

Calorimetric investigation of the Au–Pb system

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Abstract

The enthalpy of formation h^f of Au–Pb alloys was measured at 695, 871 and 1123 K by direct reaction calorimetry (drop method) with the help of a high temperature Calvet calorimeter. The measurements led to the following equations: h^f (kJ mol^{-1}) = $x_{\text{Au}}(1 - x_{\text{Au}})$ ($-12.2686 + 8.1423x_{\text{Au}}$) at 695 K; h^f (kJ mol^{-1}) = $x_{\text{Au}}(1 - x_{\text{Au}})$ ($-6.1750 + 3.4653x_{\text{Au}}$) at 871 K; h^f (kJ mol^{-1}) = $x_{\text{Au}}(1 - x_{\text{Au}})$ ($-4.4416 + 5.6702x_{\text{Au}}$) at 1123 K. We also obtained the boundary of the liquid+Au(s) region from the breaks in the $h^f(x_{\text{Au}})$ curves. From our enthalpic data and those of the literature for the free enthalpy of formation we calculated at 695, 871 and 1123 K the mole fractions corresponding to the gold-rich liquidus were in good agreement with our experimental values. Our investigation allows us to state definitely that the enthalpy of formation depends strongly on the temperature. The positive excess heat capacity suggests accentuated short-range order in the melts which has to be investigated with reference to associated models.

1. Introduction

The enthalpy of formation h^f of Au–Pb liquid alloys was determined by calorimetry by Kleppa at 623 and 723 K [1] and by Béja [2] at 823 and 923 K. Hager and Walker at 1200 K [3], Kameda *et al.* at 1223 K [4] and Kleppa at 873 K [5] also derived the enthalpy of mixing from their e.m.f. measurements. The trends of the enthalpy of mixing of the Au–Pb melts as a function of composition are shown in Fig. 1. h^f appears to be strongly temperature dependent. Moreover, after Kleppa at 873 K and Hultgren *et al.*, the enthalpy of mixing changes sign with respect to composition but in the opposite manner. Thus it is obvious that the temperature and composition dependences of the enthalpy of mixing are not yet well established. In contrast the free enthalpy of formation of the melts is well known, since the data of Hager and Walker [3] and of Rebouillon [6] at 1200 K are in good agreement (Fig. 2).

In their critical assessment, Okamoto and Massalski [7] considered two models for their phase diagram evaluation: the first with temperature-dependent h^f values very close to that selected by Hultgren *et al.* at 1200 K [8] and the second with temperature-independent values very close to that of Hultgren *et al.* for $x_{\text{Au}} > 0.7$ and close to that of Kameda *et al.* for $x_{\text{Au}} < 0.7$. However, things are not becoming clearer from the point of view of h^f since the phase

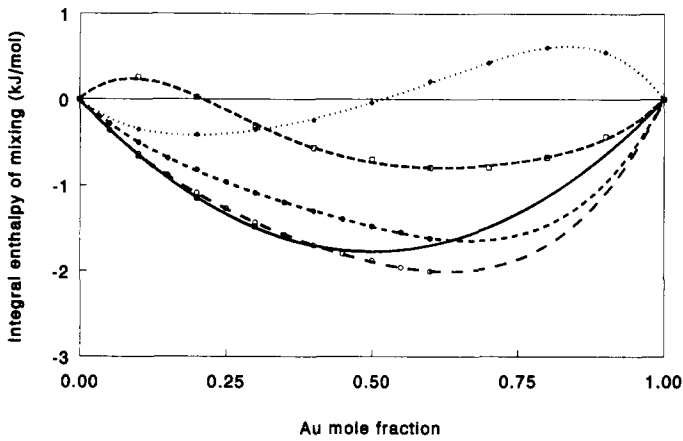


Fig. 1. Molar enthalpy of formation of the Au-Pb liquid alloys with reference to both liquid components according to the literature: ■, after Kleppa, 723 K [1]; ○, after Béja, 823 K [2]; ●, after Béja, 923 K [2]; ◆, after Kleppa, 873 K [5]; □, after Hultgren *et al.*, 1200 K [8].

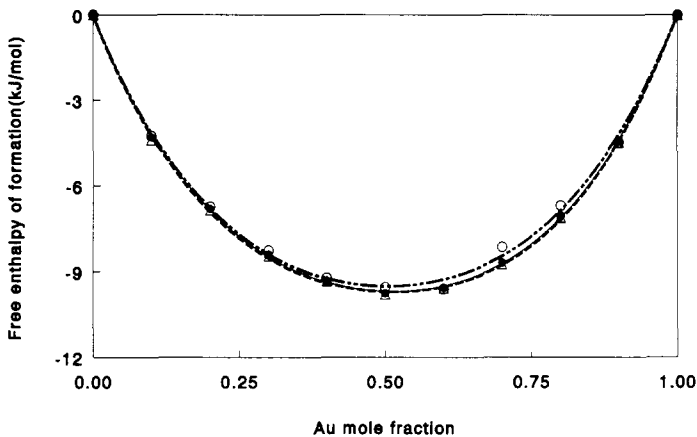


Fig. 2. Molar free enthalpy of formation at 1200 K of the Au-Pb liquid alloys according to the literature: ●, after Hultgren *et al.* [8]; △, after Hager and Walker [3]; ○, after Rebouillon [6].

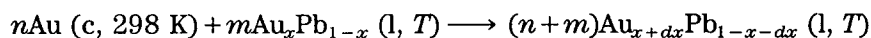
diagrams calculated according to these two situations are very close to each other and calculations did not allow Okamoto and Massalski to settle the question of temperature dependence of the enthalpy of mixing.

Since available experimental results on the enthalpy of formation of the liquid phase are conflicting and cannot be settled by phase diagram calculations, we carried out calorimetric determinations of the enthalpy of mixing of the Au-Pb liquid alloys with respect to temperature and composition by direct reaction calorimetry.

2. Calorimetric method

The apparatus employed was a high temperature Calvet calorimeter ($T < 1400$ K). The drop method used (direct reaction calorimetry) has already been described [9]. The enthalpy of formation h^f was deduced from the heat effects corresponding to successive additions of small quantities of gold (from about 20 to 200 mg according to the gold content) at T_0 (near 298 K) into an $\text{Au}_x\text{Pb}_{1-x}$ binary alloy placed in an Al_2O_3 crucible at the bottom of the calorimetric cell at temperature T . Before the first addition of gold the melt was pure lead (about 800 mg).

Thus the thermal effects correspond to the reaction



where c and l denote crystalline and liquid phase respectively. These effects lead to the integral enthalpy of formation of the melt with respect to composition. The enthalpy difference between two successive additions of gold allows us to determine a mean value of the partial enthalpy of gold in the liquid referred to the averaged composition.

The pure metals used were purchased from Koch-Light with metallic impurities less than 10^{-3} mass%. The calibration of the calorimeter was performed by adding small quantities of pure lead (c, 298 K) into pure lead (l, T). The enthalpy change of lead was taken from ref. 10. The calibration data were controlled by adding some small pieces of $\alpha\text{-Al}_2\text{O}_3$ whose enthalpy change from T_0 to T is well known [11].

The enthalpy of formation of liquid Au–Pb alloys was determined at three temperatures between the melting points of lead and gold (695, 871 and 1123 K). The breaks in the integral enthalpy of mixing curve with respect to composition allowed us to determine the liquidus mole fractions at the temperatures investigated.

3. Results

Figure 3 shows the molar integral enthalpy of formation of the melt at 695 K with reference to the pure liquid components. The corresponding data given in Table 1 lead to the following equation:

$$h^f (\text{kJ mol}^{-1}) = x_{\text{Au}}(1 - x_{\text{Au}})(-12.2686 + 8.1423x_{\text{Au}})$$

The break at $x_{\text{Au}} = 0.47$ corresponds to the liquid–(liquid + pure solid Au) boundary (the extrapolation up to $x_{\text{Au}} = 1$ of the straight line for $x_{\text{Au}} > 0.47$ leads to the enthalpy of crystallization of gold). The phase boundary was determined as the intersection between the extrapolations of the linear dependence in the two-phase region and the enthalpy of the liquid single phase. The smooth variation near the liquidus (instead of an angular break) was already observed in the case of Ag–Te alloys [12].

The integral enthalpy of mixing is negative in the whole range of concentrations with a minimum of $h_{\text{min}}^f = -2.16 \text{ kJ mol}^{-1}$ at $x_{\text{Au}} = 0.39$

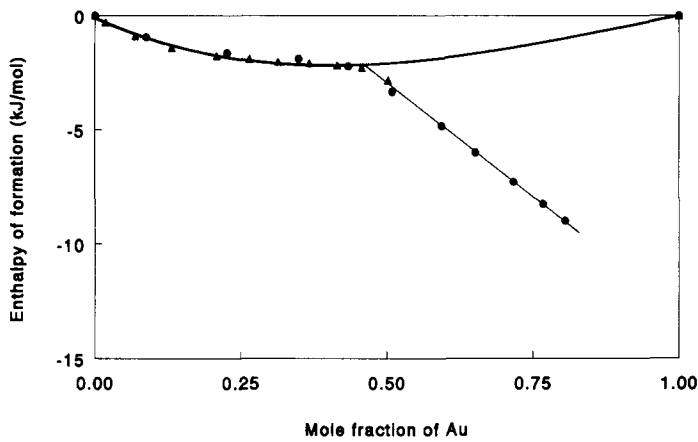


Fig. 3. Molar enthalpy of formation of the Au-Pb alloys at 695 K (this work) referred to both liquid components. The two symbols refer to independent sets of measurements. The break corresponds to the liquid-[liquid+Au(s)] boundary.

TABLE 1

Molar integral enthalpy of formation h^f of the Au-Pb alloys at 695 K referred to both pure liquid components with respect to gold mole fraction x_{Au}

x_{Au}		h^f (J mol ⁻¹)	
1 ^a	2	1	2
0.018	0.088	-290	-945
0.069	0.227	-891	-1629
0.132	0.349	-1407	-1887
0.209	0.434	-1756	-2218
0.265	0.509	-1894	-3340
0.314	0.594	-2013	-4844
0.367	0.652	-2074	-6013
0.415	0.717	-2173	-7301
0.457	0.767	-2272	-8267
0.502	0.805	-2829	-8998

^aSet of experimental results.

obtained from extrapolation and corresponding to a metastable liquid. The molar partial enthalpy of gold in the alloy is plotted in Fig. 4 with reference to solid gold at 695 K. The jump at $x_{Au}=0.47$ corresponds to the liquidus at 695 K (for higher values of gold molar fractions, heat effects due to the drops of gold correspond only to the heating of the samples).

The results obtained at 871 K shown in Fig. 5 are given in Table 2. They correspond to the following equation:

$$h^f \text{ (kJ mol}^{-1}\text{)} = x_{Au}(1 - x_{Au})(-6.1750 + 3.4653x_{Au})$$

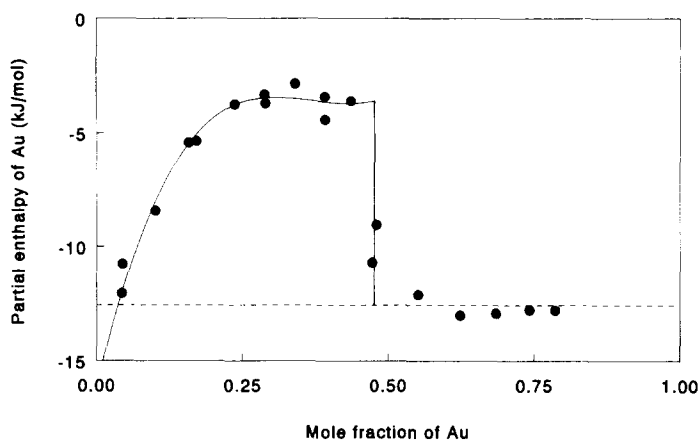


Fig. 4. Partial molar enthalpy of gold in the Au–Pb alloys at 695 K (this work) referred to liquid gold. The jump corresponds to the liquid–[liquid+Au(s)] boundary.

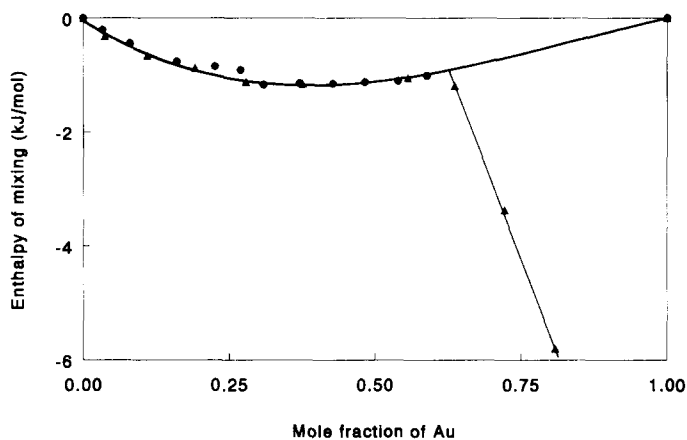


Fig. 5. Molar enthalpy of formation of the Au–Pb alloys at 871 K (this work) referred to both liquid components. The two symbols refer to independent sets of measurements. The break corresponds to the liquid–[liquid+Au(s)] boundary.

As at 695 K the molar integral enthalpy of mixing is negative in the whole range of concentration. The minimum lies in the stable liquid domain ($h_{\min}^f = -1.16 \text{ kJ mol}^{-1}$ at $x_{\text{Au}} = 0.35$). The liquid–(liquid + solid Au) boundary corresponds to $x_{\text{Au}} = 0.63$.

Finally the results at 1123 K are plotted in Fig. 6 and given in Table 3. At this temperature the enthalpy changes sign with respect to the mole fraction. It is negative up to $x_{\text{Au}} = 0.78$ with a minimum ($h^f = -0.58 \text{ kJ mol}^{-1}$) at $x_{\text{Au}} = 0.28$ and can be plotted with respect to composition according to the following equation:

$$h^f (\text{kJ mol}^{-1}) = x_{\text{Au}}(1 - x_{\text{Au}})(-4.4416 + 5.6702x_{\text{Au}})$$

TABLE 2

Molar integral enthalpy of formation h^f of the Au–Pb alloys at 871 K referred to both pure liquid components with respect to gold mole fraction x_{Au}

x_{Au}		h^f (J mol ⁻¹)	
1 ^a	2	1	2
0.033	0.037	-208	-320
0.080	0.110	-445	-661
0.161	0.192	-761	-876
0.226	0.279	-847	-1120
0.270	0.376	-908	-1156
0.309	0.557	-1166	-1048
0.371	0.637	-1143	-1188
0.428	0.722	-1149	-3366
0.483	0.809	-1123	-5797
0.540		-1101	
0.590		-1007	

^aSet of experimental results.

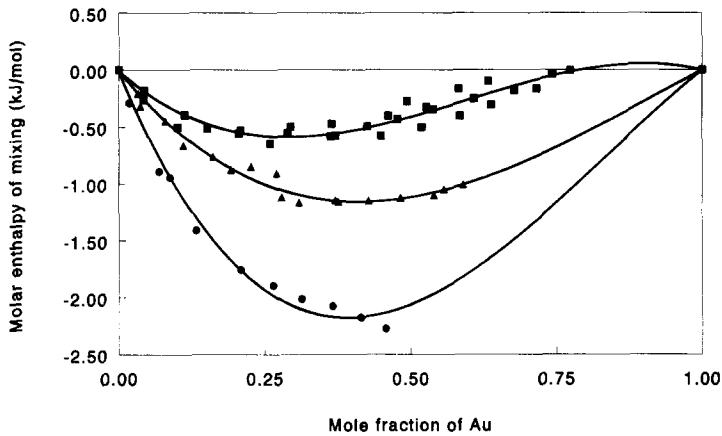


Fig. 6. Molar enthalpy of formation of the Au–Pb liquid alloys at the three temperatures investigated with reference to both liquid components (the experimental data have been extrapolated on the gold-rich side): ●, 695 K; ▲, 871 K; ■, 1123 K.

4. Discussion

Figure 6 shows the selected values for the single liquid phase at the three temperatures investigated. As can be seen h^f depends strongly on the temperature but differs from the calorimetric data of the literature and especially from those of Béja [2] obtained at temperatures not much different from ours. They correspond obviously to strong short-range order which disappears when the temperature increases. The smoothed numerical values

TABLE 3

Molar integral enthalpy of formation h^f of the Au–Pb alloys at 1123 K referred to both pure liquid components with respect to gold mole fraction x_{Au}

x_{Au}	h^f (J mol ⁻¹)				
	1 ^a	2	3	1	2
0.044	0.049	0.042	-182	-276	-261
0.113	0.151	0.102	-392	-514	-502
0.209	0.259	0.206	-529	-646	-558
0.295	0.363	0.289	-499	-582	-551
0.365	0.462	0.372	-470	-401	-574
0.426	0.538	0.449	-494	-343	-576
0.478	0.609	0.519	-431	-251	-501
0.527	0.677	0.585	-324	-177	-402
0.582	0.743	0.638	-166	-40	-305
0.633		0.716	-99		-164
		0.773			-6

^aSet of experimental results.

TABLE 4

Molar integral enthalpy of formation h^f of the Au–Pb liquid alloys at the three temperatures investigated referred to both pure liquid components with respect to gold mole fraction x_{Au} ^a

x_{Au}	h^f (kJ mol ⁻¹)		
	695 K	871 K	1123 K
0.05	-0.56	-0.29	-0.20
0.10	-1.03	-0.53	-0.35
0.15	-1.41	-0.72	-0.46
0.20	-1.70	-0.88	-0.53
0.25	-1.92	-1.00	-0.57
0.30	-2.06	-1.08	-0.58
0.35	-2.14	-1.13	-0.56
0.40	-2.16	-1.15	-0.52
0.45	-2.13	-1.14	-0.47
0.50	-2.05	-1.11	-0.40
0.55	-1.93	-1.06	-0.33
0.60	-1.77	-0.98	-0.25
0.65	-1.58	-0.89	-0.17
0.70	-1.38	-0.79	-0.10
0.75	-1.16	-0.67	-0.04
0.80	-0.92	-0.54	+0.02
0.85	-0.68	-0.41	+0.05
0.90	-0.45	-0.28	+0.06
0.95	-0.22	-0.14	+0.05

^aSmoothed values; values on the gold-rich side have been extrapolated and correspond to undercooled melts.

are given in Table 4. They lead to positive mean values of the heat capacity (Fig. 7) which decrease when the temperature increases:

$$C_P \text{ (J mol}^{-1} \text{ K}^{-1}\text{)} = x_{\text{Au}}(1 - x_{\text{Au}})(6.85 + 8.79x_{\text{Au}})$$

from 1123 to 871 K and

$$C_P \text{ (J mol}^{-1} \text{ K}^{-1}\text{)} = x_{\text{Au}}(1 - x_{\text{Au}})(18.26 - 5.72x_{\text{Au}})$$

from 871 to 695 K. In the temperature ranges 1123–871 K and 871–695 K C_P is maximum respectively at $x_{\text{Au}} = 0.58$ and 0.37 (2.92 J mol⁻¹ K⁻¹ and 5.79 J mol⁻¹ K⁻¹).

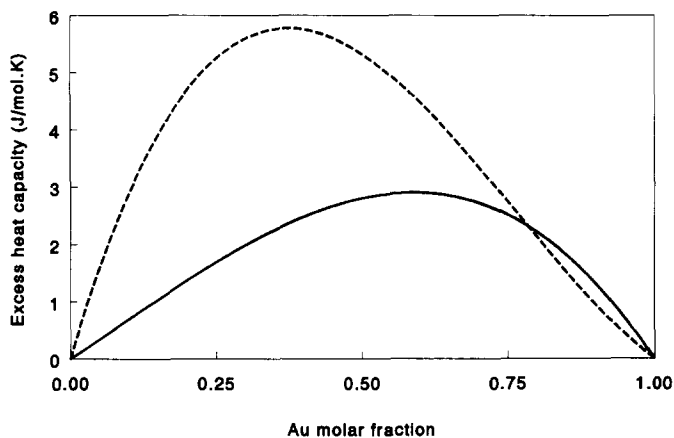


Fig. 7. Mean values of the excess heat capacity of the Au–Pb liquid alloys in the temperature ranges 1123–871 K (—) and 871–695 K (---).

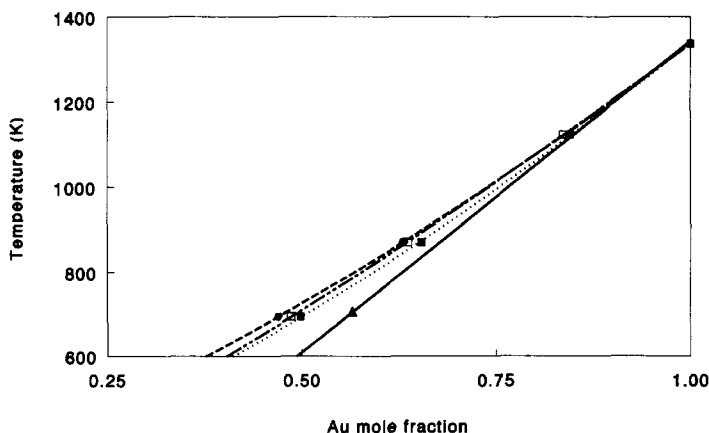


Fig. 8. Liquid–[liquid + Au(s)] boundary of the Au–Pb phase diagram: —, after Okamoto and Massalski [7] (\blacktriangle , eutectic composition); ---, \bullet , obtained from the breaks in the $h^f(x_{\text{Au}})$ curves (this work); - · - ·, \square , calculated from our calorimetric data (h^f) and those of Rebouillon (g^f) [6]; · · · ·, \blacksquare , calculated from our calorimetric results (h^f) and those of Hultgren *et al.* (g^f) [8].

Using the Gibbs free energy of mixing at 1200 K of Hultgren *et al.* [8]

$$g^{xs} \text{ (kJ mol}^{-1}\text{)} = x_{\text{Au}}(1 - x_{\text{Au}})(-11.838 + 4.843x_{\text{Au}} - 7.704x_{\text{Au}}^2)$$

and that of Rebouillon [6]

$$g^{xs} \text{ (kJ mol}^{-1}\text{)} = x_{\text{Au}}(1 - x_{\text{Au}})(-11.142 + 2.885x_{\text{Au}} - 3.651x_{\text{Au}}^2)$$

we calculated the liquid–(liquid + solid Au) phase boundary. The gold mole fractions corresponding to the liquidus are plotted in Fig. 8 with those obtained from the breaks in the $h^f(x_{\text{Au}})$ curves. The agreement between our experimental data and the calculations using Rebouillon's free enthalpy values is not bad. In contrast they differ strongly from the selected data of Okamoto and Massalski. Thus the strong temperature dependence of the thermodynamic quantities of the Au–Pb melts has now been definitely established. The thermodynamic behaviour of the liquid will be described in a future paper with reference to associated models.

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