)(1+\beta)}\right\}^{z/2}$$
(6)

here γ_A and γ_B are activity coefficients of atoms A and B, respectively. The activities of the components in a binary liquid alloy are given by:

$$a_i = c\gamma_i \quad ; \quad (i = A,B)$$
(7)

The standard error is computed by:

$$S_i = \pm\left[\sum \frac{(a_i i_{,pre}^2 ,exp}{n}[]\right]^{1/2}$$
(8)

Table 1: Fitted values of the interaction parameters for the binary liquid alloys.

Alloys	T(K)	Z	$\omega(eV)$
Au-Cu	1550	10	-0.2467
Au-Zn	1080	10	-0.7042
Au-Pb	1200	10	-0.1218
Au-Ni	1150	10	0.1825
Au-Sn	823	10	-0.4562
Al-Au	1338	10	-1.1322
Ti-Si	2000	10	-1.6260
Ti-Si	2400	10	-1.5723
Ti-Si	2473	10	-1.5567

Table 2: Predicted and Experimental free energy of mixing values along with the calculated activity of Au in binary liquid Au-Cu alloys at 1550 K, respectively [1]. ($S_{G_M} = \pm0.0072$ $S_{a_{Au}} = \pm0.0145$)

	Au-Cu			
C_{Au}	$G_M/RT^{(Pre.)}$	$G_M/RT^{(Expt.*)}$	$a_{Au}^{(Pre.)}$	$a_{Au}^{(Expt.*)}$
0.1	-0.49387	-0.49504	0.021	0.022
0.2	-0.80427	-0.80204	0.058	0.061
0.3	-1.01346	-1.00671	0.115	0.120
0.4	-1.13583	-1.12534	0.198	0.240
0.5	-1.17620	-1.16412	0.308	0.314
0.6	-1.13583	-1.12534	0.444	0.445
0.7	-1.01346	-1.00671	0.595	0.592
0.8	-0.80427	-0.80204	0.746	0.742
0.9	-0.49387	-0.49504	0.885	0.883

Table 3: Predicted and Experimental free energy of mixing values along with the calculated activity of Au in binary liquid Au-Zn alloys at 1080 K, respectively [1]. ($S_{G_M} = \pm 0.2560$, $S_{a_{Au}} = \pm 0.0720$)

C_{Au}	Au-Zn			
	$G_M/RT^{(Pre.)}$	$G_M/RT^{(Expt.*)}$	$a_{Au}^{(Pre.)}$	$a_{Au}^{(Expt.*)}$
0.1	-1.03948	**-1.78672**	0.0001	0.0001
0.2	-1.82901	-1.93359	0.0006	0.0006
0.3	-2.42389	-2.52012	0.0028	0.0026
0.4	-2.80293	-2.87139	0.0127	0.0117
0.5	-2.93450	-2.98925	0.0531	0.0485
0.6	-2.80293	-2.84847	0.1721	0.1470
0.7	-2.42389	-2.45604	0.3871	0.3280
0.8	-1.82901	-1.84846	0.6430	0.5980
0.9	-1.03948	-1.04491	0.8592	0.6580

Table 4: Predicted and Experimental free energy of mixing values along with the calculated activity of Au in binary liquid Au-Pb alloys at 1200 K, respectively [1]. ($S_{G_M} = \pm 0.0212$, $S_{a_{Au}} = \pm 0.0137$)

C_{Au}	Au-Pb			
	$G_M/RT^{(Pre.)}$	$G_M/RT^{(Expt.*)}$	$a_{Au}^{(Pre.)}$	$a_{Au}^{(Expt.*)}$
0.1	-0.43216	-0.45756	0.038	0.039
0.2	-0.69232	-0.69549	0.092	0.103
0.3	-0.86426	-0.86021	0.165	0.179
0.4	-0.96367	-0.95173	0.258	0.261
0.5	-0.99629	-0.97003	0.369	0.368
0.6	-0.96367	-0.92427	0.495	0.472
0.7	-0.86426	-0.84191	0.630	0.608
0.8	-0.69232	-0.67719	0.764	0.750
0.9	-0.43216	-0.44841	0.890	0.880

Table 5: Predicted and Experimental free energy of mixing values along with the calculated activity of Au in binary liquid Au-Ni alloys at 1150 K, respectively [1]. ($S_{G_M} = \pm 0.0308$, $S_{a_{Au}} = \pm 0.0624$)

C_{Au}	Au-Sn			
	$G_M/RT^{(Pre.)}$	$G_M/RT^{(Expt.*)}$	$a_{Au}^{(Pre.)}$	$a_{Au}^{(Expt.*)}$
0.1	-0.16230	-0.17702	0.423	0.577
0.2	-0.21479	-0.23281	0.611	0.673
0.3	-0.23933	-0.25301	0.701	0.683
0.4	-0.25061	-0.25345	0.747	0.693
0.5	-0.25390	-0.23984	0.775	0.717
0.6	-0.25061	-0.21699	0.799	0.754
0.7	-0.23933	-0.19064	0.827	0.799
0.8	-0.21479	-0.16253	0.865	0.848
0.9	-0.16230	-0.12563	0.918	0.914

where $a_{i,exp}$ and $a_{i,pre}$ are the experimental data and the predicted values of component i in the liquid alloys, respectively.

3. RESULTS AND DISCUSSION

In quasi-chemical approximation model, the interaction energy parameter ω and the coordination number Z = 10 [19, 25] are the parameters required for the computation of the thermodynamic properties of the binary liquid alloys. The parameter ω in this model is assumed to be temperature independent and it has been estimated by simultaneously fitting the experimental data of free energy of mixing and activity throughout the whole concentration range. The best fit values of the parameter ω optimized via Eqn. (4) for the six binary liquid alloys investigated at different working temperatures are listed in Table 1. These parameters remain unchanged throughout the computations. The positive value of ω ensures that the attraction between unlike atoms (A-B) is less than that of like atoms (A-A or B-B), indicating that there is a tendency of homo-coordination of atoms in the binary liquid Au-Ni alloys. On the other hand, negative values of ω for binary liquid Au-Cu, Au-Zn, Au-Pb, Au-Sn and Al-Au alloys imply that the attraction between unlike atoms (A-B) is more favoured than that of like atoms (A-A or B-B), thus suggesting the presence of chemical short-range order in the liquid alloys.

The results of the predicted free energy of mixing calculated using Eqn. (5) along with the experimental data are presented in Tables 2 through 7. It is evident from the tables that the theoretical predicted values are in reasonable agreement with the experimental observation taken from Hultgren et al. [1] . Al-Au at 1338 K exhibits the highest tendency for compound formation and is the most interacting out of the six gold-based binary alloys studied with calculated minimum G_M value of -3.72808 RT (in RT unit) at c_{Au} = 0.5, which correlates well with experimental value of -3.72820. This is closely followed by Au-Zn at 1080 K, Au-Sn at 823 K, Au-Cu at 1550 K and Au-Pb at 1200 K with calculated minimum G_M values of -2.93450 RT, -2.55563 RT, -1.17620 RT and -0.99629 RT, respectively. Au-Ni at 1150 K in the liquid state is the least interacting alloy. The experimental values of $\frac{G_M}{RT}$ in Hultgren et al. [1] as given in Tables 3 and 6 when c_{Au} = 0.1 (**bold face**), perhaps appear in non-smart form.

In Fig. 8(a, b, c), we present the results of the predicted free energy of mixing calculated using the QACM along with the experimental free energy of mixing data of Kostov et al. [10] obtained using the FactSage Thermochemical software to further show the suitability of the QACM in predicting thermodynamic properties for binary liquid alloys. Activity is another important thermodynamic quantity which can be obtained directly from experimental studies [18]. The interactions among the constituent components of a binary liquid system are assumed to be

Table 6: Predicted and Experimental free energy of mixing values along with the calculated activity of Au in binary liquid Au-Sn alloys at 823 K, respectively [1]. ($S_{G_M} = \pm0.03655$, $S_{a_{Au}} = \pm0.0160$)

	Au-Sn			
C_{Au}	$G_M/RT^{(Pre.)}$	$G_M/RT^{(Expt.*)}$	$a_{Au}^{(Pre.)}$	$a_{Au}^{(Expt.*)}$
0.1	-0.92936	**-1.90949**	0.00035	0.00072
0.2	-1.61799	-1.94693	0.00166	0.00240
0.3	-2.12732	-2.37843	0.00642	0.00650
0.4	-2.44625	-2.57238	0.02315	0.01700
0.5	-2.55563	-2.55151	0.07703	0.04500
0.6	-2.44625	-2.35203	0.20624	0.10700
0.7	-2.12732	-1.98806	0.41652	0.23400
0.8	-1.61799	-1.48168	0.65702	0.44200
0.9	-0.92931	-0.83966	0.86223	0.48500

Table 7: Predicted and Experimental free energy of mixing values along with the calculated activity of Au in binary liquid Al-Au alloys at 1338 K, respectively [1]. ($S_{G_M} = \pm0.1984$, $S_{a_{Au}} = \pm0.0753$)

	Au-Sn			
C_{Au}	$G_M/RT^{(Pre.)}$	$G_M/RT^{(Expt.*)}$	$a_{Au}^{(Pre.)}$	$a_{Au}^{(Expt.*)}$
0.1	-1.26002	-1.18736	0.00001	0.00003
0.2	-2.25616	-2.11611	0.00008	0.00016
0.3	-3.03232	-2.86401	0.00049	0.00058
0.4	-3.54501	-3.42277	0.0034	0.0023
0.5	-3.72808	-3.72820	0.0240	0.0116
0.6	-3.54501	-3.70630	0.1213	0.0545
0.7	-3.03233	-3.33367	0.3432	0.1880
0.8	-2.25616	-2.59671	0.6213	0.4770
0.9	-1.26002	-1.49128	0.8542	0.8100

determined by the magnitude of the activities, which in turn determines the bond energies. Experimental determination of activities for a class of similar system can be expected to provide, at least, a basis for correlating the mixing behaviour, which may be useful in extrapolating the behaviour of more complex system. Using Eqn. (7), the activities of Au in the six gold-based binary liquid alloys were calculated. The results of the predicted activities of Au alongside experimental data are also given in Tables 2 through 7. The predicted activities values correlate well with the experimental values. The activity values of Au in liquid Au-Cu, Au-Zn, Au-Pb, Au-Sn and Al-Cu alloys show negative deviations from ideal mixture behaviour, whereas the activity values for liquid Au-Ni show large positive deviations from the ideal.

In addition, the deviations between the predicted and experimental values for the free energy of mixing and activities were assessed by computing the standard errors using Eqn.(8). It can be seen that the predicted average deviations when compared with the experimental data vary between ±0.0072 - ±0.3655 for the free energy of mixing and between ±0.0145 to ±0.1984 for the activity. The relatively small deviations observed between the calculated and experimental values thus show that the quasi-chemical approximation model may be an alternative method for predicting the thermodynamic properties of binary liquid alloys. The model is quite efficient and reliable because it has a physical meaning from the viewpoint of statistical thermodynamics.

5. Conclusion

The quasi-chemical approximation model which is based on statistical thermodynamics has been employed to predict the thermodynamic properties of some binary liquid alloys. The predicted results of the free energy of mixing and activities of Au in the selected Au-based binary liquid alloys have been compared with experimental values. It is found that the predicted values with the model are in good agreement with those of experimental data; thus, indicating that the model is reliable, efficient and cost effective with a good physical basis.

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Table 8: Predicted and Experimental free energy of mixing values of binary liquid Ti-Si alloys at 2000 K, 2400 K and 2473 K, respectively [1]. ($S_{G_M} = \pm 0.1984$, $S_{a_{Au}} = \pm 0.0753$)

(a) Ti-Si at 2000 K ([11], $S_{G_M} = \pm 0.2121$)

C_{Au}	$G_M/RT^{(Pre.)}$	$G_M/RT^{(Expt.*)}$
0.1	-1.22218	-1.12485
0.2	-2.18251	-2.08932
0.3	-2.92670	-2.90267
0.4	-3.41520	-3.49568
0.5	-3.58872	-3.79329
0.6	-3.41520	-3.73514
0.7	-2.9267	-3.29109
0.8	-2.18251	-2.47468
0.9	-1.22218	-1.35247

(b) Ti-Si at 2400 K ([11], $S_{G_M} = \pm 0.2214$)

C_{Au}	$G_M/RT^{(Pre.)}$	$G_M/RT^{(Expt.*)}$
0.1	-1.04297	-0.96900
0.2	-1.83572	-1.78450
0.3	-2.43373	-2.46820
0.4	-2.81439	-2.96513
0.5	-2.94671	-3.21420
0.6	-2.81439	-3.16469
0.7	-2.43337	-2.79174
0.8	-1.83572	-2.10558
0.9	-1.04297	-1.15868

(b) Ti-Si at 2473 K ([11], $S_{G_M} = \pm 0.1844$)

C_{Au}	$G_M/RT^{(Pre.)}$	$G_M/RT^{(Expt.*)}$
0.1	-1.03562	-0.94599
0.2	-1.82159	-1.73941
0.3	-2.41341	-2.40395
0.4	-2.79028	-2.88680
0.5	-2.92103	-3.12851
0.6	-2.79028	-3.08051
0.7	-2.41341	-2.71808
0.8	-1.82159	-2.05111
0.9	-1.03562	-1.13007

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