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Enthalpies of liquid–liquid mixing in the systems Cu–Ag, Cu–Au and Ag–Au by using an in-situ mixing device in a high temperature single-unit differential calorimeter

K. Fitzner[a,b], Qiti Guo[a,c], Junwen Wang[a,d], O.J. Kleppa[a,]*

[a]*The James Franck Institute, The University of Chicago, 5640 South Ellis Avenue, Chicago, IL 60637, USA*
[b]*Institute of Metallurgy and Materials Engineering, 25 Reymonta Street, 30-059 Krakow, Poland*
[c]*Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, Guizhou Province 550002, People's Republic of China*
[d]*Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, Guangdong Province 510640, People's Republic of China*

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Abstract

The enthalpies of mixing of the binary liquid alloys of copper with silver, copper with gold and silver with gold have been re-determined using a new in-situ mixing technique at 1375±2 K. In this paper we report the following analytical expressions for ΔH_{mix}, derived from the experimental results:

Cu–Ag: $\Delta H_{\text{mix}} = X_{\text{Cu}}X_{\text{Ag}}(16{,}959 - 7{,}620X_{\text{Ag}} + 4{,}287X_{\text{Ag}}^2)$ J/mol

Cu–Au: $\Delta H_{\text{mix}} = X_{\text{Cu}}X_{\text{Au}}(-29{,}506 - 2{,}616X_{\text{Au}} + 9{,}360X_{\text{Au}}^2)$ J/mol

Ag–Au: $\Delta H_{\text{mix}} = X_{\text{Ag}}X_{\text{Au}}(-16{,}803 - 3{,}233X_{\text{Au}} + 4{,}525X_{\text{Au}}^2)$ J/mol

We note that in all of these systems the enthalpy interaction parameter is described by a nonlinear relation to the composition. These new results are compared with earlier data of Kleppa and Watanabe [O.J. Kleppa, S. Watanabe, Met. Trans. 13B (1982) 391–401] and of Topor and Kleppa [L. Topor, O.J. Kleppa, Met. Trans. 15A (1984) 203–208], obtained by dropping one of the two components into the high-temperature calorimeter from room temperature.

Keywords: Enthalpy of mixing; Copper liquid alloys; Silver liquid alloys; Gold liquid alloys; High temperature in-situ mixing calorimetry

1. Introduction

Enthalpy of mixing data for binary systems provide important thermochemical information for industry and for theoretical studies in physics, chemistry and metallurgy. In the past years a large number of heat of mixing data have been determined experimentally and published in the literature. As far as the liquid alloys Cu–Ag, Cu–Au and Ag–Au are concerned, due to the then important discrepancies in the pertinent published thermochemical data, Kleppa and Watanabe [1] and Topor and Kleppa [2] carried out a systematic reinvestigation of these alloys in the early 1980s. During this reinvestigation the basic technique adopted was to drop one solid metal from room temperature into a calorimeter which was maintained at high temperature. In this calorimeter it was mixed with the other metal which was present in the liquid state. We may call this technique the ''solid drop'' mixing technique. The major disadvantages of this technique are well known: In order to obtain the liquid–liquid heat of mixing, it is necessary to correct for the heat content of the solid metal. This correction is usually a large quantity, and is often a value cited from a handbook (e.g., Hultgren et al. [3]). In this case, in addition to the experimental errors in the calorimetric measurements, any errors in the cited heat contents will transfer to the measured heats of mixing. Moreover, at high temperatures the heats of mixing are usually relatively small quantities compared to the heat contents. Hence, no matter whether the enthalpy of mixing is positive or negative, when a solid metal is introduced from room temperature to mix with a different liquid metal at high temperature, the result will usually be a large

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*Corresponding author.

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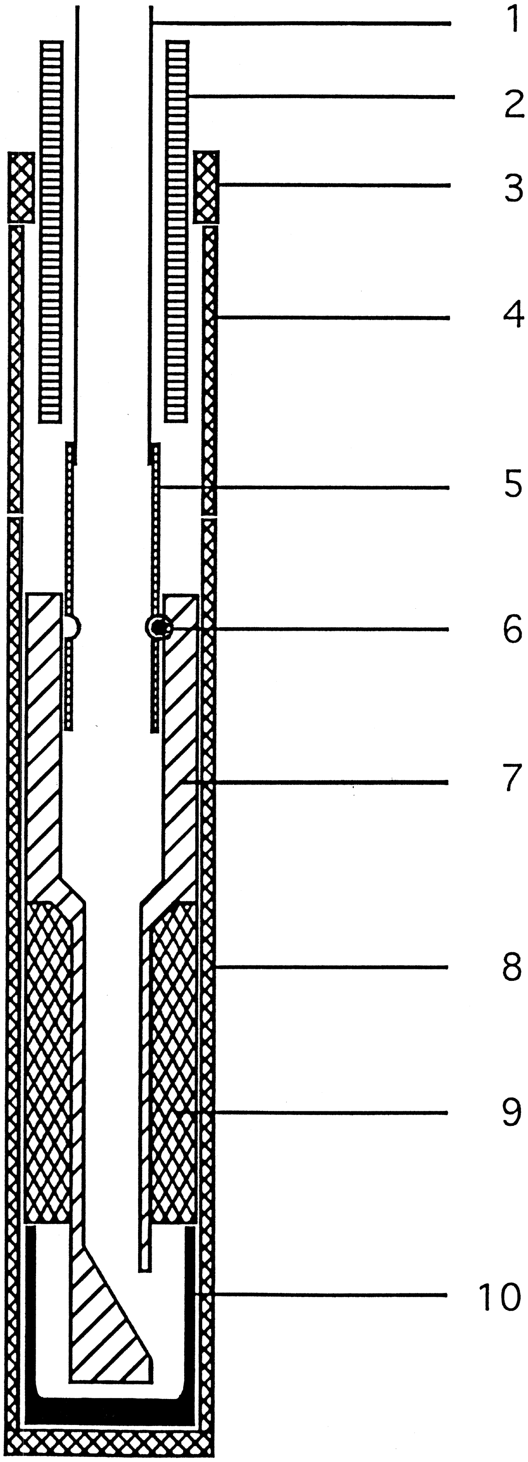

Fig. 1. Schematic diagram of the in-situ mixing device. Part #1: 6-mm O.D. thin wall stainless steel tube. Part #2: alumina tube. Part #3: boron nitride (BN) protective ring. Part #4: BN extension sleeve. Part #5: inconel tip connecting the stainless steel tube and the boron nitride hollow plug. Part #6: tungsten wire. Part #7: movable BN hollow plug. Part #8: BN outer crucible. Part #9: immovable BN collar. Part #10: BN inner (reaction) crucible.

endothermic change in enthalpy. Because the difference between this observed enthalpy change and the large heat content correction is the targeted enthalpy of mixing, the calculated enthalpy of mixing may be associated with a large experimental uncertainty.

To overcome these disadvantages we report in this paper on a new technique, which is designed to allow two liquid metals to be mixed in-situ at high temperatures in our single-unit differential micro-calorimeter [4]. We may call this new technique an ‘‘in-situ’’ mixing technique.

The unique structure of our calorimeter, which has a 20 mm I.D. Pt20Rh liner, provides a big enough space to make room for a specially designed in-situ mixing device (see Fig. 1). With this device, the in-situ mixing can be completed in a two step process. In the first step, a solid metal sample is dropped from room temperature into the BN hollow plug (Part #7) in the calorimeter. At this time the hollow plug is in the ‘‘upper’’ position and the solid metal melts at the calorimeter temperature. In the second step, this melted metal is introduced into the BN crucible (Part #10) in the calorimeter, where it mixes with the other liquid metal. In this second step the heat of mixing is measured. The principles and usefulness of this new technique will be demonstrated in this paper by measuring the enthalpies of mixing of the three binary alloys Cu–Ag, Cu–Au and Ag–Au at 1375±2 K. The results will be compared with the previous values reported by Kleppa and Watanabe [1] and by Topor and Kleppa [2], all obtained by the ‘‘solid-drop’’ technique.

2. In-situ mixing device and experimental procedures

2.1. In-situ mixing device

The in-situ mixing device is schematically shown in Fig. 1. Inside the 20 mm I. D. Pt20Rh liner we place the outer boron nitride (BN) protective crucible (Part #8) with the BN extension (Part #4). This BN extension is closed at the top by the BN ring (Part #3). This ring is designed to prevent zirconium getters to slide into the outer BN crucible (Part #8) along the alumina tube (Part #2).

In the bottom of the outer BN crucible there is an inner BN crucible (Part #10), in which the actual mixing of the two liquid metals takes place. Sitting on top of the inner BN crucible are two parts; both are crucial for the in-situ mixing. Part #9 is an immovable BN collar, while Part #7 is a movable BN hollow plug. This hollow plug is closed at the bottom, but has an opening in its wall close to the bottom. The plug can be moved up and down readily by raising and lowering the stainless steel tube (Part #1). It can be set in two positions by a special mechanism maintained at room temperature. This mechanism holds the stainless steel tube in place and limits the magnitude of its up and down movements. It is set to stay at the ‘‘upper’’ and ‘‘lower’’ positions of the hollow plug. It can be inferred from Fig. 1 that in the upper position the opening of the hollow plug is closed. In this position it retains a liquid metal. In the lower position the retained liquid metal is allowed to flow into the inner crucible (Part #10). The stainless steel tube, which guides samples into the hollow plug when they are dropped into the calorimeter from room temperature, is attached to the hollow plug (Part #7) by a piece of tungsten wire (0.58 mm in diameter) (Part #6). This tungsten wire is kept in position through two small holes through Part #7 and a groove in the inconel tip (Part #5) of the stainless steel tube. The hollow plug also functions as a stirrer.

2.2. Calibration

In our routine direct synthesis experiments, calibration of the calorimeter is achieved by dropping pieces of high purity copper wire of known mass from room temperature into the calorimeter at high temperatures. The enthalpy of pure copper at high temperatures is taken from Hultgren et al. [3]. The calibrations are reproducible within ±1%.

However, when we tried to calibrate our calorimeter with the in-situ mixing device we encountered two problems. The first problem is associated with the mass of the preexisting metals in the crucible. This problem may be explained as follows. Our routine calibration starts with an empty inner crucible and the accumulated mass of copper which is dropped into the calorimeter is usually quite small (<1 g). For this reason, we never tried to determine the calibration factor as a function of the accumulated mass of copper in the crucible. However, when we measure heats of mixing, the situation is different. The experiments usually start with a significant amount of one liquid metal in the crucible and thus end up with more mass accumulated in the crucible. In this case, our first concern was to find out whether there was a noticeable dependence of the calibration factor on the mass of metal in the crucible. To solve this problem, a series of comparisons were made between the calibration factors obtained with an empty starting crucible and the calibration factors measured with a partially filled (3–6 g of liquid Cu) starting crucible. These comparisons showed that within our experimental errors there was no detectable difference between these calibration factors.

The second problem is associated with our in-situ mixing device itself. With this device calibrations have to be done with the hollow plug set in its lower position. Otherwise, copper pieces cannot be dropped into the crucible. In the lower position the plug is located close to the bottom of the inner crucible. This not only significantly reduces the volume for receiving copper pieces in the inner crucible, but it also forces copper pieces to move to the side to fill in the narrow gap between the plug and the crucible. Since the surface tension of liquid copper is quite significant, even after six pieces of copper wire have been dropped into the calorimeter, the liquid copper will not form a ring surrounding the plug. This creates a locally asymmetrical environment within the symmetrical structure of the calorimeter. Obviously, this is a significantly different situation from what happens when the actual mixing is carried out. The actual mixing takes place without the hollow plug located near the bottom of the inner crucible. Hence, the liquid metals are mixed in the central area of the crucible. In order to eliminate this problem we prepared a special plug which is otherwise identical to the hollow plug, but has an open bottom. This special plug is used for calibration only. With this special plug, calibrations may be carried out when the plug is set in its upper position. A comparison was made between the calibration factors obtained from experiments with the hollow plug in the lower position and the calibration factors obtained with the special plug in the upper position. This comparison indicated that the latter was numerically larger than the former by more than 4%. At the same time, the latter also was associated with a much smaller uncertainty than the former.

2.3. Experimental procedures

For mixing experiments, one of the two metals must be pre-placed in the inner crucible of the calorimeter. Before each series of calorimetric experiments, including the calibrations, the liner is flushed at room temperature for about 1 h in a stream of purified argon gas. The liner is then carefully inserted into the calorimeter at 1375±2 K, and is maintained there overnight to attain thermal equilibrium. At this temperature, the metal in the inner crucible is, of course, in the liquid state.

The measurements are carried out in the inert atmosphere of argon. This gas was purified by passing it through a silica tube full of sponge titanium chips, maintained at about 1173 K. This eliminates possible traces of oxygen and nitrogen in the argon gas.

The copper metal used in our experiments was OFHC of 99.99% purity (metal basis), in the form of 2-mm diameter wire. The silver used was electrolytic silver shots of 99.92% purity (metal basis). The 2-mm diameter wire of gold was purchased from Engelhard, and was 99.99% pure (metal basis).

The mixing experiments were initiated by dropping the sample of the solid metal from room temperature into the hollow plug of the mixing device in its upper position in the calorimeter. Here the solid metal melts and attains the calorimeter temperature. During this period, the heat content of this solid metal could be measured if the calorimeter had been calibrated in this position before. Then, the hollow plug is lowered to its lower position to let the liquid metal be introduced into the inner crucible, where it is mixed with the other metal. To promote the mixing, we usually stir the liquid metal mixture by moving the plug up and down two times immediately after the liquid metal in the plug is introduced into the inner crucible. The heat generated from this stirring effect was measured in a separate set of experiments, so that a small correction for the heat of stirring could be made in our final calculations. After the stirring the hollow plug is raised to its upper position again and the heat of mixing of the two liquid metals is then measured.

The heat effect observed in the calorimeter can be assigned to the following reaction.

$$n_1\mathrm{A}(l, 1375\mathrm{K}) + n_2\mathrm{B}(l, 1375\mathrm{K}) = (n_1\mathrm{A} + n_2\mathrm{B})(l, 1375\mathrm{K}) \quad (1)$$

Here, n_1 represents the number of moles of metal A which was placed in the inner crucible before each series of mixing experiments; n_2 is the number of moles of metal B which was dropped into the calorimeter at the beginning of each individual experiment.

3. Results and discussions

Our preliminary and final experimental results for the enthalpies of mixing of the liquid alloys Cu–Ag, Cu–Au and Ag–Au are listed in Tables 1–6. The results are also presented graphically in Figs. 2–4. In these figures our new data are compared with previous calorimetric values

Table 1
Preliminary results of enthalpies of mixing for Cu (liquid)+Ag (liquid) at 1378±2 K

No	n_{Cu} (mmol)	n_{Ag} (mmol)	$n_{Cu}+n_{Ag}$ (mmol)	X_{Ag} (mol%)	ΔH_{mix} (J/mol)
P1	47.6458		47.6458	0	0
P2	1.6256		49.2714	0	0
P3		2.5457	51.8171	0.0491	667
P4		2.8414	54.6585	0.0986	1291
P5		1.2747	55.9332	0.1191	1519
P6		1.9394	56.8726	0.1512	1825
P7		2.6884	60.5610	0.1864	2164
P8	40.4290		40.4290	0	0
P9	1.4777		41.9067	0	0
P10		3.5265	45.4332	0.0776	1108
P11		2.9758	48.4090	0.1343	1785
P12		3.3911	51.8001	0.1910	2296
P13		3.5098	55.3099	0.2423	2674
P14		2.9573	58.2672	0.2808	2902
P15		3.6062	61.8734	0.3227	3108
P16		19.7720	19.7720	1.0000	0
P17		1.9106	21.6826	1.0000	0
P18	0.7742		22.4568	0.9655	463
P19	1.1016		23.5584	0.9204	994
P20	1.2338		24.7922	0.8746	1460
P21		11.6585	11.6585	1.0000	0
P22		1.6223	13.2808	1.0000	0
P23	1.2652		14.5460	0.9130	1066
P24	1.8679		16.4139	0.8091	2132
P25	1.8711		18.2850	0.7263	2737
P26	1.7719		20.0569	0.6622	3031
P27	2.0395		22.0964	0.6010	3221
P28	2.0190		24.1154	0.5507	3329

Table 2
Final results of enthalpies of mixing for Cu (liquid)+Ag (liquid) at 1375±2 K

No	n_{Cu} (mmol)	n_{Ag} (mmol)	$n_{Cu}+n_{Ag}$ (mmol)	X_{Ag} (mol%)	ΔH_{mix} (J/mol)
F1	47.2949		47.2949	0	0
F2	1.9608		49.2557	0	0
F3		2.5476	51.8032	0.0492	750
F4		2.9068	54.7100	0.1000	1389
F5		3.2141	57.9241	0.1497	1927
F6		3.6378	61.5619	0.1999	2375
F7		4.1041	65.6660	0.2499	2730
F8	31.5425		31.5425	0	0
F9	1.9694		33.5119	0	0
F10		6.0639	39.5758	0.1532	2091
F11		6.0574	45.6332	0.2656	3000
F12	25.2573		25.2573	0	0
F13	2.1669		27.4242	0	0
F14		3.7611	31.1853	0.1206	1703
F15		4.4388	35.6241	0.2302	2740
F16		5.2935	40.9176	0.3298	3362
F17		7.2116	48.1291	0.4302	3598
F18	47.8409		47.8409	0	0
F19	1.9860		49.8269	0	0
F20		1.0253	50.8522	0.0202	350
F21		1.0596	51.9119	0.0402	665
F22		1.0939	53.0058	0.0600	957
F23		1.1570	54.1628	0.0801	1225
F24		19.9735	19.9735	1.0000	0
F25		1.9301	21.9036	1.0000	0
F26	1.1472		23.0508	0.9502	621
F27	1.2920		24.3428	0.8998	1206
F28	1.4305		25.7732	0.8499	1700
F29	1.6177		27.3910	0.7997	2188
F30	1.8207		29.2117	0.7498	2555
F31	2.0820		31.2936	0.6999	2837
F32		23.2729	23.2729	1.0000	0
F33		1.9487	25.2219	1.0000	0
F34	3.4447		28.6675	0.8798	1476
F35	4.0821		32.7483	0.7702	2443
F36	5.4433		38.1917	0.6604	3052
F37		23.2302	23.2302	1.0000	0
F38		1.8745	25.1047	1.0000	0
F39	9.2893		34.3940	0.7299	2889
F40	6.0964		40.4904	0.6200	3433
F41	2.7980		43.2884	0.5799	3515
F42	6.9210		50.2094	0.5000	3640
F43	8.6583		8.6583	0	0
F44	1.6020		10.2603	0	0
F45		10.2523	20.5126	0.4998	3523
F46	8.1736		8.1736	0	0
F47	2.0332		10.2068	0	0
F48		10.2051	20.4118	0.5000	3518
F49	10.1391		10.1391	0	0
F50	1.8931		12.0322	0	0
F51		8.0255	20.0578	0.4001	3479
F52		4.0058	24.0636	0.5000	3538
F53		8.8617	8.8617	1.0000	0
F54		1.8328	10.6945	1.0000	0
F55	10.6930		21.3876	0.5000	3559
F56		9.3308	9.3308	1.0000	0
F57		1.8078	11.1386	1.0000	0
F58	4.7729		15.9115	0.7000	2721
F59		9.4866	9.4866	1.0000	0
F60		1.7614	11.2480	1.0000	0
F61	7.4938		18.7418	0.6002	3349

Table 3
Preliminary results of enthalpies of mixing for Cu (liquid) + Au (liquid) at 1378±2 K

No	n_{Cu} (mmol)	n_{Au} (mmol)	$n_{Cu}+n_{Au}$ (mmol)	X_{Au}	ΔH_{mix} (J/mol)
P1		10.9509	10.9509	1.0000	0
P2		0.6169	11.5678	1.0000	0
P3	0.8451		12.4129	0.9319	−1678
P4	0.8608		13.2737	0.8715	−2820
P5	1.1016		14.3753	0.8047	−3930
P6	1.0087		15.3840	0.7519	−4764
P7	1.1330		16.5170	0.7004	−5501
P8		10.7164	10.7164	1.0000	0
P9		0.6260	11.3424	1.0000	0
P10	0.9772		12.3196	0.9207	−1742
P11	0.9946		13.3142	0.8519	−3227
P12	1.1472		14.4614	0.7843	−4477
P13	1.1645		15.6259	0.7259	−5291
P14	1.1991		16.8250	0.6741	−5963
P15	11.0393		11.0393	0	0
P16	1.5485		12.5878	0	0
P17		0.7001	13.2879	0.0527	−1482
P18		0.9392	14.2271	0.1152	−2959
P19		0.9814	15.2085	0.1723	−4247
P20		0.9667	16.1751	0.2218	−5213
P21		0.8986	17.0737	0.2627	−5873
P22		1.0357	18.1094	0.3049	−6403
P23	19.9021		19.9021	0	0
P24	1.4950		21.3971	0	0
P25		1.0920	22.4891	0.0486	−1478
P26		1.1885	23.6776	0.0963	−2810
P27		1.1692	24.8468	0.1388	−3728
P28		1.2611	26.1079	0.1804	−4573

Table 4
Final results of enthalpies of mixing for Cu (liquid) + Au (liquid) at 1375±2 K

No	n_{Cu} (mmol)	n_{Au} (mmol)	$n_{Cu}+n_{Au}$ (mmol)	X_{Au} (mol%)	ΔH_{mix} (J/mol)
F1	15.9979		15.9979	0	0
F2	1.6508		17.6487	0	0
F3		0.8443	18.4929	0.0457	−1309
F4		1.0824	19.5754	0.0984	−2608
F5		1.2276	20.8030	0.1516	−3807
F6		1.2619	22.0649	0.2002	−4706
F7		1.4657	23.5306	0.2500	−5538
F8		2.0425	25.5731	0.3099	−6329
F9	12.7829		12.7829	0	0
F10	1.6382		14.4211	0	0
F11		5.3131	19.7341	0.2692	−5789
F12		2.4502	22.1843	0.3499	−6648
F13		1.8689	24.0532	0.4005	−6978
F14		2.1803	26.2335	0.4503	−7125
F15		2.5911	28.8245	0.4997	−7135
F16		12.0990	12.0990	1.0000	0
F17		1.2614	13.3604	1.0000	0
F18	1.4887		14.8491	0.8998	−2213
F19	1.8522		16.7013	0.8000	−4037
F20	2.3762		19.0775	0.7003	−5511
F21	3.2087		22.2862	0.5995	−6589
F22	2.0096		24.2958	0.5499	−6962
F23	2.4234		26.7192	0.5000	−7209
F24	13.2203		13.2203	0	0
F25	2.0001		15.2205	0	0
F26		3.1269	18.3474	0.1704	−4105
F27		2.5032	20.8506	0.2700	−5834
F28		2.5690	23.4196	0.3501	−6774
F29		2.8370	26.2566	0.4203	−7190
F30		2.4563	28.7129	0.4699	−7294
F31		1.1357	29.8486	0.4901	−7285
F32		12.4950	12.4950	1.0000	0
F33		1.2525	13.7475	1.0000	0
F34	0.7648		14.5123	0.9473	−1192
F35	1.6846		16.1969	0.8488	−3241
F36	2.1355		18.3324	0.7499	−4851
F37	2.8405		21.1728	0.6493	−6142
F38	2.5273		23.7001	0.5801	−6649
F39	3.7894		27.4895	0.5001	−7021

obtained for these systems by the ''solid drop'' technique by Kleppa and Watanabe [1] and by Topor and Kleppa [2]. For the sake of simplicity, we will not compare our new results with data other than those in [1] and [2]. Kleppa and Watanabe [1] and Topor and Kleppa [2] already compared their data with earlier values in the literature [5–13].

The preliminary results and the final results are different for the following reasons:

All the results that are considered as final were obtained with a brand new Pt20Rh liner. The preliminary results were obtained with the old Pt20Rh liner. This liner was later proved to have a small leak in a position just above the mixing device. The possible consequences of this leak may be summarized as follows. A) This leak may let small amounts of air get into the liner of the calorimeter at high temperatures. Therefore, when the calorimeter was calibrated with pure copper, the copper might be slightly oxidized, resulting in a small exothermic effect. Because calibrations with pure copper always give rise to an endothermic value, this exothermic effect may have lowered the calibration factor f_{Cu} (in counts/Joule). This may affect all the later enthalpy calculations. B) During experiments on Cu-containing systems, oxidation of Cu may influence the total counts, thus adding an additional error to the final calculated enthalpy values. C) The correction for the heat of stirring in our preliminary experiments was not accurate. This correction was measured in the leaking liner. To determine the heat generated by the stirring the hollow plug was moved up and down 25 times in a pool of Cu in the inner BN crucible. The up and down movement is in fact equivalent to switching the inner crucible between closing and opening. This movement inevitably introduces more gas into the inner crucible. Hence, the heat of oxidation of copper is added to the effect of stirring, which results in a numerically higher correction value. This effect can be seen very clearly from a comparison between the heat of stirring corrections in the old liner and in the new liner. With the old liner we found a stirring heat correction of about −0.25 J/stir; with the new liner this correction was reduced to about −0.077

Table 5
Preliminary results of enthalpies of mixing for Ag (liquid)+Au (liquid) at 1378±2 K

No	n_{Ag} (mmol)	n_{Au} (mmol)	$n_{Ag}+n_{Au}$ (mmol)	X_{Au}	ΔH_{mix} (J/mol)
P1	16.3614		16.3614	0	0
P2	0.6397		17.0011	0	0
P3		1.1184	18.1195	0.0617	−910
P4		1.2540	19.3735	0.1225	−1723
P5		1.0428	20.4163	0.1673	−2266
P6		1.1438	21.5601	0.2115	−2792
P7		1.6561	23.2162	0.2677	−3238
P8	13.3846		13.3846	0	0
P9	0.8102		14.1948	0	0
P10		0.8900	15.0848	0.0590	−878
P11		1.0509	16.1357	0.1203	−1636
P12		1.1398	17.2755	0.1783	−2356
P13		1.0748	18.3503	0.2265	−2930
P14		1.1423	19.4926	0.2718	−3288
P15		1.1555	21.8036	0.2960	−3370
P16		9.6634	9.6634	1.0000	0
P17		0.6346	10.2980	1.0000	0
P18	0.7240		11.0220	0.9343	−1007
P19	0.7110		11.7330	0.8777	−1788
P20	1.1366		12.8696	0.8002	−2683
P21	1.1245		13.9941	0.7359	−3260
P22	0.9919		14.9860	0.6872	−3523
P23		8.2058	8.2058	1.0000	0
P24		0.6874	8.8932	1.0000	0
P25	1.1505		10.0437	0.8855	−1638
P26	1.4035		11.4472	0.7769	−2851
P27	1.4175		12.8647	0.6913	−3594
P28	1.5296		14.3943	0.6178	−4015
P29	1.5108		15.9045	0.5591	−4222
P30	1.5176		17.4221	0.5104	−4347

Table 6
Final results of enthalpies of mixing for Ag (liquid)+Au (liquid) at 1375±2 K

No	n_{Ag} (mmol)	n_{Au} (mmol)	$n_{Ag}+n_{Au}$ (mmol)	X_{Au} (mol%)	ΔH_{mix} (J/mol)
F1		10.2190	10.2190	1.0000	0
F2		1.0520	11.2710	1.0000	0
F3	1.2543		12.5253	0.8999	−1490
F4	1.5686		14.0938	0.7997	−2746
F5	2.0089		16.1028	0.6999	−3580
F6	2.6977		18.8005	0.5995	−4115
F7	3.7323		22.5328	0.5002	−4327
F8		10.4901	10.4901	1.0000	0
F9		1.1535	11.6436	1.0000	0
F10	1.2970		12.9406	0.8998	−1378
F11	1.6307		14.5713	0.7991	−2604
F12	2.0711		16.6423	0.6996	−3538
F13	2.7673		19.4096	0.5999	−4042
F14	3.8705		23.2800	0.5002	−4301
F15	9.5663		9.5663	0	0
F16	1.8634		11.4297	0	0
F17		0.8575	12.2872	0.0698	−1112
F18		1.1677	13.4549	0.1505	−2154
F19		1.7856	15.2405	0.2500	−3199
F20		2.3430	17.5835	0.3500	−3920
F21		3.2579	20.8414	0.4516	−4266
F22	9.4755		9.4755	0	0
F23	1.9607		11.4362	0	0
F24		0.4917	11.9279	0.0412	−660
F25		0.8006	12.7285	0.1015	−1607
F26		1.5663	14.2948	0.2000	−2761
F27		2.0422	16.3370	0.3000	−3683
F28		2.7192	19.0563	0.3999	−4248

J/stir. This correction was used in the calculation of all the final measurements. D) The stainless steel tube suffered pronounced oxidation during our preliminary experiments using the old liner. For this reason, we were forced to replace this tube quite frequently. This oxidation may also have slightly influenced our heat of mixing measurements. Because our new Pt20Rh liner eliminated this leak, in our final experiments the stainless steel tube came out from the calorimeter still shiny, indicating a negligible oxidation of the tube.

Another difference between our preliminary and final experiments was in the reaction time setting. All the final experiments were set to react for 2000 s and 2000-s calibration factors were also used. However, in our preliminary experiments the reaction time was sometimes set for a somewhat shorter time.

3.1. The Cu–Ag system

Tables 1 and 2 give the results of our new experiments in detail. In these tables, as in all later tables, the preliminary experiments are prefixed with the letter P, while the final experiments are prefixed with the letter F. Our new results for heats of mixing, ΔH_{mix}, and the corresponding enthalpy interaction parameters λ ($\lambda = \Delta H_{mix}/(X_{Cu}X_{Ag})$) are plotted against alloy composition in Fig. 2. The previous values given by Kleppa and Watanabe [1] are also shown in the same figure. The final results for the enthalpies of mixing for the Cu–Ag system can be described by the following equation:

$$\Delta H_{mix} = X_{Cu}X_{Ag}(16\,959 - 7\,620X_{Ag} + 4\,287X_{Ag}^2)\ \mathrm{J/mol} \tag{2}$$

Fig. 2 shows that our final results for ΔH_{mix} are in very good agreement with the preliminary values in the composition range from $X_{Ag}=0.66$ to $X_{Ag}=1.00$, but are more endothermic from $X_{Ag}=0$ to $X_{Ag}=0.66$. This difference may well be caused by the slight oxidation of Cu in our preliminary experiments, which were carried out in the old leaking liner. Our final results for ΔH_{mix} are in reasonable agreement with the values of Kleppa and Watanabe [1] for low values of X_{Ag}, and are slightly more endothermic for high values of X_{Ag}. However, in the middle of the system both our preliminary and final results are somewhat less endothermic than those determined by Kleppa and Watanabe. Significant difference between our results and those of Kleppa and Watanabe is seen in the enthalpy interaction parameter λ. Kleppa and Watanabe's λ was

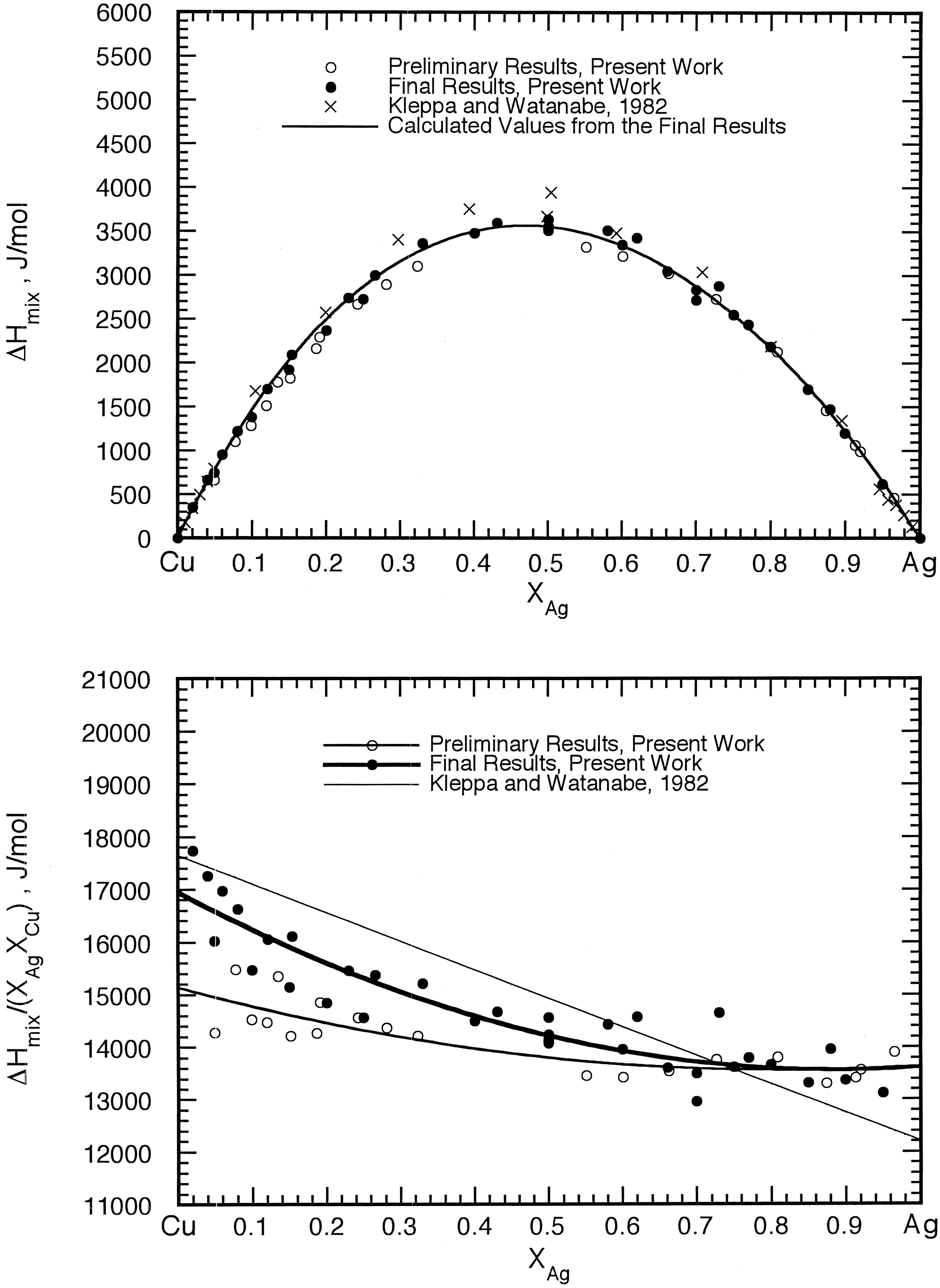

Fig. 2. Molar enthalpy of mixing (upper figure) and the enthalpy interaction parameter (lower figure) in the liquid system of Cu–Ag. The solid curve in the heat of mixing figure is calculated from Eq. (2).

presented as a linear function of composition, while our λ shows a definite nonlinear character. This reflects the fact that in-situ liquid–liquid mixing is more sensitive to details of the dependence of the enthalpy interaction parameter on composition.

3.2. The Cu–Au system

Our new experimental data are listed in Tables 3 and 4. The enthalpy of mixing, ΔH_{mix}, and the enthalpy interaction parameter, λ, are also shown graphically in Fig. 3

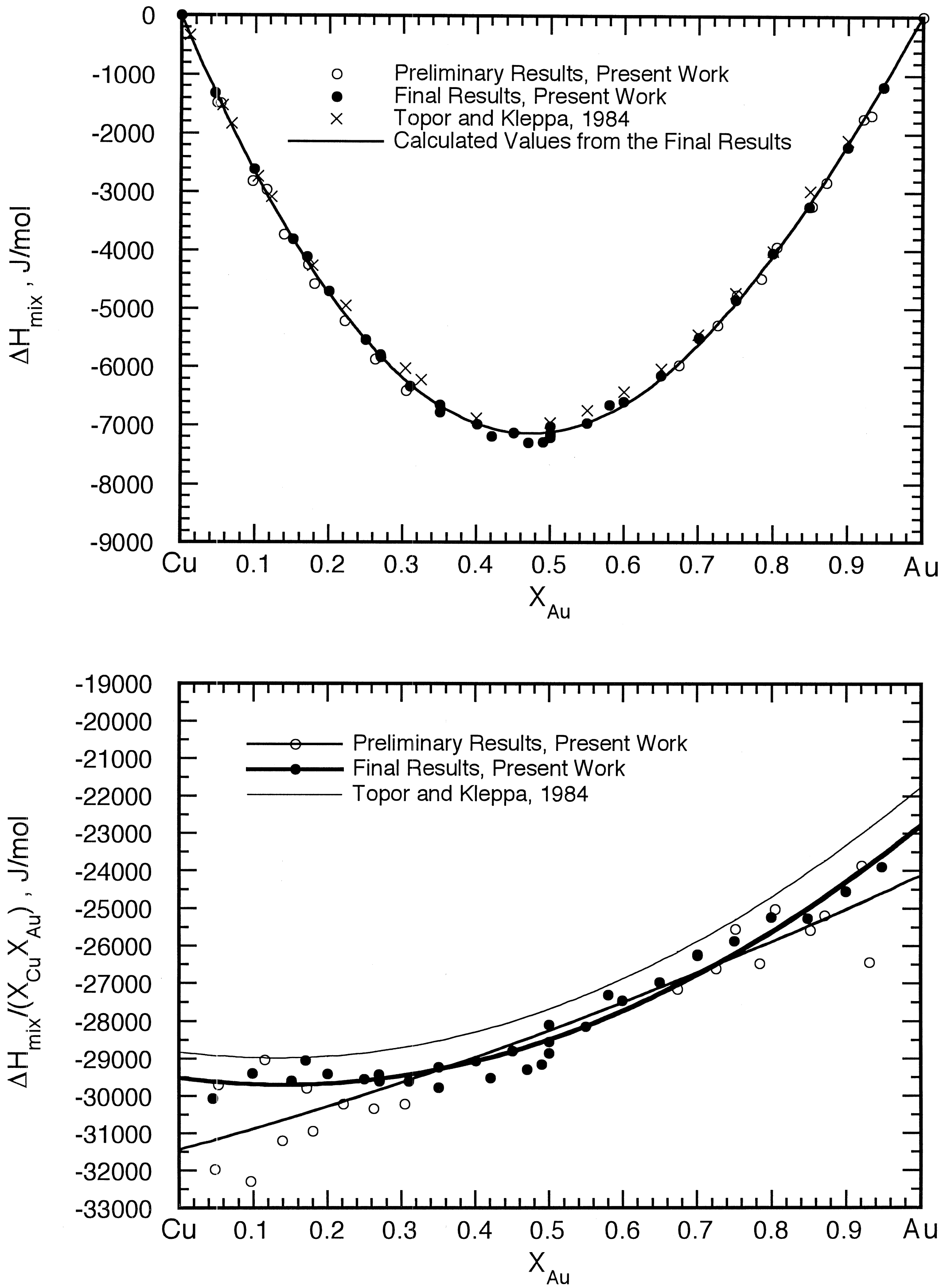

Fig. 3. Molar enthalpy of mixing (upper figure) and the enthalpy interaction parameter (lower figure) in the liquid system of Cu–Au. The solid curve in the heat of mixing figure is calculated from Eq. (3).

along with the earlier data of Topor and Kleppa [2]. Both from the tables and from the figure we see that the agreement between our preliminary and final values of ΔH_{mix} is generally good for alloy compositions ranging from $X_{\mathrm{Au}}=0.68$ to $X_{\mathrm{Au}}=1.00$. However, from $X_{\mathrm{Au}}=0.1$ to $X_{\mathrm{Au}}=0.3$ our final results are slightly less exothermic than our preliminary results. The previous values published by Topor and Kleppa [2] are, in general, in good agreement with our final results, but are somewhat less exothermic over the whole range of compositions.

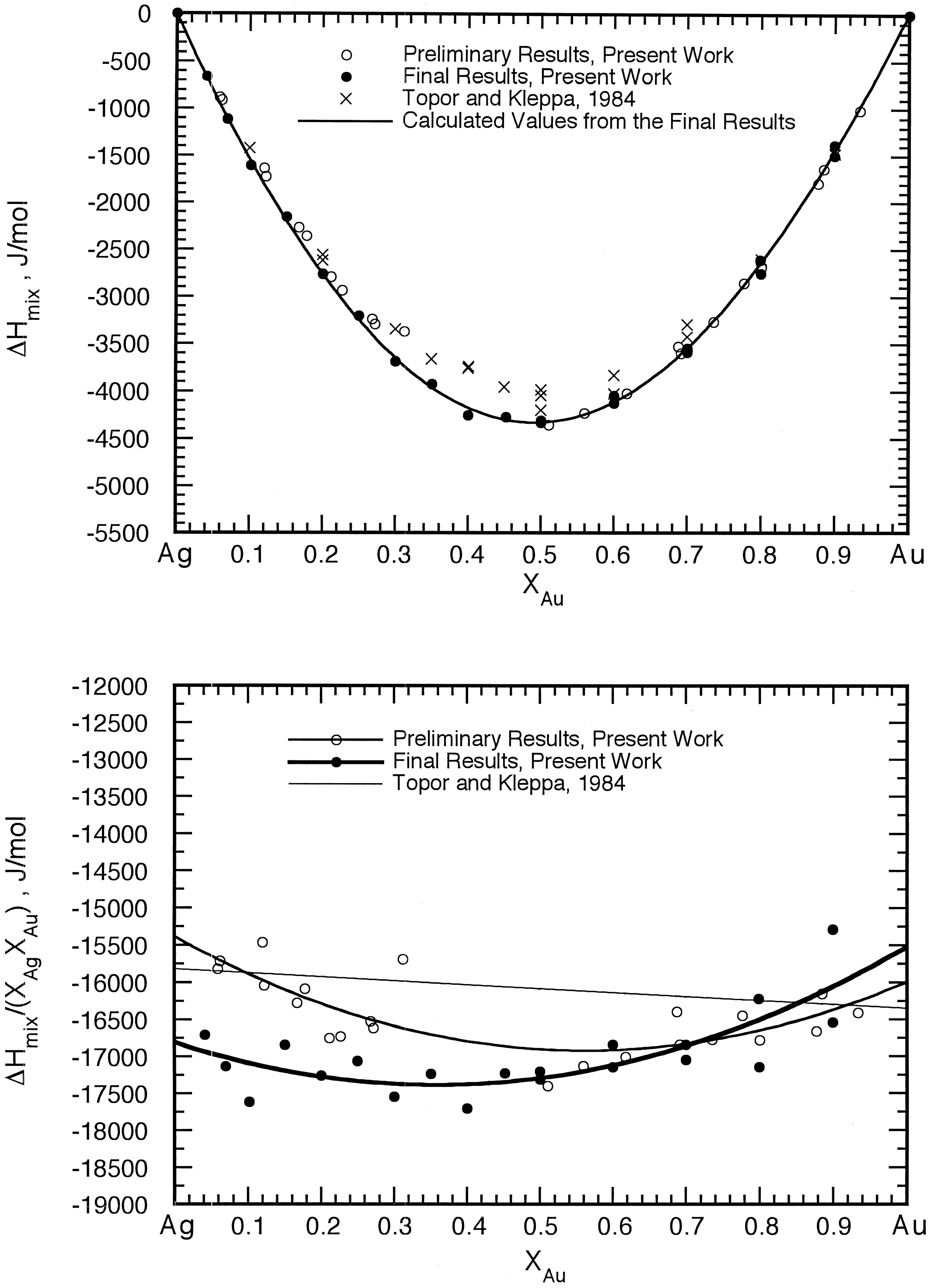

Fig. 4. Molar enthalpy of mixing (upper figure) and the enthalpy interaction parameter (lower figure) in the liquid system of Ag–Au. The solid curve in the heat of mixing figure is calculated from Eq. (6).

The enthalpies of mixing for liquid alloys of Cu with Au can be described by the analytical expression

$$\Delta H_{\mathrm{mix}} = X_{\mathrm{Cu}} X_{\mathrm{Au}} (-29\,506 - 2\,616 X_{\mathrm{Au}} + 9\,360 X_{\mathrm{Au}}^{2})\ \mathrm{J/mol} \qquad (3)$$

It is well known that negative enthalpies of mixing indicate a tendency toward short-range order in the solution. This phenomenon can be described by the quasi-chemical theory [14], which also predicts a nonlinear dependence of the enthalpy interaction parameter on composition. The observed negative enthalpy data in the present work are consistent with the fact that ordering is observed in the solid solution of Cu–Au at lower temperatures where the ordered compounds Cu_3Au, CuAu and $CuAu_3$ are formed. As for the enthalpy interaction parameter, λ, our preliminary values failed to show an obvious nonlinear dependence on the composition. However, our final experiments reveal a definite nonlinear curve, very similar to that indicated by the results of Topor and Kleppa [2]. This nonlinear curve clearly indicates that certain aspects of quasi-chemical theory [14] should apply to the Cu–Au system, as already suggested by Topor and Kleppa [2]. It is also interesting to see from Fig. 3 that our curve for λ is essentially parallel to the curve given by Topor and Kleppa [2]. It implies that there is only a small systematic shift in the heat of mixing from the values of Topor and Kleppa [2] to our final values.

Based on the quasi-chemical theory [14], Topor and Kleppa [2] estimated the nearest neighbor coordination number, z, in liquid Cu–Au alloys from the following equation:

$$z \approx -\frac{2\lambda^2}{cRT} \tag{4}$$

Here, R is the gas constant, T is the thermodynamic temperature, while λ is the average value of the enthalpy interaction parameter, which equals to $a+\frac{b}{2}$, and a, b and c are all the coefficients in the following equation:

$$\Delta H_{\text{mix}} = X_{\text{Au}}(1-X_{\text{Au}})[a+bX_{\text{Au}}+cX_{\text{Au}}(1-X_{\text{Au}})] \tag{5}$$

As mentioned in [2] for closed-packed liquid metals, such as pure copper and pure gold, one would expect a value of z somewhat lower than 12. A comparable value should be found in liquid copper–gold alloys. The value of z actually calculated from the experimental enthalpy of mixing data in [2] was 11.7. This is probably too high, but is in reasonable agreement with our expectation. From the new experimental results, the calculated value of $z \approx 12.8$, also is in fair agreement with the expectation. Note, however, that the Cu–Au system is energetically very asymmetrical. Therefore, the estimate of $\lambda \approx a+\frac{b}{2}$ is somewhat uncertain.

3.3. The Ag–Au system

The results of our experiments on this system are listed in Tables 5 and 6. The heats of mixing, ΔH_{mix}, and the enthalpy interaction parameters, λ, are plotted against the liquid alloy composition in Fig. 4. For this system, our preliminary results are very close to the values published by Topor and Kleppa [2] in the composition ranges from $X_{\text{Au}}=0$ to about 0.30 and from $X_{\text{Au}}=0.70$ to 1.00, but are more exothermic in the middle of the system. Our final results are in excellent agreement with our preliminary results in the composition range between $X_{\text{Au}}=0.50$ and $X_{\text{Au}}=1.00$, but are more exothermic between $X_{\text{Au}}=0$ and $X_{\text{Au}}=0.50$. The heats of mixing can be described by the following Eq.:

$$\Delta H_{\text{mix}} = X_{\text{Ag}}X_{\text{Au}}(-16{,}803-3{,}233X_{\text{Au}}+4{,}525X_{\text{Au}}^2)\ \text{J/mol} \tag{6}$$

It is interesting to mention how the value of the heat of mixing in this system has changed with time since the early 1930s. In the first high temperature calorimetric study carried out at 1473 K, Kawakami [15] found that the heats of mixing for both Cu–Ag and Ag–Au were close to 0. Years later Wagner [16] pointed out that the accepted phase diagram for Ag–Au was not in accord with the then available thermodynamic properties of solid and liquid alloys in this system. Six years later, Kleppa [17] showed that the difference between the free energies of formation of the solid alloy and the liquid alloy must be very small to be compatible with the narrow liquidus–solidus gap that was predicted by Wagner [16]. Consequently, they must both be negative since the enthalpies of mixing for the liquid alloys are negative. The study by Topor and Kleppa [2] showed negative enthalpies of mixing for liquid Ag–Au alloys, which are in reasonable agreement with our new data. However, as in the system Cu–Ag, a significant difference is observed in the enthalpy interaction parameters. Topor and Kleppa's λ was presented as a linear function of the alloy composition, while our λ is a nonlinear function (see Fig. 4). This nonlinear dependence suggests the possible presence of short-range order in the liquid alloys and one should also expect some ordering to take place in the solid Ag–Au alloys at low temperatures. However, to the best of our knowledge this ordering has not as yet been observed.

Using the quasi-chemical theory, we also carried out a calculation of z, the nearest neighbor coordination number, from our experimental enthalpy of mixing data for Ag–Au liquid alloys. The result was $z \approx 10.1$, in remarkably good agreement with our expectation. Since this system is energetically nearly symmetrical, the estimate of $\lambda \approx a+\frac{b}{2}$ is more realistic than for the Cu–Au system.

4. Concluding remarks

It is apparent from this reinvestigation of the heats of mixing of the liquid alloys Cu–Ag, Cu–Au and Ag–Au, that our in-situ mixing technique is a better method to determine the liquid–liquid heats of mixing at high temperatures than the traditional ‘‘solid drop’’ technique. It has, for example, allowed us to obtain good information on the nonlinear character of the enthalpy interaction parameters for all the three liquid alloy systems. Moreover, the in-situ technique has the following additional advantages. A) It avoids the introduction of errors associated with the heat contents of dropped solid samples. This is particularly important when small heats of mixing are involved. B) It enables us to work on quite small samples. This is especially meaningful when hazardous materials (say, radioactive elements) are involved. C) This technique may also be used to measure the heat effects associated with dissolution of solid metals and alloys in appropriate liquid metals. However, our in-situ technique also has some restrictions. The most important restriction is that only those metals that do not wet boron nitride (BN) in the liquid state can be investigated. Also, any small difference in temperature (in our case about 1.5 K) between the upper position and the lower position of the hollow plug in the calorimeter may give rise to small errors in the measurements when the plug is moved up and down. Finally, our present construction of the in-situ mixing device does not allow a large amount of liquid solvent to be used in the experiments.

Acknowledgements

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