Letter

Note on the standard enthalpies of formation of Ta_5Ge_3 and $OsGe_2$ by direct synthesis calorimetry

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1. Introduction

During recent years we have, in this laboratory, pursued a systematic study of the thermochemistry of 3d, 4d and 5d transition metal germanides. The enthalpies of formation of these compounds are reported in four papers by Kleppa and Jung [1] and by Jung and Kleppa [2–4]. In order to complete this systematic study we are presently reporting on the standard enthalpies of formation of Ta_5Ge_3 and $OsGe_2$, 5d compounds which were not covered in the earlier communications.

To the best of our knowledge, there is no experimental information on the enthalpies of formation of these compounds in the literature. However, we will compare our results with the data available for other 5d germanides, for 3d and 4d germanides and with predicted values from Miedema's semi-empirical model [5].

2. Experimental and materials

The calorimetric experiments were carried out at 1473 ± 2 K in a single unit differential microcalorimeter; this unit has been described in an earlier communication from this laboratory [6]. All experiments were performed under a protective atmosphere of argon gas; this gas was purified by passing it over titanium chips at about 900 °C. A boron nitride (BN) crucible was used to contain the samples.

The Ta, Os and Ge elements were purchased as powders from Johnson-Matthey/Aesar and were reported to be 99.98%, 99.8% and 99.999% pure, respectively. The Ta sample had a particle size of -325

mesh, while the Os was -100 mesh. These two metals were used as purchased. The Ge sample, as purchased, had a particle size of -10 mesh. This sample was ground in an agate mortar and sifted through a 150 mesh sieve to get a powder suitable for the calorimetric experiments.

The pure components were checked by X-ray diffraction in order to detect possible oxide contamination or other impurities. None were found. The powdered elements were carefully mixed in the appropriate molar ratio, pressed into 4 mm pellets, and dropped into the calorimeter from room temperature. In a subsequent set of experiments the reaction products were also dropped into the calorimeter from room temperature in order to measure their heat contents. This allowed us to refer all the observed enthalpies of formation to 298 K.

Calibration of the calorimeter was achieved by dropping weighed segments of 2 mm high purity copper wire from room temperature into the calorimeter at 1473 ± 2 K. The enthalpy of pure copper at this temperature was obtained from Hultgren et al. [7]. The calibrations were reproducible to within $\pm 1.4\%$.

3. Measurements

The standard enthalpies of formation of germanides were obtained from the difference between the results of two sets of measurements. In the first set the following reaction took place in the calorimeter:

$$Me\ (s,\ 298\ K) + mGe\ (s,\ 298\ K)$$

$$= MeGe_m\ (s,\ 1473\ K) \tag{1}$$
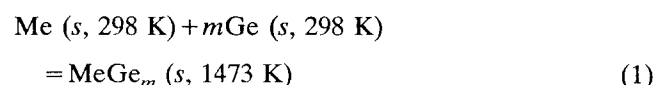
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Here m represents the molar ratio Ge:Me, Me is the considered metal while s denotes solid. The reaction pellets were reused in a subsequent set of measurements to determine their heat contents:

$$\text{MeGe}_m \ (s, \ 298 \ K) = \text{MeGe}_m \ (s, \ 1473 \ K) \qquad (2)$$
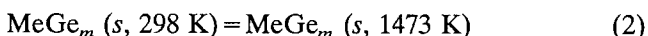
The standard enthalpy of formation is given by:

$$\Delta H_f^0 = \Delta H(1) - \Delta H(2) \qquad (3)$$

where $\Delta H(1)$ and $\Delta H(2)$ are the enthalpy changes associated with reactions (1) and (2) in kJ (g. atom)$^{-1}$.

The germanide samples were examined by X-ray diffraction to assess their structures and ascertain the absence of unreacted metals. In addition, the samples were also subjected to SEM and X-ray microprobe analysis.

There is no established experimental phase diagram for the Ta–Ge system [8,9], however, an estimated phase diagram is reported by Moffat [10]. For this system the ASTM powder diffraction file lists two tetragonal crystal structures for the high and low temperature modifications of Ta_5Ge_3. Some structural data are also available for the compounds Ta_3Ge and $TaGe_2$ [11–14]. We prepared Ta_5Ge_3 in our calorimetric experiments. The X-ray diffraction pattern of our reaction product matched quite well the pattern of the high temperature modification of Ta_5Ge_3 in the ASTM file. There was no evidence for any unreacted metal. However, we found a minor amount of a second phase, less than 5%, which was probably Ta_3Ge. The pattern of Ta_3Ge is not listed in the ASTM file. We generated a pattern from the reported unit cell dimensions and the atomic coordinates [13].

The SEM analysis confirmed that this sample was nearly single phase. A very minor amount of a second phase was found, estimated at about 2%.

There is no published phase diagram for the Os–Ge system [8,10]. The structures of two compounds are reported, namely those of Os_2Ge_3 and $OsGe_2$ [15,16]. We prepared both compounds in calorimetric experiments. When the reaction products were checked by X-ray diffraction, we found that $OsGe_2$ was the dominant phase in all experiments. The pattern of our Os_2Ge_3 sample showed a mixture of Os_2Ge_3 and $OsGe_2$. The pattern was, however, largely that of $OsGe_2$ with approximately 15% of Os_2Ge_3. The pattern of our $OsGe_2$ sample matched quite well the structure in the ASTM powder diffraction file. There was no evidence for any unreacted metal. However, we did notice the presence of a minor amount of a second phase, Os_2Ge_3, estimated at less than 5%. The SEM analysis confirmed that this sample was essentially single phase.

4. Results and discussion

The experimental results are summarized in Table 1. The heat effects associated with reactions (1) and (2) are given in kJ (g. atom)$^{-1}$ as the averages of five or six consecutive measurements with the appropriate standard deviations. The last column shows the standard enthalpies of formation of the phases considered.

Table 2 presents a comparison of the standard enthalpies of formation reported presently with values from Miedema's semi-empirical model [5]. To the best of our knowledge there is no experimental information for the heats of formation of these two germanides. Table 2 shows that for these two compounds, Miedema's semi-empirical model predicts enthalpies of formation which are in reasonably good agreement with our results.

In Fig. 1 we present a systematic plot of the enthalpies of formation of all the 3d, 4d and 5d transition metal germanides studied in the laboratory [1–4]. We also include a value for $ReGe_2$ which was measured by Searcy et al. [17]. The W–Ge system has no stable compound at the calorimeter temperature used [8,10].

Table 1
Summary of standard enthalpies of formation for two 5d germanides

Compound	m = Ge:Me	$\Delta H(1)$	$\Delta H(2)$	ΔH_f^0
		kJ (g. atom)$^{-1}$		
Ta_5Ge_3	0.6	$-11.6 \pm 0.5(6)$	$30.4 \pm 1.0(5)$	-42.0 ± 1.1
$OsGe_2$	2.0	$26.8 \pm 2.2(6)$	$30.5 \pm 1.3(5)$	-3.7 ± 2.5

Table 2
Comparison of ΔH_f^0 values for Ta_5Ge_3 and $OsGe_2$ with predicted values from Miedema's semi-empirical model [5]

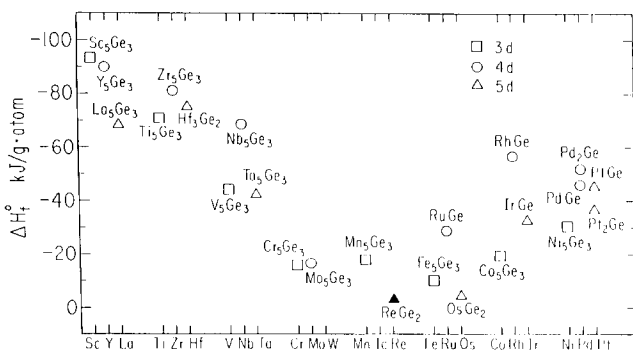|	ΔH_f^0 (expt.) kJ (g. atom)$^{-1}$	ΔH^0 (predicted) kJ (g. atom)$^{-1}$
Ta_5Ge_3	-42.0 ± 1.1	-41
$OsGe_2$	-3.7 ± 2.5	0

Fig. 1. Standard enthalpies of formation of 3d, 4d and 5d germanides from Refs. [1–4] and from the present work. The value for $ReGe_2$ is from Ref. [17].

Fig. 1 shows some interesting trends. The absolute values of the enthalpies of formation of the 3d, 4d and 5d transition metal germanides decrease systematically from the (Sc,Y,La) group to (Cr,Mo,W) and (Mn,Tc,Re) and then increase significantly to the (Ni,Pd,Pt) group. There is a noticeable minimum in the middle of the series. Our new value for the heat of formation of $OsGe_2$ is quite comparable with that for $ReGe_2$ measured by Searcy et al. [17]. It is noteworthy that in most triads of the 3d, 4d and 5d transition metal elements, the magnitude of the enthalpy of formation increases from the 3d to the corresponding 4d compound and then decreases from the 4d to the 5d germanide. Our new values for the enthalpies of formation of Ta_5Ge_3 and $OsGe_2$ reflect this effect.

In recent communications on the 3d, 4d and 5d aluminides we found no correlation between the observed enthalpies of formation and the difference in the electronegativities of the component elements [18]. This also holds for the 5d germanides. For example, the electronegativity difference between the elements in the $Os + Ge$, $Ir + Ge$ and $Pt + Ge$ systems is the same, while the heats of formation differ by a factor of nearly 10. This suggests strongly the importance of covalent bonding in these systems.

Since we have found that experimental melting points for the 5d germanides are available in literature only for Hf_5Ge_3 and La_5Ge_3 [8,10], we are unable to test the correlation between the enthalpies of formation of the germanides and their melting points. Theoretical studies of bonding in transition metal compounds to not extend directly to the treatment of transition metal germanides [19,20].

Acknowledgements

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