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A THERMODYNAMIC EVALUATION OF THE Au–Sb AND Au–Tl SYSTEMS

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ABSTRACT

The two binary systems Au–Sb and Au–Tl have been thermodynamically assessed in the framework of a long term programme to provide thermodynamic data bases in order to perform calculations in multi-component systems. For each of these systems, two different sets of self-consistent parameters have been obtained by using the optimization procedure developed by Lukas et al. (Calphad, 6 (1977) 225). Phase diagram and characteristic thermodynamic functions have been calculated and compared with the corresponding experimental values using the THERMODATA software. The reasons why a definitive set of coefficients cannot yet be selected for the two systems are discussed, and proposals for further experimental work are given in order to conclude that work.

INTRODUCTION

Several gold-based binary systems have been previously assessed in this programme: Au–Sn [1], Au–Bi [2], Au–Si and Au–Ge [3]. The main aim of this work is to be able to thermodynamically model multi-component systems (ternary or higher order systems) and by this approach to minimize the number of necessary experiments. Another aim is also to determine missing experimental information and thus to avoid duplication of efforts.

For each of the two systems Au–Sb and Au–Tl, the available experimental information has been compiled using the bibliographic data base THERMDOC integrated in the THERMODATA system [4] and presented for both phase diagram and thermodynamic properties. This information is needed in order to obtain a set of self-consistent parameters for each of the systems using the optimization procedure of Lukas et al. [5].

EVALUATION METHOD

The Gibbs free energy of different solution phases (liquid, f.c.c.) has been described using a simple substitution model. An expression for the excess

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Gibbs free energy has been developed using a Redlich–Kister polynomial equation of the form

$$\Delta G^{\mathrm{E}} = x_{\mathrm{Au}} x_{\mathrm{M}} \sum_{\nu=0}^{n} (x_{\mathrm{Au}} - x_{\mathrm{M}})^{\nu} L_{\mathrm{Au,M}}^{(\nu)}(T) \tag{1}$$

with M = Sb or Tl.

The interaction terms $L_{\mathrm{Au,M}}^{(\nu)}$ are linear functions of the temperature

$$L_{\mathrm{Au,M}}^{(\nu)}(T) = a_{\mathrm{Au,M}}^{(\nu)} + b_{\mathrm{Au,M}}^{(\nu)} T \tag{2}$$

i.e., $a_{\mathrm{Au,M}}^{(\nu)}$ and $b_{\mathrm{Au,M}}^{(\nu)}$ correspond to the temperature independent values of the enthalpy and the excess entropy of mixing.

The Gibbs free energy of the compounds referred to the pure solid components has been represented by a three-term expression

$$\Delta G = A - BT + CT(1 - \ln T) \tag{3}$$

which can be written

$$\Delta G = a + bT + cT \ln T \tag{4}$$

where the term C is the first constant term of the C_p development: $a = A$, $b = C - B$, $c = -C$.

The values used for the lattice stabilities of the pure components come from the S.G.T.E. assessment [6] for the stable solid and liquid phases, and those of the metastable structures (Sb f.c.c.), Tl f.c.c.) have been evaluated by Saunders et al. [7]. They are reported in Table 1.

TABLE 1

Lattice-stabilities for M = Au, Sb and Tl for stable structures [6] and metastable structures [7]

M	Transformation	$\Delta G^{\ominus}$	Temperature range (K)
Au	f.c.c. → liquid	$12589.413 - 9.416744T + 8140.249 \times 10^{-25}\ T^{7}$	298.15–1337.58
		$12522.901 - 9.364532T + 398805.149 \times 10^{+23}\ T^{-9}$	1337.58–3200.0
Sb	rho → liquid	$19822.595 - 21.920597T - 173784.951 \times 10^{-25}\ T^{7}$	298.15– 903.90
		$19913.982 - 22.026755T - 16104.421 \times 10^{+23} T^{-9}$	903.90–2000.0
	rho → f.c.c.	$19874.0 - 13.7T$	298.15–2000.0
Tl	h.c.p. → liquid	$4654.235 - 8.157775T - 5946859.963 \times 10^{-25}\ T^{7}$	298.15– 577.00
		$4789.301 - 8.403563T - 418.897 \times 10^{+23}\ T^{9}$	577.00–3000.0
	h.c.p. → b.c.c.	$137.793 - 9.055306T - 4.42 \times 10^{-3}\ T^{2} + 1.77T \ln T$	298.15– 577.00
		$801.583 - 1.465674T - 1513.730 \times 10^{+23}\ T^{9}$	577.00–3000.0
	h.c.p. → f.c.c.	$151 - 0.06T$	298.15–3000.0

EXPERIMENTAL INFORMATION

The Au–Sb system

Phase diagram

The equilibrium phase diagram of the Au–Sb system has been assessed by Okamoto and Massalski [8]. The liquidus was determined by Vogel [9] and Grigorjew [10] using thermal analysis and microscopic examination. The solid solubility of Sb in gold was measured parametrically with an accuracy of 0.05 at.% by Owen and Roberts [11]: $x_{Sb} = 0.0112$ at $T = 893$ K, 0.0115 at 822 K, 0.0108 at 769 K, 0.0105 at 721 K, 0.009 at 678 K, 0.0087 at 675 K, 0.0085 at 661 K, 0.0070 at 637 K, 0.0038 at 583 K and 0 at 473 K. An approximate value of 0.0045 at 598 K was obtained by Muller and Merl [12] from electrical resistivity data. The solid solubility of Au in pure antimony has not been studied and is assumed to be negligible. The different phases of the system are the liquid phase (L), the terminal gold-based solid solution (f.c.c.), and the Fe_2S-type intermetallic line compound $AuSb_2$, whose existence has been confirmed by several authors [8]. Pure antimony has a rhombohedral (A7) structure isotypic with As (Sb rho). There are two invariant reactions: a eutectic one, liquid (L) + Sb rho $\Leftrightarrow$ $AuSb_2$, and a peritectic one, liquid (L) $\Leftrightarrow$ f.c.c. + $AuSb_2$.

The eutectic temperature has been determined by: Vogel [9], eight values between 630.15 and 634.15 K, mean value 632.8 K (thermal analysis); by Grigorjew [10], seven values between 624.15 and 628.15 K, mean value 627.15 K (thermal analysis); by Gasgnier et al. [13], 633.15 K (specific heat); by Gaither and Blachnik [14], 633.15 K (X-rays and metallography); and by Wallbrecht et al. [15], 634.15 K (specific heat). The eutectic composition was determined by Vogel [9] as $x_{Sb} = 0.348$. The eutectic point assessed by Okamoto and Massalski [8] was $T = 633.15$ K, $x_{Sb}(L) = 0.355 \pm 0.025$.

The peritectic temperature was measured by: Vogel [9], six values between 723.15 and 733.15 K, mean value 729.5 K; by Grigorjew [10], seven values between 725.15 and 738.15 K, mean value 730.4 K; by Gaither and Blachnik [14], 733.15 K; and by Okamoto and Massalski [8], 740 K. The peritectic point assessed by Okamoto and Massalski [8] is $T = 733.15$ K, $x_{Sb}(L) = 0.66$.

Thermodynamic properties

The heat of formation of the intermetallic compound $AuSb_2$ referred to the pure solid components was measured calorimetrically by: Jena and Bever [16], $T = 273$ K, $\Delta H = -4351$ J (g at.)$^{-1}$; by Kleppa [17], $T = 723$ K, $\Delta H = -3138$ J (g at.)$^{-1}$; and by Biltz et al. [18], $T = 363$ K, $\Delta H = -4895$ J (g at.)$^{-1}$. The enthalpy of formation of $AuSb_2$ referred to the pure liquid elements was determined as -20 kJ (g at.)$^{-1}$ by Wallbrecht et al. [15], which yields a value of -2570 J (g at.)$^{-1}$ for the heat of formation referred to the pure solid elements, by assuming that ΔC_p for both components are zero. The heat of formation selected by Kubaschevski et al. [19] is $\Delta H = -6485$ J (g at.)$^{-1}$ at $T = 298.15$ K. It can be seen that the enthalpies of formation are very scattered.

The heat capacity of $AuSb_2$ was given by Kelley [20] ($0 < T < 773$ K) as $C_p = 23.88 \pm 6.47 \times 10^{-3}\ T$ J (g at.)$^{-1}$ K^{-1}, and by Itagaki [21] ($473 < T < 623$ K) as $C_p = 21.924 \pm 8.368 \times 10^{-3} \times T$ J (g at.)$^{-1}$ K^{-1}. The calculated value of ΔC_p in the temperature range 300–800 K taking Kelley's values of C_p for $AuSb_2$ and the values of Hultgren et al. [22] for the pure elements can be approximated by a mean constant value equal to 0.62 J (g at.)$^{-1}$ K^{-1}.

The activity of Sb in Au–Sb liquid alloys has been measured using the e.m.f method by Kasuo et al. [23] ($T = 973$–1073 K); $x_{Sb} = 0.2$–0.85. The activities of antimony were also determined from the vapour pressures by Mitsuhisa et al. [24] using the transportation method ($T = 1273$–1473 K); $x_{Sb} = 0.1$–0.9.

The Au–Tl system

Phase diagram

The liquid curve of the Au–Tl system has been determined by Levin [25] by the thermal analysis of only six alloys. The solid solubility of Tl in gold was parametrically measured by Raub and Engel [26] as $x_{Tl} = 0.0048$ at $T = 1313$ K, 0.0075 at 1273 K, 0.0079 at 1173 K, 0.0090 at 1073 K, 0.0082 at 873 K, 0.0071 at 771 K, 0.0051 at 723 K, 0.0035 at 673 K, 0.0021 at 573 K and 0.0017 at 473 K. No measurement of the solubility of Au in thallium has been reported and it was neglected. The different phases of the system are the liquid phase (L), the terminal gold-based solid solution (f.c.c.), pure thallium, with an h.c.p (A3) structure isotypic with Mg (Tl h.c.p.) which transforms at 507 K to a b.c.c. (A2) structure isotypic with W (Tl b.c.c.). There is eutectic reaction liquid (L) ⇔ f.c.c. + Tl h.c.p. and the eutectic point was located by Hajicek [27] at $T = 415$ K and $x_{Tl} = 0.708$.

Thermodynamic properties

The heat of formation of Au–Tl liquid alloys referred to solid gold and liquid thallium has been measured calorimetrically by Kleppa [28]; $T = 723$ K, $x_{Au} = 0$–0.313. The values of the enthalpy of mixing referred to the pure liquid components are negative (up to -583 J for $X_{Au} = 0.3128$ assuming the heat of transformation between solid and liquid gold is equal to 12552 J).

The activity of thallium in the liquid phase has been measured using the e.m.f. method by Kleppa [29]; $T = 973$ K, $x_{Tl} = 0.177$–0.895. We can note that the two points corresponding to $x_{Tl} = 0.177$ and 0.243 are not in the monophasic liquid region according to the phase diagram. The calculated enthalpy of mixing resulting from this method is very slightly positive over all the composition range (maximum equal to 167 J). The activity of thallium in liquid Au–Tl alloys has also been determined using the e.m.f. method by Kasuo et al. [30]; $T = 973$, 1073 K, $x_{Tl} = 0$–1. Their results show a small dependency of the activity on temperature and are similar to those of Kleppa at 973 K. The calculated heat of mixing shows a minimum equal to -251 J at $x_{Tl} = 0.6$.

RESULTS AND DISCUSSION

The published experimental information was used to obtain a set of self-consistent parameters for each phase of the system using the optimization procedure developed by Lukas et al. [1]. Table 2 shows the optimized parameters of the excess Gibbs free energy according to expressions (1) and (2) for the various solution phases referred to the pure elements having the same structure as the corresponding phase.

Table 3 shows the optimized parameters of the Gibbs free energy of formation of the stoichiometric compound $AuSb_2$ referred to the pure solid

TABLE 2

Excess Gibbs free energy for the liquid and f.c.c. solid solution phases of the Au–M systems (M = Sb, Tl)

$$\Delta G^{E} = x_{Au}x_{M}\sum_{\nu=0}^{n}(x_{Au}-x_{M})^{\nu}L^{(\nu)}_{Au,M}(T) \qquad (1)$$

$$L^{(\nu)}_{Au,M}(T) = a^{(\nu)}_{Au,M} + b^{(\nu)}_{Au,M}T \ (\nu = 0,\dots,2) \qquad (2)$$

M	Phase	ν	$a^{(\nu)}_{Au,M}$ (J)	$b^{(\nu)}_{Au,M}$ (J K^{-1})	Temperature range (K)
Sb	liquid	0	−15437.35 (a)	−4.63455 (a)	298.15–2000
			−824.90 (b)	−33.16207 (b)	
		1	−18854.10 (a)	15.64707 (a)	
			−6115.60 (b)	−3.99516 (b)	
		2	−4271.85 (a)	0.00000 (a)	
			0.00 (b)	0.00000 (b)	
	f.c.c.	0	7580.00 (a)	0.00000 (a)	
			36445.10 (b)	−46.04160 (b)	
Tl	liquid	0	−8003.30 (a)	0.72432 (a)	298.15–2100
			−9142.70 (a)	2.37236 (b)	
		1	−8895.50 (a)	13.33760 (a)	
			−8061.40 (b)	12.23521 (b)	
	f.c.c.	0	23222.30 (a)	0.00000 (a)	
			23293.40 (b)	0.00000 (b)	

TABLE 3

Gibbs free energy of formation of the stoichiometric compound Au Sb_2 referred to the pure solid components (Au f.c.c. and Sb rho)

$$\Delta G = A - BT + CT(1 - \ln T) \text{ (J)} \tag{3}$$

$$\Delta G = a + bT + cT \ln T \text{ (J)} \tag{4}$$

Compound	A a	B b	C c	Temperature range (K)
$AuSb_2$	−5594.6	−6.72499	0.62000 (a)	298.15–2000.0
	−5594.6	−7.34499	−0.62000 (a)	
	−6549.2	−6.34957	0.62000 (b)	
	−6549.2	6.96957	−0.62000 (b)	

components according to expressions (3) and (4). For the two systems, two different data sets are proposed and discussed. The first optimization is symbolized by (a), the second by (b).

The Au–Sb System

Results

Two different optimizations have been performed for the Au–Sb system. The first has five coefficients in the liquid phase and one in the f.c.c. solid solution, and the second has four coefficients in the liquid phase and two in the f.c.c. solid solution. The phase diagram has been calculated using the two sets of optimized coefficients and compared with the experimental data in Fig. 1. The calculated eutectic point is: $x_{Sb} = 0.349$, $T = 630.9$ K for the first set; and $x_{Sb} = 0.353$, $T = 629.4$ K for the second set which are in satisfactory agreement with the mean experimental value, $T = 632$ K, and the composition determined by Vogel [9], $x_{Sb} = 0.348$, in the two cases.

The calculated peritectic point is: $T = 732.4$ K, $x_{Sb} = 0.66$, for the first optimization; and $T = 734.3$ K, $x_{Sb} = 0.663$, for the second optimization, and is in good agreement with the values assessed by Okamoto and Massalski [8]: $T = 733.15$ K, $x_{Sb} = 0.66$, in both cases. The calculated solid solubility of Tl in f.c.c. at the eutectic temperature is equal to 0.01 in the first case and 0.0076 in the second case, and the general agreement over all the temperature range is better with the second set of coefficients. Moreover, the calculated liquidus curve in the gold-rich region is closer to the experimental values in the second case.

In the optimization procedure, the heat capacity of $AuSb_2$ referred to the pure solid components, ΔC_p, has been fixed to the mean constant experimental value of 0.62 J (g at.)$^{-1}$ K^{-1}. The calculated enthalpy of formation of $AuSb_2$ was assumed to be a linear function of the temperature, which yields a value of −5410 (a) or −6364 (b) J (g at.)$^{-1}$ at 298.15 K. These values seem to be appreciably more negative than the experimental ones.

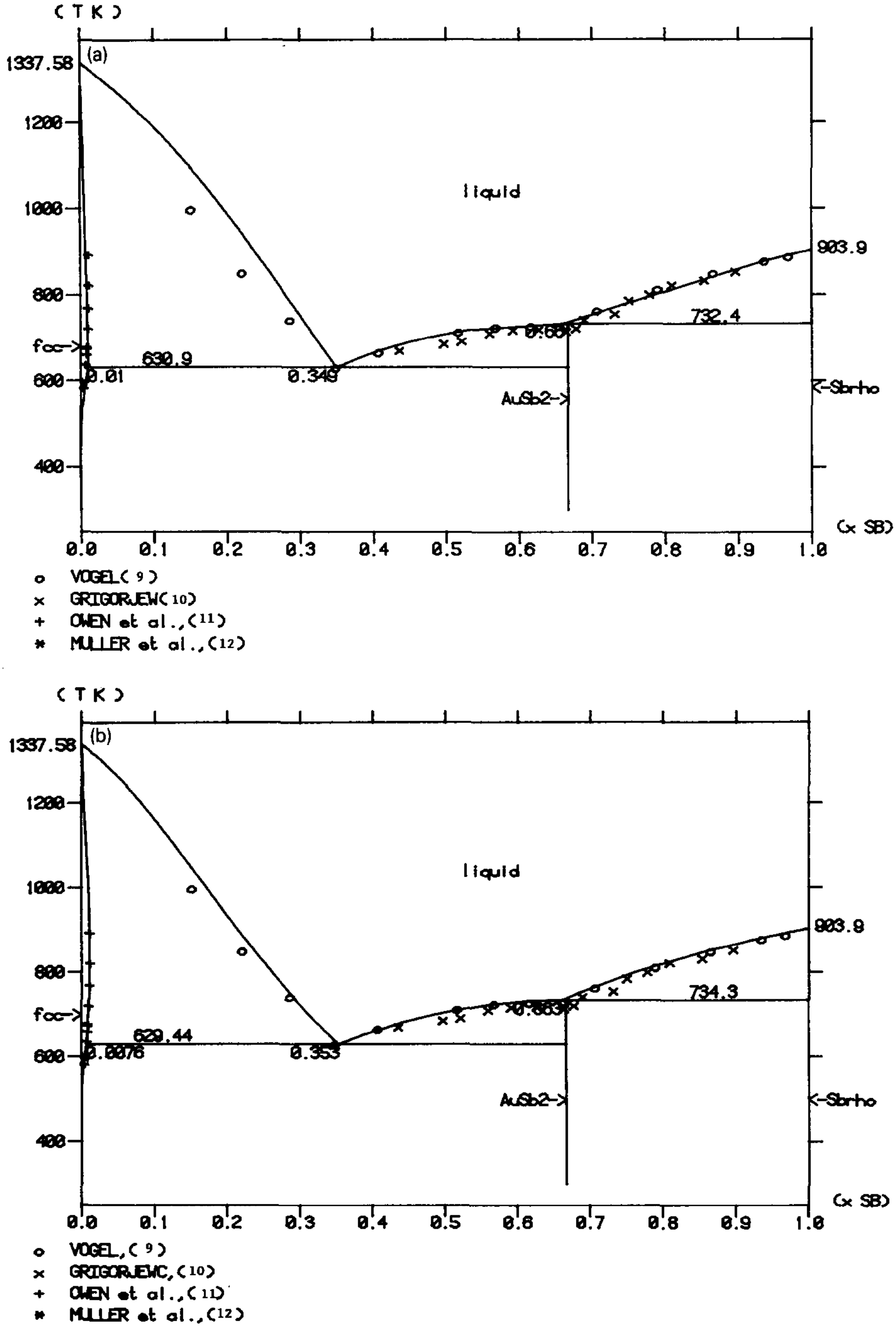

Fig. 1. Calculated Au–Sb phase diagram compared with selected experimental data: a, first optimization; b, second optimization.

The calculated activity of thallium in the liquid phase has been compared to the experimental results of Kasuo et al. [23] at 973 and 1073 K, and the agreement is rather poor with the two data sets, even if the second one seems

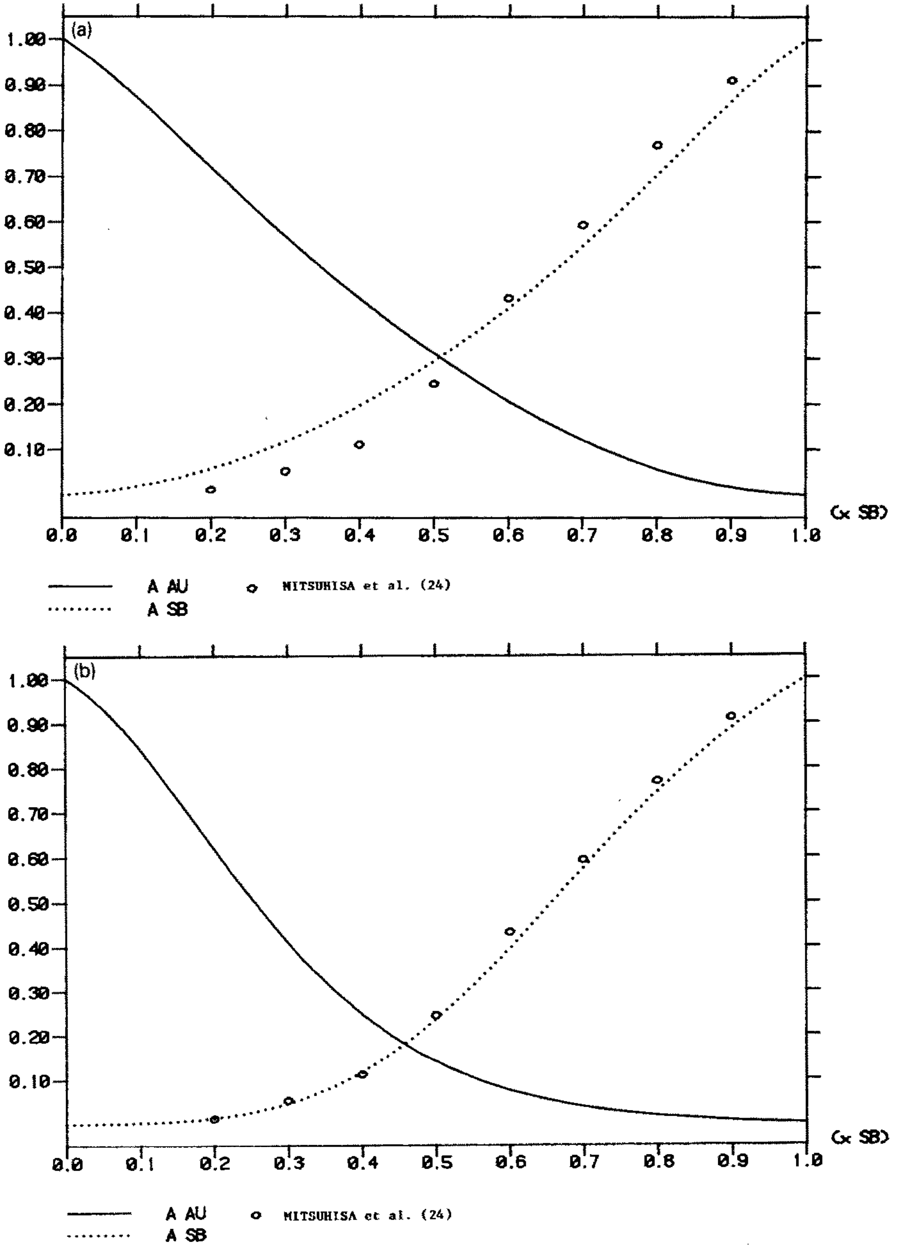

Fig. 2. Calculated activity of Au and Sb in the liquid phase at $T = 1273$ K referred to the pure liquid components and compared with selected experimental data of Mitsuhisa et al. [24]. a, first optimization; b, second optimization.

to be better in the gold-rich region. The comparison with the results of Mitsuhisa et al. [24] at $T = 1273$ K is shown in Fig. 2. The agreement is much better with the second set of coefficients.

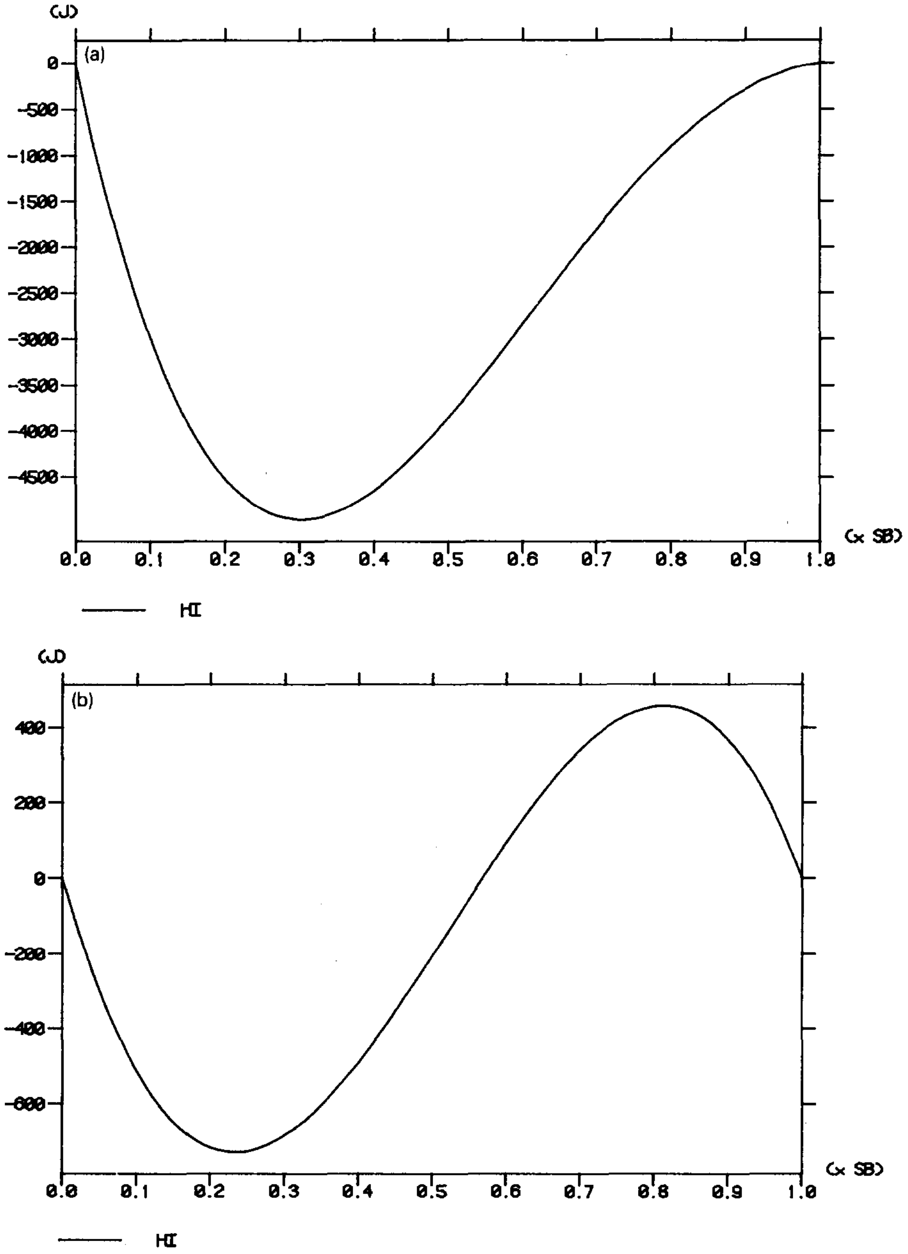

Fig. 3. Calculated enthalpy of mixing of the Au–Sb liquid phase (assumed to be temperature independent): a, first optimization; b, second optimization.

The calculated enthalpy of mixing with the two sets of coefficients is presented in Fig. 3 and is very different in the two cases. In the first case, it is negative over all the composition range and shows a minimum equal to -4800 J at $x_{\mathrm{Sb}} = 0.3$ while in the second case, the enthalpy of mixing is very small (less than 1 kJ) with a minimum in the gold-rich region and a maximum in the antimony-rich region. It cannot be compared with directly measured experimental values.

Discussion

It is difficult to select one or other data set for the Au–Sb system for the following reasons: the general agreement with all the experimental values, phase diagram and activity of thallium in the liquid phase, is better with the second set of coefficients, but the calculated enthalpy of mixing of the liquid phase is very different in the two cases.

Consequently, further experimental work would be very useful in order to directly measure, by calorimetry for example, the enthalpy of mixing of the liquid phase and to select a definitive set of parameters after having included these new experimental values in the optimization procedure. Other experimental points could also be more accurately determined, such as the enthalpy of formation of $AuSb_2$ and the liquidus curve in the gold-rich region.

The Au–Tl system

Results

As with the Au–Sb system, two different optimizations have been performed. The first takes into account the enthalpy of mixing of the liquid phase according to Kleppa [28], and the second does not. The phase diagram was calculated with the two sets of data and compared with the experimental data, see Fig. 4. The agreement is better for the eutectic temperature in the second case: $T = 418$ K, $x_{\mathrm{Tl}} = 0.722$, for (a); $T = 409$ K, $x_{\mathrm{Tl}} = 0.719$, for (b), compared with $T = 404$ K [25] and $T = 415$ K [27]. The calculated solid solubility of Tl in the f.c.c. solid solution is the following: $x_{\mathrm{Tl}} = 0.0013$ (a), 0.0010 (b) at the eutectic temperature; 0.0021 (a), 0.0019 (b) at 473 K; 0.0038 (a), 0.0036 (b) at 573 K; 0.0055 (a), 0.0053 (b) at 673 K; 0.0063 (a), 0.0060 (b) at 723 K; 0.0070 (a), 0.0069 (b) at 773 K, 0.0080 (a, b) at 873 K, 0.0081 (a), 0.0084 (b) at 1073 K and 0.004 (a, b) at 1273 K.

The calculated enthalpy of mixing of the liquid phase referred to the pure liquid components is compared with the experimental calorimetric values of Kleppa [28] in Fig. 5.

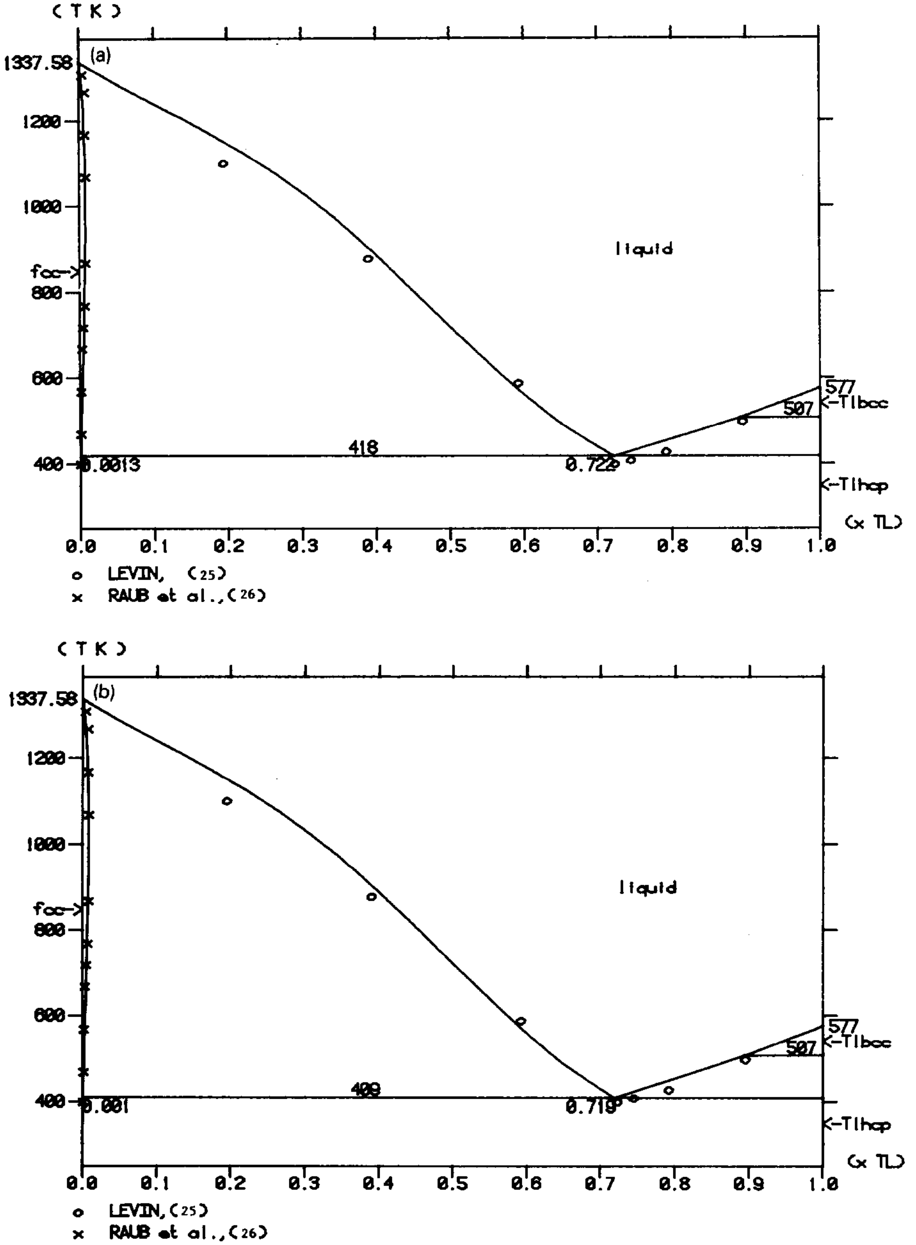

Fig. 4. Calculated Au–Tl phase diagram compared with selected experimental data: a, first optimization; b, second optimization.

The activities of the pure components in the liquid phase have been calculated at $T = 973$ and $T = 1073$ K and compared with the experimental values of Kleppa [29] and Kasuo et al. [30] in Fig. 6 and 7. The agreement is very good and is the same with the two optimizations.

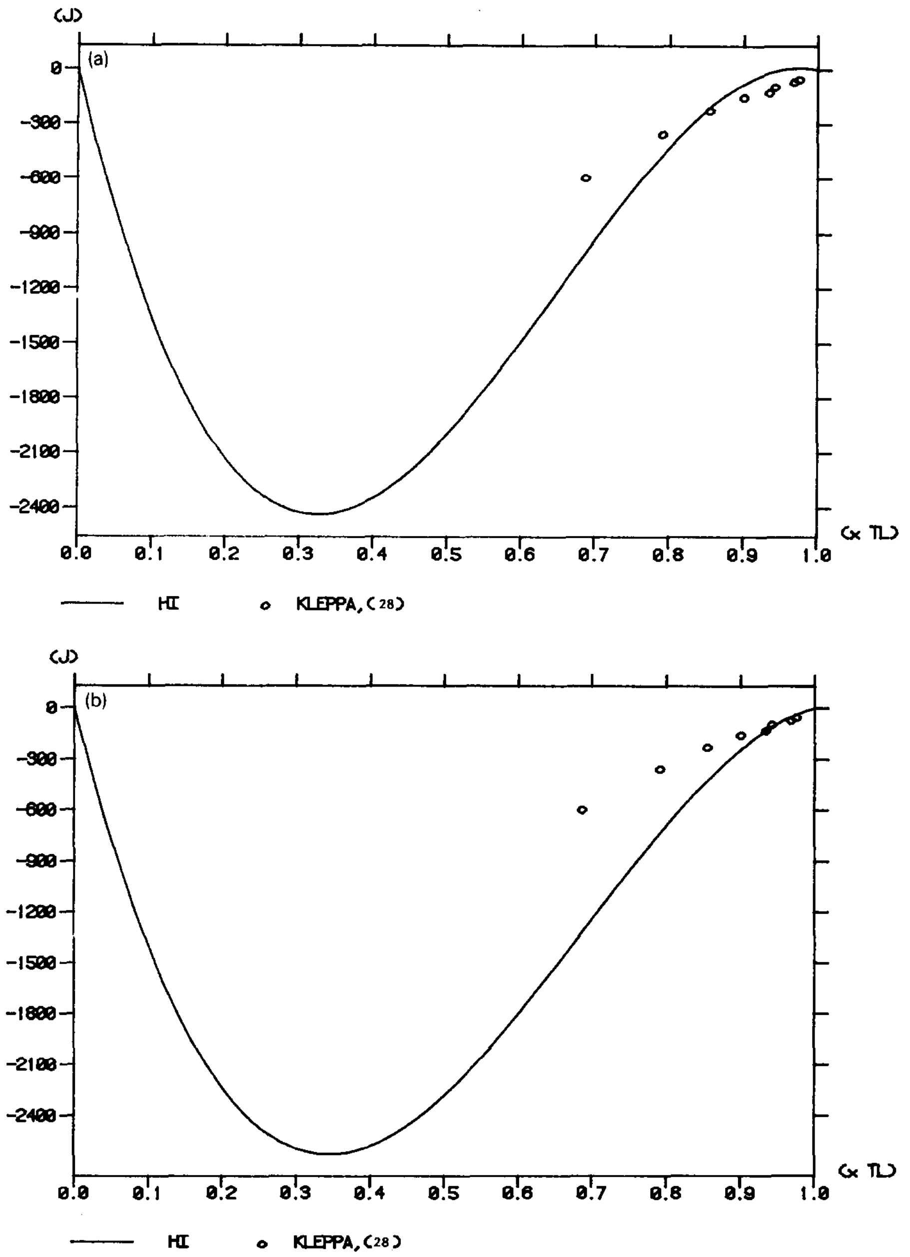

Fig. 5. Calculated enthalpy of mixing of the liquid phase referred to the pure liquid components and compared with selected experimental data: a, first optimization; b, second optimization.

Discussion

The calculated phase diagram is in better agreement with the experimental one with the second set of coefficients, which does not take into account

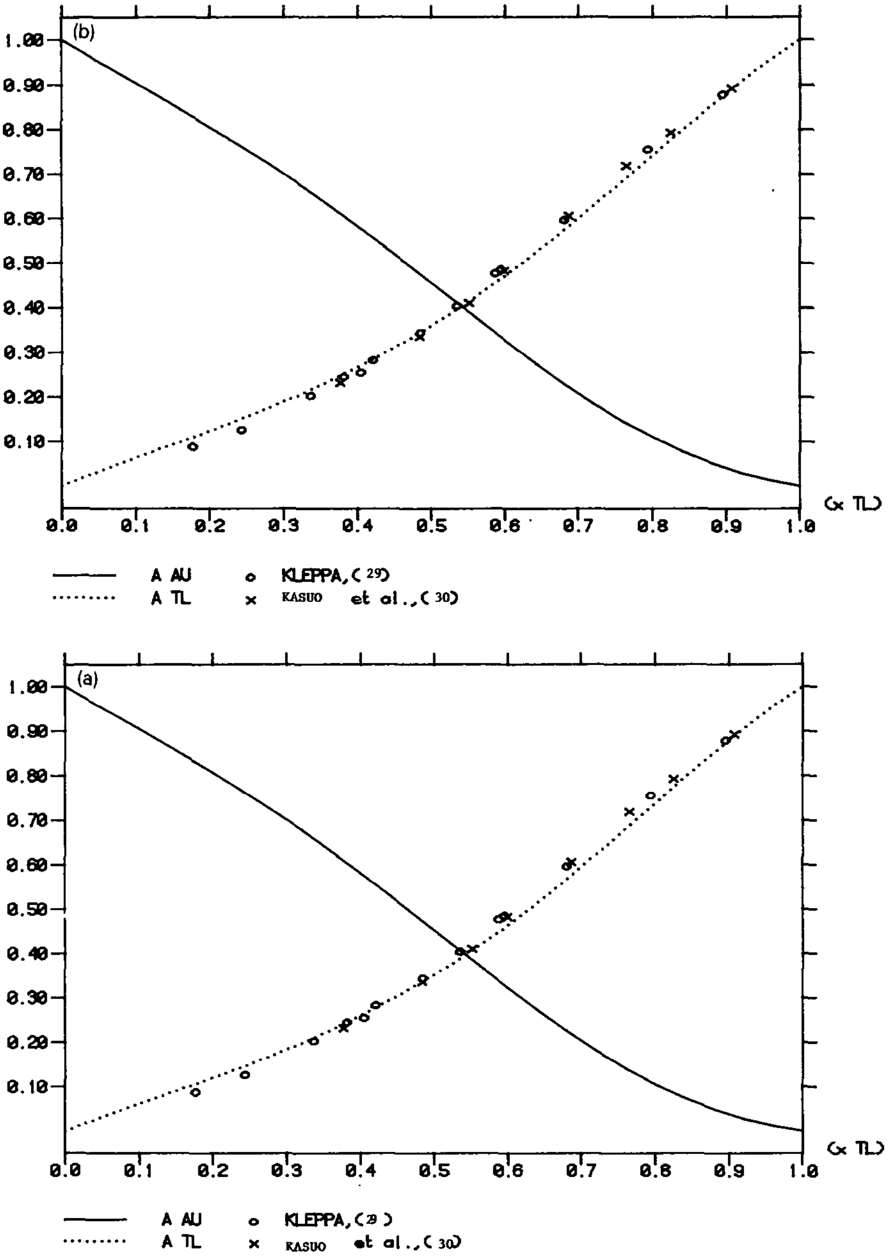

Fig. 6. Calculated activity of Au and Tl in the liquid phase at $T = 973$ K referred to the pure liquid components and compared with selected experimental data: a, first optimization; b, second optimization.

the enthalpy of mixing of Kleppa [28]. A new experimental determination of this function over the whole composition range and also of other points of the liquidus would be helpful in completing the assessment.

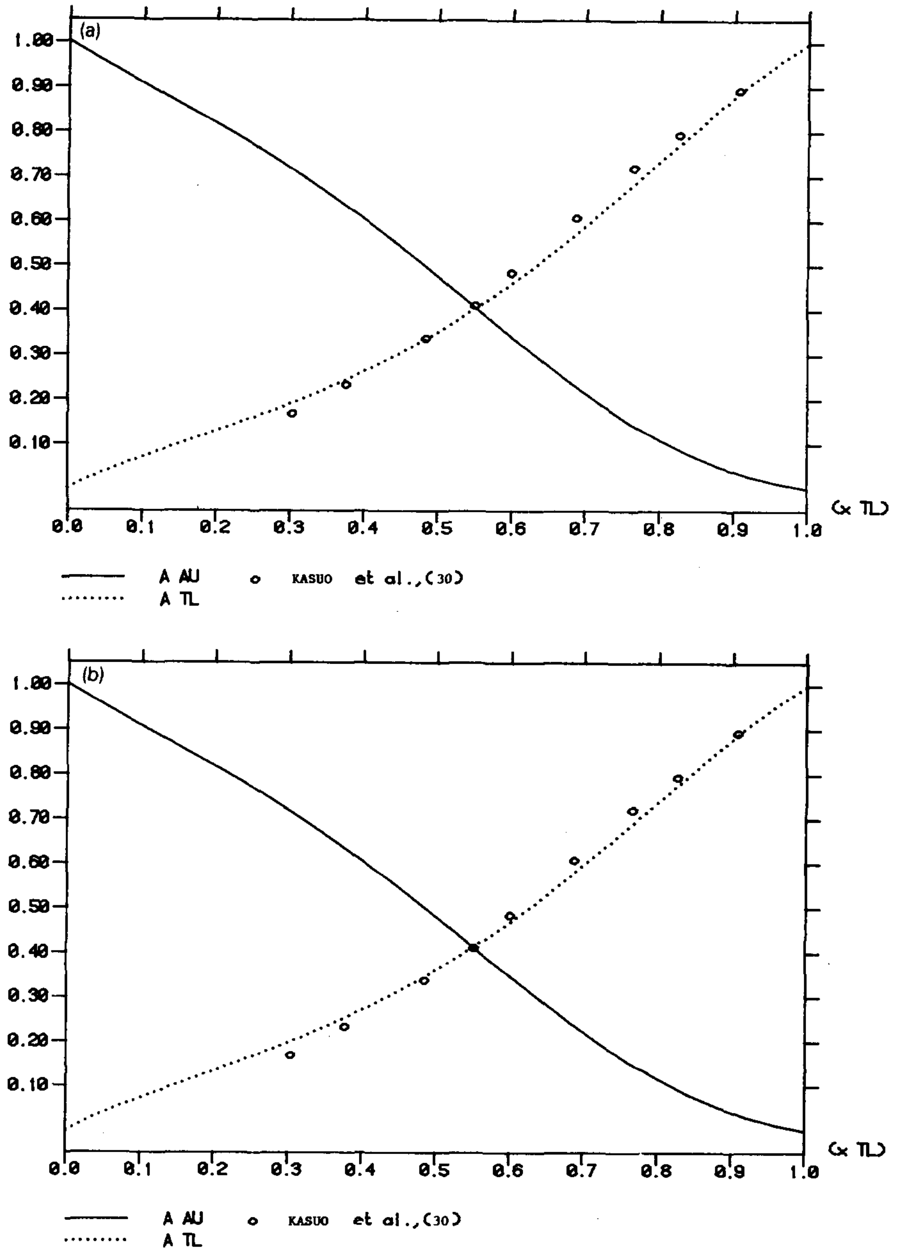

Fig. 7. Calculated activity of Au and Tl in the liquid phase at $T = 1073$ K referred to the pure liquid components and compared with selected experimental data: a, first optimization; b, second optimization.

SUMMARY

A complete thermodynamic evaluation of the Au–Sb and Au–Tl systems is presented. The liquid phase (L), the terminal gold-based solid solutions (f.c.c.) and the stoichiometric compound $AuSb_2$ have been modelled. For each system, two sets of self-consistent parameters have been proposed; however, it is still difficult to select one of them, especially because experimental information on the enthalpy of mixing of the liquid phase over the whole composition range is either lacking or not sufficiently accurate. The heat of formation of the stoichiometric compound $AuSb_2$ should also be improved. A definitive set of coefficients could be established as soon as new experimental information is available for these different points.

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