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Standard enthalpies of formation of some holmium alloys, Ho + Me (Me = Ni, Ru, Rh, Pd, Ir, Pt), determined by high temperature direct synthesis calorimetry

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Abstract

The standard enthalpies of formation of 13 holmium alloys with late transition metals have been determined by direct synthesis calorimetry at 1474 ± 2 K. The following values of ΔH_f^0 (kJ (mol atoms) $^{-1}$) are reported: HoNi₅, $-(29.9 \pm 0.8)$; HoRu₂, $-(26.8 \pm 1.3)$; Ho₃Rh₂, $-(73.4 \pm 2.0)$; HoRh, $-(87.2 \pm 2.3)$; HoRh₂, $-(70.4 \pm 1.5)$; HoPd, $-(91.5 \pm 2.2)$; Ho₃Pd₄, $-(94.2 \pm 2.1)$; HoPd₃, $-(87.4 \pm 2.3)$; HoIr, $-(80.7 \pm 2.3)$; HoIr₂, $-(74.4 \pm 2.0)$; HoPt, $-(121.8 \pm 5.1)$; HoPt₂, $-(106.6 \pm 4.8)$; HoPt₃, $-(95.3 \pm 2.3)$. The results are compared with predicted values from the Miedema model and with available literature data for HoPd and HoPt.

Keywords: Enthalpies of formation; Holmium alloys; High temperature direct synthesis calorimetry

1. Introduction

The thermodynamic properties of the binary alloys formed between early transition metals and late transition metals are of great interest both in technology and in theoretical studies of the solid state. Since the early 1980s, systematic experimental studies of the standard enthalpies of formation of such alloys have been a long-term project of this laboratory. The early work included a pioneering investigation of the thermochemistry of liquid alloys of copper with titanium at 1372 K [1], and studies of the thermochemistry of the binary alloys formed between copper and all the elements from group IV in the periodic table [2], of the binary alloys formed between lanthanum, an element from group III, and nickel, an element from group VIII [3], and of the binary alloys formed between Sc, Y, La, and Lu, elements from group III, and Cu which is from group IB [4]. These early studies included heats of mixing measurements on liquid alloys as well as direct synthesis calorimetry of intermetallic compounds and solution calorimetry in liquid copper at 1373 K. However, when these studies were extended to alloys formed between elements from group IV and elements from group VIII, it was

inferred that the direct synthesis method might not work at this temperature because these alloys have much higher melting points than the alloys studied previously.

In 1984, a new calorimetric method, now called "solute–solvent drop calorimetry", was developed in this laboratory by Topor and Kleppa in their study of the thermochemistry of LaB₆ [5]. This compound has a melting point of about 2973 K and is an important electron emitter. The new method was used in 1986–1988 to determine the standard enthalpies of formation of 18 equiatomic alloys of the group IV elements Ti, Zr and Hf with a number of elements from group VIII. A review of these studies was given by Topor and Kleppa in 1989 [6].

When work on these equiatomic alloys was initiated, the enthalpies of formation of some of the same compounds had been determined by direct synthesis calorimetry at somewhat higher temperatures by Gachon et al. [7]. A comparison of the solute–solvent drop data with the corresponding data of Gachon et al. indicated that in most cases the agreement was good to excellent. This encouraged us to return to the less cumbersome and less time-consuming direct synthesis approach when our investigations were extend-

ed to the intermetallic compounds formed between transition metals from group III and group VIII. Consequently, Selhaoui and Kleppa in 1993 reported new standard enthalpy of formation data for alloys of Sc + Me [8], Y + Me [9], La + Me [10], and Ce + Me and Lu + Me [11]. More recently, the present authors have reported new enthalpy of formation values for alloys of Pr + Me [12], Nd + Me [13], Gd + Me [14], Tb + Me [15], and Dy + Me [16]; in all cases Me stands for an element from group VIII in the periodic table. Because some of the earlier data seemed to fall out of line, the standard enthalpies of formation for LaPt, LuPt and LuPt₃ were also redetermined by the present authors [17].

In another recent study we have reported on the standard enthalpies of formation for some intermetallic compounds formed between elements from group V and elements from group VIII [18]. In order to obtain a systematic comparison of the standard enthalpies of formation for A₃B-type alloys, where A stands for an element from group VIII, while B is an element from group III, from group IV, or from group V, we have very recently reported the standard enthalpies of formation for four compounds of this type [19]. All of these measurements have been based on direct synthesis calorimetry at about 1473 K. Generally speaking, if solid + solid reactions proceed without complications at temperatures of the order of 1473 K or below, direct synthesis calorimetry is now our preferred method.

In the present communication our investigation of intermetallic compounds formed between group III and group VIII elements is extended to the alloys of Ho. As far as we know, the only earlier calorimetric studies of the enthalpies of formation of these alloys were carried out by Palenzona and Cirafici (Ho₆₈Pd₂₈, HoPd and HoPt) [20–22]. We have in the present investigation attempted to determine the standard enthalpies of formation for a total of 14 alloys of Ho. According to Massalski et al. [23], 2 of the 14 alloys, HoRh and HoPt₂, are peritectic compounds, while the rest of the alloys which we studied are reported to be congruently melting compounds. However, we found that the direct synthesis reaction was completely unsuccessful for Ho₃Ru₂.

There is no ASTM standard X-ray diffraction pattern for this compound. Scanning electron microscopy (SEM) with energy-dispersive X-ray microanalysis indicated that, in addition to some Ho₂O₃, there were two phases in the reaction product at this composition. These phases were Ho₃Ru + HoRu₂, in roughly equal proportions, and we found no Ho₃Ru₂. Hence, we report below standard enthalpies of formation for only 13 Ho alloys. Most of these enthalpy values are the first values ever reported in the literature. All of the results will be compared with predicted values from

the Miedema model [24]. For HoPd and HoPt our results are also compared with the earlier values of Palenzona and Cirafici [21,22].

2. Experimental and starting materials

The experiments were all carried out at 1474 ± 2 K in a single-unit differential microcalorimeter which has been described in detail earlier [25]. Since July 1994 we have changed the mode of the temperature control of our calorimetric system. Previously, the temperature of the furnace, in which the calorimeter is inserted and mounted, was controlled at about 1490 K automatically by a Leeds & Northrup temperature controller. Each day, about 4 h before we started dropping our samples into the calorimeter, we switched the circuit from automatic control to a constant power input. This resulted in a fairly constant small decrease in temperature. The temperature changed relatively rapidly at first, but gradually approached a steady state at 1 or 2 K above 1473 K. At this time the first sample was dropped into the calorimeter. The disadvantage of this procedure was the long waiting period before a series of measurements could be initiated. In order to overcome this disadvantage, we decided to attempt to control the temperature of the furnace and calorimeter completely by using a Sola constant voltage transformer. After about one year of observations we have concluded that this procedure has in fact improved the stability of our temperature and of our calorimeter baseline.

All experiments were conducted in an inert atmosphere of argon. This gas was purified by passing it through a silica tube full of titanium grains which were maintained at about 900 °C in order to eliminate possible traces of oxygen and nitrogen in the gas. The actual synthesis reactions were carried out in boron nitride (BN) crucibles.

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. [26]. The calibrations were reproducible within ±1%.

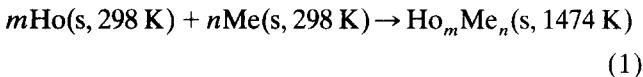
The metallic purities of the metals used for the experiments ranged from 99.9% for Ho, Ni, Ru, Rh and Pt, to 99.95% for Pd and Ir. The particle sizes were –200 mesh for Rh, Pd, Ir and Pt and –325 mesh for Ru and Ni.

Samples were prepared by mixing two metal powders that were accurately weighed according to the appropriate stoichiometry. This mixture was then pressed into 4 mm diameter pellets. The nickel powder used for the preparation of the HoNi₅ compound was

reduced in pure hydrogen at about 873 K for 1 h; the powder was then passed through a 325 mesh sieve just before the pellets were prepared. The Ho metal was purchased as ingot and stored in a vacuum desiccator. Fine filings of this metal passed through an 80 mesh sieve were prepared just before we prepared the 4 mm diameter pellets. All the metals were purchased from Johnson Matthey, *ÆSAR* Group, except for Rh and Pt, which were obtained from Engelhard. The platinum powder was purchased as platinum black, which was fired in air overnight at about 973 K. This promoted a growth in the grain size of the metal, 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. Ir metal was purchased as –60 mesh powder. This powder was ground in an agate mortar, and was then passed through a 200 mesh sieve.

3. Experimental results

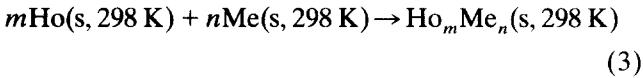
The standard enthalpy of formation of the compound Ho_mMe_n is obtained from the difference between two sets of measurements. In the first set the following reaction takes place in the calorimeter:



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



From Eqs. (1) and (2) we have



and the standard enthalpy of formation is given by

$$\Delta H_f^0(\text{Ho}_m\text{Me}_n) = \Delta H(1) - \Delta H(2)$$

where $\Delta H(1)$ and $\Delta H(2)$ are the observed enthalpy changes per mole of atoms for Eqs. (1) and (2) respectively.

Table 1 summarizes all the experimental results obtained for Ho + Me alloys (Me = Ni, Ru, Rh, Pd, Ir or Pt). The reported values of $\Delta H(1)$ and $\Delta H(2)$ are averages of five to ten individual determinations with standard deviations δ_1 and δ_2 respectively. If the standard deviation for the calibration is δ_3 , the overall uncertainty in the reported standard enthalpy of formation is calculated from $\delta = (\delta_1^2 + \delta_2^2 + \delta_3^2)^{1/2}$.

It will be seen from Table 1 that the values of $\Delta H(1)$ for HoPt and HoPt₂ exhibit the largest uncertainties

Table 1

Observed heats of reaction, average heat contents at 1474 K, and calculated standard enthalpies of formation, in kilojoules per mole of atoms^a

Compound	$\Delta H(1)$	$H_{1474}^0 - H_{298}^0 = \Delta H(2)$	ΔH_f^0
HoNi ₅	5.64 ± 0.51(6)	35.49 ± 0.54(6)	-29.9 ± 0.8
HoRu ₂	5.20 ± 0.44(5)	32.03 ± 1.13(6)	-26.8 ± 1.3 ^b
Ho ₃ Rh ₂	-42.48 ± 1.65(6)	30.96 ± 0.85(9)	-73.4 ± 2.0
HoRh	-54.60 ± 1.69(6)	32.61 ± 0.64(5)	-87.2 ± 2.3
HoRh ₂	-38.07 ± 1.31(6)	32.34 ± 0.66(6)	-70.4 ± 1.5
HoPd	-58.34 ± 0.54(6)	33.12 ± 2.09(6)	-91.5 ± 2.2
Ho ₃ Pd ₄	-61.51 ± 1.52(6)	32.70 ± 1.36(6)	-94.2 ± 2.1
HoPd ₃	-56.71 ± 1.77(5)	30.64 ± 1.35(6)	-87.4 ± 2.3
HoIr	-48.42 ± 1.58(6)	32.31 ± 1.44(6)	-80.7 ± 2.3
HoIr ₂	-44.57 ± 1.17(5)	29.82 ± 1.35(5)	-74.4 ± 2.0
HoPt	-89.68 ± 5.03(10)	32.08 ± 0.36(5)	-121.8 ± 5.1
HoPt ₂	-75.05 ± 4.67(6)	31.51 ± 0.89(6)	-106.6 ± 4.8
HoPt ₃	-62.74 ± 1.61(6)	32.52 ± 1.49(6)	-95.3 ± 2.3

^a Numbers in parentheses indicate numbers of experiments averaged.

^b Indicative value.

(5.03 kJ (mol atoms)⁻¹ for HoPt and 4.67 kJ (mol atoms)⁻¹ for HoPt₂). This was because the direct synthesis reactions for these two samples were very fast and evolved large amounts of heat. As a result, it sometimes happened that sample droplets were ejected from the bottom to the upper portion of the BN crucible, and sometimes even to the inner surface of the surrounding protective BN sleeves. In order to minimize this uncertainty, we carried out as many as ten individual determinations of $\Delta H(1)$ for HoPt. Even so, we failed to obtain any better precision.

After the measurements all alloys samples were examined by powder X-ray diffraction and by SEM with energy-dispersive X-ray microanalysis. The results of these examinations are summarized in Table 2. As can be seen from this table, very small percentages of Ho_2O_3 were found by either X-ray diffraction or SEM or by both in all samples. This oxide may well be formed during the sample preparation.

It will be seen from Table 2 that 2 of the 13 Ho compounds which we studied had no ASTM files of standard X-ray diffraction patterns. These compounds were Ho₃Rh₂ and Ho₃Pd₄. Without an ASTM standard it is difficult to make an accurate identification by X-ray powder diffraction of what phase or phases were formed during the direct synthesis reactions. However, from our X-ray diffraction patterns we are still able to say for sure that there were no unreacted elements in these two samples. SEM examination with energy-dispersive X-ray microanalysis indicated that the major phases formed in these two samples during the direct synthesis reactions were in fact our desired phases, namely Ho₃Rh₂ and Ho₃Pd₄ respectively. However, in addition to Ho_2O_3 , both X-ray diffraction

Table 2

Summary of X-ray diffraction and scanning electron microscopy examination results

Compound	X-ray diffraction	SEM examination
HoNi ₅	HoNi ₅ + minor Ho ₂ O ₃	HoNi ₅ + Ho ₃ Ni ₂ (1%–2%) + Ho ₂ O ₃ (1%–2%)
HoRu ₂	HoRu ₂ + minor Ru + minor Ho ₂ O ₃	HoRu ₂ + Ru (≈5%) + Ho ₂ O ₃ (1%–2%)
Ho ₃ Rh ₂ ^a	No unreacted elements + minor HoRh + minor Ho ₂ O ₃	Ho ₃ Rh ₂ + HoRh (≈5%) + Ho ₂ O ₃ (1%–2%)
HoRh	HoRh + minor Ho ₂ O ₃	Single phase of HoRh + Ho ₂ O ₃ (1%–2%)
HoRh ₂	HoRh ₂ + minor Ho ₂ O ₃	Single phase of HoRh ₂ + Ho ₂ O ₃ (1%–2%)
HoPd	HoPd + weak unknown peaks + minor Ho ₂ O ₃	Single phase of HoPd + Ho ₂ O ₃ (1%–2%)
Ho ₃ Pd ₄ ^a	No unreacted elements + minor Ho ₂ O ₃	Ho ₃ Pd ₄ + HoPd ₃ (<5%) + Ho ₂ O ₃ (1%–2%)
HoPd ₃	HoPd ₃	Single phase of HoPd ₃ + Ho ₂ O ₃ (<1%)
HoIr	HoIr + minor HoIr ₂ + minor Ho ₂ O ₃	HoIr + HoIr ₂ (10%–15%) + Ho ₂ O ₃ (1%–2%)
HoIr ₂	HoIr ₂ + minor HoIr + minor Ho ₂ O ₃	HoIr ₂ + HoIr (<5%) + Ho ₂ O ₃ (1%–2%)
HoPt	HoPt + minor HoPt ₃ + minor Ho ₂ O ₃	HoPt + HoPt ₃ (1%–2%) + Ho ₂ O ₃ (1%–2%)
HoPt ₂	HoPt ₂ + minor HoPt ₃ + minor Ho ₂ O ₃	HoPt ₂ + HoPt ₃ (<5%) + Ho ₂ O ₃ (1%–2%)
HoPt ₃	HoPt ₃	HoPt ₃ + HoPt ₅ (<5%) + Ho ₂ O ₃ (<1%)

^a There is no ASTM standard file for the compound.

and SEM examination verified the formation of HoRh in our Ho₃Rh₂ sample; SEM examination also indicated that a small amount of HoPd₃ was formed in our Ho₃Pd₄ samples. Because the percentages of these undesired phases are very small (less than 5% in both cases), they cannot introduce any significant error in our reported values of the standard enthalpy of formation.

Both X-ray diffraction and SEM examination with energy-dispersive X-ray microanalysis indicated that there was a minor amount of unreacted Ru (about 5%) in our HoRu₂ samples. For this reason, we have marked our reported value of ΔH_f^0 for HoRu₂ as indicative, i.e. it may be possible to improve on this value by another calorimetric method.

SEM examination revealed the formation of a small amount of Ho₃Ni₂ (about 1%–2%) in our HoNi₅ samples. SEM also showed that a small amount of HoPt₅ (less than 5%) was formed in our HoPt₃ samples. Both X-ray diffraction and SEM examination showed that second phases, which were HoIr₂ (10%–15%), HoIr (less than 5%), HoPt₃ (1%–2%) and HoPt₅ (less than 5%), were formed in our samples of HoIr, HoIr₂, HoPt and HoPt₂ respectively. However, because the percentages of these second phases are all small, it is unlikely that their formation will introduce any significant error in our reported values of ΔH_f^0 . We accordingly infer that our reported standard enthalpies of formation for HoNi₅, HoIr, HoIr₂, HoPt, HoPt₂ and HoPt₃ are all very acceptable.

It will also be seen from table 2 that, apart from the small amounts of Ho₂O₃, only single phases were formed in the direct syntheses of the HoRh, HoRh₂, HoPd and HoPd₃ samples. Overall, we believe that our new values of ΔH_f^0 reported for all the 13 compounds of Ho are reliable.

4. Discussion

Fig. 1 shows plots of all our experimental results for the standard enthalpies of formation of Ho + Me alloys (Me = Ni, Ru, Rh, Pd, Ir, Pt). All values are given in kilojoules per mole of atoms. The earlier calorimetric values for HoPd and HoPt by Palenzona and Cirafici [21,22] are also included. However, it should be noted that the data of Palenzona and Cirafici apply at temperatures higher than 298.15 K, namely at 1158 K for HoPd and at 1183 K for HoPt. Even so, because the differences between enthalpy of formation data at 298.15 K and 1158 or 1183 K usually are not very significant, conclusions drawn from a comparison should still hold true. It is apparent that Palenzona and Cirafici's values for HoPd and HoPt, $-60.2 \text{ kJ (mol atoms)}^{-1}$ and $-83.7 \text{ kJ (mol atoms)}^{-1}$, are much less exothermic than our new values, which are $-91.5 \text{ kJ (mol atoms)}^{-1}$ and $-121.8 \text{ kJ (mol atoms)}^{-1}$ respectively.

Plotted in Fig. 1 are also the predicted values of the standard enthalpies of formation for all considered and some related alloys which were calculated from the semiempirical model of Miedema [24]. We see that the Miedema model gives values that are in perfect agreement with our observed results for HoPd₃, HoPt₂ and HoPt. However, the same model gives less exothermic values than observed for HoNi₅, HoRh, Ho₃Rh₂, HoIr₂, HoIr and HoPt₃, and more exothermic values for HoRu₂, HoRh₂, Ho₃Pd₄, HoPd. Although somewhat different from the experimental values, the predicted values for HoRh₂, Ho₃Rh₂, HoIr₂, HoIr, and HoPt₃ are still in very good agreement with the experiments when the experimental uncertainties are taken into account.

In Fig. 2 we compare our results for PrNi₅ [12],

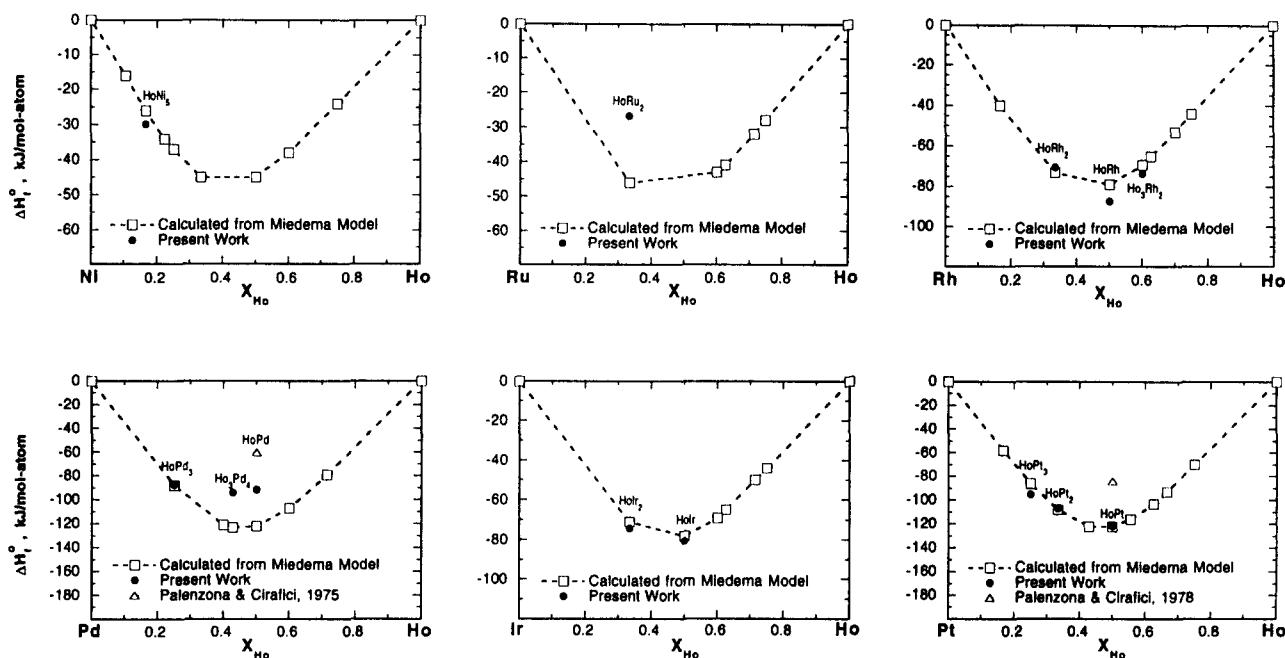


Fig. 1. Standard enthalpies of formation for alloys of Ho with Ni, Ru, Rh, Pd, Ir and Pt compared with earlier data for HoPd by Palenzona and Cirafici [21], for HoPt by the same researchers [22], and with predicted values from the Miedema model of Niessen et al. [24].

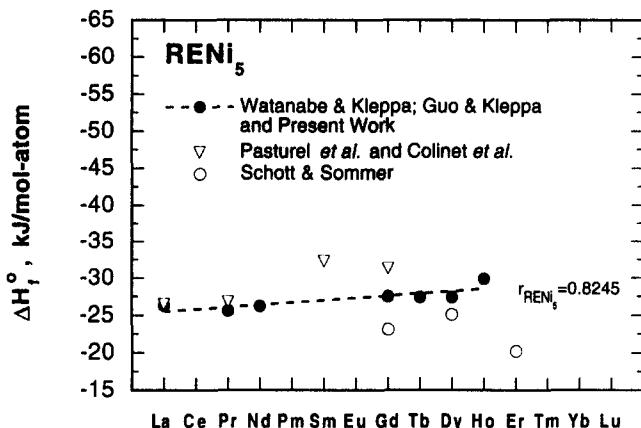


Fig. 2. Standard enthalpies of formation for RENi_5 alloys. Guo and Kleppa's data for PrNi_5 [12], NdNi_5 [13], GdNi_5 [14], TbNi_5 [15], DyNi_5 [16] and HoNi_5 (present work) are compared with the earlier value for LaNi_5 of Watanabe and Kleppa [3], with data from Pasturel et al. [27] for LaNi_5 , PrNi_5 and SmNi_5 , from Colinet et al. [28] for GdNi_5 , and from Schott and Sommer [29] for GdNi_5 , DyNi_5 and ErNi_5 . All RENi_5 alloys have the same CaCu_5 structure.

NdNi_5 [13], GdNi_5 [14], TbNi_5 [15], DyNi_5 [16] and HoNi_5 with the value of Watanabe and Kleppa for LaNi_5 [3], with data from Pasturel et al. [27] for LaNi_5 , PrNi_5 and SmNi_5 , with a value from Colinet et al. [28] for GdNi_5 , and with data from Schott and Sommer [29] for GdNi_5 , DyNi_5 and ErNi_5 . Although our value for HoNi_5 is considerably more exothermic than all our earlier values, it will be seen that the values from

this laboratory all fall within a narrow range from $-25.6 \text{ kJ (mol atoms)}^{-1}$ for PrNi_5 to $-29.9 \text{ kJ (mol atoms)}^{-1}$ for HoNi_5 . Note that our values for LaNi_5 and PrNi_5 agree very well with the data of Pasturel et al. [27]. However, the value of Colinet et al. for GdNi_5 ($-31.3 \text{ kJ (mol atoms)}^{-1}$) is much more exothermic than the corresponding value of Schott and Sommer ($-23.1 \text{ kJ (mol atoms)}^{-1}$), while our own value ($-27.5 \text{ kJ (mol atoms)}^{-1}$) falls very close to their average. Generally speaking, the values of Pasturel et al. [27] and Colinet et al. [28] for RENi_5 are somewhat more exothermic, while the values of Schott and Sommer [29] are somewhat less exothermic than our own values. Unlike the data from the French group [27,28] and from the German group [29], the seven values of ΔH_f^0 for RENi_5 from our own laboratory exhibit a very small change from compound to compound. In Fig. 2 we have fitted a straight line to our seven experimental enthalpy values for RENi_5 . The r values given in Fig. 2, as well as in the following figures, is the correlation coefficient of the linear regression. This line suggests a slight increase in the exothermic character of the compound with an increasing number of f electrons. We plan to extend our measurements of the standard enthalpies of formation to other RENi_5 alloys. This will allow us to explore this problem further.

In Figs. 3, 4 and 5 we compare our new results for the Ho alloys with corresponding enthalpy of formation data published by this laboratory for the equiva-

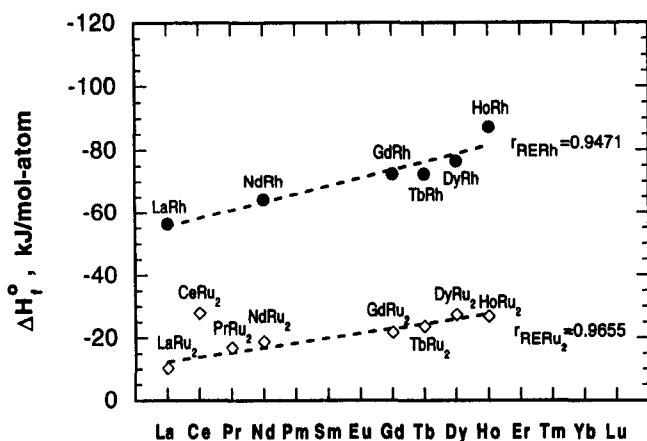


Fig. 3. Standard enthalpies of formation for RERu_2 and RERh alloys. Data for the La, and Ce alloys are from Selhaoui and Kleppa [10,11], and for Pr, Nd, Gd, Tb and Dy alloys are from Guo and Kleppa [12–16]. The values for the Ho alloys are from the present work. LaRu_2 , CeRu_2 , and PrRu_2 have the MgCu_2 structure, NdRu_2 has the MgCu_2 structure at lower pressures but the MgZn_2 structure at higher pressures. All the other RERu_2 compounds included in this figure have the MgZn_2 structure. The MgCu_2 structure was also reported for GdRu_2 . LaRh and NdRh have the CrB structure, while the other RERh compounds in this figure have the CsCl structure.

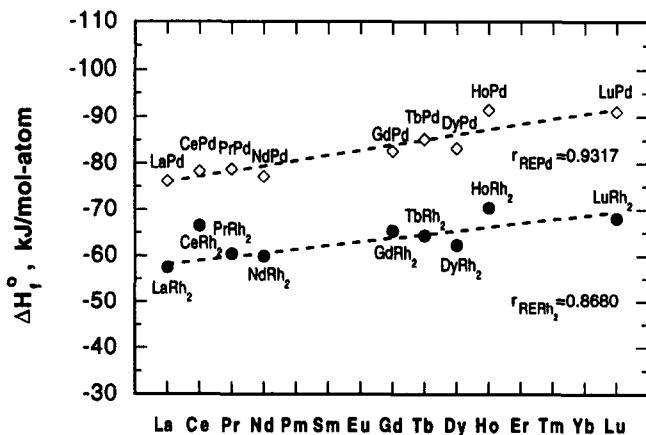


Fig. 4. Standard enthalpies of formation for RERh_2 and REPd alloys. Data for the La, Ce and Lu alloys are from Selhaoui and Kleppa [10,11], and for the Pr, Nd, Gd, Tb and Dy alloys are from Guo and Kleppa [12–16]. The values for the Ho alloys are from the present work. All the RERh_2 alloys have the MgCu_2 structure. LaPd , CePd , PrPd , NdPd , GdPd , and TbPd have the CrB structure. DyPd and HoPd have the FeB structure. LuPd has the CsCl structure.

lent La, Ce, Pr, Nd, Gd, Tb, Dy and in some cases also for the Lu alloys. First, we see that, if we exclude Ce alloys, for all the families of compounds compared in these figures except for the family of RERu_2 , the Ho alloys have so far the most exothermic values of ΔH_f° . Second, we always find a steady increase in the exothermic character of the enthalpies of formation of the alloy with increasing number of f electrons. As we did above for the RENi_5 alloys, we have fitted straight lines to the experimental data. However, we have

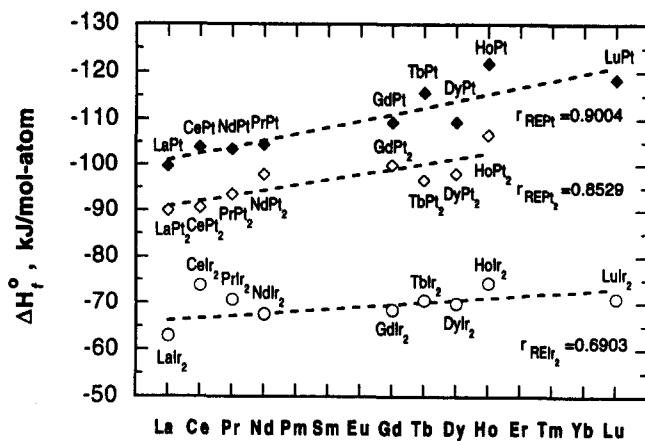


Fig. 5. Standard enthalpies of formation for alloys of Ir and Pt with La, Ce, Pr, Nd, Gd, Tb, Dy, Ho and Lu. Data for the La and Ce alloys are from Selhaoui and Kleppa [10,11]. However, the values for LaPt and LuPt are from Guo and Kleppa [17]. Data for the Pr, Nd, Gd, Tb and Dy alloys are also from Guo and Kleppa [12–16], and the values for the Ho alloys are from the present work. All REIr_2 compounds have the MgCu_2 structure. The structure of PrPt_2 is unknown, but is believed to be MgCu_2 . All the other REPt_2 compounds have the MgCu_2 structure. LaPt and CePt have the CrB structure, PrPt has the FeB structure at low temperatures and the CrB structure at high temperatures. All the other REPt compounds have the FeB structure.

excepted from these fits the values for CeRu_2 in Fig. 3, for CeRh_2 in Fig. 4, and for CeIr_2 in Fig. 5. The values for these three compounds clearly are significantly more exothermic than the values for the neighboring alloys. On the contrary, it is worth noting that the enthalpies of formation of CePd in Fig. 4 and of CePt and CePt_2 in Fig. 5 seem to fit in well with the values for the neighboring alloys; these three Ce alloys have been included in the linear fits.

We believe that the exceptional character of the Ce compounds probably relates to the fact that the characteristic valency of Ce at times may be higher than +3. Of course, we have no enthalpy of formation data in Figs. 3–5 for the related compounds of Eu and Yb which both have the characteristic valency of +2. Any plot of the enthalpies of formation against the number of f-electrons which includes data also for alloys of Eu and Yb would be expected to exhibit significantly less negative values for these two metals. This is well known from the systematic study of REAL_2 compounds by Colinet et al. [30].

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