

Letter

Redetermination of the standard enthalpies of formation of LaPt, LuPt and LuPt₃ by high temperature direct synthesis calorimetry

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The thermodynamic properties of the binary intermetallic compounds formed between early transition metals and late transition metals are important both from a theoretical and a technological point of view. Since the early 1980's this laboratory has pursued a long-term goal of experimental determination of the standard enthalpies of formation of these compounds. During the 1980's the senior author, in collaboration with Watanabe and Topor first studied the binary alloys between Cu and the elements in Group IV [1] and Group III [2] in the periodic table. They then studied the alloys between La and Ni [3], as well as 18 equiatomic alloys of Ti, Zr and Hf with late transition metals [4]. Recently, this systematic investigation has been extended to the intermetallic compounds formed between Group III and lanthanide metals on the one hand, and Group VIII transition metals on the other hand [5–11]. As more standard enthalpies of formation of the intermetallic compounds formed between the rare earth elements and the elements of Group VIII have become available, we have noticed that some values seem to fall out of line. For example, as already mentioned in an earlier paper [11], we find that the standard enthalpies of formation of ScPt [5], YPt [6], CePt [8], PrPt [9] and NdPt [10] (-104.8 ± 5.4 , -104.0 ± 2.3 , -103.8 ± 4.0 , -103.4 ± 2.7 , and -104.4 ± 2.6 kJ (g.atom)⁻¹, respectively) are very similar in magnitude, while the value for GdPt [11] (-109.3 ± 2.8 kJ (g.atom)⁻¹) is a little more exothermic. However, the values for LaPt [7] and LuPt [8] (-92.1 ± 4.6 kJ (g.atom)⁻¹ and -90.6 ± 7.7 kJ

(g.atom)⁻¹, respectively) appear to be too low; they also have quite large experimental uncertainties. Apart from this, we noticed another peculiar phenomenon among these values: we found very little difference between the reported values for LaPt (-92.1 ± 4.6 kJ (g.atom)⁻¹) and LaPt₂ (-90.0 ± 2.9 kJ (g.atom)⁻¹) [7], and between the values for LuPt (-90.6 ± 7.7 kJ (g.atom)⁻¹) and LuPt₃ (-89.2 ± 2.3 kJ (g.atom)⁻¹) [8]. These facts gave us some concern, and we therefore decided to redetermine these values. In this short note we report our new results for the standard enthalpies of formation of LaPt, LuPt and LuPt₃.

The experiments were all carried out at 1474 ± 2 K in a single-unit differential microcalorimeter which has been described in detail earlier [12]. All experiments were conducted in an inert atmosphere of argon gas. In order to eliminate possible traces of oxygen and nitrogen this gas was purified by passing it through a silica tube filled with pure titanium grains maintained at about 900 °C. The actual synthesis reactions took place in a boron nitride (BN) crucible.

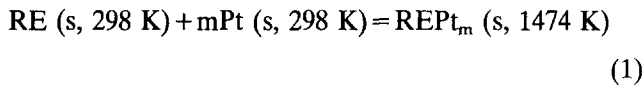
Calibration of the calorimeter was achieved by dropping pieces of 2 mm diameter high purity copper wire of known mass from room temperature into the calorimeter at 1474 ± 2 K. The enthalpy of pure copper at this temperature, $46\,498$ J mol⁻¹, was taken from Hultgren et al. [13]. The calibrations were reproducible within $\pm 1\%$.

The metallic purities of La, Lu and Pt were all 99.9%. Both La and Lu were purchased from Johnson Matthey as ingots. Fine filings of La and Lu were prepared just before we prepared the samples. Pt was obtained from Engelhard as platinum black. The black powder was

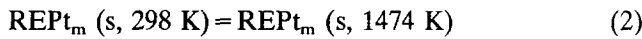
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fired in air overnight at about 700 °C. This promoted a growth in the grain size of Pt, and was accompanied by a significant contraction in volume and a change in color from black to light gray. After this treatment the platinum powder was passed through a 200 mesh sieve. Samples were prepared by mixing two powders that were accurately weighed according to the appropriate stoichiometry and then pressing the powdered mixtures into 4 mm diameter pellets.

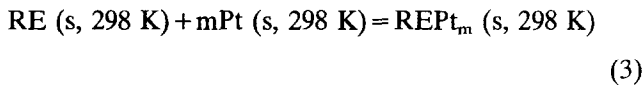
The standard enthalpy of formation of the compound REPt_m is obtained from the difference between two sets of determinations. In the first set the following reaction takes place in the calorimeter:



The products of reaction (1) were reused in a subsequent set of measurements to determine the corresponding heat contents:



From equations (1) and (2) we have



and the standard enthalpy of formation is given by

$$\Delta H_f^\circ(\text{REPt}_m) = \Delta H(1) - \Delta H(2)$$

where $\Delta H(1)$ and $\Delta H(2)$ are the enthalpy changes per gram atom for equations (1) and (2), respectively.

Table 1 summarizes all the experimental results obtained for LaPt, LuPt and LuPt₃. The reported values of $\Delta H(1)$ and $\Delta H(2)$ are averages of four to six individual determinations with standard deviations δ_1 and δ_2 . If the standard deviation for the calibration is δ_3 , the overall uncertainty in the reported standard enthalpy of formation is calculated from $\delta = \sqrt{\delta_1^2 + \delta_2^2 + \delta_3^2}$.

After the measurements all alloy samples were examined by powder X-ray diffraction and by scanning electron microscopy (SEM) with energy-dispersive microanalysis. The results of these examinations are listed in Table 2. As can be seen from this table, a trace amount (<1%) of Lu₂O₃ was found in our LuPt and LuPt₃ samples. A larger percentage (~3–5%) of La₂O₃

Table 1
Observed heats of reaction, average heat contents at 1474 K, and calculated standard enthalpies of formation, in kJ (g.atom)⁻¹

Compound	$\Delta H(1)$	$H_{1474}^\circ - H_{298}^\circ = \Delta H(2)$	ΔH_f°
LaPt	$-67.73 \pm 2.75(6)$	$31.94 \pm 0.49(4)$	-99.7 ± 2.9
LuPt	$-88.97 \pm 0.90(6)$	$29.40 \pm 0.95(6)$	-118.4 ± 2.2
LuPt ₃	$-71.73 \pm 1.52(6)$	$31.67 \pm 1.25(6)$	-103.4 ± 2.7

* Numbers in parentheses indicate numbers of experiments averaged.

Table 2
Summary of X-ray diffraction and SEM examination results

Compound	X-ray diffraction	SEM examination
LaPt	LaPt + Unknown peaks + La ₂ O ₃ (~3–5%)	LaPt + La ₃ Pt ₂ (~10–15%) + La ₂ O ₃ (<5%)
LuPt	LuPt + trace Lu ₂ O ₃	Single phase of LuPt
LuPt ₃	No ASTM standard file. No unreacted Lu or Pt, with trace Lu ₂ O ₃	Single phase of LuPt ₃

was found in our LaPt sample. These oxides may be formed during the sample preparation. From Table 2 it will be seen that there is no ASTM standard file for LuPt₃. However, the X-ray diffraction pattern of LuPt₃ showed no unreacted Lu or Pt. The X-ray diffraction pattern of our LaPt sample showed the existence of some other phase or phases in addition to LaPt, but there was no unreacted La or Pt. SEM examination showed LuPt and LuPt₃ to be single phase, but revealed the existence of about 10%–15% of La₃Pt₂ in the LaPt sample. In comparison with our random experimental errors, the formation of a second phase in an amount of less than 15% will not introduce a very significant error in our reported value for LaPt. We believe accordingly that our new values for all the three alloys are acceptable.

If we compare our redetermined values (Table 1) with the previous values in references [7] and [8], we find that the redetermination has mainly corrected $\Delta H(2)$ for LaPt and $\Delta H(1)$ for LuPt and LuPt₃. The value of $\Delta H(2)$ for LaPt reported in reference [7] (26.34 ± 1.06 kJ (g.atom)⁻¹) is undoubtedly too low; this is clearly the main reason that the previous value was less exothermic (-92.1 ± 4.6 kJ (g.atom)⁻¹) than our new value (-99.7 ± 2.9 kJ (g.atom)⁻¹). The values of $\Delta H(1)$ for LuPt and LuPt₃ reported in reference [8] (-61.48 ± 7.6 and -57.87 ± 1.93 kJ (g.atom)⁻¹, respectively) are responsible for the significantly less exothermic values for these compounds (-90.6 ± 7.7 and -89.2 ± 2.3 kJ (g.atom)⁻¹, respectively).

Our redetermined values of ΔH_f° for LaPt and LuPt fall in line with the available values for the other REPt compounds [5,6,8,9–11]. The new value for LaPt is still less exothermic than the other values, but is well separated from the reported value for LaPt₂ (-90.0 ± 2.9 kJ (g.atom)⁻¹). The new value for LuPt is about 8% more negative than the value for GdPt (-109.3 ± 2.8 kJ (g.atom)⁻¹) [11]; it is the most exothermic value we have found for any REPt compounds. Our values for GdPt and LuPt clearly indicate that the magnitude of the standard enthalpy of formation for REPt alloys generally increases from La to Lu.

Acknowledgments

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