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Thermodynamic reassessment of Au–Pt–Sn system

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Abstract

Au–Pt–Sn alloys are a novel class of materials with promising catalytic properties. This study provides updated information on phase equilibrium structures and thermodynamics of the Au–Pt–Sn ternary system. The formation enthalpies of Au–Sn and Pt–Sn binary subsystems were predicted by first principles calculations and these values were further refined by CALPHAD method. The results obtained accurately reproduced the experimental data. The reassessed phase diagram of the Au–Pt–Sn ternary system accurately described the phase composition of several Au–Pt–Sn alloys, which is essential for further modifications of these materials.

1. Introduction

Due to excellent physicochemical and biological properties, Au–Pt–based alloys are widely applied in microelectronics, catalysis, and biomedical fields. Among these materials, Au–Pt bimetallic catalysts draw particular attention in recent years [1, 2]. Pt–Sn catalysts are highly active materials applied for catalytic reforming, electrocatalytic oxidation, and catalytic dehydrogenation of alkanes [3, 4]. However, the main problems with these catalysts are low conversion rate and easy deactivation. Recent studies showed that the addition of Au in Pt–Sn alloys using a volume immersion method results in ternary Au–Pt–Sn catalysts with improved catalytic activity [5]. To find the optimum composition of a catalyst, the first step is the analysis of a phase diagram to determine all phases in the system and how the phases change with temperature and composition. Afterward, the thermodynamic parameters of each phase should be determined. This paper reassesses Au–Sn and Pt–Sn binary systems and uses these data for the reconstruction of the ternary Au–Pt–Sn system. The predicted data are compared with the experimental results for several Au–Pt–Sn alloys.

2. Literature review

2.1. Binary Au–Pt system

The phase diagram of Au–Pt system is highly complex due to the presence of a miscibility gap in a solid solution phase and the ambiguous shape of liquidus and solidus line [6]. Previous study found that the critical point of the miscibility gap in this system lies at 61 at.% Pt and at 1533 K, and that the shape of miscibility gap is highly asymmetric due to differences in enthalpies of formation in a solid state [7]. The cooling of Au–Pt alloy via miscibility gap results in a spontaneous separation into Au-rich and Pt-rich phases. Moreover, at 1223 K this alloy forms a single-phase region on the phase diagram between the miscibility gap and the solidus line [8]. This phase corresponds to the thermodynamically stable solid solution where the atoms are randomly positioned in the lattice. In another study by Xu et al [9], the phase diagram of a binary Au–Pt system was reevaluated using the combination of CALPHAD method and the most recent experimental data. In addition, the Gibbs free energies of face-centered cubic (FCC) and liquid phase have been studied using the Redlich–Kister mixing model. To accurately model the thermodynamic (TD) quantities of a solid phase and predict the experimental phase equilibrium data, the authors included the activity coefficients and the mixing enthalpy along with the constraints imposed by the Third Law of TD. This model revealed that the miscibility gap is slightly shifted to the...
Au-rich side compared with [7], with the critical point at about 1473K and Au-56% Pt (figure 1). Some TD data of binary Au–Pt system are listed in table 1.

### Table 1. The evaluated TD parameters of Au–Pt binary system. Reprinted from [9], Copyright (2012), with permission from Elsevier.

| Phase type | Thermodynamic parameters |
|------------|--------------------------|
| Liquid     | $f_{\text{Lag}}^{\text{Au, Pt}} = 12800 + 7T$ |
| FCC        | $f_{\text{FCC}}^{\text{Lag}} = 15000 + 6.1T$ |
| FCC        | $f_{\text{FCC}}^{\text{Lag}} = -7600 + 3.55T$ |

### Table 2. TD parameters of Au–Sn system. Reprinted by permission from [11], Springer Nature Customer Service Centre GmbH: Springer (Springer) Journal of Electronic Materials, Copyright (2003).

| Phase type | Phase | Thermodynamic parameters |
|------------|-------|--------------------------|
| Liquid     |       |                          |
| Solid solution | FCC | $f_{\text{FCC}}^{\text{Lag}} = -28802.84 - 5.5753T$ |
| Solid solution | HCP | $f_{\text{HCP}}^{\text{Lag}} = -19184.81 - 25.1676T$ |
| Solid solution | DO24 | $L_{\text{DO24}}^{\text{Sn}} = 0.796 + 125 + 0.79T$ |
| Stoichiometric compounds | Au₅Sn | $G_{\text{Au₅Sn}}^{\text{fcc}} = -4050 - 3.3T + 0.84G_{\text{Au}}^{\text{bcc}} + 0.16G_{\text{Sn}}^{\text{bcc}}$ |
| Stoichiometric compounds | Au₅Sn | $G_{\text{Au₅Sn}}^{\text{bct}} = -14976.31 + 1.0206T + 0.5G_{\text{Au}}^{\text{bcc}} + 0.5G_{\text{Sn}}^{\text{bcc}}$ |
| Stoichiometric compounds | AuSn₂ | $G_{\text{AuSn₂}}^{\text{fcc}} = -17419.12 + 10.9048T + 0.33333G_{\text{Au}}^{\text{bcc}} + 0.66667G_{\text{Sn}}^{\text{bcc}}$ |
| Stoichiometric compounds | AuSn₄ | $G_{\text{AuSn₄}}^{\text{fcc}} = -9770.27 + 4.43357T + 0.2G_{\text{Au}}^{\text{bcc}} + 0.8G_{\text{Sn}}^{\text{bcc}}$ |

2.2. Binary Au–Sn system

The phase diagram and thermodynamic (TD) data of binary Au–Sn system have been modeled by Chevalier [10], Liu et al[11], and Vincent Grolier [12] using the CALPHAD method. The work of Chevalier [10] was eliminated from further considerations in multicomponent systems as it did not use the data from Scientific Group Thermodata Europe (SGTE) unary compilation. Some shortages of the valuable work of Liu et al[11]
were clarified in Grolier et al. [12] and Dong et al. [13]. On the other hand, the results of Grolier’s work [12] have been reassessed in [11] and [13] by taking into account the additional experimental data. The phase diagram of Au–Sn system reported in [11] was modified by Dong et al. [13] using the ab initio method for the calculation of the enthalpies of formation of several phases. Furthermore, the work of Dong et al. [13] provided more information on how liquid phase mixing enthalpy depends on the temperature of the optimization process. The TD parameters of Au–Sn system are given in Table 2.

Other authors also studied the formation enthalpies ($\Delta H_f$) of various stoichiometric Au–Sn systems. The $\Delta H_f$ values obtained by Liu et al. [11] are somewhat different from the experimental ones. This discrepancy is most pronounced for AuSn$_2$, which has a lower $\Delta H_f$ value compared with the experimental one. Dong et al. [13] also constructed a TD model for the Au–Sn system but these predictions were rough and significantly different from the experiment. Therefore, a novel methodology for the determination of $\Delta H_f$ is presented in this study, where first principles predictions have been used as input values followed by the optimization of the weight of each phase.

Dong et al. [13] calculated the $\Delta H_f$ values of NiAs-type AuSn, AuSn$_2$, and AuSn$_4$ by ab initio method in order to evaluate the correlations in the binary systems and extrapolate data to ternary system. The calculated $\Delta H_f$ of AuSn is $\sim 18.77$ kJ mol$^{-1}$. This result deviates from the experimental value of $\sim 14.88$ kJ mol$^{-1}$. The main reason for this deviation is an inconsistent selection of reference states. The experimental values in the previous papers selected diamond-type Sn as the reference state, while Dong et al. [13] used body-centered tetragonal (BCT)-type Sn as the reference state to calculate the formation enthalpy. In order to compare the accuracy of two results, Dong et al. [13] took BCT-type Sn as the reference state and the experimental value of AuSn at 78K was set to $\sim 15.69$ kJ mol$^{-1}$ but there was still a certain deviation from the calculated value of $\sim 18.77$ kJ mol$^{-1}$. The reason for this deviation is further analyzed. Some studies [10] show that NiAs-type AuSn is a non-stoichiometric compound, but they do not consider the vacancies in the lattice or the substitution between atoms in the ab initio calculation process, and only build a simple atomic model due to the limited computing power. This is most likely the main reason for the observed differences between the calculated and the measured value of $\Delta H_f$ for AuSn. Therefore, Dong et al. [13] have taken the calculated enthalpy of formation as the initial value in the

| Phase            | Experimental at 78K (kJ mol$^{-1}$) | ab initio, this study (kJ mol$^{-1}$) | Assessed value (kJ mol$^{-1}$) |
|------------------|-------------------------------------|--------------------------------------|-------------------------------|
| NiAs-type AuSn   | $-15.69$ (modified)                 | $-18.77$                             | $-15.75$                      |
| AuSn$_2$         |                                     | $-13.10$                             | $-13.38$                      |
| AuSn$_4$         |                                     | $-7.19$                              | $-7.20$                       |
process of Au–Sn optimization and set a small weight for these values to reduce the impact of calculation error on the optimization results. The formation enthalpy was finally optimized by Dong et al [13] and the results are listed in table 3. It can be seen from table 3 that the optimized ΔHf values of AuSn are very close to the experimental results.

The phase diagram of Au–Sn system optimized by Dong et al [13] and compared with the data of Liu et al [11] is shown in figure 2. The diagram reveals the increase of decomposition and formation temperatures of HCP phase, which indicates that its stability decreased. Also, the formation temperature of AuSn4 is decreased.

The thermodynamic parameters predicted for several alloy phases are shown in table 2. The optimization process and the obtained results of two abovementioned models are analyzed and compared in detail. Due to the rough selection of the calculation model by Dong [13], the predicted formation enthalpies are quite different from the experimental values. The optimization parameters by Liu [11] are selected more precisely but the formation enthalpy of each compound still deviated from the experimental values. Therefore, the aim of this study was to use the results of high-accuracy first principles calculations as the input, fine-tune the thermodynamic parameters of Liu et al [11], re-optimize the thermodynamic data of Au–Sn binary system, and extrapolate to the ternary system.

2.3. Binary Pt-Sn system

The phase diagram of a binary Pt-Sn system optimized by Su et al [14] includes miscibility gap of the liquid phase. Recalculation of phase diagram in Pandat software revealed demixing of the liquid phase in the Sn-rich region above 900 °C. This type of inverted miscibility gap of the liquid phase is not physically meaningful and has never been observed experimentally; the experimental phase diagram published by Su et al [14] did not show this artifact. However, this type of artifact has been observed in other systems and its origin is described in more detail in the literature [15]. A comprehensive thermodynamic (TD) characterization of the Pt-Sn system in

![Figure 3. The phase diagram of Pt-Sn binary system.](image-url)
CALPHAD software has been described by Vincent Grolier [16]. Special attention was given to the artifacts observed in [14]. This reassessment was based on a critical evaluation of published experimental data on phase equilibria and TD properties of alloys. The formation of strong PtSn associates in the liquid phase was applied in model construction, and the possibility for short-range ordering or cluster formation was considered. The solution phase (Pt) was treated as a substitutional solution, which means that there was a possibility for the formation of intermediate Pt3Sn, PtSn, Pt2Sn3, PtSn2, PtSn4 phases in a stoichiometric ratio. The absolute entropy and the entropy of fusion of intermetallic compounds were taken into consideration for the correct assignment of TD parameters. The phase diagram of Pt-Sn system reassessed by Grolier is shown in figure 3. Five intermetallic compounds identified in the system are listed in table 4.

2.4. Ternary Au–Pt–Sn system
The isothermal section of Au–Pt–Sn phase diagram in the Sn-rich region (> 50 at. % Sn) at 400 °C was studied by Alexandra Neumann Torgersen [17]. The results given in figure 4 indicate the presence of a limited solid-solubility with the exchange between Au and Pt in the majority of binary phases. On the other hand, substantial homogeneity ranges are observed for AuSn and Pt2Sn3. The Au-to-Pt replacement is possible for up to 50% of gold in the AuSn phase, and Pt-to-Au exchange is allowed in Pt2Sn3 phase until Pt content reaches 20%. Moreover, a new, ternary AuPt2Sn4 phase is observed in the phase diagram and this phase was homogeneous between Au137Pt293Sn570 and Au196Pt241Sn563.
In this study, the properties of solid-state species were calculated using density functional theory (DFT) implemented in the CASTEP module of Materials Studio 2016 software [19]. For the correct treatment of the exchange-correlation energy of electron-electron interactions, PW91 generalized gradient approximation (GGA) functional was used [20]. In the calculations, plane wave basis sets has been applied, and the kinetic energy cut-off was set to 380 eV for Au–Sn systems and 350 eV for Pt–Sn systems. SCF convergence limit was $5.0 \times 10^{-7}$ eV/atom. Thermo-Calc and Pandat software were applied for the calculation and optimization of a phase diagram.

### 3. Calculation methods and thermodynamic modeling

In this study, the properties of solid-state species were calculated using density functional theory (DFT) implemented in the CASTEP module of Materials Studio 2016 software [19]. For the correct treatment of the exchange-correlation energy of electron-electron interactions, PW91 generalized gradient approximation (GGA) functional was used [20]. In the calculations, plane wave basis sets has been applied, and the kinetic energy cut-off was set to 380 eV for Au–Sn systems and 350 eV for Pt–Sn systems. SCF convergence limit was $5.0 \times 10^{-7}$ eV/atom. Thermo-Calc and Pandat software were applied for the calculation and optimization of a phase diagram.

#### 3.1. Pure element

The TD data of pristine Au, Pt, and Sn were obtained from the SGTE pure component database.

#### 3.2. Liquid phase

Thermodynamics of the liquid and solution phase of Au–Pt–Sn ternary system is described using a substitutional solution model shown in (1):

$$G_i^\theta = \sum_j x_j^\theta G_j^\theta + RT \sum_j x_j \ln x_j + E_i^\theta$$  \hspace{1cm} (1)$$

In this equation, $G_i^\theta$ represents a Gibbs free energy or pure component $\theta$ and $E_i^\theta$ denotes excess function. The excess G can be calculated according to (2):

$$G_\text{excess} = \sum_{i>j} x_i x_j G_{ij}$$

### Table 5. TD parameters of Au–Pt–Sn system. Reprinted from [18], Copyright (2016), with permission from Elsevier.

| Phase | Thermodynamic parameters |
|-------|-------------------------|
| NiAs (represent AuSn and PtSn) | $(\text{Sn}_3, \text{Sn}_2, \text{Va})(\text{Au}, \text{Pt})$ |
| $G_{\text{NiAs}}^{\text{AuSn}}$ | $= -2000$ |
| $G_{\text{NiAs}}^{\text{PtSn}}$ | $= -14000$ |
| $G_{\text{NiAs}}^{\text{AuSn}}$ (Au–Sn) | $= -28980.8006 + 11.4109 T$ |
| $G_{\text{NiAs}}^{\text{PtSn}}$ (Pt–Sn) | $= -31906.3444 + 14.1994 T$ |
| $G_{\text{NiAs}}^{\text{AuSn}}$ (Au–Pt) | $= -5000 - 1.575 + 0.75 \times \text{GHSERAU}$ |
| $G_{\text{NiAs}}^{\text{PtSn}}$ (Pt–Sn) | $= 0.25 \times \text{GHSERSN}$ |
| $G_{\text{NiAs}}^{\text{AuSn}}$ (Au–Sn) | $= -1000$ |
| $G_{\text{NiAs}}^{\text{PtSn}}$ (Pt–Sn) | $= -10200$ |
| $G_{\text{NiAs}}^{\text{AuSn}}$ (Au–Pt) | $= -162981.9235 + 10.3167 T$ |

Dong [18] reevaluated the TD description of the Au–Pt–Sn ternary alloy by remodeling the ternary compound, AuSn, PtSn, and the solubility of the third element in the corresponding binary phase. The authors calculated the isothermal sections of Au–Pt–Sn system at 150 °C and 320 °C and experimentally studied Au-20 wt%Sn–Pt reaction couples. Based on negligible changes in the microstructure of aged samples, it was concluded that the Au-20 wt%Sn–Pt system is stable at 150 °C. The phase diagram reassessed by Dong [18] is given in figure 5 and the corresponding thermodynamic parameters are listed in table 5. However, the Au–Pt–Sn phase diagram, particularly a part with low Au content (below 20 at.%) needs an additional investigation due to the lack of data about the high-temperature isothermal section of Au–Pt–Sn system and the influence of alloy components on the spinodal decomposition of Au–Pt system.
3. Results and discussion

According to the literature data

3.3. Intermetallic compounds

In this case, the thermodynamics of binary intermetallic compounds in the ternary Au–Pt–Sn system can be determined from the sublattice model (Au, Pt)\textsubscript{m}Sn\textsubscript{n}.

The Gibbs free energy of this system can be calculated from the equation

\[ \mathbf{E}_\text{G} = \mathbf{z}_\text{Au} \mathbf{X}_\text{Au} \mathbf{X}_\text{Pt} \sum_{i=0}^{N} \mathbf{I}_\text{Au-Pt}(X_{\text{Au}} - X_{\text{Pt}}) + \mathbf{z}_\text{Sn} \mathbf{X}_\text{Sn} \sum_{i=0}^{N} \mathbf{I}_\text{Sn}(X_{\text{Sn}} - X_{\text{Sn}}) \]

\[ + \mathbf{X}_\text{Pt} \mathbf{X}_\text{Sn} \sum_{i=0}^{N} \mathbf{I}_\text{Pt-Sn}(X_{\text{Pt}} - X_{\text{Sn}}) + \mathbf{X}_\text{Au} \mathbf{X}_\text{Pt} \mathbf{X}_\text{Sn} \mathbf{I}_\text{Au-Pt-Sn} \]  

(2)

The \( \mathbf{I} \) terms represent binary (Au–Pt, Au–Sn, and Pt–Sn) or ternary (Au–Pt–Sn) interaction parameters of a solute phase. The ternary interaction parameter can decompose to the contributions of Au-rich, Pt-rich, and Sn-rich terms as represented in (3):

\[ \mathbf{I}_\text{Au-Pt-Sn} = \mathbf{X}_\text{Au} \mathbf{X}_\text{Pt} \mathbf{X}_\text{Sn} \mathbf{I} \]

(3)

3.3. Intermetallic compounds

According to the literature data [18], solid-state structure is complex due to partial solid solubility of Au and Pt. In this case, the thermodynamics of binary intermetallic compounds in the ternary Au–Pt–Sn system can be determined from the sublattice model (Au, Pt)\textsubscript{m}Sn\textsubscript{n}.

The Gibbs free energy of this system can be calculated from the equation (4):

\[ G^{(\text{Au, Pt}) \text{Sn}_m} = X'_{\text{Au}} G^{(\text{Au, Pt}) \text{Sn}_{m + n}} + X'_{\text{Pt}} G^{(\text{Pt}) \text{Sn}_{m + n}} + (m / (m + n)) \]

\[ \times RT(X'_{\text{Au}} \ln X'_{\text{Au}} + X'_{\text{Pt}} \ln X'_{\text{Pt}} + X'_{\text{Pt}} X'_{\text{Pt}} \sum_{i=0}^{N} L_i^{(\text{Au, Pt}) \text{Sn}_m} (X'_{\text{Au}} - X'_{\text{Pt}})) \]  

(4)

Where \( X'_{\text{Au}} \) and \( X'_{\text{Pt}} \) are the molar percentages of Au and Pt in the first sublattice, \( G^{(\text{Au, Pt}) \text{Sn}_m} \) and \( G^{(\text{Pt}) \text{Sn}_{m + n}} \) are the molar Gibbs free energies of Au\textsubscript{m}Sn\textsubscript{n} and Pt\textsubscript{m}Sn\textsubscript{n}, and \( L_i^{(\text{Au, Pt}) \text{Sn}_m} \) represents interaction term between Au and Pt in the first sublattice when the second sublattice is occupied with Sn.

3.4. Ternary compound

The molar Gibbs free energy of ternary compound \( \tau \text{(AuPt}_2\text{Sn}) \) can be calculated from (5):

\[ G^{(\text{AuPt}_2\text{Sn}_n)} = a + bT + \frac{1}{7} G^{\text{FCC}_{\text{Au}}} + \frac{2}{7} G^{\text{FCC}_{\text{Pt}}} + \frac{4}{7} G^{\text{BCT}_{\text{Sn}}} \]  

(5)

Here, \( a \) and \( b \) represent optimized coefficients, and \( G^{\text{FCC}_{\text{Au}}} \), \( G^{\text{FCC}_{\text{Pt}}} \), and \( G^{\text{BCT}_{\text{Sn}}} \) are the Gibbs free energies of neat elements.

4. Results and discussion

The formation enthalpies (\( \Delta H_f \)) of various intermetallic components are required for the optimization of a ternary phase diagram of Au–Pt–Sn. The crystal structure parameters and \( \Delta H_f \) are predicted using DFT
calculations with PW91 GGA functional (table 6). The predicted data were very close to experimental values, confirming the reliability of the theoretical model. Moreover, negative values of $\Delta H_f$ for all compounds indicate their stability.

The PARROT program within Thermo-Calc software is applied for further optimization of Au–Sn and Pt–Sn binary intermetallic systems to obtain agreement with the experiment for the ternary Au–Pt–Sn system. In the beginning, each $\Delta H_f$ obtained either by ab initio calculations or taken from the literature is given a certain weight based on its importance and reliability. These weights change during the optimization until the predicted values are within the estimated experimental error range.
Other authors also studied the formation enthalpies of various stoichiometric Au–Sn systems. The ΔHf values obtained by Liu \[11\] are somewhat different from the experimental values. This discrepancy is most pronounced for AuSn2 with a lower value compared with the experimental one. Dong \[13\] also constructed a TD model for the Au–Sn system but these predictions were rough and significantly different from the experiment. Therefore, the novel methodology for the determination of ΔHf is presented in this study, where first principles predictions served as input values and the appropriate weights of each phase were optimized. Because of the close relationship between HCP on one side and AuSn and Au5Sn on the other side, all three phases were optimized. The comparison between the optimized ΔHf values from this work and the previous literature reports for AuSn and Au5Sn is shown in figure 6. It should be noted that the optimized values for two binary compounds were in excellent agreement with the experiment (table 6). The results of this study for Au5Sn are lower than those of Liu and Dong \[11, 13\], and the optimized ΔHf for AuSn2 and AuSn4 are between the values reported in these two studies. Therefore, the methodology applied in this study provided ΔHf values that better reproduce experimental data compared with the previous works \[11, 13\].

The other optimized TD quantities of the Au–Sn system are given in table 7. Figure 6 shows a good agreement between the optimized phase diagram and the experimental values for the Au–Sn system. This graph also shows that the formation temperatures of Au5Sn and AuSn4 are lower than the values found by

| Phase type | Phase | ΔHf (predicted by DFT) |
|------------|-------|------------------------|
| Stoichiometric compounds | Pt3Sn | \( G^{\text{Pt3Sn}} = -35936.4 - 0.5T + \left(\frac{3}{2}\right)G^{0\text{Pt}}_{\text{Pt}} + \left(\frac{1}{2}\right)G^{0\text{Sn}}_{\text{Sn}} \) |
| | PtSn | \( G^{\text{PtSn}} = -58942.6 + 3.973T + \left(\frac{3}{2}\right)G^{0\text{Pt}}_{\text{Pt}} + \left(\frac{1}{2}\right)G^{0\text{Sn}}_{\text{Sn}} \) |
| | Pt3Sn3 | \( G^{\text{Pt3Sn3}} = -52273.8 + 4.858T + \left(\frac{3}{2}\right)G^{0\text{Pt}}_{\text{Pt}} + \left(\frac{1}{2}\right)G^{0\text{Sn}}_{\text{Sn}} \) |
| | PtSn2 | \( G^{\text{PtSn2}} = -47033.1 + 5.919T + \left(\frac{3}{2}\right)G^{0\text{Pt}}_{\text{Pt}} + \left(\frac{1}{2}\right)G^{0\text{Sn}}_{\text{Sn}} \) |
| | PtSn4 | \( G^{\text{PtSn4}} = -31359.3 + 5.096T + \left(\frac{3}{2}\right)G^{0\text{Pt}}_{\text{Pt}} + \left(\frac{1}{2}\right)G^{0\text{Sn}}_{\text{Sn}} \) |

Table 8. Optimized thermodynamic parameters of stoichiometric compounds in Pt–Sn system.

| Phase | ΔHf (DFT), J mol\(^{-1}\) | ΔHf (CALPHAD), J mol\(^{-1}\) |
|-------|------------------------|------------------------|
| Pt3Sn | -35904 | -35940.3 |
| PtSn | -58944 | -58946.6 |
| Pt3Sn3 | -52320 | -52277.8 |
| PtSn2 | -47712 | -47037.1 |
| PtSn4 | -30816 | -31363.3 |

Table 9. Enthalpies of formation of various Pt–Sn components calculated by first principles method and optimized using CALPHAD.
Liu [11], suggesting their stability at a lower temperature. The comparison between the optimized formation enthalpies and experimental values for various Au–Sn components (figure 7) further explains this result.

The same methodology was applied for the optimization of thermodynamic quantities and the construction of phase diagram for a Pt–Sn binary system. The results are presented in table 8 and figure 8. Excellent agreement with the experimental phase diagram [16] confirms the reliability of calculated formation enthalpies.

The first principles-calculated ΔHf of various Pt–Sn components and the values refined by CALPHAD method are given in table 9. Very good agreement between two sets of data is observed, which confirms that the DFT results are a good starting point for further optimization.

As can be seen from figure 9, the optimized formation enthalpies of different Pt–Sn compounds are generally consistent with the previous literature reports [16].

After successful optimization of Au–Sn and Pt–Sn binary systems, we continued with the optimization of interaction parameters of the ternary system using Pandat software. The reassessment of Au–Pt–Sn system was done using the experimental data reported in literature [24]. The calculated TD parameters of Au–Pt–Sn alloys are listed in table 10.

Table 10. Optimized TD data of Au–Pt–Sn system.

| Phase type                        | Thermodynamic parameters                          |
|-----------------------------------|--------------------------------------------------|
| Liquid                            |                                                   |
| Liquid                            | $\text{L}_{\text{Pt,PtSn}} = -71062.3 + 25.6461 \times T$ |
| Liquid                            | $\text{L}_{\text{Pt,Sn}} = -10754.4$              |
| Liquid                            | $\text{L}_{\text{Pt,Sn}} = -35610 + 18.8021 \times T$ |
| Liquid                            | $\text{L}_{\text{Pt,Sn}} = -15500 + 6 \times T$   |
| Liquid                            | $\text{L}_{\text{Pt,Sn}} = 7000$                  |
| Liquid                            | $\text{L}_{\text{Pt,Sn}} = 5183.32 + 0.0072 \times T$ |
| NiAs (represent AuSn and PtSn)    |                                                   |
| NiAs (represent AuSn and PtSn)    | $\text{L}_{\text{NiAs}} = 2003.05$               |
| NiAs (represent AuSn and PtSn)    | $\text{L}_{\text{Sn}} = -13982.5$                |
| NiAs (represent AuSn and PtSn)    | $\text{L}_{\text{Pt,Sn}} = -5000 - 1.5 \times T + 0.75 \times \text{GHSERSN}$ |
| NiAs (represent AuSn and PtSn)    | $\text{L}_{\text{Pt,Sn}} = -1577.45$             |
| NiAs (represent AuSn and PtSn)    | $\text{L}_{\text{Pt,Sn}} = -10692.9$             |
| NiAs (represent AuSn and PtSn)    | $\text{L}_{\text{Pt,Sn}} = -4300 + 0.33333 \times \text{GHSERSN}$ |
| NiAs (represent AuSn and PtSn)    | $\text{L}_{\text{Pt,Sn}} = +0.666667 \times \text{GHSERSN}$ |
| NiAs (represent AuSn and PtSn)    | $\text{L}_{\text{Pt,Sn}} = -3913.25$             |
| NiAs (represent AuSn and PtSn)    | $\text{L}_{\text{Pt,Sn}} = -30900 + 0.2 \times \text{GHSERAU} + 0.8 \times \text{GHSERSN}$ |
| NiAs (represent AuSn and PtSn)    | $\text{L}_{\text{Pt,Sn}} = -5802.58$             |
| NiAs (represent AuSn and PtSn)    | $\text{L}_{\text{Pt,Sn}} = -47695.3 + 15.0436 \times T + 3 \times \text{GHSERAU}$ |
| NiAs (represent AuSn and PtSn)    | $\text{L}_{\text{Pt,Sn}} = +4 \times \text{GHSERSN}$ |
| NiAs (represent AuSn and PtSn)    | $\text{L}_{\text{Pt,Sn}} = -377634 + 62.3202 \times T + 3 \times \text{GHSERPT}$ |
| NiAs (represent AuSn and PtSn)    | $\text{L}_{\text{Pt,Sn}} = +4 \times \text{GHSERSN}$ |
| NiAs (represent AuSn and PtSn)    | $\text{L}_{\text{Pt,Sn}} = -162901 + 10.35 \times T$ |

Figure 9. The correlation between the optimized formation enthalpies of the Pt–Sn system and the literature values.
The first step of ternary system optimization was to calculate the isothermal sections of Au–Pt–Sn system at 400 °C and 700 °C. When the calculated phases were approximately consistent with the experiment, the data on invariant reactions were optimized and fitted into the experimentally determined vertical sections. The result of this model is a set of self-consistent TD quantities that describe the system within the entire composition range. Starting from the data in table 10, vertical sections of the Au–Pt–Sn system were calculated at two temperatures and compared with the experimental values. Figure 10(b) shows that the optimized equilibrium junction lines of two-phase and three-phase regions (red line) for the system at 700 °C match well the experimental data. The slight deviation was found only for the liquidus line most probably owing to partial oxidation of liquid observed in DTA analysis.

Figure 10. Optimized isothermal section of Au–Pt–Sn system at 700 °C and its comparison with the experimental data: (a) Optimized (blue line) and experimental values (color dots); (b) Optimized (red line) and experimental values (blue line).

Figure 11. Optimized isothermal section of Au–Pt–Sn mixture at 400 °C and its agreement with the experimental data: (a) Optimized (blue line) and experimental values (color dots); (b) Optimized (red line) and experimental values (blue line).
The isothermal section of the Au–Pt–Sn system at 400 °C given in figure 11 shows good matching between the optimized and the experimental equilibrium junction lines for the two-phase and three-phase region near ternary phase \( \tau \) (orange circle). Moreover, each of the phases fits well with the experimental data (figure 11(b)).

To reproduce the vertical sections and construct the Au–Pt–Sn ternary phase diagram, we chose the alloy composition that matches the experimental data [24]. The atomic percentage of Au is fixed at 16%, and the composition of Pt and Sn varied between 0 and 84%. According to the results shown in figure 12, the calculated phase composition of alloy \#1 is FCC + FCC + Pt3Sn, which is in line with the experimental data [24]. The predicted vertical sections for alloys 2–5 were also close to the experimental data, confirming the reliability and accuracy of the Au–Pt–Sn phase diagram optimized in this study.

5. Conclusions

This study provides new insights into the equilibrium phase structures and the character of phase transitions of the Au–Pt–Sn ternary system. Thermodynamics of binary Au–Sn and Pt–Sn subsystems is reassessed through the combination of first principles calculations and CALPHAD optimization. These data were further utilized to construct the optimized phase diagram of a ternary alloy. The optimized formation enthalpies were in better agreement with the experimental data compared with the previous studies [11–13]. The reassessed Au–Pt–Sn phase diagram is essential for further improvement of these alloys as catalysts and functional materials. Besides, this study provides a new methodology for the thermodynamic reassessment of other technologically important ternary alloys.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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