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The standard enthalpies of formation of the compounds of early transition metals with late transition metals and with noble metals as determined by Kleppa and co-workers at the University of Chicago — A review

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Abstract

Since the early 1980s, experimental studies of the standard enthalpies of formation of the binary intermetallic compounds of early transition metals with late transition metals and with noble metals have been a major long-term research project in this laboratory. Tabulated in this review are 290 enthalpy of formation values for 273 such compounds, all determined in this laboratory during the last two decades. The calorimetric methods used in these investigations have included solution calorimetry, solute–solvent drop calorimetry, and direct synthesis calorimetry. Among these methods, the direct synthesis approach has been the most frequently used technique. In this review, our results will be compared with values published by other laboratories and with values predicted by the Miedema semi-empirical model. However, the emphasis will be placed on the systematic variation from group to group in the periodic table. A few examples will be presented to show the correlation between the enthalpy of formation and the pertinent atomic number in the binary alloy families.

Keywords: Enthalpies of formation; Intermetallic compounds; High-temperature direct synthesis calorimetry

1. Introduction

If you take a look at the periodic table you will find that more than 3/4 of the chemical elements are metals. As a result, intermetallic compounds represent a very significant part of inorganic chemistry.

More than 60 years ago, Hume-Rothery et al. empirically found some of the physical factors which govern the formation of intermetallic compounds [1]. The principal factors recognized by Hume-Rothery et al. were: (a) the 'size factor', which limits solid solubility; (b) the 'electrochemical factor', namely, the difference in electronegativity between the two metals, which provides an important driving force for intermetallic compound formation; and (c) the 'valence factor', which decides energetic asymmetry and controls the formation of certain types of intermetallic compounds. The studies of Hume-Rothery and his school were of crucial importance for the development of the field and in particular for obtaining an understanding of alloy formation between the noble metals and other Group B metals. However, Hume-Rothery's theories proved less useful in the area of transition metal alloys.

Thirty-two years ago, Brewer predicted that very stable intermetallic compounds should form when early transition metals are alloyed with late transition metals [2,3]. He attributed the high stability of such compounds to a strong Lewis acid–base interaction between late transition metal d electron donors (Lewis bases) and early transition metal acceptors (Lewis acids). His prediction was later proved by experiments: almost all experimental determinations carried out since then have indicated large negative enthalpies of formation for such compounds.

Although the binary intermetallic compounds formed between early transition metals and late transition metals are of great interest both in technology and in theoretical studies of the solid state, very few people were involved in investigations of the thermodynamic properties of these compounds until the early 1980s. However, stimulated by the pioneering studies of Miedema and co-workers [4–6], during the last two decades there has been an increasing interest in the thermodynamics of such compounds.

In the early 1980s, under the leadership of the senior author of this paper, a long-term project was initiated in

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this laboratory, which was designed to provide systematic experimental data on the thermochemistry of such compounds. This project has involved two major goals: (a) to obtain reliable standard enthalpy of formation data, and (b) to get information on the systematic variation of ΔH_f^o in various families of such compounds. In this project, Kleppa's early work included: (1) a pioneering investigation of the thermochemistry of liquid alloys of copper with titanium at 1372 K [7]; (2) a study of the thermochemistry of the binary alloys formed between copper, an element from Group IB, and all the elements from Group IV in the periodic table [8]; (3) a study of the binary alloys formed between lanthanum, an element from Group III, and nickel, an element from Group VIII [9]; and (4) a study of the binary alloys formed between Sc, Y, La, and Lu, all elements from Group III, and copper [10]. Since that time, this laboratory, supported by the National Science Foundation and also by the Department of Energy of the United States since 1988, has been perhaps the major contributor in the world to information on the thermodynamic properties of such compounds.

Technically, the early studies included heat of mixing measurements on liquid alloys, solution calorimetry in liquid copper at 1373 K, as well as high-temperature direct synthesis calorimetry of relatively low-melting intermetallic compounds. However, when these studies were extended to alloys formed between elements from Group IV and from Group VIII, it was inferred that the direct synthesis method might not work at 1373 K because these alloys have much higher melting points than the alloys studied in the earlier work.

In 1984, a new calorimetric method, which is now called 'solute–solvent drop calorimetry', was developed in this laboratory by Topor and Kleppa in their study of the thermochemistry of LaB_6 [11]. This compound has a melting point of about 2973 K and is an important electron emitter. This new method was used from 1986 through 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 [12–18]. A review of these studies was given by Topor and Kleppa in 1989 [19].

When work on these equiatomic alloys was initiated, the enthalpies of formation of some of the same compounds had recently been determined by direct synthesis calorimetry at somewhat higher temperatures by Gachon et al. [20]. 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 the laboratory to adopt the less cumbersome and less time-consuming direct synthesis approach when the investigations were extended to the intermetallic compounds of Group III elements with Group VIII elements, of Group III, Group IV and Group V elements with noble metals and of uranium with Group VIII elements. Consequently, Fitzner and coworkers in 1991 reported new enthalpy of formation data for alloys of Sc + Me, Y + Me and La + Me (Me = Ag, Au) [21], while Jung and Kleppa in 1991 reported new data for alloys of uranium with Ru, Rh and Pd [22]. In 1992, Fitzner and Kleppa reported new enthalpy of formation values for alloys of Ti + Me, Zr + Me and Hf + Me (Me = Ag, Au) [23], while Fitzner and coworkers reported new data for alloys of V + Au, Nb + Au and Ta + Au [24]. In 1993, Selhaoui and Kleppa reported new standard enthalpy of formation data for alloys of Sc + Me [25], Y + Me [26], La + Me [27], Ce + Me and Lu + Me [28]. In 1993 and 1994, Fitzner and Kleppa reported new values for alloys of Ce with Cu, Ag, and Au [29] and for alloys of Pr and Nd with Cu, Ag, and Au [30].

In more recent years, the present authors have published new standard enthalpy of formation values for alloys of Pr + Me [31], Nd + Me [32], Sm + Me [33], Gd + Me [34], Tb + Me [35], Dy + Me [36], Ho + Me [37], Er + Me [38], and Tm + Me [39]. In all cases, Me stands for elements from Group VIII in the periodic table. We also found new values for $LuNi_5$, Lu_3Pd_4 and LuPd [40] and for $CeNi_5$ and RENi (RE = Ce, Pr, Nd, Sm, Gd, Tb, Ho, Tm and Lu) [41]. Moreover, we published new values for alloys formed between elements from Group V and elements from Group VIII [42], and for alloys of Sc with Pt, of Hf with Ni and Pd, and of V with Ni [43].

As new enthalpy of formation data for such compounds have become available, we have sometimes found that our earlier data, for some reason, were associated with significant experimental uncertainties. Sometimes we also found that some of the data fell out of line. In such cases, we sometimes redetermined the earlier values. For example, in 1995 we redetermined the enthalpies of formation for LaPt, LuPt and $LuPt_3$ [44], and for LuPd [40]. For the same reason, we also reinvestigated the thermochemistry of some alloys formed between Group IV elements and Group VIII elements [45,46].

All of the mentioned recent investigations have been based on application of the high-temperature direct synthesis method. Generally speaking, if solid–solid reactions proceed without complications at temperatures of the order of 1473 K or below, direct synthesis calorimetry is now the preferred method in this laboratory.

2. Tabulation of enthalpies of formation for intermetallic compounds as determined by Kleppa and co-workers since 1980

Summarized in Table 1 are the enthalpy of formation values for all intermetallic compounds that were studied in the last two decades by the senior author and his coworkers. Listed in the first column of the table are the chemical formulae of the compounds studied. Listed, respectively, in the second and the third columns are the calorimetric values reported and the methods used for their measurements. It will be apparent from the first three

Table 1
Standard enthalpies of formation of the intermetallic compounds of early transition metals with late transition metals and with noble metals as determined by Kleppa and co-workers at the University of Chicago[a]

Compound	ΔH_f^o (kJ/(mol atom))	Calorimetric method	Other calorimetric values in the literature (kJ/(mol atom))	Miedema value (kJ/(mol atom))
$ScFe_2$	−11.2±1.2 [25]	Direct synthesis	None	−16
$ScCo_2$	−32.5±2.1 [25]	Direct synthesis	None	−41
Sc_2Co	−26.7±1.9 [25]	Direct synthesis	None	−32
La_3Ni	−13.1±0.5 [9]	Direct synthesis	None	−19
ScNi	−44.7±2.3 [25]	Direct synthesis	None	−57
LaNi	−24.8±1.1 [9]	Direct synthesis	None	−38
CeNi	−30.3±1.4 [41]	Direct synthesis	None	−40
PrNi	−28.1±1.1 [41]	Direct synthesis	None	−42
NdNi	−25.0±1.5 [41]	Direct synthesis	None	−42
SmNi	−36.4±0.7 [41]	Direct synthesis	None	−44
GdNi	−29.9±1.1 [41]	Direct synthesis	−25.8±1.8 [55] −36.3 [56]	−44
TbNi	−36.8±1.4 [41]	Direct synthesis	None	−46
DyNi	−35.2±1.5 [36]	Direct synthesis	−33.4±1.9 [55]	−46
HoNi	−41.7±1.4 [41]	Direct synthesis	None	−45
ErNi	−42.1±1.8 [38]	Direct synthesis	−30.6±1.1 [55]	−48
TmNi	−46.4±1.6 [41]	Direct synthesis	None	−48
LuNi	−47.3±2.2 [41]	Direct synthesis	None	−52
$ScNi_2$	−43.0±2.3 [25]	Direct synthesis	None	−53
$LaNi_5$	−26.3±4.6 [9]	La solution	−21.5±1.3 [50] −22.0±2.0 [51] −26.5±1.4 [52] −26.5 [53]	−24
$CeNi_5$	−28.1±1.3 [41]	Direct synthesis	−33.2 [54]	−24
$PrNi_5$	−25.6±1.0 [31]	Direct synthesis	−26.8 [53]	−25
$NdNi_5$	−26.2±1.1 [32]	Direct synthesis	None	−25
$SmNi_5$	−27.4±0.5 [33]	Direct synthesis	−30.3 [53]	−26
$GdNi_5$	−27.5±1.2 [34]	Direct synthesis	−23.1±0.7 [55] −31.3 [56]	−26
$TbNi_5$	−27.4±0.9 [35]	Direct synthesis	None	−27
$DyNi_5$	−27.4±0.7 [36]	Direct synthesis	−25.1±0.9 [55]	−27
$HoNi_5$	−29.9±0.8 [37]	Direct synthesis	None	−26
$ErNi_5$	−29.2±0.8 [38]	Direct synthesis	−20.2±0.5 [50]	−27
$TmNi_5$	−29.1±0.7 [39]	Direct synthesis	None	−27
$LuNi_5$	−30.0±0.8 [40]	Direct synthesis	None	−29
ScRu	−44.5±2.2 [25]	Direct synthesis	None	−65
$LaRu_2$	−10.3±2.8* [27]	Direct synthesis	−11±1 [47]	−39
$CeRu_2$	−27.9±1.5* [28]	Direct synthesis	None	−42
$PrRu_2$	−16.9±1.5* [31]	Direct synthesis	None	−44
$NdRu_2$	−18.8±1.2 [32]	Direct synthesis	−19±1 [47]	−44
$GdRu_2$	−21.7±1.9 [34]	Direct synthesis	None	−46
$TbRu_2$	−23.6±1.7 [35]	Direct synthesis	None	−48
$DyRu_2$	−27.3±0.9 [36]	Direct synthesis	None	−48
$HoRu_2$	−26.8±1.3 [37]	Direct synthesis	None	−46
$ErRu_2$	−26.2±1.3 [38]	Direct synthesis	None	−50
Y_5Ru_2	−27.3±3.1 [26]	Direct synthesis	None	−31
Nd_5Ru_2	−17.2±1.9 [32]	Direct synthesis	None	−29
Tb_5Ru_2	−29.9±1.9 [35]	Direct synthesis	None	−33

Table 1. Continued

Compound	ΔH_f^o (kJ/(mol atom))	Calorimetric method	Other calorimetric values in the literature (kJ/(mol atom))	Miedema value (kJ/(mol atom))
ScRh	−94.5±1.5 [25]	Direct synthesis	None	−91
YRh	−76.1±3.4 [26]	Direct synthesis	None	−79
LaRh	−56.3±2.3 [27]	Direct synthesis	None	−73
NdRh	−64.2±2.0 [32]	Direct synthesis	None	−77
GdRh	−72.4±2.1 [34]	Direct synthesis	None	−79
TbRh	−72.3±1.1 [35]	Direct synthesis	None	−82
DyRh	−76.5±2.0 [36]	Direct synthesis	None	−81
HoRh	−87.2±2.3 [37]	Direct synthesis	None	−79
ErRh	−87.4±1.7 [38]	Direct synthesis	None	−83
TmRh	−88.9±2.0 [39]	Direct synthesis	None	−83
YRh_2	−65.4±1.3 [26]	Direct synthesis	None	−74
$LaRh_2$	−57.5±1.7 [27]	Direct synthesis	None	−70
$CeRh_2$	−66.5±2.3 [28]	Direct synthesis	None	−72
$PrRh_2$	−60.4±1.7 [31]	Direct synthesis	None	−73
$NdRh_2$	−59.9±1.1 [32]	Direct synthesis	None	−73
$SmRh_2$	−65.5±1.2 [33]	Direct synthesis	None	−74
$GdRh_2$	−65.4±1.6 [34]	Direct synthesis	None	−74
$TbRh_2$	−64.4±1.5 [35]	Direct synthesis	None	−76
$DyRh_2$	−62.3±0.8 [36]	Direct synthesis	None	−75
$HoRh_2$	−70.4±1.5 [37]	Direct synthesis	None	−73
$ErRh_2$	−69.8±2.0 [38]	Direct synthesis	None	−76
$TmRh_2$	−73.0±2.0 [39]	Direct synthesis	None	−76
$LuRh_2$	−68.1±3.2 [28]	Direct synthesis	None	−79
$ScRh_3$	−51.7±1.4 [25]	Direct synthesis	None	−62
$CeRh_3$	−55.2±1.6 [28]	Direct synthesis	None	−58
$NdRh_3$	−44.4±1.6 [32]	Direct synthesis	None	−59
Ho_3Rh_2	−73.4±2.0 [37]	Direct synthesis	None	−69
Lu_3Rh_2	−58.7±1.9* [28]	Direct synthesis	None	−76
Ce_5Rh_4	−70.5±1.9 [28]	Direct synthesis	None	−70
Nd_5Rh_4	−59.9±2.5 [32]	Direct synthesis	None	−72
Sm_5Rh_4	−66.5±1.0 [33]	Direct synthesis	None	−74
Dy_7Rh_3	−56.8±2.2 [36]	Direct synthesis	None	−54
ScPd	−89.3±2.2 [25]	Direct synthesis	−106±15 [20]	−128
YPd	−94.9±3.8 [26]	Direct synthesis	None	−123
LaPd	−76.2±1.8 [27]	Direct synthesis	−56.5 (883 K) [48]	−119
CePd	−78.3±1.5 [28]	Direct synthesis	−63.6 (828 K) [48]	−121
PrPd	−78.8±2.5 [31]	Direct synthesis	−63.2 (873 K) [48]	−122
NdPd	−77.2±2.7 [32]	Direct synthesis	−67.4 (913 K) [48]	−122
SmPd	−82.4±2.0 [33]	Direct synthesis	−63.2 (958 K) [48]	−124
GdPd	−82.6±1.1 [34]	Direct synthesis	−62.8 (1038 K) [48] −85.7 [57]	−123
TbPd	−85.2±1.6 [35]	Direct synthesis	−61.1 (1073 K) [48]	−125
DyPd	−83.3±2.0 [36]	Direct synthesis	−61.1 (1108 K) [48]	−124
HoPd	−91.5±2.2 [37]	Direct synthesis	−60.3 (1158 K) [48]	−122
ErPd	−91.1±2.2 [38]	Direct synthesis	−59.8 (1183 K) [48]	−126
TmPd	−92.6±2.0 [39]	Direct synthesis	−59.4 (1203 K) [48]	−125
LuPd	−91.1±5.2 [28]	Direct synthesis	−58.6 (1243 K) [48]	−128
LuPd	−95.0±1.4 [40]	Direct synthesis	−58.6 (1243 K) [48]	−128
$PrPd_2$	−82.7±3.1 [31]	Direct synthesis	None	−113
Y_3Pd_4	−92.8±3.7 [26]	Direct synthesis	None	−125
Sm_3Pd_4	−87.2±2.5 [33]	Direct synthesis	None	−125
Gd_3Pd_4	−88.5±2.9 [34]	Direct synthesis	−88.3 [57]	−125
Tb_3Pd_4	−85.5±1.4 [35]	Direct synthesis	None	−126
Dy_3Pd_4	−86.6±2.1 [36]	Direct synthesis	None	−125
Ho_3Pd_4	−94.2±2.1 [37]	Direct synthesis	None	−123

Table 1. Continued

Compound	ΔH_f^o (kJ/(mol atom))	Calorimetric method	Other calorimetric values in the literature (kJ/(mol atom))	Miedema value (kJ/(mol atom))
Er_3Pd_4	−94.6±1.8 [38]	Direct synthesis	None	−126
Tm_3Pd_4	−93.0±1.7 [39]	Direct synthesis	None	−125
Lu_3Pd_4	−98.4±2.2 [40]	Direct synthesis	None	−128
YPd_3	−79.0±6.5 [26]	Direct synthesis	None	−90
$LaPd_3$	−77.1±2.2 [27]	Direct synthesis	None	−92
$CePd_3$	−73.0±3.8 [28]	Direct synthesis	None	−91
$NdPd_3$	−73.3±2.3 [32]	Direct synthesis	None	−91
$SmPd_3$	−82.9±2.5 [33]	Direct synthesis	None	−91
$GdPd_3$	−79.7±2.7 [34]	Direct synthesis	−89.2 [57]	−90
$TbPd_3$	−78.8±1.5 [35]	Direct synthesis	None	−90
$DyPd_3$	−76.2±1.5 [36]	Direct synthesis	None	−90
$HoPd_3$	−87.4±2.3 [37]	Direct synthesis	None	−88
$ErPd_3$	−90.2±1.4 [38]	Direct synthesis	None	−89
$TmPd_3$	−86.8±1.6 [39]	Direct synthesis	None	−89
$LuPd_3$	−88.7±2.7 [28]	Direct synthesis	None	−90
YOs_2	−24.8±2.8 [26]	Direct synthesis	None	−38
$LaOs_2$	−9.0±1.1* [27]	Direct synthesis	None	−30
ScIr	−89.7±3.0 [25]	Direct synthesis	None	−92
YIr	−65.9±3.8 [26]	Direct synthesis	None	−78
HoIr	−80.7±2.3 [37]	Direct synthesis	None	−78
ErIr	−82.9±2.1 [38]	Direct synthesis	None	−83
LuIr	−85.5±4.8 [28]	Direct synthesis	None	−87
$ScIr_2$	−66.3±1.3 [25]	Direct synthesis	None	−79
YIr_2	−59.4±2.8 [26]	Direct synthesis	None	−72
$LaIr_2$	−62.9±2.2 [27]	Direct synthesis	None	−67
$CeIr_2$	−73.8±2.8 [28]	Direct synthesis	None	−69
$PrIr_2$	−70.7±2.8 [31]	Direct synthesis	None	−71
$NdIr_2$	−67.6±1.5 [32]	Direct synthesis	None	−70
$GdIr_2$	−68.5±2.2 [34]	Direct synthesis	None	−72
$TbIr_2$	−70.6±2.6 [35]	Direct synthesis	None	−74
$DyIr_2$	−69.9±2.1 [36]	Direct synthesis	None	−73
$HoIr_2$	−74.4±2.0 [37]	Direct synthesis	None	−71
$ErIr_2$	−75.9±2.2 [38]	Direct synthesis	None	−75
$LuIr_2$	−71.0±1.2 [28]	Direct synthesis	None	−78
$LaIr_3$	−49.7±2.2 [27]	Direct synthesis	None	−54
Nd_5Ir_3	−59.7±2.7 [32]	Direct synthesis	None	−62
ScPt	−104.8±5.4 [25]	Direct synthesis	None	−132
YPt	−104.0±2.3 [26]	Direct synthesis	None	−123
LaPt	−92.1±4.6 [27]	Direct synthesis	−87.0 (903 K) [49]	−117
LaPt	−99.7±2.9 [44]	Direct synthesis	−87.0 (903 K) [49]	−117
CePt	−103.8±4.0 [28]	Direct synthesis	−102.9 (883 K) [49]	−119
PrPt	−103.4±2.7 [31]	Direct synthesis	−101.7 (923 K) [49]	−121
NdPt	−104.4±2.6 [32]	Direct synthesis	−99.2 (973 K) [49]	−121
SmPt	−108.7±3.5 [33]	Direct synthesis	−93.3 (993 K) [49]	−123
GdPt	−109.3±2.8 [34]	Direct synthesis	−89.5 (1153 K) [49]	−123
TbPt	−115.7±2.9 [35]	Direct synthesis	−87.0 (1153 K) [49]	−125
DyPt	−109.4±1.8 [36]	Direct synthesis	−85.4 (1193 K) [49]	−125
HoPt	−121.8±5.1 [37]	Direct synthesis	−83.7 (1183 K) [49]	−122
ErPt	−118.7±2.3 [38]	Direct synthesis	−81.2 (1293 K) [49]	−127
TmPt	−121.0±2.0 [39]	Direct synthesis	−78.7 (extrapolated) [49]	−126
LuPt	−90.6±7.7 [28]	Direct synthesis	−74.5 (extrapolated) [49]	−130
LuPt	−118.4±2.2 [44]	Direct synthesis	−74.5 (extrapolated) [49]	−130

Table 1. Continued

Compound	ΔH_f^o (kJ/(mol atom))	Calorimetric method	Other calorimetric values in the literature (kJ/(mol atom))	Miedema value (kJ/(mol atom))
$LaPt_2$	−90.0±2.9 [27]	Direct synthesis	None	−109
$CePt_2$	−90.6±3.5 [28]	Direct synthesis	None	−110
$PrPt_2$	−93.5±2.4 [31]	Direct synthesis	None	−110
$NdPt_2$	−97.9±2.4 [32]	Direct synthesis	None	−110
$SmPt_2$	−100.2±2.6 [33]	Direct synthesis	None	−111
$GdPt_2$	−100.0±2.6 [34]	Direct synthesis	−94.2 [57]	−111
$TbPt_2$	−96.7±3.1 [35]	Direct synthesis	None	−112
$DyPt_2$	−98.1±2.8 [36]	Direct synthesis	None	−111
$HoPt_2$	−106.6±4.8 [37]	Direct synthesis	None	−108
$ErPt_2$	−107.8±2.8 [38]	Direct synthesis	None	−112
$TmPt_2$	−112.4±3.1 [39]	Direct synthesis	None	−111
$ScPt_3$	−94.6±2.0 [43]	Direct synthesis	None	−86
YPt_3	−86.9±2.0 [26]	Direct synthesis	None	−88
$TbPt_3$	−85.6±2.9 [35]	Direct synthesis	None	−89
$DyPt_3$	−82.8±2.2 [36]	Direct synthesis	None	−88
$HoPt_3$	−95.3±2.3 [37]	Direct synthesis	None	−86
$ErPt_3$	−93.6±1.8 [38]	Direct synthesis	None	−88
$TmPt_3$	−91.1±2.1 [39]	Direct synthesis	None	−87
$LuPt_3$	−89.2±2.3 [28]	Direct synthesis	None	−89
$LuPt_3$	−103.4±2.7 [44]	Direct synthesis	None	−89
$NdPt_5$	−55.0±3.1 [32]	Direct synthesis	None	−59
Cu_4Sc	−14.0±0.43 [10]	Direct synthesis	None	−22
Cu_2Sc	−17.37±1.14 [10]	Direct synthesis	None	−33
CuSc	−20.85±1.28 [10]	Copper solution	None	−36
Ag_2Sc	−27.1±0.6 [21]	Direct synthesis	None	−36
AgSc	−26.2±1.6 [21]	Direct synthesis	None	−43
AuSc	−76.1±3.0 [21]	Direct synthesis	None	−111
Cu_4Y	−16.04±0.63 [10]	Direct synthesis	None	−22
Cu_2Y	−19.5 [10]	Direct synthesis	None	−32
CuY	−19.34±0.22 [10]	Direct synthesis	None	−32
$Ag_{51}Y_{14}$	−22.2±1.3 [21]	Direct synthesis	None	−28
AgY	−26.8±3.2 [21]	Direct synthesis	None	−44
AuY	−78.7±2.5 [21]	Direct synthesis	None	−110
Cu_6La	−9.91±1.75 [10]	Direct synthesis	None	−16
Cu_2La	−16.16±1.59 [10]	Direct synthesis	None	−30
$Ag_{51}La_{14}$	−21.4±2.0 [21]	Direct synthesis	None	−29
AgLa	−16.9±2.3 [21]	Direct synthesis	None	−43
AuLa	−69.9±2.3 [21]	Direct synthesis	None	−108
Cu_6Ce	−20.9±2.4 [29]	Direct synthesis	None	−16
Cu_6Ce	−10.1±3.2 [30]	Direct synthesis	None	−16
Cu_2Ce	−21.2±3.0 [29]	Direct synthesis	None	−31
Cu_2Ce	−14.8±3.9 [30]	Direct synthesis	None	−31
$Ag_{51}Ce_{14}$	−19.3±4.1 [29]	Direct synthesis	None	−29
AgCe	−13.5±4.3* [29]	Direct synthesis	None	−44
$Au_{51}Ce_{14}$	−49.5±2.2 [29]	Direct synthesis	None	−67
Au_2Ce	−57.5±4.7 [29]	Direct synthesis	None	−97
AuCe	−62.8±4.2 [29]	Direct synthesis	None	−109

Table 1. Continued

Compound	ΔH_f^o (kJ/(mol atom))	Calorimetric method	Other calorimetric values in the literature (kJ/(mol atom))	Miedema value (kJ/(mol atom))
Cu_6Pr	−11.3±2.7 [30]	Direct synthesis	None	−16
Cu_2Pr	−14.5±2.6 [30]	Direct synthesis	None	−32
$Ag_{51}Pr_{14}$	−22.1±2.8 [30]	Direct synthesis	None	−29
AgPr	−24.4±2.8 [30]	Direct synthesis	None	−44
$Au_{51}Pr_{14}$	−54.9±3.7 [30]	Direct synthesis	None	−67
Au_2Pr	−64.2±3.0 [30]	Direct synthesis	None	−97
AuPr	−72.2±4.4 [30]	Direct synthesis	None	−110
Cu_6Nd	−13.3±3.1 [30]	Direct synthesis	None	−16
Cu_2Nd	−16.9±2.7 [30]	Direct synthesis	None	−31
$Ag_{51}Nd_{14}$	−17.7±2.9 [30]	Direct synthesis	None	−29
AgNd	−19.8±3.7 [30]	Direct synthesis	None	−44
$Au_{51}Nd_{14}$	−49.3±4.9 [30]	Direct synthesis	None	−67
Au_2Nd	−69.7±3.7 [30]	Direct synthesis	None	−97
AuNd	−70.2±3.7 [30]	Direct synthesis	None	−110
CoTi	−41.3±0.9 [46]	Direct synthesis	−44.3±0.5 (1490 K) [58]	−42
$Co_2Zr(\epsilon)$	−35.8±0.6 [46]	Direct synthesis	−41.0±1.6 (1708 K) [58]	−56
$CoZr(\zeta)$	−35.8±0.7 [46]	Direct synthesis	−42.2±1.0 (1512 K) [58]	−60
$CoZr_2(\eta)$	−26.4±1.0 [46]	Direct synthesis	−33.0±2.0 (1290 K) [58]	−44
Co_2Hf	−39.4±0.9 [46]	Direct synthesis	−49.0±1.2 (1573 K) [58]	−48
CoHf	−47.5±3.1 [18]	Solute–solvent drop	−51.0±1.5 (1653 K) [58]	−51
CoHf	−42.8±1.1 [46]	Direct synthesis	−51.0±1.5 (1653 K) [58]	−51
Ni_3Ti	−42.2±1.2 [46]	Direct synthesis	−42.9±1.0 (1513 K) [58] −34.9 [59]	−37
NiTi	−33.1±1.1 [46]	Direct synthesis	−34.0±2.0 (1475 K) [58] −33.9 [59]	−52
Ni_7Zr_2	−40.6±0.7 [46]	Direct synthesis	−39.5±0.5 (1670 K) [58] −45.94±3.48 [60]	−50
NiZr	−50.5±1.5 [46]	Direct synthesis	−51.5±2.0 (1405 K) [58] −48.53±2.47 [60]	−72
$NiZr_2$	−31.2±0.9 [46]	Direct synthesis	−36.8±1.0 (1230 K) [58] −37.24±6.11 [60]	−53
Ni_7Hf_2	−44.1±1.5 [46]	Direct synthesis	−50.7±2.0 (1623 K) [58]	−43
NiHf	−59.3±2.5 [18]	Solute–solvent drop	−47.9±1.8 (1573 K) [58]	−63
NiHf	−48.3±1.0 [46]	Direct synthesis	−47.9±1.8 (1573 K) [58]	−63
Ni_3Hf	−47.8±1.4 [43]	Direct synthesis	−50.7±2.0 (1623 K) [58]	−48
RuTi	−77.0±3.7 [15]	Solute–solvent drop	None	−65
RhTi	−71.5±4.9 [14]	Solute–solvent drop	−75.0±5.0 (1673 K) [58]	−78
RhTi	−74.4±0.8 [45]	Direct synthesis	−75.0±5.0 (1673 K) [58]	−78
PdTi	−51.6±6.4 [12]	Solute–solvent drop	−53.1±3.0 (1523 K) [58] −53.0±1.1 (1578 K) [20]	−97
PdTi	−53.3±1.8 [45]	Direct synthesis	−53.1±3.0 (1523 K) [58] −53.0±1.1 (1578 K) [20]	−97
OsTi	−68.5±3.6 [17]	Solute–solvent drop	None	−61
IrTi	−84.3±3.8 [17]	Solute–solvent drop	−84.0±3.2 (1723 K) [58]	−86
PtTi	−79.7±6.5 [16]	Solute–solvent drop	−77.1±3.1 (1673 K) [58]	−112
PtTi	−90.7±2.8 [45]	Direct synthesis	−77.1±3.1 (1673 K) [58]	−112
Pd_3Ti	−65.0±0.9 [45]	Direct synthesis	−50.7±1.8 (1573 K) [58]	−62

Table 1. Continued

Compound	ΔH_f^o (kJ/(mol atom))	Calorimetric method	Other calorimetric values in the literature (kJ/(mol atom))	Miedema value (kJ/(mol atom))
RuZr	−68.7±3.4 [15]	Solute–solvent drop	None	−88
RhZr	−75.9±3.6 [14]	Solute–solvent drop	−75.8±5.0 (1700 K) [58]	−107
RhZr	−79.0±1.2 [45]	Direct synthesis	−75.8±5.0 (1700 K) [58]	−107
PdZr	−61.3±3.5 [13]	Solute–solvent drop	−62.0±5.0 (1667 K) [58]	−136
PdZr	−66.1±1.1 [45]	Direct synthesis	−62.0±5.0 (1667 K) [58]	−136
IrZr	−85.7±3.9 [17]	Solute–solvent drop	−81.0±2.0 (1723 K) [58]	−114
PtZr	−96.0±6.2 [16]	Solute–solvent drop	−90.0±10.0 (1629 K) [58]	−150
PtZr	−104.1±1.8 [45]	Direct synthesis	−90.0±10.0 (1629 K) [58]	−150
Pd_3Zr	−84.4±1.7 [45]	Direct synthesis	−82.8±3.6 (1573 K) [58]	−93
RuHf	−91.8±5.2 [15]	Solute–solvent drop	None	−77
RhHf	−95.8±2.2 [14]	Solute–solvent drop	−82.0±8.4 (1723 K) [58]	−95
PdHf	−67.4±3.9 [13]	Solute–solvent drop	−65.6±2.5 (1623 K) [58]	−121
PdHf	−69.5±1.7 [45]	Direct synthesis	−65.6±2.5 (1623 K) [58]	−121
IrHf	−96.7±4.8 [17]	Solute–solvent drop	−97.7±1.5 (1723 K) [58]	−102
PtHf	−113.7±6.6 [16]	Solute–solvent drop	−113.0±6.0 (1336 K) [58]	−134
Pd_3Hf	−88.6±1.8 [43]	Direct synthesis	−100.1±1.2 (1673 K) [58]	−82
Pd_3Hf	−88.5±1.4 [45]	Direct synthesis	−100.1±1.2 (1673 K) [58]	−82
CuTi	−9.61±0.37 [8]	Direct synthesis	None	−13
Au_2Ti	−45.93±2.03 [23]	Direct synthesis	None	−57
AuTi	−44.20±1.49 [23]	Direct synthesis	None	−71
$AuTi_3$	−31.39±0.50 [23]	Direct synthesis	None	−48
Cu_3Zr	−14.07±1.24 [8]	Copper solution	None	−26
Cu_3Zr_2	−12.31±0.24 [8]	Direct synthesis	None	−34
CuZr	−9.05±1.18 [8]	Direct synthesis	None	−34
$CuZr_2$	−10.95±0.69 [8]	Direct synthesis	None	−25
AgZr	−3.12±3.13* [23]	Direct synthesis	None	−31
$AgZr_2$	−1.47±2.89* [23]	Direct synthesis	None	−24
Au_3Zr	−51.41±2.93 [23]	Direct synthesis	None	−73
Au_2Zr	−61.00±2.34 [23]	Direct synthesis	None	−93
Au_4Zr_5	−47.15±3.04 [23]	Direct synthesis	None	−109
$AuZr_3$	−30.07±1.92 [23]	Direct synthesis	None	−71
Cu_4Hf	−13.65±0.24 [8]	Copper solution	None	−16
Cu_3Hf_2	−12.64±0.49 [8]	Direct synthesis	None	−25
$CuHf_2$	−15.23 [8]	Copper solution	None	−19
AgHf	−10.74±2.00* [23]	Direct synthesis	None	−19
Au_3Hf	−54.77±2.64 [23]	Direct synthesis	None	−62
Au_2Hf	−61.98±2.11 [23]	Direct synthesis	None	−79
AuHf	−57.03±1.29 [23]	Direct synthesis	None	−96
$AuHf_2$	−40.76±4.14* [23]	Direct synthesis	None	−79
Ni_3V	−21.7±1.0 [43]	Direct synthesis	None	−18
Pt_3V	−27.4±3.0 [42]	Direct synthesis	−30* [61]	−40
Pt_2V	−37.2±2.5 [42]	Direct synthesis	None	−53
Pt_3Nb	−46.6±3.7 [42]	Direct synthesis	None	−63
Ni_3Ta	−20.4±2.3 [42]	Direct synthesis	None	−31
Pd_3Ta	−36.1±2.0 [42]	Direct synthesis	None	−51

Table 1. Continued

Compound	ΔH_f^o (kJ/(mol atom))	Calorimetric method	Other calorimetric values in the literature (kJ/(mol atom))	Miedema value (kJ/(mol atom))
Au_4V	−9.79±2.50 [24]	Direct synthesis	None	−13
Au_2V	−10.37±3.45 [24]	Direct synthesis	None	−22
AuV_4	−9.74±1.29 [24]	Direct synthesis	None	−17
Au_2Nb	−13.36±2.04 [24]	Direct synthesis	None	−39
Au_2Ta_3	−20.56±2.21 [24]	Direct synthesis	None	−46
Ru_3U	−31.0±1.2 [22]	Direct synthesis	None	−38
Rh_3U	−69.7±2.2 [22]	Direct synthesis	None	−48
Pd_3U	−73.7±0.9 [22]	Direct synthesis	−131±7.8 [62]	−61
Pd_3U	−71.5±5.4 [22]	Solute–solvent drop	−131±7.8 [62]	−61

[a] Number in square brackets after each value indicates the reference cited. Temperature in Kelvin in parentheses after a value indicates the temperature to which the value applies.

* Indicative values.

columns of this table that some compounds were investigated two times by using the same method or a different technique in different years. The reasons for the second measurements are generally described above in the Introduction. However, for one compound, Pd_3Hf, the purpose of the second measurement was to check the reproducibility of the value determined in this laboratory. Table 1 shows that for this compound, the second value (−88.5±1.4 kJ/(mol atom)), which was determined 3 years later than the first one, is in perfect agreement with the first value (−88.6±1.8 kJ/(mol atom)). This indicates that the reproducibility of our data is very good. Generally speaking, if two different values were published by this laboratory, the more recent value is the preferred value.

In the fourth column, we list the calorimetric values for the same compounds published in the literature by other investigators. However, we have not included enthalpy data which were derived either from e.m.f. or from vapor-pressure measurements. It is evident from this column that about 70% of the compounds were never studied calorimetrically by other investigators. A comparison of our values with data reported by other investigators shows that the agreement is sometimes very good, but sometimes poor.

In the last column we list the predicted values calculated from the Miedema semi-empirical model [6]. The predicted values are sometimes very close to our measured values, but often fall far away from our data.

3. Systematics of standard enthalpies of formation for various alloy families formed between early transition metals and late transition metals

As repeatedly stated before [41–43,45,46] and above, one of our principal objectives in carrying out investigations of the standard enthalpies of formation for intermetallic compounds between early and late transition

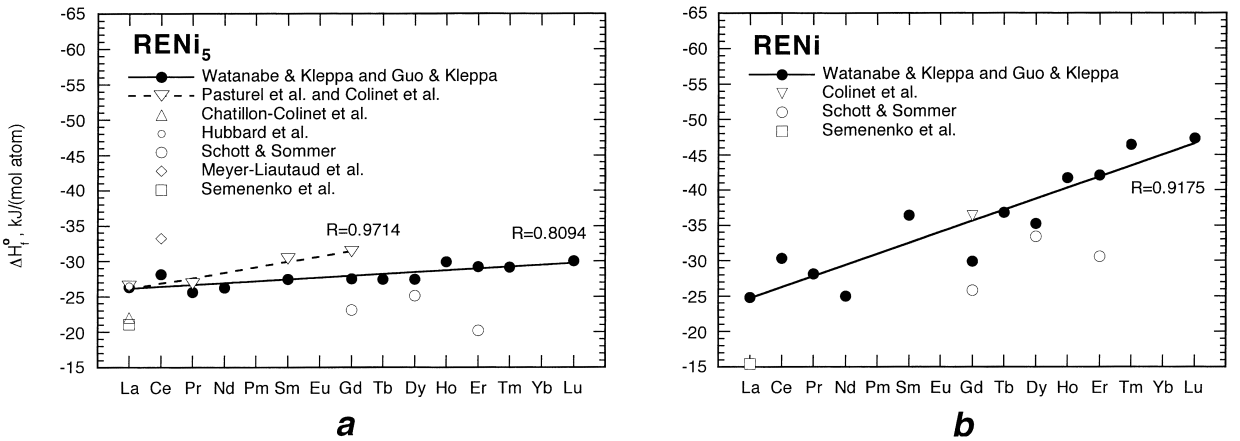

Fig. 1. Standard enthalpies of formation for compounds in the $RENi_5$ family and in the RENi family (RE, lanthanide elements). (a) The systematic variation of the standard enthalpies of formation in the $RENi_5$ family. All the $RENi_5$ compounds have the $CaCu_5$ structure. (b) The systematic variation of the standard enthalpies of formation in the RENi family. LaNi, CeNi, PrNi, NdNi and SmNi have the CrB structure. The structures of PmNi and EuNi are unknown. GdNi, DyNi, HoNi, ErNi, TmNi, YbNi and LuNi have both the CrB and the FeB structures. TbNi has both the CrB and the TbNi structures.

metals has been to find the dependence of this quantity, for characteristic alloys, from group to group in the periodic table. During the past two decades, the accumulation of new enthalpy data has made it possible to explore some of the regularities in the changes of the enthalpy of formation within some alloy families. In this section we will first discuss the systematic variation of ΔH_f^o for alloys of Group III elements with Group VIII elements. We will then extend this discussion to alloys of Group IV elements with Group VIII elements. Finally, we will explore the change of ΔH_f^o for A_3B type alloys formed between elements of Groups III, IV or V and elements of Group VIII.

3.1. Alloys of Group III elements with Group VIII elements

In this sub-section we will discuss the alloys formed between rare earth elements, which belong to Group III in the periodic table, and Group VIII elements.

Based on the numerical values listed in Table 1, Fig. 1a,b presents comprehensive graphical comparisons between the experimental results obtained in this laboratory and the available earlier calorimetric data for intermetallic compounds of the rare earth elements with Ni ($RENi_5$ and RENi). The sources of the earlier calorimetric values are indicated in the figure. The structure of each of the compounds in Fig. 1a,b is described in the figure caption. The details of each structure type can be found in [63].

It is clear from Fig. 1a that our value of ΔH_f^o for $LaNi_5$ is in excellent agreement with the two values reported, respectively, by Hubbard et al. [52] and by Pasturel et al. [53]. However, it is significantly more exothermic than the values of Semenenko et al. [50] and of Chatillon-Colinet et al. [51]. Our value for $PrNi_5$ is slightly less exothermic, but is in good agreement with the value of Pasturel et al. [53]. Our values for $SmNi_5$ and $GdNi_5$ are both somewhat less exothermic than the values reported by the French group [53,56]. At the same time, our values for $GdNi_5$, $DyNi_5$ and $ErNi_5$ are all more exothermic than the values reported by Schott and Sommer [55]. In Fig. 1b we see that our value for LaNi is much more exothermic than the value of Semenenko et al. [50]. Also, our value for GdNi is less exothermic than the value reported by Colinet et al. [56], but more exothermic than the value of Schott and Sommer [55]. Our value for DyNi is close to, but more exothermic than the value of Schott and Sommer [55]. Finally, our value for ErNi is significantly more exothermic than the value of Schott and Sommer [55].

In order to inspect the general trend of the variation of ΔH_f^o from one compound to another within the two families, we have fitted straight lines to our own experimental data in Fig. 1a,b. Of course, these fittings did not include data for the corresponding Pm, Eu and Yb compounds. The correlation coefficients of the fits (R) are marked within the figures. In Fig. 1a we have also fitted a straight line to the four values published by Pasturel et al. [53] and by Colinet et al. [56].

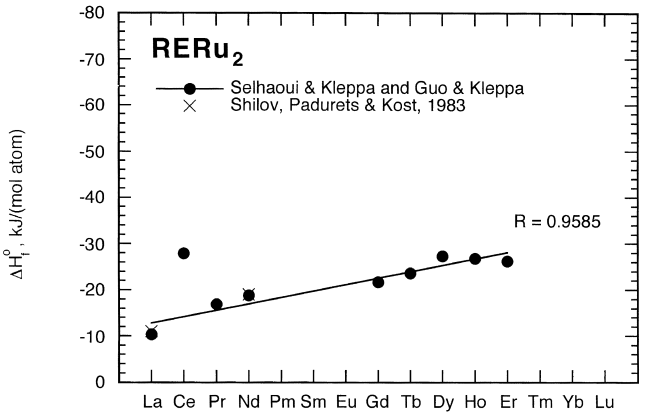

Fig. 2. Standard enthalpies of formation for the $RERu_2$ family. $LaRu_2$, $CeRu_2$, $PrRu_2$, $NdRu_2$ and $SmRu_2$ have the $MgCu_2$ structure. The structure of $EuRu_2$ is unknown. All the other $RERu_2$ compounds have the $MgZn_2$ structure.

There are two striking features in Fig. 1a,b: (1) Our values exhibit a steady increase, with increasing atomic number of the rare earth elements, in the exothermic character of the enthalpy of formation for both $RENi_5$ and RENi alloys. This is in agreement with the tendency shown by the four values reported by Pasturel et al. [53] and by Colinet et al. [56]. (2) The slope of the fitting line in Fig. 1b is significantly steeper than that in Fig. 1a, indicating that the exothermic character of the enthalpy of formation increases more rapidly for RENi alloys than for $RENi_5$ alloys. An empirical explanation for this more rapid increase is that the atomic percentage of the rare earth element in the RENi alloys (50%) is significantly higher than that in the $RENi_5$ alloys (16.7%). Better explanations are awaited with interest from possible future theoretical studies.

Figs. 2–10 present our experimental results for ΔH_f^o for

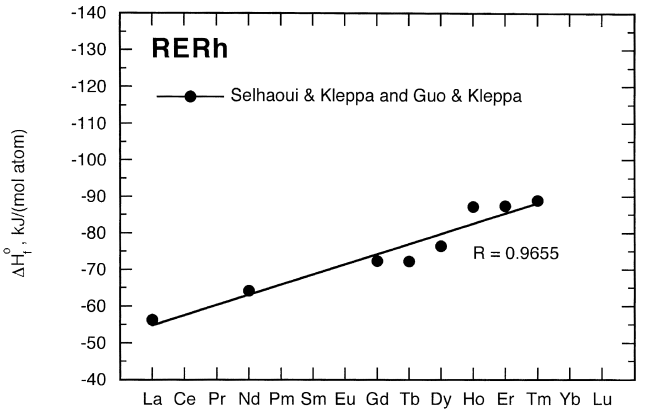

Fig. 3. Standard enthalpies of formation for the RERh family. LaRh, CeRh, PrRh and NdRh have the CrB structure. The structure of EuRh is unknown. All the other RERh compounds have the CsCl structure.

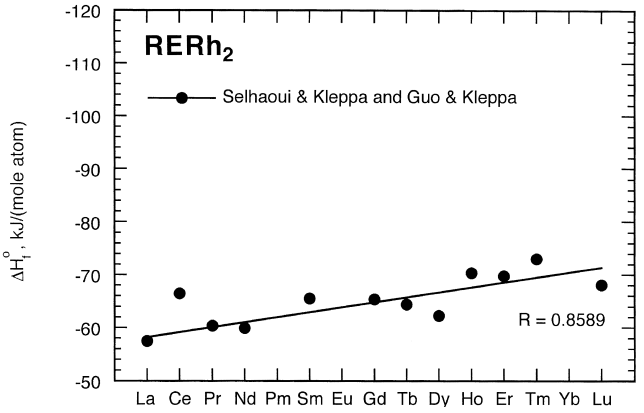

Fig. 4. Standard enthalpies of formation for the $RERh_2$ family. The structure of $EuRh_2$ is unknown. All the other $RERh_2$ compounds have the $MgCu_2$ structure.

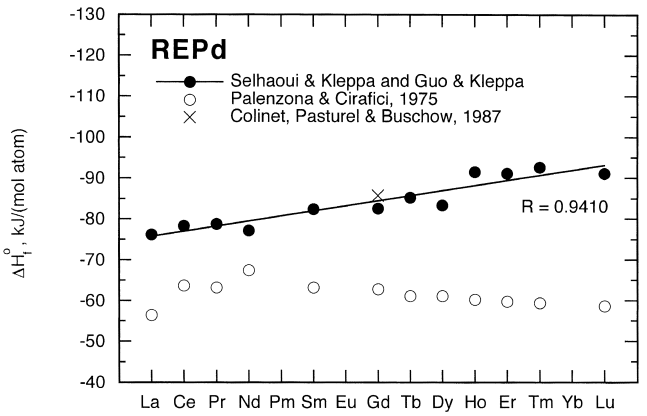

Fig. 5. Standard enthalpies of formation for the REPd family. LaPd, CePd, PrPd, NdPd, SmPd, EuPd, GdPd and TbPd have the CrB structure. DyPd and HoPd have the FeB structure. ErPd, TmPd, YbPd and LuPd have the CsCl structure.

various alloy families of rare earth elements with Ru, Rh, Pd, Ir and Pt. In each case, the structure type of each of the compounds is stated in the figure captions. For comparison, these figures also include the available calorimet-

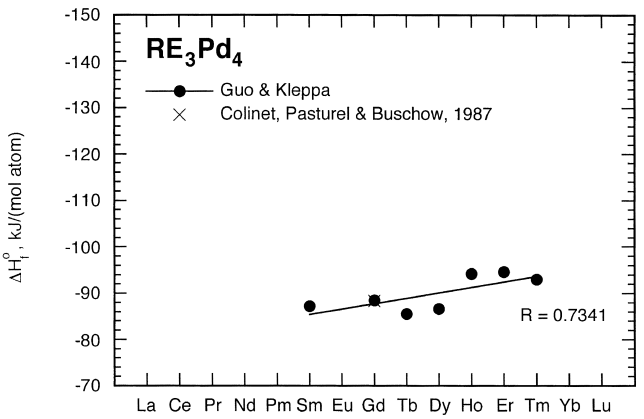

Fig. 6. Standard enthalpies of formation for the RE_3Pd_4 family. All RE_3Pd_4 compounds have the Pu_3Pd_4 structure.

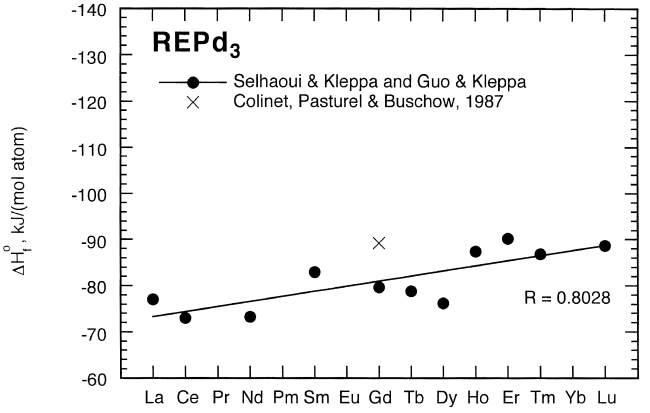

Fig. 7. Standard enthalpies of formation for the $REPd_3$ family. All the $REPd_3$ compounds have the $AuCu_3$ structure.

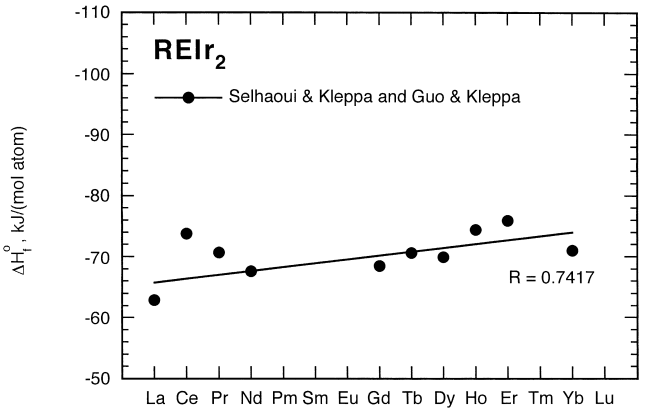

Fig. 8. Standard enthalpies of formation for the $REIr_2$ family. All the $REIr_2$ compounds have the $MgCu_2$ structure.

ric values, if any, reported in the literature. However, it should be noted that some of the enthalpy values cited from the literature are not standard enthalpies of formation, but enthalpies of formation at elevated temperatures. Even

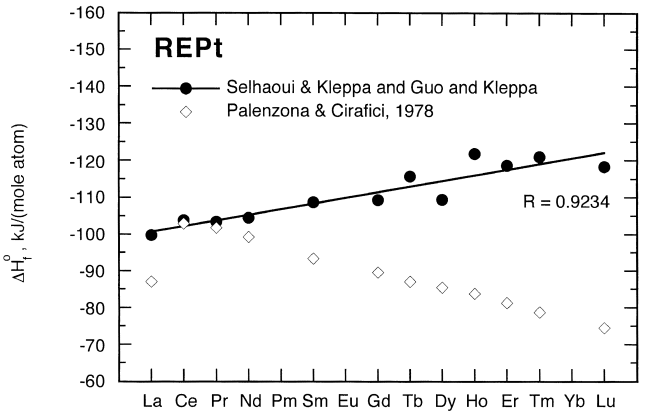

Fig. 9. Standard enthalpies of formation for the REPt family. LaPt and CePt have the CrB structure. PrPt has the FeB structure at low temperatures and the CrB structure at high temperatures. The compound EuPt does not exist. All the other REPt compounds have the FeB structure.

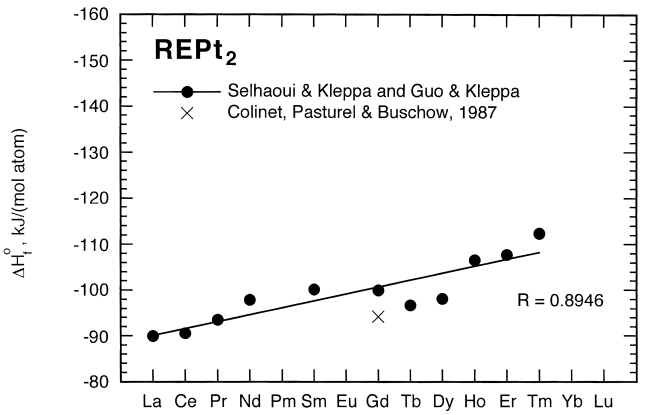

Fig. 10. Standard enthalpies of formation for the $REPt_2$ family. The structure of $PrPt_2$ is unknown but is believed to be the $MgCu_2$ structure. The compound $LuPt_2$ does not exist. All the other $REPt_2$ compounds have the $MgCu_2$ structure.

so, because the differences between 298.15 K data and the data at higher temperatures usually are not very significant, conclusions drawn from comparisons should still hold true. In Table 1, for non-standard enthalpies of formation, the temperatures at which the values apply are given in parentheses immediately after the values cited.

It will be seen from Fig. 2 that the two values of Shilov et al. [47] are in very good agreement with our own values. In Fig. 5 a value for GdPd reported by Colinet et al. [57] is in good agreement with our own value. However, the values of Palenzona and Cirafici [48] for REPd alloys (Fig. 5) are all significantly less exothermic than ours. The value of Colinet et al. [57] for Gd_3Pd_4 is in perfect agreement with our own value (Fig. 6). The values of Colinet et al. [57] for $GdPd_3$ (Fig. 7) and for $GdPt_2$ (Fig. 10) are either somewhat more exothermic (for $GdPd_3$) or less exothermic (for $GdPt_2$). In Fig. 9, the values reported by Palenzona and Cirafici [49] are all significantly less exothermic than our own values, except for CePt and PrPt.

As we did previously for the $RENi_5$ and RENi families, in order to explore the systematic variation of the standard enthalpy of formation within individual alloy families, we have fitted straight lines to all of our own experimental results in Figs. 2–10. However, we have excepted from these fits the values for $CeRu_2$ in Fig. 2, $CeRh_2$ in Fig. 4, and $CeIr_2$ in Fig. 8. The values for these compounds clearly are significantly more exothermic than the values for the neighboring alloys. On the other hand, it is worth noting that the enthalpies of formation of CePd in Fig. 5, of $CePd_3$ in Fig. 7, of CePt in Fig. 9 and of $CePt_2$ in Fig. 10 seem to fit in well with the values for the neighboring alloys. These four Ce alloys therefore 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, in all the figures (Figs. 2–10), we have no enthalpy of formation data for the compounds of Eu and Yb, which both have the characteristic valency of +2. Any plot of the enthalpies of formation against the atomic number of rare earth elements, which includes data also for alloys of Eu and Yb, would be expected to show significantly less exothermic values for these two metals. This is well known from the systematic study of Colinet et al. [64].

It was suggested by Gschneidner [65,66] that the

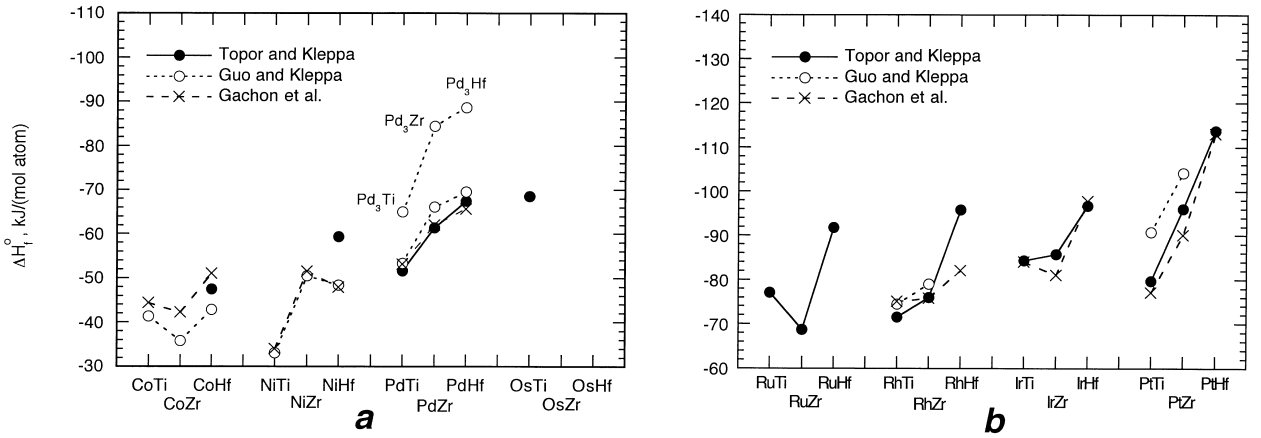

Fig. 11. Standard enthalpies of formation for some equiatomic compounds formed between Group IV elements and Group VIII elements and for Pd_3Me (Me = Ti, Zr, or Hf). (a) Standard enthalpies of formation for CoTi, CoZr, CoHf, NiTi, NiZr, NiHf, PdTi, PdZr, PdHf, Pd_3Ti, Pd_3Zr, Pd_3Hf, and for OsTi. All the three compounds of Co with Ti, Zr, and Hf have the CsCl structure. NiTi has both the CsCl structure and the NiTi structure. NiZr and NiHf have the CrB structure. PdTi has the CsCl structure, but the structures of PdZr and PdHf are unknown. Pd_3Ti and Pd_3Zr have the Ni_3Ti structure, while Pd_3Hf has both the Ni_3Ti and the Cu_3Au structures. OsTi has the CsCl structure. (b) Standard enthalpies of formation for RuTi, RuZr, RuHf, RhTi, RhZr, RhHf, IrTi, IrZr, IrHf, PtTi, PtZr, and PtHf. All Ru compounds with Ti, Zr and Hf have the CsCl structure. RhTi has the AuCu structure, but RhZr and RhHf have the CsCl structure. IrZr has the CsCl structure, but the structures of IrTi and IrHf are unknown. PtTi has both the CsCl structure and the AuCd structure. PtZr and PtHf have both the CsCl structure and the CrB structure.

enthalpies of formation of rare earth alloys, their reduced melting temperatures, and their relative molar volumes all should be related to the lanthanide contraction in the compounds compared to the contraction in the pure metals. For example, if the lanthanide contraction in the compounds is greater than in the corresponding metals, then the enthalpies of formation are predicted to become more exothermic from La to Lu. In this scheme, the ratio of the molar volume of the compound ($V^{o}_{REMe_x}$) to the atomic volume of the element (V^{o}_{RE}), normalized with respect to this ratio for the first member of the lanthanide series ($V^{o}_{LaMe_x}/V^{o}_{La}$), is used as an indicator to predict the systematic change in the stability of the compounds.

We have checked the validity of these predictions for all the binary rare earth compounds reviewed in the present work. From Figs. 1–10, we see that as a general rule, the magnitude of the negative enthalpy of formation increases with the increasing atomic number of the rare earth element. However, when we consider Gschneidner's molar volume ratios [$(V^{o}_{REMe_x}/V^{o}_{RE})/(V^{o}_{LaMe_x}/V^{o}_{La})$], we find little or no change in this ratio with increasing atomic number for RERh and REPd and positive rather than negative changes for the remaining alloy families. This suggests that the Gschneidner prediction does not apply to the rare earth alloy systems reviewed in this paper.

3.2. Alloys of Group IV elements with Group VIII elements

Fig. 11a,b shows a comprehensive comparison of the standard enthalpies of formation of the equiatomic compounds formed between Group IV elements and Group VIII elements. The structure of each of the compounds included in the figure is described in the figure caption. We have included in this figure the two sets of data for these compounds that were reported by this laboratory: one set was published by Topor and Kleppa in the 1980s, while the other was published recently by Guo and Kleppa. Also included are data reported by Gachon et al. [58]. It will be seen from Fig. 11a,b that in most cases the agreement among these data reported by different investigators is from good to excellent. However, the agreement between the values of different authors for CoTi, CoZr and CoHf is poor. The data of Guo and Kleppa [45] are less exothermic than the data of Gachon et al. [58], while the only value reported by Topor and Kleppa for CoHf [18] is more exothermic than Guo and Kleppa's value, but less exothermic than the value of Gachon et al. [58]. Apart from this, Topor and Kleppa's value for NiHf [18] is significantly more exothermic than the values of both Guo and Kleppa [45] and Gachon et al. [58]. The recently published values of Guo and Kleppa [45] for PtTi and PtZr are also significantly more exothermic than the values of both Gachon et al. [58] and of Topor and Kleppa [16]. The value of Topor and Kleppa for RhHf [14] is significantly more exothermic than the value of Gachon et al. [58].

Although there are some discrepancies between the values of different authors, it is still indicated that the magnitude of the negative enthalpies of formation increases in the sequence Ti<Zr<Hf for alloys with Rh, Pd, Ir and Pt. However, alloys of Co and Ru with Ti, Zr and Hf show a different tendency: the magnitude of the enthalpy of formation first decreases from Ti to Zr, and then increases from Zr to Hf. This is in striking contrast to the alloys of Ni with Ti, Zr and Hf. From Fig. 11a we see that the magnitude of the negative enthalpy of formation for alloys of Ni with Ti, Zr and Hf first increases from Ti to Zr, and then decreases from Zr to Hf.

In addition to the equiatomic compounds formed between Group IV elements and Group VIII elements, it is also interesting to consider the A_3B type alloys formed between the elements in these two groups. Although we do not have enough data to compare all the alloys of this type, we will consider Pd_3Me (Me=Ti, Zr, or Hf) as an example. Fig. 11a shows the standard enthalpies of formation for Pd_3Ti, Pd_3Zr and Pd_3Hf, compared with the values for their equiatomic counterparts. The enthalpies of formation for these three A_3B type compounds show the usual tendency, i.e. they become more exothermic in the sequence Ti<Zr<Hf. Moreover, it is also evident that these three A_3B type compounds have much more exothermic enthalpies of formation than their equiatomic counterparts.

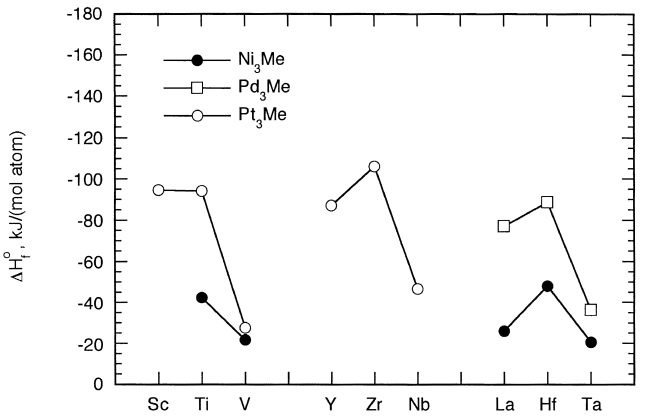

Fig. 12. Standard enthalpies of formation for A_3B type compounds formed between early and late transition metals (A stands for one of the Group VIII elements, while B stands for an element from either Group III, or Group IV, or Group V). Pt_3Sc has the $AuCu_3$ structure. Three different structures have been found for Pt_3Ti. They are Pt_3Ti structure, Cu_3Au structure and Ni_3Ti structure. Pt_3V has the Al_3Ti structure at low temperature and the Cu_3Au structure at high temperature. The structure of Ni_3Sc is unknown. Ni_3Ti has the Ni_3Ti structure. Ni_3V has the Al_3Ti structure. Pt_3Y has both the Fe_3C and the Cu_3Au structures. Pt_3Zr has both the Ni_3Ti and Cu_3Au structures. Pt_3Nb has both the Cu_3Ti and Pt_3Nb structures. Ni_3La has the Be_3Nb structure. Ni_3Hf has both the Pb_3Ba and Pd_3Ta structures. Ni_3Ta has the Pt_3Nb structure at low temperature and the Al_3Ti structure at high temperature. Pd_3La has the Cu_3Au structure. Pd_3Hf has both the Cu_3Au and the Ni_3Ti structures. Pd_3Ta has both the Al_3Ti and the Pd_3Ta structures.

3.3. A_3B type alloys of Groups III, IV, and V elements with Group VIII elements

Fig. 12 presents a comparison of the enthalpies of formation for A_3B type alloys formed between elements of Groups III, IV, and V with elements from Group VIII. The structure of each compound included in this figure is described in the figure caption. Among the 14 alloys included in Fig. 12, 11 have enthalpy of formation values determined in this laboratory. These 11 alloys are Pt_3Sc [43], Pt_3V [42], Ni_3V [43], Pt_3Y [26], Pt_3Nb [42], Ni_3Ti [46], Ni_3Hf [43], Ni_3Ta [42], Pd_3La [27], Pd_3Hf [43,45], and Pd_3Ta [42]. ΔH_f^o values for Pt_3Ti, Pt_3Zr, and Ni_3La are cited, respectively, from Gachon et al. [58], Selhaoui [67] and Shilov et al. [47]. Fig. 12 shows that the magnitude of the enthalpy of formation for all Ni_3Me, Pd_3Me and Pt_3Me type alloys increases somewhat from the compounds in which Me is a Group III element to the compounds in which Me is a Group IV element. While there is virtually no change from Pt_3Sc to Pt_3Ti, there is always a drastic decrease in all the compounds in which Me is a Group V element.

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