Journal of Alloys and Compounds, 176 (1991) 301–308
JAL 0014

Standard molar enthalpies of formation of Hf_3Ge_2, MeGe (Me ≡ Ir, Pt) and Pt_2Ge

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(Received May 8, 1991)

Abstract

The standard molar enthalpy of formation of Hf_3Ge_2 has been determined by solute–solvent drop calorimetry and those of IrGe, PtGe and Pt_2Ge by the direct combination method. The data have been obtained using a high temperature calorimeter at 1473 ± 2 K. The following values are reported: $\Delta H_f°(Hf_3Ge_2) = -(373.2 \pm 39.5)$ kJ mol^{-1}, $\Delta H_f°(IrGe) = -(66.2 \pm 11.8)$ kJ mol^{-1}, $\Delta H_f°(PtGe) = -(90.8 \pm 2.4)$ kJ mol^{-1}, $\Delta H_f°(Pt_2Ge) = -(111.3 \pm 4.7)$ kJ mol^{-1}. Comparisons are made with our earlier values for 3d and 4d transition metal germanides, with some available values for silicides, and with predicted values.

1. Introduction

During recent years we have pursued a systematic study of the thermochemistry of transition metal borides, silicides, and intermetallic compounds using high temperature calorimetry. In three recent papers [1–3] we extended our study to the germanides of 3d and 4d transition metals and to Me_5Ge_3 compounds formed by group III metals.

For 5d transition metal germanides, experimental enthalpies of formation are very scarce in the literature. In the present investigation, we determined the standard molar enthalpy of formation of Hf_3Ge_2 by solute–solvent drop calorimetry and those of IrGe, PtGe and Pt_2Ge by the direct combination method. The results are compared with our values for other germanides reported in the earlier papers, with some data for the silicides, and with predicted values.

2. Experimental details

The experiments were carried out in a modified Setaram-type high temperature calorimeter. Details of this apparatus and of the calorimeter liner assembly have already been given in our earlier reports [1, 4]. Boron nitride (BN) and beryllium oxide (BeO) crucibles were used as containers.

Table 1 gives the metallic purity and description of the starting materials used in the calorimetric experiments. Hafnium in the form of a 17 mm rod

0925-8388/91/$3.50

TABLE 1

Metallic purity and description of the materials used in the calorimetric measurements

Metal	Metallic purity (%)	
Hf	(2% Zr)	17 mm rod, −100 mesh shavings
Ir	99.95	−160 mesh powder
Pt	99.9	−325 mesh powder
Ge	99.999	2–4 mm pieces −200 mesh powder
Pd	99.99	0.025 mm foil
Cu	99.999	0.025 mm foil

with about 2 wt.% Zr was obtained from Alfa Products, iridium powder from Johnson–Matthey AESAR group (lot 19389) and platinum powder from Baker & Co. Inc. (lot 145). The germanium sample was high purity, semiconductor grade. Palladium and copper foils 0.025 mm thick were obtained from Engelhard and Johnson–Matthey AESAR group (lot 101882) respectively. The palladium foil was annealed in argon at about 1100 K for several hours; the surface of the copper foil was polished with sandpaper and the foil was annealed at about 900 K for a few hours in a stream of hydrogen gas. The foils were used for making small capsules of about 4 mm diameter for the solute–solvent drop experiments. Small pieces of germanium were put into the palladium or copper capsule in the desired ratio. In the calorimeter, these materials form liquid Pd+Ge or Cu+Ge solvents which dissolve (metal+germanium) or the germanide compound.

The Hf_3Ge_2 compound was synthesized by arc melting on a water-cooled copper hearth in an atmosphere of argon. The arc melting was repeated several times, the alloy button being reversed to obtain a homogeneous phase. The arc-melted button was examined by scanning electron microscopy (SEM) and by energy-dispersive X-ray (EDX) analysis. The analysis indicated that the Hf_3Ge_2 button was homogeneous and of a stoichiometric composition. The Hf_3Ge_2 alloy was crushed into small pieces, ground in a mortar and sifted through a 100 mesh sieve.

Calibration of the calorimeter was achieved by dropping small pieces of 2 mm diameter high purity copper wire into the calorimeter. The enthalpy of pure copper was taken from Hultgren *et al.* [5]: 46 465 J mol^{-1} at 1473 K. The calibrations were reproducible within ± 1.5% in a single series of measurements.

3. Results and discussion

With the exception of the Pt–Ge system the phase diagrams [6–11] of the alloys considered in the present work have not been investigated much.

The hafnium germanides are very refractory with melting temperatures near 2500 K. For these compounds we applied solute–solvent drop calorimetry. On the contrary, the Pt–Ge alloys studied are liquid at our experimental temperature of 1473 K. In analogy to the RhGe compound studied in our previous communication [3], a strong chemical interaction was expected between iridium and germanium. Hence, we adopted the direct combination method for IrGe, PtGe and Pt_2Ge.

In our synthesis of hafnium germanide by arc melting, we first tried to prepare Hf_5Ge_3 on the basis of the available phase information [6–10]. However, we could not obtain a single phase at this composition. On the contrary, a single phase was obtained at the Hf_3Ge_2 composition. This is analogous to hafnium silicide covered in a recent report [12] by Topor and one of the present authors.

Liquid Cu + Ge and Pd + Ge alloys were used as solvents in the solute–solvent drop experiments. The standard enthalpy of formation was obtained from the enthalpy effects associated with the formation of a liquid alloy of the same composition from the elements and from the compound. The reactions generating the liquid alloy $Cu_{0.60}Ge_{0.355}Hf_{0.045}$ in the calorimeter were

$$0.60\mathrm{Cu}(\mathrm{s},\ 298\ \mathrm{K}) + 0.355\mathrm{Ge}(\mathrm{s},\ 298\ \mathrm{K}) + 0.045\mathrm{Hf}(\mathrm{s},\ 298\ \mathrm{K}) \longrightarrow \mathrm{Cu}_{0.60}\mathrm{Ge}_{0.355}\mathrm{Hf}_{0.045}(\mathrm{l},\ 1473\ \mathrm{K}) \quad (1)$$

and

$$0.60\mathrm{Cu}(\mathrm{s},\ 298\ \mathrm{K}) + 0.325\mathrm{Ge}(\mathrm{s},\ 298\ \mathrm{K}) + 0.015\mathrm{Hf}_3\mathrm{Ge}_2(\mathrm{s},\ 298\ \mathrm{K}) \longrightarrow \mathrm{Cu}_{0.60}\mathrm{Ge}_{0.355}\mathrm{Hf}_{0.045}(\mathrm{l},\ 1473\ \mathrm{K}) \quad (2)$$

where s and l denote solid and liquid respectively. From reactions (1) and (2) we have

$$0.045\mathrm{Hf}(\mathrm{s},\ 298\ \mathrm{K}) + 0.03\mathrm{Ge}(\mathrm{s},\ 298\ \mathrm{K}) \longrightarrow 0.015\mathrm{Hf}_3\mathrm{Ge}_2(\mathrm{s},\ 298\ \mathrm{K}) \quad (3)$$

Hence, the standard enthalpy of formation can be obtained from

$$\Delta H_f^\circ(\mathrm{Hf}_3\mathrm{Ge}_2) = \Delta H_\mathrm{m}(1) - \Delta H_\mathrm{m}(2) \quad (4)$$

where $\Delta H_\mathrm{m}(1)$ and $\Delta H_\mathrm{m}(2)$ designate the molar enthalpy change for reactions (1) and (2) with respect to Hf_3Ge_2. Similar equations can be written for the liquid alloy $Pd_{0.325}Ge_{0.63}Hf_{0.045}$. After the experiments, the solidified alloys were examined by SEM and EDX analysis; these examinations confirmed the complete dissolution of the elements and the compounds in the melts.

The experimental results for Hf_3Ge_2 obtained by this approach are summarized in Tables 2 and 3. In these tables, the average values of ΔH_m for each reaction are given with their standard deviations δ_1 and δ_2. The uncertainties in $\Delta H_\mathrm{f}^\circ$ were calculated from $\delta = (\delta_1^2 + \delta_2^2)^{1/2}$. Since the standard enthalpies of formation obtained in the two different series of measurements have different uncertainties, we calculated the weighted average of the two results using the relation

TABLE 2

Standard enthalpy of formation of Hf_3Ge_2 obtained by generating the liquid alloy $Cu_{0.60}Ge_{0.355}Hf_{0.045}$ at 1473 ± 2 K

Experiment	n(Cu) (mmol)	n(Ge) (mmol)	n(Hf) (mmol)	$n(Hf_3Ge_2)$ (mmol)	ΔH_{obs} (J)	$\Delta H_m(1)$ (kJ mol^{-1})	$\Delta H_m(2)$ (kJ mol^{-1})
1-1	2.2222	1.2037	–	0.0556	168.4	–	3029.4
1-2	2.1717	1.1763	–	0.0543	170.7	–	3143.0
1-3	2.0203	1.0943	–	0.0505	151.6	–	3001.9
1-4	2.3728	1.2852	–	0.0593	183.1	–	3088.4
1-5	2.3278	1.2608	–	0.0582	181.8	–	3124.4
2-1	2.5989	1.5377	0.1949	–	172.6	2654.6	–
2-2	2.3666	1.4003	0.1775	–	161.3	2723.8	–
2-3	2.2061	1.3053	0.1655	–	149.0	2699.0	–
2-4	2.2206	1.3139	0.1665	–	145.8	2627.0	–
2-5	2.1661	1.2816	0.1625	–	142.0	2619.7	–
Mean values						2664.8 ± 45.4	3077.4 ± 60.5

ΔH_f° (kJ mol^{-1}) = 2664.8 ± 45.4 − (3077.4 ± 60.5) = −(412.6 ± 75.6)

TABLE 3

Standard enthalpy of formation of Hf_3Ge_2 obtained by generating the liquid alloy $Pd_{0.325}Ge_{0.63}Hf_{0.045}$ at 1473 ± 2 K

Experiment	n(Pd) (mmol)	n(Ge) (mmol)	n(Hf) (mmol)	$n(Hf_3Ge_2)$ (mmol)	ΔH_{obs} (J)	$\Delta H_m(1)$ (kJ mol^{-1})	$\Delta H_m(2)$ (kJ mol^{-1})
1-1	1.4712	2.7161	–	0.0679	118.8	–	1749.1
1-2	1.7043	3.1464	–	0.0787	136.1	–	1729.5
1-3	1.4852	2.7418	–	0.0685	114.5	–	1670.9
1-4	1.4363	2.6517	–	0.0663	116.9	–	1763.8
2-1	1.4001	2.7141	0.1939	–	90.4	1399.1	–
2-2	1.3766	2.6685	0.1906	–	85.5	1346.0	–
2-3	1.3450	2.6071	0.1862	–	84.8	1366.0	–
2-4	1.6388	3.1767	0.2269	–	103.4	1368.3	–
Mean values						1369.8 ± 21.9	1728.3 ± 40.8

ΔH_f° (kJ mol^{-1}) = 1369.8 ± 21.9 − (1728.3 ± 40.8) = −(358.5 ± 46.3)

$$\Delta H_f^\circ(\text{mean}) = \sum(\Delta H_f^\circ/\delta_i^2)/\sum(1/\delta_i^2) \tag{5}$$

The standard deviation δ_m of the mean was obtained from

$$\delta_m = \{1/\sum(1/\delta_i^2)\}^{1/2} \tag{6}$$

In this way, the mean value of the standard molar enthalpy of formation of Hf_3Ge_2 was found to be given by

$\Delta H_f°(Hf_3Ge_2) = -(373.2 \pm 39.5)$ kJ mol^{-1}

We tried a similar treatment for Ta_3Ge_2, and obtained a single phase by arc melting. However, we have not as yet found a suitable solvent for Ta_3Ge_2.

In the direct combination experiments iridium or platinum powder and germanium powder were weighed carefully in the desired ratios and mixed thoroughly. These mixtures were compressed into 4 mm diameter pellets. The pellets were dropped from room temperature into the calorimeter at 1473 ± 2 K and the enthalpy effects were measured. After the measurements, the alloy products were removed from the crucible, broken into pieces of suitable size, and then used for the heat content measurements. These procedures can be expressed by the following equations, here shown for PtGe as an example.

$$\mathrm{Pt(s, 298\ K) + Ge(s, 298\ K) \longrightarrow PtGe(l, 1473\ K)} \tag{7}$$

and

$$\mathrm{PtGe(s, 298\ K) \longrightarrow PtGe(l, 1473\ K)} \tag{8}$$

From reactions (7) and (8), we obtain

$$\mathrm{Pt(s, 298\ K) + Ge(s, 298\ K) \longrightarrow PtGe(s, 298\ K)} \tag{9}$$

Thus, the standard enthalpy of formation is obtained from

$$\Delta H_f°(\mathrm{PtGe}) = \Delta H_m(7) - \Delta H_m(8) \tag{10}$$

After the experiments the reaction products were examined by SEM and EDX and by powder X-ray diffraction. The examinations indicated only one phase in the PtGe sample, and a minor presence of Pt_3Ge in the Pt_2Ge sample. This does not influence the heat content of Pt_2Ge significantly. For the IrGe sample, 23% of the Ir_4Ge_5 phase was found in the analysis. For this reason we made another series of measurements on IrGe using solute–solvent drop calorimetry.

The experimental results are summarized in Tables 4 and 5 for IrGe, and in Tables 6 and 7 for PtGe and Pt_2Ge respectively. Finally, the standard molar enthalpies of formation of IrGe, PtGe, and Pt_2Ge were found to be as follows:

$\Delta H_f°(IrGe) = -(66.2 \pm 11.8)$ kJ mol^{-1}

$\Delta H_f°(PtGe) = -(90.8 \pm 2.4)$ kJ mol^{-1}

$\Delta H_f°(Pt_2Ge) = -(111.3 \pm 4.7)$ kJ mol^{-1}

The value for IrGe is the average of the two results obtained by the direct combination method and by solute–solvent drop calorimetry.

Figure 1 shows the standard enthalpies of formation of some 5d transition metal germanides. Because the compositions of the compounds are different, $\Delta H_f°$ is given in kilojoules per gram-atom. Tungsten and rhenium do not form compounds with germanium at the considered compositions. We

TABLE 4

Standard enthalpy of formation of IrGe by the direct combination method at 1473±2 K

Experiment	n(Ir) (mmol)	n(Ge) (mmol)	n(IrGe) (mmol)	ΔH_{obs} (J)	$\Delta H_m(7)$ (kJ mol^{-1})	$\Delta H_m(8)$ (kJ mol^{-1})
1-1	1.0169	1.0169	–	−3.5	−3.4	–
1-2	2.0338	2.0338	–	−8.9	−4.4	–
1-3	1.9918	1.9918	–	−4.4	−2.2	–
1-4	2.0693	2.0693	–	−6.9	−3.3	–
1-5	2.0757	2.0757	–	−7.8	−3.8	–
2-1	–	–	1.1313	75.4	–	66.1
2-2	–	–	1.9110	123.3	–	64.5
2-3	–	–	1.8174	113.2	–	62.3
2-4	–	–	2.0674	131.6	–	63.7
2-5	–	–	2.0315	128.2	–	63.1
Mean values					−3.4±0.8	64.0±1.7

$\Delta H_f°$ (kJ mol^{-1}) = −3.4±0.8−(64.0±1.7) = −(67.4±1.8)

TABLE 5

Standard enthalpy of formation of IrGe obtained by generating the liquid alloy $Ni_{0.50}Ge_{0.45}Ir_{0.05}$ at 1473±2 K

Experiment	n(Ni) (mmol)	n(Ge) (mmol)	n(Ir) (mmol)	n(IrGe) (mmol)	ΔH_{obs} (J)	$\Delta H_m(1)$ (kJ mol^{-1})	$\Delta H_m(2)$ (kJ mol^{-1})
1-1	3.3185	2.6548	–	0.3318	166.3	–	501.2
1-2	3.1457	2.5165	–	0.3146	156.1	–	496.2
1-3	3.0884	2.4707	–	0.3088	151.8	–	491.5
1-4	2.7802	2.2242	–	0.2780	136.3	–	490.2
1-5	2.7930	2.2344	–	0.2793	141.0	–	504.9
2-1	3.0544	2.7489	0.3054	–	128.9	422.0	–
2-2	3.0276	2.7248	0.3028	–	129.4	427.3	–
2-3	2.9792	2.6813	0.2979	–	132.8	445.8	–
2-4	2.8403	2.5563	0.2840	–	124.4	438.1	–
2-5	2.9151	2.6237	0.2915	–	124.1	425.6	–
Mean values						431.8±9.9	496.8±6.3

$\Delta H_f°$ (kJ mol^{-1}) = 431.8±9.9−(496.8±6.3) = −(65.0±11.7)

attempted to study OsGe by the direct combination method, but this did not work well. The value for Hf_3Ge_2 reported by Golutvin *et al.* [13](−152 kJ g-atom^{-1}) is very different from ours, approximately double in magnitude. Our result for PtGe agrees very well with that of Castanet [14], −46.3 kJ g-atom^{-1}. No experimental values for IrGe and Pt_2Ge could be found in the literature. However, the figure shows the predicted values of de Boer *et al.* [15]. On the whole they agree reasonably well with our experimental values.

TABLE 6

Standard enthalpy of formation of PtGe by the direct combination method at 1473±2 K

Experiment	n(Pt) (mmol)	n(Ge) (mmol)	n(PtGe) (mmol)	ΔH_{obs} (J)	$\Delta H_m(7)$ (kJ mol^{-1})	$\Delta H_m(8)$ (kJ mol^{-1}
1-1	2.2876	2.2876	–	62.4	27.3	–
1-2	2.9025	2.9025	–	76.2	26.3	–
1-3	2.8514	2.8514	–	68.1	23.9	–
1-4	2.7643	2.7643	–	70.2	25.4	–
1-5	2.8368	2.8368	–	73.6	26.0	–
2-1	–	–	1.1228	133.6	–	119.0
2-2	–	–	1.1171	127.7	–	114.3
2-3	–	–	1.1149	127.4	–	114.2
2-4	–	–	1.1295	132.5	–	117.3
2-5	–	–	1.1731	136.6	–	116.5
2-6	–	–	1.1558	137.1	–	118.6
Mean values					25.8±1.2	116.6±2.1

ΔH_f° (kJ mol^{-1}) = 25.8 ± 1.2 − (116.6 ± 2.1) = −(90.8 ± 2.4)

TABLE 7

Standard enthalpy of formation of Pt_2Ge by the direct combination method at 1473±2 K

Experiment	n(Pt) (mmol)	n(Ge) (mmol)	(Pt_2Ge) (mmol)	ΔH_{obs} (J)	$\Delta H_m(7)$ (kJ mol^{-1})	$\Delta H_m(8)$ (kJ mol^{-1})
1-1	0.9624	0.4812	–	14.1	29.3	–
1-2	2.7880	1.3940	–	45.8	32.8	–
1-3	2.5434	1.2717	–	40.0	31.4	–
1-4	2.4556	1.2278	–	38.7	31.5	–
2-1	–	–	0.6137	90.3	–	147.1
2-2	–	–	0.4903	66.9	–	136.5
2-3	–	–	0.9689	139.5	–	144.0
2-4	–	–	1.0599	151.3	–	142.8
Mean values					31.3±1.5	142.6±4.4

ΔH_f° (kJ mol^{-1}) = 31.3 ± 1.5 − (142.6 ± 4.4) = −(111.3 ± 4.7)

Also, the general trend in ΔH_f° for Me_3Ge_2 or Me_5Ge_3 for 5d transition metals in the left-hand part of the figure is quite similar to the trends for 3d and 4d transition metal germanides and silicides as shown in Fig. 2 of our recent publication [3].

Acknowledgments

This investigation has been supported by DOE under Grant DE-FG02-88 ER 45363; it has also benefitted from the general support of Materials

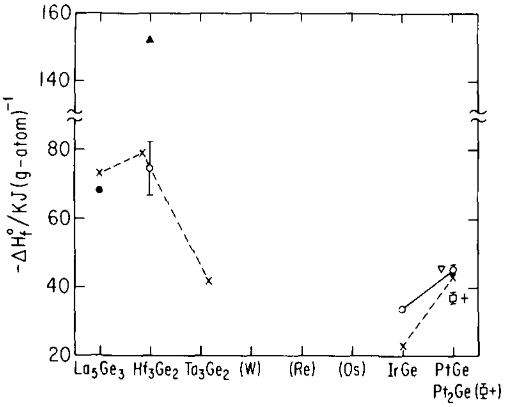

Fig. 1. Standard enthalpies of formation of some 5d transition metal germanides: ○, □, present work; ●, Jung and Kleppa [2]; ▲, Golutvin *et al.* [13]; ▽, Castanet (PtGe) [14]; ×, +, de Boer *et al.* (estimated) [15].

Science at the University of Chicago provided by NSF–MRL. We are indebted to Dr. A. M. Davis who carried out the SEM and EDX analyses.

References

1 O. J. Kleppa and W.-G. Jung, *High Temp. Sci.*, *29* (1990) 109.
2 W.-G. Jung and O. J. Kleppa, *J. Less-Common Met.*, *169* (1991) 85.
3 W.-G. Jung and O. J. Kleppa, *J. Less-Common Met.*, *169* (1991) 91.
4 O. J. Kleppa and L. Topor, *Thermochim. Acta*, *139* (1989) 291.
5 R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley and D. D. Wagman, *Selected Values of the Thermodynamic Properties of the Elements, American Society for Metals*, Metals Park, OH, 1973.
6 A. B. Gokhale and R. Abbaschian, *Bull. Alloy Phase Diagr.*, *11* (1990) 253.
7 T. B. Massalski, H. Okamoto, P. R. Subramanian and L. Kacprzak (eds.), *Binary Alloy Phase Diagrams*, American Society for Metals, Metals Park, OH, 2nd edn., 1990.
8 M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
9 R. P. Elliott, *Constitution of Binary Alloys, First Supplement*, McGraw-Hill, New York, 1965.
10 F. A. Shunk, *Constitution of Binary Alloys, Second Supplement*, McGraw-Hill, New York, 1969.
11 W. G. Moffatt, *The Handbook of Binary Phase Diagrams*, Genium, Schenectady, NY, 1984.
12 L. Topor and O. J. Kleppa, *J. Less-Common Met.*, *167* (1990) 91.
13 Y. M. Golutvin, L. G. Titov and E. Maslennikova, *Nauchn. Tr. Mosk. Inst. Stali Splav.*, *117* (1979) 108.
14 R. Castanet, *J. Chem. Thermodyn.*, *14* (1982) 639.
15 F. R. de Boer, R. Boom, W. C. M. Mattens, A. R. Miedema and A. K. Niessen, *Cohesion in Metals, Transition Metal Alloys*, North-Holland, Amsterdam, 1988.