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Calorimetric investigations of Au–In, In–Sb and Au–In–Sb systems at 973 K

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ABSTRACT

The molar enthalpies of mixing of the Au–In, In–Sb and Au–In–Sb alloys have been determined at 973 K using a Calvet high-temperature microcalorimeter by the drop method. Measurements in the ternary system Au–In–Sb were performed along four sections, $x_{Au}/x_{In} = 1/3–1/1$ and $x_{In}/x_{Sb} = 1/1–3/1$. The experimental calorimetric data and estimated values with a Redlich–Kister–Muggianu formulation are compared.

1. Introduction

In recent years, substantial efforts were made to develop lead-free solders that are suitable substitute for classic tin–lead eutectic solders. Despite numerous studies already conducted, there are only a limited number of reports on the research and development for high temperature lead-free alternative solders. High-temperature lead-free solders are needed for both the electronics and automobile industries. Unfortunately, limited choices are available as high temperature solders. Gold-based alloys are known for good mechanical and thermal properties, as well as corrosion consistency and can be considered as potential candidates. Among these systems, the Au–In–Sb ternary alloys may be taken in consideration.

In order to predict the interface reactions between In-based solders and Au-substrate, knowledge of thermodynamic behaviour and phase diagram of the ternary Au–In–Sb system is essential.

As no direct measurement of the thermodynamic functions of mixing of this ternary system is available in the literature, the main purpose of this study is the determination of the enthalpies of mixing of the liquid phase in the ternary system Au–In–Sb at 973 K. The measurements were performed along four sections, $x_{Au}/x_{In} = 1/3–1/1$ and $x_{In}/x_{Sb} = 1/1–3/1$ that require knowledge of the enthalpies of mixing for the two limiting Au–In and In–Sb binary systems.

2. Bibliographic survey

2.1. The binary systems

2.1.1. Au–In system

Several thermodynamic investigations of Au–In alloys have been reported in the literature. Kameda et al. [1] determined thermodynamic activities of In in liquid Au–In alloys by e.m.f. measurements in the temperature range 973–1223 K. Predel and Schallner [2] used the same method to determine the partial molar free enthalpy of zinc in ternary Au–In–Zn alloys and obtained the excess values of liquid Au–In alloys by extrapolation. Béjà [3] measured the enthalpy of mixing at 873 and 1028 K by direct reaction calorimetry. Itagaki and Yazawa [4] performed measurements of heats of mixing by adiabatic calorimetry at 1373 K. Kleppa [5] determined the molar heats of formation of gold–indium alloys by tin solution technique at 723 K in the liquid range $0.02 < x_{Au} < 0.16$.

Castanet et al. [6] determined the enthalpies of mixing of liquid Au–In alloys, between 720 K and 1300 K, by using a high temperature Calvet-type calorimeter, and the activities of indium in liquid gold–indium alloys by e.m.f. method between the liquidus

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temperature and 973 K. The calorimetric results of Castanet et al. [6] are more exothermic than those of Kameda et al. [1] and Itagaki and Yazawa [4].

Gather and Blachnik [7] built a heat-flow calorimeter and made some measurements at 900 K to test it. Their minimum value of the enthalpy of mixing lies between the results of Béjà [3] and Castanet et al. [6].

The data of Castanet et al. [6] and Béjà [3] show that the enthalpies of mixing of Au–In alloys are temperature dependent. They deduced from their data, the $Cp^E = (\partial \Delta_{mix} H_m)/\partial T$ values that are positive and pass through a maximum at about $x_{Au} = 0.55$. Castanet et al. [6] show that Cp^E decreases with increasing temperature indicating strongly the existence of associates in liquid alloys which dissociate with increasing temperature.

The thermodynamic functions were assessed by Ansara and Nabot [8], and Liu et al. [9]. The calculated enthalpies of mixing of liquid Au–In alloys obtained by both the descriptions are similar and show the same dependence on temperature.

2.1.2. *Au–Sb system*

The liquid Au–Sb alloys have been studied between 973 K and 1073 K by Kameda et al. [1] using the e.m.f. method and by Hino et al. [10] by vapour-pressure measurements between 1273 K and 1473 K. The enthalpies of formation deduced from both methods are in good agreement. However, the enthalpies of formation obtained by Béjà [3] using the direct-reaction calorimetry at 923 K are very different from these two previous authors. Anres et al. [11] have also measured the enthalpies of mixing at 916 K and Hayer and Castanet [12] between 906 K and 1028 K using calorimetric method. The data of both these investigations are in good agreement with each other only in the rich part of antimony, between $0.5 < x_{Sb} < 1$. Hayer and Castanet [12] found out that the Béjà's enthalpy data were in fair agreement with their results and considered the enthalpies derived by Kameda et al. [1] and by Hino et al. [10] as erroneous probably because they come from indirect methods. Larger uncertainty may exist in such deduced values of the enthalpy of mixing compared with the data obtained directly by using calorimetry.

Unfortunately, the assessment given by Okamoto and Massalski [13] was based on the data of Kameda et al. [1] and Hino et al. [10]. New optimizations were carried out subsequently by several authors [14–17]. Only Liu et al. [16] considered the temperature dependence of mixing enthalpy of the liquid phase. Although the improvement is not very noticeable in the phase diagram of Au–Sb binary system, Liu et al. [16] considered that the temperature dependence is more thermodynamically reasonable.

2.1.3. *In–Sb system*

For this system, the calorimetric investigations were carried out by several authors: Wittig and Gehring [18] by using the liquid tin solution calorimetry at 973 K; Yazawa et al. [19] used a new adiabatic calorimeter to achieve measurements at 946 K. A heating process method was developed by Itagaki and Yazawa [20,21] to measure the enthalpy of mixing.

A high-temperature calorimeter was used by Predel and Oehme [22], Oehme and Predel [23] at 953 K and Rosa et al. [24] at various temperatures between 957 K and 1184 K. The data of Rosa et al. [24] show that the enthalpies of mixing of In–Sb alloys increase with increasing temperature.

The thermodynamic assessment of In–Sb binary system was performed by Ansara et al. [25] and agreement was obtained between the calculated values and experimental data for thermodynamic properties and phase relations, respectively. Liu et al. [16] re-optimized this system, while keeping the parameters of the liquid from Ansara et al. [25]. In both cases, the temperature effect is taken into account.

2.2. *Au–In–Sb system*

Few experimental calorimetric data concerning the ternary Au–In–Sb system were available. The only existing investigation was carried out by Gomidzelovic and Zivkovic [26] that relate a study using Oelsen calorimetry at 873 K. Applying the predicting methods of Toop and Muggianu in the temperature range 873–1673 K, they determined the thermodynamic properties in the AuIn–Sb section.

In a second study, Gomidzelovic et al. [27] used Chou's general solution model to predict the thermodynamic properties of the Au–In–Sb system in a wide temperature range from 873 to 1673 K. In a third study, Gomidzelovic et al. [28] have calculated the enthalpies of mixing for three sections with Au/In molar ratio equal to 1/3, 1/1, and 3/1 using derived form of the Gibbs–Helmholtz equation.

The equilibrium phase diagram of this system has been the subject of many experimental investigations especially by Nikitina and Lobanova [29], Babitsyna and Luzhnaya [30], Kubiak and Schubert [31], Tsai and Williams [32] and by Gomidzelovic et al. [33]. On the basis of the constituent binary systems, the Au–In–Sb system was assessed by Liu et al. [16].

3. Experimental procedure

The determinations of the enthalpies of formation of liquid Au–In, In–Sb and Au–In–Sb alloys were performed at 973 K using a Calvet high-temperature microcalorimeter with an experimental set up described elsewhere [34]. The nature of the crucible depends on the reactivity of the liquid metals and alloys: during these measurements, pure graphite crucibles were employed. A small flow of high-purity argon, $[O_2] < 2$ ppm (Argon Alphagaz from Air Liquid Company) is maintained during experiments.

High purity metals: Au (4N) wire from Engelhard C.L.A.L. (Comptoir Lyon Alemand Louyot) and Sb (5N) shot and In (6N) shot from Alfa Aesar, were employed in this study. Measurements were performed by the direct drop method [35]. The Au–In and In–Sb binary liquid alloys were formed by multiple successive additions of a lot of pieces of gold or antimony into the liquid indium at experimental temperature. The ternary alloys were synthesized by additions of samples of gold or antimony into the liquid In_xSb_{1-x} or Au_xIn_{1-x} alloys respectively.

Enthalpy contents of elements Au and Sb were taken from compilation of Hultgren et al. [37].

The calorimeter was calibrated at the end of each experiment by dropping small pieces of α-Al_2O_3 from N.I.S.T. [36] from the ambient temperature into the experimental crucible.

The standard deviation of the calibration is about 0.1% and the uncertainty in the enthalpy of formation is estimated to be 5%.

Considering the high vapour pressure of Sb at the experimental temperature (5.9×10^{-4} atm at 973 K), one would expect a significant loss in mass during the experiment. It can be noticed however that, after dissolution into the bath, the Sb vapour pressure is strongly decreased by the alloying process. The ingots weighed after experiment revealed a mass loss of about 3–6 mg for a final mass of the ingot ranging from 1000 to 1600 mg. Assuming the maximum loss in Sb of 6 mg, the uncertainty calculated on the final Sb molar fraction ($\Delta x_{Sb}/x_{Sb}$) of the ingot is estimated at about 2.7%.

4. Results and discussion

4.1. *Binary systems*

4.1.1. *Au–In system*

The enthalpies of formation of Au–In alloys have been determined at 973 K over the composition range $0 < x_{Au} < 0.55$. Results were referred to undercooled liquid gold and liquid indium with a heat of fusion for gold of 12.27 kJ mol^{-1} at 973 K [37]. All experimental results are recorded in Table 1. The measured enthalpies are adequately represented by the expression:

$$\Delta_{mix} H^{\circ}{}_m \, (\mathrm{J\ mol^{-1}}) = x_{Au}(1 - x_{Au})(-42901.38 - 49483.16 x_{Au})$$

The molar enthalpies are exothermic over the entire investigated composition range with a minimum located at $x_{Au} = 0.60$ and $\Delta_{mix} H^{\circ}{}_m = -17,422\ \mathrm{J\ mol^{-1}}$.

Table 1
Experimental values of the integral enthalpy of mixing of the Au–In system at 973 K referred to undercooled liquid gold and liquid indium.

x_{Au}	$\Delta_{mix}H^\circ{}_m$ (J mol^{-1})	x_{Au}	$\Delta_{mix}H^\circ{}_m$ (J mol^{-1})
0.0384	−1663	0.3506	−13,783
0.0549	−2407	0.3689	−14,278
0.0822	−3502	0.3880	−14,835
0.1128	−4865	0.4104	−15,358
0.1275	−5448	0.4283	−15,798
0.1683	−7158	0.4534	−16,200
0.1717	−7230	0.4595	−16,367
0.2185	−9082	0.4908	−16,759
0.2240	−9355	0.4947	−16,871
0.2658	−10,906	0.5276	−17,187
0.2751	−11,233	0.5291	−17,108
0.3083	−12,412	0.5631	−17,279
0.3245	−12,951		

Fig. 1 represents the comparison between our results and the previous calorimetric data of Béjà [3] at 1028 K and those of Castanet et al. [6] at 1000 K. All data of both authors were corrected with respect to the undercooled liquid state of gold.

Our results agree well with those of Béjà [3] at 1028 K, but are less negative than the values of Castanet et al. [6] at 1000 K.

4.1.2. In–Sb system

At the same temperature ($T = 973$ K), calorimetric measurements have been performed in the composition range $0 < x_{Sb} < 0.73$. The results are listed in Table 2 and may be represented as follows:

$$\Delta_{mix}H^\circ{}_m\,(\text{J mol}^{-1}) = x_{Sb}(1 - x_{Sb})(-12326.50 - 7276.20x_{Sb} + 14073.37x_{Sb}^2)$$

The $\Delta_{mix}H^\circ{}_m = f(x_{Sb})$ curve is asymmetrical with a minimum at $x_{Sb} = 0.448$ and $\Delta_{mix}H^\circ{}_m = -3155.9\,\text{J mol}^{-1}$.

Fig. 2 compares our results with those of the literature in the temperature range: 953–986 K.

As can be seen, our results lie between the two sets of measurements of Rosa et al. [24] at 986 K and 957 K but show a difference of about 200 J/mol with data of Wittig et al. [18] obtained at the same temperature and the data reported by Oehme and Predel [23] at 953 K. As the enthalpy of mixing seems to be temperature dependent, our values are consistent with data from Rosa et al. [24].

The heat capacity data of liquid alloys are devoted to throw some light on the temperature dependence of the enthalpies of mixing.

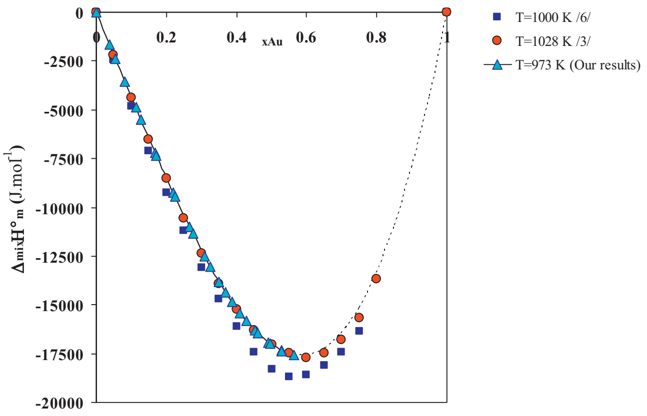

Fig. 1. Integral enthalpies of mixing of Au–In alloys. Comparison between our results and those of Béjà [3] and Castanet et al. [6] at the similar temperatures.

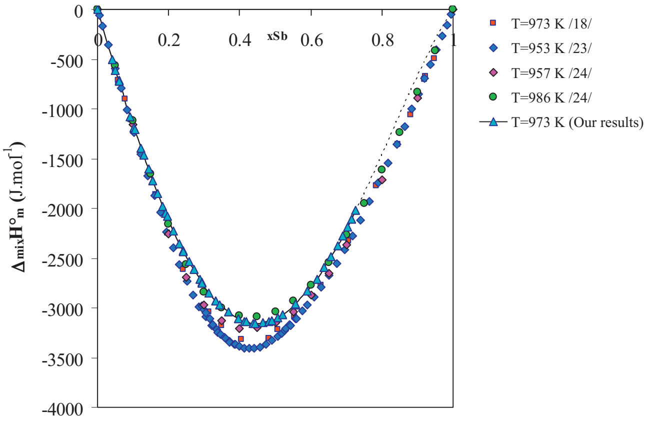

Fig. 2. Integral enthalpies of mixing of In–Sb alloys. Comparison between our results and literature at the similar temperatures.

4.2. Au–In–Sb system

For ternary liquid alloys, the enthalpies have been measured at 973 K either by addition of solid antimony or solid gold to the limiting liquid binary alloys, respectively:

$$\frac{x_{Au}}{x_{In}} = \frac{1}{3}, \frac{1}{1} \quad \text{with}\ 0 < x_{Sb} < 0.640$$

$$\frac{x_{In}}{x_{Sb}} = \frac{1}{1} \text{ and } \frac{3}{1} \quad \text{with}\ 0 < x_{Au} < 0.580$$

For each pseudo-binary section, two to four experiments were conducted. The compositions of the liquid ternary alloys investigated in the present work are shown in Fig. 3. All experimental data are collected in Table 3.

The experimental values of the integral molar enthalpy at the intersections points (A–D) (see Fig. 3) are listed in Table 4. As can be seen, the values are compatible and reinforce the reproducibility of our measurements. The maximum deviation is about 4% which is less than the experimental precision.

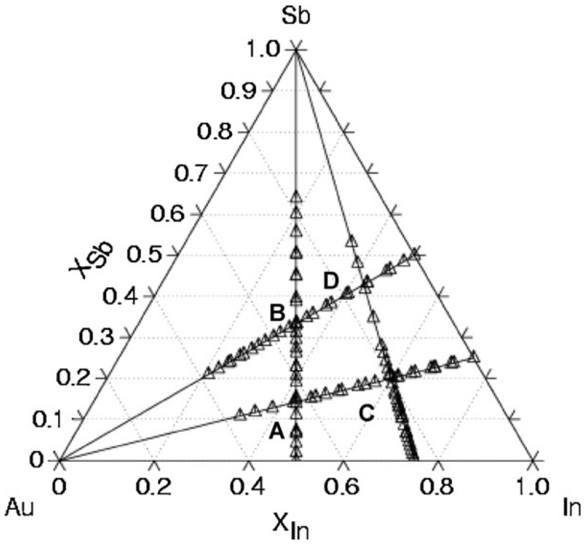

Fig. 3. Compositions of ternary Au–In–Sb alloys investigated in the present work (A–D: intersection points).

Table 2
Experimental values of the integral enthalpy of mixing of the In–Sb system at 973 K referred to liquid state.

x_{Sb}	$\Delta_{mix}H^{\circ}_{m}$ (J mol^{-1})	x_{Sb}	$\Delta_{mix}H^{\circ}_{m}$ (J mol^{-1})	x_{Sb}	$\Delta_{mix}H^{\circ}_{m}$ (J mol^{-1})	x_{Sb}	$\Delta_{mix}H^{\circ}_{m}$ (J mol^{-1})
0	0	0.1842	−1978	0.3321	−2929	0.5220	−2979
0.0419	−408	0.1924	−2072	0.3333	−3008	0.5565	−2922
0.0508	−605	0.1953	−2081	0.3446	−3007	0.5580	−2877
0.0600	−671	0.2142	−2285	0.3671	−3094	0.5912	−2827
0.0605	−703	0.2308	−2373	0.3961	−3126	0.6165	−2713
0.0919	−960	0.2406	−2446	0.4138	−3074	0.6383	−2591
0.1028	−1197	0.2417	−2450	0.4180	−3157	0.6572	−2498
0.1043	−1084	0.2570	−2566	0.4388	−3158	0.6746	−2412
0.1224	−1366	0.2701	−2674	0.4419	−3125	0.6895	−2295
0.1296	−1457	0.2868	−2730	0.4657	−3139	0.7027	−2231
0.1431	−1527	0.2926	−2812	0.4832	−3066	0.7149	−2151
0.1550	−1729	0.2939	−2814	0.4894	−3021	0.7271	−2082
0.1692	−1804	0.3141	−2936	0.5083	−3056	1	0

Table 3
Experimental values of the integral enthalpy of mixing of the Au–In–Sb ternary system at 973 K.

$x_{Au}/x_{In} = 1/1$		$x_{Au}/x_{In} = 1/3$		$x_{In}/x_{Sb} = 1/1$		$x_{In}/x_{Sb} = 3/1$	
x_{Sb}	$\Delta_{mix}H^{\circ}_{m}$ (J mol^{-1})	x_{Sb}	$\Delta_{mix}H^{\circ}_{m}$ (J mol^{-1})	x_{Au}	$\Delta_{mix}H^{\circ}_{m}$ (J mol^{-1})	x_{Au}	$\Delta_{mix}H^{\circ}_{m}$ (J mol^{-1})
0.0000	−16,909	0.0000	−10,367	0	−3112	0	−2487
0.0195	−16,311	0.0073	−10,281	0.03036	−3726	0.0480	−4082
0.0439	−15,596	0.0161	−10,193	0.06864	−4537	0.0505	−4172
0.0669	−14,817	0.0257	−10,087	0.07932	−4703	0.0933	−5518
0.0690	−14,733	0.0360	−9976	0.13287	−5759	0.0953	−5568
0.0732	−14,804	0.0466	−9864	0.13319	−5848	0.0972	−5691
0.1125	−13,765	0.0575	−9749	0.18627	−6749	0.1413	−6949
0.1394	−12,909	0.0665	−9730	0.19219	−6922	0.1417	−7024
0.1490	−12,605	0.0684	−9642	0.23511	−7533	0.1813	−8124
0.1540	−12,752	0.0866	−9459	0.24822	−7887	0.1841	−8157
0.1923	−11,803	0.1029	−9315	0.28606	−8304	0.1843	−8273
0.2078	−11,299	0.1053	−9270	0.30374	−8656	0.2261	−9405
0.2285	−10,714	0.1115	−9229	0.33143	−8887	0.2615	−10,045
0.2291	−10,994	0.1201	−9149	0.35238	−9219	0.2653	−10,388
0.2629	−10,287	0.1312	−9046	0.37745	−9435	0.3035	−11,265
0.2748	−9819	0.1321	−9033	0.39721	−9646	0.3261	−11,418
0.2953	−9717	0.1389	−8970	0.42002	−9808	0.3415	−12,032
0.3117	−9048	0.1484	−8896	0.43950	−9939	0.3764	−12,654
0.3295	−8965	0.1614	−8767	0.45810	−10,038	0.3817	−12,308
0.3353	−8602	0.1678	−8726	0.48146	−10,142	0.4353	−12,986
0.3877	−7685	0.1870	−8553	0.49150	−10,176	0.4857	−13,448
0.3957	−7430	0.2059	−8363	0.51826	−10,203	0.5276	−13,597
0.4499	−6622	0.2105	−8265	0.52416	−10,246	0.5639	−13,670
0.4507	−6444	0.2241	−8195	0.55165	−10,190		
0.5020	−5564	0.2417	−8017	0.58009	−10,171		
0.5045	−5677	0.2603	−7830				
0.5563	−4936	0.2793	−7584				
0.6008	−4334	0.3477	−6822				
0.6392	−3831	0.4177	−6032				
		0.4805	−5274				
		0.5316	−4760				

In order to have an analytical representation of the enthalpy of mixing of the ternary liquid Au–In–Sb, the Redlich–Kister–Muggianu formalism extensively described in the literature [38–40] was used in the present work.

5. Thermodynamic modeling at 973 K

The excess Gibbs energy of ternary liquid Au–In–Sb, taking both binary and ternary interactions into account, can be described as random mixtures of components Au, In and Sb by

Table 4
Values of the integral enthalpy of mixing at the intersection points (A–D).

Intersection point	Concentrations			$\Delta_{mix}H^{\circ}_{m}$ (J mol^{-1})			
	x_{Au}	x_{In}	x_{Sb}	$x_{Au}/x_{In} = 1/1$	$x_{Au}/x_{In} = 1/3$	$x_{In}/x_{Sb} = 1/1$	$x_{In}/x_{Sb} = 3/1$
A	0.429	0.429	0.142	−13,033			−12,994
B	0.333	0.333	0.334	−8697		−9054	
C	0.200	0.600	0.200		−8400		−8283
D	0.142	0.429	0.429		−6001	−5982	

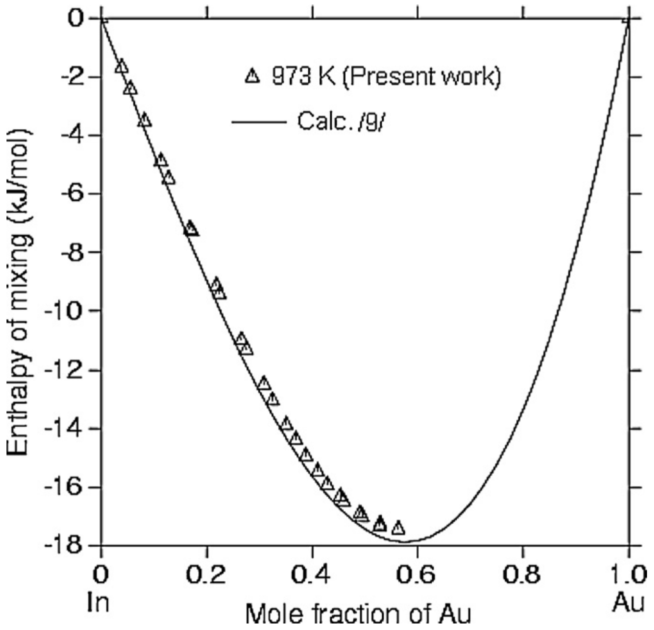

Fig. 4. Calculated enthalpies of mixing of the liquid Au–In alloys at 973 K in comparison with our experimental values. Standard states: undercooled liquid Au and liquid In.

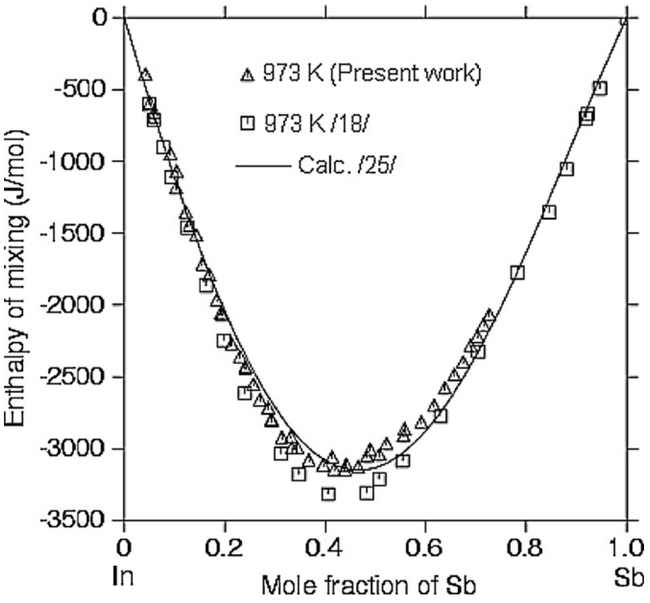

Fig. 5. Calculated enthalpy of mixing of liquid In–Sb alloys at 973 K in comparison with our results and Wittig's data. Standard states: liquid In and liquid Sb.

Redlich–Kister–Muggianu polynomial as:

$$G^{xs} = x_{\mathrm{Au}}x_{\mathrm{In}}\sum_{\nu=0}^{n} {}^{\nu}L_{\mathrm{Au,In}}(x_{\mathrm{Au}}-x_{\mathrm{In}})^{\nu} + x_{\mathrm{Au}}x_{\mathrm{Sb}}\sum_{\nu=0}^{n} {}^{\nu}L_{\mathrm{Au,Sb}}(x_{\mathrm{Au}}-x_{\mathrm{Sb}})^{\nu} + x_{\mathrm{In}}x_{\mathrm{Sb}}\sum_{\nu=0}^{n} {}^{\nu}L_{\mathrm{In,Sb}}(x_{\mathrm{In}}-x_{\mathrm{Sb}})^{\nu} + x_{\mathrm{Au}}x_{\mathrm{In}}x_{\mathrm{Sb}}(x_{\mathrm{Au}}{}^{0}L_{\mathrm{Au,In,Sb}} + x_{\mathrm{In}}{}^{1}L_{\mathrm{Au,In,Sb}} + x_{\mathrm{Sb}}{}^{2}L_{\mathrm{Au,In,Sb}}) \qquad (1)$$

where x_i is the molar fraction of element i (i = Au, In, Sb). ${}^{\nu}L^{\varphi}_{i,j}$ and ${}^{\nu}L^{\varphi}_{i,j,k}$ are the binary and ternary interaction parameters which can be temperature dependent as follows:

$${}^{\nu}L = {}^{\nu}A + {}^{\nu}BT + {}^{\nu}CTLnT \qquad (2)$$

These parameters are derived from an optimization procedure, using the module Parrot developed by Jansson [41] included in the Thermo-Calc software [42].

Only the enthalpic part to the ternary interactive parameters (${}^{\nu}W = {}^{\nu}A - {}^{\nu}CT$) was evaluated based on our present calorimetric measurements. A temperature dependence of the integral enthalpy of mixing of ternary liquid is possible considering the binary data. However, since we worked only at 973 K, the ternary interaction parameters ${}^{\nu}W$, were assumed independent of temperature i.e. ${}^{\nu}C = 0$. The binary interaction parameters of the liquid phase for the three limiting binary systems: ${}^{\nu}L^{liq}_{\mathrm{Au,In}}$, ${}^{\nu}L^{liq}_{\mathrm{Au,Sb}}$ and ${}^{\nu}L^{liq}_{\mathrm{In,Sb}}$, assessed by [9], [16] and [25] respectively, were accepted in this work.

All optimized thermodynamic parameters are given in Table 5.

Fig. 4 represents the comparison between our experimental enthalpy of mixing of Au–In liquid alloys at 973 K and the calculated curves deduced from [9]. As can be seen, the calculation is in agreement with experimental data.

The calculated enthalpies of mixing of In–Sb liquid alloys at 973 K are compared with our experimental results and those of Wittig and Gehring [18] in Fig. 5. Our data are in very good agreement with the assessment. The values of Wittig and Gehring [18] diverge slightly around $x_{\mathrm{Sb}} = 0.4$.

The calculated enthalpies of mixing along four sections $x_{\mathrm{Au}}/x_{\mathrm{In}} = 1/1$; 1/3 and $x_{\mathrm{In}}/x_{\mathrm{Sb}} = 1/1$; 3/1 at 973 K are compared with the experimental results in Figs. 6–9. A very good agreement is observed with all studied sections.

The interaction parameters listed in Table 5 were used to calculate the enthalpy of mixing of liquid at 973 K for any point of Au–In–Sb ternary system. The iso-enthalpy lines have been drawn over the whole concentration range in Fig. 10.

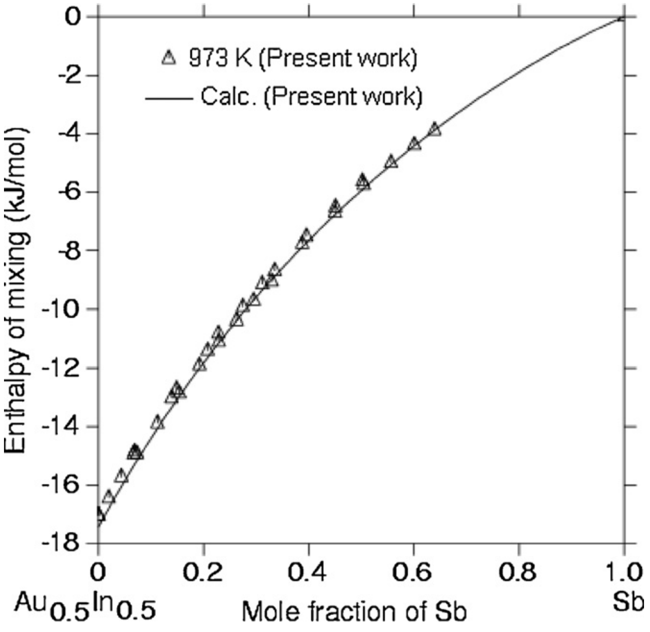

Fig. 6. Experimental and calculated enthalpy of mixing of liquid Au–In–Sb alloys at 973 K along the section $x_{\mathrm{Au}}/x_{\mathrm{In}} = 1/1$. Standard states: undercooled liquid Au, liquid In and liquid Sb.

Table 5
Values of parameters describing the excess Gibbs energy of liquid phase (in J mol^{-1}).

System	Parameters	Ref.
Au–In	${}^{0}L^{liq}_{\text{Au,In}} = -76196.19 + 64.2914T - 6.6375T\ln(T)$ ${}^{1}L^{liq}_{\text{Au,In}} = -31134.02 + 81.3582T - 8.5134T\ln(T)$	[9]
Au–Sb	${}^{0}L^{liq}_{\text{Au,Sb}} = -15067.47 + 23.15424T - 4.988235T\ln(T)$ ${}^{1}L^{liq}_{\text{Au,Sb}} = -2427.37 - 8.3278T$	[16]
In–Sb	${}^{0}L^{liq}_{\text{In,Sb}} = -25631.2 + 102.9324T - 13.45816T\ln(T)$ ${}^{1}L^{liq}_{\text{In,Sb}} = -2115.4 - 1.31907T$; ${}^{2}L^{liq}_{\text{In,Sb}} = 2908.9$	[25]
Au–In–Sb	${}^{0}W^{liq}_{\text{Au,In,Sb}} = 69432.383$; ${}^{1}W^{liq}_{\text{Au,In,Sb}} = 19165.152$; ${}^{2}W^{liq}_{\text{Au,In,Sb}} = 27989.790$	Present work

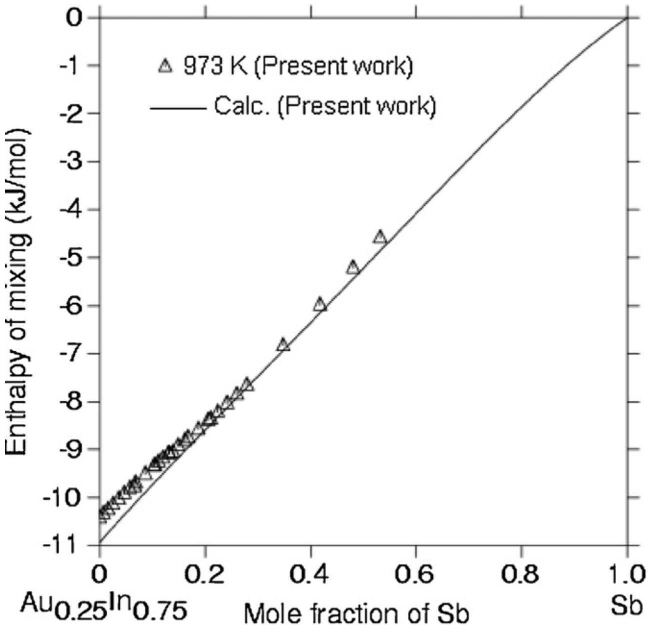

Fig. 7. Experimental and calculated enthalpy of mixing of liquid Au–In–Sb alloys at 973 K along the section $x_{\text{Au}}/x_{\text{In}} = 1/3$. Standard states: undercooled liquid Au, liquid In and liquid Sb.

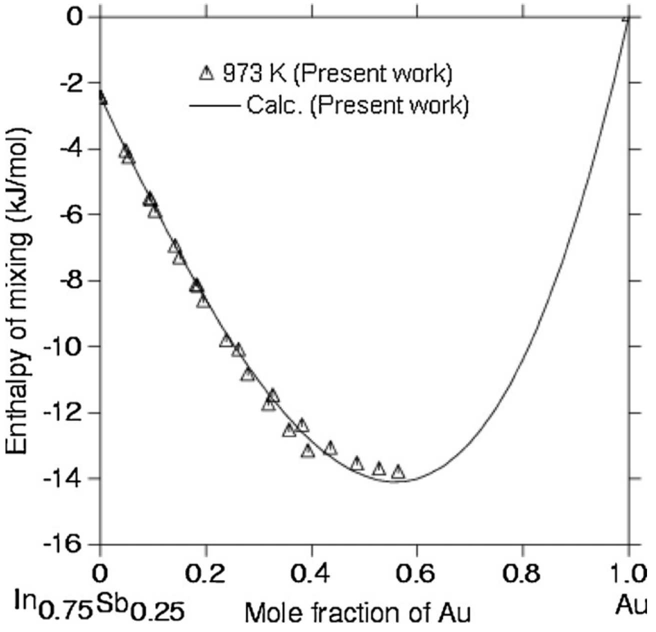

Fig. 9. Experimental and calculated enthalpy of mixing of liquid Au–In–Sb alloys at 973 K along the section $x_{\text{In}}/x_{\text{Sb}} = 3/1$. Standard states: undercooled liquid Au, liquid In and liquid Sb.

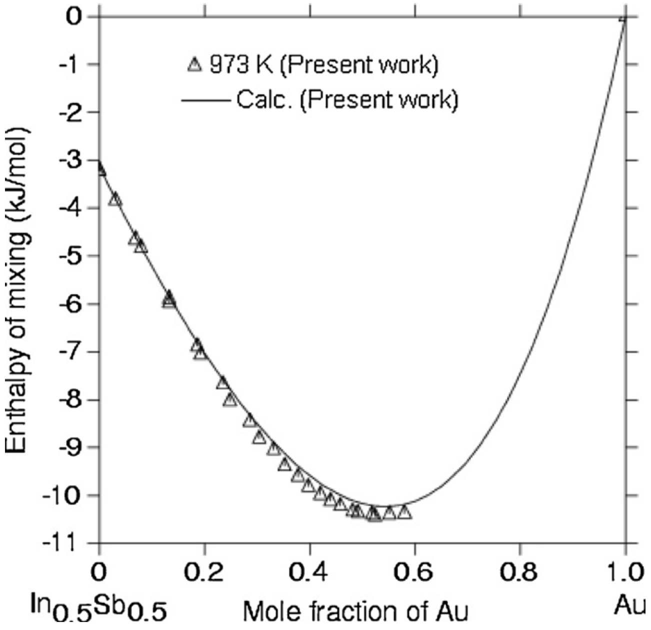

Fig. 8. Experimental and calculated enthalpy of mixing of liquid Au–In–Sb alloys at 973 K along the section $x_{\text{In}}/x_{\text{Sb}} = 1/1$. Standard states: undercooled liquid Au, liquid In and liquid Sb.

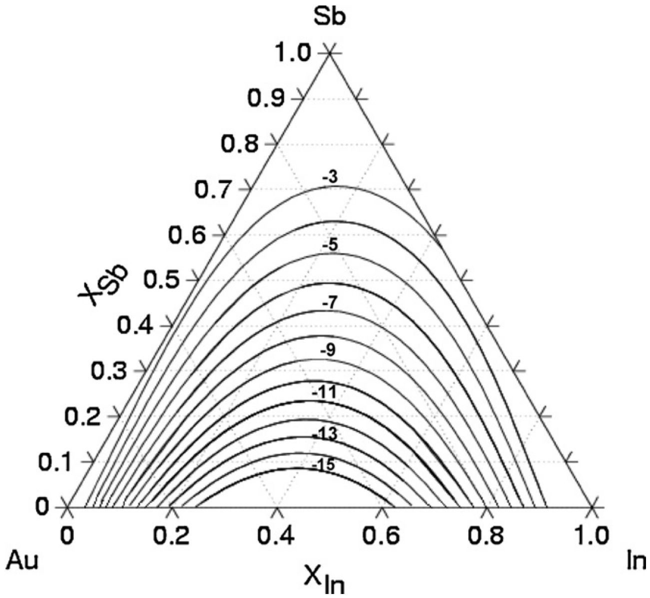

Fig. 10. Calculated isoenthalpy curves of liquid Au–In–Sb alloys at 973 K (values in kJ mol^{-1}). Standard states: undercooled liquid Au, liquid In and liquid Sb.

6. Conclusion

By using a high temperature Calvet microcalorimeter, molar enthalpies of mixing of the liquid Au–In, In–Sb and Au–In–Sb alloys have been determined at 973 K. The data of the ternary liquid were analytically described by the Redlich–Kister–Muggianu formalism. The calculated results are in good agreement with experimental data. Additional ternary interaction parameters were necessary to adequately describe the enthalpies of the ternary liquid Au–In–Sb. These parameters will be used as start values in the further optimization of the ternary Au–In–Sb system combining our present calorimetric values and all experimental data available in the literature.

The new experimental study of the phase equilibria occurring in this ternary system is already undertaken to complete this thermodynamic description.

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