Standard enthalpies of formation of some Th alloys with Group VIII elements (Co, Ni, Ru, Rh, Pd, Ir and Pt), determined by high-temperature direct synthesis calorimetry

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Abstract

The standard enthalpies of formation of seven alloys formed between Th, an element from Group III, and Co, Ni, Ru, Rh, Pd, Ir and Pt, elements from Group VIII, have been determined by high-temperature direct synthesis calorimetry at 1473 ± 2 K. The following values of ΔH_f^o, in kJ (mol atom)$^{-1}$, are reported: ThCo$_5$, -17.0 ± 2.3; ThNi$_5$, -34.8 ± 1.9; ThRu$_2$, -28.9 ± 1.6; ThRh$_3$, -60.3 ± 2.8; ThPd$_3$, -86.1 ± 3.2; ThIr$_2$, -78.0 ± 3.4; and ThPt$_3$, -89.7 ± 5.1. The results are compared with predicted values from the Miedema model and with available literature data on the Gibbs free energies of formation for ThCo$_5$, ThNi$_5$, ThRu$_2$ and ThRh$_3$. The results are also compared with an earlier calorimetric value of ΔH_f^o for ThRh$_3$ (Kubaschewski et al., Materials Thermochemistry, Pergamon, Oxford, 1993) and with the standard enthalpies of formation for URu$_3$, URh$_3$, UPd$_3$, as well as for CeNi$_5$, CeRu$_2$, CeRh$_3$, CePd$_3$ and CeIr$_2$ previously reported in investigations carried out in this laboratory. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Since the early 1980s, a systematic study of the thermochemistry of binary intermetallic compounds formed between early transition metals and late transition metals has been one of the major interests in our University of Chicago laboratory. During most of the 1980s, our investigations were focused on the binary liquid and/or solid alloys formed between Cu and elements from Group IV (Ti, Zr and Hf) and between Cu and elements from Group III (Sc, Y, La and Lu) [1–3], as well as on the equi-atomic compounds formed between elements from Group IV and elements from Group VIII [4–12]. During this period there was also a pioneering study of alloys formed between La, an element from Group III, and Ni, an element from Group VIII [13]. The calorimetric methods used in this period included solution calorimetry in liquid copper, solute–solvent drop calorimetry, and direct synthesis calorimetry.

Starting in the early 1990s, by using high-temperature direct synthesis calorimetry at 1200°C, our study was extended to the binary alloys formed between elements from Group III and elements from Group VIII in the periodic table. Very recently, Guo and Kleppa prepared a comprehensive review of the thermochemical data that were determined in this laboratory during the past two decades. This review covered binary alloys formed between early and late transition metals and between early transition metals and noble metals [14]. Tabulated in this review were 290 enthalpy of formation values for 273 such binary compounds. Among the 273 compounds, 166 were formed between elements from Group III and elements from Group VIII.

However, alloys formed between actinides, which belong to Group III, and elements from Group VIII have not as yet been extensively studied. On the one hand, very few calorimetric values have been reported in the literature for such compounds. Our recent review of the published literature in this field going back about 30 years revealed only five calorimetric studies. These studies are summarized as follows. The first of these studies, carried out by

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Dannöhl and Lukas in 1974, was based on solution calorimetry in liquid aluminum at 750°C. Four ΔH_f° values for UAl_2, UNi_2, UNi_5 and UFeAl, were reported [15]. The second calorimetric study was that of Wijbenga, who in 1982 determined the enthalpy of formation of the important compound UPd_3 by fluorine combustion calorimetry [16]. The third calorimetric study was carried out in our own laboratory in 1991 by Jung and Kleppa [17]. They reported four new values for the standard enthalpies of formation of URu_3, URh_3 and UPd_3. Of the four values, three were obtained by direct synthesis calorimetry at 1473 ± 2 K, while one was obtained by solute–solvent drop calorimetry at the same temperature. The fourth set of data was published by Kubaschewski et al. in 1993 [18]. This set includes seven values of ΔH_f° for Th_7Rh_3, ThRh, $ThRh_3$, $ThRh_5$, ThRu, Th_7Ru_3, and UFe_2, respectively. The fifth and last calorimetric study was published in 1995 by Antony et al. [19]. These authors reported on calorimetric values valid at room temperature for the enthalpies of formation of UNi_5, UNi_2 and UFe_2. In contrast to the scarce calorimetric studies, there exist much more published data of Gibbs free energy of formation for such compounds in the literature, mostly obtained by EMF measurements, but a few obtained by vapor pressure measurements [20–40].

In the present investigation we carried out calorimetric experiments on a total of 14 Th alloys with elements from Group VIII ($ThCo_5$, $ThNi_5$, ThRu, $ThRu_2$, ThRh, $ThRh_2$, $ThRh_3$, Th_7Rh_3, ThPd, $ThPd_3$, $ThIr_2$, $ThIr_3$, $ThPt_3$, and $ThPt_5$). However, we found that our experiments were not successful for half of these compounds. This was due either to the formation of mixed products or to incomplete reactions. As a result, in this paper we report only on the standard enthalpies of formation for the following seven compounds: $ThCo_5$, $ThNi_5$, $ThRu_2$, $ThRh_3$, $ThPd_3$, $ThIr_2$ and $ThPt_3$.

2. Experimental details and starting materials

The experiments were all carried out by the direct synthesis method, using a single-unit differential microcalorimeter, which has been described in detail in an earlier communication [41]. This unit was maintained at 1473 ± 2 K during the whole research project. All experiments were conducted in an inert atmosphere of pure argon gas. In order to eliminate possible traces of oxygen and nitrogen, this gas was purified by passing it through a fused-silica tube filled with pure titanium sponge (with grain size of 3 mm) maintained at about 1173 K. The actual synthesis reactions took place in boron nitride (BN) crucibles.

Calibration of the calorimeter was achieved by dropping pieces of 2-mm diameter high purity copper of known mass from room temperature into the calorimeter at 1473 ± 2 K. The enthalpy of pure copper at this temperature, 46 465 J mol^{-1}, was taken from Hultgren et al. [42]. The calibrations were reproducible within $\pm1\%$.

The metallic purity of the metals used for the direct synthesis ranged from 99.8% for Th, to 99.9% for Ru, Rh, and Pt, and to 99.95% for Pd and Ir. The particle sizes were −100 mesh for Th, −200 mesh for Rh, Pd, Ir and Pt, and −325 mesh for Co, Ni, and Ru.

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 cobalt and nickel powders used for the preparation of the $ThCo_5$ and $ThNi_5$ compounds were reduced in pure hydrogen for 1 h at about 773 and 873 K, respectively. The powders were then passed through a 325-mesh sieve just before the pellets were prepared. All the metals were purchased from Johnson Matthey, ÆSAR Group (Ward Hill, MA), except for Rh and Pt, which were obtained from Engelhard (Newark, NJ). 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 thermal treatment the platinum powder was sifted 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.

It is worth noting that Th is a radioactive element and its powder is apt to be oxidized in air, especially in the presence of moisture. The Th powder was examined by X-ray powder diffraction (XRD) at the beginning of this research project. XRD showed that the Th powder contained a small amount of ThO_2. A rough estimate from the height of the ThO_2 111 peak (100% intensity) on the XRD patterns indicated that this powder might contain as much as 3–5% of ThO_2. However, taking the low X-ray penetration depth in the very heavy Th metal into consideration, the XRD patterns obtained may mostly reflect the average composition of the surface layer and the layer near the surface of the Th particles. For this reason, we believe that the ThO_2 content in our starting material of pure Th powder should be less than the rough estimate of 3–5%. In order to avoid further oxidation after the opening of the sealed Th bottle, we tried to store the Th powder and to prepare Th sample pellets in a glove box. Pure and dry argon gas was passed through this glove box. Although the glove box was perfect for the storage of the Th powder, it did not work for sample preparation. When we tried to transfer the metal powders for the purpose of weighing or mixing, these powders flew in every direction within the glove box due to static electricity. In order to control the static electricity and to prevent charged metal particles from flying, we tried a few techniques, but without success. These techniques included a spray called Static Free purchased from Chemtronics (Kennosaw, WA), a

Table 1
Observed heats of reaction, average heat contents at 1473 K, and calculated standard enthalpies of formation, in kJ (mol atom)$^{-1}$[a]

Compound	Melting point (°C)	Structure type	$\Delta H(1)$	$\Delta H(2)$	ΔH_f°
ThCo$_5$	1425	CaCu$_5$	20.7 ± 1.1 (7)	37.7 ± 1.9 (5)	-17.0 ± 2.3
ThNi$_5$	1530	CaCu$_5$	2.4 ± 0.8 (5)	37.2 ± 1.6 (6)	-34.8 ± 1.9
ThRu$_2$	>1500	MgCu$_2$	4.2 ± 0.9 (5)	33.1 ± 0.8 (5)	-28.9 ± 1.6
ThRh$_3$	–	AuCu$_3$	-25.1 ± 1.2 (6)	35.3 ± 2.3 (5)	-60.3 ± 2.8
ThPd$_3$	>1500	TiNi$_3$	-51.7 ± 2.5 (5)	34.4 ± 1.7 (4)	-86.1 ± 3.2
ThIr$_2$	–	MeCu$_2$	-44.2 ± 2.7 (4)	33.8 ± 1.2 (7)	-78.0 ± 3.4
ThPt$_3$	>1500	Unknown	-56.8 ± 4.6 (5)	33.0 ± 1.7 (4)	-89.7 ± 5.1

[a] Numbers in parentheses indicate numbers of experiments averaged.
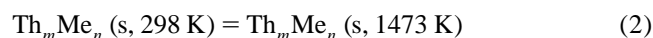
non-fan ionizer purchased from Vacuum/Atmospheres Company (Hawthorne, CA), and an anti-static instrument called Zerostat purchased from Aldrich (St. Louis, MO). In the end, we had to carry out the entire process of sample preparation in a separate room. We tried to keep this room as cool and dry as possible. When a sample pellet was prepared, it was immediately transferred into a vacuum desiccator and was stored there until use. The starting material of Th powder was examined again by XRD after the completion of the research project. A comparison was made between the XRD patterns obtained before and after the project. It was difficult to tell whether there was an increase in the amount of ThO$_2$ in the Th powder.
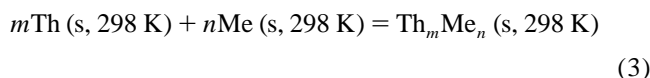
3. Results

The standard enthalpy of formation of the compound Th$_m$Me$_n$ is obtained from the difference between two sets of measurements. In the first set the following reaction takes place in the calorimeter

$$m\text{Th (s, 298 K)} + n\text{Me (s, 298 K)} = \text{Th}_m\text{Me}_n \text{ (s, 1473 K)} \tag{1}$$
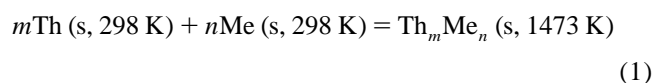
The products of reaction (1) were reused in a subsequent set of measurements to determine the corresponding heat contents

$$\text{Th}_m\text{Me}_n \text{ (s, 298 K)} = \text{Th}_m\text{Me}_n \text{ (s, 1473 K)} \tag{2}$$

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

$$m\text{Th (s, 298 K)} + n\text{Me (s, 298 K)} = \text{Th}_m\text{Me}_n \text{ (s, 298 K)} \tag{3}$$

The standard enthalpy of formation is given by

$$\Delta H_f^{\circ}(\text{Th}_m\text{Me}_n) = \Delta H(1) - \Delta H(2) \tag{4}$$

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

Table 1 summarizes all the experimental results obtained for the seven alloys. The reported values of $\Delta H(1)$ and $\Delta H(2)$ are averages of four to seven individual determinations with standard deviations of 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

$$\delta = \sqrt{\delta_1^2 + \delta_2^2 + \delta_3^2}$$

After the measurements, all the alloy samples were examined by XRD. The results of these examinations are listed in Table 2. This table shows that ThPt$_3$ does not have a standard XRD pattern. At the same time, no crystallographic data for this compound were found in the Pearson's Handbook of Crystallographic Data for Intermetallic Phases [43]. Hence, it was impossible to calculate a diffraction pattern for ThPt$_3$ by using the VersaTerm-Pro software, purchased from Abelbeck Software. However, because we had the standard XRD patterns for Th, Pt, and

Table 2
Summary of X-ray diffraction examination results

Compound	XRD examination result
ThCo$_5$	ThCo$_5$ + minor Th$_2$Co$_{17}$ + ThO$_2$ (~5%)
ThNi$_5$	ThNi$_5$ + minor ThNi and Th$_2$Ni$_{17}$ + ThO$_2$ (~5%)
ThRu$_2$	ThRu$_2$ + ThRu (<2%) + ThO$_2$ (~5%)
ThRh$_3$	ThRh$_3$ + two weak unknown peaks + ThO$_2$ (~5%)
ThIr$_2$	ThIr$_2$ + minor ThIr and ThIr$_3$ + ThO$_2$ (~5%)
ThPd$_3$	ThPd$_3$ + ThPd (<2%) + four weak unknown peaks + ThO$_2$ (~5%)
ThPt$_3$	No unreacted elements, ThPt (<5%) + ThO$_2$ (~5%)

ThPt, as well as the calculated patterns for Th_3Pt_5 and Th_7Pt_3, we were able to establish that our $ThPt_3$ sample did not contain any unreacted elements and that it contained less than 5% of ThPt and about 5% of ThO_2. By eliminating the reflection peaks for ThPt and ThO_2, we concluded that the XRD pattern we obtained from our $ThPt_3$ sample was in fact the pattern for the $ThPt_3$ compound.

All the other six alloys have standard XRD patterns. From Table 2 we see that a small amount of ThO_2 was found in all these samples. We believe that most of the ThO_2 found in the reacted samples had its origin in the Th starting material. However, we cannot completely exclude the possibility that a part of the ThO_2 was formed during the sample preparation. The pre-existing ThO_2 will not participate in the reaction. Hence, it will not contribute to the difference between the enthalpy changes of Eqs. (1) and (2). The probability that there formed additional ThO_2 during the direct synthesis is minimal since the reaction took place in a very good inert atmosphere.

In addition to ThO_2, a second and, in some cases, a third alloy phase was found in the reacted samples. There was a minor amount of Th_2Co_{17} in our $ThCo_5$ samples, and minor amounts of $ThNi + Th_2Ni_{17}$ in the $ThNi_5$ samples. Very small amounts of ThRu and ThPd were found in the $ThRu_2$ and $ThPd_3$ samples, respectively. Very small amounts of $ThIr + ThIr_3$ were found in the $ThIr_2$ samples. Although it is impossible to make a quantitative estimate of the percentage of a second or a third alloy phase in the reacted samples solely based on the XRD patterns, a very rough estimate may be good enough for our purpose. Once we are sure that the total percentage of the alloy phases other than the principal phase will not be more than 10%, we feel confident in the reported enthalpy values. We believe that the formation of up to 10% of other alloy phases during the direct synthesis reactions will not introduce any significant errors in our reported enthalpy values. This is because the heats of formation of these second and third phases usually are roughly comparable in magnitude to the heat of formation of the principal phase.

4. Discussion

Fig. 1 shows plots of our experimental results for the standard enthalpies of formation of Th + Me alloys (Me stands for Co, or Ni, or Ru, or Rh, or Pd, or Ir, or Pt). All values are given in kJ (mol atom)$^{-1}$. Also plotted in Fig. 1 are the predicted values calculated from the semi-empirical model of Miedema and co-workers [44]. There is only one earlier calorimetric value in the literature, which is for $ThRh_3$ by Kubaschewski et al. [18]. This value is plotted in Fig. 1 as well. From this figure, we see that the Miedema model usually gives somewhat more exothermic values than we observed. However, for $ThNi_5$, the predicted value (-35 kJ (mol atom)$^{-1}$) is in excellent

agreement with our result (-34.8 ± 1.9 kJ (mol atom)$^{-1}$). Fig. 1 also shows that the value given by Kubaschewski et al. for $ThRh_3$ (-80.4 kJ (mol atom)$^{-1}$) is significantly more exothermic than our result (-60.3 ± 2.8 kJ (mol atom)$^{-1}$). It is also more exothermic than the predicted value (-74 kJ (mol atom)$^{-1}$) for this compound.

Due to the scarcity of calorimetric values for these compounds in the literature, we are not able to compare our enthalpy of formation values with earlier calorimetric values for six of the seven compounds studied in this investigation. In principle, we may compare our results with enthalpy of formation values derived indirectly from Gibbs free energies of formation. Usually these enthalpy values are calculated by correcting the Gibbs energies using the temperature dependence of the EMF measurements. However, our experience tells us that one must be very cautious when using enthalpy values derived indirectly in this way from Gibbs free energy of formation data. On the other hand, Gibbs free energies of formation at elevated temperatures often are not very different from the enthalpies of formation for the same compounds. For this reason, we decided to compare our results directly with corresponding Gibbs free energies of formation.

In Fig. 2 we compare our standard enthalpies of formation for $ThCo_5$ and $ThNi_5$ with the Gibbs free energies of formation for the same alloys at 973 K. The Gibbs energy values were determined using EMF cells with solid CaF_2 as the electrolyte in the temperature range 841–1141 K [20,22]. It is apparent from Fig. 2 that our values of ΔH_f^o for $ThCo_5$ (-17.0 ± 2.3 kJ (mol atom)$^{-1}$) and for $ThNi_5$ (-34.8 ± 1.9 kJ (mol atom)$^{-1}$) are in reasonable agreement with the $\Delta G_{973\ K}^o$ values for the same compounds, -21.3 ± 0.29 kJ (mol atom)$^{-1}$ for $ThCo_5$ and -36.4 ± 0.13 kJ (mol atom)$^{-1}$ for $ThNi_5$ [20,22]. In Fig. 2 we also compare our results for $ThNi_5$ and $ThIr_2$ with our earlier values of ΔH_f^o for $CeNi_5$ [45] and $CeIr_2$ [46]. Ce and Th occupy equivalent positions in the lanthanide and actinide series, respectively, in the periodic table. The comparison indicates that the magnitude of the standard enthalpy of formation increases somewhat from Ce alloys to Th alloys. Also plotted in Fig. 2 are two earlier calorimetric values for UNi_5, determined by Dannöhl and Lukas (-30.1 kJ (mol atom)$^{-1}$) [15] and by Antony et al. (-39.5 ± 8.6 kJ (mol atom)$^{-1}$) [19], respectively. Note that these two values differ from each other significantly and that the uncertainty associated with Antony's value is very significant. Therefore, it is difficult to discuss the tendency in the magnitude variation of ΔH_f^o from $ThNi_5$ to UNi_5.

In Fig. 3 we compare our values of ΔH_f^o for $ThRu_2$ and $ThRh_3$ with the values of $\Delta G_{1100\ K}^o$ for the same alloys [28,34]. Obviously, the values of $\Delta G_{1100\ K}^o$ are more exothermic than our values of ΔH_f^o for both of these two compounds. It is interesting to note that the two values of $\Delta G_{973\ K}^o$ for $ThCo_5$ and $ThNi_5$ and the two values of $\Delta G_{1100\ K}^o$ for $ThRu_2$ and $ThRh_3$ are all more negative than
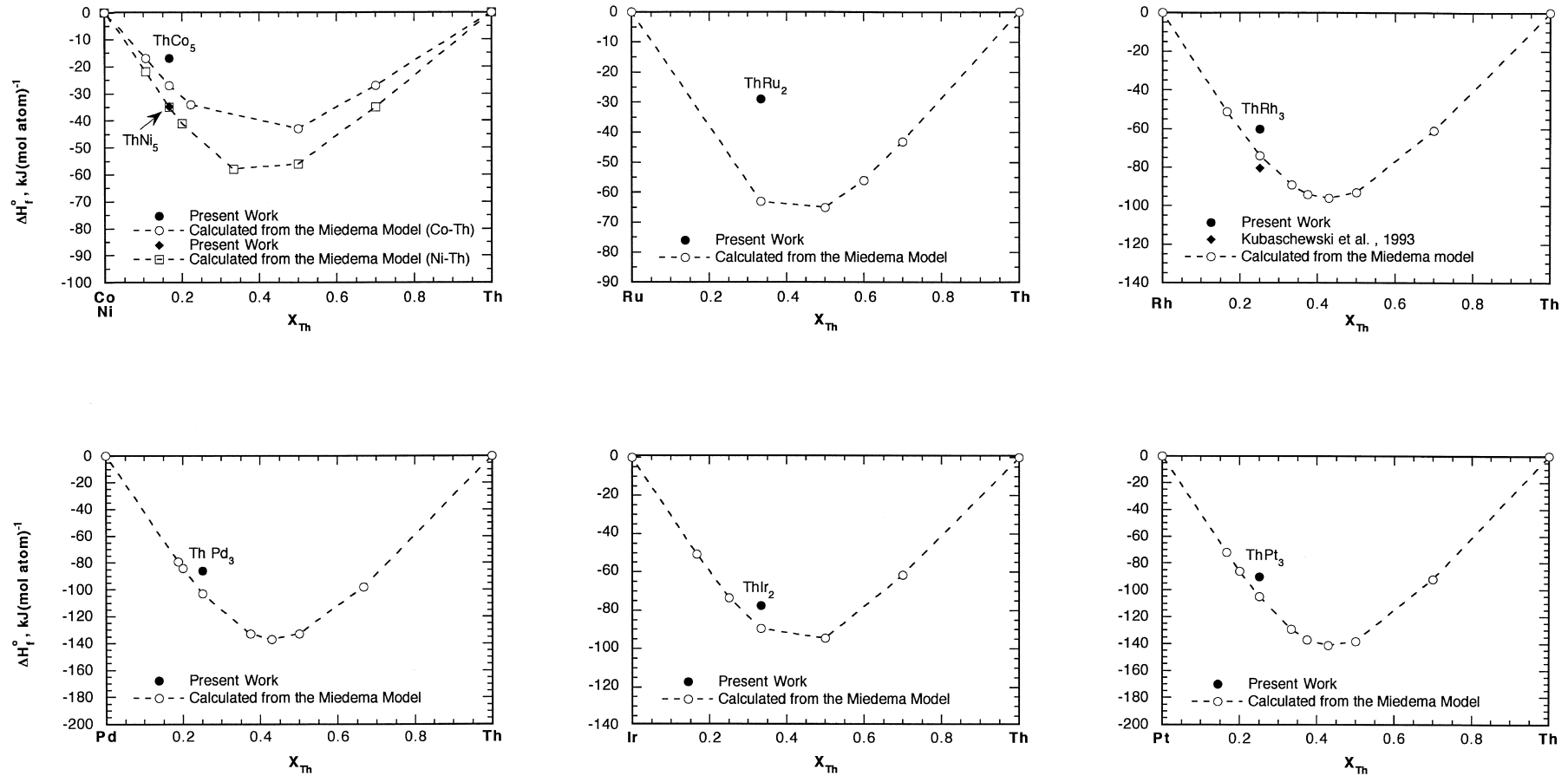
Fig. 1. Standard enthalpy of formation for $ThCo_5$, $ThNi_5$, $ThRu_2$, $ThRh_3$, $ThPd_3$, $ThIr_2$ and $ThPt_3$, compared with predicted values calculated from the Miedema model [44].
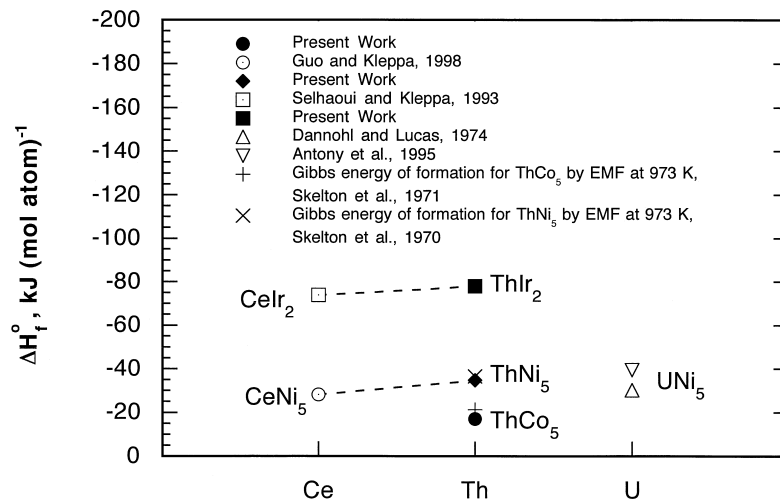
Fig. 2. Standard enthalpies of formation for $ThCo_5$, $ThNi_5$ and $ThIr_2$, compared with earlier values for $CeNi_5$ by Guo and Kleppa [45] and for $CeIr_2$ by Selhaoui and Kleppa [46], and with earlier values of Gibbs free energy of formation for $ThCo_5$ and $ThNi_5$ by Skelton et al. [20,22].

their corresponding values of ΔH_f°. This might suggest that the entropy changes of the four reactions of formation for these four compounds are all small positive values. In Fig. 3 our value of ΔH_f° for $ThRh_3$ is also compared with an earlier calorimetric value given by Kubaschewski et al. [18]. As mentioned above in the discussion of Fig. 1, Kubaschewski's value is significantly more exothermic than our own value for this compound. As we did in Fig. 2, we compare our new results with our earlier calorimetric values of ΔH_f° for $CeRh_3$ [46], $CeRu_2$ [46], as well as for URh_3 [17]. It is evident that the magnitude increases from $CeRh_3$ to $ThRh_3$, then to URh_3, and also from $CeRu_2$ to $ThRu_2$. Although we do not have a value for URu_2, we have plotted the value of ΔH_f° for URu_3 in Fig. 3. We believe that the value of ΔH_f° for URu_2 may be somewhat

more negative, but not very different from the value for URu_3. If this is the case, it is possible that the magnitude of ΔH_f° may increase slightly from $ThRu_2$ to URu_2. The tendency observed in the variation of ΔH_f° in Fig. 3 is in a striking contrast to that observed in Fig. 4, which shows that the magnitude of ΔH_f° increases significantly from $CePd_3$ to $ThPd_3$, and then decreases drastically from $ThPd_3$ to UPd_3.

In Fig. 5 we plot our values of ΔH_f° for the $ThMe_5$ family (Me=3d metals in Group VIII), for the $ThMe_3$ family (Me=4d metals in Group VIII), and for the $ThMe_2$ family (Me=5d metals in Group VIII). These values are compared with the values of ΔH_f° for the UMe_3 family (Me=4d metals in Group VIII), which were determined by Jung and Kleppa in 1991 [17]. For the $ThMe_5$ family we
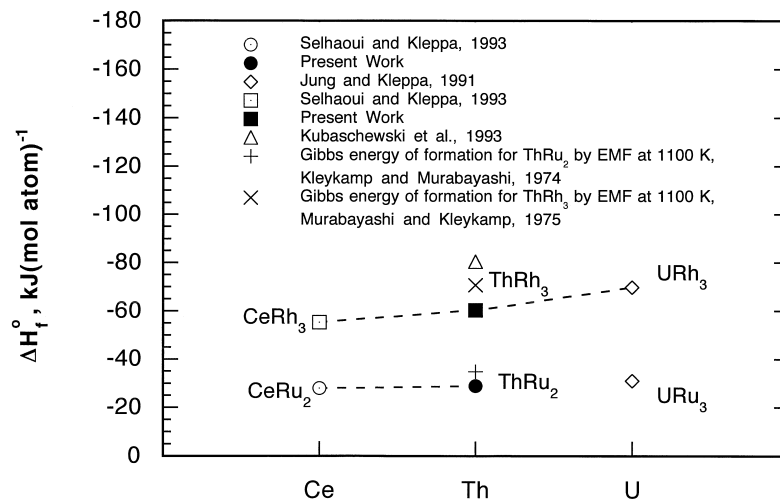

Fig. 3. Standard enthalpies of formation for $ThRu_2$ and $ThRh_3$, compared with earlier values for $ThRh_3$ by Kubaschewski et al. [18], for URu_3 and URh_3 by Jung and Kleppa [17], for $CeRu_2$ and $CeRh_3$ by Selhaoui and Kleppa [46], and with earlier values of Gibbs free energy of formation for $ThRu_2$ by Kleykamp and Murabayashi [28] and for $ThRh_3$ by Murabayashi and Kleykamp [34].
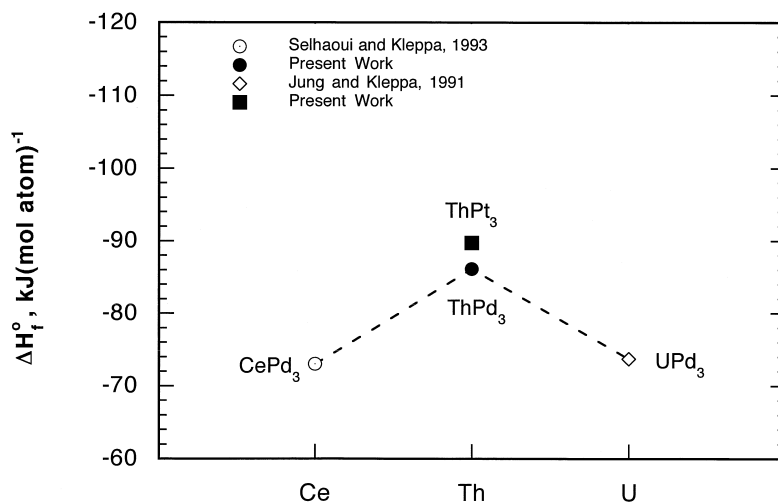
Fig. 4. Standard enthalpies of formation for $ThPd_3$ and $ThPt_3$, compared with earlier values for $CePd_3$ by Selhaoui and Kleppa [46] and for UPd_3 by Jung and Kleppa [17].

did not determine ΔH_f^o for $ThFe_5$. We plotted instead $\Delta G_{973\ K}^o$ for this compound, as determined by Skelton et al. [25]. In the $ThMe_3$ family we did not study $ThRu_3$. Instead, we determined ΔH_f^o for $ThRu_2$. Because we believe that ΔH_f^o for $ThRu_3$ should not be very different from ΔH_f^o for $ThRu_2$, we have plotted our value of ΔH_f^o for $ThRu_2$ in Fig. 5. For the $ThMe_2$ family we did not study the compound of $ThOs_2$. However, Kleykamp investigated this compound in 1979 by EMF measurements in the temperature range 1020–1220 K [37]. We calculated the Gibbs energy of formation for this compound at 1100 K from the equation given by Kleykamp, -35.2 kJ (mol atom)$^{-1}$. However, the value of ΔH_f^o, 1200 K derived by

Kleykamp was -53.5 ± 4.2 kJ (mol atom)$^{-1}$. We have plotted both of these values in Fig. 5. We also did not investigate $ThPt_2$. Instead, in the present project we studied the compound of $ThPt_3$, whose value of ΔH_f^o is also plotted in Fig. 5. It is possible that ΔH_f^o may be more negative for $ThPt_2$ than for $ThPt_3$. From Fig. 5 we may draw three conclusions.

1. In general, the magnitude of ΔH_f^o increases substantially with increasing atomic number of the Group VIII metals in each of the three families of Th alloys. For example, ΔH_f^o ($ThNi_5$) is more negative than ΔH_f^o ($ThCo_5$), while ΔH_f^o ($ThCo_5$) is more negative than ΔH_f^o ($ThFe_5$).
2. The magnitude of ΔH_f^o for the UMe_3 family (Me stands for a 4d metal in Group VIII) varies somewhat differently. We see a substantial increase in magnitude of ΔH_f^o from URu_3 to URh_3, but only a slight increase from URh_3 to UPd_3 is observed.
3. Generally, the magnitude of ΔH_f^o increases with increasing number of d-electrons of the late transition metal in the alloys of Th with Group VIII metals. For example, ΔH_f^o for $ThMe_x$, where Me is a 3d transition metal, is less negative than ΔH_f^o for the same type of Th alloy if Me is a 4d transition metal; the latter is less negative than ΔH_f^o for the same type of Th alloy if Me is a 5d transition metal.
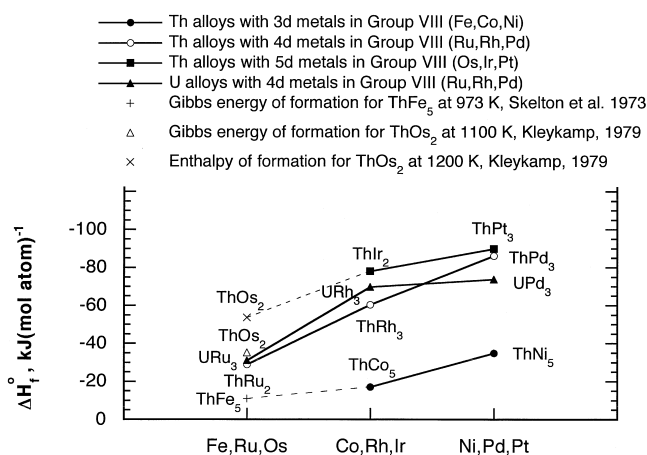

Fig. 5. Standard enthalpies of formation for the indicated compounds of Th and U with 3d-, 4d- and 5d-transition metals in Group VIII. The values for $ThCo_5$, $ThNi_5$, $ThRu_2$, $ThRh_3$, $ThPd_3$, $ThIr_2$ and $ThPt_3$ are from the present work. The earlier values of ΔH_f^o for URu_3, URh_3 and UPd_3 are taken from Jung and Kleppa [17]. The $\Delta G_{f,\ 973\ K}^o$ value for $ThFe_5$ is from Skelton et al. [25]. The $\Delta G_{f,\ 1100\ K}^o$ value and the $\Delta H_{f,\ 1200\ K}^o$ value for $ThOs_2$ are from Kleykamp [37].

Acknowledgements

References

[1] H. Yokokawa, O.J. Kleppa, J. Chem. Thermodyn. 13 (1981) 703–715.

[2] O.J. Kleppa, S. Watanabe, Met. Trans. 13B (1982) 391–401.

[3] S. Watanabe, O.J. Kleppa, Met. Trans. 15B (1984) 357–368.

[4] L. Topor, O.J. Kleppa, J. Chem. Thermodyn. 16 (1984) 993–1002.

[5] L. Topor, O.J. Kleppa, Z. Metallk. 77 (1986) 633–636.

[6] L. Topor, O.J. Kleppa, Met. Trans. 18A (1987) 1989–1994.

[7] L. Topor, O.J. Kleppa, J. Less Common Metals 135 (1987) 67–75.

[8] L. Topor, O.J. Kleppa, Met. Trans. 19A (1988) 1061–1066.

[9] L. Topor, O.J. Kleppa, Met. Trans. 19A (1988) 1827–1831.

[10] L. Topor, O.J. Kleppa, J. Chem. Thermodyn. 20 (1988) 1271–1282.

[11] L. Topor, O.J. Kleppa, High Temp. Sci. 25 (1988) 163–174.

[12] L. Topor, O.J. Kleppa, J. Less Common Metals 155 (1989) 61–73.

[13] S. Watanabe, O.J. Kleppa, J. Chem. Thermodyn. 15 (1983) 633–644.

[14] Q. Guo, O.J. Kleppa, Presented at the Kleppa Symposium on High Temperature Thermochemistry of Materials, TMS 2000 the 129th Annual Meeting and Exhibition, March 12–16, 2000, Nashville, TN, USA, in press.

[15] H.-D. Dannöhl, H.L. Lukas, Z. Mettallkd. 65 (1974) 642–649.

[16] G. Wijbenga, J. Chem. Thermodyn. 14 (1982) 483–493.

[17] W.-G. Jung, O.J. Kleppa, J. Chem. Thermodyn. 23 (1991) 147–153.

[18] O. Kubaschewski, C.B. Alcock, P.J. Spencer, in: Materials Thermochemistry, 6th Edition, Pergamon, Oxford, 1993.

[19] M.P. Antony, R. Babu, C.K. Mathews, U.V. Varada Raju, J. Nucl. Mater. 223 (1995) 213–217.

[20] W.H. Skelton, N.J. Magnani, J.F. Smith, Met. Trans. 1 (1970) 1833–1837.

[21] H. Holleck, H. Kleykamp, J. Nucl. Mater. 35 (1970) 158–166.

[22] W.H. Skelton, N.J. Magnani, J.F. Smith, Met. Trans. 2 (1971) 473–476.

[23] N. Lorenzelli, J.P. Marcon, J. Nucl. Mater. 44 (1972) 57–63.

[24] H. Holleck, H. Kleykamp, J. Nucl. Mater. 45 (1972/73) 47–54.

[25] W.H. Skelton, N.J. Magnani, J.F. Smith, Met. Trans. 4 (1973) 917–920.

[26] V.A. Lebedev, N.V. Nazarov, V.I. Pyatkov, I.F. Nichkov, S.P. Raspopin, Electrokhimiya 9 (1973) 920–926.

[27] M. Kanno, J. Nucl. Mater. 51 (1974) 24–29.

[28] H. Kleykamp, M. Murabayashi, J. Less Common Met. 35 (1974) 227–233.

[29] K. Yoshihara, M. Kanno, J. Inorg. Nucl. Chem. 36 (1974) 309–312.

[30] N. Schmidt, Thermodynamics of Coupled Reductions, Thesis, Inst. Radiochemie, Kernforschungszentrum Karlsruhe, 1974.

[31] V.A. Lebedev, V.I. Pyatkov, R.R. Abdrakhmanov, I.F. Nichkov, S.P. Raspopin, N.V. Nazarov, Russ. J. Phys. Chem. 48 (1974) 1489–1491.

[32] G.M. Campbell, J. Chem. Thermodyn. 6 (1974) 1110–1112.

[33] M.G. Naraine, H.B. Bell, J. Nucl. Mater. 50 (1974) 83–90.

[34] M. Murabayashi, H. Kleykamp, J. Less Common Met. 39 (1975) 235–246.

[35] H. Holleck, H. Kleykamp, J.I. Franco, Z. Metallkd. 66 (1975) 298–302.

[36] G.M. Campbell, in: H. Blank, R. Lindner (Eds.), Plutonium 1975 and other Actinides, North Holland, Amsterdam, 1976, pp. 95–104.

[37] H. Kleykamp, J. Less Common Met. 63 (1979) 25–33.

[38] J.G. Edwards, J.S. Starzynski, D.E. Peterson, J. Chem. Phys. 73 (1980) 908–912.

[39] D.E. Peterson, J. Nucl. Mater. 91 (1980) 306–310.

[40] G. Wijbenga, E.H.P. Cordfunke, J. Chem. Thermodyn. 14 (1982) 409–417.

[41] O.J. Kleppa, L. Topor, Thermochim. Acta 139 (1989) 291–297.

[42] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley, D.D. Wagman, in: Selected Values of Thermodynamic Properties of the Elements, ASM, Metal Park, OH, 1973.

[43] P. Villars, L.D. Calvert, in: Pearson's Handbook of Crystallographic Data for Intermetallic Phases, Vol. 3, ASM, Metals Park, OH, 1985.

[44] A.K. Niessen, F.R. de Boer, R. Boom, P.F. de Chatel, W.C.M. Mattens, A.R. Miedema, Calphad 7 (1983) 51–70.

[45] Q. Guo, O.J. Kleppa, J. Alloys Compounds 270 (1998) 212–217.

[46] N. Selhaoui, O.J. Kleppa, Z. Metallkd. 84 (1993) 744–747.