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Enthalpies of mixing of liquid systems for lead-free soldering: Cu–Sb–Sn system

Dominika Jendrzejczyk-Handzlik[a,*], Meryem Rechchach[b,c], Wojciech Gierlotka[a,d], Herbert Ipser[c], Hans Flandorfer[c]

[a] *Faculty of Non-Ferrrous Metals, University of Science and Technology in Krakow, Mickiewicza Ave 30, 30-059 Krakow, Poland*
[b] *Faculté des Sciences, Université Mohammed V, Laboratoire de Chimie Physique Générale, Av. Ibn Batouta, B.P. 1014, Rabat, Morocco*
[c] *University of Vienna, Department of Inorganic Chemistry/Materials Chemistry, Waehringer Str. 42, A-1090 Wien, Austria*
[d] *Yuan Ze University, Chemical Engineering and Material Science Department, 35 Yuan-Tung Road, Chung-Li, Taiwan, ROC*

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ABSTRACT

Using two different types of high temperature drop calorimeters, partial and integral enthalpies of mixing of liquid alloys were determined in the ternary Cu–Sb–Sn system. The system was investigated along four sections at 1100 K. Experimental data were used to find ternary interaction parameters by applying the Redlich–Kister–Muggianu model for substitutional solutions, and a full set of parameters describing the concentration dependence of the enthalpy of mixing was derived. From these, the isoenthalpy curves were constructed for 1100 K. The entire system shows exothermic enthalpy of mixing at the given temperature.

1. Introduction

Since high-temperature solders with lead had to be replaced by new materials which are safe for the environment the search for lead-free solders has started in Europe several years ago. The present work is a contribution to the European COST Action MP 0602 “Advanced Solder Materials for High-Temperature Application” which was initiated in 2007. Among the potential new materials are also systems based on Sb–Sn alloys, one of them being the ternary Cu–Sb–Sn system. To obtain the necessary knowledge on phase diagram and melting behavior of Cu–Sb–Sn alloys, new experimental data are needed. The present work refers to high-temperature calorimetric measurements on liquid Cu–Sb–Sn alloys performed along the following cross-sections: $x_{Cu}/x_{Sb} = 1{:}1$, $x_{Sb}/x_{Sn} = 1{:}3$, $x_{Cu}/x_{Sn} = 1{:}2$ and $x_{Cu}/x_{Sn} = 2{:}1$ at 1100 K.

In the literature one can find a number of results of calorimetric measurements in the binary systems Cu–Sn, Cu–Sb and Sb–Sn at various temperatures. They are summarized as follows:

1.1. Cu–Sb system

Calorimetric measurements carried out on liquid Cu–Sb alloys indicate a noticeable temperature dependence of the heat of mixing. Hayer et al. [1] measured $\Delta_{mix}H_m$ at eleven different temperatures, i.e. 843, 863, 911, 929, 952, 1003, 1108, 1128, 1247, 1347, and 1375 K, and the results clearly showed temperature dependence. Lee at al. [2] measured $\Delta_{mix}H_m$ at 1000 K, and Kleppa [3] at 723 K. Experimental data determined by Lee et al. [2] and Hayer et al. [1] are in good agreement. In contrast, there are also data by Kawakami [4] which show the heat of mixing as temperature independent. Gierlotka and Jendrzejczyk-Handzlik [5] described the liquid phase in Cu–Sb system by a substitutional solution model suggesting that the heat of mixing depends on temperature. Calculated values of the enthalpy of mixing at 1003 and 1375 K are in good agreement with the data taken from experiments, and differences are smaller than the uncertainty of the calorimetric measurements.

1.2. Sb–Sn system

Experimental data for the heat of mixing do not show any temperature dependence in this system. $\Delta_{mix}H_m$ was measured by Kawakami [4], Wittig and Gehring [6], Yazawa et al. [7], Sommer et al. [8] and Azzaoui et al. [9] in the temperature range from 783 to 1108 K. Kleppa [10] studied the dissolution of solid antimony in liquid tin at 723 K. Chen et al. [11] described the liquid phase in the Sb–Sn system using a regular solution model and assuming temperature independent heat of mixing. Experimental data by Azzaoui et al. [9], Wittig and Gehring [6] and Sommer et al. [8] are in good agreement with one other and also with calculated values of the enthalpy of mixing [11].

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* Corresponding author. Tel.: +48 12 617 41 25.
E-mail address: djendrze@agh.edu.pl (D. Jendrzejczyk-Handzlik).

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1.3. Cu–Sn system

The heat of mixing in the liquid binary Cu–Sn system was determined by several authors. Kleppa [3] measured enthalpies of mixing of liquid alloys as well as enthalpies of formation of solid alloys – both at 723 K. Hultgren et al. reported enthalpies of mixing at 1400 K [12], whereas Takeuchi et al. [13], Itagaki and Yazawa [14], Iguchi et al. [15], Pool et al. [16], and Lee et al. [2] measured $\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ at 1363, 1373, 1393, 1440, and 997 K, respectively. Moreover, Flandorfer et al. [17] measured the enthalpy of mixing of liquid Cu–Sn alloys at 773, 973, 1173, 1373 and 1523 K. The results were described by the Redlich–Kister model and also using an association model. Gierlotka et al. [18] used a substitutional solution model to describe the liquid phase. By comparing the data of Itagaki and Yazawa [14] at 1373 K and Lee et al. [2] at 997 K, they suggested a temperature dependence of the enthalpy of mixing for liquid Cu–Sn alloys.

As far as the ternary Cu–Sb–Sn system is concerned, there is only one study by Lee et al. [2] who determined the enthalpy of mixing in this system at 1000 K for the following sections: $x_{\mathrm{Cu}}/x_{\mathrm{Sb}} = 3{:}7$, $x_{\mathrm{Sb}}/x_{\mathrm{Sn}} = 7{:}3$, $x_{\mathrm{Sb}}/x_{\mathrm{Sn}} = 4{:}6$, $x_{\mathrm{Cu}}/x_{\mathrm{Sn}} = 6{:}4$, and $x_{\mathrm{Cu}}/x_{\mathrm{Sn}} = 3{:}7$. Additional calorimetric measurements will help in a precise description of the thermodynamic properties of liquid Cu–Sb–Sn solutions and to answer the question of possible temperature dependence in the ternary liquid system.

2. Experimental procedure

Two different calorimeters were used for the experiments: (1) A Calvet-type twin micro-calorimeter HT 1000 (Setaram, Lyon, France) with two thermopiles consisting of more than 200 thermocouples each, a wire wound resistance furnace and an automatic drop device for up to 30 drops. Control of the entire equipment and data evaluation is performed with LabView and HiQ as described by Flandorfer et al. [19]. (2) A MHTC high-temperature Calvet-type calorimeter (Setaram, Lyon, France) with a thermopile of 20 thermocouples, a graphite tube resistance furnace and a manual drop device for up to 23 drops. Control and data evaluation is performed using the software provided by the producer.

Heats of mixing along the two cross-sections $x_{\mathrm{Cu}}/x_{\mathrm{Sb}} = 1{:}1$ and $x_{\mathrm{Sb}}/x_{\mathrm{Sn}} = 1{:}3$ were measured with both calorimeters, measurements along the two cross-sections $x_{\mathrm{Cu}}/x_{\mathrm{Sn}} = 2{:}1$ and $x_{\mathrm{Cu}}/x_{\mathrm{Sn}} = 1{:}2$ were carried out using the HT1000 high-temperature calorimeter only (see Fig. 1). In both calorimeters the measurements were performed under Ar-flow (approximately 30 ml/min). At the end of each series the calorimeters were calibrated by five additions (approximately 40 mg each) of NIST standard α-Al_2O_3 (National Institute of Standards and Technology, Gaithersburg, MD).

Starting materials for all experiments were Cu wire (99.98+%; Alfa Aesar), Sb shots (99.999%; Koch-Light Lab.), and Sn rod (99.9985%; Alfa Aesar). The Cu wire was treated under flowing H_2 at 250 °C for 2 h to remove oxide layers; Sb was purified by filtering the liquid metal under vacuum through quartz wool to remove oxides; Sn was used without further purification.

Samples of pure metals (Cu, Sn, or Sb) were introduced into a bath of binary alloys (Sb–Sn, Cu–Sb, or Cu–Sn) of chosen starting compositions (see Fig. 1). All measurements were carried out in a graphite crucible ($\varnothing_{\mathrm{i}} = 9$ mm, h = 90 mm) which was heated at 973 K for 10 min before using it to remove surface impurities.

The enthalpy of mixing was determined for the following compositions:

- along the cross-section $x_{\mathrm{Cu}}/x_{\mathrm{Sb}} = 1{:}1$ the mole fraction of Sn was varied from 0.0192 to 0.5187 by dropping pieces of pure Sn (19–50 mg) into a molten binary Cu–Sb alloy;
- along the cross-section $x_{\mathrm{Sb}}/x_{\mathrm{Sn}} = 1{:}3$ the mole fraction of Cu was varied from 0.032 to 0.668 by dropping pieces of pure Sn (20–50 mg) into a molten binary Sb–Sn alloy;
- along the cross-section $x_{\mathrm{Cu}}/x_{\mathrm{Sn}} = 1{:}2$ the mole fraction of Sb was varied from 0.0204 to 0.5907 by dropping pieces of pure Sb (18–38 mg) into a molten binary Cu–Sn alloy;
- along the cross-section $x_{\mathrm{Cu}}/x_{\mathrm{Sn}} = 2{:}1$ the mole fraction of Sb was varied from 0.0430 to 0.6011 by dropping pieces of pure Sb (20–37 mg) into a molten binary Cu–Sn alloy.

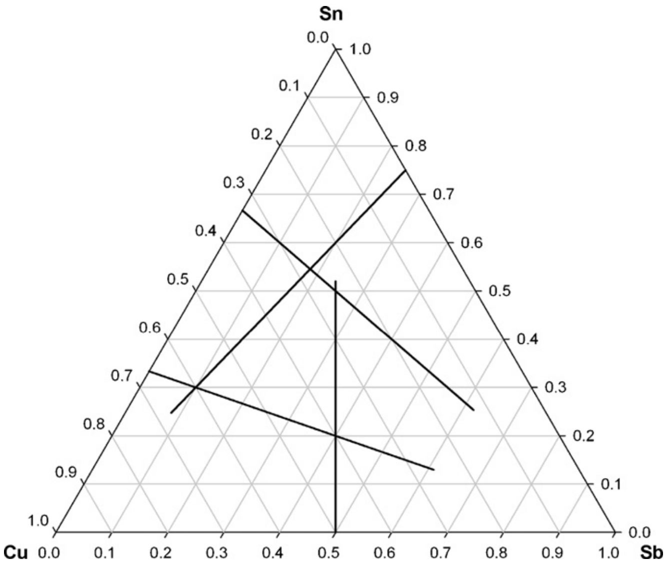

Fig. 1. Chosen sections in the ternary Cu–Sb–Sn system, measurements performed at 1100 K.

The furnace temperature was set at 1100 K. The time interval between individual drops was usually 40 min. The obtained signals were recorded and integrated. The measured enthalpy (integrated heat flow at constant pressure) is:

$$\Delta H_{\mathrm{Signal}} = n_i(H_{\mathrm{m},i,T_{\mathrm{M}}} - H_{\mathrm{m},i,T_{\mathrm{D}}}) + \Delta H_{\mathrm{Reaction}} \tag{1}$$

where n_i is the number of moles of the added sample, H_{m} denotes molar enthalpies, T_{D} is the drop temperature, and T_{M} is the calorimeter temperature of the respective measurement in Kelvin. The molar enthalpy difference $(H_{\mathrm{m},i,T_{\mathrm{M}}} - H_{\mathrm{m},i,T_{\mathrm{D}}})$ was calculated using the so-called Dinsdale polynomials [20]. Because of the rather small masses added, the partial enthalpies can be directly given as

$$\Delta_{\mathrm{mix}}\bar{H}_i = \frac{\Delta H_{\mathrm{Reaction}}}{n_i} \tag{2}$$

Random errors as well as systematic errors of calorimetry depend on the construction of the calorimeter, calibration procedure, signal integration and “chemical errors”, e.g. incomplete reactions or impurities. Considering many calibration measurements done by dropping NIST standard sapphire, the standard deviation can be estimated to be less than ±1% for the HT-1000 and less than ±1.5% for the MHTC instrument. The systematic errors are mainly caused by parasitic heat flows, base line problems at signal integration and dropping and mixing problems. One can estimate that the overall error connected with a specific calorimeter is ±150 J/mol for measurements with the Calvet-type calorimeter and ± 300 J/mol for the MHTC calorimeter.

Table 1
Partial and integral enthalpies of mixing of liquid Cu–Sb–Sn alloys, 1100 K, cross-section Cu:Sb = 1:1; standard states: liquid pure components; Series A – HT1000 calorimeter, Series B – MHTC calorimeter.

Mole dropped	Drop enthalpy	Partial enthalpy		Integral enthalpy		
n_{Sn} (mmol)	ΔH_{Signal} (J)	x_{Sn}	$\Delta_{mix}\bar{H}_i$ (J/mol)	x_{Cu}	x_{Sb}	$\Delta_{mix}H_m$ (J/mol)
Series A: starting amount: n_{Cu} = 3.701 mmol; n_{Sb} = 3.709 mmol; σ (drop enthalpy) = ±150 (J/mol)						
0	–	0	–	0.4995	0.5005	−2974
0.1871	32,039	0.0246	2130	0.4872	0.4882	−2849
0.1968	29,790	0.0493	−118	0.4749	0.4759	−2780
0.2010	29,729	0.0732	−179	0.4629	0.4639	−2714
0.2141	28,504	0.0973	−1404	0.4508	0.4518	−2680
0.2279	30,306	0.1217	397	0.4387	0.4396	−2597
0.2525	30,027	0.1472	118	0.4259	0.4268	−2518
0.2694	30,074	0.1729	165	0.4131	0.4140	−2437
0.2764	30,579	0.1976	670	0.4007	0.4016	−2344
0.2849	31,265	0.2217	1356	0.3887	0.3896	−2234
0.3014	30,902	0.2455	993	0.3768	0.3776	−2135
0.3166	31,196	0.2691	1287	0.3651	0.3659	−2028
0.3204	29,891	0.3119	−18	0.3437	0.3444	−1910
0.3297	31,605	0.3323	1696	0.3335	0.3342	−1803
0.3361	30,854	0.3519	945	0.3237	0.3244	−1722
0.3469	31,084	0.3710	1175	0.3141	0.3148	−1637
0.3603	30,840	0.3897	931	0.3048	0.3055	−1561
0.3669	31,759	0.4076	1850	0.2959	0.2965	−1461
0.3722	30,119	0.4247	210	0.2873	0.2880	−1412
0.3795	32,025	0.4412	2116	0.2791	0.2797	−1311
0.3993	30,730	0.4575	821	0.2709	0.2715	−1249
0.4182	30,773	0.4736	864	0.2629	0.2635	−1186
0.4316	31,174	0.4893	1265	0.2551	0.2556	−1113
0.4357	30,954	0.5042	1045	0.2476	0.2482	−1050
0.4505	30,625	0.5187	716	0.2404	0.2409	−999
Series B: starting amount: n_{Cu} = 5.600 mmol; n_{Sb} = 5.584 mmol; σ (drop enthalpy) = ±300 (J/mol)						
0	–	0	–	0.5007	0.4993	−2993
0.2189	31,546	0.0192	1636	0.4911	0.4897	−2904
0.2612	33,308	0.0412	3399	0.4801	0.4787	−2763
0.3809	28,885	0.0715	−1023	0.4649	0.4636	−2708
0.3868	30,130	0.1004	221	0.4505	0.4492	−2617
0.3795	27,685	0.1270	−2223	0.4371	0.4359	−2605
0.4898	31,777	0.1592	1868	0.4210	0.4198	−2441
0.4045	28,730	0.1840	−1178	0.4086	0.4074	−2403
0.4779	32,268	0.2115	2359	0.3948	0.3937	−2243
0.4712	27,800	0.2368	−2108	0.3821	0.3810	−2239
0.4257	27,653	0.2584	−2255	0.3714	0.3703	−2239
0.5166	32,171	0.2829	2262	0.3591	0.3580	−2090
0.4677	33,057	0.3038	3149	0.3486	0.3476	−1937
0.4740	32,937	0.3238	3028	0.3386	0.3376	−1795
0.4890	33,239	0.3432	3330	0.3289	0.3279	−1648
0.4052	30,409	0.3584	500	0.3212	0.3203	−1598
0.4733	31,002	0.3754	1093	0.3127	0.3119	−1527
0.4960	25,971	0.3922	3938	0.3043	0.3035	−1592
0.4960	30,805	0.4082	896	0.2963	0.2955	−1527
0.4090	31,442	0.4207	1533	0.2901	0.2892	−1462

3. Results and discussion

3.1. Experimental results

The drop enthalpy and the partial and integral molar enthalpy of mixing of alloys obtained in nine separate experiments at a constant temperature of 1100 K are given in Tables 1–4. They also provide information to the number of moles of pure metals dropped into the liquid alloys.

All experimental results are also shown in Figs. 2–5. The starting values of $\Delta_{mix}H_m$ for the binary systems, necessary for the evaluation of the measurements, were taken from literature according to Table 5. In Fig. 2 data for the section x_{Cu}/x_{Sb} = 1:1 are shown, together with the calculated values (see Section 3.2).

One can see that the results of the experimental series from both calorimeters are in good agreement with each other. The integral enthalpies of mixing along this section become almost linearly less negative with increasing mole fraction of Sn. Accordingly, the partial enthalpy values fluctuate around zero (see Table 1).

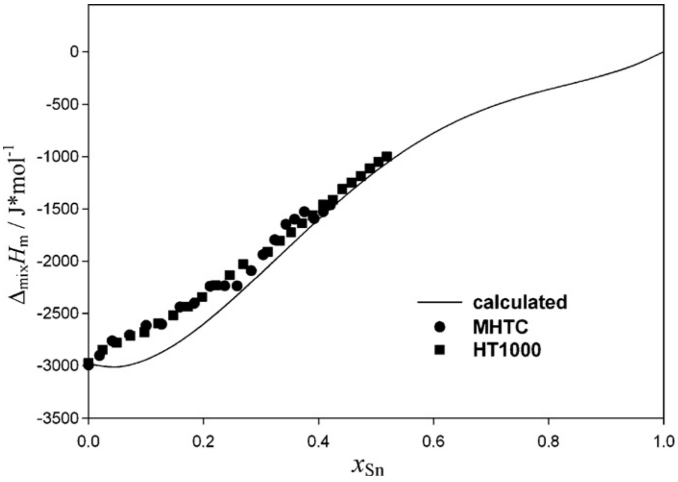

Fig. 2. Integral molar enthalpies of mixing of liquid Cu–Sb–Sn alloys at 1100 K for the section x_{Cu}/x_{Sb} = 1:1; standard states: pure liquid metals.

Table 2
Partial and integral enthalpies of mixing of liquid Cu–Sb–Sn alloys, 1100 K, cross-section Sb:Sn = 1:3, standard states: liquid pure components; Series A – HT1000 calorimeter, Series B and C – MHTC calorimeter.

Mole dropped	Drop enthalpy	Partial enthalpy		Integral enthalpy		
n_{Cu} (mmol)	ΔH_{Signal} (J)	x_{Cu}	$\Delta_{mix}\bar{H}_i$ (J/mol)	x_{Sn}	x_{Sb}	$\Delta_{mix}H_m$ (J/mol)
Series A: starting amount: n_{Sn} = 5.112 mmol; n_{Sb} = 1.704 mmol; σ (drop enthalpy) = ±150 (J/mol)						
0	–	0	–	0.7500	0.2500	−1036
0.3016	37,787	0.0424	3050	0.7182	0.2394	−863
0.3143	37,393	0.0829	2657	0.6878	0.2293	−714
0.3277	36,536	0.1216	1799	0.6588	0.2196	−608
0.3304	35,395	0.1575	658	0.6319	0.2107	−556
0.3562	34,678	0.1930	−58	0.6052	0.2018	−535
0.3789	34,021	0.2277	−715	0.5792	0.1931	−543
0.4132	33,378	0.2622	−1358	0.5533	0.1845	−579
0.4485	32,534	0.2964	−2202	0.5277	0.1759	−654
0.4651	31,578	0.3286	−3159	0.5035	0.1679	−769
0.4905	31,439	0.3595	−3297	0.4803	0.1601	−886
0.5149	30,478	0.3891	−4258	0.4582	0.1527	−1041
0.5282	29,923	0.4167	−4813	0.4375	0.1458	−1212
0.5486	29,416	0.4429	−5321	0.4178	0.1393	−1396
0.5695	28,947	0.4676	−5790	0.3993	0.1331	−1591
0.5875	28,469	0.4910	−6267	0.3817	0.1273	−1796
0.5993	27,891	0.5128	−6846	0.3654	0.1218	−2013
0.6212	27,668	0.5335	−7068	0.3499	0.1166	−2228
0.6450	26,912	0.5532	−7824	0.3351	0.1117	−2464
0.6632	27,119	0.5718	−7618	0.3211	0.1071	−2679
0.6975	26,828	0.5898	−7909	0.3076	0.1026	−2898
0.7211	26,360	0.6069	−8376	0.2948	0.0983	−3126
0.7549	26,092	0.6233	−8644	0.2825	0.0942	−3357
0.7754	26,075	0.6388	−8661	0.2709	0.0903	−3574
0.8211	25,659	0.6538	−9078	0.2596	0.0866	−3804
0.8483	26,124	0.6681	−8613	0.2489	0.0830	−4003
Series B: starting amount: n_{Sn} = 6.329 mmol; n_{Sb} = 2.102 mmol; σ (drop enthalpy) = ±300 (J/mol)						
0	–	0	–	0.7506	0.2494	−1034
0.2812	34,459	0.0320	−277	0.7264	0.2413	−1010
0.2958	35,967	0.0641	1231	0.7026	0.2334	−936
0.3142	36,785	0.0956	2049	0.6789	0.2255	−835
0.3362	35,737	0.1271	1001	0.6553	0.2177	−771
0.3525	36,543	0.1578	1806	0.6322	0.2100	−681
0.3835	32,982	0.1889	−1755	0.6089	0.2023	−720
0.4235	35,694	0.2206	957	0.5850	0.1944	−655
0.4442	37,761	0.2514	3024	0.5620	0.1867	−510
0.4798	30,968	0.2819	−3769	0.5390	0.1791	−643
0.5357	31,358	0.3133	−3378	0.5155	0.1712	−762
0.5518	29,417	0.3428	−5320	0.4933	0.1639	−958
0.5890	29,660	0.3717	−5077	0.4717	0.1567	−1139
0.6378	29,846	0.4002	−4891	0.4503	0.1496	−1309
0.6644	30,811	0.4272	−3926	0.4299	0.1428	−1427
0.7356	27,493	0.4545	−7244	0.4095	0.1360	−1704
0.7676	26,524	0.4803	−8212	0.3901	0.1296	−2012
0.7880	31,105	0.5044	−3632	0.3720	0.1236	−2087
0.8189	28,390	0.5271	−6347	0.3550	0.1179	−2283
0.8732	25,148	0.5493	−9589	0.3383	0.1124	−2626
Series C: starting amount: n_{Sn} = 6.734 mmol; n_{Sb} = 2.243 mmol; σ (drop enthalpy) = ±300 (J/mol)						
0	–	0	–	0.7502	0.2498	−1035
0.2968	34,232	0.0320	−505	0.7261	0.2419	−1018
0.3066	32,297	0.0630	−2439	0.7029	0.2341	−1064
0.3636	36,478	0.0973	1742	0.6772	0.2256	−961
0.3968	34,333	0.1319	−408	0.6512	0.2169	−940
0.4462	33,942	0.1678	−795	0.6243	0.2079	−934
0.4906	31,728	0.2040	−3008	0.5971	0.1989	−1024
0.5109	34,064	0.2385	−673	0.5712	0.1903	−1009
0.5581	29,501	0.2729	−5235	0.5454	0.1817	−1200
0.5910	30,791	0.3061	−3946	0.5205	0.1734	−1325
0.6393	28,291	0.3388	−6445	0.4960	0.1652	−1566
0.6561	30,558	0.3693	−4179	0.4731	0.1576	−1687
0.6862	29,867	0.3983	−4870	0.4514	0.1503	−1833
0.7321	30,236	0.4264	−4501	0.4303	0.1433	−1958
0.7539	26,888	0.4528	−7849	0.4105	0.1367	−2229
0.7913	26,614	0.4780	−8122	0.3916	0.1304	−2500
0.8319	27,711	0.5021	−7026	0.3735	0.1244	−2709
0.8461	26,614	0.5244	−8123	0.3568	0.1188	−2951
0.8702	25,338	0.5454	−9399	0.3411	0.1136	−3236
0.9161	25,663	0.5665	−9074	0.3259	0.1086	−3494

Table 3
Partial and integral enthalpies of mixing of liquid Cu–Sb–Sn alloys, 1100 K, cross-sections Cu:Sn = 1:2; standard states: liquid pure components; Series A and B – HT1000 calorimeter.

Mole dropped	Drop enthalpy	Partial enthalpy		Integral enthalpy		
n_{Sb} (mmol)	ΔH_{Signal} (J)	x_{Sb}	$\Delta_{mix}\bar{H}_i$ (J/mol)	x_{Cu}	x_{Sn}	$\Delta_{mix}H_m$ (J/mol)
Series A: starting amount: n_{Cu} = 1.487 mmol; n_{Sn} = 3.030 mmol; σ (drop enthalpy) = ±300 J mol						
0	–	0	–	0.3290	0.6710	−786
0.1813	43,503	0.0386	−4719	0.3163	0.6452	−938
0.1996	43,622	0.0777	−4600	0.3034	0.6189	−1087
0.2374	43,762	0.1204	−4460	0.2894	0.5903	−1243
0.2386	43,530	0.1594	−4691	0.2765	0.5641	−1396
0.2426	43,914	0.1957	−4307	0.2646	0.5397	−1522
0.2382	43,933	0.2284	−4289	0.2538	0.5178	−1634
0.2511	44,005	0.2601	−4216	0.2434	0.4965	−1740
0.2518	44,821	0.2894	−3401	0.2338	0.4768	−1806
0.2550	44,803	0.3168	−3418	0.2247	0.4585	−1868
0.2695	45,360	0.3436	−2862	0.2159	0.4405	−1907
0.2921	45,300	0.3703	−2921	0.2072	0.4226	−1948
0.3008	45,872	0.3956	−2350	0.1988	0.4056	−1965
0.3012	46,144	0.4190	−2078	0.1911	0.3899	−1969
0.3019	46,333	0.4407	−1889	0.1840	0.3753	−1966
0.3174	46,162	0.4619	−2060	0.1770	0.3611	−1970
0.3178	46,675	0.4815	−1547	0.1706	0.3479	−1954
0.3213	46,946	0.4999	−1276	0.1645	0.3356	−1930
0.3178	46,540	0.5169	−1682	0.1589	0.3242	−1922
0.3311	47,335	0.5334	−887	0.1535	0.3131	−1886
0.3352	47,083	0.5490	−1139	0.1484	0.3026	−1861
0.3387	47,063	0.5638	−1159	0.1435	0.2927	−1838
0.3492	47,143	0.5780	−1079	0.1388	0.2832	−1813
0.3513	47,180	0.5914	−1042	0.1344	0.2742	−1789
0.3519	46,986	0.6040	−1236	0.1303	0.2657	−1772
0.3702	46,869	0.6164	−1353	0.1262	0.2574	−1759
Series B: starting amount: n_{Cu} = 1.493 mmol; n_{Sn} = 3.030 mmol; σ (drop enthalpy) = ±300 J/mol						
0	–	0	–	0.3298	0.6702	−792
0.1922	43,169	0.0407	−5053	0.3164	0.6429	−966
0.2006	43,035	0.0798	−5187	0.3035	0.6167	−1138
0.2121	43,503	0.1178	−4719	0.2909	0.5912	−1286
0.2247	43,284	0.1549	−4938	0.2787	0.5664	−1439
0.2359	43,576	0.1905	−4646	0.2670	0.5425	−1574
0.2570	44,348	0.2261	−3874	0.2553	0.5187	−1675
0.2573	44,999	0.2587	−3223	0.2445	0.4968	−1741
0.2731	42,420	0.2904	−5801	0.2340	0.4756	−1914
0.2741	45,384	0.3196	−2838	0.2244	0.4560	−1952
0.2808	45,505	0.3472	−2717	0.2153	0.4375	−1983
0.2824	45,925	0.3727	−2297	0.2069	0.4204	−1996
0.2861	46,116	0.3966	−2106	0.1990	0.4044	−2000
0.2935	45,224	0.4194	−2997	0.1915	0.3891	−2037
0.3058	44,075	0.4413	−4147	0.1843	0.3745	−2117
0.3081	48,341	0.4617	119	0.1775	0.3607	−2035
0.3134	42,365	0.4811	−5857	0.1712	0.3478	−2172
0.3457	47,223	0.5008	−999	0.1646	0.3345	−2128
0.3512	47,516	0.5195	−706	0.1585	0.3221	−2075
0.3546	47,202	0.5369	−1020	0.1527	0.3104	−2036
0.3547	44,559	0.5531	−3663	0.1474	0.2995	−2093
0.3624	46,223	0.5685	−1999	0.1423	0.2892	−2090
0.3806	47,039	0.5836	−1183	0.1373	0.2790	−2058
0.3834	43,698	0.5978	−4524	0.1326	0.2695	−2035

Similarly, experimental measurements from both calorimeters are compared for the section Sb:Sn = 1:3 in Fig. 3, and again the data are in good agreement. This section is characterized by a pronounced minimum around $x_{Cu} = 0.75$. This is in agreement with the fact that both binary systems, Cu–Sb and Cu–Sn, exhibit a minimum of $\Delta_{mix}H_m$ at $x_{Cu} = 0.75$, caused by the respective most stable compounds Cu_3Sb and Cu_3Sn. Fig. 4 shows the section $x_{Cu}/x_{Sn} = 1{:}2$ where a minimum of approx. 2000 J/mol appears around $x_{Sb} = 0.5$. Fig. 5 shows the section $x_{Cu}/x_{Sn} = 2{:}1$ where $\Delta_{mix}H_m$ becomes less negative with increasing x_{Sb}, again in a close to linear shape. The experimental values at the four intersections of the vertical sections (see Fig. 1) are listed in Table 6. The maximum deviation is 900 J/mol which is rather low but significant.

3.2. Ternary modeling

The experimental results were described by a least square fit to the Redlich–Kister–Muggianu [21,22] polynomial which is given by the following equation:

$$\Delta_{mix}H_m = \sum_i \sum_{j>i} \left[x_i x_j \sum_{\nu} {}^{\nu}L_{i,j} (x_i - x_j)^{\nu} \right] + x_i x_j x_k \left({}^{(0)}M_{i,j,k} x_i + {}^{(1)}M_{i,j,k} x_j + {}^{(2)}M_{i,j,k} x_k \right) \quad (3)$$

where i, j, k are equal to 1, 2, 3 for the element Cu, Sb and Sn. The binary parameters ${}^{\nu}L_{i,j}$ were determined from experimental enthalpies of mixing from literature: Cu–Sb [1], Cu–Sn [17] and

Table 4
Partial and integral enthalpies of mixing of liquid Cu–Sb–Sn alloys, 1100 K, cross-sections Cu:Sn = 2:1; standard states: liquid pure components; Series A and B – HT1000 calorimeter.

Mole dropped	Drop enthalpy	Partial enthalpy		Integral enthalpy		
n_{Sb} (mmol)	ΔH_{Signal} (J)	x_{Sb}	$\Delta_{mix}\bar{H}_i$ (J/mol)	x_{Cu}	x_{Sn}	$\Delta_{mix}H_m$ (J/mol)
Series A: starting amount: n_{Cu} = 3.263 mmol; n_{Sn} = 1.605 mmol; σ (drop enthalpy) = ±300 (J/mol)						
0	–	0	–	0.6704	0.3296	−4188
0.1997	50,189	0.0394	1967	0.6439	0.3167	−3945
0.2153	47,995	0.0786	−227	0.6177	0.3037	−3794
0.2176	48,269	0.1150	48	0.5933	0.2917	−3642
0.2401	46,753	0.1520	−1469	0.5684	0.2795	−3551
0.2632	46,849	0.1892	−1373	0.5435	0.2673	−3455
0.2707	47,041	0.2242	−1181	0.5201	0.2557	−3357
0.2754	47,785	0.2568	−437	0.4982	0.2450	−3235
0.2770	47,070	0.2870	−1152	0.4780	0.2350	−3150
0.2806	46,898	0.3151	−1324	0.4591	0.2258	−3078
0.2878	48,211	0.3418	−11	0.4413	0.2170	−2959
0.2911	47,079	0.3667	−1143	0.4245	0.2088	−2890
0.2994	48,516	0.3904	294	0.4086	0.2009	−2770
0.2996	45,132	0.4125	−3090	0.3938	0.1937	−2782
0.3068	50,170	0.4335	1948	0.3798	0.1868	−2613
0.3267	47,952	0.4542	−270	0.3659	0.1799	−2527
0.3313	44,912	0.4738	−3310	0.3528	0.1735	−2555
0.3395	48,333	0.4924	111	0.3403	0.1673	−2461
0.3415	48,231	0.5098	9	0.3286	0.1616	−2376
0.3427	46,342	0.5262	−1880	0.3176	0.1562	−2359
0.3456	47,001	0.5416	−1221	0.3073	0.1511	−2322
0.3504	47,903	0.5563	−319	0.2975	0.1463	−2258
0.3583	47,747	0.5703	−475	0.2881	0.1416	−2202
0.3619	49,253	0.5836	1031	0.2791	0.1373	−2102
0.3651	48,297	0.5962	75	0.2707	0.1331	−2036
0.3652	48,070	0.6081	−151	0.2627	0.1292	−1981
Series B: starting amount: n_{Cu} = 3.266 mmol; n_{Sn} = 1.601 mmol; σ (drop enthalpy) = ±300 (J/mol)						
0	–	0	–	0.6711	0.3289	−4193
0.2185	50,596	0.0430	2374	0.6422	0.3148	−3911
0.2234	48,268	0.0832	47	0.6152	0.3015	−3765
0.2268	46,739	0.1208	−1483	0.5900	0.2892	−3671
0.2303	47,392	0.1559	−830	0.5665	0.2776	−3558
0.2550	47,214	0.1916	−1008	0.5425	0.2659	−3450
0.2578	45,167	0.2248	−3055	0.5202	0.2550	−3434
0.2706	46,126	0.2569	−2096	0.4987	0.2444	−3378
0.2819	46,095	0.2875	−2127	0.4781	0.2344	−3327
0.2848	48,010	0.3160	−212	0.4590	0.2250	−3202
0.2852	47,969	0.3424	−252	0.4413	0.2163	−3088
0.2931	46,536	0.3674	−1686	0.4245	0.2081	−3035
0.3103	48,136	0.3920	−86	0.4080	0.2000	−2921
0.3145	48,160	0.4149	−62	0.3926	0.1924	−2813
0.3182	47,971	0.4365	−250	0.3782	0.1854	−2718
0.3378	48,413	0.4577	191	0.3639	0.1784	−2609
0.3380	47,749	0.4774	−473	0.3507	0.1719	−2531
0.3388	48,233	0.4957	11	0.3384	0.1659	−2442
0.3526	47,271	0.5135	−951	0.3265	0.1600	−2389
0.3526	47,442	0.5301	−780	0.3154	0.1546	−2335
0.3640	48,083	0.5460	−139	0.3047	0.1493	−2260
0.3649	48,348	0.5610	126	0.2946	0.1444	−2182
0.3698	49,163	0.5751	941	0.2851	0.1398	−2081
0.3711	48,343	0.5885	121	0.2762	0.1354	−2012
0.3761	47,887	0.6011	−335	0.2677	0.1312	−1960

Sb–Sn [8]. The three ternary parameters $M_{i,j,k}$ were obtained from the experimental enthalpies of mixing from the present investigation. The parameters $M_{i,j,k}$ represent the additional mixing enthalpy due to ternary interactions. All binary and ternary interaction parameters are listed in Table 5. Calculated values for the enthalpy of mixing in the liquid Cu–Sb–Sn system are shown in Figs. 2–5 as solid lines and are compared with the experimental results. Figs. 2 and 3 show two series of experimental data each for both sections obtained with the two different calorimeters, i.e. the HT1000 and the MHTC, compared with calculated data. In both sections the two different sets of experimental data are in good agreement with each other, but also with the calculated enthalpies of mixing. Differences between them are within ±250 J/mol which is in the range of the measuring error of this method. A similarly good agreement can be seen in Fig. 5 where differences between experimental and calculated enthalpy of mixing values are again not higher than ±250 J/mol. Clearly, the least satisfactory agreement is found for the section x_{Cu}/x_{Sn} = 1:2 in Fig. 4 although this has to be seen with respect to the expected experimental uncertainties and the rather small absolute values. This deviation is a consequence of the behavior of the ternary interaction parameters of the employed Redlich–Kister–Muggianu model. An extensive discussion of the properties of these ternary interaction parameters was presented by Janz and Schmid-Fetzer [23].

The model parameters listed in Table 5 were used to calculate the enthalpy of mixing of liquid alloys at 1100 K for the entire binary system Cu–Sb–Sn. Fig. 6 shows the corresponding isoenthalpy curves where values in the Cu-corner refer to metastable liquid alloys.

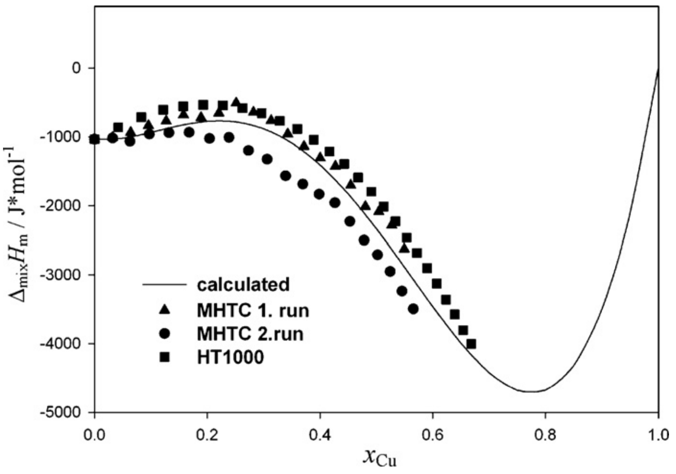

Fig. 3. Integral molar enthalpies of mixing of liquid Cu–Sb–Sn alloys at 1100 K for the section x_{Sb}/x_{Sn} = 1:3; standard states: pure liquid metals.

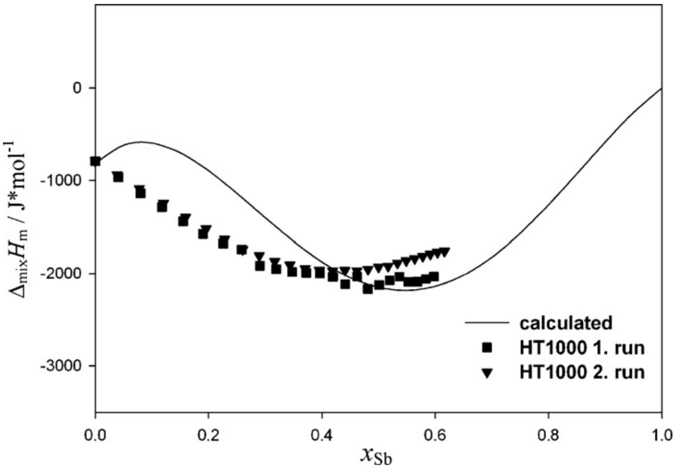

Fig. 4. Integral molar enthalpies of mixing of liquid Cu–Sb–Sn alloys at 1100 K for the section x_{Cu}/x_{Sn} = 2:1; standard states: pure liquid metals.

Table 5
Binary and ternary interaction parameters.

System	Temperature (K)	Literature	Interaction parameters (J/mol)
Cu–Sb	1108	[1]	$^{0}L = -11929.8$
			$^{1}L = -30148.1$
			$^{2}L = -22185.0$
Cu–Sn	1100	[17]	$^{0}L = -9768.4$
			$^{1}L = -22557.2$
			$^{2}L = -12898.2$
Sb–Sn	1108	[8]	$^{0}L = -5269.4$
			$^{1}L = 507.4$
Cu–Sb–Sn	1100	This work	$^{(0)}M = 175{,}135$
			$^{(1)}M = -119{,}539$
			$^{(2)}M = 29{,}801$

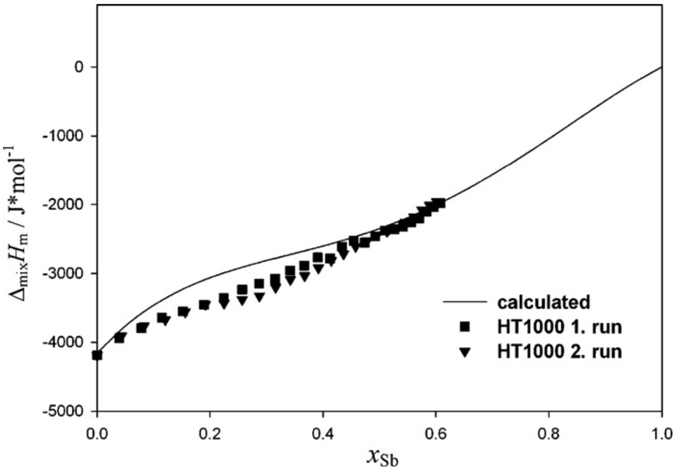

Fig. 5. Integral molar enthalpies of mixing of liquid Cu–Sb–Sn alloys at 1100 K for the section x_{Cu}/x_{Sn} = 1:2; standard states: pure liquid metals.

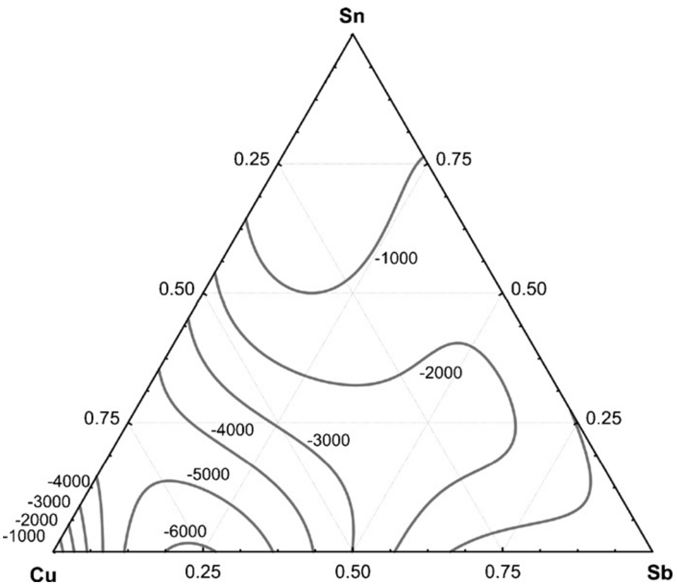

Fig. 6. Isoenthalpy curves of liquid Cu–Sb–Sn alloys at 1100 K; standard states: pure liquid metals. Values in the Cu-corner refer to metastable liquid alloys.

A comparison to the results of Lee et al. [2] who determined $\Delta_{mix}H_m$ for Cu–Sb–Sn at 1000 K generally shows slightly less exothermic values at the lower temperature. This is mainly caused by the chosen enthalpy curve for the limiting binary system Cu–Sn. The authors [2] used literature values at temperatures from 1363 to 1573 K. However, the work of Flandorfer et al. [17] clearly showed a temperature dependence of $\Delta_{mix}H_m$ in Cu–Sn with more exothermic values at temperatures below 1200 K.

Table 6
Values of the integral enthalpy of mixing at the intersection points.

Concentration			Integral enthalpy of mixing (J/mol)[a]			
x_{Cu}	x_{Sb}	x_{Sn}	Cu/Sb = 1:1	Sb/Sn = 1:3	Cu/Sn = 1:2	Cu/Sn = 2:1
0.25	0.24	0.51	−1050	–	−1700	–
0.27	0.18	0.55	–	−600	−1500	–
0.40	0.40	0.20	−2300	–	–	−2800
0.60	0.10	0.30	–	−3100	–	−3700

[a] Rounded to 50 J/mol.

4. Summary and conclusions

Enthalpies of mixing in the liquid Cu–Sb–Sn system were measured along four sections at constant temperature $T = 1100$ K. For two sections: $x_{Cu}/x_{Sb} = 1{:}1$ and $x_{Sb}/x_{Sn} = 1{:}3$ calorimetric measurements were done with two different calorimeters. The obtained experimental data from both instruments are in good agreement with each other and also with the calculated data. For the other two sections, i.e. $x_{Cu}/x_{Sn} = 1{:}2$ and $x_{Cu}/x_{Sn} = 2{:}1$, experiments were only done with one instrument (the HT1000 calorimeter). A comparison of experimental and calculated values for the enthalpy of mixing shows that both sets of data are in good agreement too.

Based on the experimental data from the present work, three ternary interaction parameters $M_{i,j,k}$ were obtained to be used in the Redlich–Kister–Muggianu polynomials which is a standard CALPHAD procedure [23,24]. Enthalpies of mixing determined in this work for liquid Cu–Sb–Sn solutions will be helpful in a future optimization of the thermodynamic properties and the phase equilibria of the entire ternary Cu–Sb–Sn system.

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