Application of Engel-Brewer and Miedema Semi-Empirical Models Combined with Entropy Models to Thermodynamic Modeling of Binary Systems

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ABSTRACT

Application of Engel-Brewer and Miedema Semi-Empirical Models Combined with Entropy Models to Thermodynamic Modeling of Binary Systems

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Thermodynamic modeling of phase diagrams provides fundamental information for applications such as solidification, crystal growth, joining, solid-state reaction, casting, phase transformations and oxidations. CALPHAD method has been widely used to predict phase diagrams and thermodynamic properties. However, for systems with no or few experimental phase equilibrium data and/or thermodynamic properties, CALPHAD method cannot be applied. For these systems, predicting thermodynamic properties using theoretical and/or empirical formulae is of great interest. Engel-Brewer and Miedema tried to predict enthalpy of mixing based on electronic properties. Whereas, Faber, Guggenheim, Sommer and Wituciewicz formulated excess entropy of mixing.

In this study, Engel-Brewer method is used to calculate thermodynamic properties and phase relations for 5 binary systems and the results are compared with the experimental data from the literature. Then, Engel-Brewer method and Miedema model are applied to calculate enthalpy of mixing of 50 liquid and solid solutions and the results are compared with the experimental data from the literature. Analysis of the results indicates that the Engel-Brewer method is not robust, while Miedema model with some modifications is evaluated as an appropriate model to predict enthalpy of mixing of liquid and solid solutions. Moreover, the models of Faber, Guggenheim, Sommer and Wituciewicz are used to predict entropy of mixing of 50 liquid alloys and the results are then compared with the experimental data from the literature. A critical review of each of these entropy relations is presented and it is concluded that the Wituciewicz relation is the most appropriate model to predict entropy of mixing of liquid alloys. Finally, based on the current work, a combined Miedema-Wituciewicz model is suggested to parameterize Gibbs free energy of mixing for liquid solutions. This model can be used to predict thermodynamic properties and consequently, binary phase diagrams without relying on the experimental thermochemical data.

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Chapter 1

Introduction

1.1 Introduction to thermodynamic modeling

Phase diagrams are graphical representations of equilibrium relationships between phases as a function of temperature, pressure and concentrations of constituent components. “They can be used as roadmaps for alloy design, development and processing” [1]. Moreover, phase diagrams provide basic information applied in fields such as solidification, crystal growth, joining, solid-state reaction, casting, phase transformations and oxidations [2].

Experimental calculation of phase diagrams is a long and expensive task and even more complicated for multi-component systems. Calculation of phase diagrams reduces the time and effort used to find equilibrium conditions for binary and multi-component systems. The correlation between thermodynamics and phase equilibria was established by J.W.Gibbs [3]. Later, Kaufman and Bernstein [4] founded CALPHAD method which is based on the minimization of the Gibbs free energy.

Consequently, considering the fact that minimization of Gibbs energy can result in an optimized phase diagram, there is a mutual relationship between phase diagram and thermodynamic properties. In other words, calculation of phase diagram provides information about thermodynamic properties such as enthalpy and entropy of mixing and activity. On the other hand, calculation of thermodynamic properties of the system leads to the prediction of the phase diagram.

A thermodynamic database containing model parameters would provide the thermodynamic properties of all the phases as a function of temperature and composition at a desired pressure and thus will result in the determination of the required phase diagrams. Thermodynamic description of the constituent binary systems is obtained based on the experimental phase equilibrium data. Then, using an appropriate extrapolation method [5-7], thermodynamic description of higher order systems can be obtained. As binary phase diagrams are the base for the calculation of multi-component systems, it is of great importance to build a database which correctly predicts thermodynamic properties and phase equilibrium data of the binary systems. A schematic representation of CALPHAD method is summarized in Figure 1-1.

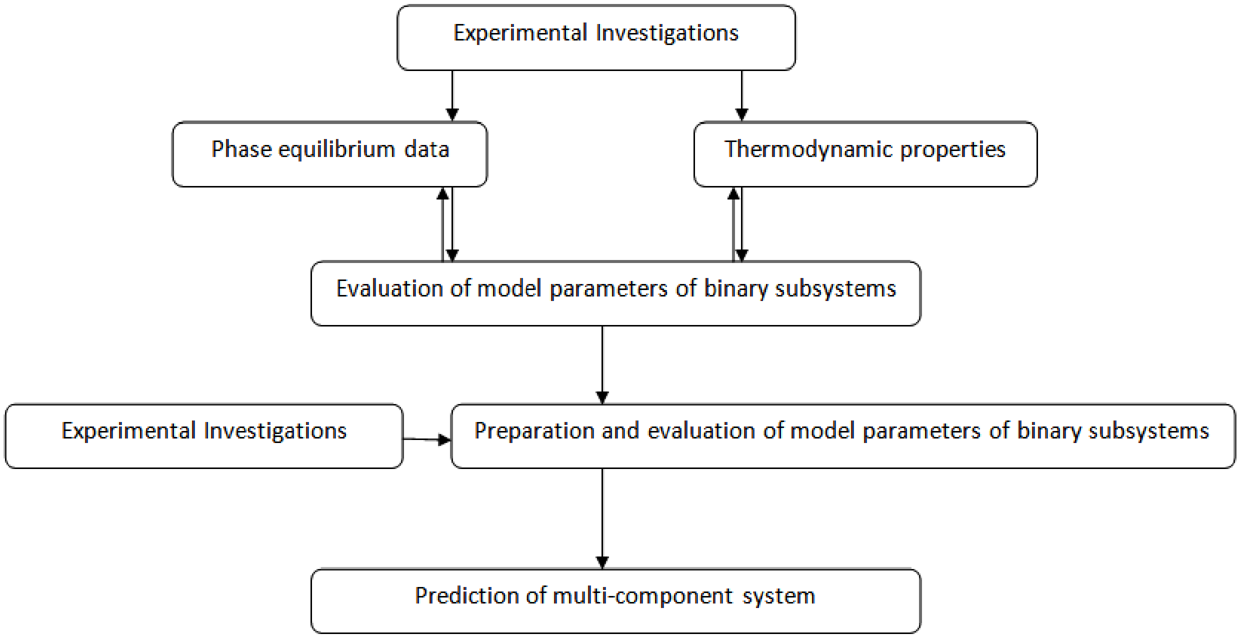


Figure 1-1. Schematic of the CALPHAD method

1.1 Motivation

Nowadays, CALPHAD method is widely used to predict phase diagrams. However, for systems with no or few experimental phase equilibrium data and/or thermodynamic properties, CALPHAD method cannot be applied. For this reason, it is of great importance to establish a valid method able to predict thermodynamic properties and phase diagrams for systems lacking experimental data. Since Gibbs energy is $\Delta G = \Delta H - T\Delta S$, phase diagram prediction is possible only if theoretical methods can be used to predict excess enthalpy and entropy terms.

Firs-principles quantum mechanics based on density functional theory [8] can provide information about enthalpy and entropy of formation for solids and compounds, bulk modulus, thermal expansion, entropy, etc. For these calculations the only information needed is the structure of constituent atoms. However, firs-principles calculations cannot be applied to the liquid phases and multi-component systems. Using approximation of electron densities, ab-initio molecular dynamics (AIMD) [9,10] makes possible the prediction of thermodynamic properties of liquid, super-cooled liquid and glass phases. However, first-principles and ab-initio molecular dynamics are both complicated and time consuming and they do not lead to accurate predictions.

On the other hand, the free electron theory of Sommerfeld [11] was a breakthrough in the prediction of thermodynamic properties of metals and alloys. Empirical models developed by Hume-Rothery [12,13], Darken and Gurry [14], Engel and Brewer [15-18] and Miedema [19,20], coupled with the free electron theory, allow for correlation of electronic properties to physical stability [21]; Free electron theory

[11] led to some electronic models capable of correlating phase stability and electronic properties of pure elements and alloys. Hume-Rothery [12,13] developed some rules regarding the trends of alloying of pure metals based on size factor, electrochemical factor and valence effect. Darken and Gurry [14] extended some of Hume-Rothery rules to predict solid solution formation. Engel [15] used the same correlation as Hume-Rothery for all the metals. Later, Brewer developed the Engel-Brewer method by applying Hildebrand formula [22,23] to Engel method in order to calculate the mixing properties and phase transformations and predict the phase diagram of binary and multi-component systems [15 -18]. 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 Gibbs energy of mixing. Also, Miedema model [19, 20] uses electron density at the boundary of Wigner-Sritz cell [19], electronegaivity and hybridization to describe enthalpy of mixing.

In addition, some efforts have been made to find excess entropy of mixing of different phases. Faber et al. [24], Guggenheim [25] and Kleppa et al. [26] attempted to find volume-based formulae for excess entropy of mixing while Sommer et al. [27] formulated excess entropy of mixing based on energy and volume changes resulting from alloying. Tanaka et al. [28], Kubachenski [29] and Wituciewicz et al. [30,31] found empirical relationships for the entropy of mixing based on the heat of mixing and melting and boiling temperatures.

Accordingly, all these efforts can result in the prediction of thermodynamic properties which consequently leads to the prediction of the phase diagram. A schematic diagram of this approach for binary systems is summarized in Figure 1-2.

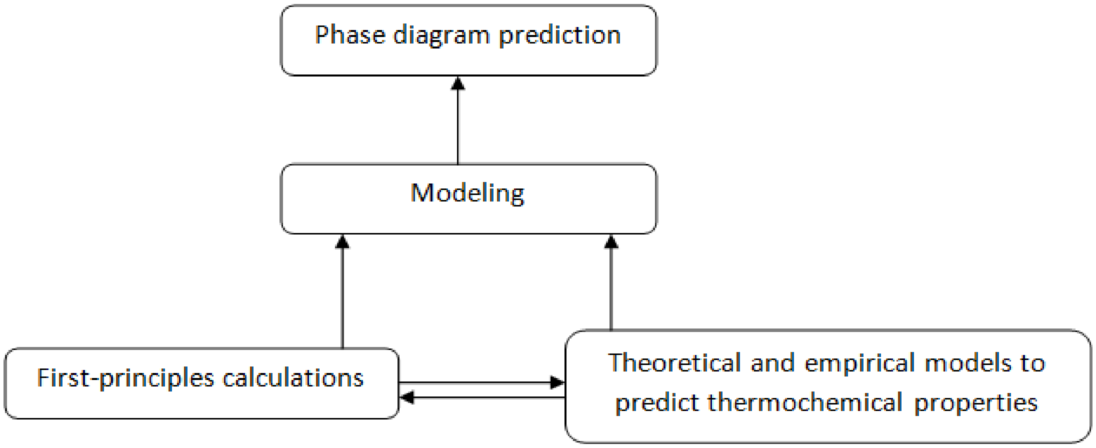


Figure 1-2. Methodology of phase diagram prediction for systems lacking experimental phase equilibrium data and thermodynamic properties data

1.2 Objectives and Thesis layout

The objective of the present study is to review and discuss the ability of different theoretical and empirical models to parametrize Gibbs free energy and thus, predict thermodynamic properties and phase relations of liquid and solid solutions.

This goal is achieved by:

- Application of Engel-Brewer method to find thermodynamic description of 5 binary systems and comparing the results with the experimental data from literature.
- Application of Miedema model and Engel-Brewer method to calculate enthalpy of mixing for large number of liquid alloys that represent different groups of elements and comparing the results with the experimental data.

- Application of Miedema model to calculate enthalpy of mixing of large number of solid solutions that represent different groups of elements and comparing the results with the experimental data.
- Comparison of Engel-Brewer method with Miedema model.
- Application of Faber, Guggenheim, Sommer and Wituciewicz relations to obtain excess entropy of mixing of liquid alloys and comparing the results with the experimental data from the literature.

The entire thesis is divided into five chapters; the following describes the contents of the remaining chapters. Chapter 2 presents a review of different theoretical and empirical models to describe mixing properties of liquid and solid solutions. Chapter 3 describes the fundamentals behind thermodynamic modeling and discusses elaborately the formulae and models used in this study. Chapter 4 presents the results of enthalpy of mixing obtained using Miedema model and Engel-Brewer method and discusses the results in relation to the experimental data from the literature. In addition, this chapter tabulates the results of entropy of mixing calculated using Faber, simplified Guggenheim, Sommer and modified Wituciewicz relations and compares them with the experimental data. This chapter reviews all these models and discusses about their limitations and possible improvements. Finally, chapter 5 summarizes the conclusions and contributions of this thesis and suggests possible directions for future work.

Chapter 2

Literature Review

2.1 Hildebrand theory on enthalpy of non-electrolytic solutions

For non-polar molecules, the dominant intermolecular force is the van der Waals forces. In these molecules bonding is the result of temporary dipoles which are formed by dispersion forces. Therefore, the cohesive energy is stemmed from these temporary dipoles.

From Berthelot relation [32], the adhesion energy for two van der Waals atoms in a molecule AB is the geometrical mean of the adhesion energy in molecule AA and that of BB.

$$-\gamma_{A-B}^{adhesion,T} = -2\varphi\sqrt{\gamma_A^T \gamma_B^T} \qquad 2\text{-}1$$

In this formula, φ is an approximate constant for large families of materials and its value can be determined experimentally [33-35]. For similar substances such as two noble metals, φ can be taken as unity [36].

Good [37] applied Bertholot's relation to interfacial adhesion as follows:

$$-\gamma_{A-B}^{adhesion,T} = \gamma_A + \gamma_B - \gamma_{A-B}^{interface,T} \qquad 2\text{-}2$$

and, from equations 2-1 and 2-2 he concluded that:

$$\gamma_{A-B}^{interface,T} = \left[\sqrt{\gamma_A^T} - \sqrt{\gamma_B^T}\right]^2 \qquad 2\text{-}3$$

Hildebrand [23] assumed, however, linear relationship between enthalpy of vaporization and the product of molar volume and interfacial energy. Therefore, he suggested that eqn. 2-3 can be changed to eqn. 2-4 as follows:

$$\Delta H_{A-B}^{solution,T} = V\left[\sqrt{\left(\frac{\Delta H^{vap}}{V}\right)_A} - \sqrt{\left(\frac{\Delta H^{vap}}{V}\right)_B}\right]^2 \qquad 2\text{-}4$$

In this formula $\frac{\Delta H^{vap}}{V}$ is called the solubility parameter. Predictions regarding the immiscibility or miscibility of van der Waals liquids using solubility parameter are of great accuracy [19].

Hence heat of mixing can be obtained if a concentration factor is added which describes specie A randomly surrounded by similar and dissimilar species. Hildebrand [23] described this concentration factor as:

$$f(c) = C_A^V . C_B^V \qquad 2\text{-}5$$

In which C_A^V means volume concentration of A.

In addition to the application of this solubility parameter to van der Waals molecules, Hildebrand and Scott [23] used this solubility parameter to liquid metal alloys and found that the liquid immiscibility is predictable when no intermediate compounds are involved in the system. As will be discussed later in this chapter, Brewer [16-18] modified Hildebrand formula and used Engel theory [15] to predict cohesive energy for alloys.

2.2 Previous works on enthalpy of mixing

As mentioned earlier, the solubility parameter of Hildebrand can be used not only for van der Waals molecules, but also for metals in systems where no intermetallic compounds are formed. This solubility parameter adds a positive contribution to enthalpy of mixing. However, in order to predict the formation of compounds, a negative contribution to enthalpy of formation is needed. Pauling [38] used the difference in electronegativities of the constituent substances in the system to describe enthalpy of formation (ΔH^{for}) of ionic compounds as follows:

$$\Delta H^{for} = -96M(X_A - X_B) \qquad \textit{2-6}$$

Where X_A and X_B are Pauling electronegativities of the elements and M is the number of shared electron pairs. Although, the concept of shared electron pairs cannot be applied to metals, Mott [39] tried to define M for different binary systems of metals. In other words, attempts of Hildebrand and Pauling were proceeded by Mott [39] who used negative contribution of Pauling together with positive contribution of Hildebrand to predict immiscibility for metallic alloys. Kumar [40] replaced enthalpy of vaporization with enthalpy of fusion in Hildebrand's solubility parameter and introduced a modified Mott's approach to obtain enthalpy of mixing. All these studies are compared later in this chapter with Miedema model.

2.3 Introduction to Engel-Brewer method

2.3.1 Electronic configurations of bonding

Engel [41,42] stated that a relationship exists between the crystal structure and electronic configuration of atoms for all the metals. He proposed that B.C.C. lattice structure has stability between 1 to 1.75 *sp* electrons per atom, H.C.P. lattice structure is stable between 1.8-2.2 *sp* electrons per atom and F.C.C lattice structure is stable between 2.25-3 electrons per atom. Later, Brewer [17] confirmed that Engel's metallic correlation can be used to predict most of the structures of pure metals as well as intermetallic compounds and applied it to predict phase diagrams of some binary systems of transition metals [16].

In order to explain what happens during bonding, Brewer used the valence bond approach [18]. In the valence bond approach, the starting state is separated atoms and the molecule is made by different atomic electronic states. Therefore, bonding takes place when the unpaired electrons of the atoms pair with each other. Atoms can simply pair with each other on their ground electronic state, for instance, diatomic molecules such as Cl_2, S_2, etc. However, when the bonding energies offset the promotion energies of the electrons to excited states, atoms make bonds in electronic configurations different from their ground electronic state. As an example, silicon has two unpaired p electrons in its ground state. But it can be excited to sp^3 valence state with four unpaired electrons provided that the energy of the two additional bonds covers the required promotion energy. Hence, silicon has four electron pair bonds and a diamond structure [43].

2.3.2 Prediction of the crystal structure of pure metals

In the valence bond approach first, it is assumed that the metal evaporates to a gaseous ground state. Then different promoted electronic states are studied and the promotion energies for each of these electronic states are found using experimental data. At last, the enthalpy of atomization can be found as follows:

$$Bonding\ Energy \times n - Promotion\ Energy = Enthalpy\ of\ atomization \quad 2\text{-}7$$

For example, B.C.C phase of Ti has an electronic configuration of d^2sp. The bonding enthalpy of 4s electron and 3d electrons for Ti are reported to be 222, 126 $kJ/electron\,mole$, respectively [43]. Since Ti has two *s,p* and two d electrons, these amounts are multiplied by 2 and hence, the total bonding enthalpy is 695 $kJ/mole$. The promotion energy for d^2sp configuration of Ti is reported by [44] to be around 209 $kJ/mole$. Subtracting these two amounts (eqn. 2-7) results in the atomization energy of 486 $kJ/mole$. Using the same procedure for electronic configuration d^3s results in the atomization energy of 465 $kJ/mole$. The value of these two atomization energies are so close that it can be concluded that for Ti, at lower temperatures the H.C.P structure is stable and it changes to B.C.C. structure at higher temperatures [43]. If the atomization enthalpy for any of these two phases were much lower compared to the other, it could be concluded that the phase with lower enthalpy of atomization is unstable. It should be mentioned that the reason that for Ti, B.C.C. crystal structure is more stable in higher temperatures is that it has the coordination number of 8 which compared to H.C.P. structure, with the coordination number of 12, has higher entropy [43]. Experimental data of Leyens et al. [45] confirms that B.C.C. crystal structure of Ti is stable in higher temperatures. The promotion energies to different electronic configurations for different elements are collected in [44,46] from the analysis of elemental optical spectra.

This cycle which is called modified Born-Haber cycle [47] for the phase stability of pure metals is shown in Figure 2-1.

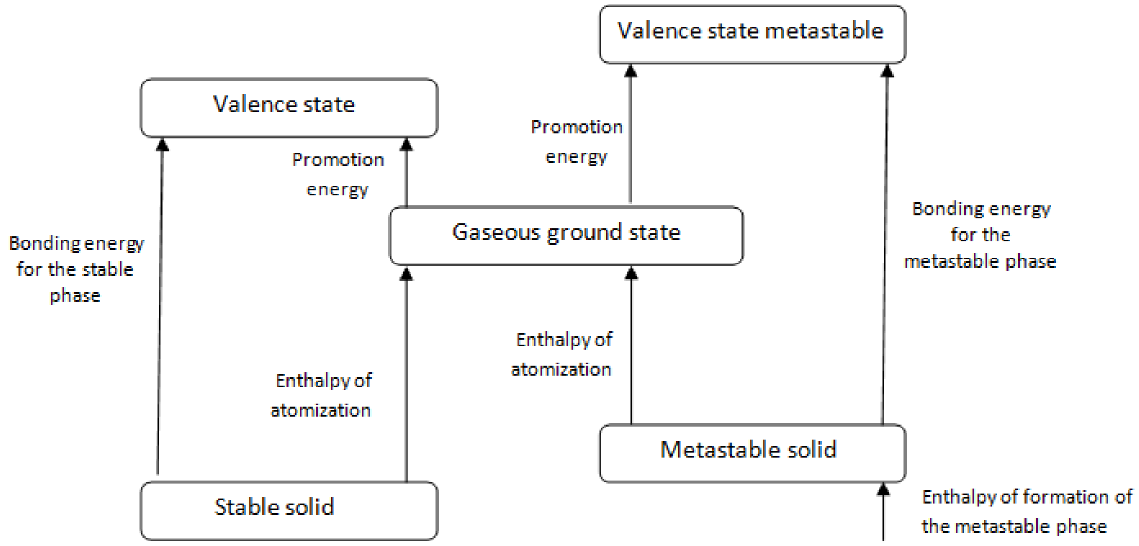


Figure 2-1. Modified Born-Haber cycle for metallic elements [47]

The application of Engel-Brewer correlation is shown in Figure 2-2. It can be seen from the figure that a band of energy states presents a certain electronic configuration. In the Engel-Brewer method, only the lowest state of the electronic configuration is used in the calculations [47]. In this figure, energy levels of both of the excited states of Sr to Mo are presented. It can be seen that for Sr and Y, the energy levels of B.C.C. and H.C.P. structures are close enough. Therefore, these elements have both B.C.C and H.C.P crystal structures. However, for Nb and Zr, the energy level of H.C.P. electronic configuration is so high compared to the B.C.C. phase that one expects only B.C.C. structure for these two elements. For these transition metals energy of S^2 valence state is so high that it is not stable at all [43].

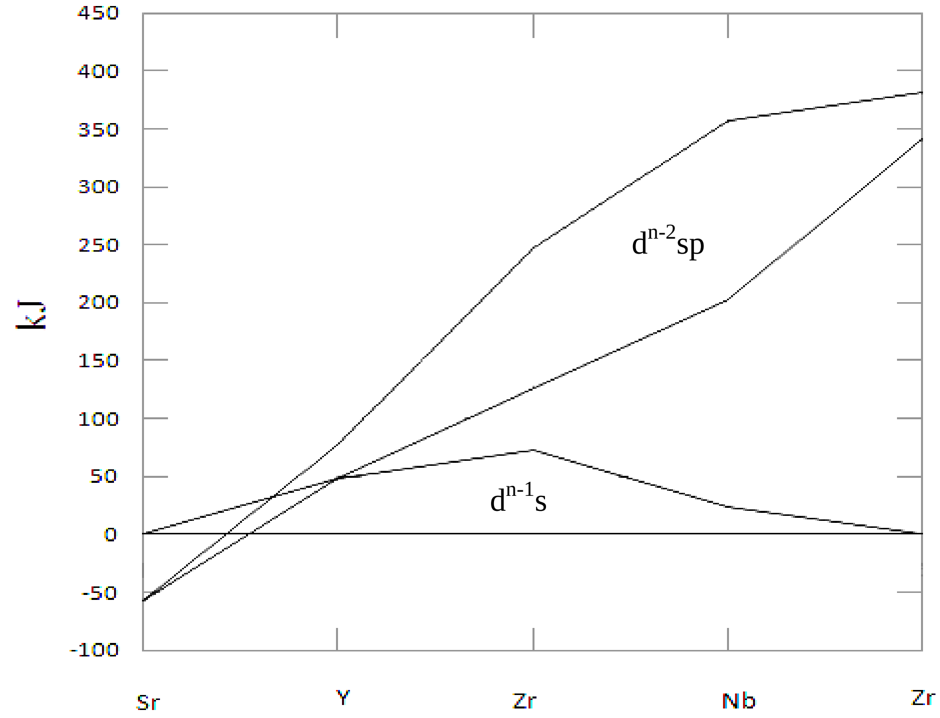


Figure 2-2. Stabilities of $d^{n-1}s$ *and* $d^{n-2}sp$ *electronic configurations for 3d transition metals [18]*

From the previous discussions, it can be concluded that in the Engel-Brewer method, d and f electrons take part in bonding but phase stability is specified based on the number of sp electrons. Brewer [48] explains that the effect of d and f electrons in phase stability is through their excitation to sp valence states. However, in some cases such as lanthanides and actinides, the existence of f electrons provides a large number of valence configurations with the same number of sp electrons. For instance, light actinides can promote to configurations with f^{n-4} in americium to f^{n-6} in uranium and neptunium [48]. In these cases, the choice of the best valence state is more challenging.

The promotion energies for bonding configurations with less than f^{n-3}can be found in [48,49].

2.3.3 Bonding of different elements

Brewer suggested that when two unlike atoms bond together to form an alloy, their electronic configuration affect the crystal structure of the final alloy. For example, he discussed the bonding of thorium with different elements of the periodic table [48]. According to Engel theory [41,42], the B.C.C. structure of thorium has the electronic configuration of d^3s while the electronic configuration of F.C.C. structure is dp^2s. In other words, the number of unpaired *d* electrons for thorium in B.C.C. structure is more compared to F.C.C. structure. In addition, d orbitals of the transition metals overlap easier with d orbitals rather than s or p orbitals [48]. Since, all the transition metals between group 4th to 11th have more than two bonding d electrons, they stabilize the B.C.C. structure of thorium. Whereas, non-transition metals or transition metals with less than two d bonding electrons (group 1st and 11th) stabilize more the F.C.C. crystal structure [48].

Therefore, Brewer developed Engel-Brewer method by adding the effect of electronic configuration to Hildebrand theory [22,23]. According to Hildebrand theory [22,23] for van der Waals molecules, when two elements are mixed, the internal pressure differences and size effects should be considered. The differences in internal pressures are represented by $\frac{\Delta E}{V}$ in which ΔE is the energy of vaporization and V is the molar volume of the element. In Hildebrand proposed model, which later was called regular solution model, the activity coefficient is written as [23]:

$$ln\gamma_1 = V_1 a \varphi_1^2$$

$$ln\gamma_2 = V_2 a \varphi_2^2 \qquad \textit{2-8}$$

where $\varphi_1$and φ_2 are the volume fractions of pure elements 1 and 2, V_1 and V_2 are the molar volumes of pure elements 1 and 2. And a is a parameter function of internal pressures and size differences.

The formulas above can be changed to mole fraction instead of volume fraction with the expansion of φ^2 and therefore, Hildebrand rewrote eqn. 2-8 [22,23,50] as:

$$ln\gamma_1 = bx_2^2 + cx_2^3$$

$$ln\gamma_2 = (b + 1.5c)x_1^2 + cx_1^3 \qquad \textit{2-9}$$

Where $\gamma_1$and γ_2 are activity coefficients of elements 1 and 2. x_1 and x_2 are the mole fractions and b and c are partial dependant parameters defined as $b = V_1 a$ and $V_2/V_1 = (b + c)/(b + 0.5c)$. To formulate a, Hildebrand [22,23] 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” [50], the mixing is taking place under constant volume conditions and the excess entropy of mixing is negligible (i.e. entropy of mixing is ideal). Hence, Hildebrand [22] suggested that a can be written as:

$$a = (\frac{1}{RT})\left(\left(\frac{\Delta E_1}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2}{V_2}\right)^{1/2}\right)^2 \qquad \textit{2-10}$$

This formula does not always result in the correct a parameter because $\Delta E/V$ is also a function of temperature. Besides, mixing does not take place at a constant volume and the entropy of mixing is not ideal. Moreover, for the case of metallic solutions this relationship does not lead to a correct prediction of the Gibbs free energy. Metals have electrons moving freely in their valence electronic layer. Thus metal's vapor does not necessarily have the same electronic configuration as the predominant solid state. To describe the case of metals, Brewer [50] gave a simple example: the enthalpy of vaporization from lanthanum to samarium and from gadolinium to thulium decreases, which may imply that from lanthanum to samarium and from gadolinium to thulium the bonds become weaker and thus cohesion energy decreases. Therefore, it can be predicted that the melting point decreases in this direction. Nevertheless, this is not the case and the melting point increases. Moreover, considering only $\Delta E/V$ to calculate the mutual solubility of actinides, it can be expected that they have small solubility in each other. However, actinides have large such solubility [50]. Brewer [50] stated that this increase in the melting point from lanthanum to samarium and from gadolinium to thulium and the large mutual solubility of actinides can be justified by taking into consideration energies of vaporization to the gaseous state with the same electronic configuration as the final solid metal. In other words, Brewer [43,50] suggested that the ΔE in the formula should be changed to ΔE^* which is energy of vaporization to the gaseous atom with the same valence state of the condensed solid.

In addition, the actual behavior of the elements indicate that their interaction energy is between arithmetic and geometric mean rather than just geometric mean [50]. Thus, Brewer rewrote eqn. 2-10 as [50]:

$$b + c = (\frac{V_1}{2RT})\left(\left(\frac{\Delta E_1^*}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2^*}{V_2}\right)^{1/2}\right)^2 \qquad \textit{2-11}$$

The values of ΔE^* and V needed to calculate the internal pressure of the elements are reported in [18,51,52].

2.3.4 Phase boundaries by activity formulae

In order to define the phase boundaries between two phases, the choice of standard state for the Gibbs free energy of the pure element is important. The standard state Gibbs energies of metals are listed in [53]. If the deviations from Raoult's law are small, stable crystal form can be used as the standard state. But on the other hand, if other components stabilize one structure or if the element has different crystal structures in different temperatures and pressures, then metastable structure should be used as the standard state [53].

To make the phase boundaries between two adjacent phases, one can use the equality of their chemical potential. Since for all real solutions neither Raoult's law nor Henry's law is applicable [53] the partial Gibbs energies can be formulated as:

$$\Delta G_A = \Delta G_A^{\circ}(RL) + RTlnx_A + RTln\gamma_A \qquad \textit{2-12}$$

Where γ_A and x_A are the activity coefficient and concentration of element A, respectively. Using eqn. 2-9, Brewer [50,53,54] described the equality of the chemical potential between two phases as:

$$lnx + b(1-x)^2 + c(1-x)^3 + e_x = ln(1-y) + (b+1.5c)y^2 - cy^3 \qquad \textit{2-13}$$

$$lny + b(1-y)^2 + c(1-y)^3 + e_y = ln(1-x) + (b+1.5c)x^2 - cx^3 \qquad \textit{2-14}$$

Where x is the mole fraction of component 1 in the phase richest in component 2 and y is the mole fraction of component 2 in the phase richest in component 1. Brewer [54] proposed that *e* terms are the standard Gibbs energy of transformation. For example, if the equation is for solid/liquid then he considered that *e* will be the Gibbs free energy of fusion as follows [54]:

$$e_x = \frac{\Delta G_{f,1}^{\circ}}{RT} = \frac{\Delta H_{f,1}^{\circ}}{RT} - \frac{\Delta S_{f,1}^{\circ}}{R} \qquad \textit{2-15}$$

$$e_y = -\frac{\Delta G_{f,2}^{\circ}}{RT} = \frac{\Delta H_{f,2}^{\circ}}{RT} + \frac{\Delta S_{f,2}^{\circ}}{R} \qquad \textit{2-16}$$

Using eqn. 2-12 to 2-16, Brewer [53] proposed that partial excess Gibbs energy of mixing for the constituent components of the system can be found as:

$$\frac{\Delta G_1^E}{R} = Tln\gamma_1 = b_g {x_2}^2 + C_g {x_2}^3 \; when \; x_2 \to 0 \qquad \textit{2-17}$$

$$\frac{\Delta G_2^E}{R} = Tln\gamma_2 = (b_g + 1.5C_g){x_1}^2 - C_g {x_1}^3 \; when \; x_1 \to 0 \qquad \textit{2-18}$$

Therefore, Brewer [53] suggested the excess Gibbs energy of mixing as:

$$\frac{\Delta G^E_{Mix}}{R} = (n_1 + n_2)x_1x_2\left[b_g + c_g(1 - 0.5x_1)\right] \qquad 2\text{-}19$$

This formula is a special case of Redlich-Kister formulation which is a mathematical formulation for the regular solution model.

$$\Delta G^E = \sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\sum_{p=0}^{m_{ij}} A^p_{ij}X_iX_j(X_i - X_j)^p + \sum_{i=1}^{n-2}\sum_{j=i+1}^{n-1}\sum_{k=j+1}^{n} C_{ijk}X_iX_j\,X_k \qquad 2\text{-}20$$

Neglecting the ternary interaction parameters, Ogawa [55] implied the model parameters as

$$b + c = \alpha \qquad 2\text{-}21$$

$$\beta = \frac{2(V_j - V_i)}{V_i - V_j} \qquad 2\text{-}22$$

$$A^0_{ij} = \propto + A^1_{ij} \qquad 2\text{-}23$$

$$A^1_{ij} = \frac{-\beta\alpha}{4(1 + \beta)} \qquad 2\text{-}24$$

Eqn. 2-21 to 2-24 are used in this study to find Gibbs energy of mixing for liquid and solid solutions.

2.3.5 Previous works on the application of Engel-Brewer method

Engel-Brewer method has been used in several articles. Smith et al. [56] used this method to calculate the binary phase diagrams of Pu-U, Pu,Zn, U-Zn. His predictions were consistent with the experimental data. Then he extrapolated the binary systems to predict the Pu-U-Zn ternary phase diagram. Brewer [57,58] calculated the phase diagrams of a large number of elements with Mo. For most of them not much experimental data was available and for the rest the prediction was done based on his model and experimental data. In addition, Brewer [16] studied the phase behavior and crystal structure for binary systems of the 30 metals of the 3 transition series from the alkali metals to the Ni-Pt group. Wu et al. [59] used this method to calculate binary phase diagrams of some refractory metals such as Re, Tc, W, Ta with actinides like Am, Bk and Cm. His results were consistent with the experimental data. Ogawa [55] applied Engel-Brewer method to predict phase diagrams of some light actinides such as U-Pu, U-Np, Np-Pu, U-Am and Np-Am. His predictions except the case of Pu-U were in agreement with the experimental data. Then, he extrapolated the binary sub-systems to find phase diagrams for the systems U-Pu-Am and Np-Pu-Am. Oyama et al. [60] used Engel-Brewer method and predicted successfully the crystal structures occurring in early transition metal nitrides and carbides. Wu et al. [61] based on Engel-Brewer method, calculated the enthalpy of formation of the intermetallics forming between transition metals and Al and Mg. Their predictions were consistent with the experimental data. It should be mentioned that in all these works, only the phase diagrams obtained from 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.

2.3.6 Limitations of Engel-Brewer Method

Several previous works have criticized Engel-Brewer method [62-69]. Using band theory [62] and by DFT calculations [64], Pettifor showed that the number of sp electrons for 4d transition metals remains constant and the situation does not change even if the hybridization between *sp* and *d* bands are taken into account. This fact contradicts Engel-Brewer method that specifies phase stability based on the number of *sp* valence electrons. Moreover, Pettifor in [65] used long-range oscillatory contribution to the pair potential to find structural stability. The results indicate that the stability of Na, Mg, Al which are non-transition metals are determined not only by their valence *sp* electrons, but also by their core size of constituent ions and valence electron density through the phase shift. Hume Rothery [66] in his note on Engel-Brewer method provided examples which prove the inconsistency of Engel-Brewer method in many cases. For instance, he mentioned the high temperature Be since B.C.C structure of Be is stable at high temperatures but there cannot be any *sd* configuration. Furthermore, he stated the same problem mentioned by Pettifor that in transition metals hybridization of *spd* electrons exists which opposes the claim of Engel-Brewer that *d* orbitals only contribute to bonding not to crystal structures. Engel [67] in a reply to Hume-Rothery’s note stated that only outer shell orbitals contribute to crystal structure. He also mentioned that the existence of B.C.C. high temperature crystal structure of Be is doubtful from the data of [68]. But he did not give a clear explanation about the critics on hybridization. Pecora [69] highlighted the same problem as Hume-Rothery; *d* electrons do not directly affect the crystal structure but it contributes to bonding and he stated that this is problematic since *d* electrons have more directional properties than *s* and *p* electrons. He also mentioned the shortcomings of the method when dealing with alkaline metals since there is no justification for the presence of the F.C.C. phase in some alkaline metals such as Ca and Sr. The other problems mentioned by Pecora [69] are ferromagnetism and the inability of the model to predict the absence of B.C.C. crystal structures for late transition metals. Hunter-Hill [63] mentioned the inability of the model to predict some of the crystal structures in rare-earth metals when there is *sd-f* hybridization rather than *f-f* overlap. Moreover, as Brewer mentioned in [58], this model adds only positive contribution to cohesive energies. Therefore the model is not applicable when the system has negative enthalpy of mixing.

2.4 Introduction to Miedema model

In order to describe the heat of formation of alloys and intermetallic compounds, Miedema considered atoms as pieces of metal [70]. In other words, atoms as they are embedded in pure metals are considered as reference systems. Therefore, the first assumption of the model is that many of the considerations applied when two macroscopic pieces of metal are brought into contact is valid on atomic scale [19]. Hence the alloying effects can be looked upon as the result of the changes in boundary conditions when the atom is transferred from pure metal to an alloy. The relationship between the interaction energy of two blocks of atoms and the heat of alloying of their corresponding binary system is assumed to be linear [71]. Miedema et al. called this approach “Macroscopic atom picture” [19,20].

Before introducing Miedema model, an insight should be given into two parameters of the pure metals that are used in the model description.

The first property used in the model is electron density at the boundary of Wigner-Seitz cell [72] (n_{ws}). Previously, this parameter was only available for non-transition metals [73]. It was assumed for these metals that total electronic charge distribution in a metal crystal is the summation of atomic charge densities [73]. Later, Miedema et al. [74] stated that electron density at the boundary of Wigner-Sietz cell can be well represented as:

$$(n_{ws})^2 = K/V \qquad \textit{2-25}$$

Where K is the experimental value of bulk modulus and V is the molar volume of pure metal. Hence, Miedema obtained electron density at the boundary of Wigner-Sietz cell for all the metals. Boom et al. [75] changed the values of n_{ws} calculated from eqn. 2-25 within the range of uncertainty of the experimental data to have a better consistency with experimental enthalpy of formation of solid alloys. This empirical set of electron densities are in good agreement with the values of the interstitial electron density obtained by self-consistent band-structure calculations of Moruzzi et al. [76].

The second property used in Miedema model is the value of the chemical potential for electronic charge. Similar to electron density, Miedema et al. [20] changed experimental values of work function (φ) within the uncertainty range to have a better consistency with experimental enthalpy of formation of solid alloys. Miedema et al. [20] stated that the new set of values (φ^*) show good consistency with experimental values of work function [77] and electronegativities of Pauling [38]. Miedema [71] discussed in detail how this curve fitting is carried out for transition metals.

List of values for φ^* and $n_{ws}^{1/3}$ used for the calculations were proposed by Miedema et al. [19,20,78] and by Boom et al. [79]. However, these values which are properties of the pure solid metals are also used in Miedema model to calculate heats of mixing for liquid alloys based on two reasons; First, Boom et al. [79] explained that

Miedema model is not dependant on the crystal structure and hence the properties of solid metals can be used to calculate heat of mixing for liquid alloys as well. Second, it is clear that φ^* and n_{ws} depend on temperature and molar volume. The volume increase caused by phase transformation from solid to liquid will result in a decrease in φ^* and n_{ws} and hence $\Delta\varphi^*, \Delta n_{ws}$. However, the area of contact between atoms in liquid phase increases compared to solid phase which in turn can compensate for the decrease in $\Delta\varphi^*$and , Δn_{ws} [79]. Boom et al. [79] used the same argument for $n_{ws}^{1/3}$. Therefore, Boom et al. [79] concluded that the same set of parameters used for solid alloys can be applied to liquid alloys. In this work for Miedema predictions of enthalpy of mixing, the same values as Miedema et al. [19,20,78] for $\Delta\varphi^*, \Delta n_{ws}$ and V are used.

2.4.1 Development of Miedema model

Miedema model is introduced in [20,71,75,78,80-83]. Miedema et al. [70] suggested that the heat of solution of liquid A in liquid B can be formulated in eqn. 2-26.

$$\Delta H^{sol.}_{A\,in\,B} = -P\frac{V_A^{2/3}}{\left(n_{ws}^{-\frac{1}{3}}\right)_{avg}}(\Delta\varphi^*)^2 + \acute{Q}V_A^{2/3}\left(\Delta n_{ws}\right)^2 \qquad 2\text{-}26$$

In this formula, the first term is related to the energy of the dipole layer. This term is introduced to describe ionicity in metals. When two different metals are brought into contact, there will be a charge transfer governed by the difference in chemical potential of the electrons between two metals $(\Delta\varphi^*)$. This charge transfer corresponds to a negative contribution to enthalpy of mixing or formation of alloys [71]. This term is proportional to the area of interface $\left(V_A^{2/3}\right)$ and the square of the difference in work function of the two elements $(\Delta\varphi^*)$ and inversely proportional to the average electrostatic shielding length $(n_{ws}^{-\frac{1}{3}})_{avg}$ which is the width of the dipole layer. V_A is the molar volume of element A [70]. In other words, the interface of two blocks of atoms in contact can be looked at as a plate capacitor with a potential difference of $\Delta\varphi^*$, a surface area of $V_A^{2/3}$ and a distance between plates of $(n_{ws}^{-\frac{1}{3}})_{avg}$ [19].

Since at the macroscopic scale, electron density (n_{ws}) across A-B interface should be continuous, Miedema et al. [78] introduced the second term in eqn. 2-26. When two dissimilar atoms are brought into contact, the discontinuity of the electron densities at the boundary of dissimilar atoms should be smoothed. Since original densities at the cell boundaries of pure metals correspond to their minimum energies, smoothing this discontinuity will add a positive contribution to the enthalpy of formation or mixing [78]. So far, two approaches have been applied to explain how electron density changes in alloying. Alonso et al. [84] proposed that the change in electron density is caused by the change in molar volumes of the two metals. Hence, molar volume of the atom with larger electron density is increased and molar volume of the other one is decreased. Whereas, using first-principle calculations, Williams et al. [85] demonstrated that changing the electronic configuration of metals in contact with each other can equalize their electron densities. For instance, for the atom with lower electron density, the amount of s-type electrons is increased and that of d or f-type electrons is decreased. However, It is plausible that volume changes and changes in electronic configuration both play role in equalization of the mismatch in n_{ws}. Consequently, this positive contribution from discontinuity of electron density can be compared to Engel-Brewer method. Miedema et al. [19,20] proposed that a linear relationship exists between enthalpy of vaporization and the product of $V^{2/3}$and electron density at the boundary of Wigner-Seitz cell (n_{ws}). Thus, n_{ws} can be taken as ${}^{\Delta H}\!/_{V^{2/3}}$ which is very similar to Hildebrand solubility parameter (${}^{\Delta H}\!/_{V}$) that is the basis of Engel-Brewer method [15- 18]. Although, while Brewer adds promotion energy to ΔH in order to take into account the effect of electronic configuration on bonding, Williams et al. [85] demonstrated that n_{ws} by itself, includes the effect of electronic configuration.

Using Hildebrand Formula (eqn. 2-4) [22], interfacial energy can be substituted by $\frac{\Delta H^{vap}}{V^{2/3}}$ which by itself is proportional to n_{ws} . The constant for this linear relationship in eqn. 2-26 is taken as $\acute{Q}$.

Later, de Boer et al. [19] concluded that it is better to change Δn_{ws} in eqn. 1-27 to $\Delta n_{ws}^{1/3}$ and hence, he proposed the following relationship:

$$\Delta H^{for} \propto P\left[-(\Delta\varphi^{*})^{2} + Q/P\left(\Delta n_{ws}^{1/3}\right)^{2}\right] \qquad \textit{2-27}$$

Comparing the sign of enthalpy of formation with existing experimental data showed that $\acute{Q}/P$ in eqn. 2-26 is not constant for different groups of binary systems. Whereas Q/P can be considered as constant for different alloy systems [71]. Furthermore, Chelikowsky et al. [86] expressed that φ^{*} and $n_{ws}^{1/3}$ are of compatible dimensions. This is observed in a linear relationship between chemical potential for electrons and average electron densities with the power of 1/3 proposed by Miedema et al. [87] as shown in eqn. 2-28:

$$\mu^{\mathrm{e}} = 5.2\left(\frac{N_z}{V}\right)^{1/3} + 0.7 \qquad \textit{2-28}$$

Where N_z is the number of valence electrons per atom and V is the molar volume. Therefore, Δn_{ws} is changed to $\Delta n_{ws}^{1/3}$. For relatively small differences in electron densities of metals, Miedema et al. [20] combined the two terms in eqn. 2-26 as follows:

$$\Delta H_{A\,in\,B}^{sol.} = -P\frac{V_A^{2/3}}{\left(n_{ws}^{-\frac{1}{3}}\right)_{avg}}\left[-P(\Delta\varphi^*)^2 + Q\left(\Delta n_{ws}^{1/3}\right)^2\right] \qquad \textit{2-29}$$

Hence, enthalpy of solution is proportional to interface area and the square of the difference in electron densities of the two metals on the boundary of Wigner-Seitz cell, $\Delta n_{ws}^{1/3}$. The values for $n_{ws}^{1/3}$ and φ^* are reported in [19,20]. P and Q are empirical constants.

2.4.2 Comparison between Miedema model and previous models on enthalpy of formation of alloys

Eqn. 2-29 is compatible with some previous studies on enthalpy of alloy formation. It can be looked at as a different presentation of Mott's model [39] in which the positive contribution with slight changes is comparable with the solubility parameter of Hildebrand [22] and the negative contribution corresponds to Pauling's formula for enthalpy of formation of ionic compounds [38]. In addition, since enthalpy of alloy formation is linearly related to electron densities, this model can be compared with Kumar's model [40] as well. All these models are described briefly in section 2.1and 2.2.

2.4.3 The concentration dependence of Miedema model

A simple approach to calculate heat of mixing of liquid alloys is to neglect the difference in the atomic size of the components in the system. In this case, heat of mixing is proportional to the product of the atomic concentrations of the constituent elements. Thus, heat of mixing can be formulated as [23]:

$$\Delta H^{mix} = c_A(1 - c_A)\Delta H^{sol.}_{A\ in\ B} \qquad \textit{2-30}$$

In other words, in regular solution approach, the degree to which A atoms are surrounded by B atoms (f_B^A) equals to $(1 - c_A)$. This fact will explain, why regular solution model predicts symmetric enthalpy of mixing. However, size difference cannot always be neglected. Predel et al. [88] introduced a relationship between positive heat of alloy formation and molar volumes of the constituent elements. Miedema et al. [70] modified Predel et al. [88] relation. He compared the experimental data for heat of solution of A in B to that of B in A for 25 binary systems. For the majority of these systems, the ratio of the heat of solution of A in B to that of B in A were almost equal to $\left(\frac{V_A}{V_B}\right)^{2/3}$. Miedema et al. [70] concluded that when $\left(\frac{V_A}{V_B}\right)^{2/3} > 1.33$ the concentration dependence of enthalpy of mixing is asymmetric.

Therefore, Miedema model should be modified to account for asymmetry. Miedema et al. [70] solved the problem by replacing atomic concentration with the surface area concentration as in eqn. 2-32:

$$c_A^S = \frac{c_A V_A^{2/3}}{c_A V_A^{2/3} + c_B V_B^{2/3}} \qquad 2\text{-}31$$

In addition, the new term c_A^S, gives a better physical explanation of the “macroscopic atom picture” [19,20] since in the “microscopic atom picture” all the interactions are happening at the surface of atomic blocks. Substituting eqn. 2-31 in eqn. 2-30, final concentration dependence for statistically ordered alloys (solutions) is [70]:

$$f_B^A = c_A^S(1 - c_A^S) \qquad 2\text{-}32$$

However, for compounds, the area of contact will be larger compared to solutions and hence Miedema et al. [71] introduced a different concentration dependent formula described as [70]:

$$f_B^A = c_B^S(1 + 8(c_A^S c_B^S)^2) \qquad 2\text{-}33$$

Later, Weeber [89] suggested that for crystalline alloys in order to take into account short range ordering, f_B^A should be changed to:

$$f_B^A = c_B^S(1 + 5(c_A^S c_B^S)^2) \qquad 2\text{-}34$$

2.4.4 Volume corrections

As explained earlier in section 2.4.1, electron density changes caused by changes in molar volume proposed by Alonso et al. [84] are insignificant and can be neglected. But the volume of the atomic cell changes depending on the charge transfer ($\Delta\varphi$). To take into account the volume change during alloying, de Boer et al. [19] proposed:

$$\frac{\left(V_A^{2/3}\right)_{alloy}}{\left(V_A^{2/3}\right)_{pure\ A}} = \left[1 + af_B^A(\varphi_A^* - \varphi_B^*)\right] \qquad \textit{2-35}$$

Where a is a constant and can be found from experimental volume contractions in compounds. De Boer et al. [19] listed the values of a for different groups of metals. It should be mentioned that Miedema takes into account volume change during alloying while volume is taken as constant in Engel-Brewer method [16-18].

2.4.5 Miedema model for enthalpy of formation or mixing for binary alloys

As will be discussed later in section 2.4.7, from the analysis of the sign of enthalpy of alloy formation for systems involving transition metals alloyed with polyvalent non-transition metals, it turns out to be necessary to add another negative contribution to the enthalpy of formation. Miedema defined this term to be related to hybridization of *d*-type orbitals with *p*-type orbitals [20,71,75,78,80-83]. Values of R for different metals are listed in [19,20,75,81].

Consequently, by introducing the R term, concentration dependence and volume corrections, Miedema et al. [20,71,75,78,80-83] described enthalpy of formation or that of mixing for binary alloys as:

$$\Delta H = \frac{2f(c)\left(c_A V_A^{\frac{2}{3}} + c_B V_B^{\frac{2}{3}}\right)}{{n_{ws}^A}^{-1/3} + {n_{ws}^B}^{-1/3}} \times \left[-P(\Delta\varphi^*)^2 + Q\left(\Delta n_{ws}^{\frac{1}{3}}\right)^2 - R\right] \qquad \textit{2-36}$$

Eqn. 2-36 can be used for compounds and liquid solutions. However, it is not always applicable to solid solutions. When size mismatch for the constituent solid components is significant, eqn. 2-36 by itself does not show consistency with the experimental data. In these cases, elastic contribution originating from size mismatch needs to be considered [19]. Eqn. 2-36 is also used in this study to find enthalpy of mixing for different binary systems.

2.4.6 Miedema model for enthalpy of mixing of solid solutions

Niessen et al. in [90] proposed a formula to estimate the enthalpy of mixing of solid solutions. Enthalpy of solid solution has three contributions as follows [91]:

$$\Delta H^{Solid\ sol.} = \Delta H^{Chemical} + \Delta H^{Elastic} + \Delta H^{Structural} \qquad 2\text{-}37$$

The chemical contribution can be calculated from 2-36. However, for solid solutions the difference in molar volumes has a significant effect on enthalpy of mixing. Therefore, Niessen et al. [91] proposed to take the chemical contribution average value between enthalpy of solution of A in B and that of B in A and hence, Loeff et al. [91] described the chemical contribution as:

$$\Delta H^{Ch.} = c_A c_B \left[c_B \Delta H^{sol.}_{A\ in\ B} + c_A \Delta H^{sol.}_{B\ in\ A} \right] \qquad 2\text{-}38$$

The elastic contribution arises from an elastic energy created when a matrix atom is replaced by a solute atom of different size [92]. This elastic energy is taken from Eshelby-Friedel elastic continuum theory [93,94]. This model explains the elastic contribution with sphere and hole. It means that a spherical hole with volume V_B in the matrix will be partly filled with a volume V_A . Elastic deformation of the matrix and inclusion will force the remaining volume $(V_B - V_A)$ to disappear [19]. Therefore both the matrix and inclusion will be subject to hydrostatic pressure. The pressure on inclusion is related to its bulk modulus (K_A) while the one on the hole is related to effective bulk modulus. Eshelby-Friedel assumed this value as 4/3 times the shear modulus of the matrix. Niessen et al. [90] formulated this contribution as:

$$\Delta H^{el}_{A\ in\ B} = \frac{2S_B(V_A^* - V_B^*)^2}{3V_B^* + 4SK_AV_A^*} \qquad \textit{2-39}$$

Where S_B is shear modulus of the solvent. K_A is compressibility of the solute and V_A^* and V_B^* are molar volumes as corrected using eqn. 2-35.

According to Loeff et al. [91], the same argument for chemical contribution can be applied to elastic contribution. Hence, the elastic contribution to the heat of formation can be written as [91]:

$$\Delta H^{el.} = c_A c_B\left[c_B \Delta H^{el.}_{A\ in\ B} + c_A \Delta H^{el.}_{B\ in\ A}\right] \qquad \textit{2-40}$$

Structural contribution accounts for variation of structure dependent energies. This term can be explained using lattice stability. In a metal, lattice stability changes with the number of valence electrons. Loeff et al. [91] discussed two cases. In the first case, since during alloying, metals make a common d band. Therefore, lattice stability for average number of the valence electrons (which is the most negative of the lattice stabilities of the three energies $(E^{str}_{H.C.P.}(\bar{z}), E^{str}_{B.C.C.}(\bar{z}), E^{str}_{F.C.C.}(\bar{z}))$ is subtracted from a reference lattice stability which is estimated as the linear interpolation between lattice stabilities of pure metals in their equilibrium state. Thus, Loeff et al. [91] proposed that the structural contribution can be formulated as:

$$\Delta H^{struct} = E^{str}(\bar{z}) - E^{ref}(\bar{z}) \qquad \text{2-41}$$

For the second case, there is no common d band (e.g. alloys of transition with noble metals). In this case, first an interpolation is taken between lattice stabilities of all the crystal structures (e.g. $E^{str}_{F.C.C.}(A)$ and $E^{str}_{F.C.C.}(B)$, $E^{str}(z)$) and then $E^{str}(\bar{z})$ is taken as the minimum of the results of interpolations. $E^{ref}(\bar{z})$ is the same as in the previous case.

Bakker et al. [95] suggested another formula for structural enthalpy as follows :

$$\Delta H^{Struct}_{B\ in\ A} = (Z_A - Z_B)\frac{\partial E^{struc}}{\partial Z} + E^{Struct}_{B} - E^{Struct}_{A} \qquad \text{2-42}$$

However, eqn. 2-42 is valid only for the metals with common d band. In this sense, the formulae suggested by Loeff et al. [91] are more general compared to the ones suggested by Bakker et al. [95] since they can be can also be applied to transition metals without common d bands. However, the formulae suggested by Loeff et al. [91], Bakker et al. [95] and Niessen et al. [90] cannot be applied to non-transition metals and hence, for the case of non-transition metals, Miedema model cannot be applied to obtain structural contribution.

Recently, Basu et al. [96] stated that structural difference has negligible effect on the enthalpy of formation of solid alloys. The result of his calculations for enthalpy of mixing of (Zr-Ti-Hf)-(Cu-Ni) alloys show consistency with the experimental data.

2.4.7 Qualitative approach to enthalpy of formation of intermetallic compounds and enthalpy of mixing of solutions

Provided that P and Q are constant for metals A and B, and referring to eqn. 2-36, Miedema et al. [20] suggested that the sign of enthalpy of alloy formation can be defined by the ratio shown in eqn. 2-43:

$$W = \frac{|\Delta\varphi^{*}|}{|\Delta n_{ws}|} \qquad \textit{2-43}$$

If the square root of Miedema models' constants (P and Q) taken from eqn. 2-36 is less than W in eqn. 2-43, then the enthalpy of alloy formation would be negative and vice versa.

Miedema et al. [20,70,71,75,78,82] plotted the $\varphi - n_{ws}$ diagram for three groups of systems; two transition metals, two non-transition metals, and transition metals alloyed with non-transition metals. From the slope of these figures, the amount of $\frac{Q}{P}$ for all of these groups was:

$$\frac{Q}{P} = 9.4\ \frac{volt^{2}}{empirical\ density\ units^{2/3}} \qquad \textit{2-44}$$

This approach can be shown in Figure 2-3. This figure indicates electronegativity versus density for liquid alloys of two non-transition metals. It can be seen that for the majority of the systems the demarcation line is the boundary between positive and negative enthalpy of mixing. It should be mentioned that since for small heat of mixing ($-600\frac{cal}{mol} < \Delta H_{mix} < +600\frac{cal}{mol}$) the sign of heat of mixing cannot be accurately predicted, the + sign in Figure 2-3 is defined as $\Delta H_{mix} > +600\frac{cal}{mol}$ and the - sign as $\Delta H_{mix} < -600\frac{cal}{mol}$. On the other hand, the demarcation curve for transition metals alloyed with non-transition metals, as can be seen in Figure 2-4 is more parabolic. Miedema suggested that this parabolic shape is the effect of the R term and he worked a rather elaborate way for defining R [75,78]. Miedema et al. [75,78] concluded that contrary to $\frac{Q}{P}$, $\frac{R}{P}$ is not universal for all the binary systems, but can be taken constant for each group of non-transition metals in the periodic table. However, for some of non-transition metals, this constant is different in the same group of elements. Moreover, from this analysis, it was concluded that

$$\left(\frac{R^*}{P}\right)_{liq.} = 0.73\left(\frac{R}{P}\right)_{sol.}$$

$\frac{R}{P}$ for different elements is estimated empirically and is listed in [19,20,75,78]. Afterall, $\frac{R}{P}$ is the only term that is not defined clearly in Miedema model.

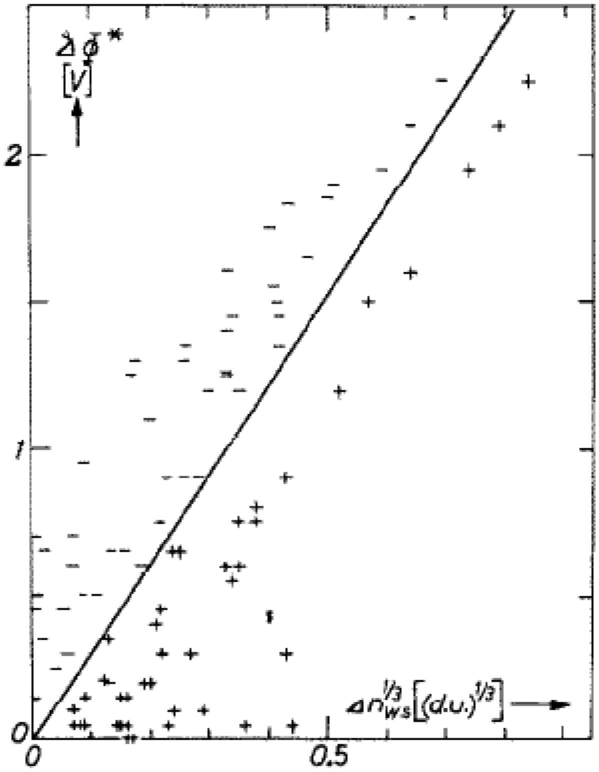


Figure 2-3. The sign of heat of mixing for binary liquid alloys of two non-transition metals at equiatomic composition plotted as a function of $\Delta\varphi^{*}$ *and* Δn_{ws}*. The* $-$ *sign means* $\Delta H_{mix} < -2511\frac{kJ}{mol}(-600\frac{cal}{mol})$ *and the sign + means* $\Delta H_{mix} > 2511\,kJ/mol(+600\frac{cal}{mol})$ *or the solubility of one of the metals is very small at temperatures near 1000K or higher [75]*

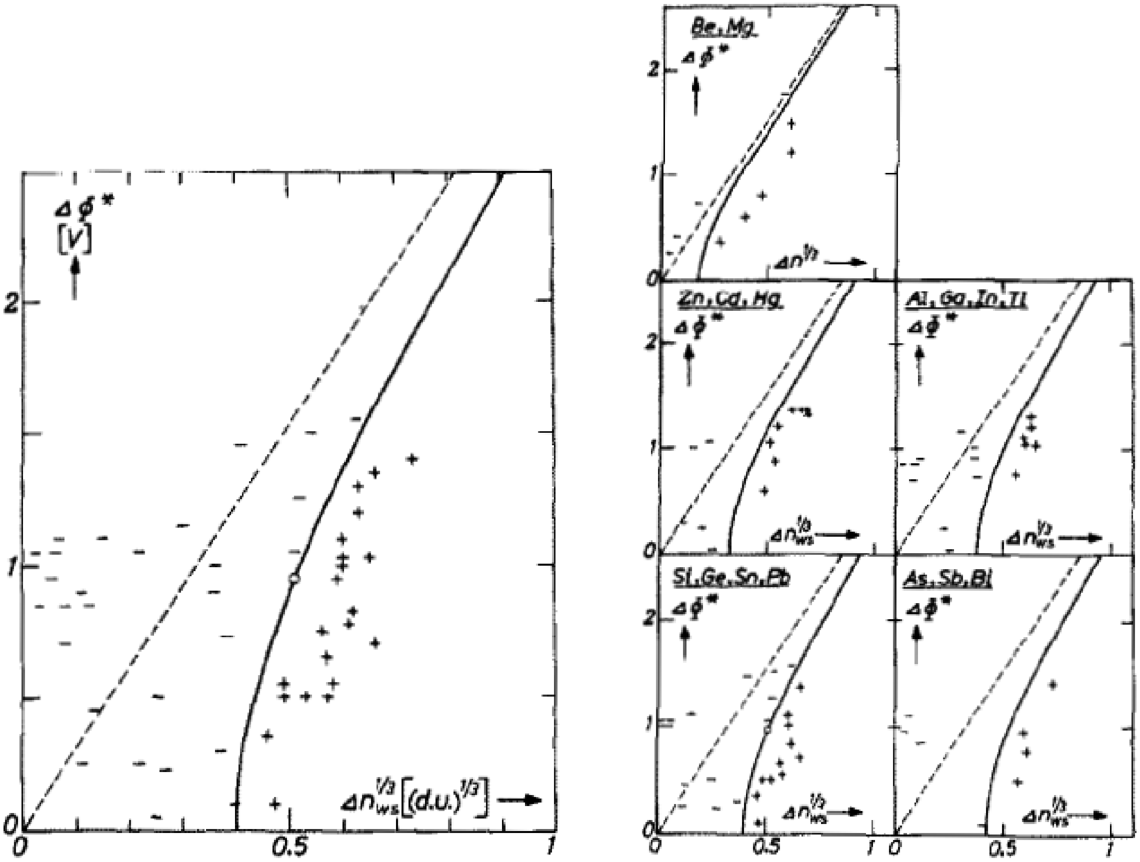


Figure 2-4. The sign of heat of mixing for liquid binary alloys of transition metals with non-transition metals at equiatomic composition. The $-$ *sign means* $\Delta H_{mix} < -2511\frac{kJ}{mol}(-600\frac{cal}{mol})$ *and the + sign means* $\Delta H_{mix} > 2511\frac{kJ}{mol}(+600\frac{cal}{mol})$ *or the solubility of one of the metals is very small at temperatures near 1000K or higher. The dashed line represents chemical contribution without considering the R term and the curve represents chemical contribution after R term. [75]*

2.4.8 Quantitative approach to enthalpy of formation of intermetallic compounds and enthalpy of mixing of solutions

Miedema et al. [92,97,98,99-101] published the result of their calculations in relation to the experimental data for solid solutions, for intermediate compounds [80,81] and for alloys of two transition metals [19,20,92,97,98,99-101].

From available experimental data, Miedema et al. [19] estimated three different values for P. For alloys of two metals with a valence larger than two, $P = 14.2$ and for alloys of two monovalent or divalent metals $P = 10.7$ and for alloys between a metal belonging to the first group ($P = 14.2$) and the other to the second group ($P = 10.7$), the average $P = 12.35$ is applid to eqn. 2-36 in order to calculate heat of mixing of liquid and solid solutions.

2.4.9 Previous works on application of Miedema model

Miedema model has been widely used to calculate the enthalpy of formation of compounds and enthalpy of mixing of solutions. Several years after the publication of the model, Zhang [102] used Miedema model to predict enthalpy of formation of binary amorphous alloys. He found consistency between his results and the experimental data. Combining Miedema model with CALPHAD method, Zhou et al. [103] successfully assessed Fe-Br binary system. Application of the model was not only limited to binary alloys. Zhang et al. [104] presented a simple extended Miedema model for ternary systems and introduced the model to 12 ternary systems. The results were in overall agreement with experiments. Lin et al. [105] calculated formation energies of different solute components in Er-X binary system and Al-Er-X ternary system based on Miedema model and extended Miedema model. Recently, Sun et al. [106] applied Miedema model along with Toops model to calculate glass forming range of some ternary alloys systems. The systems studied are Al-Ni-RE (Ce,La,Y). The results showed consistency with the experimental data. Basu et al. [96] used the model to predict the glass forming ability of some binary and ternary alloys of (Zr,Ti,Hf)-(Cu,Ni).

Moreover, some previous studies modified model parameters (φ^{*}, n_{ws}) and/or model constants $(P, \frac{Q}{P}, \frac{R}{P})$ to find more consistency with the experimental data. Shubin et al. [107] used Miedema model to calculate heats of formation for more than 200 systems of rare-earth metals with p-metals and compared the results with the experimental data. In their study, they made slight changes to model parameters n_{ws} and φ and the constants P and $\frac{R}{P}$. The accuracy of their results is not so high but their calculations can be used as the first estimation. Chen et al. [108] considered the case of Zr alloys where Miedema model failed and comparing the calculated enthalpy with ab-initio calculations and calorimetric data of the intermetallic compounds, they modified the φ parameter of Zr. The heats of formation of Zr-based alloys obtained by their new φ parameter showed more consistency with the experimental data compared to classic Miedema model. Zhang et al. [109] optimized the model parameters for metals by ab-initio HTDM method and found a better consistency compared to classical Miedema model with the experimental data of some binary systems of transition metals.

2.5 Entropy of mixing

“Entropy is a measure of randomness in a system and its microscopic definition in terms of statistic mechanics is based on the number of configurations of the system.” [8]. Calculation of entropy of mixing is more complicated compared to enthalpy of mixing. However, in order to find the phase relations for a system, both enthalpy and entropy of mixing should be obtained.

Entropy of the crystalline elements consists of [27]:

$$S = S^{vib} + S^{elc} + S^{mag} \qquad \textit{2-45}$$

Where S^{vib} is the contribution due to lattice vibrations; S^{elc} is electrical contribution and S^{mag} is the contribution from magnetic moments. Usually, entropy is found from Helmholtz energy by Maxwell equation:

$$S = \left(\frac{\partial F}{\partial T}\right)_V \qquad \textit{2-46}$$

Helmholtz energy is calculated from partition function as follows:

$$F = -k_B T lnQ \qquad \textit{2-47}$$

Where T is the absolute temperature and k_B is the Boltzmann constant. The partition function can be found from [110] as:

$$lnQ = \frac{N\xi}{k_B T} - N \int_0^{\infty} g(\upsilon) \ln\left(1 - e^{\frac{h\nu}{k_B T}}\right) d\nu \qquad \textit{2-48}$$

Where N is Avogadro number, h is the Planck constant, υ is the vibration frequency. $\frac{N\xi}{k_B T}$ represents the zero point energy of the *3N* harmonic oscillators.

Einstein's model considers that all *3N* oscillators vibrate with the same frequency (υ_E), and thus simplifies eqn. 2-48 simplifies to:

$$lnQ = \frac{N\xi}{k_BT} + 3Nln(1 - e^{\frac{-h\nu_E}{k_BT}}) \qquad \textit{2-49}$$

Afterall, vibration entropy can be found from combining eqn. 2-46, eqn. 2-47 and eqn. 2-49 as follows:

$$S = S^{ref} + \ 3Nk_Bln\frac{k_BT}{h\nu_E} + O(\frac{h\nu_E}{k_BT})^2 \qquad \textit{2-50}$$

In eqn. 2-50 and 2-51 $O(\frac{h\nu_E}{k_BT})^2$ represents the remaining part of entropy in taylor series with the power of two or more which is small and can be neglected.

Debye model would lead to a similar formula as eqn. 2-50

$$S^{vib} = S^{ref} + 3Nk_Bln\frac{T}{\Theta} + O\left(\frac{\Theta}{\mathrm{T}}\right)^2 \qquad \textit{2-51}$$

Where Θ is Debye temperature and equals to $\Theta = \frac{\mathrm{h}\nu_\mathrm{D}}{\mathrm{k_B}}$ and ν_D is a cutoff frequency. Randhall et al. [111] listed the values of ν_D.

All the formulae mentioned above are for the vibrational entropy of solids. However, there should be an entropy change during melting. Considering that vibrational entropy of solid is given in terms of its characteristic vibration frequency (eqn.2-51), Mott et al. [112] assumed that a similar formula as eqn. 2-50 can be applied to vibrational entropy of liquids. They proposed that there should be a reciprocal relation between density and frequency and thus they suggested that the entropy increase in melting is explained as [112]:

$$\Delta S = 3/2Nk_B\log\left(\frac{\rho_L}{\rho_S}\right) \qquad 2\text{-}52$$

However, Faber [24] stated that the change in ρ_L and ρ_S is not only dependant on ν_L and ν_S but also on several other factors. Faber [24] suggested that Mott et al. [112] has ignored the configurational entropy during melting which arises from disorder in the rest positions about which the molecules are vibrating. He [24] suggested that this configurational entropy can be estimated using the extra volume introduced upon melting. His proposed formula is shown in eqn. 2-53.

$$S^{Conf} = Nk_B\frac{\Delta\Omega_\mathrm{m}}{\Omega_\mathrm{m}}\left(1 - ln\frac{\Delta\Omega_\mathrm{m}}{\Omega_\mathrm{m}}\right) \qquad 2\text{-}53$$

Where Ω_m is the volume of the liquid phase at melting temperature. As can be seen from eqn. 2-35, this configurational entropy cannot be ignored since even with the small change in $\frac{\Delta\Omega_\mathrm{m}}{\Omega_\mathrm{m}}$, it will amount to $0.2Nk_B$.

Guggenheim [25] discussed that difference in size for the constituent atoms of a binary mixture will lead to configurational contribution to entropy of mixing of the system. He developed a formula to calculate entropy of mixing based on lattice sites and coordination number. Assuming A atoms occupy γ_1 lattice sites and B atoms occupy γ_2 lattice sites:

$$\frac{\Delta S}{Nk_B} = -c_A \ln\left(\frac{c_A}{c_A+\gamma c_B}\right) - c_B \ln\left(\frac{\gamma c_B}{c_A+\gamma c_B}\right) - 1/2zq_A c_A \ln\left(\frac{c_A+\gamma c_B}{c_A+qc_B}\right) - 1/2zq_B c_B \ln\left(\frac{c_B+\frac{c_A}{\gamma}}{c_B+\frac{c_A}{q}}\right) \qquad 2\text{-}54$$

Where $\gamma = \frac{\gamma_2}{\gamma_1}$ and $q = \frac{q_2}{q_1}$ and q is related to z (the coordination number) by

$$\gamma_i = 1 + 1/2z(\gamma_i - q_i) \qquad 2\text{-}55$$

The relation proposed by Guggenheim [25] assumes no energetic effect. Whereas, the question is raised whether the effect of energy on entropy of mixing can be ignored. In chapter 4, a simplified form of eqn. 2-54 is applied to different binary liquid solutions and the results are compared with the experimental data from the literature.

Going back to eqn. 2-45, the electronic contribution in eqn. 2-45 arises from electronic heat capacity contribution and is formulated as [27]:

$$S^{el} = \int_0^T \gamma dT \qquad 2\text{-}56$$

Where γ is the electronic heat capacity constant and finally the magnetic contribution arises from the magnetic moments. Swalin [113] proposed this contribution as:

$$S^{mag.} = Nk_B \ln(\mu + 1) \qquad 2\text{-}57$$

Where μ is the average magnetic moment per atom. Electronic and magnetic contributions originate from electronic scale while vibrational contribution and configurational contribution originate from interatomic and atomic scales, respectively.

In the literature, there are several studies on correlating the entropy of mixing to other thermophysical properties. Faber [24] attempted to correlate entropy of mixing with molar volume. His formula for entropy of mixing can be written as:

$$\Delta S^{xs} = c_A c_B (\Omega_B - \Omega_A)(\frac{\alpha_A}{\kappa_A} - \frac{\alpha_B}{\kappa_B}) \qquad \textit{2-58}$$

Where α_i is the coefficient of thermal expansion and κ_i is the isothermal compressibility of the element. Faber formula (eqn. 2-58) is used in this study to find entropy of mixing of different binary liquid solutions. Kleppa [26] suggested a method to calculate excess volume of mixing and applied his method to five binary systems. He compared the results with available information on excess entropy of mixing and concluded that 70% of entropy of mixing can be attributed to excess volumes of mixing.

In some other studies, an attempt has been made to correlate entropy of mixing with enthalpy of mixing. Tanaka et al. [28] based on free volume theory, derived a formula for entropy of mixing for liquid binary alloys as:

$$\Delta \bar{S}_i^{xs} = \frac{\frac{1}{T_A^m} + \frac{1}{T_B^m}}{14} \Delta \bar{H}_i \qquad \textit{2-59}$$

Their calculated values [28] were reported to be in good agreement with available experimental data. Kubachenski [29] showed that there is a linear relationship between

$\Delta S_{max}^{xs}/R$ and $(2\Delta H_{max}/T_A^b + T_B^b)$ where ΔS_{max}^{xs} and ΔH_{max} are the maximum absolute values of excess entropy and integral enthalpy of formation and T_i^b is the boiling point of element *i*. Spencer [114] showed that the plot of partial enthalpy versus partial excess entropy of formation both, at infinite dilution for 150 liquid and solid solutions results in a linear relation. Witusiewicz [30] suggested that, if a relation exists between excess entropy of mixing and enthalpy of mixing for binary alloys for infinite dilute solutions or for maximal points, then similar relations will be applicable for the whole concentration range. He generalized the experimental data for thermodynamic functions for the formation of binary 3d transition metal-metalloid liquid alloys and reproduced partial and integral enthalpy of mixing by a self-consistent series representation and finally obtained an empirical relation for excess entropy of mixing for these systems as follows [30]:

$$\Delta S^{xs} = 6Rc_A c_B \left(\frac{\bar{T}^m}{\bar{T}^b}\right)^{\frac{5}{2}} + 4\frac{\bar{T}^m}{(\bar{T}^b)^2}\Delta H \qquad \textit{2-60}$$

The least squares analysis was then carried out resulting in eqn.2-60 to describe the experimental data for systems of transition metals-metalloids with a standard deviation of $4.7\frac{J}{mol.K}$.

Following the same procedure, Witusiewicz et al. [31] based on reliable experimental enthalpy data, modified eqn. 2-60 to estimate entropy of mixing of different types of liquid alloys.

$$\Delta \bar{S}^{xs}(x,T) = \Omega\left[\frac{\Delta H(x,T)}{T} + x(1-x^2)RP_T\right] \qquad \textit{2-61}$$

Where

$$\Omega = \frac{1}{2\pi}\left(\frac{\overline{\mathrm{T}}_{\mathrm{m}}}{\overline{\mathrm{T}}_{\mathrm{b}}} + 1\right)^{\mathrm{e}} \qquad 2\text{-}62$$

$$P_T = \frac{1}{2} + \frac{4\overline{\mathrm{T}}_{\mathrm{m}}}{3T} + 2\ln\left(\frac{T}{\overline{\mathrm{T}}_{\mathrm{b}} - \overline{\mathrm{T}}_{\mathrm{m}}}\right) \qquad 2\text{-}63$$

His estimations were then compared with the experimental data of 30 systems and it was concluded that eqn. 2-61 describes the experimental data with a standard deviation of $5.3 \frac{j}{mol.K}$. In addition, from eqn. 2-61, a relationship for estimation of excess heat capacities were derived which showed standard deviation of $3.8 \frac{j}{mol.K}$ from the experimental data of more than 40 binary systems. The empirical relation proposed by Wituciewicz et al. [31] (eqn. 2-61) has the advantage that since it takes into account energy effect, it can be used to find excess heat capacity as well.

Sommer [27] developed a relationship for excess entropy of formation of liquid alloys based on physical properties of the components and some empirical constants. In his formula, he solely considered ΔS^{vib} and ΔS^{conf}. He derived ΔS^{conf} from Guggenheim’s formula. Sommer’s formula is then used to calculate entropy of mixing for around 100 binary systems. Except for alloys containing components with magnetic properties, the results were in a good agreement with the experimental data. Contrary to Wituciewicz [31], Sommer [27] proposed a theoretical relation for entropy of mixing which takes into account both energy and volume effects. In this sense, Sommer’s formula can be more reliable. However, he used several empirical formulae for properties of alloys which can reduce its accuracy. Wituciewicz [31] and Sommer [27] relations are compared later in Chapter 4.

Chapter 3

Research Methodology

3.1 Thermodynamic modeling

Phase diagram is a graphical representation of equilibrium relationships among phases. These phase relationships should be based on thermodynamic laws [115]. Gibbs free energy relates thermodynamics to phase equilibria. Minimization of the Gibbs energy can then be used as a guideline for phase stability. In other words, in order to calculate the phase equilibria, the total Gibbs free energy of all the phases taking part in equilibria should be minimized [1].

For a pure element, Gibbs free energy is dependent on temperature, pressure and average magnetic moment per atom. The temperature dependency of the Gibbs free energy is derived from specific heat capacities. Dinsdale [116] represented specific heat capacities at constant pressure for pure elements by an empirical polynomial indicated in eqn. 3-1.

$$C_P(T) = a + b \times T + c \times T^2 + d \times T^{-2} + e \times ln(T) + \sum_{n>2} a_n \times T^n \qquad \textit{3-1}$$

Where a, b, c, d, e, a_n are empirical constants. Then, the change in enthalpy and entropy can be calculated as:

$$\Delta H = \int_{298}^{T} C_p dT \qquad 3\text{-}2$$

$$\Delta S = \int_{0}^{T} \frac{C_p}{T} dT \qquad 3\text{-}3$$

And Gibbs free energy can be calculated as follows:

$$\Delta G = \Delta H - T\Delta S \qquad 3\text{-}4$$

Therefore, using eqns 3-1 to 3-3, Gibbs free energy for pure elements at constant pressure can be obtained as follows:

$$G_i(T) = a + b \times T + c \times T \times ln(T) + \sum_{\mathrm{n}=1}^{\mathrm{m}} d_n \times T^n \qquad 3\text{-}5$$

Where T is the absolute temperature.

Gibbs free energies of pure elements and sometimes pressure and magnetic contribution are listed in Dinsdale [116]. In this work, Gibbs free energy for the unary phases is taken from the same reference [116].

For a multi-component system, Gibbs free energy depends not only on temperature, pressure, magnetic moment, but also on concentration. When phase diagram is calculated at constant pressure and no ferromagnetic, anti-ferromagnetic and ferri-magnetic properties exist in the system, pressure and magnetic contributions can be neglected [117]. Finally, the concentration dependence of the Gibbs energy of a phase for a multi-component system can be described as:

$$G^{\varphi} = G^{0} + G^{ideal} + G^{ex} \qquad 3\text{-}6$$

Where, G^{0} corresponds to the contribution from mechanical mixing of the pure components, G^{ideal} is the entropy of mixing for an ideal solution and G^{ex} is the excess Gibbs free energy term which arises from deviation from ideality. Considering a binary system with A and B as constituent components, eqn. 3-6 can be rewritten as:

$$G^{\varphi} = x_A G_A^0 + x_B G_B^0 - RT(x_A ln x_A + x_B ln x_B) + G^{ex} \qquad 3\text{-}7$$

Where x_i is the concentration of component i and G_i^0 is Gibbs free energy of pure component i at standard state. Afterall, the most complicated part of thermodynamic modeling is to find excess Gibbs free energy (G^{ex}). Excess Gibbs free energy is defined as:

$$G^{ex} = H^{ex} - TS^{ex} \qquad 3\text{-}8$$

Where H^{ex} and S^{ex} are excess enthalpy and excess entropy of mixing respectively. Several structural models such as regular solution model [22] and ionic liquid model [118] for disordered solutions, compound energy formalism [119] for ordered solution phases can be used to calculate Gibbs free energies of different phases. Since Engel-Brewer method has used regular solution model to describe the excess Gibbs energy of mixing, in the following part, this model is introduced more elaborately.

3.1.1 Regular solution model

Regular solution model is based on random distribution of atoms. In this model, enthalpy of mixing only depends on the bonds formed between adjacent atoms. For this assumption to be valid, volume of pure A and pure B should be equal and should not change during mixing so that bond energies and interatomic distances are independent of composition [120]. Thus, enthalpy of mixing can be found by estimating bonding energies and counting nearest neighbor bonds when the atoms are mixed randomly. The entropy of mixing for regular solution model is assumed to be zero. Therefore, calculation of the enthalpy of mixing can provide the Gibbs free energy of mixing. This model is explained elaborately in section 2.1. In the first part of this study, modified regular solution model in the form of Engel-Brewer method is used to calculate phase equilibria.

Usually, binary liquid and disordered solid solutions are described as random mixtures and their Gibbs free energies are represented by Redlich-Kister polynomial [121] as follows:

$$G^{ex} = x_i x_j \sum_{n=0}^{k} ({}^{n}L^{\varphi}_{i,j}\left(x_i - x_j\right)^{n}$$

3-9

With

$${}^{n}L^{\varphi}_{i,j} = a_n + b_n T \ \ , n = 0, \dots, m$$

3-10

Where ${}^{n}\,L_{i,j}^{\varphi}$ are the interaction parameters and a_n and b_n are the model parameters. When $L_{i,j}^{\varphi}$ is constant and independent of temperature, one talks about regular solution whereas when $L_{i,j}^{\varphi}$ is dependant on temperature ($b_n \neq 0$), the solution is called subregular.

Using CALPHAD method, the model parameters (a_n,b_n) can be optimized with respect to experimental phase diagram and thermodynamic data. On the other hand, for a subregular solution model, comparing eqn. 3-8 and 3-10, then a_n and b_n can be taken equal to H^{ex} and $-S^{ex}$, respectively. Therefore, the model parameters (a_n, b_n) can be found by application of different theoretical or empirical models to find excess enthalpy and entropy of mixing.

In the first part of this study, model parameters (a_i in eqn. 3-10 are calculated using Engel-Brewer method.

3.1.2 Estimation of excess Gibbs energies of mixing by Engel-Brewer method

Hildebrand [22,23] introduced a regular solution model with solubility parameter ($\frac{\Delta H^{vap}}{V}$) for van der Waals molecules. Hildebrand formula has been discussed elaborately in section 2.1. Using Engel theory [41,42], Brewer extended Hildebrand formula to metals. He changed ΔE^{vap} in the formula to ΔE^{*} which is energy of vaporization to the gaseous atom with the same valence state of the condensed solid [43,50]. In addition, he used Redlich-Kister polynomial [121] to represent excess Gibbs energy of mixing.

In this study, eqn. 1-10 and eqns 2-20 to 2-18 are used to estimate Gibbs energies of mixing for five binary systems with positive deviation from ideality. Since Brewer focused mostly on alloys of transition metals and actinides [17,47,48,57,58], three actinide binary systems and one transition metal binary system are analyzed in this thesis. The first system is Ag-Cu with two transition metals. Then, Engel-Brewer method is examined for Al-Ga which has filled *d* orbitals for both elements. Finally, the model is used to predict phase diagrams and thermodynamic properties of light actinides (Np-Pu,Np-U, Pu-U) for which the experimental data are usually scarce.

Molar volumes and energies of vaporization to the gaseous valence state used for calculations are listed in Table 3-1. The values obtained from eqns 2-20 to 2-24 are collected in a database. In this database the amount of excess entropy of mixing is assumed to be zero. Afterwards, phase diagrams and thermodynamic properties such as enthalpy and entropy of mixing are calculted by importing the excess parameters to FactSage program [126]. The results for phase equilibrium and thermodynamic properties are then compared with CALPHAD assessments and the experimental data. For systems Ag-Cu and Al-Ga, SGTE database [127] and for actinide systems, optimized databases of Kurata [128,129] are used as CALPHAD assessment.

Table 3-1. Molar volumes and energies of vaporization to the gaseous valence state for Cu, Al, Ga, Np, Pu and U pure elements. Molar volumes for the liquid phases are taken at their melting point.

Element	Phase	V (g/cm^3)	Ref.	ΔE^* (kJ/mol)	Ref.
Ag	Liquid	11.56	[122]	823.328	[52]
	F.C.C.	10.28	[123]	840.984	[51]
Al	Liquid	11.29	[122]	661.047	[52]
	F.C.C.	9.96	[123]	674.042	[51]
Cu	Liquid	7.91	[122]	800.608	[52]
	F.C.C.	7.11	[123]	820.064	[51]
Ga	Liquid	11.81	[122]	720.736	[52]
	F.C.C.	11.43	[123]	725.506	[51]
Np	Liquid	13.1	[55]	708.770	[52],[48]
	B.C.C.	14.78	[124]	736.384	[51],[48]
Pu	Liquid	14.64	[122]	545.552	[52],[48]
	B.C.C.	13.1	[124]	554.798	[51],[48]
U	Liquid	13.78	[122]	767.910	[52],[48]
	B.C.C.	12.23	[125]	790.776	[51],[48]

3.1.3 Estimation of Gibbs energy with Miedema model and an entropy model

Another approach that is used in the second part of this work is to obtain enthalpy of mixing and entropy of mixing using empirical or theoretical relationships. Enthalpy of mixing is calculated using Miedema model and entropy of mixing is estimated using Faber [24], simplified Guggenheim [27], Sommer [27] and Wituciewicz et al. [31] relations.

3.1.3.1 Calculation of enthalpy of mixing using Miedema model

In this study, Miedema model is used to calculate enthalpy of mixing for disordered solution phases. Miedema model is explained in section 2-1. For liquid alloys eqns 2-36 , 2-32 and 2-35 are used to calculate enthalpy of mixing.

For solid solutions, an elastic contribution arises from an elastic energy created when a matrix atom is replaced by a solute atom of different size [92]. This contribution which is described in eqns 2-39 and 2-40 is then added to the chemical contribution obtained by eqn. 2-36 to give the total enthalpy of mixing of solid solutions. Electronegativities (φ), electron densities at the boundary of Wigner-Seitz cell (n_{ws}) and volumes of the pure solid elements (V) are taken from de Boer et al. [19]. Bulk and rigidity moduluii for solid metals used in eqn. 1-40 to calculate elastic contribution are listed in Table 3-2.

As discussed earlier, in the semi-empirical model of Miedema $P, Q/P$ and R/P are adjustable parameters. Miedema et al. [19,20,75,78] defined these parameters as follows:

Q/P equals to 9.4 $\left(\frac{V^2}{(du)^{2/3}}\right)$ and is constant for all groups of binary alloys

P equals to 14.1 if both of the elements have valences less than two. It is equal to 10.7 when both of the elements have valences larger than two. For the case of one element with less than two valence electrons and the other one with more than two valence electrons, the average value of 12.35 is used.

R/P for compounds and solid solutions can be found from the tables of de Boer et al. [19]. According to the sign of experimental enthalpy of mixing, they have assigned different values to different elements. For the liquid solutions, de Boer et al. [19] proposed:

$$R_{liq.} = 0.73 \times R_{Sol.} \qquad 3\text{-}11$$

Miedema et al. [20,71,75,78,80-83] applied these parameters to all systems of alloys. However, these parameters are changed in some previous works such as Zhang et al. [109] and Shubin et al. [107] 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 change the value of the parameters for each group to find the best consistency with the experimental data.

3.1.3.2 Calculation of excess entropy of mixing using Miedema model

Excess entropy of mixing for liquid alloys have been studied in previous works which were mentioned in section 2.5. However, very little work has been done on entropy of mixing for solid solutions. Therefore, this study focuses on finding an appropriate relationship for excess entropy of mixing for liquid alloys.

In the previous works [24-31], two approaches have been used to calculate excess entropy of mixing of liquid alloys. In the first approach, the deviation of entropy of mixing from ideality is taken just as the result of volume change during alloy formation. Faber [24] and Guggenheim [25] can be categorized in this group. In the second approach, excess entropy of mixing is considered as the result of energetic effect.

Wituciewicz et al. [31] is one of the examples of this group. Sommer [27] takes into account both energetic and volumetric effects to estimate excess entropy of mixing of liquid alloys.

Faber [24] proposed a relationship for entropy of mixing of liquid alloys which is described as:

$$\Delta S^{xs} = c_A c_B (\Omega_B - \Omega_A) \left(\frac{\alpha_A}{\kappa_A} - \frac{\alpha_B}{\kappa_B} \right) \qquad 3\text{-}12$$

Where α and κ are coefficient of themal expansion and isothermal compressibility of the constituents.

Guggenheim [25] suggested a correlation between excess entropy of mixing and volume change which is described in eqn. 2-54. Sommer [27] assumed long-range ordering for liquid alloys and thus he assumed the coordination number as $z \rightarrow \infty$. In addition, for simplicity, he assumed $\gamma_B/\gamma_A = \Omega_B/\Omega_A$. Hence, he simplified eqn. 2-54 as [27]:

$$\frac{\Delta S}{Nk_B} = -\sum c_i ln c_i - \sum c_i ln \Omega_i + \ln \sum c_i \Omega_i \qquad 3\text{-}13$$

Sommer [27] considered the excess entropy of mixing for liquid alloys as the summation of vibrational and configurational contributions. His formula is as follows [27]:

$$\Delta S^{xs,l}(c,T) = Rln\frac{c_i\Omega_{l,i}}{\prod_i \Omega_{l,i}^{c_i}} + \frac{1}{\sum_i c_i\Omega_i}c_Ac_B\left[3 - 20abs\left(n_{ws,A}^{\frac{1}{3}} - n_{ws,B}^{\frac{1}{3}}\right) - \frac{1}{3(\Phi_A^* - \Phi_B^*)^2}\right]$$

$$+ \frac{2}{\sum_i c_i T^{b,i}}Rc_Ac_BT\left(\frac{\Omega_{l,B} - \Omega_{l,A}}{\sum_i c_i\Omega_{l,i}}\right) \qquad 3\text{-}14$$

$$+ 3R\left[ln\prod_i \Theta_{l,i}^{c_i} - ln\left\{\sum_i c_i\Theta_{l,i} + 34.1 \times 10^{-3}(-\Delta H_{Miedema}R^{-1}\right\}\right]$$

Where Ω is the molar volume, c is the atomic composition and Θ_l is the debye-like temperature for liquid alloys. Sommer [27], for this model, used several empirical assumptions. He used positive excess entropy data near equiatomic composition to find the right hand sides of eqns 3-15 and 3-16.

$$\frac{\alpha_{l,alloy}}{\kappa_{l,alloy}} = \frac{1}{\sum c_i\Omega_i} \qquad 3\text{-}15$$

$$\alpha_{l,alloy}\left(\frac{\kappa_{l,B} - \kappa_{l,A}}{\kappa_{l,alloy}}\right) = \frac{1}{\sum c_i\Omega_i} \qquad 3\text{-}16$$

Where κ is the isothermal compressibility and α is the coefficient of thermal expansion. The value of isothermal compressibility and coefficient of thermal expansion for different solid metals are listed in Table 3-2.

Moreover, Sommer [27] introduced debye like temperature for the liquid phase as:

$$\Theta_{l,alloy} = \sum c_i\Theta_{l,i} + \Delta\Theta_{l,alloy} \qquad 3\text{-}17$$

Where he defined $\Delta\Theta_{l,alloy}$ empirically as follows [27]:

$$\Delta\Theta_{l,alloy} = 34.1 \times 10^{-3}(\Delta H_{Miedema} R^{-1}) \qquad \textit{3-18}$$

The first and second terms in eqn. 3-14 account for configurational contribution. The first term is obtained from Guggenheim relation (eqn. 3-13) and the second term from Maxwell's equation combined with Miedema's relation for volume change during alloy formation (eqn. 2-35). The third term accounts for energetic contribution and is obtained from Flory's expression [130] and the last term is the vibrational contribution taken from Debye theory.

In addition to all these theoretical formulae, Wituciewicz et al. [31] proposed an empirical relationship between entropy of mixing and enthalpy of mixing for liquid alloys as follows:

$$\Delta\bar{S}^{xs}(x,T) = \Omega\left[\frac{\Delta H(x,T)}{T} + x(1-x^2)RP_T\right] \qquad \textit{3-19}$$

$$\Omega = \frac{1}{2\pi}\left(\frac{\overline{\mathrm{T}}_{\mathrm{m}}}{\overline{\mathrm{T}}_{\mathrm{b}}} + 1\right)^{\mathrm{e}} \qquad \textit{3-20}$$

$$P_T = \frac{1}{2} + \frac{4\overline{\mathrm{T}}_{\mathrm{m}}}{3T} + 2\ln\left(\frac{T}{\overline{\mathrm{T}}_{\mathrm{b}} - \overline{\mathrm{T}}_{\mathrm{m}}}\right) \qquad \textit{3-21}$$

Where T_m and T_b are melting and boiling temperature of the constituents and Ω and P_T are functions of melting and boiling temperatures as described in eqns. 3-20 and3-21.

In this work, Faber relation (eqn. 3-12), simplified Guggenheim relation (eqn. 3-13), Sommer relation (eqns 3-14 to 3-18) and the relation proposed by Wituciewicz et al. (eqns 3-19 to 3-21) are used to estimate entropy of mixing for liquid alloys of 49 binary systems at equiatomic composition. The results are then compared with the experimental data to find the most reliable relation for the excess entropy of mixing of liquid alloys. The physical properties required for the calculations are summarized in Table 3-2 and Table 3-3.

Table 3-2. Bulk and rigidity modulus for pure solid metals

Element	Bulk Modulus, K (Gpa)	RigidityModulus, G (Gpa)	Ref.
Ag	103.6	30.3	[131]
Au	171	26	[131]
Al	75.2	26.2	[131]
Cd	51	24	[131]
Cr	160.2	115.3	[131]
Cu	137.8	48.3	[131]
Fe	169.8	81.6	[131]
Ga	62	6.67	[132,133]
Mn	120	79.5	[131,133]
Mo	230	66	[131,133]
Nb	170.3	37.5	[131]
Ni	177.3	76	[131]
Pb	45.8	5.59	[131]
Pd	187	43.6	[131]
Pt	276	60.9	[131]
Tl	28.5	2.71	[131]
V	158	46.7	[131]
Zn	69.4	41.9	[131]

Table 3-3. Physical properties of pure liquid metals

Element	Volume expansion coefficient $\alpha \times 10^5\ 1/K$ [24,122]	Bulk modulus, $K(\ Gpa)$ [134]	$V_L(cm^3/mol)$ [27,135, 136]	Liquid Debye temperature$\theta_{D,l}\ (K)$ [27,135, 136]	Boiling point,$T_b\ (K)$ [133]	Melting point,$T_m\ (K)$ [133]
Ag	9.70	72.60	11.56	164.10	2435	1234.9
Al	12.20	49.70	11.29	294.00	2792	933.5
Au	0.83	114.40	11.36	121.60	3129	1337.3
Bi	11.00	26.98	20.83	86.90	1837	544
Cd	15.10	40.70	14.06	143.20	1040	594.2
Cu	10.00	95.70	7.91	244.40	3200	1357
Fe	12.40	124.22	7.82	364.70	3134	1811
Ga	12.60	48.70	11.82	233.60	2477	302.9
Ge	11.70	39.80	13.24	273.00	3093	1211.4
Hg	17.80	31.25	14.65	51.20	629.9	234
In	12.00	38.31	16.36	82.80	2345	429.7
Li	23.70	10.68	13.48	275.20	1615	453.6
Mg	16.60	26.26	15.29	289.40	1363	923
Na	27.50	6.07	24.17	124.20	1156	370.8
Ni	13.00	129.21	7.52	324.70	3186	1728
Pb	12.70	35.11	19.57	80.60	2022	600.6
Pu	9.22	23.80	14.65	96.40	3503	912.5
Sb	9.60	107.00	20.04	154.00	1860	903.8

Table 3.3. Continued.

Element	Volume expansion coefficient $\alpha \times 10^5\ 1/K$ [24,122]	Bulk modulus, $K(\ Gpa)$ [134]	$V_L(cm^3/mol)$ [27,135, 136]	Liquid Debye temperature$\theta_{D,l}\ (K)$ [27,135, 136]	Boiling point,$T_b\ (K)$ [133]	Melting point,$T_m\ (K)$ [133]
Si	14.30	38.80	11.13	471.00	3173	1687
Sn	8.80	42.34	17.02	118.90	2875	505.1
Tl	14.00	30.55	18.21	61.40	1746	577
U	9.35	76.11	13.78	124.10	4200	1405.3
Zn	15.00	53.22	9.98	226.60	1180	692.7

Chapter 4

Results and Discussion

4.1 Application of Engel-Brewer method to thermodynamic modeling of binary systems

The results of the phase diagrams calculated with Engel-Brewer method, their comparison with modified Engel-Brewer database, CALPHAD method and the experimental data are shown in Figure 4-1 to Figure 4-5. The invariant points or some liquidus and solidus points for these 5 binary systems are listed in Appendix A-1. It should be mentioned that in order to improve the consistency of Engel-Brewer method with the experimental phase diagram data and thermodynamic properties, the original Engel-Brewer equation has been modified. In this regard, promotion energies are changed and entropy parameters are added to the Redlich-Kister equation (eqn. 3-9 and 3-10) to reproduce the phase diagrams reported by Kurata [128,129] and SGTE [116]. In all the figures of this section (Figure 4-1 to Figure 4-20), the results after the modifications mentioned above, are referred to as “Modified”. Modified Engel-Brewer database will be discussed elaborately later in this section.

From Figure 4-1 to Figure 4-5, it can be seen that for all of the systems except Np-U, Engel-Brewer method was not able to predict the phase diagram. It can be seen from Figure 4-1 that Ag-Cu is a simple binary eutectic system with two terminal solid solutions. The phase diagram of this system has a large area of solid immiscibility gap.

Therefore, it can be expected that enthalpy of mixing for the solid solutions is large and positive. As can be seen in Figure 4-1, the liquidus line predicted by Engel-Brewer method is not far above the one calculated using CALPHAD assessment but the solid immiscibility gap needs to be shifted up to form the eutectic point. Therefore, for this system Engel-Brewer method was not even able to predict the general shape of the phase diagram. For the Al-Ga system, as can be seen from Figure 4-2, Engel-Brewer method was able to predict the eutectic point very close to that from the CALPHAD assessment. However, the maximum solid solubility for the Engel-Brewer method prediction is at 72 at% Al which shows a great difference from the CALPHAD assessment.

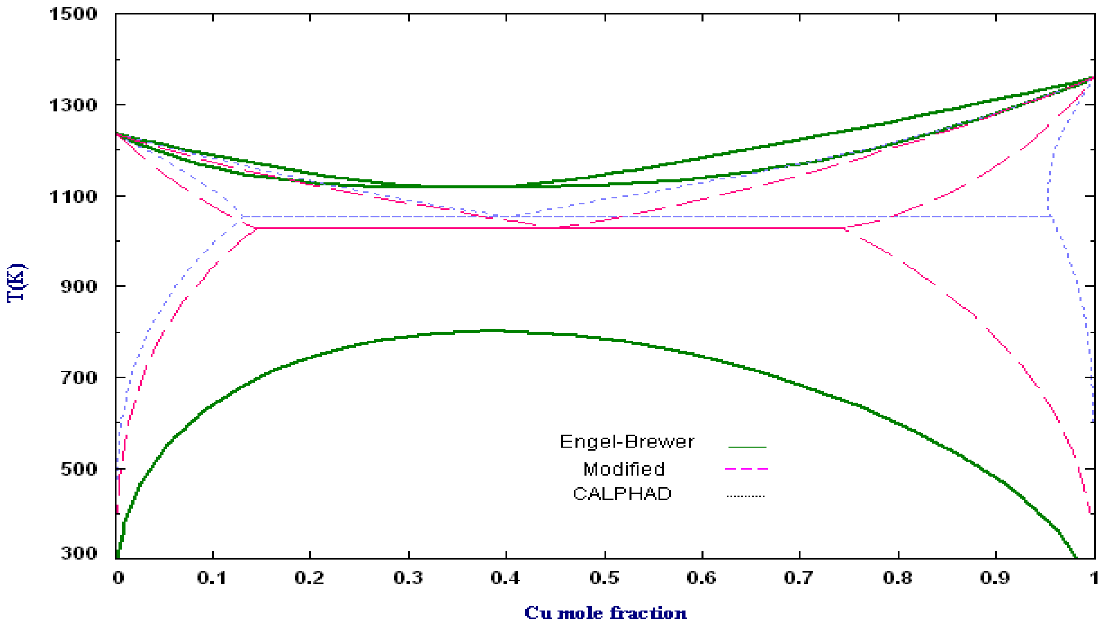


Figure 4-1. Phase diagram of the Ag-Cu system predicted by Engel-Brewer method __ compared with the phase diagram obtained by modifying enthalpy parameters of Engel-Brewer method and adding entropy parameters to the Redlich-Kister equation - - - and CALPHAD results taken from SGTE database [116] ....

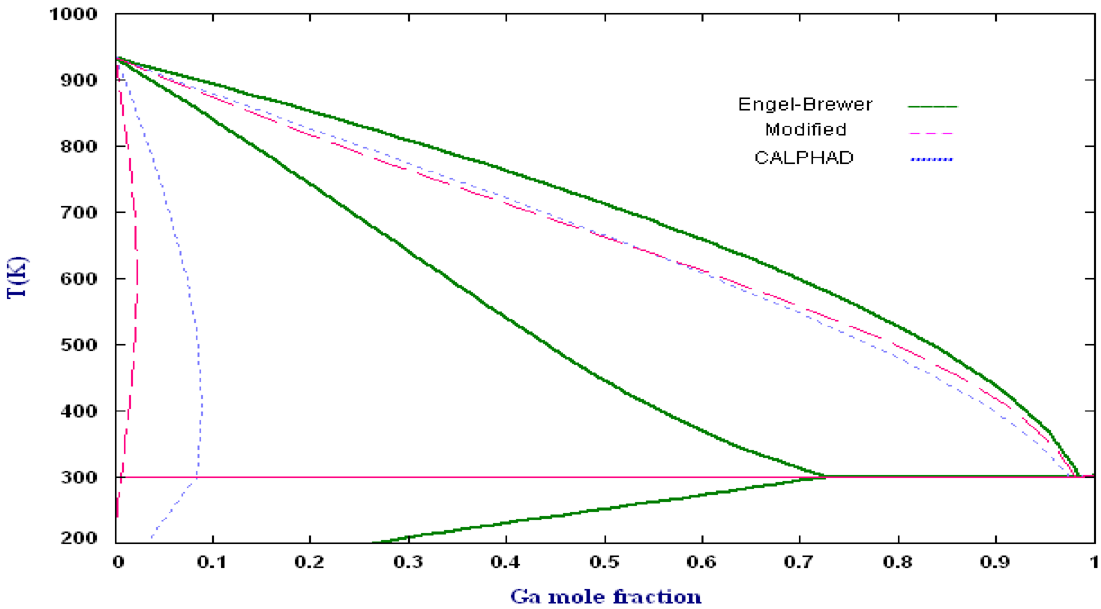


Figure 4-2. Phase diagram of the Al-Ga system predicted by Engel-Brewer method — *compared with the phase diagram obtained by modifying enthalpy parameters of Engel-Brewer method and adding entropy parameters to the Redlich-Kister equation* - - - *and CALPHAD results taken from SGTE database [116]* ....

Moreover, for this system liquidus line is shifted higher than the CALPHAD assessment. Engel-Brewer prediction was not successful even for light actinides except for the Pu-U system. As can be seen in Figure 4-3, the phase diagram developed by Engel-Brewer method for the Pu-U system is far above the experimental data of Peterson et al. [137]. At *x=20* at% U, the solidus and liquidus points are overestimated about 300K and 445K compared to the experimental data of Peterson et al. [137]. At *x=80* at% U, the difference is 203K and 292K for the solidus and liquidus lines predicted by Engel-Brewer method in relation to the experimental data of Peterson et al. [137].

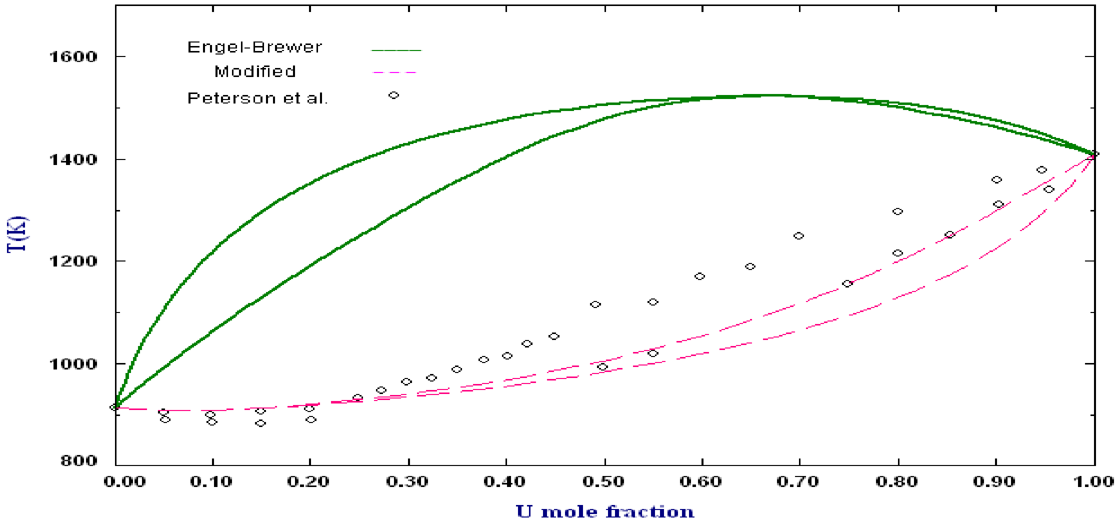


Figure 4-3. Phase diagram of the Pu-U system predicted by Engel-Brewer method — *compared with the phase diagram obtained by modifying enthalpy parameters of Engel-Brewer method and adding entropy parameters to the Redlich-Kister equation* - - - *and the experimental data of Peterson et al. [137]* ○

For the Np-Pu system, it can be seen from Figure 4-4 that Engel-Brewer method underestimated the liquidus and solidus lines. At *x=50* at%, the difference between liquidus and solidus temperatures for Engel-Brewer prediction compared to the experimental data of Mardon et al. [138] is 111K and 121K, respectively. The only case for which Engel-Brewer method was able to successfully predict the phase diagram was the Np-U system. For this system, the prediction of Engel-Brewer method is close to the experimental data of Mardon et al. [139]. However the phase diagram is shifted down compared to the results of Mardon et al. [139]. From Figure 4-5, it can be seen that at *x=30* at% U, the liquidus line is 40K below the data reported by Mardon et al. [139] and the solidus line is 60K below experimental results of Mardon et al. [139]. and at *x=50* at% U, the difference between the solidus line predicted by Engel-Brewer method and the data of Mardon et al. [139] reaches 50K. The results of the enthalpy of mixing obtained by Engel-Brewer method for these five binary systems are depicted in Figure 4-6 to Figure 4-15 and listed in Appendix A-2. For the Ag-Ca and Al-Ga systems, enthalpies of mixing for solid and liquid solutions are underestimated while for all the actinides, they are overestimated.

The results of the enthalpy of mixing obtained by Engel-Brewer method for these five binary systems are depicted in Figure 4-6 to Figure 4-15 and the parameters are listed in Appendix A-2. For the Ag-Ca and Al-Ga systems, enthalpies of mixing for solid and liquid solutions are underestimated while for all the actinides, they are overestimated.

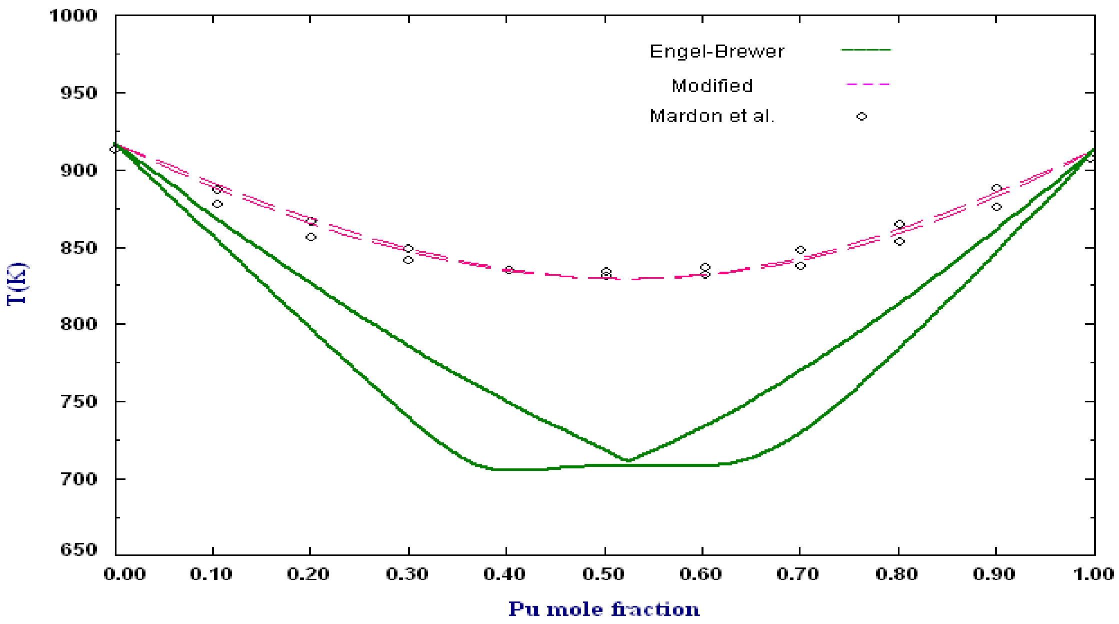


Figure 4-4. Phase diagram of the Np-Pu system predicted by Engel-Brewer method — *compared with the phase diagram obtained by modifying enthalpy parameters of Engel-Brewer method and adding entropy parameters to Redlich-Kister equation* --- *and the experimental data of of Mardon et al. [138]* ○

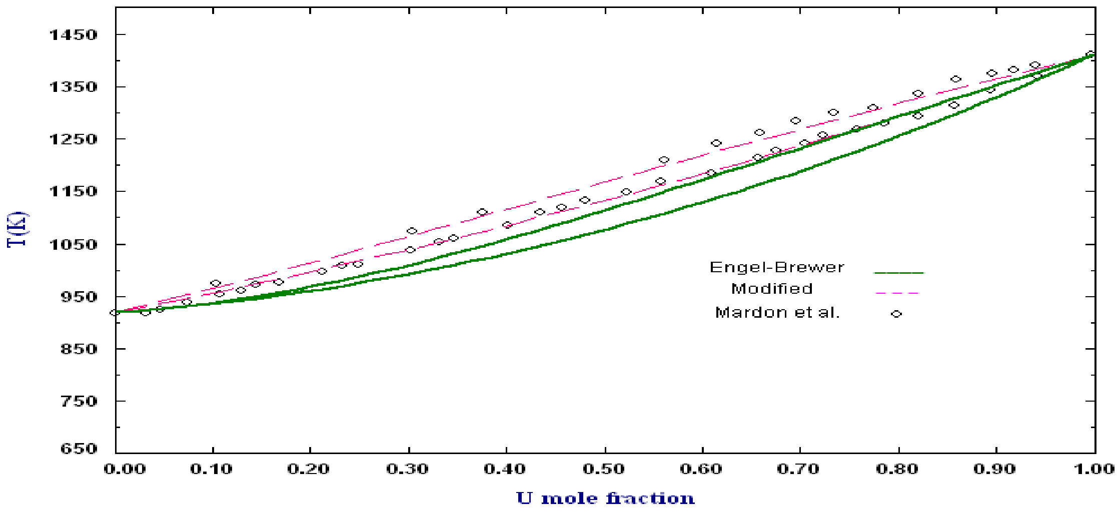
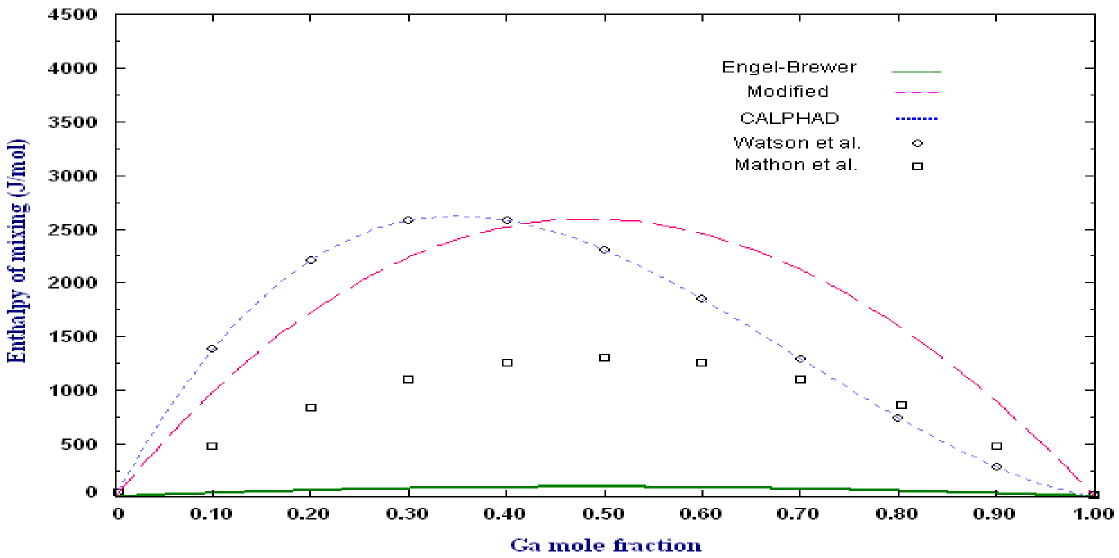


Figure 4-5. Phase diagram of the Np-U system predicted by Engel-Brewer method ___ compared with the phase diagram obtained by modifying enthalpy parameters of Engel-Brewer method and adding entropy parameters to the Redlich-Kister equation - - - and the experimental data of of Mardon et al. [139] ◊

It should be mentioned that for the Ag-Ca liquid phase, Subramanian et al. [140] reported data in two different temperatures but the difference in enthalpy of mixing for these two temperatures is negligible and both of them are used in Figure 4-6 for comparison.

Figure 4-6 and Figure 4-7 show that for the Ag-Cu liquid phase, the difference in enthalpy of mixing at equiatomic composition between Engel-Brewer prediction and the experimental data of Subramanian et al. [140] ranges from 2000 to 2800 J/mol while for the Ag-Cu solid solution, the difference between Engel-Brewer prediction and thermodynamic assessment of Hultgren et al. [141] and Rafii-Tabar et al. [142] is around 1200 to 1500 J/mol. For the Al-Ga liquid phase, enthalpy of mixing at equiatomic composition predicted by Engel-Brewer method is 400 to 600 J/mol below the experimental data of Jayaganthan et al. [143] and the thermodynamic assessment of

Hultgren et al. [141] while for the Al-Ga solid solution, enthalpy of mixing at equiatomic composition is 1200 to 1500 J/mol below the experimental data reported by Mardon et al. [144] and Watson et al. [145]. Moreover, and Figure 4-9 show that for the Al-Ga system, the enthalpy of mixing for the liquid and the solid solutions is asymmetric. Since Engel-Brewer method does not take into account size mismatch in alloying, it is not able to predict asymmetry.



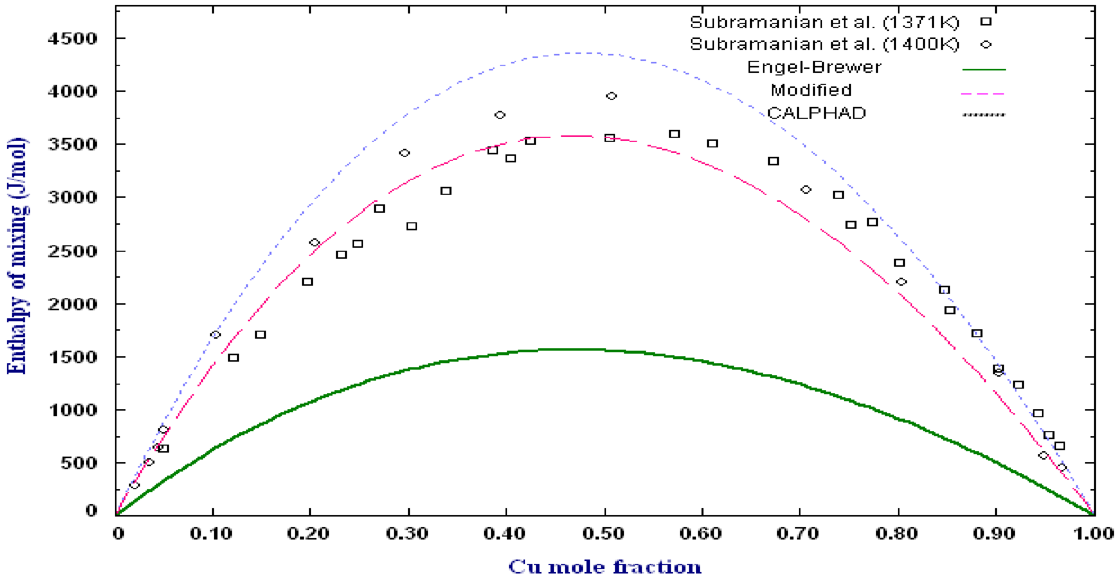


Figure 4-6. Enthalpy of mixing of liquid Ag-Cu at 1400K calculated using Engel-Brewer method ___ compared with CALPHAD results taken from SGTE database [116] ……. , the enthalpy of mixing obtained by modifying enthalpy parameters of Engel-Brewer method - - - , and the experimental data of Subramanian et al. [140] ○ , □

For actinides, the results are different from the Al-Ga and Ag-Cu systems. Kurata [128,129] predicted Np-U and Np-Pu systems to have close to ideal enthalpy of mixing. From Figure 4-10 and Figure 4-11, it can be seen that for the Np-U system, Engel-Brewer method predicted ideal enthalpy of mixing as well. However, Figure 4-12 and Figure 4-13 indicate that for the Np-Pu system, the difference between mixing enthalpy of both liquid and solid phases calculated by Engel-Brewer method in relation to the data reported by Kurata [129] is about 2500 to 2800 J/mol.

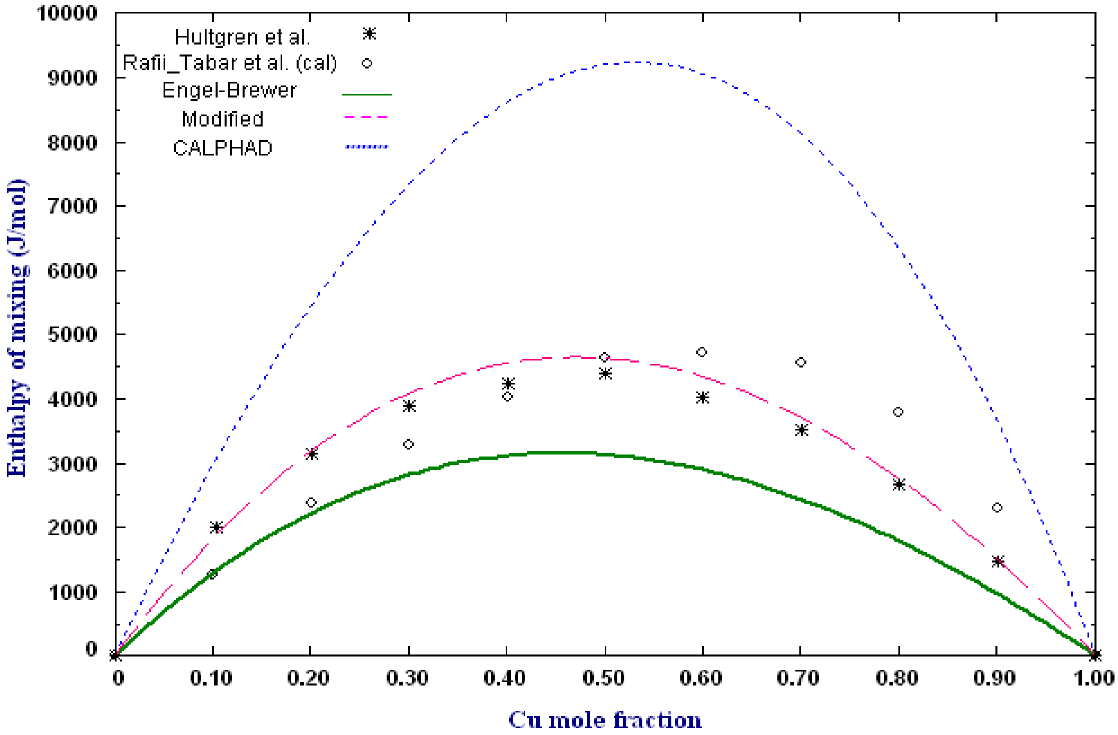


*Figure 4-7. Enthalpy of mixing of the the Ag-Cu solid solution at 300K calculated using Engel-Brewer method ⸻ compared with CALPHAD results taken from SGTE database [116] ……, the enthalpy of mixing obtained by modifying enthalpy parameters of Engel-Brewer method - - - , and thermodynamic assessment of Hultgren et al. * [141] and Rafii-Tabar et al. [142] ◊*

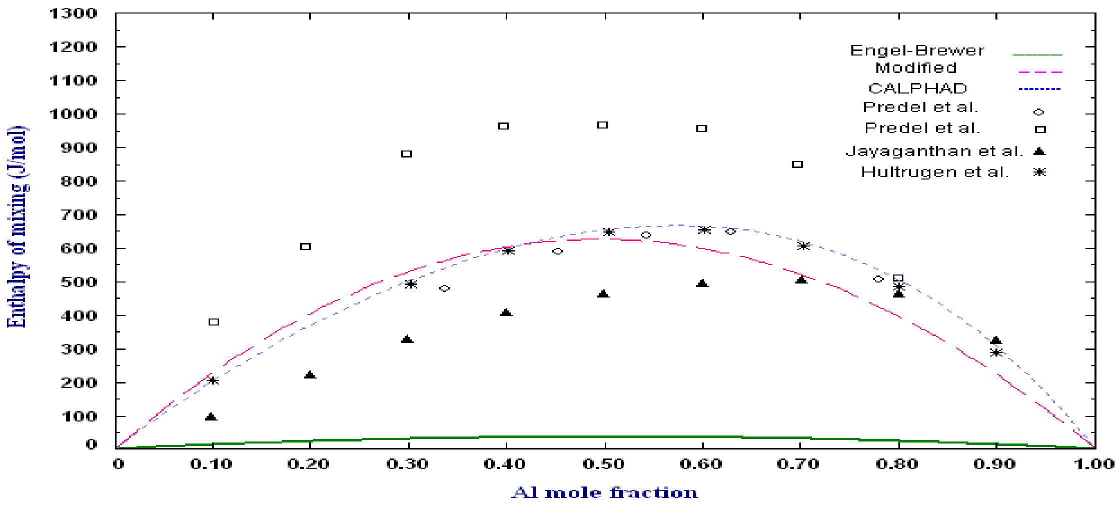


*Figure 4-8. Enthalpy of mixing of liquid Al-Ga at 1300K calculated using Engel-Brewer method __ compared with CALPHAD results taken from SGTE database [116] …… , the enthalpy of mixing obtained by modifying enthalpy parameters of Engel-Brewer method _ _ _, and the experimental data of Predel et al. [146] ◊, Predel et al. [147] □, Jayaganthan et al. [143] ▲ and thermodynamic assessment of Hultgren et al. [141] **

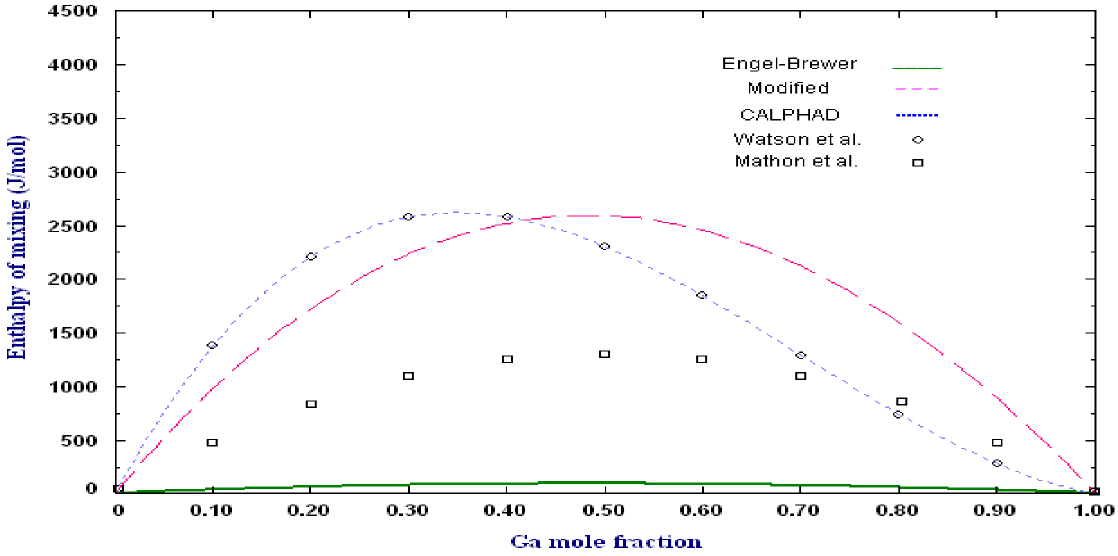


Figure 4-9. Enthalpy of mixing of the Al-Ga solid solution at 1073K calculated using Engel-Brewer method __ compared with CALPHAD results taken from SGTE database [116] …… , the enthalpy of mixing obtained by modifying enthalpy parameters of Engel-Brewer method to _ _ _ , and the experimental data of Mardon et al. [144] ◊ and Watson et al. [145] □

For the Pu-U system, enthalpy of mixing for the liquid phase as can be seen in Figure 4-14 is predicted as 2640 J/mol higher than the thermodynamic assessment of Kurata [128]. However, Figure 4-15 shows that for the solid solution phase of this system, Kurata [128] predicted negative enthalpy of mixing. Since Engel-Brewer method only adds positive contribution to the enthalpy of mixing, it was unable to predict at all the enthalpy of mixing of the Pu-U solid solution phase. It can be concluded that one of the possible reasons that Engel-Brewer method was not able to predict the general shape of the phase diagram of the Pu-U system may be due to the fact that it predicted a positive value for enthalpy of mixing of the solid phase. This possibility is examined later in this section by adjusting enthalpy of mixing to match the assessment of Kurata [128].

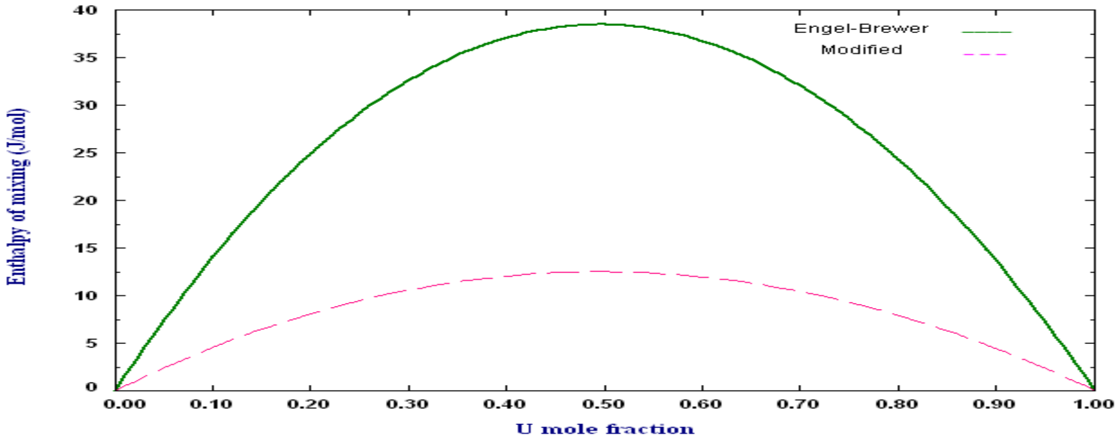


Figure 4-10. Enthalpy of mixing of liquid Np-U at 1500K calculated using Engel-Brewer method —— compared with the enthalpy of mixing obtained by modifying enthalpy parameters of Engel-Brewer method - - - . For this phase, Kurata [129] predicted ideal enthalpy of mixing ——

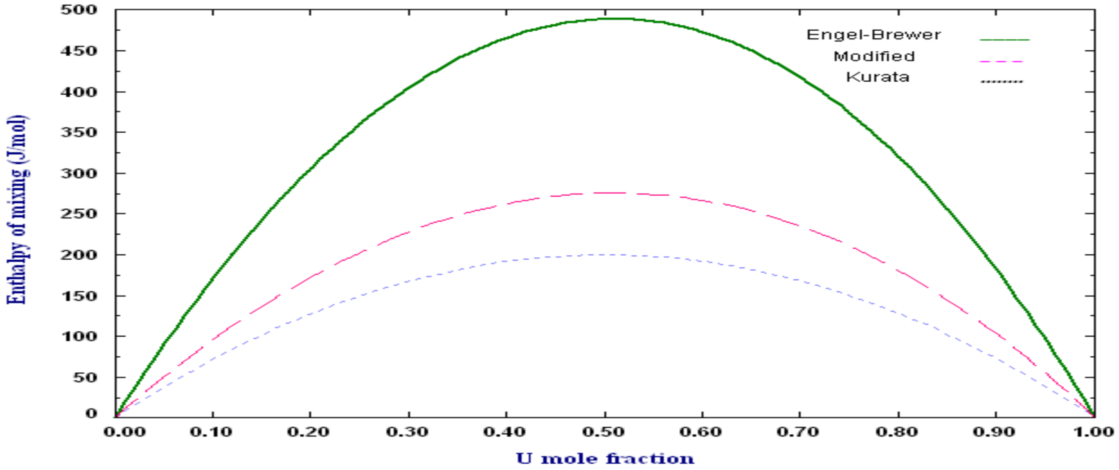


Figure 4-11. Enthalpy of mixing of the Np-U solid solution at 900K calculated using Engel-Brewer method compared with thermodynamic assessment of Kurata [129] and the enthalpy of mixing obtained by modifying enthalpy parameters of Engel-Brewer method - - -

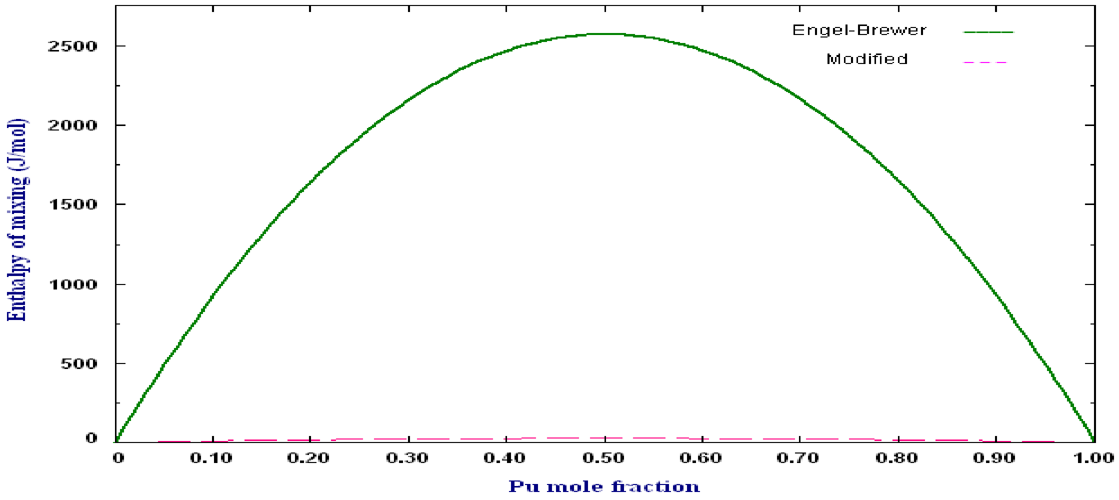


Figure 4-12. Enthalpy of mixing of liquid Np-Pu at 1050K calculated using Engel-Brewer method — compared with enthalpy of mixing obtained by modifying enthalpy parameters of Engel-Brewer method - - - - . For this phase Kurata [129] predicted ideal enthalpy of mixing —

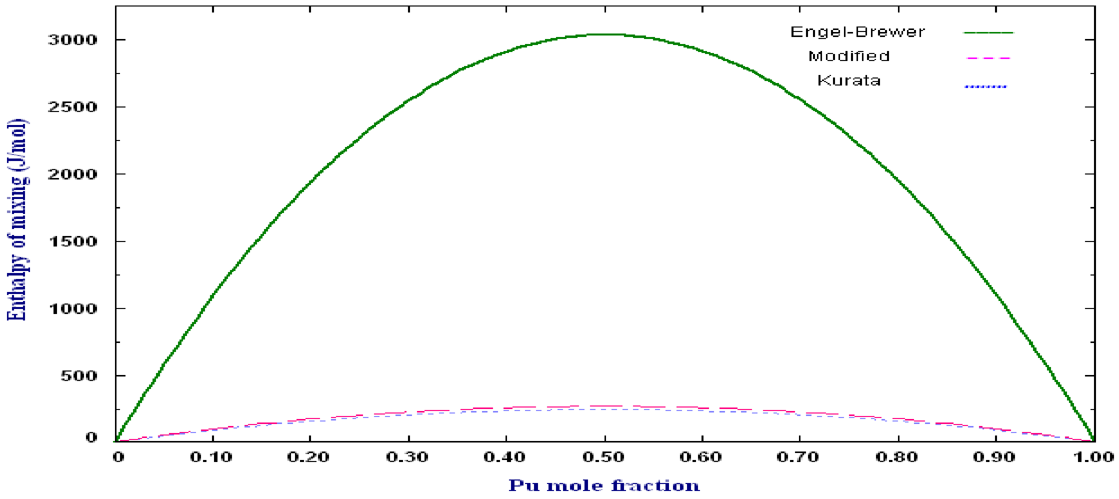


Figure 4-13. Enthalpy of mixing of Np-Pu solid solution at 850K calculated using Engel-Brewer method — compared with thermodynamic assessment of Kurata [129] …… and the enthalpy of mixing by modifying enthalpy parameters of Engel-Brewer method [129] - - -

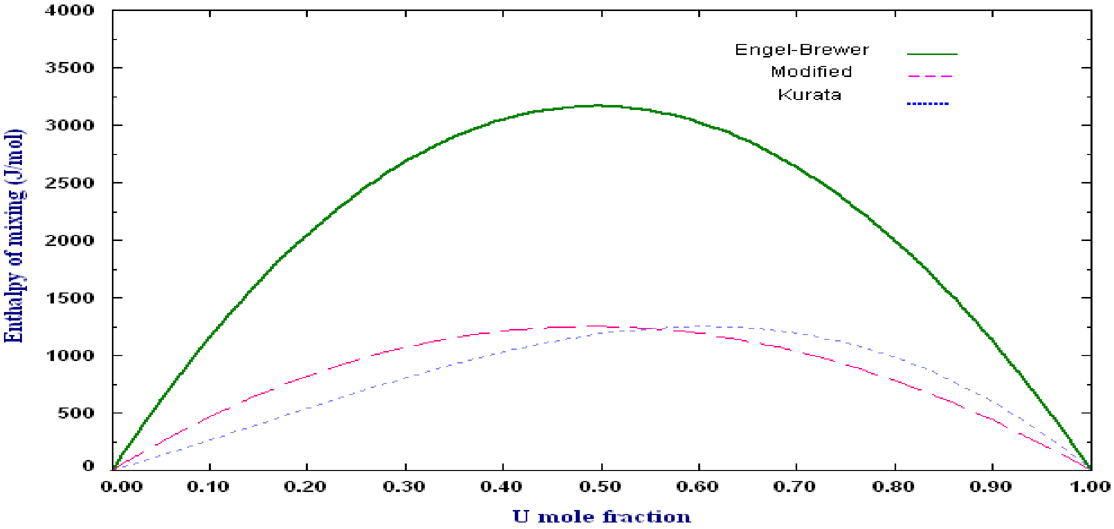


Figure 4-14. . Enthalpy of mixing of liquid Pu-U at 1500K calculated using Engel-Brewer method ⎯ compared with thermodynamic assessment of Kurata [128] …. and the enthalpy of mixing obtained by modifying enthalpy parameters of Engel-Brewer method ---

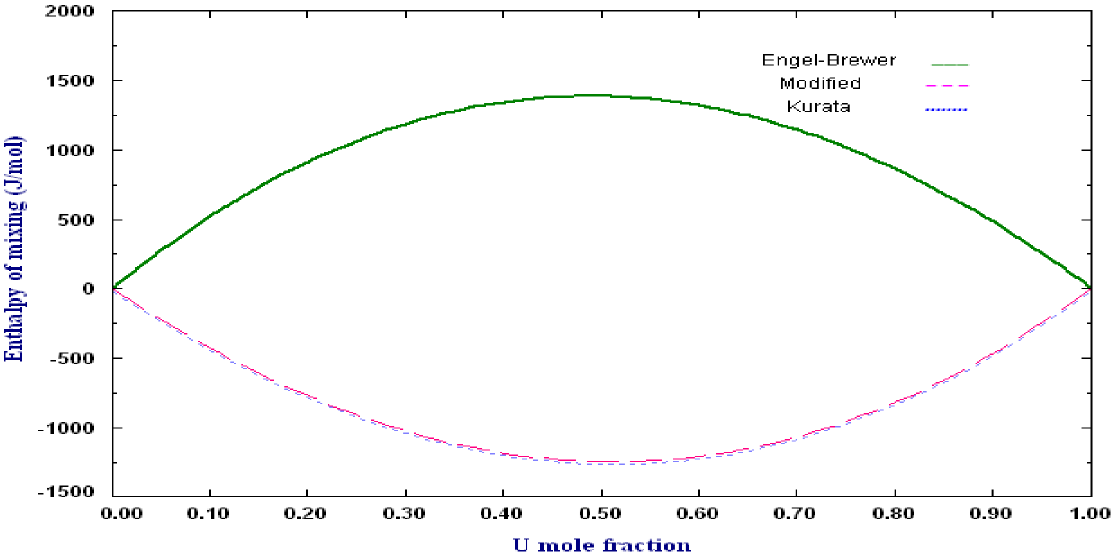


Figure 4-15. Enthalpy of mixing of the Pu-U solid solution at 900K calculated using Engel-Brewer method ⎯ compared with thermodynamic assessment of Kurata [128] …. and the enthalpy of mixing obtained by modifying enthalpy parameters of Engel-Brewer method to reproduce the phase diagram reported by Kurata [128] ---

As explained in section 3.1.2, the entropy of mixing in Engel-Brewer method is assumed to be ideal. The results of entropy of mixing and their comparison with the thermodynamic assessment of Hultgren et al. [141] and the optimized databases of Kurata [128,129] and SGTE [116] are shown in Figure 4-16 toFigure 4-25. The results of entropy of mixing are compared at equiatomic composition with the optimized databases of Kurata [128,129] and SGTE [116] in Appendix A-3. Most of the actinide systems studied in this work have ideal entropy of mixing. Therefore, the assumption of zero excess entropy of mixing in Engel-Brewer method is valid for these systems. This fact can be seen in Figure 4-16 and Figure 4-17 for Np-U, in Figure 4-18 and Figure 4-19 for Np-Pu and in Figure 4-20 for the Pu-U solid solution. However, as can be seen from Figure 4-21, for the Pu-U liquid phase, the entropy of mixing at equiatomic composition shows a difference of 34% from the data reported by Kurata [128]. Considering the fact that for this system, liquid phase does not show ideal behavior explains the failure of Engel-Brewer method to predict the phase diagram of this system. However, as can be seen in Figure 4-22 and Figure 4-23, for the Ag-Cu system the entropy of mixing for the liquid and solid solutions predicted by Engel-Brewer at equiatomic composition deviates 15 to 32%, respectively from the CALPHAD assessment [116]. Figure 4-24 and Figure 4-25 indicate that for the Al-Ga solid solution phase, this difference in entropy of mixing at eqiatomic composition reaches to 56.4%.

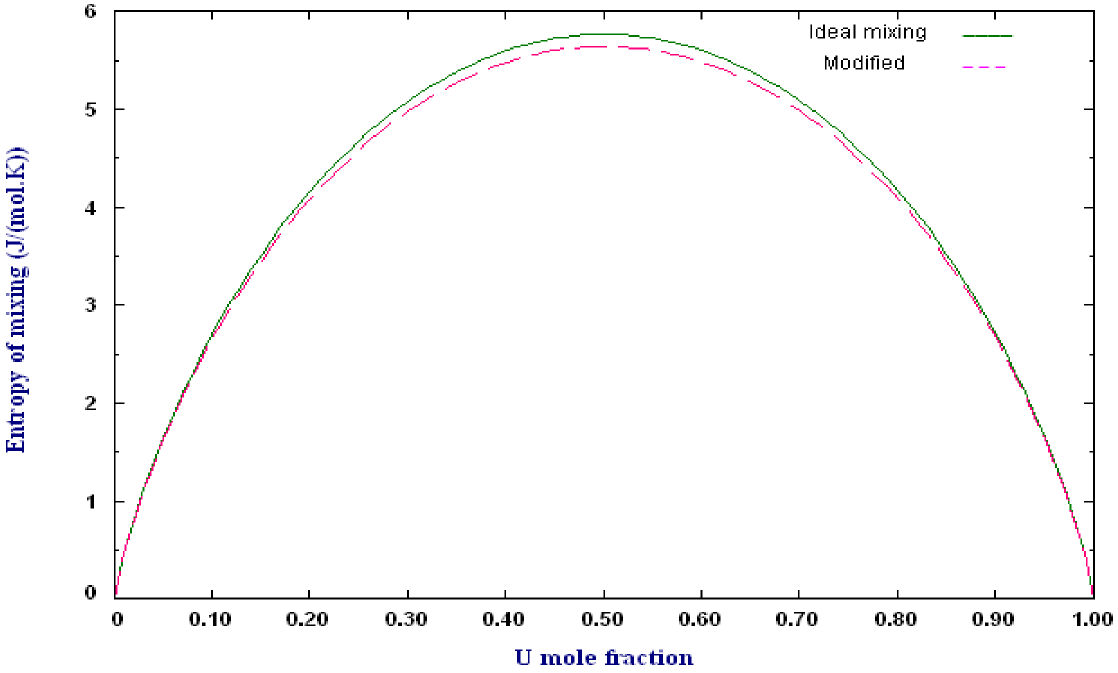


Figure 4-16. Entropy of mixing of liquid Np-U at 1500K obtained by adding entropy parameters to modified Engel-Brewer database - - - , ideal mixing and the prediction of Kurata [129] and Engel-Brewer method —

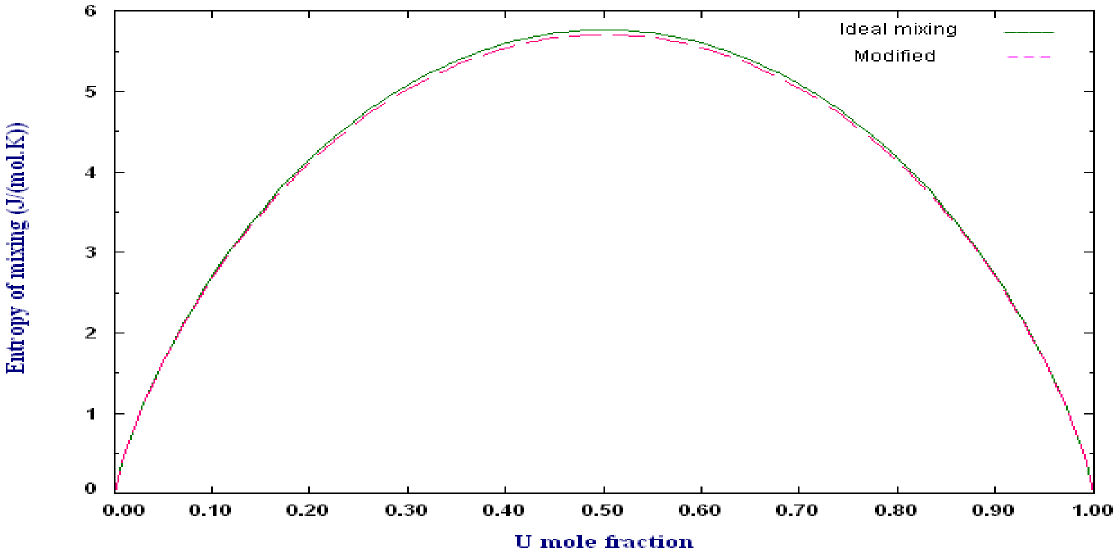


Figure 4-17. Entropy of mixing of the Np-U solid solution at 900K obtained by adding entropy parameters to modified Engel-Brewer database - - - , ideal mixing and the prediction of Kurata [129] and Engel-Brewer method __

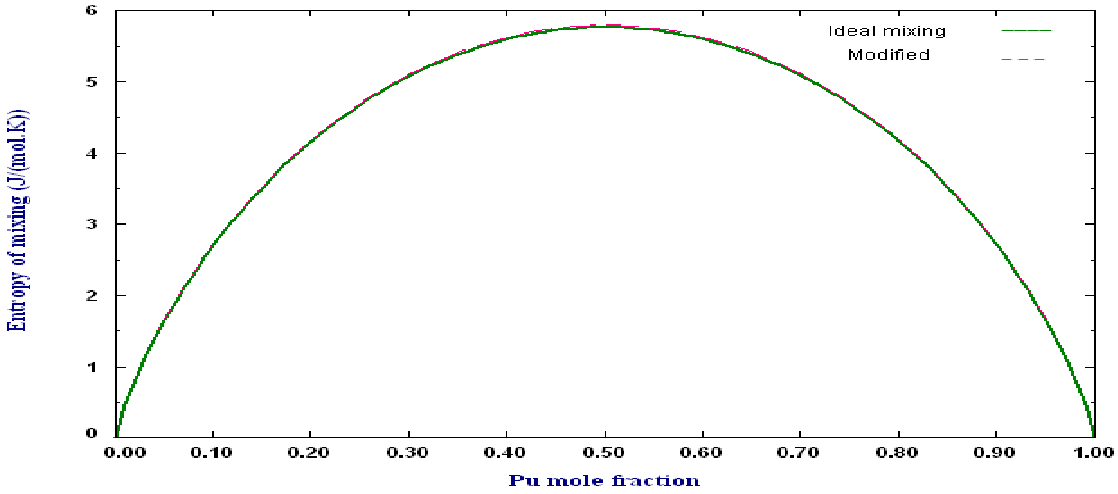


Figure 4-18. Entropy of mixing of liquid Np-Pu at 1050K obtained by adding entropy parameters to modified Engel-Brewer database - - - , ideal mixing and the prediction of Kurata [129] and Engel-Brewer method __

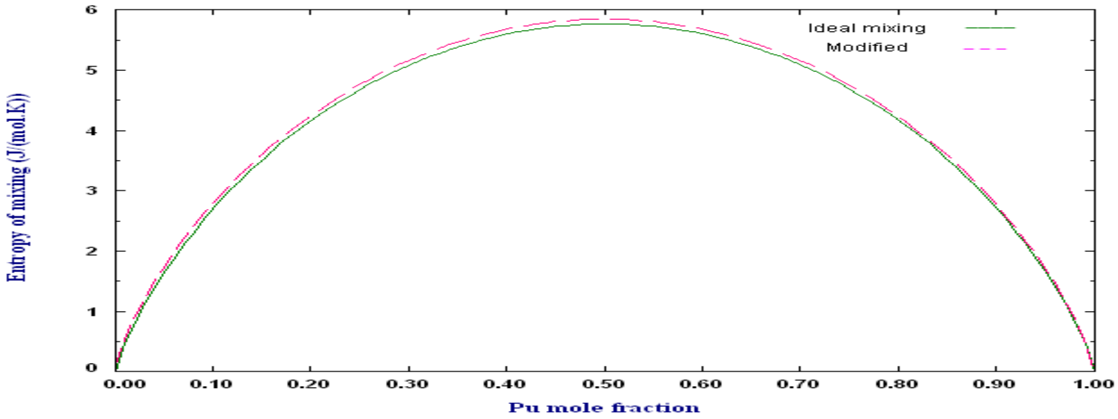


Figure 4-19. Entropy of mixing of the Np-Pu solid solution at 850K obtained by adding entropy parameters to modified Engel-Brewer database - - - , ideal mixing and the prediction of Kurata [129] and Engel-Brewer method __

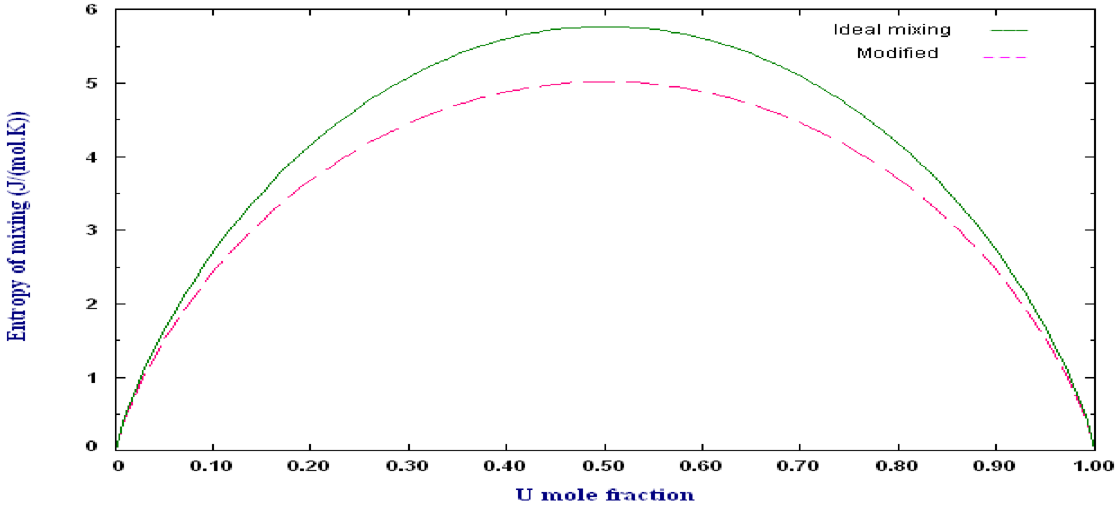


Figure 4-20. Entropy of mixing of the Pu-U solid solution at 900K obtained by adding entropy parameters to modified Engel-Brewer database ---, ideal mixing and the prediction of Kurata [128] and Engel-Brewer method —

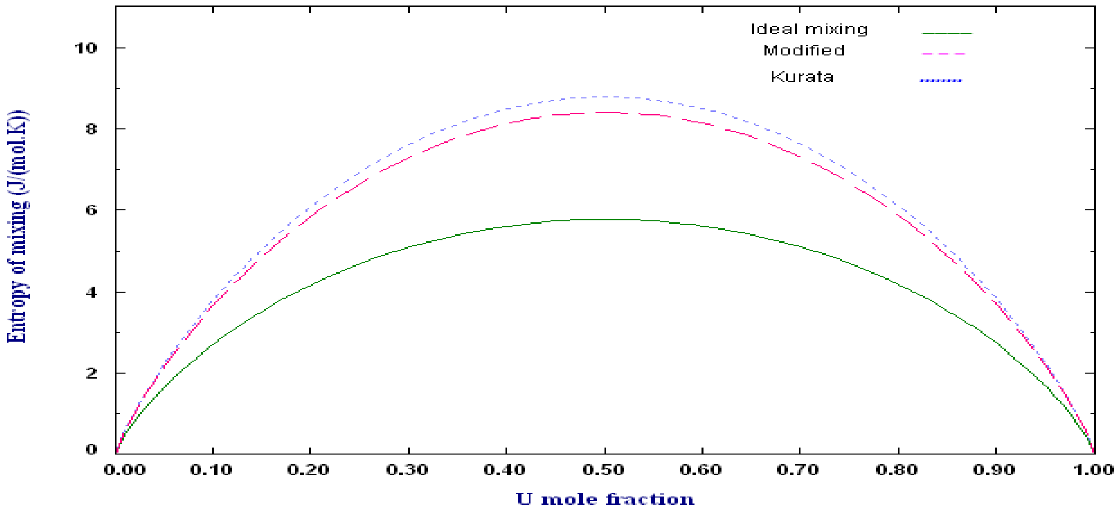


Figure 4-21. Entropy of mixing of liquid Pu-U at 1050K calculated obtained by adding entropy parameters to modified Engel-Brewer database ---, thermodynamic assessment of Kurata [128] ..... and ideal mixing and the prediction of Engel-Brewer method —

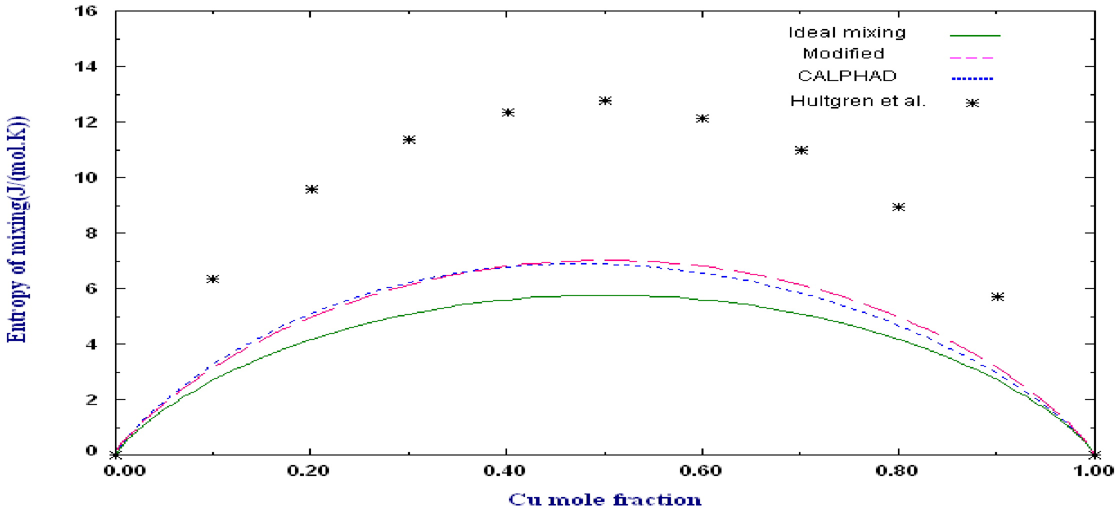


Figure 4-22. Entropy of mixing of liquid Ag-Cu at 1400K obtained by adding entropy parameters to modified Engel-Brewer database - - - , CALPHAD results taken from SGTE database [116] …… , thermodynamic assessment of Hultgren et al. [141] * *and ideal mixing and the prediction of Engel-Brewer method* —

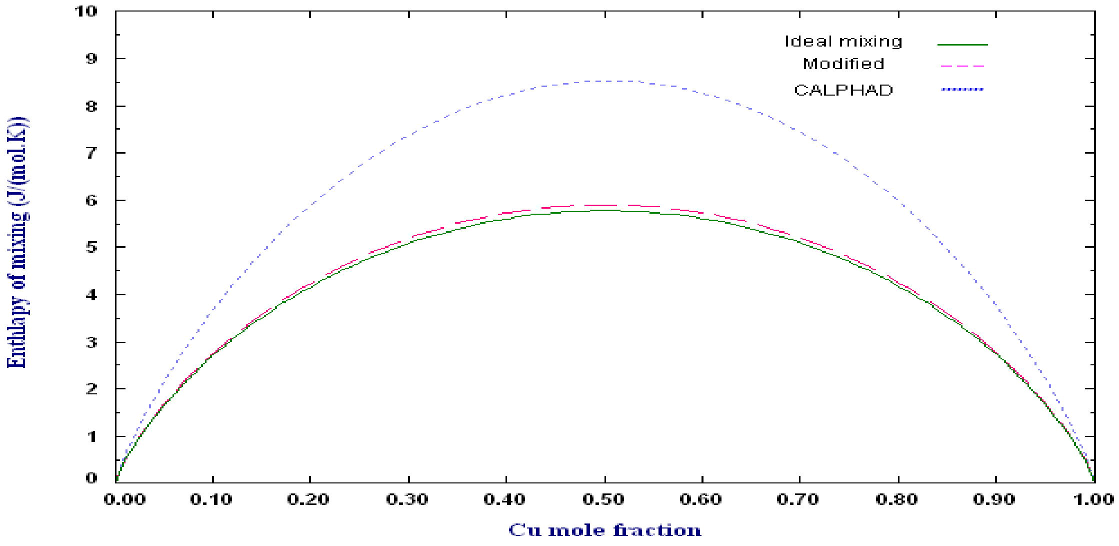


Figure 4-23. Entropy of mixing of the Ag-Cu solid solution at 300K obtained by adding entropy parameters to modified Engel-Brewer database - - - , CALPHAD results taken from SGTE database [116] …… and ideal mixing and the prediction of Engel-Brewer method —

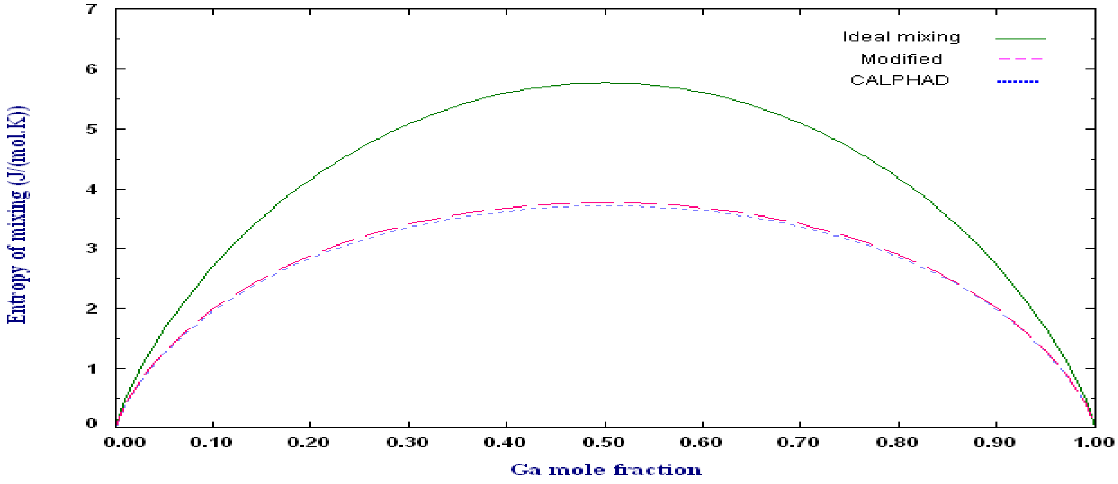


Figure 4-24. Entropy of mixing of the Al-Ga solid solution at 1073K obtained by adding entropy parameters to modified Engel-Brewer database ---, CALPHAD results taken from SGTE database [116] …… and ideal mixing and the prediction of Engel-Brewer method —

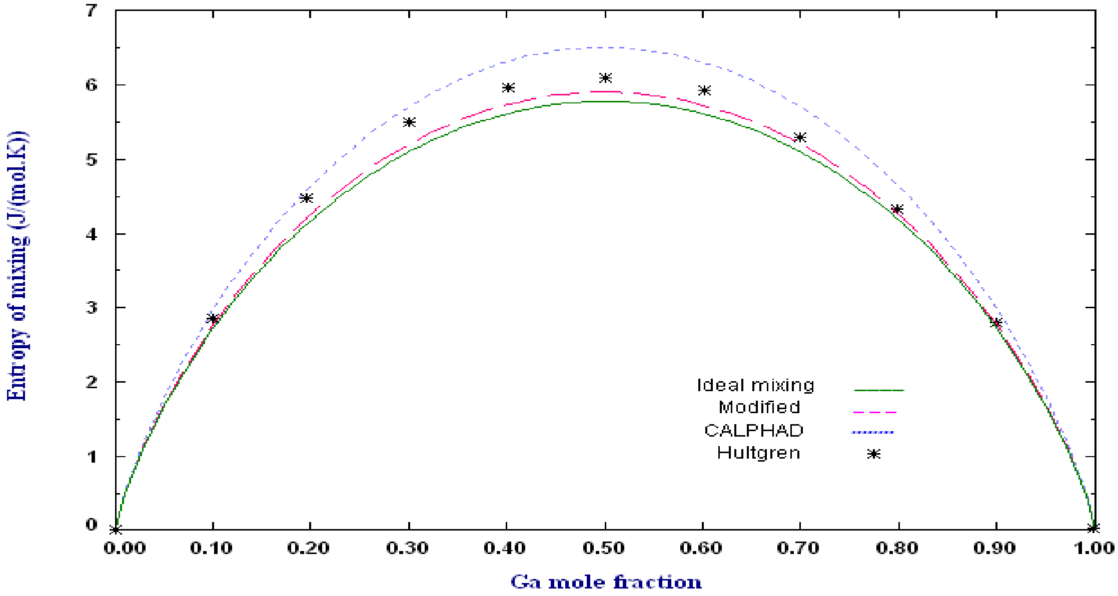
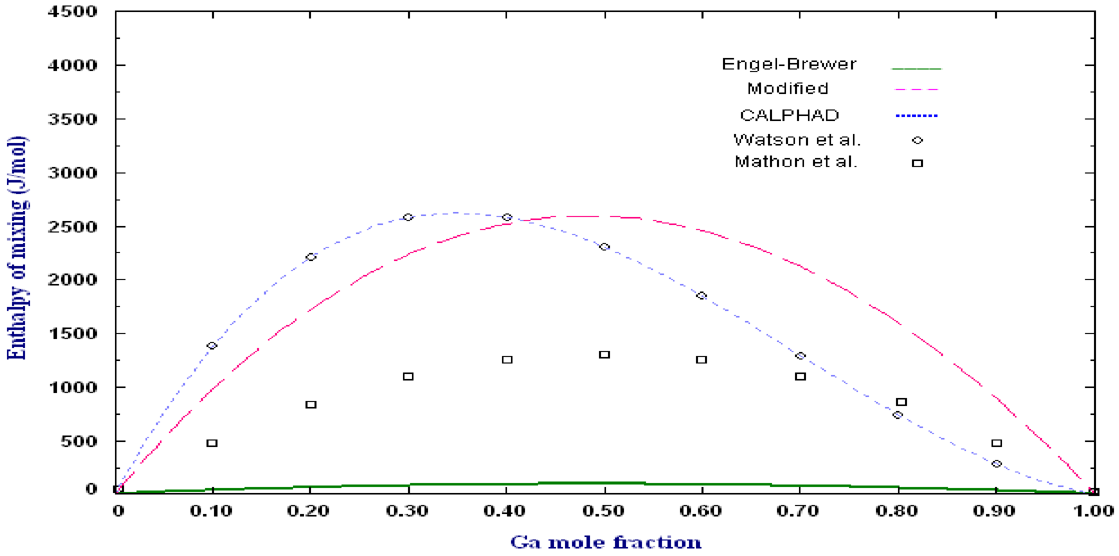


*Figure 4-25. Entropy of mixing of liquid Al-Ga at 1073K obtained by adding entropy parameters to modified Engel-Brewer database ---, CALPHAD results taken from SGTE database [116] ……, assessment of Hultgren et al. [141] * and ideal mixing and the prediction of Engel-Brewer method —*

From Figure 4-7 to Figure 4-25, it can be seen that the results enthalpy and entropy of mixing at equiatomic composition after modifying Engel-Brewer database show good consistency with the experimental data and/or the optimized databases of Kurata [128,129] and SGTE [116]. Although, for the Ag-Cu, Al-Ga and Pu-U systems, attempts have been made to find the best consistency with the experimental data, still differences can be observed between the modified Engel-Brewer database and experimental phase equilibrium data. The possible reasons would be that the formula used for the enthalpy of mixing can never lead to appropriate parameters for a phase diagram while having consistency with mixing properties. The second reason would be the possibility of the existence of additional enthalpy or entropy contributions in eqn. 2-20. The third reason would be the inability of the method to predict assymmetric mixing properties. The modified Engel-Brewer database for Np-U and Np-Pu reproduced phase diagrams consistent with the experimental data. It should be mentioned that these two systems have mixing behavior close to ideal. For the Ag-Cu system, it is clear from Figure 4-1 that still not a good consistency with phase equilibrium data can be obtained. Adding the entropy term shifts the immiscibility gap significantly up. Thus the calculated phase diagram becomes closer to the CALPHAD assessment compared to Engel-Brewer method. The eutectic composition was predicted well with this modified database whereas the eutectic temperature has been shifted down from 1047K to 1027K. It should be mentioned since there are no adjustable parameters in Engel-Brewer method, the prediction of this method for liquid phase of Ag-Ca is excellent. The limits of solid solubility especially for the Cu-rich F.C.C. solid solution extend far beyond the values from the CALPHAD assessment. Although the maximum solubility in the Ag-rich part is consistent with the experimental data, the main part of the problem still remains in the maximum solubility in the Cu-rich side which is underestimated to be 26 at% Cu instead of 5 at% Cu. As can be seen in Figure 4-2, for the Al-Ga system, addition of entropy parameters to the excess Gibbs energy and modifying the promotion energy resulted in more consistency with CALPHAD assessment. For this phase diagram, the maximum solid solubility of Ga in Al is reduced from 72 at% Ga to 0.7 at% Ga which is closer to the value of 8 at% Ga from CALPHAD assessment. However, the maximum solid solubility still has significant difference from CALPHAD assessment. It is clear from Figure 4-8 and Figure 4-9 that the differences in enthalpy of mixing for the liquid and solid solutions arise from the inability of Engel-Brewer method to predict asymmetry. Figure 4-22 shows that the percentage of difference in calculation of the entropy of mixing at equiatomic composition for the liquid phase is negligible. However, from Figure 4-23, it can be seen that for the solid solution phase the percentage of difference is decreased significantly from 56.4% to 2.1%. In the Np-U system, the modification of Engel-Brewer



parameters and addition of entropy parameters resulted in a better prediction of the phase diagram compared to Engel-Brewer method. The temperature difference between solidus and liquidus lines of the modified Engel-Brewer database with the experimental data of Mardon et al. [139] at *x=30* at% U are reduced to the range of ±7K and ±17K, respectively. As can be seen from Figure 4-10 and Figure 4-11, the predicted enthalpy of mixing for both of the phases is closer to the results of Kurata [129]. The temperature dependant parameter made a subtle decrease in the entropy of mixing for the liquid and solid solution phases. The phase diagram calculated by the modified Engel-Brewer database for the Pu-U system is displayed in Figure 4-3. It can be seen that the result is more consistent with the experimental data of Peterson et al. [137]. The difference between the solidus line obtained by the modified Engel-Brewer database and the experimental data of Peterson et al. [137] at *x=20* at% U is reduced to 26K and for the liquidus line, this difference is reduced to 9K. Similarly, at *x=80* at% U the difference between solidus lines and liquidus lines compared with the experimental data of Peterson et al. [137] is reduced to 85K and 100K, respectively. Moreover, contrary to Engel-Brewer results, the shape of the modified Engel-Brewer phase diagram is concave which is closer to the data reported by Peterson et al. [137]. The size of the two-phase region is smaller at compositions lower than *x=50* at% U and bigger at compositions higher than x=50 at% which is more consistent with the experimental data of Peterson et al. [137] compared to Engel-Brewer results. Figure 4-14 shows that the maximum enthalpy of mixing predicted by the modified Engel-Brewer database is close to the results reported by Kurata [128]. As can be seen in Figure 4-15, the enthalpy of mixing for the solid solution phase of this system agrees well with the reported data by Kurata [128]. The modified Engel-Brewer database has decreased the deviation of the entropy of mixing at equiatomic composition from the results of Kurata [128] from 34 to 4%. However, it has increased the deviation of the solid solution phase from the results of Kurata [128]. The phase diagram of the Np-Pu system obtained by the modified Engel-Brewer database is presented in Figure 4-4. This phase diagram shows a good consistency with the experimental data of Mardon et al. [138]. Figure 4-12 and Figure 4-13 demonstrate the little difference between enthalpy of mixing found by the modified Engel-Brewer database and the results of Kurata [129]. It can be seen from Figure 4-18 and Figure 4-19 that the difference between entropy of mixing for the solid solution and liquid phase found by the modified Engel-Brewer database and the results of Kurata [129] is very small.

The comparison between adjusted promotion energies and the ones used by Engel-Brewer method are listed in

Table 4-1. The difference range from 2.2% to 85.2%. For the cases of Ag-Cu and Al-Ga, although the difference in promotion energies is subtle and not exceeding 19%, it affects the phase diagram and thermodynamic properties significantly. Thus, the question is raised whether promotion energy alone, is an appropriate term to be used as a base for calculating phase diagrams.

Taking all the systems into account, only for Np-U and Np-Pu, Engel-Brewer method showed consistency with the existing phase equilibrium data and thermodynamic properties. However, for the Np-Pu system, further modification was required regarding the enthalpy of mixing. This is probably because the model takes into account the electronic configuration in bonding as the only factor to calculate cohesive energies and to estimate Gibbs free energies while other important chemical and physical factors in bonding such as bulk modulus, electronegativities, etc. are neglected.

Furthermore, for the Pu-U system, Engel-Brewer prediction was unsuccessful even to predict the shape of the phase diagram. Whereas, most of the systems assessed by this method in previous works were actinides and transition metals [16,55,56,58,59] and some of them such as Ag-Cu do not have ideal entropy of mixing and close to ideal enthalpy of mixing. Thus, this study raises the question of the ability of the Engel-Brewer method to predict the phase diagrams and thermodynamic properties even for actinides and lanthanides. It should be mentioned that the previous studies that used this method [16,55,56,58,59] were only comparing the predicted phase with experimental phase diagram data but optimization is the simultaneous consistency of phase diagram and thermodynamic properties. Ogawa et al. [55] in their study of light actinide phase diagrams used Engel-Brewer method but they changed the parameters to fit the experimental phase equilibrium data, defeating the purpose of using this method as a predictive tool.

Engel-Brewer method is an expansion of the regular solution model for gases to metals and alloys. Therefore it is unable to predict asymmetry. In a regular solution model, cohesive energy is treated as Gibbs free energy of mixing which implies that there is no excess entropy. This assumption cannot be reasonable even for transition metals, lanthanides and actinides and thus leads to deviation from the experimental data. In order to have a reliable prediction of phase diagram and thermodynamic properties, excess entropy of mixing should be taken into account.

Moreover, Engel-brewer method is not able to predict negative enthalpy of mixing. The only contribution to cohesive energy taken into account in this model is because of the promotion of electrons from ground electronic state to valence state which is positive. This can lead to completely invalid results as was outlined in this study for the case of the Pu-U system. In order to take into account negative contributions, Miedema et al. [19,20] proposed a model for calculating enthalpy of mixing which includes positive contribution for the continuity of electron density at the boundary of Wigner-Seitz cell (n_{ws}) and negative contributions of electronegativies $\Delta\varphi$ and for the case of transitional metals alloyed with non-transitional metals, they included negative hybridization contribution. Miedema model is described elaborately in section 2.4.

Above all, Engel-Brewer method was not able to predict phase diagram and thermodynamic properties in most of the cases studied here. In this work, in order to predict phase diagram and mixing properties, the parameters obtained from Engel-Brewer method needed to be adjusted. In this sense, if the model by its own cannot predict the phase diagram and thermodynamic properties, then it can be stated that the use of other methods that require adjustable parameters can be a better choice. In order to take into account more physical considerations, nearest neighbor bond energies with random mixing [148] or short range ordering in quasi-chemical model [149-151] and cluster site approximation [152] or long-range and short range ordering together [148] for liquid phase and compound energy formalism [119] for solids and compounds can be better choices. Despite the fact that using these models can be more complicated, their application using CALPHAD [4] can lead to more reliable results. Furthermore, firs-principles quantum mechanics based on density functional theory [8] and ab-initio molecular dynamics (AIMD) [9,10] are powerful tools that can help find enthalpy of mixing and other thermodynamic properties. However, ab-initio calculations cannot be used for multi-component systems and solid solutions. Moreover, the use of Miedema model [19,20] as a first approximation of enthalpy of mixing while considering the contribution of the excess entropy of mixing to the excess Gibbs energy [27,31,107] can be another approach for the prediction of thermodynamic properties.

In the proceeding parts of this chapter, first the reliability of Miedema model compared to Engel-Brewer method is examined and then different models for excess entropy of mixing are compared.

Table 4-1. Adjusted promotion Energies of liquid and different solid crystal structures of Ag, Cu, Al, Ga, Np, Pu and U used in the modified Engel-Brewer database compared to the ones reported by [48,51,52] which are used in Engel-Brewer method.

System	Element forms	Element Form	$\Delta E_P (kJ/mol)$	optimized $\Delta E_P (kJ/mol)$	Difference %
Ag-Cu	Ag	Liquid	556.455	494.128	11.2
		F.C.C.	556.47	525.488	5
	Cu	Liquid	483.666	512.108	5.5
		F.C.C	483.67	514.456	6
Al-Ga	Al	Liquid	347.272	281.225	19
		F.C.C.	347.272	322.129	7.2
	Ga	Liquid	454.369	473.634	4.2
		F.C.C	454.382	238.876	4.7
Np-U	U	Liquid	272.231	250.281	8.1
		B.C.C.	262.755	242.816	7.9
		Liquid	294.554	286.364	2.8

	Np	B.C.C	284.512	290.828	2.2
Pu-U	U	Liquid	272.231	235.681	13.4
		B.C.C.	262755	142.816	45.6^{*}
	Pu	Liquid	213.802	279.799	30.8
		B.C.C	213.802	395.904	85.2^{*}
Np-Pu	Np	Liquid	294.554	215.584	26.8
		B.C.C	284.512	205.928	27.6
	Pu	Liquid	213802.4	348250	62.8
		B.C.C.	213802.4	339004	58.6

Note1: * refers to cases when enthalpy of mixing is negative. Since Engel-Brewer method is not able to predict negative deviation from ideality, the amount reported here is the limit when $\propto$ in eqn. 2-21 equals to zero.

Note 2: Promotion energies used in Engel-Brewer method are used as adjustable parameters to obtain consistency with the experimental data or previously optimized databases.

4.2 Miedema Model

4.2.1 Prediction of enthalpy of mixing for liquid alloys

Calculated enthalpy of mixing using Miedema model in relation to the experimental data of 50 binary systems is listed in Table 4-2 and demonstrated in Figure 4-26. For simplicity, only extremum values of enthalpy of mixing are compared. As can be seen from this table, contrary to Engel-Brewer method, Miedema model accounts for both negative and positive deviations from ideality. Therefore, it can be applied to all binary systems. In a qualitative approach, Figure 4-26 shows that using Miedema model, the sign of the enthalpy of mixing is identical to the experimental data for almost all of the systems except for the case of Fe-C system. Boom et al. [101] relates this inaccuracy to uncertainties in estimation of the transformation enthalpy of C-graphite to C-metal and 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. Visual representation of the correlation between calculated and experimental values of enthalpy of mixing for liquid alloys using Miedema model is shown in Figure 4-26. It can be seen that apart from the Fe-C and Al-Au systems which are outerlayers, other systems show good consistency with the experimental data. Miedema model estimated enthalpy of mixing for liquid alloys with standard deviation of $5844\ \mathrm{J/mol}$ and prediction band of $\pm 1597\ \mathrm{J/mol}$ at confidence level of 90%. It should be mentioned that throughout this section, least square analysis is used to calculate standard deviations and prediction bands with confidence level of 90%.

Figure 4-27 indicates the same correlation for Engel-Brewer method for the 20 binary systems studied. Enthalpy of mixing of liquid alloys of the other 30 systems cannot be calculated by Engel-Brewer method since they have negative deviation from ideality. It can be seen that the best fit line has a slope close to zero and the data points are too scattered to make a linear regression. Since the slope of the fitted line is small, it can be concluded that for most of the systems, Engel-Brewer method overestimates the enthalpy of mixing. Standard deviation for this case is extremely high ($32210\ \mathrm{J/mol}$).

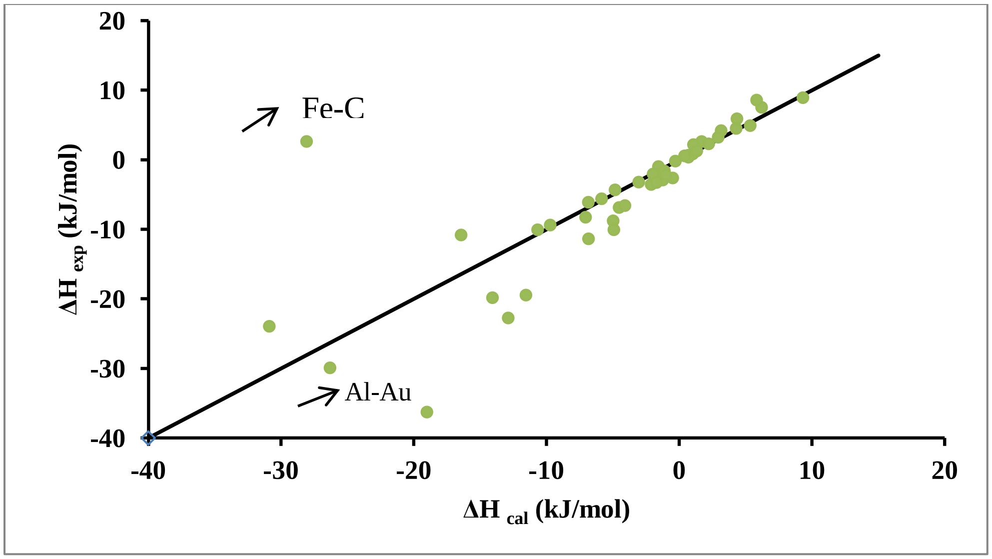


Figure 4-26. Extremum enthalpy of mixing calculated using Miedema model compared with the experimental enthalpy of mixing for liquid alloys of 50 binary systems listed in Table 4-2.

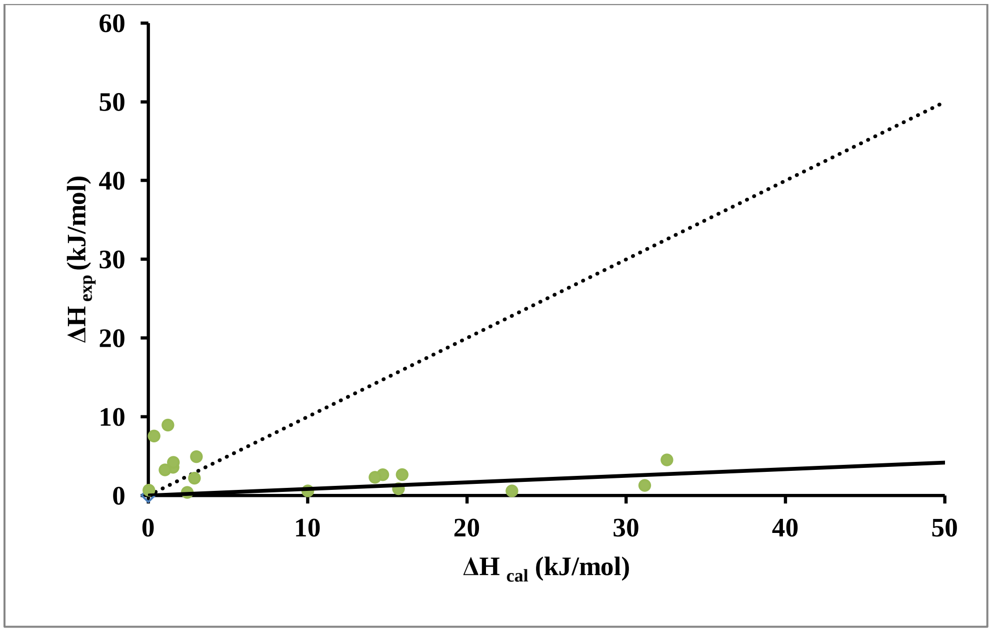


Figure 4-27. Extremum enthalpy of mixing calculated using Engel-Brewer method compared with the experimental enthalpy of mixing for liquid alloys of 20 binary systems listed in Table 4-2.

Table 4-2. Extremum enthalpy of mixing of liquid solution for binary alloys calculated using Miedema model and Engel-Brewer method compared with the experimental data

System	Miedema			Engel-Brewer		T (K)	Ref.
	H (J/mol)	H exp. (J/mol)	Difference %	H (J/mol)	Difference %		
Ag-Au	-3963	-4100	3	----	----	1400	[141]
Ag-Cu	1802	3558	49	1557	56	800	[140]
Ag-Ga	-3446	-2669	29	----	----	1000	[141]
Ag-Pb	1897	3766	50	56229	1393	1000	[141]
Al-Au	-19006	-36275	48	----	----	1400	[141]
Al-Cu	-4973	-8786	43	----	----	1373	[141]
Al-Fe	-6842	-6109	12	----	----	1873	[141]
Al-Ga	693	648	7	38	94	1073	[141]
Al-Ge	-1560	-980	59	----	----	1200	[141]

Table 4-2. Continued

System	Miedema			Engel-Brewer		T (K)	Ref.
	H (J/mol)	H exp. (J/mol)	Difference %	H (J/mol)	Difference %		
Al-In	5354	4908	9	3023	38	1173	[141]
Al-Mg	-2108	-3556	41	----	----	1073	[141]
Al-Sn	3162	4184	24	1577	62	973	[141]
Au-Cu	-4830	-4330	12	----	----	800	[141]
Au-Ni	6212	7531	18	364	95	1150	[141]
Au-Sn	-6828	-11366	40	----	----	823	[141]
Au-Zn	-12880	-22744	43	----	----	1080	[141]
Bi-Cd	1028	837	23	15710	1777	773	[141]
Bi-In	-1112	-1619	31	----	----	900	[141]

Bi-Mg	-11544	-19456	41	----	----	975	[141]
Bi-Na	-26307	-29916	12	----	----	773	[141]
Bi-Sb	592	561	6	10017	1686	1200	[141]
Bi-Zn	4295	4498	4	32568	624	873	[141]
Cd-Hg	-484	-2623	82	----	----	600	[141]
Cd-Mg	-5844	-5611	4	----	----	543	[141]
Cd-Pb	1694	2615	35	14727	463	773	[141]
Cd-Sb	-1962	-2050	4	----	----	773	[141]
Cd-Tl	2228	2284	2	14235	523	750	[141]
Cd-Zn	1079	2176	50	2900	98	800	[141]
Cu-Bi	4355	5887	26	91928	1461	1200	[141]
Cu-Fe	9327	8920	4	1233	86	1823	[141]
Cu-Sb	-1234	-2916	58	----	----	1190	[141]
Cu-Tl	5837	8577	32	82235	858	1573	[141]
Fe-C	-28071	2628	1168	15942	506	1873	[141]
Fe-Si	-10664	-10067	6	----	----	1873	[141]

Table 4-2 continued

System	Miedema			Engel-Brewer		T (K)	Ref.
	H (J/mol)	H exp. (J/mol)	Difference%	H (J/mol)	Difference%		
Ga-Mg	-4919	-10066	51	----	----	923	[141]
Hg-In	-1004	-2251	55	----	----	298	[141]
Hg-Na	-14065	-19832	29	----	----	673	[141]
Hg-Zn	697	368	89	2449	96	573	[141]
In-Mg	-4525	-6870	34	----	----	923	[141]
In-Na	-7049	-8263	14	----	----	713	[141]
In-Sb	-3047	-3217	5	----	----	900	[141]
In-Sn	-284	-197	44	----	----	700	[141]

In-Tl	408	556	26	22836	4003	723	[141]
In-Zn	2942	3230	9	1051	67	700	[141]
K-Pb	-30882	-23941	29	----	----	848	[141]
K-Tl	-16430	-10816	52	----	----	798	[141]
Mg-Li	-1706	-3276	48	----	----	1000	[141]
Mg-Pb	-9714	-9389	3	----	----	973	[141]
Mg-Tl	-4085	-6590	38	----	----	923	[141]
Pu-U	1325	1255	6	31175	2384	1500	[128]

These systems are then divided into different groups. Extremum enthalpy of mixing for liquid alloys of transition metals with transition metals using both methods are listed in Table 4-3 and demonstrated in Figure 4-28. Since, Miedema and co-workers have studied alloys of transition metals with transition metals [75,78,97-101], model parameters (*P*, *Q/P*) are taken directly from these references.

The highest percentage of difference for Miedema model is 49.3% for Ag-Cu system while for Engel-Brewer method, the difference reaches to 95.2%. For this group of metals, Miedema model predicted the data with standard deviation of $1323\ \mathrm{J/mol}$ and prediction band of $\pm 2992\ \mathrm{J/mol}$. Engel-Brewer method is completely unable to predict enthalpy of mixing of the Ag-Au and Au-Cu systems since they have negative enthalpy of mixing. This fact is in contrast with what Brewer claimed regarding the success of Engel-Brewer method for transition metals and actinides [43,48].

Table 4-3. Extremum Enthalpy of mixing for liquid solution for different groups of metals calculated using Miedema model and Engel-Brewer method compared with the experimental data

system	Miedema	Engel-Brewer	T(K)	Ref.

	H (J/mol)	H exp. (J/mol)	Difference%	H (J/mol)	Difference%		
Transition metals+ Transition metals							
Ag-Au	-3963	-4100	3	----	----	1400	[141]
Ag-Cu	1802	3558	49	1557	56	800	[140]
Au-Cu	-4830	-4330	12	----	----	800	[141]
Au-Ni	6212	7531	18	364	95	1150	[141]
Cu-Fe	9327	8920	5	1233	86	1823	[141]
Transition metals+ Non-transition metals							
Ag-Ga	-3101	-2669	16	----	----	1000	[141]
Ag-Pb	4074	3766	8	56229	1393	1000	[141]
Al-Au	-20589	-36275	43	----	----	1400	[141]
Al-Cu	-7258	-8786	17	----	----	1373	[141]
Al-Fe	-6019	-6109	1	----	----	1873	[141]
Au-Sn	-11072	-11366	3	----	----	823	[141]
Au-Zn	-14847	-22744	35	----	----	773	[141]

Table 4-3. Continued

system	Miedema			Engel-Brewer		T(K)	Ref.
	H (J/mol)	H exp. (J/mol)	Difference%	H (J/mol)	Difference%		
Transition metals+ Non-transition metals							
Cu-Bi	4392	5887	25	91928	1462	1200	[141]
Cu-Sb	-2707	-2916	7	----	----	1190	[141]
Cu-Tl	6651	8577	22	82235	859	1573	[141]
Fe-C	-32331	2628	1330	15942	507	1873	[141]
Fe-Si	-10856	-10067	8	----	----	1873	[141]
p-metals+ *p*-metals							
Al-Ga	693	648	7	38	94	1073	[141]
Al-Ge	-1560	-980	59	----	----	1200	[141]

Al-In	5354	4908	9	3023	38	1173	[141]
Al-Sn	3162	4184	24	1577	62	973	[141]
Bi-In	-1112	-1619	31	----	----	900	[141]
Bi-Sb	592	561	6	10017	1687	1200	[141]
In-Sb	-3047	-3217	5	----	----	900	[141]
In-Sn	-284	-197	45	----	----	700	[141]
In-Tl	408	556	27	22836	4004	723	[141]
p-metals+s^{10} transition metals							
Bi-Cd	1028	837	23	15710	1777	773	[141]
Bi-Zn	4295	4498	4	32568	624	873	[141]
Cd-Pb	1694	2615	35	14727	463	773	[141]
Cd-Sb	-1962	-2050	4	----	----	773	[141]
Cd-Tl	2228	2284	2	14235	523	750	[141]
Hg-In	-1004	-2251	55	----	----	298	[141]
In-Zn	2942	3230	9	1051	67	700	[141]

Table 4.3. Continued

System	Miedema			Engel-Brewer		T(K)	Ref.
	H (J/mol)	H exp. (J/mol)	Difference%	H (J/mol)	Difference%		
Hg-In	-1004	-2251	55	----	----	298	[141]
In-Zn	2942	3230	9	1051	67	700	[141]
p-metals+ Alkali and alkaline earth metals							
Al-Mg	-2151	-3556	40	----	----	1073	[141]
Bi-Mg	-11776	-19456	39	----	----	975	[141]
Bi-Na	-26835	-29916	10	----	----	773	[141]
Ga-Mg	-5018	-10066	50	----	----	923	[141]
In-Mg	-4616	-6870	33	----	----	923	[141]
In-Na	-7191	-8263	13	----	----	713	[141]

K-Pb	-25657	-23941	7	----	----	848	[141]
K-Tl	-13752	-10816	27	----	----	798	[141]
Mg-Pb	-9910	-9389	6	----	----	973	[141]
Mg-Tl	-4167	-6590	37	----	----	923	[141]
s^{10} transition metals+ Alkali and alkaline metals							
Cd-Mg	-5844	-5611	4	----	----	543	[141]
Hg-Na	-14065	-19832	29	----	----	673	[141]
Actinides							
Pu-U	1325	1255	6	31175	2384	1500	[128]
s^{10} transition metals+ s^{10} transition metals							
Cd-Hg	-484	-2623	82	----	----	600	[141]
Cd-Zn	1079	2176	50	2900	98	800	[141]
Hg-Zn	697	368	89	2449	96	573	[141]
Alkali and alkaline earth metals+ Alkali and alkaline earth metals							
Mg-Li	-1706	-3276	48	----	----	1000	[141]

The second group of metals studied is transition metals alloyed with non transition p-metals or d^{10} transition metals. For this group, adjustable parameters are changed to $P = 12.87$ and $Q/P = 9.64$. In addition, R/P for Cu, Ag, Au and Fe are changed to 0.35, 0.1, 0.4 and 0.9 respectively. This set of new adjustable parameters gave the best consistency with the experimental data. Calculated enthalpy of mixing using Miedema model and Engel-Brewer method for this group of metals is listed in Table 4-3. The percentage of difference with the experimental data for the Fe-C system with new parameters increases from 1168% to 1330%. However, the extremely high deviation (1168%) in Miedema calculations for Fe-C shows that the main reason of this inaccuracy is more the uncertainty of the electronegativity and electron density rather than the mismatch of adjustable parameters. The standard deviation using the new set of adjustable parameters decreased from $11720\ \mathrm{J/mol}$ to $5941\ \mathrm{J/mol}$ and the prediction band is $\pm 6029\ \mathrm{J/mol}$. The results are indicated in Figure 4-29.

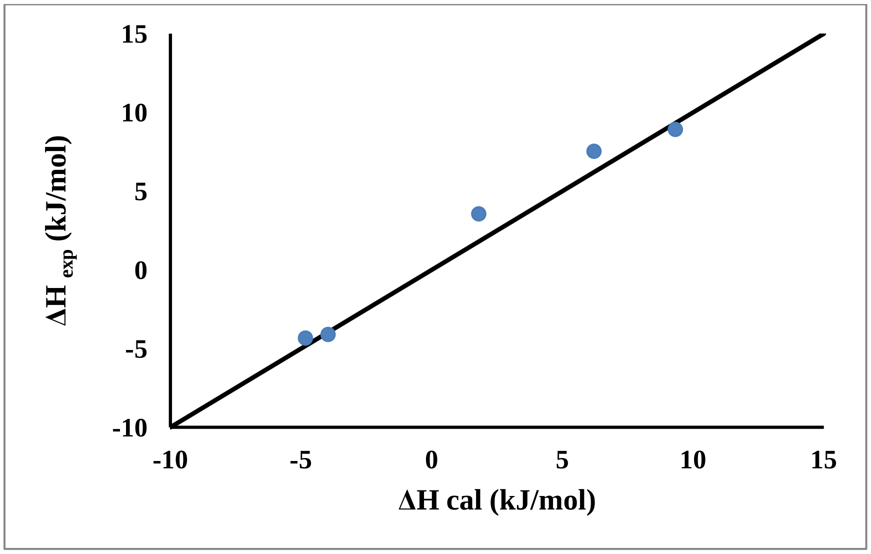


Figure 4-28. Extremum enthalpy of mixing calculated using Miedema model compared with the experimental enthalpy of mixing for the liquid phase of transition metals alloys listed in Table 4-3.

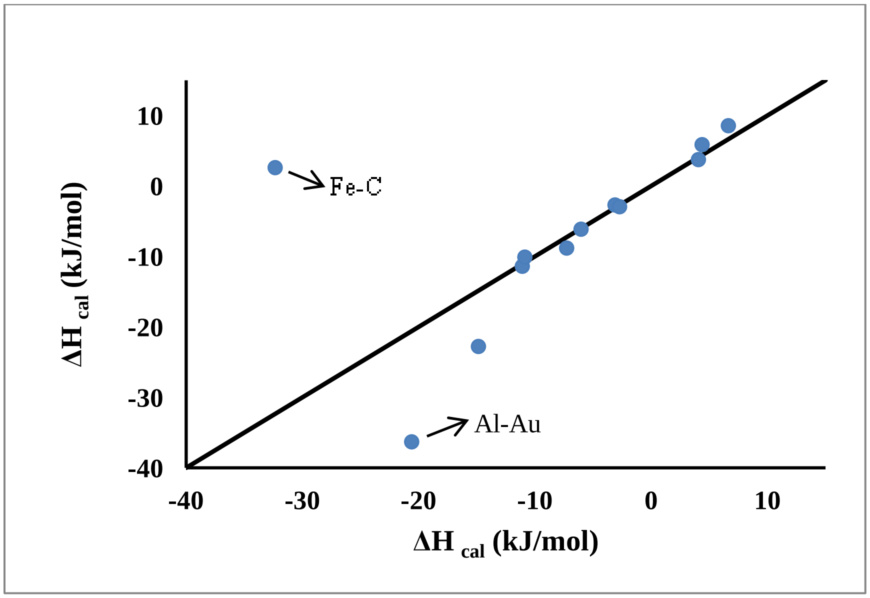


Figure 4-29. Extremum enthalpy of mixing calculated using Miedema model compared with maximum experimental enthalpy of mixing for the liquid phase of transition metals alloyed with non-transition p-metals or d^{10} *transition metals listed in Table 4-3.*

The results of the enthalpy of mixing of liquid *p*-metals alloyed with other *p*-metals are listed in Table 4-3 and presented in Figure 4-30. It can be seen that the percentage of difference in Miedema calculations reaches around 60% for Al-Ge system, 45% for In-Sn system and 36% for Bi-In system. This deviation can be explained by semi-conducting behavior of these metals. For ordinary *p*-metals, entropy of fusion is in the same range as transition metals but semi-conductors are exceptions. This difference in behavior can be related to the transformation energy from a semi-conducting state to metallic state. In other words, the semi-conductor by means of this transformation energy can be converted into a hypothetical metallic state [19]. For this group, the adjustable parameters are taken from Miedema et al. [19,20]. The standard deviation of Miedema calculations is $521\ \mathrm{J/mol}$ and the prediction band is $\pm 450\ \mathrm{J/mol}$.

Engel-Brewer method is not able to predict successfully enthalpy of mixing for *p*-metals alloyed with *p*-metals. For Bi-Sb and In-Tl, Engel-Brewer method highly overestimates enthalpy of mixing and the percentage of difference reaches to 4003% and for Al-Ga and Al-Sn, it underestimates the enthalpy of mixing.

For *p*-metals alloyed with d^{10} transition metals, the results are listed in Table 4-3 and presented in Figure 4-31. The highest deviation for Miedema calculations is for the Hg-In system (56%). For other systems, deviations are less than 35%. Standard deviation of Miedema calculations for this group of metals is $717\ \mathrm{J/mol}$ and the prediction band is $\pm 644\ \mathrm{J/mol}$.

In this group, for all of the systems with positive deviation from ideality, Engel-Brewer method overestimates the enthalpy of mixing. This can be related to the fact that in Engel-Brewer method, charge transfer caused by electronegativity is neglected.

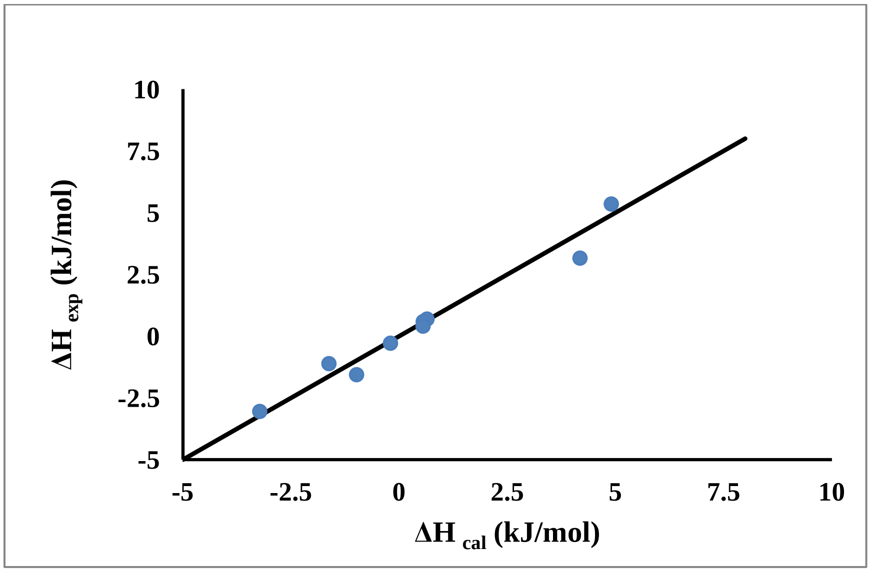


Figure 4-30. Extremum enthalpy of mixing calculated using Miedema model compared with the experimental enthalpy of mixing for the liquid phase of p-metals alloyed with other p-metals listed in Table 4-3.

Alkaline metals have very low electronegativities. For alkaline metals alloyed with *p*-metals, there is a large electronegativity difference and thus a large charge transfer. This will lead to a large volume contraction for alkaline metals during alloying. In cases of large charge transfer and large volumetric changes, parameters P, Q, n_{ws} and φ^* cannot be constant [20]. However, in order to use Miedema model to predict the enthalpy mixing of unknown systems there is no way to consider these parameters but constant. The adjustable parameters resulted in best consistency with the experimental data for $P = 14.24$ and $Q/P = 9.4$. From Table 4-3, it can be seen that, for most of the alkaline metals alloyed with *p*-metals, Miedema model overestimates the enthalpy of mixing. The results are visualized in Figure 4-32. The standard deviation of the enthalpy of mixing is estimated to be $3870\ J/mol$ and the prediction band is $\pm 5654\ kJ/mol$.

It can be seen from Table 4-3 that for alkaline metals alloyed with p-metals charge transfer plays a significant role in bonding because all of these systems have negative deviation from ideality. As charge transfer effect is neglected in Engel-Brewer method, it can be predicted that Engel-Brewer method is not at all applicable for this group. Table 4-3 indicates that this is the case for this group of alloys.

For alkali and alkaline metals alloyed with d^{10} transition metals, only two systems are studied. The percentage of difference in the results as listed in Table 4-3 are less than 30%. However it is hard to generalize the success of the model to all systems of this group. The same comment can be given for the case of actinides and alkali metals alloyed with rare earth alkaline metals for which only one system was studied.

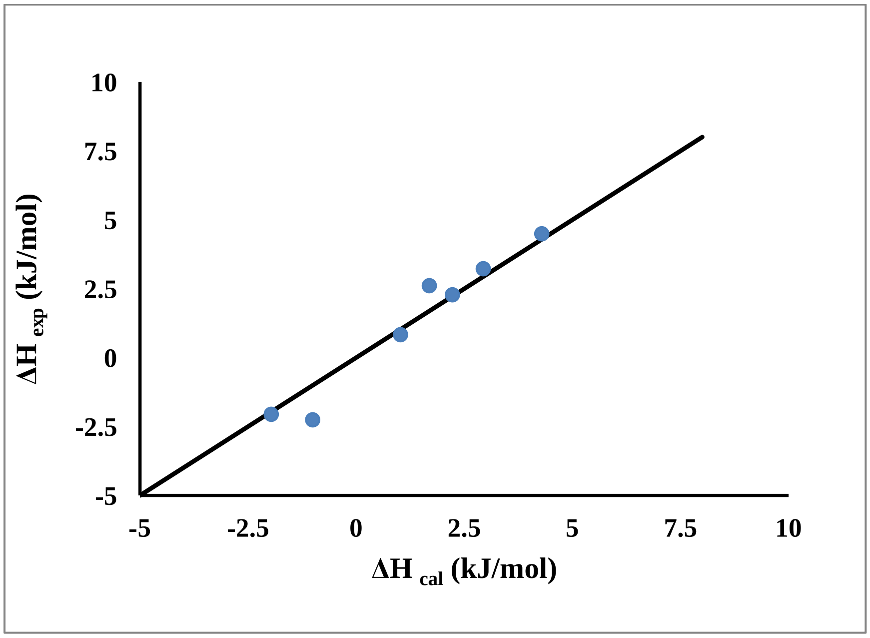


Figure 4-31. Extremum enthalpy of mixing calculated using Miedema model compared with the experimental enthalpy of mixing for the liquid phase of p-metals alloyed with d^{10} *transition metals listed in Table 4-3.*

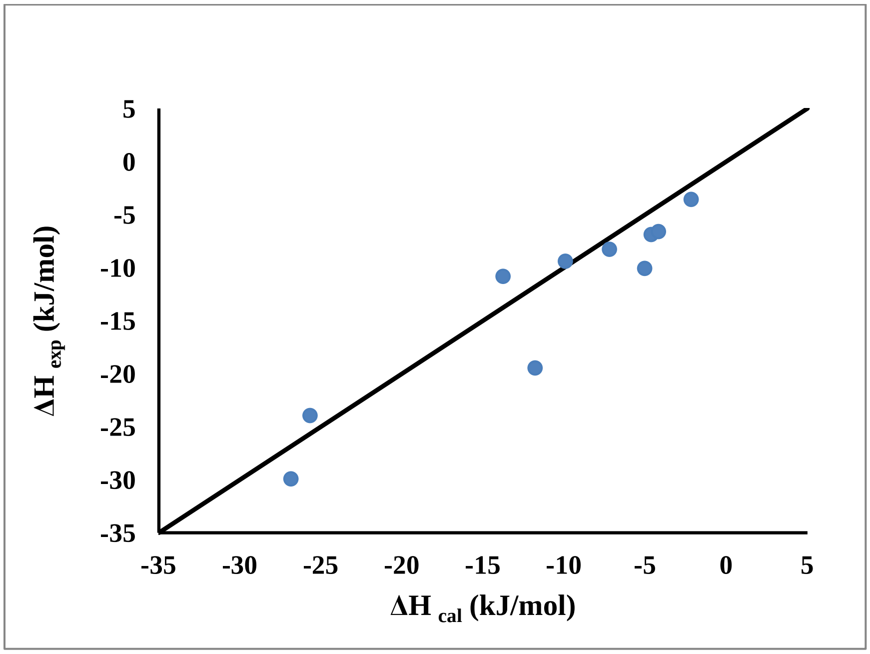


Figure 4-32. Extremum enthalpy of mixing calculated using Miedema model compared with the experimental enthalpy of mixing for the liquid phase of p-metals alloyed with alkali and alkaline earth metals listed in Table 4-3.

Since alkaline metals alloyed with d^{10} transition metals have positive deviation from ideality, Engel-Brewer method is not applicable to this group of alloys. For the case of Pu-U, while Engel-Brewer method overestimates the enthalpy of mixing, Miedema model gives a quite successful prediction of enthalpy of mixing with the deviation of 5%.

As can be seen in Table 4-3, the worst case for Miedema model is the group of d^{10} transition metals alloyed with other d^{10} transition metals. The results are presented in Figure 4-33. The deviation for this group reaches to 90% for both Engel-Brewer method and Miedema model. This can be explained by the repulsive force caused from the high stability of s^2 electronic configurations.

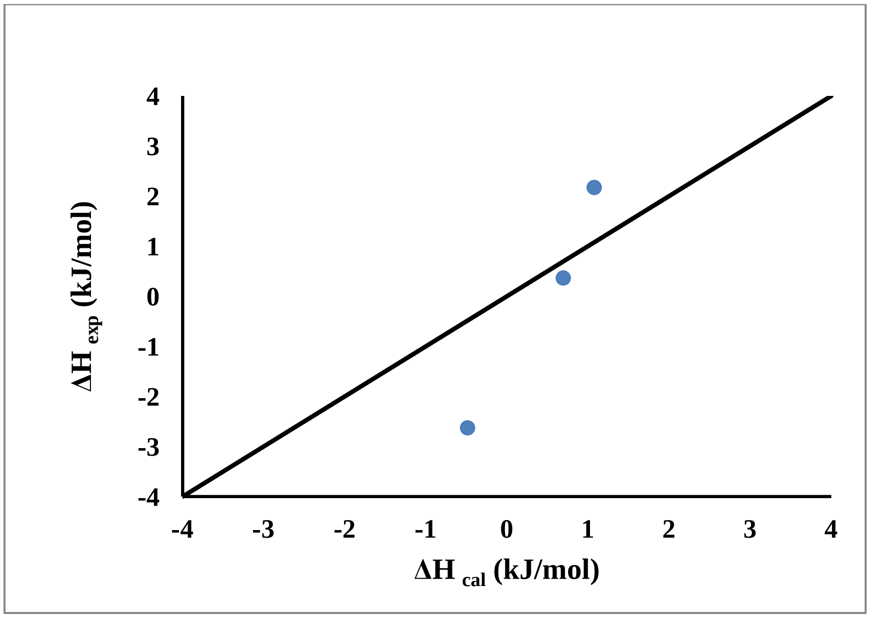


Figure 4-33. Extremum enthalpy of mixing calculated using Miedema model compared with the experimental enthalpy of mixing for liquid phase of d^{10} *transition metals alloyed with* d^{10} *transition metals listed in Table 4-3*

To summarize, Miedema model is a better choice than Engel-Brewer method to calculate enthalpy of mixing since it can predict negative contributions and asymmetry. However, there is still no clear explanation of the hybridization parameter and it is defined empirically. Miedema model can be applied to intermetallic compounds in addition to liquid and solid solutions. However, it cannot predict cohesive energies for non-stochiometric compounds.

In the formula proposed by Miedema (eqn. 2-36), the positive contribution which is the difference of electron density on the boundary of wigner-seitz cell is comparable to Hildebrand Formula [22,23] (eqn 2-4) in the following fashion [20]:

$$\Delta H^{vap} = n_{ws} \times V_m^{2/3} \qquad 4\text{-}1$$

In which $V_m$is the molar volume of the pure constituents of the system. Moreover, the electron density term is related to bulk modulus and molar volume of pure elements as shown in eqn. 2-25. In addition, the negative contribution is related to electronegativities of the pure constituents of the system. Therefore, contrary to Engel-Brewer method, Miedema model takes into account chemical and physical properties of pure elements.

From the results obtained in this section, it can be concluded that Miedema model (eqn. 2-36) can be used to find enthalpy of mixing of liquid alloys. Miedema suggested P and Q as constants for large group of metals and found them empirically; while, the results obtained in this section showed that the model can be improved if these groups of metals are divided into smaller sub groups. The proposed values for each of these sub-groups are reported in Table 4-4. Comparison of the new results with the original Miedema model indicated that, trying to describe widely alloy groups using the same set of model parameters in some cases can lead to large deviations from the experimental data. Finally, Miedema model was able to predict enthalpy of mixing for liquid alloys with maximum prediction band of about $7\ kJ/mol$ at confidence level of 90%. The confidence intervals and standard deviations for Miedema calculations are listed in Table 4-4. The accuracy of the results is not so high but it is enough as a first estimation for systems with limited or without experimental data on phase equilibrium and thermodynamic properties. Further modifications can be applied to the model if these sub groups are divided to smaller groups. For instance, Al alloyed with rare earth metals. In the next section, some of the modifications to Miedema model mentioned above are discussed.

Table 4-4. Proposed values for P and Q/P for different groups of elements with the standard deviation and prediction band at confidence level of 90%.

Group	P	Q/P $V^2/(du)^{2/3}$	Standard deviation $(\frac{J}{mol})$	Prediction band $\pm(\frac{J}{mol})$
Transition metals+ Transition metals	10.7	9.4	1323	2992
Transition metals+ Non-transition metals	12.87	9.64	5941	6029
p-metals+ *p*-metals	10.7	9.4	521	450
p-metals+d^{10} transition metals	10.7	9.4	717	644
p-metals+ Alkali and alkaline earth metals	12.35	9.4	3870	5654
d^{10} transition metals+ Alkali and alkaline metals	14.24	9.4	-----	-----
Actinides	10.7	9.4	-----	-----
d^{10} transition metals+ d^{10} transition metals	10.7	9.4	-----	-----
Alkali and alkaline earth metals+ Alkali and alkaline earth metals	14.1	9.4	-----	-----

Note: No standard deviation or prediction band is reported in cases where less than 5 systems are studied. For transition+ non-transition alloys R/P for Cu, Ag, Au, Fe is taken as 0.35, 0.1, 0.4, 0.9, respectively. Except alloys of transition-non transition metals and d^{10} transition metals-Alkali and alkaline metals, Miedema parameters taken directly from Miedema et al. [19].

4.2.2 Improvements to Miedema model

Miedema and co-workers [19] assumed that hybridization will increase when the number of P valence electrons increases. However, they assumed for the majority of transition metals, this value is constant. Therefore, for all the lanthanides, they assumed the value of R/P as 0.7.

In another attempt, Colinet et al. [153] measured heats of solution of rare earth-tin alloys. They concluded that this hybridization parameter (*R/P*) should change among rare-earth metals. Since the number of *f* electrons affects hybridization, Gschneidner et al.

[154] proposed that the participation of *4f* electrons in bonding can be presented by the ratio of metallic radius to the *4f* radius ($^{r_M}/_{r_{4f}}$) . Using this ratio, Colinet et al. [153] modified *R/P* for rare earth metals. The new results showed more consistency with the experimental data. Colinet et al. [155] used the same approach to calculate heats of mixing of rare earth metals in lead and bismuth liquid alloys. In this work, these modified *R/P* values are used to find enthalpy of mixing at $x_{RE} = 0.005\, at\%$. The results of enthalpy of mixing using the modified *R/P* values are compared with the experimental data of [156-158] and with the classical Miedema parameters in Figure 4-34. It can be seen that the new calculated values for enthalpy of mixing of Zn-RE liquid alloys are closer to the experimental data of [156-158] compared to the classical Miedema predictions.

Zhan et al. [159] studied Al-RE liquid alloys and established new φ^* parameters for rare earth elements based on their atomic radius. Similar to the electronegativities reported by Miedema et al. [20,71,75,78,80-83], the new set of parameters (φ^*) proposed by Zhan et al. [159] were all in the range of uncertainty of the work function (φ), while the enthalpies of mixing obtained by Zhan et al. [159] were much closer to the experimental results of [159-164] compared to Miedema's classical predictions. Some of their results are presented in Figure 4-35(a), (b), (c) for Al-La, Al-Ce, Al-Sc systems. Their results for Al-Nd, Al-Y and Al-Eu were also more consistent with the experimental data [159-164] compared to Miedema's classical calculations.

In another attempt, Shubin et al. [107] calculated enthalpy of formation (Al-Ga-In-Tl-Sn-Pb-Sb-Bi)-RE compounds. In their calculations, they made slight changes to φ^*

and n_{ws} to find best fit with experimental values. In addition they changed *P*, *Q/P and R/P*. The final results had better consistency with the experimental data compared to classic Miedema model.

All these examples prove that classical Miedema model can be improved if appropriate model parameters are found for each small family of elements such as Zn-RE, etc and it can result in reliable predictions for systems without enough experimental data. The results will be more reliable if model predictions of enthalpy of mixing are compared with the ones from first-principles calculations. However, this model is simple, easily parameterized and less time consuming compared to first-principles calculations. One of the significant advantages of this model is that apart from enthalpy of mixing, this model can also be applied to find physical properties such as bulk modulus for intermetallic compounds [165].

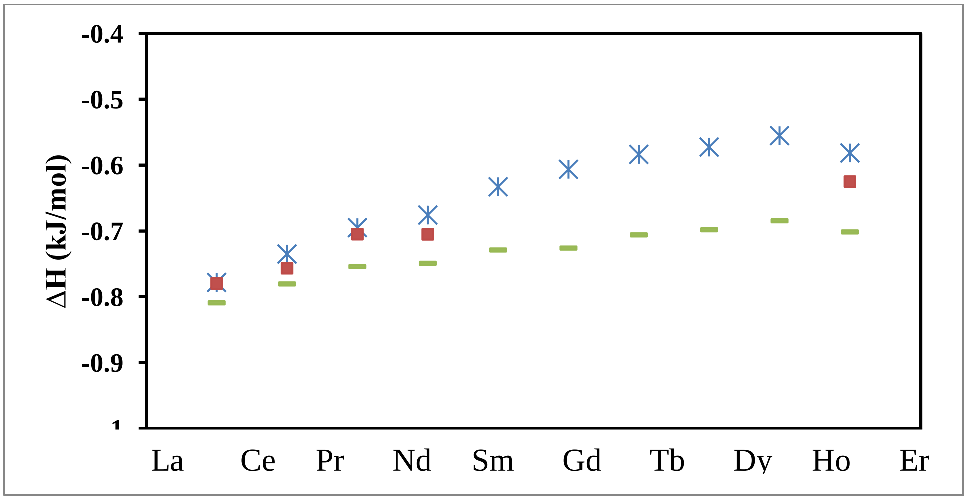


*Figure 4-34. Predicted enthalpy of mixing of Zn-RE liquid alloys at x_{RE}=0.005 using modified Miedema hybridization parameters, proposed by Colinet et al. [153] compared with the experimental data and classical Miedema parameters. ■ is the experimental data of [156-158] . * is calculated enthalpy of mixing at $x_{RE} = 0.005\ at\%$ using new Miedema hybridization parameters and _ is calculations with classical Miedema parameters.*

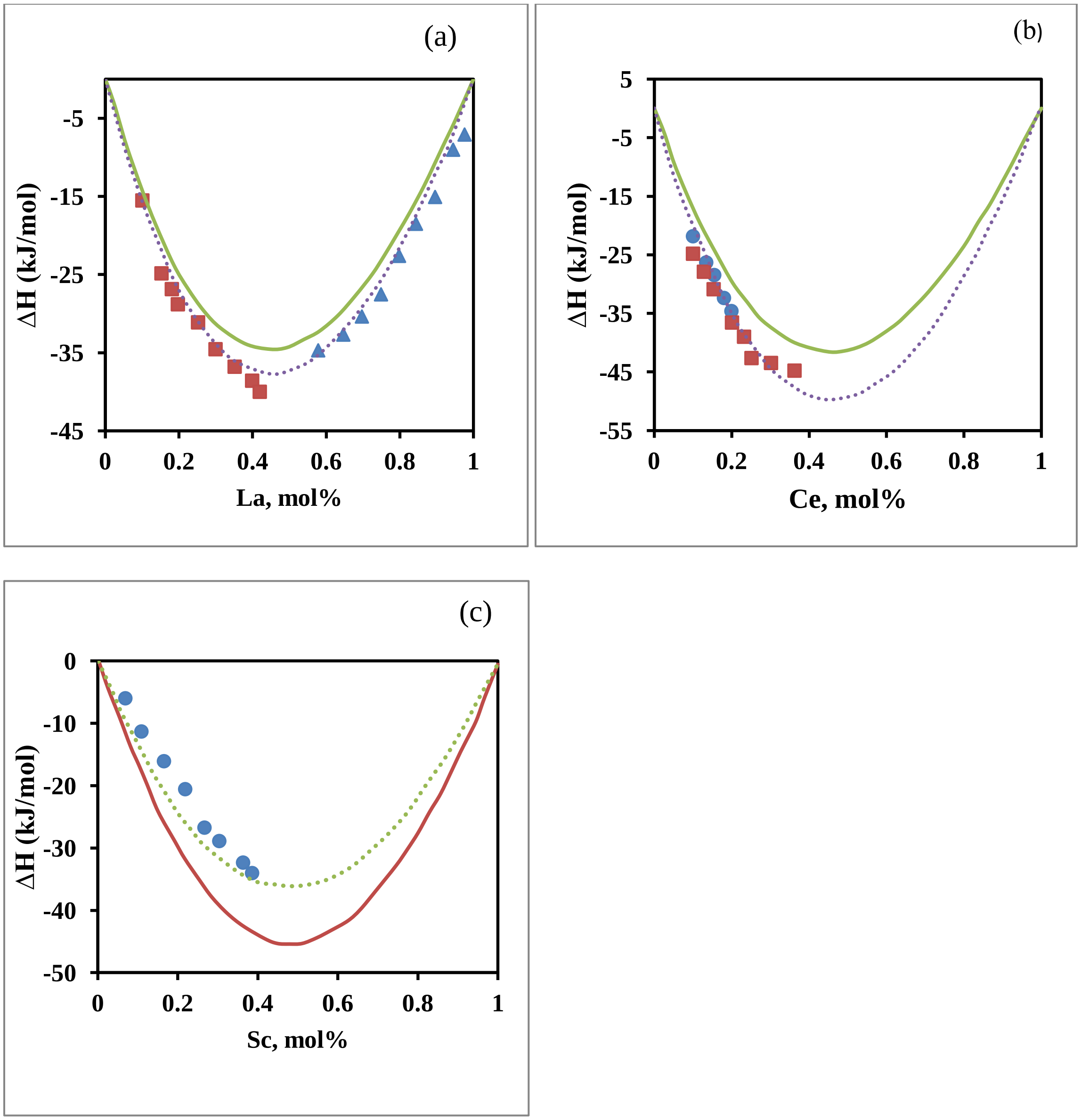


Figure 4-35. Comparison of enthalpy of mixing of Al-RE systems calculated with classical Miedema parameters and modified Miedema parameters with the experimental data. — is calculations by classical Miedema parameters and .... is calculations using new Miedema parameters by Zhan et al. [159] (a) Al-La system. ■ is the experimental data of Esin et al. [160] at 1920K, ▲ is the experimental data of Sommer et al. [161] at 1200K, (b) Al-Ce system. ■ is the experimental data of Esin et al. [162] at 1870K, ● is the experimental data of Zviadadze et al. [163] at 1250K. (c) Al-Sc system, ● is the experimental data of Litovskii et al. [164] at 1873K

4.2.3 Prediction of enthalpy of mixing for solid solutions

As discussed in section 2.4.6, for solid solutions, elastic contribution should be taken into account. Table 4-5 indicates enthalpy of mixing for 25 solid solutions. Elastic contribution arises from the elastic energy created by size mismatch. It adds a positive contribution to enthalpy of mixing of solid solutions. In order to see in detail the effect of each term, chemical and elastic contributions to enthalpy of mixing for each binary system are displayed in Table 4-5 as well. It should be mentioned that for simplicity, only extremum values of enthalpy of mixing are calculated. It can be seen that for some systems such as Ag-Au, Ag-Zn, Al-Zn, Ga-Mg, Ag-Mg, etc. Miedema's estimation of enthalpy of mixing is close to the reported data of Hultgren et al. [141]. For the majority of the systems studied such as Ag-Au, Ag-Zn, Fe-V, Nb-Zn, Cu-Pt and Al-Zn, in order to be more consistent with estimations of Hultgren et al. [141], the amount of elastic contribution should increase. For Ni-Pt, Ni-Pd, Fe-Pd and Au-Ni, the chemical contribution was closer to the estimations of Hultgren et al. [141] and the addition of elastic positive term resulted in large deviations from the estimations of Hultgren et al. [141] . For Fe-Mn and Cu-Ni, the chemical contribution is highly positive. For the Fe-Mn system, deviation of model prediction from estimations of Hultgren et al. [141] can be related to the peculiarity of Mn. Since Mn has half-filled *3d* shell electrons, it will lie between a transition metal like Fe and a non-transition metal like Zn. It can be a metal with variable molar volume and thus variable n_{ws}.

Table 4-5. Extremum enthalpy of mixing for solid solution of 25 binary systems calculated using Miedema model compared with thermodynamic the assessment of Hultgren et al. [141]

System	H chem. (J/mol)	H elastic (J/mol)	H (J/mol)	H exp. (J/mol)	Difference%	T(K)
Ag-Au	-3087	301	-2786	-1111	151	800
Ag-Mg	-8230	4739	-3931	-4400	11	773
Ag-Pd	-3954	2312	-1642	-1200	37	1200
Ag-Zn	-3299	315	-2983	-952	213	873
Al-Zn	439	190	629	825	24	653
Au-Cd	-8743	3654	-5089	-4580	11	700
Au-Cu	-4830	3279	-1550	-1221	27	800
Au-Ni	3688	9030	12718	1807	604	1150
Cd-Mg	-4673	448	-4225	-1322	220	543
Cr-Fe	-727	89	-787	1400	156	1600
Cr-Mo	189	5179	4216	1725	144	1471
Cr-Ni	-3339	961	-2379	425	660	1550
Cr-V	-1002	1683	681	-455	250	1550
Cu-Ni	729	836	1627	425	283	973
Cu-Pd	-7432	863	-6569	-2557	157	1350
Cu-Pt	-6517	1144	-5372	-2650	103	1350
Fe-Mn	117	232	349	-1130	131	1450
Fe-Pd	-2294	2019	-275	-2257	88	1273
Fe-V	-3617	2226	-1390	118	1278	1600
Ga-Mg	-3611	1198	-2413	-2406	0.28	923
Mn-Ni	-4199	1208	-2991	-3397	12	1050
Nb-Zn	-5921	1277	-4644	-2678	73	1100
Ni-Pd	-27	4178	4151	-463	996.50	1273
Ni-Pt	-2295	5507	3212	-2214	245.08	1625
Pb-Tl	-554	18	-536	-463	15.68	523

Overall, there may be some discrepancies because of neglecting structural contributions in Miedema model [101]. Pettifor [62] calculated these structural contributions theoretically. Miedema and co-workers [19] assumed that structure dependant enthalpy vary systematically with the average number of valence electrons per atom in solid solutions of transition metals if the two metals form a common band of d-type electron states. They have assigned some values to this structure-dependent enthalpy based on the number of valence electrons in solute and solvent. However, this assumption cannot be used for noble metals alloyed with other transition metals such as Cu-Ni since the valence electrons of Cu are s-type.

Overall, for 32% of the systems studied here, Miedema model predictions for solid solutions indicated good consistency with the data reported by Hultgren et al. [141] (deviations less than 36%). For the rest of the systems, Miedema model did not provide satisfactory estimations. For some systems, even the signs between the results of Hultgren et al. and Miedema's calculations are opposite. The standard deviation of Miedema predictions from estimations of Hultgren et al. [141] is $2429\,J/mol$. These deviations from reported data of Hultgren et al. [141] can be related to error in the calculation of chemical contribution like the case of Fe-Mn system or errors in the calculation of elastic contributions or neglecting structure-dependant contributions. Consequently, it can be concluded that despite the fact that application of classical Miedema model to solid solutions in systems such as Ga-Mg, Ag-Pd, etc. led to consistent results compared with the estimations of Hultgren et al. [141], this model for solid solutions has a lot of uncertainties and cannot be a reliable to predict enthalpy of solid solutions for systems with unknown thermodynamic data. However, recently, some modifications are applied to classical Miedema model [106,166,167] which proved that possible modifications to Miedema model for solid solutions can result in good consistency with the experimental data. Takeuchi et al. [167] modified the relationship for calculation of surface densities applied in equation 2-36 and thus obtained new results for enthalpy of mixing of solid solutions for 2627 systems. From these results and the results of enthalpy of mixing for amorphous alloys, Takeuchi et al. [167] predicted successfully forming ability of amorphous and glassy alloys. Sun et al. [166] used the modified formula of Takeuchi et al. [167] to obtain enthalpy of mixing of solid solutions of Al-Ni-RE alloys and predicted glass forming ranges for these alloys. Their predictions were consistent with the experimental data. Basu et al. [96] used the same method as Sun et al. [166] to predict glass forming ability in (Zr-Ti-Hf)-(Cu-Ni) systems and obtained satisfactory results. However, none of these studies focuses directly on enthalpy of mixing of solid solutions and its comparison with the experimental data. More studies should be carried out to modify Miedema model for soild solutions.

4.3 Prediction of entropy of mixing for liquid solutions

As discussed in section 2.5, Faber [24] in his proposed relation for entropy of mixing of liquid alloys assumed that the variation of entropy of mixing from ideality is the result of volume change during mixing. Meaning that, he assumed excess entropy of mixing equals to configurational entropy. Entropy of mixing calculated by his model for different binary systems are summarized in Table 4-6 and demonstrated in Figure 4-36. It should be mentioned that the results of entropy of mixing for simplicity are at equiatomic composition.

It can be seen that Faber relation [24] overestimated entropy of mixing for majority of the systems studied. From Figure 4-36 it can be seen that $Y = x$ line cannot be used at all as the best fit. However, for some systems the predictions are close to the data reported by Hultgren et al. [141], analysis of the data indicated that the majority of these systems are the systems with very small deviation from ideality such as Cd-Tl, Cd-Zn, Cu-Fe, etc. The results of the calculations are even worse for simplified Guggenheim relation [27]. From Figure 4-37 and Table 4-6, it can be seen that all the calculations are around $6\, J/mol.K$ which is close to the ideal entropy of mixing at equiatomic composition (5.76 $\frac{J}{mol.K}$). Therefore, it can be concluded that the assumptions to simplify the Guggenheim relation ($z \rightarrow \infty$ and $\gamma = \frac{\gamma_2}{\gamma_1}$) [27] are not correct. The assumption $z \rightarrow \infty$ is applied to take into account long-range ordering. However, this assumption does not have physical meaning for liquid alloys and is mostly applied to solid solutions. In addition, Guggenheim [25] has proposed his relation for the cases when energetic effect is zero. Therefore, the question is raised whether energetic effect for calculation of entropy of mixing can be neglected.

Table 4-6. Comparison of entropy of mixing at equiatomic composition for liquid alloys (J/mol.K) for different binary systems calculated using Faber [24], simplified Guggenheim [27], sommer [27] and Witusiewicz et al. [31]relations in comparison with the estimations of Hultgren et al. [141].

System	Faber [24]	Simplified Guggenheim [27]	Sommer [27]	Wituciewicz [31]	Exp. [141]	Faber Diff.%	Simplified Guggenheim Diff. %	Sommer Diff. %	Wituciewicz Diff.%	T(K)
Ag-Au	5.45	5.77	2.72	5.24	4.20	30	37	35	25	800
Ag-Cu	8.07	5.92	5.59	7.06	12.76	37	54	56	45	1400
Ag-Ga	5.82	5.77	3.91	4.89	6.10	5	5	36	20	1000
Ag-Pb	10.94	6.05	9.37	7.66	7.59	44	20	23	1	1000
Al-Au	5.85	5.77	0.06	4.43	4.48	30	29	99	1	400
Al-Cu	8.72	5.90	2.54	4.139	9.16	5	36	72	55	1373
Al-Fe	13.86	5.91	2.86	5.16	9.16	51	35	69	44	1873
Al-Ga	5.75	5.77	5.98	5.95	6.07	5	5	1	2	1073
Al-Ge	6.45	5.80	5.55	5.59	6.28	3	8	12	11	1200
Al-In	7.62	5.91	4.96	6.56	6.36	20	7	22	3	1173
Al-Mg	7.47	5.86	5.74	5.58	5.86	27	0.12	2	5	1073
Al-Sn	9.11	5.94	5.62	6.7	6.98	30	15	19	4	973
Au-Cu	13.19	5.90	1.49	3.04	5.65	133	4	73	46	800
Au-Ni	20.94	5.94	6.05	8.37	8.10	158	27	25	3	1150
Au-Sn	1.83	5.94	-1.68	1.38	7.07	74	16	124	80	823
Au-Zn	8.18	5.79	-3.20	-0.23	3.64	125	59	188	106	1080

Table 4.6. Continued

System	Faber [24]	Simplified Guggenheim [27]	Sommer [27]	Wituciewicz [31]	Exp. [141]	Faber Diff.%	Simplified Guggenheim Diff.%	Sommer Diff. %	Wituciewicz Diff. %	T(K)
Bi-Cd	11.15	5.93	5.24	6.11	7.11	57	17	26	14	773
Bi-Cu	27.09	6.71	8.10	6.87	7.58	257	11	7	9	1200
Bi-In	7.58	5.83	4.12	5.43	5.53	37	5	25	2	900
Bi-Mg	7.69	5.87	-4.79	0.57	5.02	53	17	195	89	975
Bi-Na	6.85	5.79	-12.03	-5.98	-3.30	308	276	265	81	773
Bi-Sb	7.22	5.77	5.17	5.85	8.14	11	29	36	28	1200
Bi-Zn	19.37	6.32	4.83	7.66	7.85	147	19	38	2	873
Cd-Hg	5.85	5.77	2.66	5.75	5.06	16	14	47	14	600
Cd-Mg	6.32	5.78	1.82	0.33	4.72	34	22	61	93	543
Cd-Pb	8.09	5.88	7.17	7.08	6.28	29	6	14	13	773
Cd-Sb	-0.41	5.90	5.38	5.53	7.12	106	17	24	22	773
Cd-Tl	7.71	5.84	6.58	7.59	6.77	14	13	3	12	750
Cd-Zn	7.64	5.89	4.85	7.34	5.86	30	0.56	17	25	800
Cu-Bi	27.09	6.71	8.10	6.87	7.58	258	11	7	9	1200
Cu-Fe	5.89	5.77	8.47	7.58	6.44	8	10	31	18	1823
Cu-Sb	3.63	6.64	6.29	5.26	8.19	56	19	23	36	1190
Cu-Tl	19.40	6.47	7.84	7.98	7.70	152	16	2	4	1573
Fe-Si	13.91	5.90	3.94	3.98	-4.74	394	244	183	184	1873

Table 4.6. Continued

System	Faber [24]	Simplified Guggenheim [27]	Sommer [27]	Wituciewicz [31]	Exp. [141]	Faber Diff.%	Simplified Guggenheim Diff.%	Sommer Diff. %	Wituciewicz Diff.%	T(K)
Ga-Mg	7.31	5.84	4.33	3.5	5.33	37	10	19	34	923
Hg-In	6.18	5.78	3.69	3.94	5.22	18	11	29	24	298
Hg-Na	15.03	6.03	-7.50	-1.77	-3.82	493	258	96	54	673
Hg-Zn	8.59	5.92	-0.88	6.74	4.85	77	22	118	39	573
In-Mg	5.70	5.77	-1.31	3.63	5.36	6	8	124	32	923
In-Na	11.48	5.93	-0.19	3.94	-0.77	1591	870	75	612	713
In-Sb	0.55	5.81	2.50	4.13	6.51	91	11	62	36	900
In-Sn	5.91	5.77	5.14	4.76	6.73	12	14	24	29	700
In-Tl	5.91	5.78	6.27	5.22	5.48	8	5	14	5	723
In-Zn	11.17	6.02	4.20	6.67	6.96	60	13	40	4	700
K-Pb	30.69	6.55	-17.13	-4.61	-3.12	1083	310	449	48	848
K-Tl	30.60	6.68	-13.03	-0.52	-0.76	4140	981	1339	31	798
Mg-Li	4.93	5.79	4.79	5.86	5.84	15	0.88	18	0.40	1000
Mg-Pb	5.66	5.83	-3.24	1.41	5.19	9	12	162	73	973
Mg-Tl	5.82	5.80	-2.89	3.9	6.49	10	11	144	40	923
Pu-U	6.83	5.77	6.11	6.17	8.75	21	34	30	29	1500

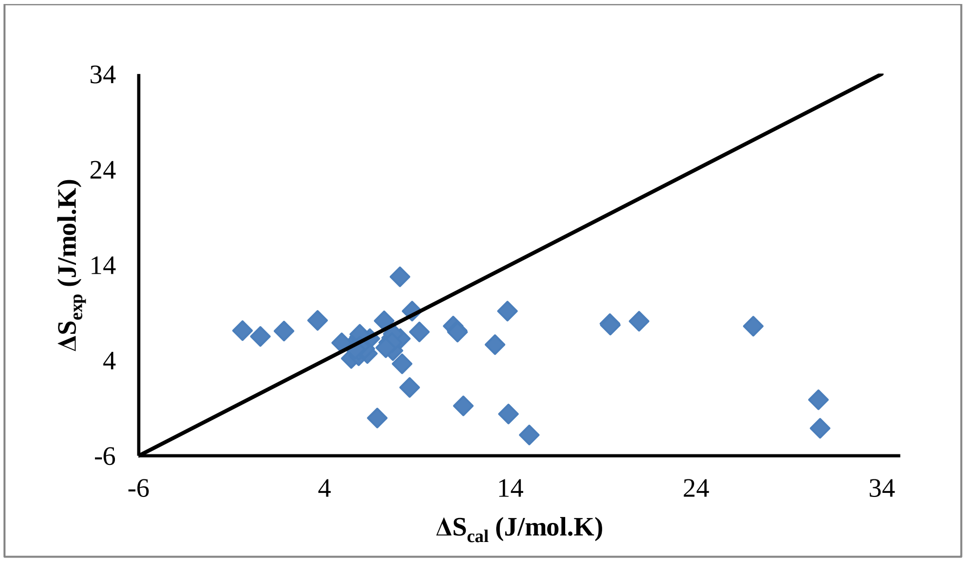


Figure 4-36. Calculated entropy of mixing by Faber relation [24] compared with the experimental entropy of mixing at equiatomic composition for liquid alloys of 49 binary systems listed in Table 4-6.

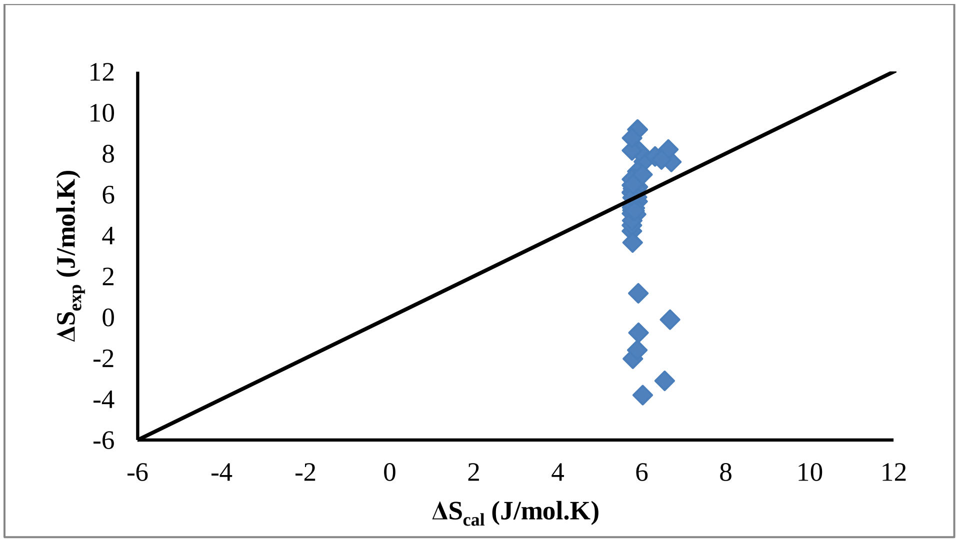


Figure 4-37. Calculated entropy of mixing by simplified Guggenheim relation [27] compared with the experimental entropy of mixing at equiatomic composition for liquid alloys of 49 binary systems listed in Table 4-6.

Sommer [27] combined Debye model taking into account vibrational entropy, simplified Guggenheim relation [27] to take into account configurational entropy and

Flory expression [130] for the energetic effects. Therefore, it is expected that his relation show more consistency with the experimental data. Table 4-6 and Figure 4-38 show that there is more consistency with the estimations of Hultgren et al. [141] compared to Faber [24]and simplified Guggenheim relation [27]. However, in some cases such as K-Tl, K-Pb, Fe-Si, In-Na, etc. there is a large difference between Sommer predictions [27] and the results of Hultgren et al. [141]. This difference can be related to errors in empirical relations he used, such as $\Delta\theta_{l,alloy}$, $\frac{\alpha_{l,alloy}}{\chi_{l,alloy}}$ and $\alpha_{l,alloy}(\frac{\chi_{l,B}-\chi_{l,A}}{\chi_{l,alloy}})$. In addition, the deviations from the results of Hultgren et al. [141] can arise from neglecting magnetic and electric contributions. For some cases such as alloys of transition metals with non transition metals, Pasturel et al. [168] showed that electronic contribution to entropy of mixing cannot be neglected. Moreover, Sommer in his proposed relation [27] used simplified Guggenheim relation [25] to take the size mismatch contribution to entropy of mixing into account. However, from Figure 4-37, it can be seen that simplified Guggenheim relation [25] results in close to ideal entropy of mixing which is almost constant for all the systems. Afterall, the deviations from the results of Hultgren et al. [141] can also be attributed to the errors in the calculation of enthalpy of mixing from Miedema model. The standard deviation of the calculations using Sommer relation is 5.08 J/(mol.K) with the prediction band of 6.44 J/(mol.K) at confidence level of 90%. In order to verify whether the deviations in calculation of entropy of mixing from Sommer relation can be attributed to the errors in calculation of enthalpy of mixing with Miedema model, the experimental enthalpy of mixing is used in Sommer relation (eqn. 3-14) for these 49 binary systems. The entropy of mixing obtained by replacing Miedema enthalpy of mixing with the experimental one is compared with the estimations of Hultgren et al. [141] in

Table 4-7 and Figure 4-39. Surprisingly, the standard deviation changed to 5.32 J/(mol.K). This subtle change in the standard deviation of entropy of mixing shows that the energetic contribution in the entropy of mixing which is neglected in Sommer relation [25] is small. Moreover, it shows that the deviation in Sommer relation [25] is more related to the two other reasons mentioned before rather than the error in Miedema predictions for enthalpy of mixing.

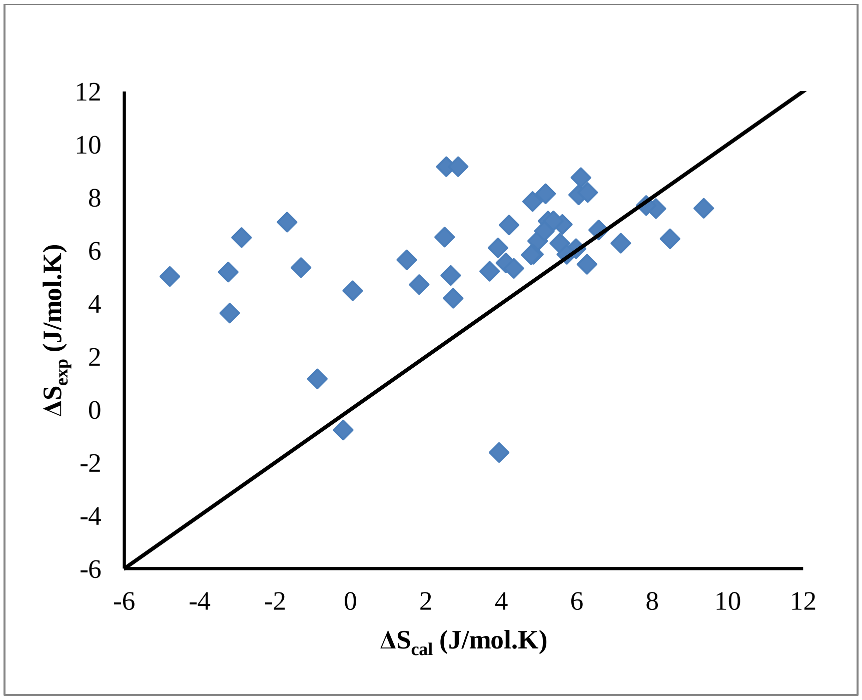


Figure 4-38. Calculated entropy of mixing using Sommer relation [27] compared with the experimental entropy of mixing at equiatomic composition for liquid alloys of the 49 binary systems listed in Table 4-6.

Compared to the theoretical relationships of Faber [24], simplified Guggenheim [27] and Sommer [27], the empirical relation of Wituciewicz et al. [31] for entropy of mixing based on average melting and boiling temperatures of the constituent elements of the system gave the best results. The calculations of entropy of mixing using Wituciewicz et al. relation [31] with enthalpy of mixing from Miedema model are compared with the experimental data in Table 4-6 and depicted in Figure 4-40. The standard deviation of this model is 2.71 J/(mol.K) with prediction band of ± 2.56 J/(mol.K) at confidence interval of 90%. The results demonstrate that the relation proposed by Wituciewicz et al. [31] compared to other relations studied [24,27], can be more reliable to predict entropy of mixing for liquid alloys. However, for some systems deviations are high. Since Miedema model is used as the enthalpy of mixing in this relation, it can be predicted that systems with high error in enthalpy of mixing deviate more from the experimental data. Table 4-6 demonstrate that this is the case for systems Hg-Zn, Fe-Si, Bi-In, etc. Wituciewicz et al. [31] estimated the accuracy of the model when experimental enthalpy of mixing is used as ± 2 J/(mol.K). Moreover, the experimental data reported are estimations of Hultgren et al. [141] and in some cases calculations for entropy of mixing are in the range of uncertainty of Hultgren estimations [141]. It should not be forgotten that experimental data for entropy of mixing are never exact because there is no way to measure entropy directly and thus they are accompanied with uncertainties. In other words, in order to obtain the experimental data for entropy of mixing, first activities of the constituents in the alloy should be measured. From the Gibbs energy obtained from the activities, the experimental data of the enthalpy and entropy of mixing are calculated. Therefore, the reported data for entropy of mixing always involve accumulated errors from each of the above mentioned steps.

Table 4-7. Comparison of the effect of replacing $\Delta H_{Miedema}$ *with* $\Delta H_{exp.}$ *on the entropy of mixing (J/mol.K) obtained by Sommer relation [27]. Entropy of mixing for liquid alloys is obtained at equiatomic composition. The experimental data are taken from estimations of Hultgren et al. [141]*

System	S with $\Delta H_{Miedema}$	S with $\Delta H_{exp.}$	exp.	System	Sommer	Sommer exp.	exp.
Ag-Au	2.72	2.64	4.20	Cd-Sb	5.38	5.32	7.12
Ag-Cu	5.59	6.52	12.76	Cd-Tl	6.58	6.64	6.77
Ag-Ga	3.91	4.12	6.10	Cd-Zn	4.85	5.48	5.86
Ag-Pb	9.37	9.07	7.59	Cu-Bi	8.10	8.10	7.58
Al-Au	0.06	-10.07	4.48	Cu-Fe	8.47	8.32	6.44
Al-Cu	2.54	2.02	9.16	Cu-Sb	6.29	6.19	8.19
Al-Fe	2.86	2.83	9.16	Cu-Tl	7.84	9.46	7.70
Al-Ga	5.98	5.96	6.07	Fe-Si	3.94	4.12	6.74
Al-Ge	5.55	5.75	6.28	Ga-Mg	4.33	4.33	-1.62
Al-In	4.96	4.69	6.36	Hg-In	3.69	1.96	5.33
Al-Mg	5.74	5.25	5.86	Hg-Na	-7.50	-11.21	5.22
Al-Sn	5.62	6.16	6.98	Hg-Zn	-0.88	-1.12	-3.82
Au-Cu	1.49	1.75	5.65	In-Mg	-1.31	-2.43	1.16
Au-Ni	6.05	6.74	8.10	In-Na	-0.19	-1.06	5.36
Au-Sn	-1.68	-1.86	7.07	In-Sb	2.50	2.36	-0.77
Au-Zn	-3.20	-6.42	3.64	In-Sn	5.14	5.23	6.51
Bi-Cd	5.24	5.06	7.11	In-Sn	5.14	5.23	6.73
Bi-In	4.12	3.55	5.53	In-Tl	6.27	6.49	5.48
Bi-Mg	-4.79	7.96	5.02	In-Zn	4.20	4.41	6.96
Bi-Na	-12.03	-13.58	-2.04	K-Pb	-17.13	-16.14	-3.12
Bi-Sb	5.17	5.15	8.14	K-Tl	-13.03	-8.32	-0.13
Bi-Zn	4.83	4.98	7.85	Mg-Li	4.79	4.24	5.84
Cd-Hg	2.66	0.16	5.06	Mg-Pb	-3.24	-3.05	5.19

Cd-Mg	1.82	1.92	4.72	Mg-Tl	-2.89	-8.32	6.49
Cd-Pb	7.17	8.08	6.28	Pu-U	6.83	6.24	8.75

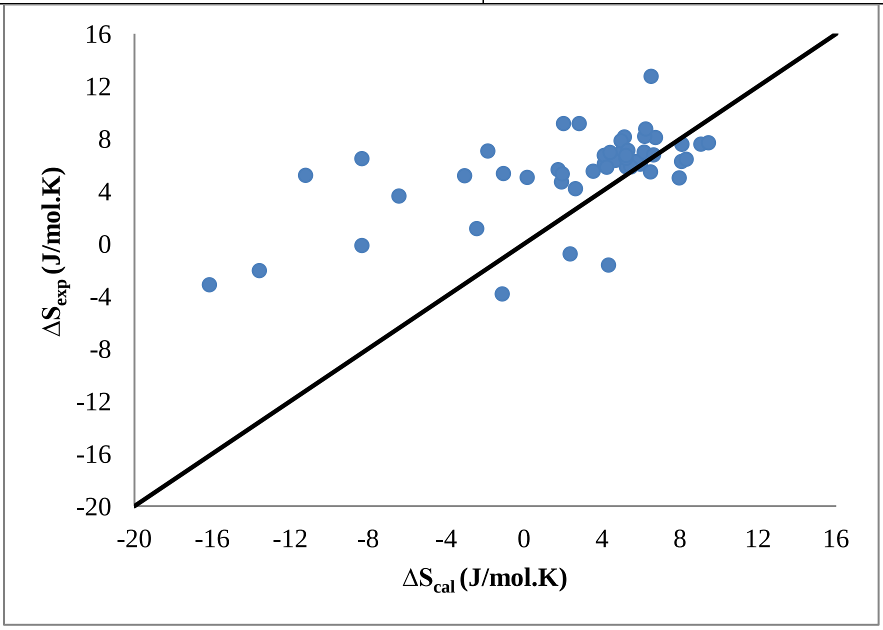


Figure 4-39. Calculated entropy of mixing using $\Delta H_{exp.}$ instead of $\Delta H_{Miedema}$ in Sommer relation [27] compared with the experimental entropy of mixing at equiatomic composition for liquid alloys of the 49 binary systems listed in

Table 4-7.

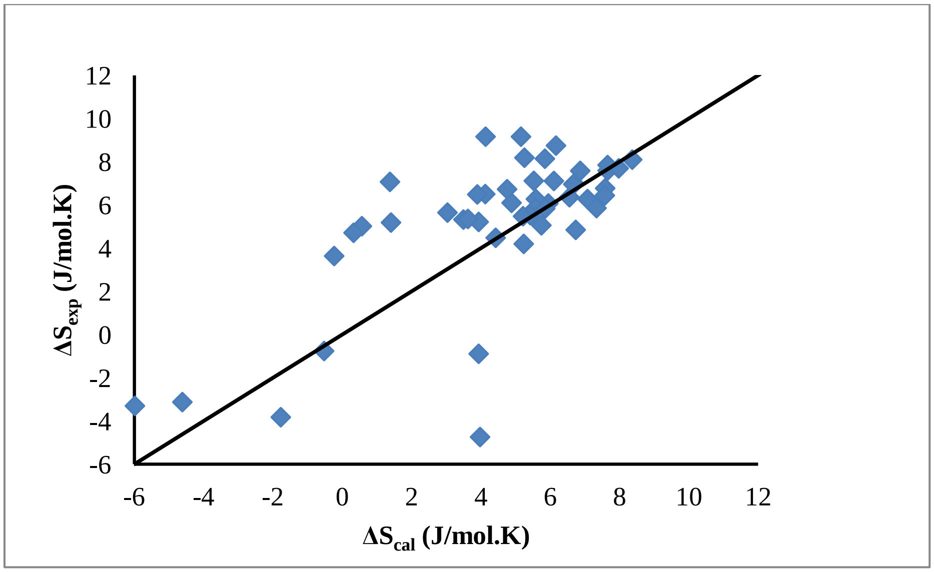


Figure 4-40. Calculated entropy of mixing using empirical relation of Witusiewicz et al. [31] compared with the experimental entropy of mixing at equiatomic composition for liquid alloys of 49 binary systems listed in Table 3-4.

4.4 Empirical description of excess heat capacity of liquid alloys

Of all the thermodynamic properties calculated in thermodynamic modeling, the excess heat capacity is the most neglected. Knowledge of excess heat capacities can result in finding temperature dependency of the excess enthalpy and excess entropy of mixing. The product of temperature and the first derivate of eqn. 2-61 proposed by Wituciewicz et al. [31] for entropy of mixing ($T \times {}^{ds}\!/_{dT}$) can be used to obtain a formula for excess heat capacity of liquid alloys. The heat capacity data obtained from this relation are compared with the experimental data of Bergman et al. [169] and are listed in Table 4-8. Figure 4-41 illustrates the correlation between the experimental and calculated results. Least square analysis of the results indicate that the results are satisfactory with standard deviation of 3.52 J/(mol.K) and prediction band of ± 2.35 J/(mol.K) at confidence level of 90%.

Table 4-8. Excess heat capacities of binary liquid alloys calculated by Wituciwicz relation [31] and compared with the experimental data [169]. Enthalpy of mixing used in the calculations are obtained from Miedema model.

System	Cp cal. ($\frac{J}{mol.K}$)	Cp exp. [169] ($\frac{J}{mol.K}$)	Difference%	T(K)	Composition (at%)
Ag-Ga	2.61	3.84	32	900	0.55
Al-Cu	4.7	4.28	10	1200	0.5
Au-Sn	7.41	6.12	21	780	0.5
Bi-In	1.47	-0.5	394	600	0.5
Cd-Pb	-0.77	0	77	623	0.5
Cd-Sb	3.87	4.78	19	693	0.57
Cu-Sb	2.65	8.9	70	1070	0.75
Ga-Mg	3.61	3	20	972	0.286
Hg-Na	13.34	12.85	4	633	0.7
In-Na	4.61	6.44	28	750	0.65
In-Sb	2.77	2.5	11	923	0.5
Li-Mg	3.16	8.4	62	800	0.5
Mg-Pb	4.49	5	10	1100	0.65

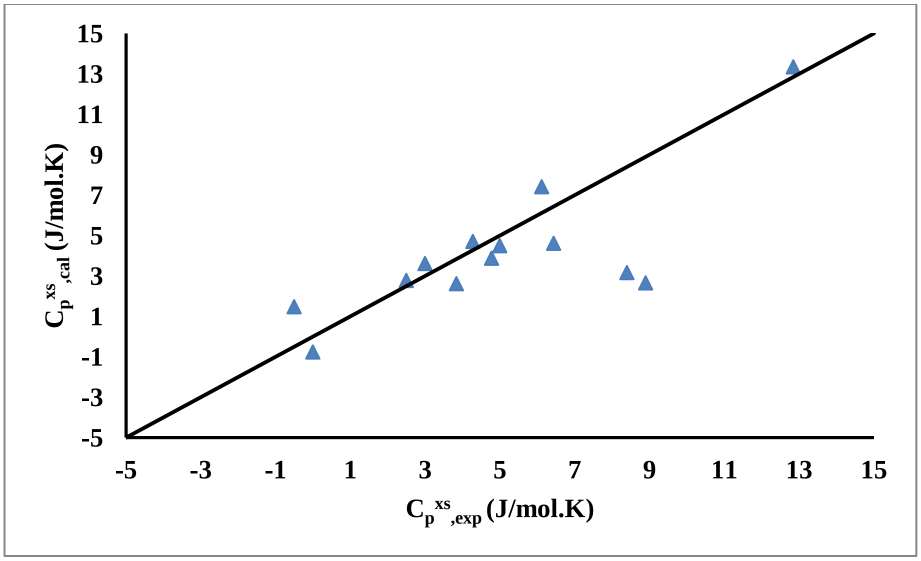


Figure 4-41. Heat capacities of binary liquid alloys calculated by Wituciwicz relation [31] and compared with the experimental data listed in Table 4-7. Enthalpy of mixing used in the calculations are obtained from Miedema model.

4.4.1 Comparison of the relations studied for entropy of mixing of liquid alloys and discussion of other possible methods for entropy of mixing of liquid alloys

The results presented in section 4.3 prove that Faber [24] and simplified Guggenheim [27] relations are not reliable to predict entropy of mixing of liquid alloys. These relations represent the configurational entropy of mixing and thus, cannot be used to predict total entropy of mixing. Sommer relation (eqn. 3-14) takes into account vibrational and configurational entropy of mixing. The results have the standard deviation of 5.08 J/(mol.K). Sommer relation [27] showed more reliability compared to the ones proposed by Faber [24] and Guggenheim [25]. However, there is still room to improve this formula by taking into account magnetic and electronic contributions and improving the configurational entropy term. The relation of Wituciewicz et al. [31] using Miedema enthalpy term was more reliable compared to other formulae studied. It is shown that their [31] empirical relation can be used with the confidence interval of ± 2.56 J/(mol.K) at confidence level of 90%. The advantage of this relation is also the ability to describe excess heat capacity of liquid alloys. Wituciewicz relation [31] can be used to find rough approximations of the excess entropy of mixing which if combined with CALPHAD method, can result in an optimized entropy of mixing. However, this model provides a simple composition dependency for entropy of mixing for systems with a strong non mixing behavior such as systems with short-range ordering, the application of this model is not recommended. For such systems, more complicated relationships [168,170,171] can be used to find more accurate results. For instance, Hard-Sphere model is a good model to describe thermodynamic properties of liquid metals [172]. Moreover, Hard-Sphere model for entropy of mixing [170,171] has shown good results in comparison with the experimental data. In this model, the existence of thermodynamic anomalies at different compositions for a special system arises from the mutual effect of packing constraints and chemical ordering forces. In this model, entropy can be written as [173]:

$$\Delta S^{HS} = \Delta S^{gas} + \Delta S^{Pack.} + \Delta S^{id.} \qquad \textit{4-2}$$

The effect of each contribution to entropy of mixing for different types of systems is discussed elaborately by Hoshino et al. [173]. Hard sphere entropy of mixing can be obtained from experimental studies [168], by analytical means [173] or by ab-initio calculations [174].

On the other hand, for all of the theoretical relations discussed in section 2.5, including Sommer [27], electronic contribution to entropy of mixing of liquid metals is neglected. However, for some systems such as transition metals alloyed with other metals, electronic entropy should be taken into account. Since transition metals have unfilled *d* bands, they have high density of states at the Fermi level. Therefore, they have high electronic entropy in pure state. In the case of a transition metal alloyed with other metals, due to s-d interaction, density of state at the Fermi level changes. Thus, electric contribution for these alloys cannot be neglected [175]. Pasturel et al. [168] combined the Hard-Sphere and electronic contributions and suggested excess entropy of mixing as follows:

$$\Delta S^{ex} = \Delta S^{el} + \Delta S^{HS} - \Delta S^{id} \qquad \textit{4-3}$$

Meyer et al. [176] suggested electronic contribution as:

$$\Delta S^{el} = \frac{1}{3}\pi^2 n(E_f) k_B^2 T \qquad \textit{4-4}$$

Where k_B is Boltzmann constant and $n(E_f)$ is the density of state at the Fermi level. In order to calculate this term, first-principles calculations should be used [177,178]. The results of Pasturel et al. [168] are depicted in Figure 4-42 to Figure 4-44. It can be seen that for the Ni-Si and Fe-Si systems, the composition dependence is dominated by electronic contribution. From Figure 4-44(a), it can be seen that Pd-Si system has two minima for entropy of mixing. Figure 4-44(b) shows that these two minima are reproduced only if the two contributions are taken into account. It can be concluded that the anomalies in entropy of mixing for Si alloyed with transition metals arise from packing and electronic effects.

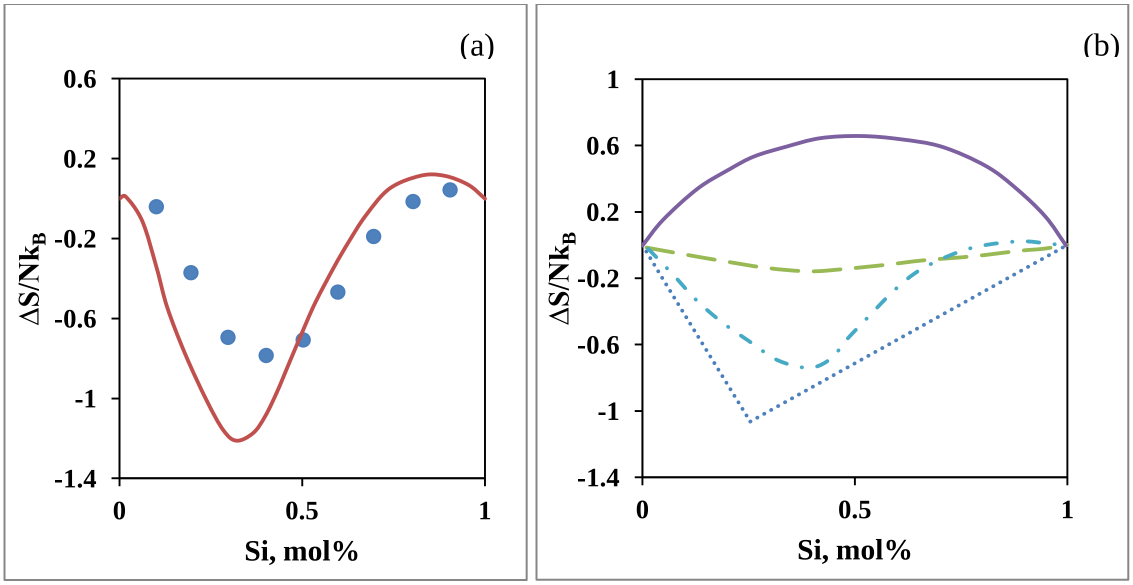


Figure 4-42. (a). Entropy of mixing of Ni-Si (T=1773K). ● *is experimental data of Schwerdtfeger et al. [179] and solid line is the calculation of Pasturel et al. [168] . (b) Individual contributions to the entropy of mixing calculated by Pasturel et al. [168]. .... is* ΔS^{el} *, -.-.. is* $\Delta S^{pack.}$*, _ _ is* ΔS^{gas} *and solid line is* ΔS^{id}*.*

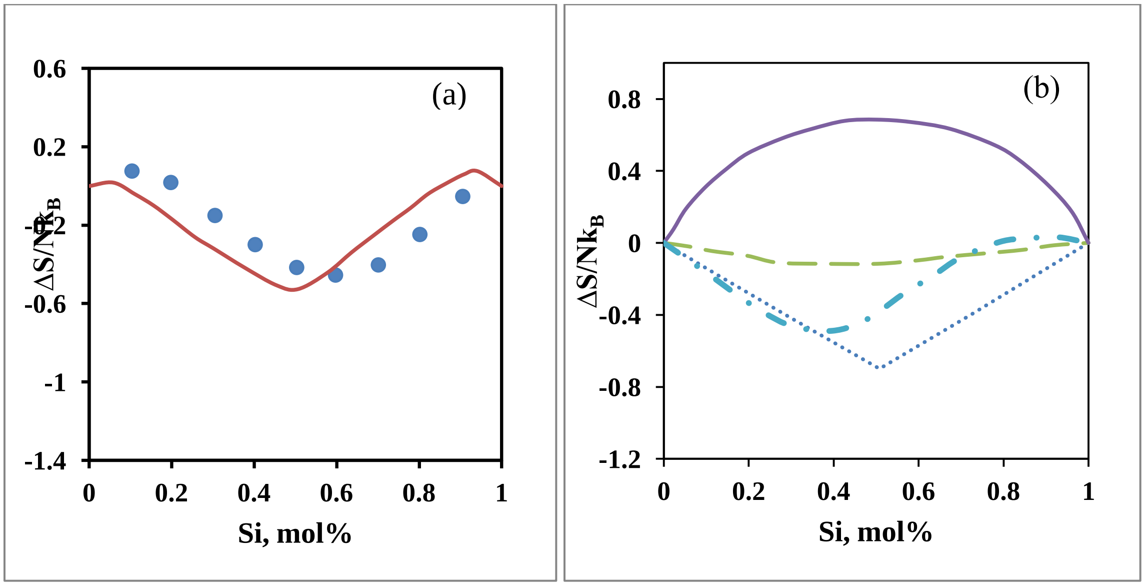


Figure 4-43. (a). Entropy of mixing of Fe-Si (T=1773K). ● *is experimental data of Schwerdtfeger et al. [180]and solid line is the calculation of Pasturel et al. [168] . (b) Individual contributions to the entropy of mixing calculated by Pasturel et al. [168]. .... is* ΔS^{el} *, -.-.. is* $\Delta S^{pack.}$*, _ _ is* ΔS^{gas} *and solid line is* ΔS^{id}*.*

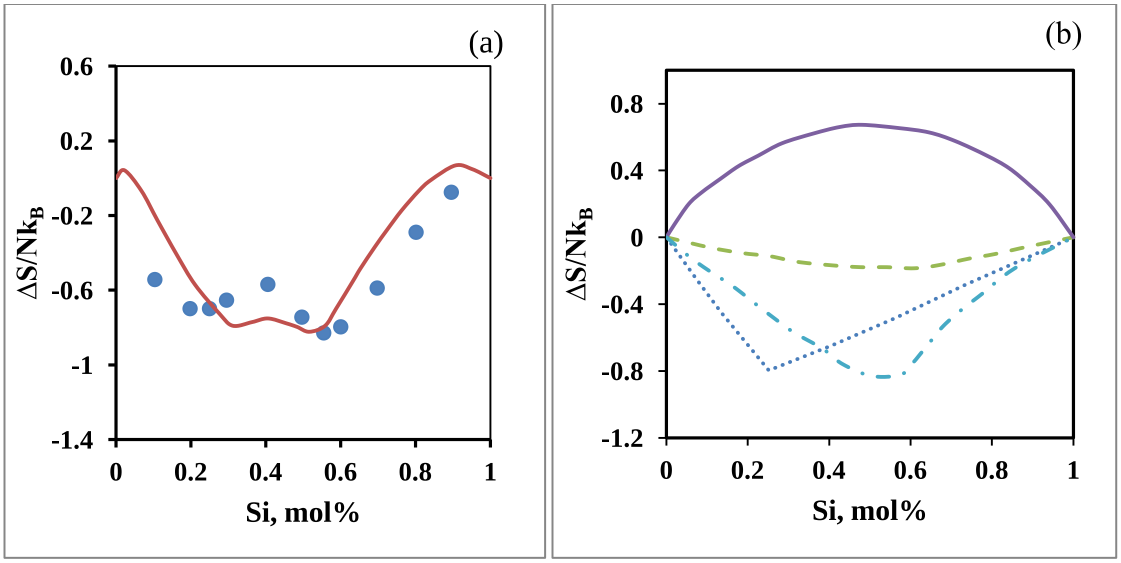


Figure 4-44. (a). Entropy of mixing of Pd-Si (T=1873K). ● *is experimental data of Bergman et al. [181]and solid line is the calculation of Pasturel et al. [168] . (b) Individual contributions to the entropy of mixing calculated by Pasturel et al. [168]. …. is* ΔS^{el} , -.-.. *is* $\Delta S^{pack.}$, – – *is* ΔS^{gas} *and solid line is* ΔS^{id}.

Afterall, application of Wituciewicz et al. [31] relation to entropy of mixing can be useful for rough approximations but the use of eqn. 4-3 combined with first-Principles calculations can result in more accurate results even for systems with more complicated mixing behaviors [168]. However, first-Principle calculations require special computational capacity (computer cluster or super computer, etc) and in addition, first-Principle calculations are more complicated and time-consuming.

Chapter 5

Concluding Remarks, Contributions and Suggestions for Future Work

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5.1 Concluding Remarks

Different theoretical and empirical models have been reviewed and evaluated for their suitability to calculate mixing properties of liquid and solid solutions. Based on the results, the following conclusions can be drawn:

- Five binary systems were calculated using Engel-Brewer method and the results were compared with the experimental data from the literature. The results show that the parameters found by Engel-Brewer method needed further adjustment to be able to reproduce the phase equilibrium data and the thermodynamic properties. It can be concluded that Engel-Brewer method has the following limitations: 1. It cannot predict negative deviation from ideal mixing. 2. Temperature dependency of the Gibbs free energy is neglected. 3. The promotion energy term added by Brewer as a modification to Hildebrand formula of regular solutions to be applicable to metals and alloys is a very sensitive term and cannot be an appropriate parameter to predict the phase diagram. 4. Physical and chemical properties such as bulk modulus and electronegativities which affect bonding are not taken into account. 5. Engel-Brewer model cannot predict asymmetry in mixing properties.

- Enthalpy of mixing for 50 binary liquid alloys is studied using Miedema model and is compared to Engel-Brewer method. New model parameters are introduced for non-transition metals alloyed with transition metals and for *p*-metals alloyed with alkali and alkaline earth metals. The new model parameters showed more consistency with the experimental data. Despite the inability of Engel-Brewer method to predict phase diagrams and thermodynamic properties for most of the cases, Miedema model was able to predict enthalpy of mixing for liquid alloys with maximum prediction band of $\pm 7\ \mathrm{kJ/mol}$ at confidence level of 90%. Therefore, it can be used as a rough approximation for systems lacking experimental data.
- The application of Miedema model has the following advantages: 1. Contrary to Engel-Brewer method, Miedema model can predict negative deviations from ideality and asymmetry and it uses physical and chemical properties such as bulk modulus and electronegativity to describe bonding. 2. Literature review of Miedema model and first-principles calculations shows that contrary to Engel-Brewer method and first-principles calculations, Miedema model can be extended to calculate enthalpy of mixing of multi component systems. 3. Miedema model is used in literature to predict physical properties like bulk modulus for intermetallic compounds. 4. Compared to first-Principles calculations, Miedema model is simple, easily parameterized and less time consuming.
- Miedema model is applied to 25 binary solid solutions in the current work and the results are compared with the experimental data. Despite the fact that the application of classical Miedema model to solid solutions in some systems led to

consistent results with the experimental data, this model for solid solutions includes many uncertainties and needs further modifications to be able to predict enthalpy of mixing of solid solutions for systems with unknown mixing properties.

- Miedema model has the following limitations: 1.The hybridization term in the formula is not well defined and is formulated empirically. 2. Miedema model cannot be applied to non-stoichiometric compounds. 3. For some metals such as Mn, Ni, etc since they have variable chemical properties (molar volume, n_{ws}, etc.) when bonding with different elements, they can cause deviations in the model predictions.
- Entropy of mixing for 49 binary liquid alloys is calculated using the relations suggested by Faber, Guggenheim, Sommer and Witusiewicz. For Wituciewicz relation, enthalpy of mixing obtained from Miedema model is used. The results are then compared to the experimental data from the literature. It is concluded that among these, Wituciewicz relation produced the closest results to the experimental data from literature.

  However, this relation offers a simple dependency relation of entropy of mixing on composition. For systems with a strong non mixing behavior such as systems with short-range ordering, the application of this model is not recommended.

  Wituciewicz relation is used to find excess heat capacity of alloys and the results show good consistency with the experimental data.

5.2 Contributions

Thermodynamic modeling of binary systems having no or few experimental thermodynamic properties data and/or equilibrium phase diagram data is always of significant interest for researchers since it reduces the cost and time required for experimental investigations. The present research suggests a combined Miedema-Wituciewicz model to parameterize Gibbs energy of mixing for liquid solutions after critical evaluation of different theoretical and empirical models for enthalpy and entropy of mixing. This combined model can be applied to predict phase relations not relying on the presence of experimental phase equilibrium data. Hence, it provides a different approach from CALPHAD assessment, which relies on curve fitting and the experimental data, to thermodynamic modeling of binary systems.

In addition, analysis of the results of enthalpy of mixing for binary systems calculated with Engel-Brewer method and Miedema model compared with the experimental data from the literature closed the door for the application of Engel-Brewer method as a robust method and proved it as a method with limited applications while Miedema model with some modifications is considered successful for calculation of enthalpy of mixing.

5.3 Suggestions for future work

- Further studies are required to predict phase diagrams and thermodynamic properties based on the Gibbs free energy predicted by Miedema model and Wituciewicz relation.

- Further studies are required to find better Miedema parameters. This goal can be achieved by focusing on small groups of metals, for instance metal A alloyed with 4*d* transition metals.
- Further studies are required to find a different approach from Miedema model or considering different parameters to reach to a general and more robust formulation for enthalpy of mixing.
- First-principle calculations studies are required to find mixing enthalpy of different systems. These first-principles calculations coupled with Miedema model can lead to more reliable predictions for enthalpy of mixing.
- The hybridization parameter in Miedema model needs to be defined more clearly and be formulated physically.
- The relation of Sommer for entropy of mixing of liquid alloys should be improved to have more consistency with the experimental data.
- Much more research is still needed on the prediction of thermodynamic properties of solid solutions.
- Further studies are required to apply First-principle calculations coupled with Hard-Spheres model and electronic contribution to describe entropy of mixing for systems with short-range ordering.

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Appendix

Appendix A-1. Invariant points or some solidus and liquidus points for 5 binary phase diagrams

Table A-1. Invariant points or some solidus and liquidus points for phase diagrams of Ag-Cu, Al-Ga, Np-U, Pu-U, Np-Pu binary systems predicted by Engel-Brewer method and modified database obtained by adjusting enthalpy parameters of Engel-Brewer method to the experimental data and adding entropy parameters to Redlich-Kister equation, compared with CALPHAD results from SGTE database [116] and the experimental data.

Systems	Invariant, solidus or liquidus points	Engel-Brewer	Modified database	CALPHAD Assessment	Exp.
Ag-Cu	Eutectic point	Not able to predict	X=0.45, T=1095K	X=0.4, T=1054.8K	X=0.42, T=1047.4K [140]
	Limit of solid sol. in Ag rich side	Not able to predict	0.14	X=0.13	X=0.15,T=1056K [182]
	Limit of solid sol. in Cu rich side	Not able to predict	X=0.75	X=0.95	X=0.95,T=1056K [140]
Al-Ga	Eutectic	X=0.98, T=303K	X=0.98, T=299K	X=0.97, T=300K	X=0.96, T=305K [183]
	Max solid sol. In Al rich side	X=0.72	X=0.007	X=0.08	X=0.094, T=301K [184]
Np-U	Liquidus at 0,3	1008K	1064K	-----	1071K [139]
	Solidus at 0.3	990K	1035K		1033K [138]
	Liquidus at 0.7	1230K	1267K	-----	1284K [42]
	Solidus at 0.7	1190K	1238K		1239K [139]

Table A-1. Continued

Systems	Invariant, solidus or liquidus points	Engel-Brewer	Modified D.B.	CALPHAD Assessment	Exp.
Pu-U	Liquidus at 0,2	1355K	919K	-----	910K [137]
	Solidus at 0.2	1191K	916K		890K [137]
Np-Pu	Liquidus at 0,5	718K	829K	-----	833K [138]
	Solidus at 0.5	708K	829K		830K [138]

Appendix A-2. Enthalpy of mixing for liquid and solid solutions of 5 binary systems

Table A-2. Enthalpy of mixing for liquid and solid solution phases in J/mol for Ag-Cu, Al-Ga, Np-U, Pu-U and Np-Pu at x=50 at % predicted by Engel-Brewer method and modified database obtained by adjusting enthalpy parameters of Engel-Brewer method to the experimental data and adding an entropy term compared with the experimental data. In cases no experimental data was available, previously optimized databases are used.

System	Phase	Engel-Brewer	Modified database	Previously Optimized databases	Exp.
Ag-Cu	Liquid	1557.7	3551	4354.6	3558.5 at 1371K [140] 4354.6 at 1450K [140]
	F.C.C	3113	4633	9193.1	4370 [141] 4633 [142]
Al-Ga	Liquid	38	623	656	698 [141] 456 [143]
	F.C.C	90	2589	2305	1294 [144] 2305 [145]
Np-U	Liquid	38.58	12.5	0 [129]	…….
	B.C.C	488	274	198 [129]	…….
Pu-U	Liquid	3175	1249	1181.5 [128]	…….
	B.C.C	1388	-1251	-1251 [128]	…….
Np-Pu	Liquid	2572	25	0 [129]	…….
	B.C.C	3040	270	240 [129]	…….

Appendix A-3. Entropy of mixing for statistically ordered phases of 5 binary systems

Table A-3. Entropy of mixing for liquid and solid solution phases in J/mol.K for Ag-Cu, Al-Ga, Np-U, Pu-U and Np-Pu at x=50 at % predicted by Engel-Brewer method and entropy of mixing obtained by adding entropy parameters to modified Engel-Brewer database, compared with existent optimized databases

System	Phase	Engel-Brewer	Modified database	Previously Optimized databases	Diff. between Engel-Brewer and previously optimized databases (%)	Diff. between modified database and previously optimized databases (%)
Ag-Cu	Liquid	5.79	7.04	6.88 [116]	15.8	2.3
	F.C.C.	5.76	5.92	8.52 [116]	32.4	30.5
Al-Ga	Liquid	5.77	5.92	6.50 [116]	11.2	8.9
	F.C.C.	5.77	3.77	3.69 [116]	56.4	2.1
Np-U	Liquid	5.76	5.65	5.76 [129]	0	1.9
	B.C.C.	5.76	5.71	5.76 [129]	0	0.8
Pu-U	Liquid	5.79	8.4	8.78 [128]	34	4.3
	B.C.C.	5.76	5	5.76 [128]	0	13
Np-Pu	Liquid	5.76	5.78	5.76 [129]	0	0.3
	B.C.C.	5.76	5.77	5.76 [129]	0	0.17