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Enthalpies of mixing of liquid alloys in the In–Pd–Sn system and the limiting binary systems

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Abstract

The partial and integral enthalpies of mixing of molten binary In–Pd (up to about 29 at.% Pd), In–Sn (entire compositional range) and Pd–Sn (up to about 53 at.% Pd) alloys were determined at 900 °C. A Calvet-type microcalorimeter was used for the measurements employing a drop calorimetric technique. Additionally, five sections in the ternary In–Pd–Sn system (compositions up to about 40 at.% Pd) were investigated at 900 °C. The ternary interaction parameters were fitted using the Redlich–Kister–Muggiano model for substitutional solutions. The isoenthalpy curves for In–Pd–Sn at 900 °C were constructed for the integral molar enthalpy of mixing. Furthermore, the experimental results in the ternary system were compared with calculated values obtained by employing different binary extrapolation models.

Keywords: Calorimetry; Enthalpy of mixing; In–Pd; In–Sn; Pd–Sn; In–Pd–Sn

1. Introduction

Lead and lead-containing materials are among the top chemicals posing a considerable threat to human life and environment [1]. Concern about the use of tin–lead solders in the electronics industry stems from occupational exposure, lead waste derived from the manufacturing process and the disposal of electronic assemblies. Although it is now widely agreed that there is no drop-in replacement for the standard tin–lead solders that are currently used worldwide, a range of possible alternatives has been investigated. One of the drawbacks of the simple Ag–Sn or Cu–Sn solder alloys is their—compared with the traditional tin–lead solders—higher melting point which creates some problems for the electronics industry: not only would the soldering processes have to be adapted to higher temperatures, but all electronic devices would also have to be manufactured to withstand these higher soldering temperatures. Thus there are serious attempts to reduce the melting temperature of the lead-free solder materials by alloying with additional elements, e.g. indium (mp: 156.6 °C). In fact, one commercial lead-free solder has already been developed based on a particular Ag–In–Sn alloy, and it is plausible to expect that other alloy compositions from this ternary system could also be developed for soldering purposes [2].

The quality and reliability of a solder joint depends, of course, on the reaction products that are formed between soldering material and substrate during the soldering process itself. One of the possible metallizations that are used in the production of integrated circuits consists of thin layers of palladium [3] or nickel–palladium alloys [4]. Thus the study of the In–Pd–Sn system as one of the limiting ternaries of the Ag–In–Pd–Sn quaternary system is important for processing and operation of lead-free solder contacts.

Our investigations are considered as a contribution to the COST 531 Action of the European Union which is mainly aiming at generating and systematizing information on thermochemistry, phase relationships and physical properties of alloy systems relevant to lead-free solder materials. A lead-free solder database will be created which forms the basis for a systematic alloy design which is desired to avoid complex and time-consuming trial and error developing methods. Information on thermochemical properties such as mixing enthalpies are indispensable for the thermodynamic optimization of phase diagrams and the estimation of several physical properties, e.g. surface tension and wettability.

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2. Literature review

2.1. The In–Pd binary system

Enthalpies of mixing of liquid In–Pd alloys were calculated by Colinet et al. [5] from experimentally determined partial enthalpies of Pd in liquid In. A minimum in the ΔH versus x_{Pd} curve is situated at 50 at.% Pd and $-35\,\mathrm{kJ\,mol^{-1}}$. Later, the enthalpy of mixing in the composition range up to 66 at.% Pd was measured by El Allam et al. [6] using direct-reaction calorimetry. They performed experiments between 1152 and 1406 °C and found the enthalpy of mixing to be temperature-independent. Jiang and Liu [7] used these experimental data in their optimization of the binary In–Pd system according to the CALPHAD approach. According to this work, the minimum in the asymmetric ΔH versus x_{Pd} curve is situated at around 60 at.% Pd and $-58\,\mathrm{kJ\,mol^{-1}}$.

2.2. The In–Sn binary system

Several calorimetric investigations of the enthalpy of mixing of liquid In–Sn alloys can be found in the literature. They cover the entire composition range and a temperature range from 248 to 450 °C. Kleppa [8] was the first to measure the integral enthalpies of mixing at 450 °C from 6 to 34 at.% In by means of liquid Sn solution calorimetry. Later, Wittig and Scheidt [9] investigated the whole composition range at 371 °C using direct-reaction calorimetry. The same method was used by Yazawa et al. [10] (450 °C; 19–90 at.% In) and finally by Bros and Laffitte [11] (248 °C; entire composition range). The agreement among these authors is generally quite good, however, no measurements at higher temperatures are available from literature. Both Lee et al. [12,13] and Korhonen and Kivilahti [2] presented assessed sets of parameters for the enthalpy of mixing in the liquid state based on the above-mentioned experimental data. Recently, Sabbar and Flandorfer [14] measured the enthalpy of mixing at 500 °C in the entire composition range.

2.3. The Pd–Sn binary system

Ghosh [15] calculated the enthalpy of mixing of liquid Pd–Sn alloys at 1577 °C based on e.m.f. measurements by Laurie and Pratt [16] and Guadagno and Pool [17]. Mathon et al. [18] measured the enthalpy of mixing at several temperatures between 679 and 1099 °C in the composition range up to 67 at.% Pd using drop calorimetry. According to this work, the enthalpy is temperature-independent showing an extrapolated minimum in the asymmetric ΔH versus x_{Pd} curve at about 71 at.% Pd and $-73\,\mathrm{kJ\,mol^{-1}}$, which is about $10\,\mathrm{kJ\,mol^{-1}}$ more negative than the value calculated by Ghosh [15].

2.4. The In–Pd–Sn ternary system

No experimental data for the enthalpy of mixing of liquid alloys in the In–Pd–Sn ternary system are available from literature.

3. Experimental procedure

The calorimetric measurements were carried out in a Calvet-type microcalorimeter (SETARAM, Lyon, France; thermopile with more than 200 thermocouples, wire wound resistance furnace, automatic drop device for up to 30 drops, control and data evaluation with LabView and HiQ as described by Flandorfer et al. [19]). To prevent oxidation all measurements were performed under Ar flow (approx. $30\,\mathrm{cm^3/min}$). At the end of each series the calorimeter was calibrated by six additions (approx. 40 mg each) of NIST standard α-Al_2O_3 (National Institute of Standards and Technology, Gaithersburg, MD).

The samples were prepared from In rods (99.999%, ASARCO, South Plainfield, NJ), Pd wire (99.9%, ÖGUSSA, Vienna, Austria) and Sn rods (99.9985%, Alfa Johnson Matthey, Karlsruhe, Germany).

In a first step the enthalpies of mixing of the binary bordering systems, i.e. In–Pd, In–Sn and Pd–Sn, respectively, were measured at 900 °C. Starting from a weighed amount (approx. 600 mg) of pure In or Sn, respectively, small pieces of Pd (20–40 mg) were added. The enthalpies of mixing in the In–Sn binary system were determined in the whole composition range. Small pieces (again 20–40 mg) of pure Sn were dropped into molten In (approx. 600 mg) and vice versa. All measurements were carried out in BN crucibles (8 mm in diameter, 68 mm in height).

In the ternary In–Pd–Sn system the enthalpies of mixing of about 120 molten samples were determined at 900 °C. Pieces of pure Pd (20–40 mg) were dropped into approximately 1000 mg of molten $In_{25}Sn_{75}$, $In_{50}Sn_{50}$ or $In_{75}Sn_{25}$ alloys, respectively. To cross-check the enthalpies of mixing at several intersections, we also added pure In to liquid $Pd_{40}Sn_{60}$ and pure Sn to liquid $In_{80}Pd_{20}$ (see Fig. 1). Again, BN was used as crucible material.

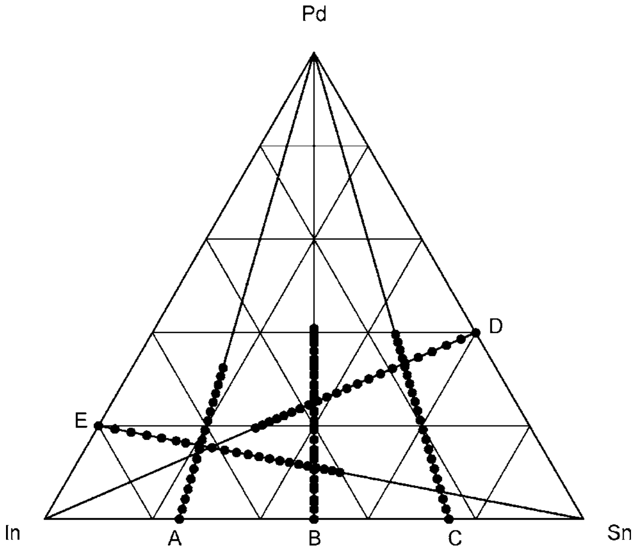

Fig. 1. Measured alloy compositions in the ternary In–Pd–Sn system at 900 °C.

The interval between individual drops was usually 40 min. The obtained signals were recorded and integrated. The measured enthalpy (integrated heatflow at constant pressure) is

$$\Delta H_{\mathrm{signal}} = n_i(H_{\mathrm{m},i,T} - H_{\mathrm{m},i,\mathrm{DT}}) + \Delta H_{\mathrm{reaction}} \qquad (1)$$

where n_i is the number of moles of the added element i, $H_{\mathrm{m},i,T}$ the molar enthalpy at the respective temperature of measurement T (in K) and $H_{\mathrm{m},i,\mathrm{DT}}$ the molar enthalpy at drop temperature. The molar enthalpy differences ($H_{\mathrm{m},i,T} - H_{\mathrm{m},i,\mathrm{DT}}$) were calculated using the Dinsdale polynomials [20]. Because of the rather small masses added, the partial enthalpies are directly given as $h_i \approx \Delta H_{\mathrm{reaction}}/n_i$.

4. Results and discussion

4.1. Experimental results

The original experimental data of the measurement series in the In–Pd, In–Sn, Pd–Sn and In–Pd–Sn systems can be found in Tables 1–4, respectively. These tables contain information on the starting amounts, added amounts and the partial and integral enthalpies of mixing of the liquid alloys.

Fig. 2 shows the experimental data of the integral molar enthalpy of mixing for the In–Pd system at 900 °C. The enthalpies are all exothermic. The curve shows a kink at about 30 at.% Pd, beyond this kink the course of the curve is more or less linear. This behaviour is obviously caused by the crystallization of a solid phase. From the In–Pd phase diagram in Massalski et al.'s compilation [21] it can be seen that the phase crystallizing at 900 °C is In Pd and the boundary between the single-phase liquid and two-phase region at this temperature is at 29 at.% Pd. This phase boundary is marked by a vertical solid line in Fig. 2. Thus our calorimetric measurements confirm the liquidus line presented in Ref. [21]. The dashed line represents the assessed enthalpy of mixing curve according to Jiang and Liu [7], which is in good agreement with our data, although it is based on measurements at slightly higher temperatures.

Table 1
Partial and integral enthalpies of mixing of liquid In–Pd alloys at 900 °C; standard states: pure liquid components

n(Pd) (mmol)	Partial enthalpy		Integral enthalpy	
	x(Pd)	h(Pd) (J mol^{-1})	x(Pd)	$\Delta_{\mathrm{mix}}H$ (J mol^{-1})
Starting amount: $n(\mathrm{In}) = 5.2364$ mmol				
0.1795	0.0166	−120403	0.0331	−3990
0.1970	0.0501	−120339	0.0671	−8074
0.2074	0.0837	−120127	0.1003	−12067
0.2130	0.1162	−121112	0.1321	−15916
0.2249	0.1477	−121859	0.1633	−19724
0.2348	0.1784	−121795	0.1935	−23415
0.2501	0.2085	−121779	0.2234	−27063
0.2577	0.2377	−122331	0.2520	−30570
0.2590	0.2654	−92933	0.2787	−32795
0.2765	0.2919	−28223	0.3052	−32627
0.2847	0.3178	−23295	0.3305	−32288
0.2928	0.3425	−23370	0.3546	−31966
0.3017	0.3662	−22755	0.3778	−31636
0.3132	0.3889	−22159	0.4001	−31295
0.3237	0.4108	−22366	0.4215	−30976
0.3256	0.4316	−20953	0.4416	−30628
0.3395	0.4514	−21448	0.4611	−30307
0.3514	0.4705	−22005	0.4799	−30018
0.3564	0.4888	−21802	0.4977	−29737
0.3659	0.5062	−21597	0.5148	−29461
0.3739	0.5229	−20802	0.5310	−29171

Table 2
Partial and integral enthalpies of mixing of liquid In–Sn alloys at 900 °C; standard states: pure liquid components

$n(i)$ (mmol)	Partial enthalpy		Integral enthalpy	
	$x(i)$	$h(i)$ (J mol^{-1})	x(In)	$\Delta_{\mathrm{mix}}H$ (J mol^{-1})
Starting amount: $n(\mathrm{Sn}) = 5.0514$ mmol; $i = \mathrm{In}$				
0.1707	0.0163	−1313	0.0327	−43
0.1846	0.0492	−856	0.0657	−71
0.1888	0.0815	−658	0.0972	−90
0.1983	0.1127	−754	0.1281	−113
0.2108	0.1434	−1057	0.1587	−146
0.2192	0.1735	−1161	0.1884	−182
0.2265	0.2026	−572	0.2169	−196
0.2325	0.2305	−916	0.2441	−221
0.2445	0.2574	−852	0.2708	−243
0.2522	0.2836	−1155	0.2964	−275
0.2596	0.3087	−712	0.3210	−290
0.2737	0.3330	−841	0.3450	−310
0.2763	0.3564	−493	0.3677	−316
0.2858	0.3786	−647	0.3895	−328
0.2972	0.4001	−359	0.4107	−329
0.3050	0.4208	−772	0.4310	−344
0.3125	0.4406	−530	0.4503	−350
0.3254	0.4597	−277	0.4691	−348
0.3324	0.4781	−660	0.4870	−358
0.3483	0.4958	−351	0.5046	−358
0.3517	0.5128	−597	0.5211	−366
Starting amount: $n(\mathrm{In}) = 5.2299$ mmol; $i = \mathrm{Sn}$				
0.2453	0.0224	−1570	0.9552	−70
0.2652	0.0669	−1273	0.9111	−126
0.2668	0.1092	−1378	0.8706	−181
0.2789	0.1487	−1231	0.8320	−228
0.2896	0.1863	−1397	0.7953	−280
0.2987	0.2219	−1006	0.7608	−311
0.3078	0.2555	−965	0.7282	−339
0.3097	0.2869	−919	0.6981	−363
0.3267	0.3165	−1338	0.6689	−404

In Fig. 3 we present our experimental data for the In–Sn binary system measured at 900 °C. Measurements starting from both pure elements were done and the system is liquid in the entire composition range at this temperature; therefore data points for the whole range of binary compositions are available. The fitted curve that is entirely exothermic shows a minimum at 58 at.% In and −380 J mol^{-1}. This is slightly more exothermic than the values previously reported [8–11] for lower temperatures (248–450 °C), but one has to take into account that absolute deviations are small. The measurement

Table 3
Partial and integral enthalpies of mixing of liquid Pd–Sn alloys at 900 °C; standard states: pure liquid components

n(Pd) (mmol)	Partial enthalpy		Integral enthalpy	
	x(Pd)	h(Pd) (J mol^{-1})	x(Pd)	$\Delta_{\mathrm{mix}}H$ (J mol^{-1})
Starting amount: $n(\mathrm{Sn}) = 5.0896$ mmol				
0.1845	0.0175	−115813	0.0350	−4051
0.1981	0.0524	−115257	0.0699	−8076
0.2107	0.0871	−114848	0.1044	−12034
0.2225	0.1213	−114552	0.1381	−15897
0.2298	0.1543	−114035	0.1704	−19573
0.2382	0.1859	−113188	0.2014	−23072
0.2433	0.2161	−112652	0.2308	−26366
0.2554	0.2451	−112408	0.2594	−29564
0.2590	0.2728	−111945	0.2863	−32556
0.2735	0.2995	−110682	0.3126	−35442
0.2788	0.3251	−110153	0.3376	−38153
0.2955	0.3498	−109517	0.3621	−40795
0.3032	0.3738	−108809	0.3855	−43285
0.3142	0.3967	−108341	0.4079	−45663
0.3231	0.4187	−107199	0.4294	−47892
0.6702	0.4493	−105940	0.4693	−51949
0.3501	0.4786	−104601	0.4879	−53804
0.3596	0.4969	−103740	0.5058	−55547
0.3674	0.5143	−86670	0.5229	−56619
0.3733	0.5309	−39498	0.5390	−56041

is in very good agreement with the data recently reported by Sabbar and Flandorfer [14] for 500 °C.

Fig. 4 shows the experimental data of the integral molar enthalpy of mixing for the Pd–Sn system at 900 °C. The enthalpies are again all exothermic. The boundary between the single-phase liquid and the two-phase region ($\mathrm{L} + \mathrm{Pd}_{20}\mathrm{Sn}_{13}$)—according to Massalski et al.'s compilation [21] at 53 at.% Pd—is marked by a vertical solid line in Fig. 4, but the kink in the curve can hardly be noticed as just one sample was situated in the two-phase field. The dashed line represents the measurements by Mathon et al. [18], which are in good agreement with our results.

Figs. 5, 6 and 8 show, as examples, the integral liquid enthalpies of mixing in the ternary In–Pd–Sn system, sections A (pure Pd dropped into liquid $\mathrm{In}_{75}\mathrm{Sn}_{25}$), B (pure Pd dropped into liquid $\mathrm{In}_{50}\mathrm{Sn}_{50}$) and C (pure Pd dropped into liquid $\mathrm{In}_{25}\mathrm{Sn}_{75}$), respectively. For section B we also included a graph showing the partial molar enthalpy of mixing h_{Pd} (Fig. 7).

The slightly negative starting values of $\Delta_{\mathrm{mix}}H^{\circ}_{\mathrm{m}}$ for the three different pure In–Sn master alloys are taken from our own measurements (Fig. 3). It can be seen that the curves of sections A (Fig. 5) and B (Fig. 6) show a kink at about 33 and 42 at.% Pd, respectively. This is again caused by the primary crystallization of a solid phase as soon as the liquidus surface is touched at a certain temperature and composition. Hitherto no liquidus surface data from the ternary In–Pd–Sn system were reported in literature. All samples measured in section C as well as all samples in the sections D and E, which are not shown here, are totally liquid at 900 °C.

Table 4
Partial and integral enthalpies of mixing of liquid In–Pd–Sn alloys at 900 °C; standard states: pure liquid components

$n(i)$ (mmol)	Partial enthalpy		Integral enthalpy		
	$x(i)$	$h(i)$ (J mol^{-1})	x(In)	x(Pd)	$\Delta_{\mathrm{mix}}H$ (J mol^{-1})
Section A—starting amount: $n(\mathrm{In}) = 6.4785$ mmol; $n(\mathrm{Sn}) = 2.1562$ mmol; $i = \mathrm{Pd}$					
0.1865	0.0106	−120981	0.7341	0.0211	−2963
0.2029	0.0321	−120434	0.7176	0.0432	−5605
0.2059	0.0538	−121970	0.7016	0.0645	−8201
0.2203	0.0754	−121596	0.6853	0.0863	−10845
0.2273	0.0970	−121443	0.6692	0.1078	−13442
0.2351	0.1184	−121348	0.6533	0.1289	−16001
0.2399	0.1392	−121882	0.6379	0.1495	−18504
0.2536	0.1599	−121729	0.6223	0.1702	−21019
0.2602	0.1804	−121771	0.6071	0.1905	−23476
0.2766	0.2007	−122123	0.5918	0.2109	−25970
0.2805	0.2208	−122065	0.5770	0.2307	−28372
0.2961	0.2406	−121940	0.5622	0.2504	−30777
0.3026	0.2600	−121477	0.5478	0.2696	−33098
0.3107	0.2790	−121152	0.5338	0.2883	−35353
0.3200	0.2975	−120677	0.5200	0.3066	−37545
0.3326	0.3156	−97156	0.5065	0.3247	−39096
0.3360	0.3333	−58797	0.4935	0.3419	−39601
0.3492	0.3505	−24545	0.4807	0.3590	−39210
0.3533	0.3672	−22177	0.4685	0.3754	−38775
0.3643	0.3834	−24350	0.4564	0.3914	−38405
0.3777	0.3993	−24777	0.4446	0.4072	−38051
Section B, first run—starting amount: $n(\mathrm{In}) = 4.2756$ mmol; $n(\mathrm{Sn}) = 4.2922$ mmol; $i = \mathrm{Pd}$					
0.1844	0.0105	−116018	0.4895	0.0211	−2893
0.1995	0.0320	−116608	0.4786	0.0429	−5427
0.2046	0.0536	−116305	0.4679	0.0643	−7905
0.2144	0.0750	−116296	0.4572	0.0857	−10384
0.2234	0.0963	−115895	0.4465	0.1070	−12841
0.2366	0.1177	−116095	0.4358	0.1285	−15326
0.2438	0.1390	−116066	0.4252	0.1496	−17764
0.2576	0.1602	−116017	0.4146	0.1708	−20214
0.2667	0.1812	−115469	0.4042	0.1916	−22611
0.2789	0.2020	−115758	0.3938	0.2124	−24999
0.2800	0.2222	−115683	0.3839	0.2321	−27275
0.2922	0.2419	−115201	0.3741	0.2517	−29519
0.2965	0.2612	−115378	0.3647	0.2706	−31686
0.3152	0.2801	−114982	0.3552	0.2897	−33863
0.3212	0.2989	−114469	0.3460	0.3081	−35954
0.3308	0.3171	−113837	0.3370	0.3261	−37980
0.3369	0.3348	−113257	0.3283	0.3435	−39923
0.3464	0.3520	−112935	0.3198	0.3605	−41811
0.3619	0.3689	−112153	0.3114	0.3773	−43661
0.3636	0.3853	−111672	0.3033	0.3933	−45412
0.3727	0.4011	−97514	0.2955	0.4089	−46752
Section B, second run—starting amount: $n(\mathrm{In}) = 2.5739$ mmol; $n(\mathrm{Sn}) = 2.5684$ mmol; $i = \mathrm{Pd}$					
0.1928	0.0181	−116281	0.4819	0.0361	−4643
0.2001	0.0536	−116138	0.4645	0.0710	−8674
0.2174	0.0885	−117326	0.4470	0.1061	−12781
0.2175	0.1224	−116639	0.4307	0.1387	−16565
0.2293	0.1546	−116987	0.4147	0.1705	−20279
0.2309	0.1854	−116526	0.3998	0.2003	−23735
0.2444	0.2149	−115901	0.3852	0.2296	−27110
0.2543	0.2437	−115972	0.3711	0.2579	−30371
0.2679	0.2717	−115078	0.3573	0.2855	−33524
0.2767	0.2987	−114543	0.3440	0.3119	−36524

Table 4 (*Continued*)

$n(i)$ (mmol)	Partial enthalpy		Integral enthalpy		
	$x(i)$	$h(i)$ (J mol^{-1})	x(In)	x(Pd)	$\Delta_{\mathrm{mix}}H$ (J mol^{-1})
0.2938	0.3250	−102251	0.3310	0.3380	−38120
0.5868	0.3612	−123536	0.3078	0.3845	−44120
0.3107	0.3955	−110123	0.2967	0.4065	−46486
0.3175	0.4170	−73656	0.2862	0.4275	−47447
0.3278	0.4376	−28441	0.2762	0.4477	−46777
0.3383	0.4574	−30822	0.2665	0.4670	−46218
0.3508	0.4764	−30412	0.2571	0.4857	−45663
0.3546	0.4945	−32378	0.2483	0.5033	−45208
0.3642	0.5118	−34243	0.2399	0.5202	−44836
0.3849	0.5285	−35693	0.2316	0.5369	−44519
Section C—starting amount: n(In) = 2.1225 mmol; n(Sn) = 6.3762 mmol; i = Pd					
0.1860	0.0107	−115573	0.2446	0.0214	−2743
0.2002	0.0324	−114941	0.2391	0.0435	−5271
0.2027	0.0541	−115148	0.2338	0.0648	−7722
0.2153	0.0756	−114799	0.2284	0.0865	−10200
0.2235	0.0972	−114977	0.2230	0.1079	−12658
0.2312	0.1185	−114772	0.2177	0.1290	−15078
0.2419	0.1396	−114394	0.2125	0.1501	−17481
0.2495	0.1604	−114146	0.2073	0.1708	−19834
0.2670	0.1813	−113785	0.2020	0.1918	−22220
0.2703	0.2020	−113534	0.1970	0.2121	−24508
0.2856	0.2223	−113802	0.1919	0.2324	−26811
0.2880	0.2421	−113137	0.1870	0.2519	−29000
0.3053	0.2617	−112652	0.1821	0.2715	−31189
0.3123	0.2810	−112020	0.1774	0.2905	−33297
0.3223	0.2997	−111871	0.1727	0.3090	−35356
0.3317	0.3181	−111436	0.1682	0.3272	−37353
0.3465	0.3362	−110857	0.1637	0.3452	−39316
0.3583	0.3539	−110326	0.1593	0.3627	−41224
0.3673	0.3713	−109903	0.1550	0.3798	−43064
0.3772	0.3881	−109193	0.1509	0.3964	−44836
Section D—starting amount: n(Pd) = 2.8193 mmol; n(Sn) = 4.2145 mmol; i = In					
0.2538	0.0174	−7514	0.0348	0.3861	−44414
0.2615	0.0515	−6530	0.0683	0.3727	−43102
0.2812	0.0850	−5685	0.1017	0.3593	−41758
0.2847	0.1175	−5084	0.1332	0.3467	−40471
0.2992	0.1486	−4676	0.1641	0.3344	−39198
0.3019	0.1785	−4338	0.1930	0.3228	−37991
0.3116	0.2069	−3527	0.2209	0.3117	−36801
0.3281	0.2345	−3382	0.2482	0.3007	−35629
0.3374	0.2613	−2849	0.2744	0.2903	−34488
0.3423	0.2867	−2938	0.2991	0.2804	−33412
0.3530	0.3110	−2399	0.3229	0.2708	−32358
0.3576	0.3342	−2216	0.3455	0.2618	−31355
0.3662	0.3562	−1782	0.3670	0.2532	−30381
0.3735	0.3773	−1861	0.3876	0.2450	−29453
0.3884	0.3976	−1517	0.4076	0.2369	−28540
0.3962	0.4172	−1062	0.4268	0.2293	−27652
0.4033	0.4359	−1244	0.4450	0.2220	−26812
0.4058	0.4536	−1168	0.4622	0.2151	−26016
0.4223	0.4706	−689	0.4790	0.2084	−25224
0.4311	0.4871	−481	0.4952	0.2019	−24458
0.4462	0.5030	−392	0.5108	0.1957	−23712
Section E—starting amount: n(In) = 5.6546 mmol; n(Pd) = 1.4111 mmol; i = Sn					
0.2497	0.0171	207	0.7727	0.1932	−23371
0.2601	0.0507	−397	0.7462	0.1865	−22582
0.2726	0.0835	131	0.7202	0.1801	−21793
0.2746	0.1149	−190	0.6959	0.1740	−21063
0.2903	0.1451	−134	0.6719	0.1680	−20341
0.1971	0.1698	1405	0.6565	0.1641	−19843
0.3021	0.1933	−341	0.6342	0.1586	−19182
0.3102	0.2205	−676	0.6129	0.1532	−18559
0.3261	0.2469	−309	0.5920	0.1480	−17936
0.3298	0.2724	−614	0.5722	0.1431	−17358
0.3361	0.2965	−800	0.5534	0.1383	−16813
0.3456	0.3196	−380	0.5353	0.1338	−16275
0.3534	0.3417	−424	0.5179	0.1295	−15762
0.3678	0.3631	−284	0.5011	0.1253	−15257
0.3702	0.3836	−336	0.4851	0.1213	−14783
0.3817	0.4032	−715	0.4698	0.1174	−14337
0.3836	0.4219	−803	0.4552	0.1138	−13919
0.3934	0.4397	−358	0.4413	0.1103	−13502
0.4047	0.4569	−476	0.4277	0.1069	−13103
0.4110	0.4734	−234	0.4148	0.1037	−12715
0.4276	0.4893	−469	0.4022	0.1006	−12343

4.2. Binary and ternary modeling

In a first step, the binary experimental data were treated by a least-squares fit using the following Redlich–Kister polynomial, as proposed by Ansara and Dupin [22] for substitutional solutions according to the CALPHAD method:

$$\Delta H_{\mathrm{mix}} = \sum_i \sum_{j>i} \left[x_i x_j \sum_\nu L^{(\nu)}_{i:j} (x_i - x_j)^\nu \right] \tag{2}$$

where i and j are equal to 1 or 2 for the two elements under consideration in alphabetical order (In and Pd, In and Sn or Pd and Sn), and $L^{(\nu)}_{i:j}$ ($\nu = 0, 1, 2, \ldots$) are the so-called binary interaction parameters of the order ν. As all three binaries in the present investigation have rather simple courses of the enthalpy of mixing curves with just one minimum each, it was sufficient to use only $L^{(0)}$ and $L^{(1)}$ for a perfect description. In this case the polynomial has the form

$$\Delta H_{\mathrm{mix}} = L^{(0)}_{1,2} x_1 x_2 + L^{(1)}_{1,2} x_1 x_2 (x_1 - x_2) \tag{3}$$

The results of the least-squares fit for all three binary systems are presented in Table 5. The calculated curves of the enthalpy of mixing versus molar fraction are included in Figs. 2–4 as solid lines.

In a second step, the ternary In–Pd–Sn experimental data were treated by a least-squares fit. In this case the so-called Redlich–Kister–Muggiano polynomial was used which also takes the additional ternary interactions into account [22]:

$$\Delta H_{\mathrm{mix}} = \sum_i \sum_{j>i} \left[x_i x_j \sum_\nu L^{(\nu)}_{i:j} (x_i - x_j)^\nu \right] + x_{\mathrm{A}} x_{\mathrm{B}} x_{\mathrm{C}} (M^{(0)}_{\mathrm{A:B:C}} x_{\mathrm{A}} + M^{(1)}_{\mathrm{A:B:C}} x_{\mathrm{B}} + M^{(2)}_{\mathrm{A:B:C}} x_{\mathrm{C}}) \tag{4}$$

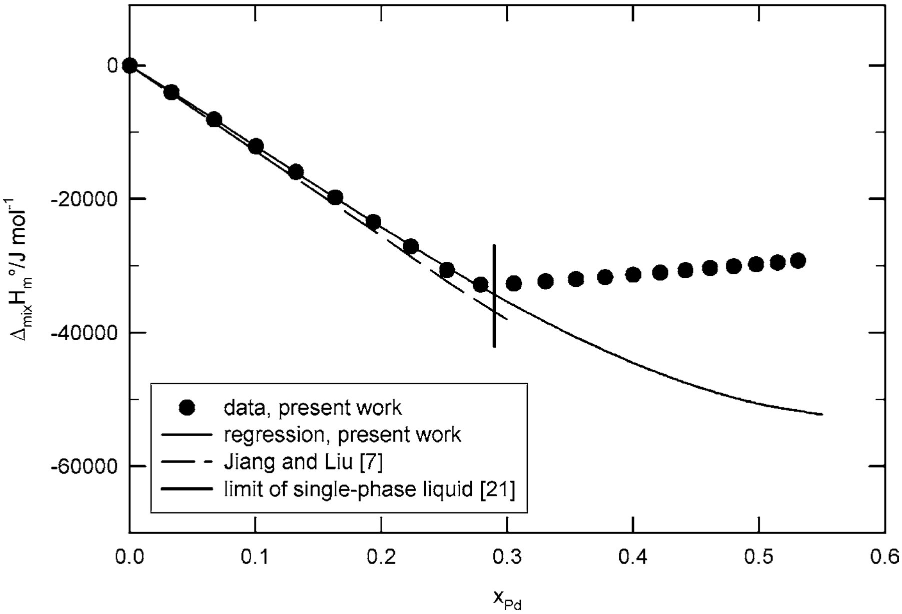

Fig. 2. Integral molar enthalpies of mixing of liquid In–Pd alloys at 900 °C; standard states: pure liquid metals.

where *i* and *j* are equal to 1, 2 or 3 for the elements In, Pd and Sn, respectively, and $L_{i:j}^{(\nu)}$ ($\nu = 0, 1, 2, \ldots$) are the interaction parameters of the constituent binaries, which were taken from Table 5. The last term represents the additional mixing enthalpy due to ternary interactions, where $M_{\mathrm{A:B:C}}^{(\alpha)}$ ($\alpha = 0, 1, 2$) are the excess ternary interaction parameters. As the result of this least-squares fit the ternary interaction parameters $M_{\mathrm{In:Pd:Sn}}^{(\alpha)}$ are also included in Table 5. The calculated enthalpies of mixing are represented by solid lines in Figs. 5, 6 and 8. In Fig. 7 we included the partial molar enthalpy h_{Pd} calculated from the fitted curve as a solid line.

The measured enthalpies of mixing close to the crossover of two sections in the ternary In–Pd–Sn system together with the values calculated using the polynomial are listed in Table 6. The different sections are marked by capital letters as in Fig. 1. The values of $D_{\mathrm{mix}}H_{\mathrm{m}}^{\circ}$ at the intersections are also shown in Figs. 5, 6 and 8. The absolute deviations from the fitted values are on the average $0.3\,\mathrm{kJ\,mol^{-1}}$ which is quite small in relative terms, as the absolute values of the enthalpy of mixing in this system are generally high. From the statistical analysis of the data it can be derived that the precision of our measurements is $\pm 0.15\,\mathrm{kJ\,mol^{-1}}$.

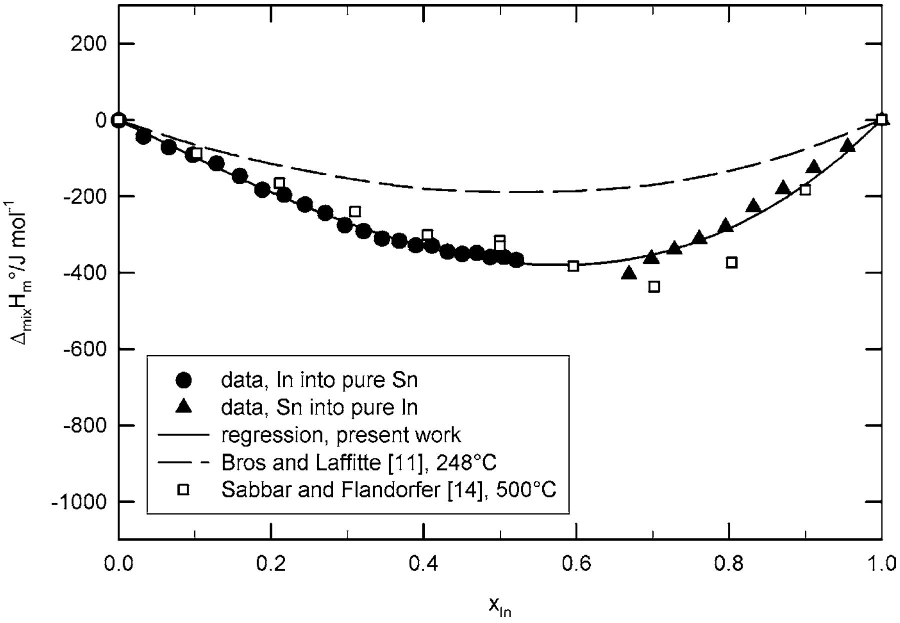

Fig. 3. Integral molar enthalpies of mixing of liquid In–Sn alloys at 900 °C; standard states: pure liquid metals.

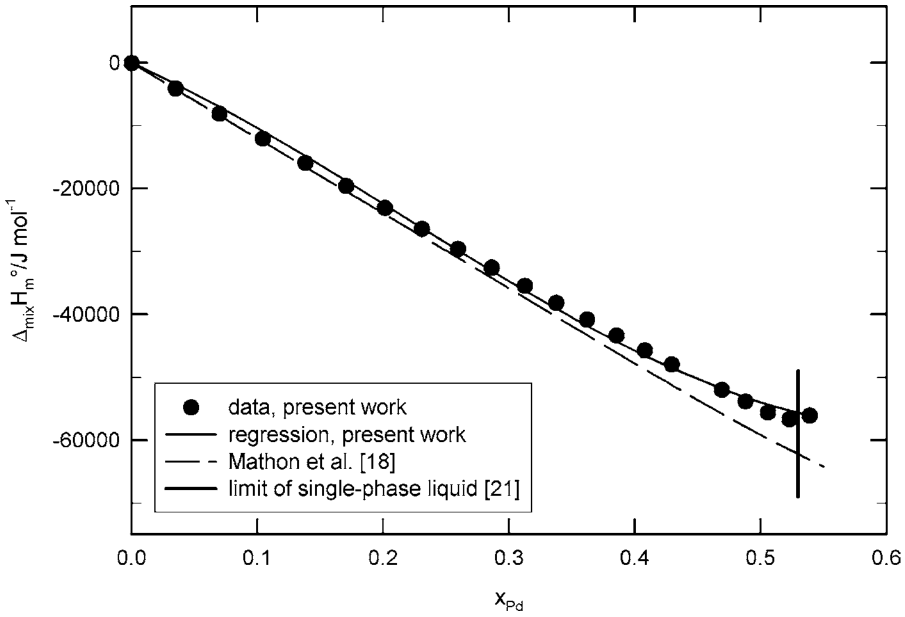

Fig. 4. Integral molar enthalpies of mixing of liquid Pd–Sn alloys at 900 °C; standard states: pure liquid metals.

Applying the polynomial (Eq. (4) and Table 5), isoenthalpy curves of the integral molar enthalpy of mixing in the liquid state were calculated and plotted on a Gibbs triangle (Fig. 9). The analytical function describes the enthalpy of mixing in the entire system, but it has to be noted that the isoenthalpy graphs can only be experimentally determined at concentrations where the alloy is completely liquid at the respective temperature. All the other calculated values refer to metastable supercooled liquid alloys. In the graphic representation, the estimated course of the liquidus isotherm at 900 °C was included showing all regions where the system is not totally liquid shaded in grey. It can be seen that the enthalpy of mixing is negative over the entire composition range and shows a minimum (i.e. is maximally exothermic) on the binary Pd–Sn edge at 56.4 at.% Pd and −57.0 kJ mol^{-1}. According to preliminary results of our phase diagram investigations in the In–Pd–Sn system, a ternary compound is likely to occur in this compositional region.

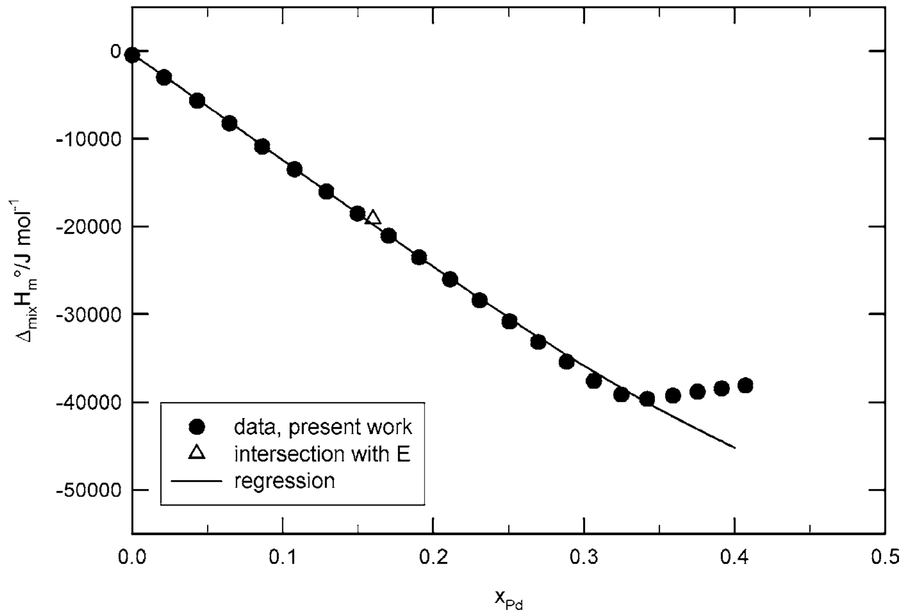

Fig. 5. Integral molar enthalpies of mixing of liquid In–Pd–Sn alloys, pure Pd dropped into molten $In_{75}Sn_{25}$ (section A) at 900 °C; standard states: pure liquid metals.

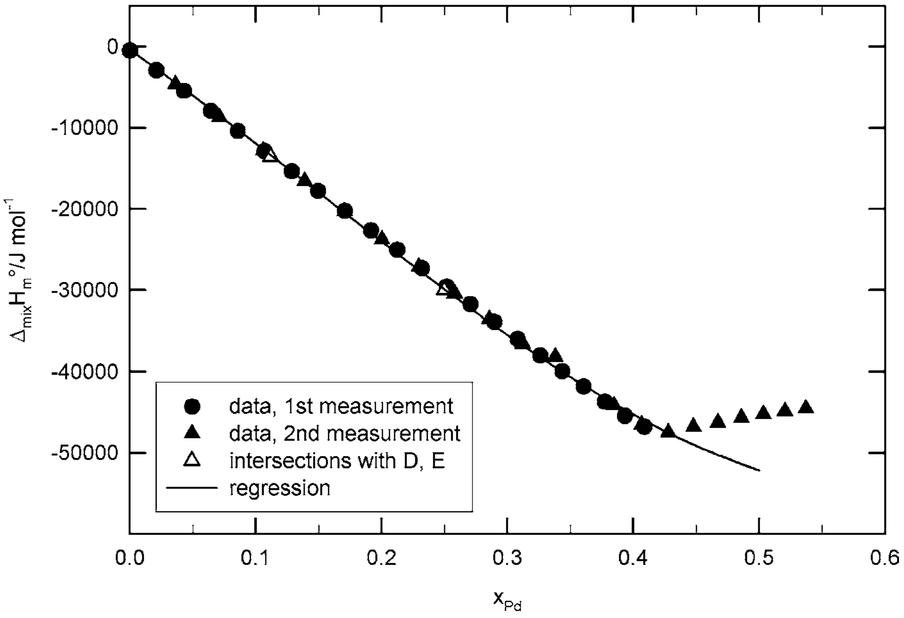

Fig. 6. Integral molar enthalpies of mixing of liquid In–Pd–Sn alloys, pure Pd dropped into molten $In_{50}Sn_{50}$ (section B) at 900 °C; standard states: pure liquid metals.

4.3. Comparison with some extrapolation models

The experimental enthalpies of mixing in the In–Pd–Sn system were compared with values obtained by an extrapolation of the binary data using three different procedures, i.e. by the methods according to Kohler [23], Muggianu et al. [24], and Toop [25]. The different approaches were discussed in detail and compared with each other by Chen et al. [26] or more recently by Chartrand and Pelton [27]. For the present study it should suffice to point out that the Kohler's approach [23] is based on a weighting scheme where the ratio of the ternary mole fractions x_i/x_j are kept constant in the binary and ternary system; the approach by Muggianu et al. [24] keeps the difference $x_i - x_j$ of two mole fractions constant, whereas Toop's relation [25] is asymmetric in a sense that one of the three mole fractions, x_k, as well as the ratio of the two others, x_i/x_j, are kept constant.

Fig. 10 shows, as an example, a comparison of the experimental results for section B of the ternary In–Pd–Sn system ($x_{In}/x_{Sn} = 1$) with the predictions according to the three

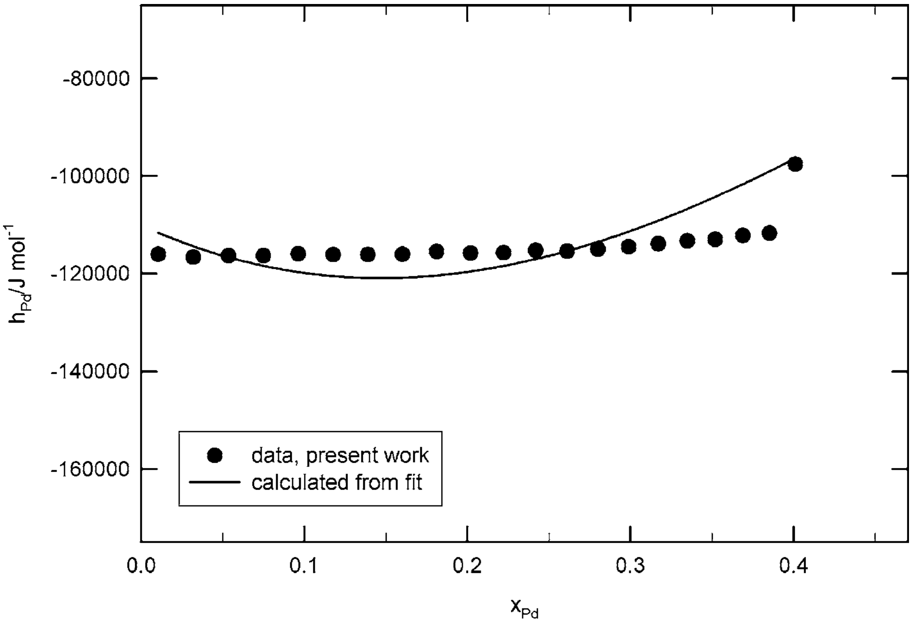

Fig. 7. Partial molar enthalpies of mixing of liquid In–Pd–Sn alloys, pure Pd dropped into molten $In_{50}Sn_{50}$ (section B) at 900 °C; standard states: pure liquid metals.

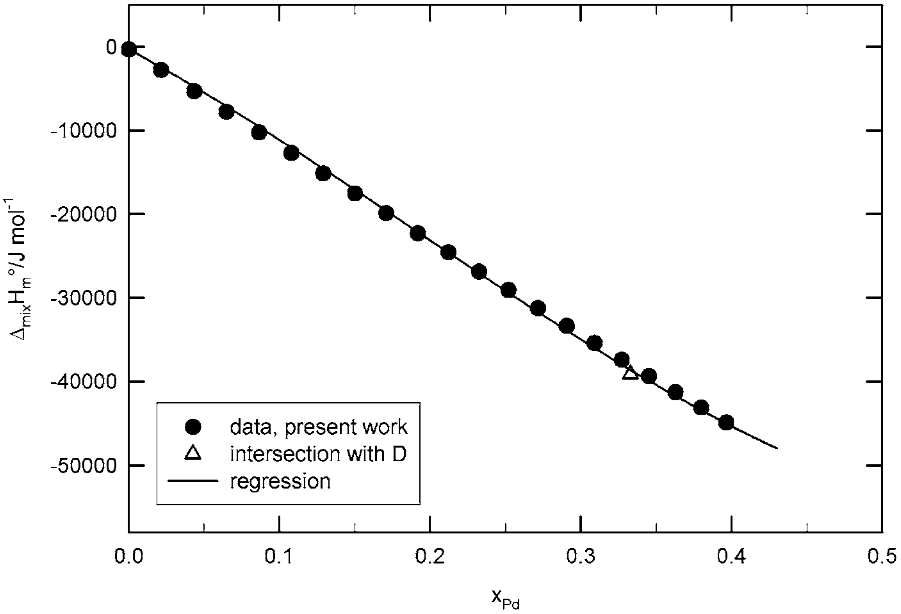

Fig. 8. Integral molar enthalpies of mixing of liquid In–Pd–Sn alloys, pure Pd dropped into molten $In_{25}Sn_{75}$ (section C) at 900 °C; standard states: pure liquid metals.

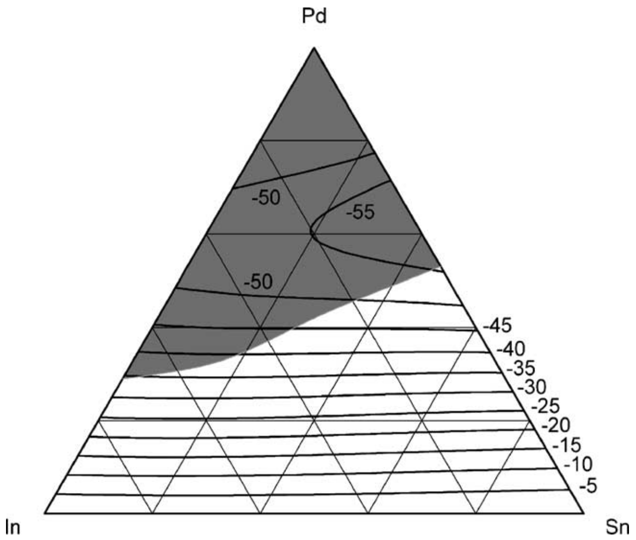

Fig. 9. Isoenthalpy curves for liquid In–Pd–Sn alloys at 900 °C (in kJ mol^{-1}); standard states: pure liquid metals; grey-shaded areas approximately indicate (partially) solid concentrations at 900 °C.

Table 5

Binary and ternary interaction parameters at 900 °C

Interaction parameter	ν, α	J mol^{-1}
$L^{(\nu)}_{\mathrm{In:Pd}}$	0	−202640
	1	85610
$L^{(\nu)}_{\mathrm{In:Sn}}$	0	−1481
	1	−499
$L^{(\nu)}_{\mathrm{Pd:Sn}}$	0	−215814
	1	−126046
$M^{(\alpha)}_{\mathrm{In:Pd:Sn}}$	0	156065
	1	253787
	2	211126

different models. It can be seen that the values calculated according to Toop's asymmetric approach agree perfectly with our measurements. Of course, Pd has to be chosen as "asymmetric" element, as the courses of the enthalpy of mixing curves of In–Pd and Pd–Sn are quite similar, whereas In–Sn shows different behaviour. The predicted values using the two other relations are still in reasonably good agreement with our experimental results, especially for low Pd

Table 6

Measured and calculated enthalpies of mixing at the intersections, In–Pd–Sn system at 900 °C; standard states: In(l), Pd(l), Sn(l)

Concentration			Experimental values in section (kJ mol^{-1})					Calculated values from polynomial (4) (kJ mol^{-1})
at.% In	at.% Pd	at.% Sn	A	B	C	D	E	
63.0	16.0	21.0	−19.8				−19.1	−19.8
37.5	25.0	37.5		−29.4		−30.0		−29.9
44.4	11.2	44.4		−13.4			−13.6	−13.4
16.7	33.3	50.0			−38.0	−39.1		−38.6

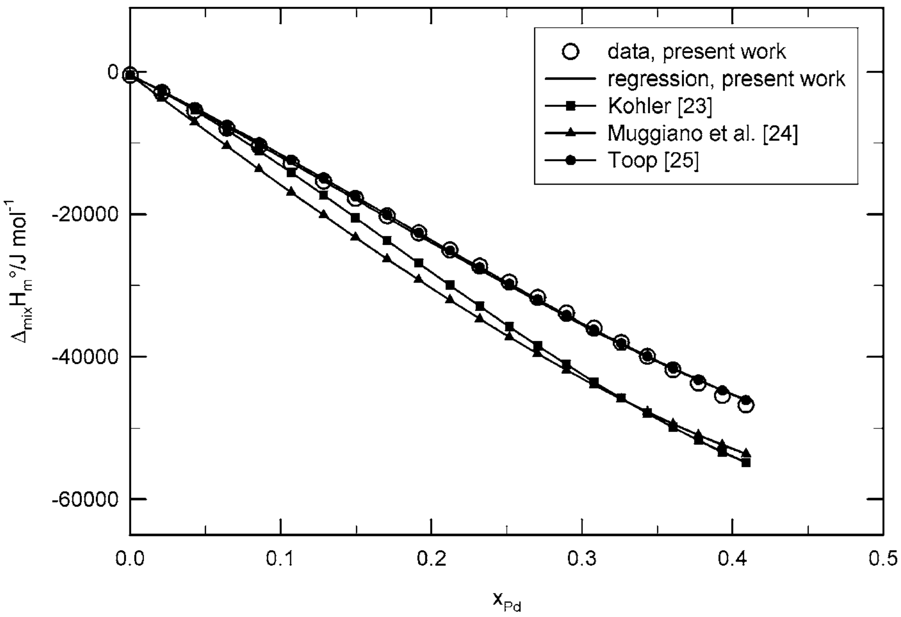

Fig. 10. Comparison of the experimental results with the predictions according to the models of Kohler, Muggianu et al. and Toop for the ternary In–Pd–Sn system at 900 °C, section B (In:Sn = 1:1).

concentrations, although the deviation increases considerably with increasing Pd content. Similar results were obtained for all other investigated sections. One reason for this good prediction of the extrapolation models is the fact that all three limiting binary systems show quite simple shapes of their enthalpy of mixing curves, with a pronounced minimum in the systems In–Pd and Pd–Sn, and a very small minimum in the In–Sn system. It indicates that under such circumstances all three models may yield a reasonable estimate of the enthalpy of mixing in a ternary system based on the binary values only.

5. Summary and conclusions

A Calvet-type calorimeter was used to study extensively the enthalpies of mixing of liquid In–Pd, In–Sn, Pd–Sn and In–Pd–Sn alloys at 900 °C. The experimental data were fitted using a Redlich–Kister–Muggiano polynomial as this is the standard CALPHAD procedure [22]. Based on our experimental values in the ternary system and the optimized binary interaction parameters, the ternary interaction parameters $M^{(\alpha)}_{\mathrm{In:Pd:Sn}}$, which were previously unknown in literature, were established. Based on the evaluated polynomial, the isoenthalpy curves of the integral molar enthalpy of mixing in the liquid state were constructed. With the set of equations obtained, it is now possible to calculate the enthalpy of mixing of liquid In–Pd–Sn alloys at any ternary concentration. For the ternary system the experimental results were compared with calculated values obtained by three simple extrapolation models to predict ternary mixing enthalpies based on binary data. It was found that these models give reasonably good results, especially for low Pd contents, whereas the asymmetric model by Toop fits perfectly to our experimental data.

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