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Thermodynamic Assessment of the Pt-Sb System

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ABSTRACT

The Pt-Sb system was critically assessed by means of CALPHAD technique. Based on the experimental data in the literature, the excess Gibbs energies of the solution phases (liquid, rhombohedral, fcc) were modeled with the Redlich-Kister equation. The five intermetallic compounds, Pt_7Sb, Pt_3Sb, Pt_3Sb_2, $PtSb$, and $PtSb_2$ were treated as stochiometric compounds and expressed as the formula $(Pt)_m(Sb)_n$. The intermetallic compound, Pt_5Sb with a homogenerity ranges 0.155 - 0.189 Sb, were treated as the formula $(Pt,Sb)_m(Pt,Sb)_n$. A set of self-consistent thermodynamic parameters of the Pt-Sb system was obtained.

Keywords: Pt-Sb Phase Diagram; Thermodynamic Assessment; Thermodynamic Properties; CALPHAD Technique

1. Introduction

The precious metals, Pt, Sb, Au, Ag and their alloys, have been widely applied as catalysts for their high thermal stability and high activity, such as decompounding hydrazine, purifying automobile gas, oxygenating selectively and so on [1-5]. Understanding the phase equilibria as well as the thermochemical behaviour of these systems is helpful for the development of the related materials. This paper intends to assess the Pt-Sb system thermodynamically and provides a set of self-consistent parameters for calculation of the phase equilibria and thermochemical properties of the system.

2. Literature Review

The Pt-Sb phase diagram consists of the liquid, the face-centered cubic (fcc), terminal solid solution (Pt); the terminal solid solution, rhombohedral (Sb) with a negligible solubility of Pt. The gas phase was estimated by Itkin and Alcock [6], which is not considered in the present work.

The liquidus was determined by thermal analysis in Refs. [7-10]. The liquidus in the Pt-Sb system was based mainly on the results made by Durussel and Feschotte [11] using differential thermal analysis (DTA), which was supported by the majority of the data [7-10].

In the Pt-Sb system, there are six intermediate phases,

Pt_7Sb, Pt_5Sb, Pt_3Sb, Pt_3Sb_2, $PtSb$, and $PtSb_2$. The Pt_7Sb compound was discovered by [11], using DTA, microprobe analysis, and X-ray powder (XRD). Pt_7Sb, a cubic structure, is formed by a peritectoid reaction. Different designations for the phase Pt_5Sb are "Pt_4Sb" [8], "$Pt_{34}Sb_7$" [10], "$Pt_{4+}Sb$" [12], and "$Pt_{82}Sb_{18}$" [13]. A compound, "Pt_5Sb_2" was reported in Ref. [7] and not confirmed in other publications [8,10,12,13]. The compound as Pt_5Sb has a cubic structure wth a homogeneity range of 0.155 to 0.189 Sb [11]. The boundaries of the phase were determined using a temperature dependence of the lattice parameter. This phase is formed at 748°C ± 4°C by peritectic reaction, which was consistent with Refs. [7-9]. It decomposed at 560°C by eutectoid reaction.

The compound Pt_3Sb was formed by peritectic reaction [9,11]. The compound was investigated using thermal arrest by [8] and explained by the phase transformation in "Pt_4Sb". The compound Pt_3Sb was examined and observed as a single phase with a composition of 0.275 Sb and as a second phase at 0.25 and 0.30 Sb by Srivastava *et al.* [14]. However, Pt_3Sb was confirmed as a stoichiometric compound in subsequent research [10].

The compound Pt_3Sb_2 was determined by Bhan *et al.* [9] and confirmed by Kim [10]. It is formed by a peritectic reaction at 732°C [9] or 739°C ± 4°C [11]. The compound $PtSb$ was determined by several researchers and the formed temperature was different, 1045°C [7], 1040°C [8], 1043°C [9], and 1046°C ± 3°C [11]. The composition of PtSb was determined by Refs. [10,11,15,16]. The re-

sults of made by Durussel and Feschotte [11], Kim [10], and Kjekshus [17] showed that the composition of PtSb can be adopted as only approximately stoichiometric compound.

The compound PtSb$_2$ was first found by chemical analysis of crystals precipitating from Pt-Sb melts containing an excess of Sb [18]. The temperature of congruent melting of PtSb$_2$ was measured as 1226°C [7], 1210°C [8], and 1225°C [11]. The enthalpy increments of PtSb$_2$ measured by drop calorimetry in the temperature interval 196°C to 620°C [19].

From the above literature [6-19], the present assessed Pt-Sb phase diagram consists of the liquid, the face-centered cubic (fcc) terminal solid solution (Pt), the terminal solid solution (Sb) with a negligible solubility of Pt and six intermediate phases, Pt$_7$Sb, Pt$_5$Sb, Pt$_3$Sb, Pt$_3$Sb$_2$, PtSb and PtSb$_2$.

3. Thermodynamic Models

3.1. Unary Phases

The Gibbs energy function $G_i^\phi(T) = G_i^\phi(T) - H_i^{SER}$ (298.15 K) for the element i (i = Pt, Sb) in the phase ϕ (ϕ = liquid, face-centered cubic(fcc) and rhombohedral) is described by an equation of the following form:

$$G_i^\phi(T) = a + bT + cT\ln(T) + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9} \tag{1}$$

where H_i^{SER} (298.15 K) is the molar enthalpy of the element i at 298.15 K in its standard element reference (SER) state, fcc for Pt and rhombohedral for Sb. The Gibbs energy of the element i, $G_i^\phi(T)$, in its SER state, is denoted by GHSER$_i$, *i.e.*,

$$\text{GHSER}_{Pt} = {}^0G_{Pt}^{fcc}(T) - H_{Pt}^{SER}(298.15\,K) \tag{2}$$

$$\text{GHSER}_{Sb} = {}^0G_{Sb}^{rhomb}(T) - H_{Sb}^{SER}(298.15\,K) \tag{3}$$

In the present work, the Gibbs energy functions are taken from the SGTE (Scientific Group Thermodata Europe) pure elements database compiled by Dinsdale [20].

3.2. Solution Phases

In the Pt-Sb system, there are three solution phases: liquid, fcc and rhombohedral. The gas phase was not considered in the Pt–Sb system, similar to the results reported by Durussel and Feschotte [11]. Their Gibbs energies are described by the following expression:

$$G_m^\phi = x_{Pt}G_{Pt}^\phi(T) + x_{Sb}G_{Sb}^\phi(T) + RT(x_{Pt}\ln x_{Pt} + x_{Sb}\ln x_{Sb}) + {}^EG_m^\phi \tag{4}$$

where R is the gas constant, x_{Pt} and x_{Sb} are the mole fraction of Pt and Sb, respectively, and ${}^EG_m^\phi$ is the excess Gibbs energy, expressed by the Redlich–Kister polynomial [21].

$$^EG_m^\phi = x_{Pt}x_{Sb}\sum_j {}^jL^\phi(x_{Pt} - x_{Sb})^j \tag{5}$$

where ${}^jL^\phi$ is the interaction parameter between element Pt and Sb, which is to be evaluated in the present work. Its general form is

$$L^\phi = a + bT + cT\ln(T) + dT^2 + eT^3 + fT^{-1} \tag{6}$$

In most cases, only the first one or two terms are used according to the temperature dependence on the experimental data.

3.3. Intermetallic Compounds

There were six intermediate phases, Pt$_7$Sb, Pt$_5$Sb, Pt$_3$Sb, Pt$_3$Sb$_2$, PtSb, and PtSb$_2$ in the Pt-Sb system. The phases crytal structure data was shown in **Table 1**. According to the composition and crystal structure data , the Sb in the five compounds, Pt$_7$Sb, Pt$_3$Sb, Pt$_3$Sb$_2$, PtSb and PtSb$_2$ of the system with no or little solid solubility will be treated as the stoichiometric compounds. While the compound Pt$_5$Sb with more homogenertiy ranges 0.155 - 0.189 Sb will treated as solid solution compound.

So the Pt$_5$Sb phase had a homogenertiy ranges, 0.155 - 0.189 Sb. The two-sublattice model, $(Pt,Sb)_{0.833}$ $(Pt,Sb)_{0.167}$ is used to describe this phase in the present work.

The parameters y_i' and y_i'' are the site fractions of Pt or Sb on the first and second sublattices, respectively; the parameter $G_{*:*}^{Pt_5Sb}$ represents the Gibbs energies of the compound Pt$_5$Sb when the first and second subletices are occupied by only one element Pt or Sb, respectively, which are relative to the enthalpies of pure fcc for Pt and rhombohedral for Sb in their SER state; ${}^jL_{Pt,Sb:*}^{Pt_5Sb}$ and ${}^jL_{*:Pt,Sb}^{Pt_5Sb}$ represent the jth interaction parameters (j = 0) between the element Pt and Sb on the first and second sublattice, respectively.

$$G_m^{Pt_5Sb} = y_{Pt}'y_{Pt}''G_{Pt:Pt}^{Pt_5Sb} + y_{Pt}'y_{Sb}''G_{Pt:Sb}^{Pt_5Sb} + y_{Sb}'y_{Pt}''G_{Sb:Pt}^{Pt_5Sb} + y_{Sb}'y_{Sb}''G_{Sb:Sb}^{Pt_5Sb} + 0.833RT(y_{Pt}'\ln y_{Pt}' + y_{Sb}'\ln y_{Sb}')$$

$$+ 0.167RT(y_{Pt}''\ln y_{Pt}'' + y_{Sb}''\ln y_{Sb}'') + y_{Pt}'y_{Sb}'\left(y_{Pt}''\sum_j {}^jL_{Pt,Sb:Pt}^{Pt_5Sb}(y_{Pt}' - y_{Sb}')^j + y_{Sb}''\sum_j {}^jL_{Pt,Sb:Sb}^{Pt_5Sb}(y_{Pt}' - y_{Sb}')^j\right) \tag{7}$$

$$+ y_{Pt}''y_{Sb}''\left(y_{Pt}'\sum_j {}^jL_{Pt:Pt,Sb}^{Pt_5Sb}(y_{Pt}'' - y_{Sb}'')^j + y_{Sb}'\sum_j {}^jL_{Sb:Pt,Sb}^{Pt_5Sb}(y_{Pt}'' - y_{Sb}'')^j\right)$$

Table 1. Pt-Sb Crystal Structure Data.

Phase	Composition, at% Sb	Pearson symbol	Space group	Strukturbericht designation	Prototype	Refs.
Fcc (Pt)	0 to 10.4	$cF4$	$Fm\bar{3}m$	$A1$	Cu	[22]
Pt$_7$Sb	12.5	$cF32$	$Fm\bar{3}m$	...	Ca$_7$Ge	[11]
Pt$_5$Sb	15.5 to 18.9	$cP4$	$Fm\bar{3}m$	$L1_2$	AuCu$_3$	[13]
Pt$_3$Sb	25.0	$tI16$	$I4/mmm$	$D0_{23}$	Al$_3$Zr	[13]
Pt$_3$Sb$_2$	40.0	$oI20$	$Ibam$	...	...	[9]
PtSb	50.0	$hP4$	$P6_3/mmc$	$B8_1$	NiAs	[23]
PtSb$_2$	66.7	$cP12$	$Pa\bar{3}$	$C2$	FeS$_2$(pyrite)	[24]
Rhombohedral (Sb)	100.0	$hR2$	$R\bar{3}m$	$A7$	αAs	[22]

The other intermediate phases, Pt$_7$Sb, Pt$_3$Sb, Pt$_3$Sb$_2$, PtSb, and PtSb$_2$ in the Pt-Sb system were treated as stochiometric compounds. The two-sublattice model, $(Pt)_m(Sb)_n$, is used to describe these phases in the present work. The Gibbs energy per mole of formula unit $(Pt)_m(Sb)_n$, was expressed as the following:

$$G_m^{Pt_mSb_n} = m\text{GHSER}_{Pt} + n\text{GHSER}_{Sb} + \Delta G_f^{Pt_mSb_n} \quad (8)$$

where $\Delta G_f^{Pt_mSb_n}$ is the Gibbs energy of formation per mole of formula unit Pt$_m$Sb$_n$. And $\Delta G_f^{Pt_mSb_n}$ can be given by the following expression:

$$\Delta G_f^{Pt_mSb_n} = a + bT \quad (9)$$

where the parameters a and b were to be evaluated in the present work.

4. Optimization

Most of the above experimental information was selected for the evaluation of the thermodynamic model parameters. In the present work, the phase relation and transformation temperatures based on the phase diagram of the Pt-Sb system compiled by Itkin and Alcock [6], determinded by Bhan *et al.* [9], and Durussel and Feschotte [11].

The optimization was carried out by means of the Thermo-Calc software [25], which can handle various kinds of experimental data. The program works by minimizing an error sum where each of the selected data values is given a certain weight. The weight is chosen by personal judgment and changed by trial and error during the work until most of the selected experimental information is reproduced within the expected uncertainty limits.

The ways to get the phase diagram summarized as several steps using the Thermo-Calc software. Firstly, it is the Unary phases to get the GES file, which is the basis of the assessment. Secondly, it is the thermodynamic models of the solution phases and the compounds to form the TCM file. The expression of the thermodynamic model was shown in Section 3.

Last is the optimization. The optimization was carried out by means of the Thermo-Calc software based on the POP file to get the PAR file. The POP file was the phases equlibria, while the PAR file was the results of the optimization. When the phase diagram is successfully optimized, all the phases in the system will get a set of consistent thermodynamic parameters to express Gibbs energies. Using the set of consistent thermodynamic parameters to reproduce the phase diagram and build the database such as the TDB file.

5. Results and Discussions

A thermodynamic description of the Pt-Sb system obtained in the present work is shown in **Table 2**. The Pt-Sb phase diagram calculated by means of the present thermodynamic parameters is presented in **Figure 1**, and nearly identical to the one determined by Bhan *et al.* [9], Durussel and Feschotte [11]. Because of the symmetry of liquid at both sides of the compound PtSb$_2$, there is great different about the liquid at 0.20 - 0.40 Sb between the calculated results and the experimental data [7-9].

The invariant equilibria of the Pt-Sb system are listed in **Table 3**. In the **Table 3**, some calculating data is nearly to experiment data but some is very different to experiment data. There is some reasons about these. The one is that the liquid at 0.20 - 0.40 Sb is deeper than others. Other is that the liquid of the sides of PtSb$_2$ is treated the symmetry during the assessed procedure. So it is very difficult to treat and optimize to get the same as the experimental data. In order not to change the types of reactions, the temperatures of reactions were revised in this work. As shown in the table, most satisfactory agreement is obtained between the calculations and experiments [7-9,11], where there is uncertainty in the invariant reaction temperature at 0.20 - 0.40 Sb.

Table 2. Thermodynamic parameters of the Pt-Sb system[a].

Phase	Models	Thermodynamic parameters
liquid	$(Pt, Sb)_1$	$^0L^{liq} = -33358.7 - 29.6508T$
		$^1L^{liq} = +4402.1 - 17.9740T$
		$^2L^{liq} = -11140.9$
rhombohedral	$(Pt, Sb)_1$	$G(\text{rhombohedral, Pt}) = + \text{GHSER}_{Pt} + 5000.0$
		$G(\text{rhombohedral, Sb}) = + \text{GHSER}_{Sb}$
fcc	$(Pt, Sb)_1$	$^0L^{fcc} = -9650.4 - 26.3403T$
		$^1L^{fcc} = -10650.4$
Pt_7Sb	$(Pt)_{0.865}(Sb)_{0.125}$	$G_{Pt:Sb}^{Pt_7Sb} = +0.865\text{GHSER}_{Pt} + 0.125\text{GHSER}_{Sb} - 7499.0 + 0.0120T$
Pt_3Sb	$(Pt)_{0.75}(Sb)_{0.25}$	$G_{Pt:Sb}^{Pt_3Sb} = +0.75\text{GHSER}_{Pt} + 0.25\text{GHSER}_{Sb} - 14002.3$
Pt_3Sb_2	$(Pt)_{0.6}(Sb)_{0.4}$	$G_{Pt:Sb}^{Pt_3Sb_2} = +0.6\text{GHSER}_{Pt} + 0.4\text{GHSER}_{Sb} - 20702.3$
$PtSb$	$(Pt)_{0.5}(Sb)_{0.5}$	$G_{Pt:Sb}^{PtSb} = +0.5\text{GHSER}_{Pt} + 0.5\text{GHSER}_{Sb} - 25012.3$
$PtSb_2$	$(Pt)_{0.333}(Sb)_{0.667}$	$G_{Pt:Sb}^{PtSb_2} = +0.333\text{GHSER}_{Pt} + 0.667\text{GHSER}_{Sb} - 30727.5 + 0.1023T$
Pt_5Sb	$(Pt,Sb)_{0.833}(Pt,Sb)_{0.167}$	$G_{Pt:Pt}^{Pt_5Sb} = +\text{GHSER}_{Pt} + 5000.0$
		$G_{Pt:Sb}^{Pt_5Sb} = +0.833\text{GHSER}_{Pt} + 0.167\text{GHSER}_{Sb} - 8357.4 - 1.3948T$
		$G_{Sb:Pt}^{Pt_5Sb} = +0.833\text{GHSER}_{Sb} + 0.167\text{GHSER}_{Pt} + 18357.4 + 1.3948T$
		$G_{Sb:Sb}^{Pt_5Sb} = +\text{GHSER}_{Sb} + 5000.0$
		$^0L_{Pt,Sb:Sb}^{Pt_5Sb} = {}^0L_{Pt,Sb:Pt}^{Pt_5Sb} = -22770.3$
		$^0L_{Pt:Pt,Sb}^{Pt_5Sb} = {}^0L_{Sb:Pt,Sb}^{Pt_5Sb} = -3981.8$

[a]In J·mole^{-1} of the formula units.

Table 3. Invariant reactions of the Pt-Sb system.

| Reaction	T (K)		x(Sb)		References
liq. + fcc(Pt) → Pt_5Sb	1021	0.275	0.100	0.166	[11]
	1139	0.2775	0.1240	0.1652	This work
fcc + Pt_5Sb → Pt_7Sb	898	0.104	0.155	0.125	[11]
	898	0.0330	0.1441	0.1250	This work
Pt_5Sb → Pt_7Sb + Pt_3Sb	833	0.164	0.125	0.250	[11]
	833	0.1530	0.125	0.2500	This work
liq. + Pt_5Sb → Pt_3Sb	948	0.302	0.189	0.250	[11]
	1128	0.2844	0.1703	0.2500	This work
liq. → Pt_3Sb + Pt_3Sb_2	903	0.315	0.250	0.400	[9]
	1127	0.2877	0.2500	0.4000	This work
liq. + $PtSb$ → Pt_3Sb_2	1012	0.352	0.500	0.400	[9]
	1133	0.2957	0.5000	0.4000	This work
liq. + $PtSb_2$ → $PtSb$	1319	0.475	0.667	0.500	[8]
	1197	0.3485	0.6667	0.5000	This work
liq. → $PtSb_2$	1499	0.667	0.667	–	[7]
	1497	0.667	0.667	–	This work
liq. → $PtSb_2$ + rhomb	899	0.990	0.667	1.000	[11]
	903	0.9974	0.6667	1.000	This work
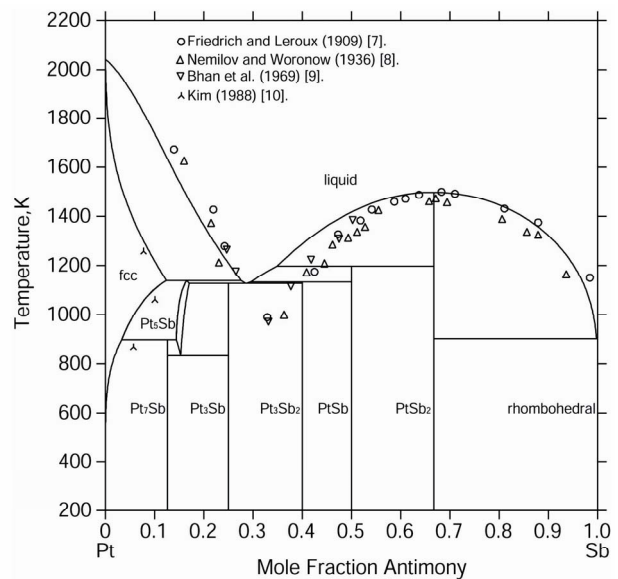
Figure 1. Calculated Pt-Sb phase diagram by the present thermodynamic escription with the experimental data measured by Friedrich and Leroux [7], Nemilov and Woronow [8], Bhan *et al.* [9] and Kim [10].

In view of the estimated experimental errors (about 0.01 - 0.02), 24 of the 26 experimental invariant reaction compositions in the Pt-Sb system are well reproduced.

6. Conclusion

The phase relations and the thermodynamic description of the Pt-Sb system were critically evaluated from the experimental information available in the literature. A set of consistent thermodynamic parameters were derived. With the thermodynamic description available, one can now make various calculations of practical interest or in the optimization of high-order systems.

7. Acknowledgements

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