



## On the prediction of Gibbs free energy of mixing of binary liquid alloys

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### ABSTRACT

Experimental measurement of thermodynamic properties and of phase equilibrium for some systems is complicated since these systems may be reactive and/or expensive to study. They may contain radioactive or scarce components and be otherwise highly unusual for bench top manipulation. For these systems, predicting thermodynamic properties using theoretical and/or empirical methods is of great interest. In this paper, the Engel–Brewer method, the Witusiewicz, Sommer and Faber relations, the Miedema and Hard-Sphere model have been reviewed and evaluated on their suitability for calculating mixing properties of liquid solutions. Analysis of the results indicated that the Engel–Brewer method is not robust, while the Miedema model, with some modifications, has been evaluated as an appropriate one for predicting enthalpy of mixing of liquid solutions. Moreover, the Witusiewicz relation and Hard-Sphere model were proved to be more reliable compared to that of Sommer and Faber for predicting entropy of mixing of liquid alloys. Finally, based on the current work, the combined Miedema–Witusiewicz or Miedema/Hard-Sphere models are recommended for parameterizing Gibbs free energy of mixing for liquid solutions.

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### 1. Introduction

Phase diagrams provide fundamental information for applications such as solidification, crystal growth, joining, solid-state reaction, casting, phase transformations and oxidations. Experimental measurement of phase diagrams is a long and expensive task that becomes more complicated for multi-component systems. Calculation of phase diagrams reduces the time and effort required to identify equilibrium conditions for binary and multi-component systems. The correlation between thermodynamics and phase equilibria was established by J.W. Gibbs [1]. Later, Kaufman and Bernstein [2] founded the CALPHAD method which is based on the minimization of the Gibbs free energy. The CALPHAD method is based on mathematically formulated models for Gibbs energies of individual phases. The model parameters are obtained from thermodynamic data of individual phases and phase equilibrium data [3]. Therefore, for systems with no or few experimental phase equilibrium data and/or thermodynamic properties, the CALPHAD method cannot be successfully applied. For this reason, it is of great importance to be able to use a valid method for predicting the thermodynamic properties and phase diagrams for systems lacking experimental data. Since the Gibbs free energy is thermodynamically formulated as  $\Delta G = \Delta H - T\Delta S$ , phase diagram prediction is

possible only if theoretical methods can be used to predict excess enthalpy and entropy terms.

First-principles simulation at 0 K, based on density functional theory [3], provides information about enthalpy and entropy of formation for pure solids and compounds, bulk modulus, thermal expansion, etc. For these calculations the only information needed is the structure of the constituent atoms. Using electron density approximations, the ab-initio molecular dynamics (AIMD) [4,5] makes possible the prediction of thermodynamic properties of liquid, super-cooled liquid and glass phases. However, first-principles simulation and ab-initio molecular dynamics are both time consuming and complicated procedures, especially when they are applied to entropy of mixing calculation.

In contrast, the free electron theory of Sommerfeld [6] was a breakthrough in the prediction of thermodynamic properties of metals and alloys. Empirical models developed by Hume-Rothery [7,8], Darken and Gurry [9], Engel [10] and Brewer [11] and Miedema et al. [12,13], coupled with the free electron theory, enable the correlation of electronic properties to physical stability [14]; Free electron theory [6] led to some electronic models capable of correlating phase stability and electronic properties of pure elements and alloys. Hume-Rothery [7,8] developed some rules regarding the trends of alloying of pure metals based on size and electrochemical factors and the valence effect. Darken and Gurry [9] extended some of the Hume-Rothery rules to predict solid solution formation. Engel [10] used this same correlation as Hume-Rothery [7,8] for all the metals. Later, Brewer [11]

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developed the Engel–Brewer method by applying the Hildebrand formula [15,16] to the Engel method in order to calculate mixing properties and phase transformations and this also enable the prediction of the phase diagram of binary and multi-component systems. The Engel–Brewer method uses electronic configurations to predict crystal structures and phase stability limits for different phases of an alloy. In other words, this method relates the number of valence electrons to the Gibbs free energy of mixing. Contrastingly, the Miedema model [12,13] uses electron density at the boundary of the Wigner–Seitz cell ( $n_{ws}$ ) [12], electronegativity ( $\phi^*$ ) and hybridization term (R/P) to describe the enthalpy of mixing.

The Engel–Brewer method has been widely used to calculate phase diagrams for actinides and transition metals [17–22]. It should be mentioned that, in all these applications, only the phase diagrams obtained from the Engel–Brewer method are compared with the experimental data and no comments are given on the consistency between the predicted thermodynamic properties and the experimental data.

The Miedema model has been widely used to calculate the enthalpy of formation of compounds and enthalpy of mixing of solutions [23–29]. Some of these studies used the Miedema model to predict the enthalpy of formation of binary alloys [24], binary amorphous alloys [23], ternary solutions and compounds [25,26] and to calculate glass forming range in some ternary systems [27,28]. Moreover, some previous studies [29] modified the model parameters ( $\phi^*$ ,  $n_{ws}$ ) and/or the model constants ( $P$ ,  $Q$ ,  $R$ ) to obtain more consistency with the experimental data.

In addition, some efforts have been made to find the excess entropy of mixing of different phases. Faber [30] and Kleppa [31] attempted to find volume-based formulae for the excess entropy of mixing while Sommer *et al.* [32] derived the excess entropy of mixing based on energy and volume changes resulting from alloying. Tanaka *et al.* [33], Kubaschewski [34] and Witusiewicz *et al.* [35,36] found empirical relationships for the entropy of mixing based on heat of mixing, melting and boiling temperatures. Moreover, the Hard-Sphere model is an appropriate for the describing the thermodynamic properties of liquid metals [37]. The Hard-Sphere model describes the entropy of mixing on the base of the effect of packing constraints and chemical ordering forces. This model was applied to the entropy of mixing [38,39] and was found to be in agreement with the experimental data.

Accordingly, all these efforts can result in the prediction of thermodynamic properties which can be used to predict the phase diagram.

The objective of the present study is to review and discuss the ability of the Engel–Brewer method and the Miedema model combined with the Witusiewicz relation, the Hard-sphere model, Faber and Sommer relations to parameterize Gibbs free energy and thus, predict thermodynamic properties and phase equilibrium.

## 2. Methodology

Fifty binary systems were studied here. They were chosen from different groups of metals to evaluate the validity of the Engel–Brewer, Miedema, Witusiewicz and Hard-Sphere models for calculating Gibbs free energy of mixing of liquid alloys. Then a statistical method was applied to determine whether these methods are suitable enough to reproduce the experimental data.

Linear regression analysis has been widely used in thermodynamics to compare the results of calculation methods with experimental data. If the methods agree, the slope of the regression line would be one. However, this ignores the measurement errors and thus the expected slope should be less than one [40]. Moreover, in regression analysis, much of the plot is empty space; if the range

of measurement is large, then the agreement will appear to be better. In addition, the bias (mean difference between two methods) is ignored [40]. Therefore, the Bland–Altman analysis [41,42] is used in this work for calculating the goodness of fit success the Engel–Brewer, Miedema, Witusiewicz and Hard-Sphere models in reproducing experimental results. The Bland–Altman analysis reveals both the magnitude of disagreement between the two methods (errors and bias) and demonstrates the trend and outliers in the data. The prediction bands shown in the plots are the confidence ranges reported in this work at 95% confidence level (indicated as CI 95% on the graphs).

### 2.1. Enthalpy of mixing

#### 2.1.1. The Engel–Brewer method

Hildebrand [15,16] introduced a regular solution model with a solubility parameter  $\Delta H^{vap}/V$  for van der Waals molecules. In these molecules, bonding is the result of temporary dipoles which are formed by dispersion forces. Therefore, the cohesive energy stems from these temporary dipoles. Hildebrand [15,16] assumed that “the interaction energy between pairs of unlike atoms is the geometric mean of the interaction energy between pairs of like atoms or molecules” [43]. The mixing takes place under constant volume conditions and the excess entropy of mixing is negligible (i.e., entropy of mixing is ideal). His solubility parameter adds a positive contribution to the enthalpy of mixing.

Engel [44,45] stated that a relationship exists between the crystal structure and electronic configuration of atoms for all the metals. Using his theory [44,45], Brewer extended the Hildebrand formula to metals. He changed  $\Delta H^{vap}$  in the formula to  $\Delta H^*$ , the energy of vaporization to the gaseous state with the same valence state of the condensed solid [43,46]. In addition, he used the Redlich–Kister polynomial (equation (1)) [47] to represent the excess Gibbs free energy of mixing as follows:

$$\Delta G^E = \Delta^m = \sum_{i=1}^{n-1} \sum_{j=i+1}^n \sum_{p=0}^{m_{ij}} A_{ij}^p X_i X_j (X_i - X_j)^p, \quad (1)$$

$$A_{ij}^0 = \alpha + A_{ij}^1, \quad (2)$$

$$A_{ij}^1 = \frac{-\beta\alpha}{4(1+\beta)}, \quad (3)$$

$$\alpha = \left( \frac{V_1}{2RT} \right) \left( \left( \frac{\Delta E_1^*}{V_1} \right)^{1/2} - \left( \frac{\Delta E_2^*}{V_2} \right)^{1/2} \right)^2, \quad (4)$$

$$\beta = \frac{2(V_j - V_i)}{V_i - V_j}, \quad (5)$$

where  $V_i$  is the molar volume of element  $i$  and  $\Delta E_i^*$  is the atomization energy to the gaseous valence state of the atom. The values of  $\Delta E^*$  and  $V$  needed to calculate the solubility parameters in equation (4) are reported in [11,48,49]. In this work, equations (1)–(5) are used to find the enthalpy of mixing of the 50 binary liquid alloys.

#### 2.1.2. Miedema model

Miedema *et al.* [12,13] proposed a so-called microscopic atomic picture to predict enthalpies of formation for binary systems. According to the Miedema model [12,13,50], the enthalpy of mixing of alloys can be obtained as follows:

$$\Delta H = \frac{2f(c) \left( x_A V_A^{2/3} + x_B V_B^{2/3} \right)}{n_{ws}^A^{-1/3} + n_{ws}^B^{-1/3}} \times \left[ -P(\Delta\phi^*)^2 + Q(\Delta n_{ws}^{1/3})^2 - R \right], \quad (6)$$

where  $x_i$  is the molar volume of element  $i$  and  $V_i$  is the volume of element  $i$  in the alloy.  $f(c)$  accounts for the concentration dependence of  $\Delta H$ .

Miedema *et al.* [51] based the formulation of the first term in equation (6) on the fact that the electron density at the boundary of Wigner–Sietz cell ( $n_{ws}$ ) [52] across the A–B interface should be continuous at the macroscopic scale. Miedema *et al.* [53] stated that the electron density at the boundary of Wigner–Sietz cell can be represented as:

$$(n_{ws})^2 = K/V, \quad (7)$$

where  $K$  is the experimental value of bulk modulus and  $V$  is the molar volume of pure metal. This term adds a positive contribution to the enthalpy of formation or mixing [51]. So far, two approaches have been applied to explain how electron density changes in alloying. Alonso and Girifalco [54] proposed that the change in electron density is caused by the difference in molar volumes of the two metals. Hence, the molar volume of the atom with larger electron density is increased and the molar volume of the other is decreased. In contrast, using first-principle calculations, Williams [55] demonstrated that changing the electronic configuration of metals in contact with each other equalizes their electron densities. Consequently, this positive contribution from discontinuity of electron density can be compared to the Engel–Brewer method. Miedema *et al.* [12,13] proposed that a linear relationship exists between enthalpy of vaporization and the product of  $V^{2/3}$  and electron density at the boundary of the Wigner–Seitz cell ( $n_{ws}$ ). Thus,  $n_{ws}$  can be taken as  $\Delta H/V^{2/3}$  which is very similar to the Hildebrand solubility parameter ( $\Delta H/V$ ) that is the basis of the Engel–Brewer method [10,11]. Although Brewer adds promotion energy to  $\Delta H$  in order to account for the effect of electronic configuration on bonding, Williams [55] demonstrated that  $n_{ws}$  by itself includes the effect of electronic configuration.

The second property used in the Miedema model is the value of the chemical potential for electronic charge. The difference in electronegativities between the two elements adds a negative contribution to the formation enthalpy in a binary alloy system. The last term in equation (6) is the hybridization parameter for the alloying of a transition metal is alloyed with a non-transition metal. This term is defined empirically for different groups of metals [12] and it adds a negative contribution to the enthalpy of formation of alloys. While the Engel–Brewer method is criticized by Pettifor [56,57], Hume Rothery [58] and Hunter–Hill [59] for ignoring hybridization of orbitals, Miedema in his model introduces a hybridization term,  $R$ , which represents the degree of mixing of d-states of the transition metal with the s-state of the non-transition metal, but he does not provide a physical explanation for this term but defines it only empirically.

In equation (6),  $P$  and  $Q$  are adjustable parameters and depend on the elements involved in the alloy. Miedema *et al.* [12,13,51,60] assigned global values to them. However,  $P$  and  $Q$  are changed in some previous studies such as Zhang *et al.* [61] and Shubin and Shunyaev [29] to obtain more consistency with the experimental data. In this study, 50 binary systems are divided into different groups of metals and an effort has been made to adjust the value of the parameters for each group to find the best consistency with the reported experimental. The values of  $V^{2/3}$ ,  $n_{ws}^{1/3}$  and  $(\phi)$  are taken from de Boer *et al.* [12].

## 2.2. Entropy of mixing

Calculation of the entropy of mixing is more complicated than the enthalpy of mixing. However, in order to find the phase relations for a system, both enthalpy and entropy of mixing must be obtained.

Following the studies of Spencer [62], Kubaschewski [34] and Tanaka [33], Witusiewicz *et al.* [36] based on reliable experimental

enthalpy data, proposed an empirical relation to estimate the entropy of mixing as:

$$\Delta \bar{S}^{xs}(x, T) = \Omega \left[ \frac{\Delta H(x, T)}{T} + x(1 - x^2)RP_T \right], \quad (8)$$

where

$$\Omega = \frac{1}{2\pi} \left( \frac{\tau_m}{\tau_b} + 1 \right)^a, \quad (9)$$

$$P_T = \frac{1}{2} + \frac{4\bar{T}_m}{3T} + 2 \ln \left( \frac{T}{\bar{T}_b - \bar{T}_m} \right), \quad (10)$$

$T_i^b$  and  $T_i^m$  are the boiling point and melting points of element  $i$ , respectively and  $\Delta H(x, T)$  is the enthalpy of mixing at a specific concentration and temperature. In this study, the enthalpy of mixing in the Witusiewicz *et al.* [36] relation is calculated using the Miedema model. Witusiewicz *et al.* [36] used the product of temperature and the first derivative of equation (8) ( $T \times ds/dT$ ) to obtain a formula for the excess heat capacity of liquid alloys as:

$$\Delta C_p^{xs}(x, T) = \frac{\Omega}{\Omega - 1} \left( \frac{\Delta H(x, T)}{T} - x(1 - x)RT \frac{dP_T}{dT} \right), \quad (11)$$

$$\frac{dP_T}{dT} = \left( 2 - \frac{4\bar{T}_m}{3T} \right) \frac{1}{T}. \quad (12)$$

Contrary to Witusiewicz *et al.* [36], Faber [31] and Sommer *et al.* [32] proposed theoretical relations for the entropy of mixing. The Faber relation [31] is based on the change in volume in alloying while Sommer *et al.* [32] take into account volume and energy changes. The relations of Faber and Sommer *et al.* are discussed in details [30,32].

In the present work, the relations of Faber [30], Sommer *et al.* [32] and Witusiewicz *et al.* [36] were applied to find the entropy of mixing of the binary systems studied in Sections 2.1 and 2.2. The Fe–C system is excluded due to its complexity and because the results of enthalpy of mixing calculations, using Miedema model, highly deviated from the experimental data. Therefore, 49 binary systems were studied. Finally, equations (11) and (12) were used to obtain the excess heat capacity of liquid alloys. Experimental data for the excess heat capacity was available only for 13 systems studied in this work. Hence the excess heat capacity was calculated only for these systems and the results are compared with the experimental data.

Although, the Witusiewicz relation [36] provides a simple composition dependence for the entropy of mixing for systems with phase separation, the application of this model is not recommended because the entropy of mixing composition curve for these systems is not symmetric and U-shaped. For such systems, more complicated relationships [38,39,63,64] can be used to derive more accurate results. For instance, the Hard-Sphere model is suitable for describing thermodynamic properties of liquid metals [37]. Moreover, the Hard-Sphere model for entropy of mixing [38,39] has shown good results in comparison with experimental data. In this model, the existence of thermodynamic anomalies at different compositions for a particular system arises from the mutual effect of packing constraints and chemical ordering forces. In this model, the entropy can be written as [65]:

$$S_{HS} = S_{gas} + S_p + S_{el} + S_{id}. \quad (13)$$

The effect of each contribution to the entropy of mixing for different types of systems is discussed in details by Hoshino [65].

The ideal gas contribution is obtained as [64]:

$$\frac{S_{gas}}{Nk_B} = \frac{5}{2} + \ln \left[ V \left( \frac{\pi m_1^{x_1} m_2^{x_2} k_B T}{2h^2} \right)^{3/2} \right], \quad (14)$$

where  $m_i$  is atomic mass of element  $i$ .

Carahan and Starling [66] suggested a formulation for the packing contribution as:

$$S_p = -Nk_B\eta(4 - 3\eta)/(1 - \eta)^2, \quad (15)$$

the packing fraction of the solution,  $\eta$ , is defined as [38–39,64]:

$$\eta = (x_1\eta_1V_1 + x_2\eta_2V_2)/V, \quad (16)$$

where  $V$  is the volume of the alloy and  $\eta_i$  is the packing fraction of the constituent elements. Packing fractions are calculated from hard-sphere diameters estimated by Jayaram *et al.* [67]. In the present study, an ideal volume is assumed for the liquid alloys, (i.e., the excess volume of mixing is taken as zero).

In the Sommerfeld theory, the electronic contribution is expressed as:

$$\frac{S_{el}}{Nk_B} = \frac{1}{3}\pi^2TN(E_F), \quad (17)$$

where  $N(E_F)$  is the electronic contribution density of state at the Fermi level.

Finally, the hard-sphere entropy of mixing is defined as:

$$\Delta S_{HS} = S_{HS} - x_1S_1 - x_2S_2. \quad (18)$$

Since there is not enough information for the packing fraction of elements, only 19 systems of the 50 binary systems are studied using Hard-Sphere model.

### 2.3. Gibbs free energy of mixing

Calculation of the enthalpy, entropy and heat capacity of mixing provides enough information for obtaining the Gibbs free energy of mixing:

$$\Delta G(T) = \Delta H(T_0) + \int_{T_0}^T Cp(T)dT - T \left[ \Delta S(T_0) + \int_{T_0}^T \frac{Cp(T)}{T} dT \right]. \quad (19)$$

In this work, all the above mentioned methods were used to obtain the phase diagram of the Pu–U and Ag–Cu systems. The Ag–Cu system is well-known, with adequate experimental data on phase equilibrium and thermodynamic properties. Therefore, it is an appropriate system that can be used to compare the application of different methods to obtain the Gibbs free energy of mixing. Moreover, Pu–U is an important system for nuclear applications. There is a lack of information on thermodynamic properties of this system. Thus, it is of great importance to evaluate the success of the application of the methods studied in this work to this system.

For the Engel–Brewer method, Eqs. (1)–(6) were applied to calculate the phase diagram of the Pu–U and Ag–Cu systems. The CALPHAD method was used to obtain parameters for liquid alloys in Redlich–Kister polynomials (equation (1)) so that the enthalpy and entropy of mixing would be consistent with the Miedema model and Witusiewicz and/or Hard-Sphere models, respectively. The phase equilibrium data obtained using this procedure are called Miedema–Witusiewicz and Miedema–Hard-Sphere data throughout this study. It should be mentioned that for the Miedema–Witusiewicz and Miedema–Hard-sphere phase equilibrium data, parameters for the solid solution phase were taken from the previously optimized databases [68,69]. Then the results were compared with the reported experimental data.

## 3. Results and discussion

### 3.1. Enthalpy of mixing

The calculated enthalpy of mixing using the Miedema model and the experimental data of 50 binary systems are presented in table 1. The Bland–Altman plot of the calculated enthalpy of mixing

using the Miedema model versus the experimental data is demonstrated in figure 1. For simplicity, only extremum values of enthalpy of mixing are compared. As can be seen from table 1, contrary to the Engel–Brewer method, the Miedema model accounts for both negative and positive deviations from ideality. Hence, it can be applied to all binary systems. Qualitatively, the sign of the enthalpy of mixing calculated by the Miedema model is identical to that of the experimental data for almost all the systems except for the system Fe–C. Boom *et al.* [70] relate this inaccuracy to uncertainties in estimating the transformation enthalpy of C-graphite to C-metal, as well as the uncertainty in other parameters that characterize the hypothetical metallic carbon atoms (such as electronegativity and electron density at the boundary of the Weigner–Seitz cell). Overall, the standard deviation of the Miedema method results is 5.9 kJ/mol and the prediction band is  $\pm 11.7$  kJ/mol. As can be seen in figure 1, the highest deviations of the Miedema model from the experimental data are for the systems: Fe–C, Al–Au, Au–Zn, Bi–Mg, Hg–Na and Ga–Mg. All these systems (except Al–Au) contain a metalloid or a  $d^{10}$  transition metal. Deviations for alloys of metalloids can be related to the transformation energy from a semi-conducting state to a metallic state. The semi-conductor by can be converted into a hypothetical metallic state by means of this transformation energy [12]. The extrapolation of the Miedema model to metals was used for metalloids resulting in higher deviations from the experimental data. Table 1 indicates that for post transition metals alloyed with metalloids, the calculated enthalpy of mixing is consistent with the experimental data. The worst case of enthalpy of mixing for alloys of metalloids occurs when they are alloyed with alkali/alkaline earth metals. In these cases, metalloids behave more as non-metallic elements and Miedema model is less suitable. In principle, resultant errors of the Miedema model for alloys of  $d^{10}$  transition metals occur because of the stability of their  $s^2$  electronic configurations; these latter produce a repulsive force in alloying. This repulsive force is not taken into account in the Miedema model. If metalloids and  $d^{10}$  transition metals are removed from the statistical analysis, the standard deviation and prediction band decrease to 2.96 kJ/mol and  $\pm 5.6$  kJ/mol, respectively.

Since the enthalpies of mixing of liquid alloys of 30 out of the 50 systems studied in this work have negative deviation from ideality, they cannot be calculated by the Engel–Brewer method. Figure 2 shows the Bland–Altman comparison plot for the remaining 20 systems studied by the Engel–Brewer method. Table 1 shows that the Engel–Brewer method is quite unsuccessful for alloys other than transition metals and actinides. For transition metals alloyed with non-transition metals, the Engel–Brewer method highly overestimates the experimental data. This can be attributed to the hybridization of  $sp$  electrons with  $d$  electrons, an effect neglected in the Engel–Brewer method. the Engel–Brewer method has been previously criticized [58,59,71] for neglecting hybridization in bonding. For alkali/alkaline earth metals alloyed with post transition metals, charge transfer plays a significant role in bonding. Consequently, all these systems have negative deviations from ideality. Thus, the Engel–Brewer method cannot be applied to these systems. Overall, the standard deviation and prediction band for the Engel–Brewer method are 26.69 kJ/mol and 68 kJ/mol, respectively.

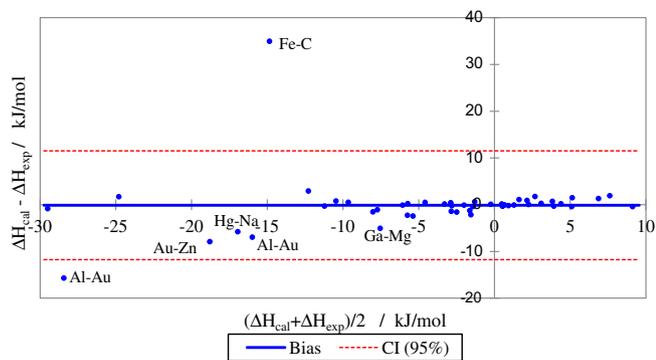
Since in almost all the previous studies, Engel–Brewer is applied to transition metals or lantnides and actinides [17–22,72], the discussion in this work will be limited to these two groups of metals. For alloys of transition metals and actinides, the Engel–Brewer method cannot be applied to 2 out of 6 systems (Ag–Au and Au–Cu) because these systems have negative deviation from ideality. For Ag–Cu and Pu–U, the results are more consistent with experimental data. However, for all the systems in this group, the Miedema predictions are more consistent with the experimental

**TABLE 1**  
Extremum enthalpy of mixing of liquid solution for binary alloys calculated using the Miedema model and the Engel–Brewer method in comparison with the experimental data.

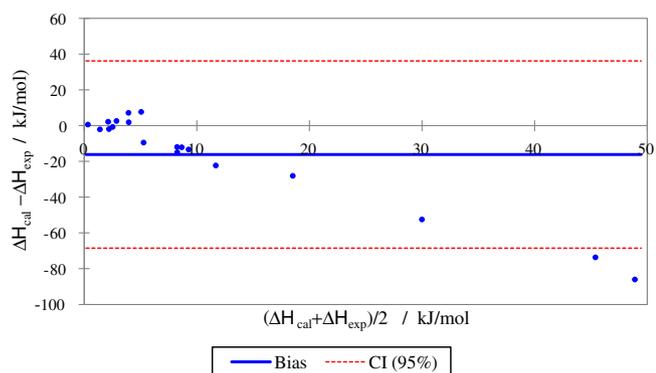
System	Miedema			Engel-Brewer		T/K	Ref.
	$\Delta H$ / kJ/mol	$\Delta H_{\text{exp.}}$ / kJ/mol	$\Delta H - \Delta H_{\text{exp.}}$ / kJ/mol	$\Delta H$ / kJ/mol	$\Delta H - \Delta H_{\text{exp.}}$ / kJ/mol		
<i>Transition metals + transition metals</i>							
Ag–Au	–4.0	–4.1	0.1			1400	[77]
Ag–Cu	1.8	3.6	1.8	1.6	2.0	800	[82]
Au–Cu	–4.8	–4.3	0.5			800	[77]
Au–Ni	6.2	7.5	1.3	0.4	7.2	1150	[77]
Cu–Fe	9.3	8.9	0.4	1.2	7.7	1823	[77]
<i>Transition metals + non-transition metals/d<sup>10</sup> transition metals</i>							
Ag–Ga	–3.1	–2.7	0.4			1000	[77]
Ag–Pb	4.1	3.8	0.3	56.2	52.5	1000	[77]
Al–Au	–20.6	–36.3	15.7			1400	[77]
Al–Cu	–7.3	–8.8	1.5			1373	[77]
Al–Fe	–6.0	–6.1	0.1			1873	[77]
Au–Sn	–11.1	–11.4	0.3			823	[77]
Au–Zn	–14.8	–22.7	7.9			773	[77]
Cu–Bi	4.4	5.9	1.5	91.9	86.0	1200	[77]
Cu–Sb	–2.7	–2.9	0.2			1190	[77]
Cu–Tl	6.7	8.6	1.9	82.2	73.7	1573	[77]
Fe–C	–32.3	2.6	35.0	15.9	13.3	1873	[77]
Fe–Si	–10.9	–10.1	0.8			1873	[77]
<i>Post transition metals + post transition metals</i>							
Al–Ga	0.7	0.6	0.1	0.0	0.6	1073	[77]
Al–In	5.3	4.9	0.4	3.0	1.9	1173	[77]
In–Sn	–0.3	–0.2	0.1			700	[77]
In–Tl	0.4	0.6	0.1	22.8	22.3	723	[77]
<i>Post transition metals + metalloids</i>							
Al–Ge	–1.6	–1.0	0.6			1200	[77]
Al–Sn	3.5	4.2	0.7	1.6	2.6	973	[77]
Bi–In	–1.2	–1.6	0.4			900	[77]
Bi–Sb	0.6	0.6	0.1	10.0	9.5	1200	[77]
In–Sb	–3.4	–3.2	0.2			900	[77]
<i>Post transition metals/metalloids + d<sup>10</sup> transition metals</i>							
Bi–Cd	1.0	0.8	0.2	15.7	14.9	773	[77]
Bi–Zn	4.3	4.5	0.2	32.6	28.1	873	[77]
Cd–Pb	1.7	2.6	0.9	14.7	12.1	773	[77]
Cd–Sb	–2.0	–2.1	0.1			773	[77]
Cd–Tl	2.2	2.3	0.1	14.2	12.0	750	[77]
Hg–In	–1.0	–2.3	1.2			298	[77]
In–Zn	2.9	3.2	0.3	1.1	2.2	700	[77]
<i>Post transition metals + alkali/alkaline earth metals</i>							
Al–Mg	–2.2	–3.6	1.4			1073	[77]
Ga–Mg	–5.0	–10.1	5.0			923	[77]
In–Mg	–4.6	–6.9	2.3			923	[77]
In–Na	–7.2	–8.3	1.1			713	[77]
K–Pb	–25.7	–23.9	1.7			848	[77]
K–Tl	–13.8	–10.8	2.9			798	[77]
Mg–Pb	–9.9	–9.4	0.5			973	[77]
Mg–Tl	–4.2	–6.6	2.4			923	[77]
<i>Metalloids + alkali/alkaline earth metals</i>							
Bi–Mg	–12.5	–19.5	6.9			975	[77]
Bi–Na	–29.1	–29.9	0.8			773	[77]
<i>d<sup>10</sup> Transition metals + alkali/alkaline metals</i>							
Cd–Mg	–5.8	–5.6	0.2			543	[77]
Hg–Na	–14.1	–19.8	5.8			673	[77]
<i>d<sup>10</sup> Transition metals + d<sup>10</sup> transition metals</i>							
Cd–Hg	–0.5	–2.6	2.1			600	[77]
Cd–Zn	1.1	2.2	1.1	2.9	0.7	800	[77]
Hg–Zn	0.7	0.4	0.3	2.4	2.1	573	[77]
<i>Actinides</i>							
Pu–U	1.3	1.3	0.1	3.2	1.9	1500	[69]
<i>Alkali/Alkaline earth metals + alkali/alkaline earth metals</i>							
Mg–Li	–2	–3	1.6			1000	[77]

data. Standard deviation for Engel–Brewer method applied to this group of metals is 5 kJ/mol with a prediction band of  $\pm 11.7$  kJ/mol, whereas for the Miedema model these are only 1.3 kJ/mol and  $\pm 2.5$  kJ/mol, respectively. Using the Engel–Brewer method,

the bias (the mean difference between calculations and the experimental data) for this group is 2.026 kJ/mol, which shows that this method overestimates the enthalpy of mixing. In order to obtain results more consistent with the experimental data, the negative



**FIGURE 1.** Bland–Altman plot of extremum enthalpy of mixing calculated using Miedema model compared with the experimental enthalpy of mixing for liquid alloys of 50 binary systems listed in table 1.



**FIGURE 2.** Bland–Altman plot of extremum enthalpy of mixing calculated using Engel–Brewer method compared with the experimental enthalpy of mixing for liquid alloys of 20 binary systems listed in table 1.

contribution to heat of mixing should be taken into account. In summary, even for transition metals and actinides, the Miedema model is more consistent with the experimental data.

In brief, the Miedema model is a better choice than the Engel–Brewer method for calculating the enthalpy of mixing, since it can predict negative contributions and asymmetry. However, there is still no clear explanation of the hybridization parameter in the Miedema model and it is defined empirically. Moreover, Miedema model can be applied to intermetallic compounds in addition to liquid and solid solutions. However, it cannot predict cohesive energies for non-stoichiometric compounds. As mentioned above, the positive contribution in the formula proposed by Miedema (equation (6)), is comparable to the Hildebrand formula [15,16]. Furthermore, the electron density term is related to the bulk modulus and molar volume of pure elements as shown in equation (6). Likewise, the negative contribution is related to electronegativities of the pure constituents of the system. Therefore, contrary to the Engel–Brewer method, the Miedema model takes into account chemical and physical properties of pure elements.

From the results obtained in this section, it can be concluded that the Miedema model can be used to calculate the enthalpy of mixing of liquid alloys. Miedema suggested  $P$  and  $Q$  as constants for a large group of metals and found them empirically; at the same time, the results obtained in this section showed that the model can be improved if these groups of metals are divided into smaller subgroups. The proposed values for each of these subgroups are reported in table 2. Comparison of the new results with the original Miedema model indicated that use of the same set of model parameters for a wide variety of alloys pairs sometimes

**TABLE 2**

Proposed values for  $P$  and  $Q/P$  parameters for the Miedema model for different groups of elements with the standard deviation and the prediction band at confidence level of 95%.<sup>a</sup>

Group	$P$	$Q/P$ $V^{2/3}$ / $(du^{2/3})$	Standard deviation / kJ/mol	Prediction band $\pm$ kJ/mol
Transition metals + transition metals <sup>b</sup>	10.7	9.4	0.9	2.3
Transition metals + non-transition metals <sup>c</sup>	12.87	9.64	5.5	12.9
Post transition metals–Post transition metals	10.32	9.2	0.4	0.7
Post transition metals–metalloids	11.25	9.4	0.6	0.8
Post transition metals– $d^{10}$ transition metals <sup>b</sup>	10.7	9.4	0.7	1.4
Post transition metals/metalloids-alkali/alkaline earth metals <sup>b</sup>	10.7	9.4	2.74	6.1
Metalloids-alkali/alkaline earth metals <sup>a,b</sup>	14.5	9.4		
$d^{10}$ Transition metals-alkali/alkaline metals <sup>a</sup>	14.24	9.4		
Actinides- Actinides <sup>a,b</sup>	10.7	9.4		
$d^{10}$ Transition metals + $d^{10}$ transition metals <sup>a,b</sup>	10.7	9.4		
Alkali/alkaline earth metals + alkali/alkaline earth metals <sup>a,b</sup>	10.7	9.4		

<sup>a</sup> No standard deviation or prediction band is reported in cases where less than five systems are studied.

<sup>b</sup> Miedema parameters are taken directly from Miedema *et al.* [12].

<sup>c</sup> For transition + non-transition alloys  $R/P$  for Cu, Ag, Au, Fe is taken as 0.35, 0.1, 0.4, 0.9, respectively.

**TABLE 3**

The Bias, the standard deviation and the prediction bands for the entropy relations of Faber [30], Sommer *et al.* [32] and Witusiewicz *et al.* [36] applied to the 49 binary systems listed in table 1<sup>a</sup>.

System	Bias / J / (mol·K)	Standard deviation / J / (mol·K)	Prediction band / $\pm$ J / (mol·K)
Faber	−4.5	8.7	$\pm 21$
Sommer <i>et al.</i>	3.0	4.1	$\pm 11$
Witusiewicz <i>et al.</i>	0.9	2.5	$\pm 5.8$

<sup>a</sup> Fe–C system is excluded in this analysis.

led to large errors in prediction. Finally, the Miedema model was able to predict the enthalpy of mixing for liquid alloys with maximum prediction band of about  $\pm 13$  kJ/mol. The prediction bands and standard deviations for Miedema calculations are listed in table 2. The accuracy of the results is not optimum but is good enough as a first estimation for systems with limited or no experimental data on phase equilibrium and thermodynamic properties. Further modifications can be applied to the model if these subgroups be divided into smaller groups [73–75]. In addition, density functional theory calculations [4] can help to improve the Miedema model parameters and thus improve the precision of the model significantly [76].

### 3.2. Entropy of mixing

The entropy of mixing calculated by the relations of Faber [30], Sommer *et al.* [32] are compared with those from Witusiewicz *et al.* [36] in table 3. Since, for the both Faber [30] and Sommer *et al.* [32] relations, standard deviations and bias are much higher than those

TABLE 4

Comparison of the entropy of mixing at equiatomic composition for liquid alloys for different binary systems calculated using the Witusiewicz *et al.* relation [36] in comparison with the experimental data [77,69].

System	$\Delta S_{\text{wit.}} / \text{J} / (\text{mol}\cdot\text{K})$	$\Delta S_{\text{exp}} / \text{J} / (\text{mol}\cdot\text{K})$	$\Delta S_{\text{wit.}} - \Delta S_{\text{exp}} / \text{J} / (\text{mol}\cdot\text{K})$	T/K
<i>Transition metals + transition metals</i>				
Ag–Au	5.2	4.2	1	800
Ag–Cu	7.1	12.8	5.7	1400
Au–Cu	3	5.7	2.6	800
Au–Ni	8.4	8.1	0.3	1150
Cu–Fe	7.6	6.4	1.1	1823
<i>Transition metals + non-transition metals/<math>d^{10}</math> transition metals</i>				
Ag–Ga	4.9	6.1	1.2	1000
Ag–Pb	7.7	7.6	0.1	1000
Al–Au	4.4	4.5	0.1	400
Al–Cu	4.1	9.2	5	1373
Al–Fe	5.2	9.2	4	1873
Au–Sn	1.4	7.1	5.7	823
Au–Zn	–0.2	3.6	3.9	1080
Bi–Cu	6.9	7.6	0.7	1200
Cu–Sb	5.3	8.2	2.9	1190
Cu–Tl	8	7.7	0.3	1573
Fe–Si	4	–4.7	8.7	1873
<i>Post transition metals + post transition metals</i>				
Al–Ga	6	6.1	0.1	1073
Al–In	6.6	6.4	0.2	1173
In–Sn	4.8	6.7	2	700
In–Tl	5.2	5.5	0.3	723
<i>Post transition metals + metalloids</i>				
Al–Ge	5.6	6.3	0.7	1200
Al–Sn	6.7	7	0.3	973
Bi–In	5.4	5.5	0.1	900
Bi–Sb	5.9	8.1	2.3	1200
In–Sb	4.1	6.5	2.4	900
<i>Post transition metals/metalloids + <math>d^{10}</math> transition metals</i>				
Bi–Cd	6.1	7.1	1	773
Bi–Zn	7.7	7.9	0.2	873
Cd–Pb	7.1	6.3	0.8	773
Cd–Sb	5.5	7.1	1.6	773
Cd–Pb	7.1	6.3	0.8	773
Cd–Sb	5.5	7.1	1.6	773
Cd–Tl	7.6	6.8	0.8	750
Hg–In	3.9	5.2	1.3	298
In–Zn	6.7	7	0.3	700
<i>Post transition metals + alkali/alkaline earth metals</i>				
Al–Mg	5.6	5.9	0.3	1073
Ga–Mg	3.5	5.3	1.8	923
In–Mg	3.6	5.4	1.7	923
In–Na	3.9	–0.8	4.7	713
K–Pb	–4.6	–3.1	1.5	848
K–Tl	–0.5	–0.8	0.2	798
Mg–Pb	1.4	5.2	3.8	973
Mg–Tl	3.9	6.5	2.6	923
<i>Metalloids + alkali/alkaline earth metals</i>				
Bi–Mg	0.6	5	4.5	975
Bi–Na	–6	–3.3	2.7	773
<i><math>d^{10}</math> Transition metals + alkali/alkaline metals</i>				
Cd–Mg	0.3	4.7	4.4	543
Hg–Na	–1.8	–3.8	2.1	673
<i><math>d^{10}</math> Transition metals + <math>d^{10}</math> transition metals</i>				
Cd–Zn	7.3	5.9	1.5	800
Cd–Hg	5.8	5.1	0.7	600
Hg–Zn	6.7	4.9	1.9	573
<i>Actinides + actinides</i>				
Pu–U	6.2	8.8	2.6	1500
<i>Alkali/alkaline earth metals + alkali/alkaline earth metals</i>				
Mg–Li	5.9	5.8	0	1000

of Witusiewicz *et al.* [36], only the results of entropy of mixing calculated by Witusiewicz *et al.* [36] are discussed in detail.

The calculations of the entropy of mixing using the Witusiewicz *et al.* relation [36] with the enthalpy of mixing from the Miedema

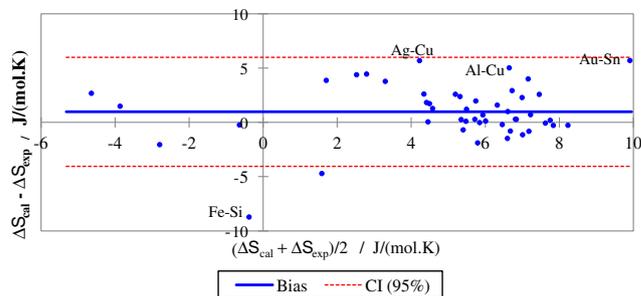


FIGURE 3. Bland-Altman plot of calculated entropy of mixing using Witusiewicz *et al.* [36] relation at equiatomic composition compared with the experimental entropy of mixing for liquid alloys of 49 binary systems listed in table 4. The enthalpy of mixing used in the calculations are obtained from Miedema model.

model are compared with the experimental data in table 4 and depicted in figure 3. As can be seen, the largest differences between the calculated entropy of mixing and the experimental data of Hultgren *et al.* [77] are in the group of transition metals alloyed with non-transition metals. Transition metals have high densities of state at their Fermi level. When they are alloyed with other metals, the difference in the Fermi levels of the two metals and the  $s$ - $d$  interaction causes a charge rearrangement [64]. Therefore, for calculating the entropy of mixing of transition metals alloyed with non-transition metals, the electronic entropy of mixing should be taken into account. The highest difference for entropy of mixing in this study occurs in the Fe–Si system which belongs to this group of alloys. Pasturel *et al.* [64] calculated the entropy of mixing for this system by taking into account the electronic term. His results are much closer to the experimental data. Some discrepancies between calculated and experimental entropy of mixing can also be seen in metalloids/ $d^{10}$  transition metals alloyed with alkali/alkaline earth metals (Bi–Mg, Cd–Mg). Similar to the Miedema model, this can be related to the unusual behavior of metalloids and  $d^{10}$  transition metals. For all the other groups, the predictions using the Witusiewicz *et al.* relation [36] are consistent with the experimental data. Other sources of error can be the use of the Miedema model for calculating enthalpy of mixing in Witusiewicz *et al.* relation [36] (equation (8)). This can be seen for systems such as Bi–Mg and Au–Zn for which application of Miedema model resulted in higher errors in estimating their entropies of mixing. Application of experimental enthalpy of mixing in the Witusiewicz *et al.* relation [36] (equation (8)) instead of the Miedema model will result in more accurate predictions. Witusiewicz *et al.* [36] estimated the accuracy of the model when the experimental enthalpy of mixing is used as  $\pm 2 \text{ J}/(\text{mol}\cdot\text{K})$ . Moreover, the experimental data reported are from Hultgren *et al.* [77] and in some cases calculations of the entropy of mixing are within experimental error. It should not be forgotten that experimental data for the entropy of mixing are never exact because there is no way to measure entropy directly and thus they are accompanied by uncertainties. In order to obtain experimental data for entropy of mixing, first activities (Gibbs free energy) of the constituents in the alloy have to be measured. From the Gibbs free energy obtained from the activities, the data of the enthalpy and entropy of mixing are calculated. Therefore, the reported data of entropy of mixing always involve accumulated errors from each of the above mentioned steps.

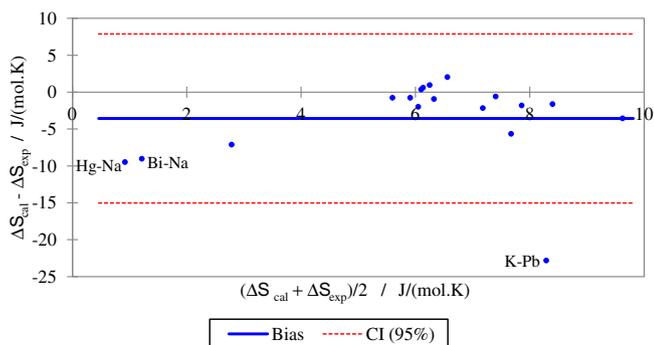
Overall, the Witusiewicz *et al.* relation [36] is successful in predicting the entropy of mixing for liquid alloys. The standard deviation of this model is  $2.5 \text{ J}/(\text{mol}\cdot\text{K})$  with a prediction band of  $\pm 5.8 \text{ J}/(\text{mol}\cdot\text{K})$ .

The calculated entropy of mixing using the Hard-Sphere model [65] is compared with the experimental data of Hultgren *et al.* [77] in table 5 and figure 4. It can be seen from figure 4 that the highest

**TABLE 5**

Comparison of the entropy of mixing at equiatomic composition for liquid alloys (J/mol.K) for different binary systems calculated using the Hard-Sphere model [65] in comparison with the Hultgren *et al.* assessment [77].

System	$\Delta S_{HS} / J / (\text{mol.K})$	$\Delta S_{Exp.} / J / (\text{mol.K})$	$\Delta S_{HS} - \Delta S_{Exp} / J / (\text{mol.K})$	T (K)
Ag–Cu	8.1	12.8	4.7	1400
Ag–Ga	8.3	6.1	2.2	1000
Ag–Pb	9.2	7.6	1.6	1000
Bi–Cd	7.7	7.11	0.6	773
Bi–Cu	5.5	7.6	2.0	1200
Bi–In	6.3	5.5	0.8	900
Bi–Na	5.7	–3.3	9	773
Bi–Zn	11.4	7.8	3.6	873
Cd–Hg	7.0	5.1	0.4	600
Cd–Pb	5.9	6.3	2	773
Cd–Zn	7.0	5.9	0.9	800
Cu–Fe	5.8	6.4	0.6	1823
Hg–In	6.0	5.2	0.8	298
Hg–Na	5.7	–3.8	9.5	673
Hg–Zn	10.5	4.8	5.7	573
In–Na	6.3	–0.8	7.1	713
In–Sn	5.8	6.7	1.0	700
In–Zn	8.8	7.0	1.8	700
K–Pb	19.7	–3.1	22.8	848



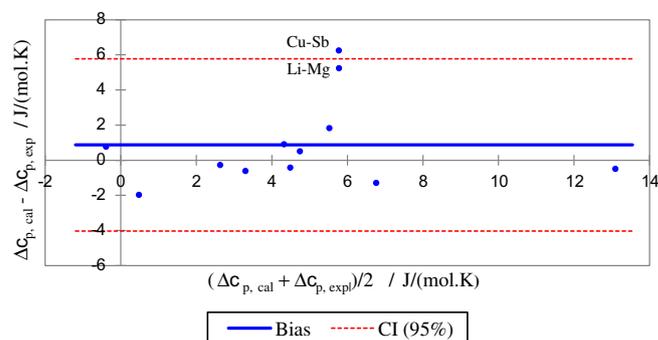
**FIGURE 4.** Bland–Altman plot of calculated entropy of mixing using Hard-Sphere model [65] at equiatomic composition compared with the experimental entropy of mixing for liquid alloys of 19 binary systems listed in table 5.

**TABLE 6**

The excess heat capacities of binary liquid alloys calculated by the Witusiewicz relation [36] and compared with the experimental data [81]. Enthalpy of mixing used in the calculations are obtained from Miedema model.

System	$\Delta C_p^{XS}_{cal} / J / (\text{mol.K})$	$\Delta C_p^{XS}_{exp.} / J / (\text{mol.K})$	$\Delta C_p^{XS}_{cal} - \Delta C_p^{XS}_{exp.} / J / (\text{mol.K})$	T / K	$x_A / (x_A + x_B) \times 100$
Ag–Ga	2.61	3.84	1.2	900	0.55
Al–Cu	4.7	4.28	0.4	1200	0.5
Au–Sn	7.41	6.12	1.3	780	0.5
Bi–In	1.47	–0.5	2.0	600	0.5
Cd–Pb	–0.77	0	0.8	623	0.5
Cd–Sb	3.87	4.78	0.9	693	0.57
Cu–Sb	2.65	8.9	6.3	1070	0.75
Ga–Mg	3.61	3	0.6	972	0.286
Hg–Na	13.34	12.85	0.5	633	0.7
In–Na	4.61	6.44	1.8	750	0.65
In–Sb	2.77	2.5	0.3	923	0.5
Li–Mg	3.16	8.4	5.2	800	0.5
Mg–Pb	4.49	5	0.5	1100	0.65

deviations from the experimental data are for the K–Pb, Hg–Na and Bi–Na systems, which contain a metalloid or a  $d^{10}$  transition metal. Therefore, similar to Witusiewicz *et al.* [36] relation, extrapolation of the Hard-Sphere model to metalloids can result in prediction er-



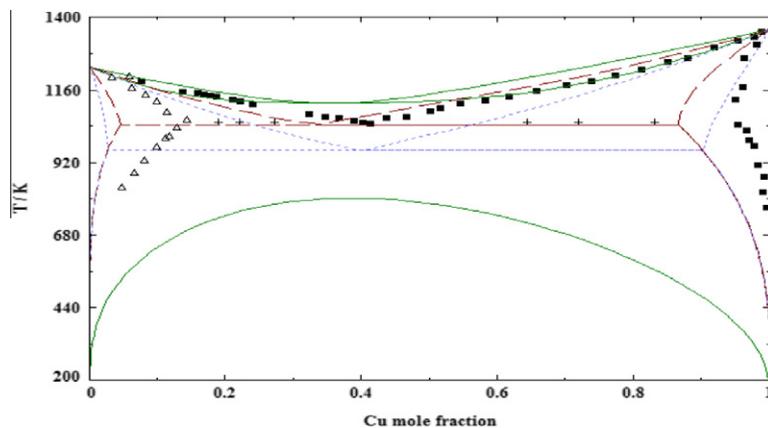
**FIGURE 5.** Bland–Altman plot of calculated heat capacity of binary liquid alloys using Witusiewicz relation [36] compared with the experimental entropy of mixing listed in table 6. The enthalpy of mixing used in the calculations are obtained from Miedema model.

rors. Also,  $d^{10}$  transition metals when alloyed with other metals show unusual behavior because of the stability of their  $s^2$  electronic configurations. Similar to the Witusiewicz *et al.* [36] relation, these deviations are more evident when metalloids/ $d^{10}$  transition metals are alloyed with alkali/alkaline earth metals. However, compared to the Witusiewicz *et al.* [36] relation, the Hard-Sphere model is more sensitive in these two groups of alloys. The standard deviation of this model is 7 J/(mol.K) with a prediction band of  $\pm 15$  J/(mol.K). Removing alloys of metalloids/ $d^{10}$  transition metals with alkali/alkaline metals pairs from the analysis decreases the prediction band to  $\pm 6$  J/(mol.K).

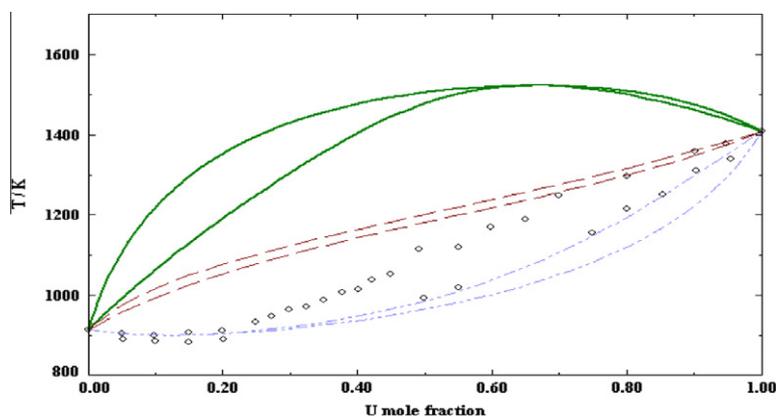
Overall, the Witusiewicz *et al.* [36] relation and the Hard-Sphere model [65] both can be applied to obtain entropy of mixing of liquid alloys. Both these methods showed good prediction for the majority of the studied systems. However, it can be said that the Witusiewicz *et al.* [36] relation is a better choice for alloys of metalloids/ $d^{10}$  transition metals with alkali/alkaline earth metals. Contrary to the Witusiewicz *et al.* [36] relation, the Hard-Sphere model [65] provides a physical description of the entropy of mixing. Recently Harvey *et al.* [78] showed that the results of the Hard-Sphere model are very consistent with Monte Carlo simulations [79] and the thermodynamic integration method [80]. This suggests that the Hard-Sphere model is physically more realistic in addition to being comparable to the Monte Carlo simulation.

### 3.3. Excess heat capacity

Of all the thermodynamic properties calculated within thermodynamic modeling, the excess heat capacity is the most neglected. Knowledge of excess heat capacities provides by definition the temperature dependence of the excess enthalpy and excess entropy of mixing. The product of temperature and the first derivative of equation (8) proposed by Witusiewicz *et al.* [36] led to equations (11) and (12) for calculating excess heat capacity of liquid alloys. The heat capacity data obtained from this relation are compared with the experimental data of Bergman and Komarek [81] and are listed in table 6. Figure 5 illustrates the correlation between the experimental and calculated results. As can be seen in table 6, the Cu–Sb and Li–Mg results deviate the most from the experimental data. For Li–Mg, this deviation is the effect of size difference. Mg and Li have a significant size difference but the effect of this size difference in the Witusiewicz *et al.* [36] relation is neglected. Considering experimental data of systems with large size difference, Witusiewicz *et al.* [36] relation can be reformulated to take into account this effect. For Cu–Sb, the deviation can be related to the unusual behavior of Sb as metalloid. A Bland–Altman analysis of the results indicates that the results are satisfactory



**FIGURE 6.** Prediction of the Ag–Cu phase diagram using Engel–Brewer method (–), Miedema–Witusiewicz (---) and the Miedema–Hard-Sphere models (...) in comparison with experimental data ([82]: ■, [68]: + and [83]: △).



**FIGURE 7.** Prediction of the Pu–U phase diagram using Engel–Brewer method (–) Miedema–Witusiewicz (---) and the CALPHAD method assuming the Miedema–Witusiewicz model as the first approximation of thermodynamic property (...) in comparison with experimental data of Peterson and Foltyn [84]: ○.

with standard deviation of  $3.52 \text{ J}/(\text{mol}\cdot\text{K})$  and prediction band of  $\pm 5.7 \text{ J}/(\text{mol}\cdot\text{K})$ .

### 3.4. Phase diagram prediction

Figures 6 and 7 present the results of the application of the different methods to calculate the phase diagrams of the Pu–U and Ag–Cu systems. It can be seen that in both cases, the Engel–Brewer method is not even able to predict the general shape of the phase diagram. For Ag–Cu, the Engel–Brewer prediction underestimates the solid miscibility gap and therefore it is not able to reproduce the eutectic point. For Pu–U, contrary to the experimental data, the Engel–Brewer method predicts a temperature maximum azeotrope-like phase diagram. For the Ag–Cu system, Miedema–Witusiewicz is more successful in predicting the eutectic point compared to the Miedema–Hard-sphere model. However, maximum solid solubility is not predicted well by both these methods. For Pu–U, since there was not enough information available for the packing fraction of Pu and U, the Miedema–Hard-Sphere cannot be used. For this system, use of Miedema–Witusiewicz leads to results closer to the experimental phase diagram compared to the Engel–Brewer method. However, there is still a large difference between Miedema–Witusiewicz and the experimental data. If the entropy of mixing (equation (1)) of the liquid phase is changed by  $1.5 \text{ J}/(\text{mol}\cdot\text{K})$  from the one predicted by the Witusiewicz *et al.* [36] relation, the dash dotted phase diagram in figure 6 will be reproduced. This phase diagram (– · –) is consistent with the

experimental phase diagram and indicates that using the Miedema–Witusiewicz or the Miedema–Hard-sphere as the first approximation for the CALPHAD method can result in the reliable prediction of phase equilibrium data and thermodynamic properties for liquid alloys.

## 4. Concluding remarks

The Engel–Brewer method and the Miedema model, the Witusiewicz, Sommer, Faber relations and the Hard-Sphere model have been reviewed and evaluated for their suitability for calculating mixing properties of liquid solutions. For this purpose, these methods have been applied to different groups of binary systems and the results have been compared with the experimental data. Analysis of the results on the enthalpy of mixing obtained by the Engel–Brewer method and the Miedema model contra-indicated the application of the Engel–Brewer method even for transition metals and actinides, while the Miedema model is considered successful for calculating the enthalpy of mixing. Moreover, the Witusiewicz relation and Hard-Sphere model successfully predicted the entropy of mixing of the majority of liquid alloys. However, it was shown that the Hard-Sphere model cannot be reliable for the case of  $d^{10}$  transition metals/metalloids alloyed with alkali/alkaline earth metals. It is proposed that for systems with no or few experimental thermodynamic property data, a Miedema/Witusiewicz model or Miedema/Hard-Sphere model can be used as thermodynamic property first approximations. When combined

with phase equilibrium data and the CALPHAD method this can result in the useful prediction of thermodynamic properties of liquid binary liquid alloys. Application of these models is not limited to binary systems. Using the Muggianu, Kohler or Toop models, Miedema/Witusiewicz or Miedema/Hard-Sphere models can also be extended to ternary systems or higher order systems.

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