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Enthalpies of formation of refractory borides of 5d elements by high temperature direct synthesis calorimetry I. $IrB_{1.35}$ and $OsB_{2.5}$

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Abstract

The standard enthalpies of formation of $OsB_{2.5}$ and $IrB_{1.35}$ have been determined by direct synthesis calorimetry at 1473 K. The following values are reported: $\Delta H_f^\circ(OsB_{2.5}) = -39.9 \pm 3.5$ kJ mol^{-1} and $\Delta H_f^\circ(IrB_{1.35}) = -49.1 \pm 2.4$ kJ mol^{-1}. The results are compared with the predicted values of Miedema *et al.* and with the previously published values for the corresponding 3d transition metal borides FeB and CoB and 4d metal borides $RuB_{1.1}$ and $RhB_{1.1}$.

1. Introduction

The borides formed by the transition elements form a group of compounds of considerable technological interest. Their refractory character, chemical inertness, hardness and high electrical and thermal conductivity make them particularly attractive for high temperature applications. During the past decade communications from this laboratory have reported new thermochemical data for a number of 3d transition metal borides [1–5] and for some borides of 4d transition metals [6, 7]. In these studies we have used high temperature solution calorimetry [1, 2], solute–solvent drop calorimetry [3–5] and high temperature direct synthesis calorimetry [6, 7]. Most recently we applied the last method to $RuB_{1.1}$ and $RhB_{1.1}$ at 1473 K [7]. Encouraged by the results of this investigation, we decided to initiate a study of the borides of 5d transition metals using the same technique.

In this paper we report on the heats of formation of some borides of osmium and iridium. Investigations of other 5d transition metal borides are in progress. We will compare our new results with data for the corresponding 3d and 4d transition metal borides and with predicted values from Miedema's semiempirical model [8, 9].

2. Experimental details

2.1. *Equipment*

The experiments were carried out at 1473 ± 2 K in a single-unit differential microcalorimeter which has been described in some detail in an earlier paper

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from this laboratory [10]. All experiments were performed under a protective atmosphere of argon which had been purified by passing the gas over titanium powder at 900 °C. A BN crucible was used to contain the samples.

2.2. *Materials*

The iridium and osmium powders were purchased from Johnson–Matthey, Aesar. Their metallic purities were reported to be 99.95% and 99.8% respectively. The boron sample was purchased from Alfa Products/Ventron. This sample consisted of crystalline material of the β rhombohedral form with a boron content of 99.5%.

The boron sample was ground to powder in an agate mortar. Prior to use all three powders were sifted through 150-mesh sieves to provide fine particles for the reactions. The powdered elements were carefully mixed in the appropriate molar ratio, pressed into pellets 4 mm in diameter and dropped into the calorimeter from room temperature. In a subsequent set of experiments the reaction products were dropped into the calorimeter to measure the heat contents of the compounds.

Calibration was performed by dropping weighed segments of high purity copper wire 2 mm in diameter from room temperature into the calorimeter at 1473 ± 2 K. The enthalpy of pure copper at 1473 K was obtained from ref. 11. The calibrations were reproducible within ±1.2%.

2.3. *Measurements and results*

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

$$\mathrm{Me(s,\ 298\ K)} + n\mathrm{B(s,\ 298\ K)} = \mathrm{MeB}_n\mathrm{(s,\ 1473\ K)} \qquad (1)$$

Here n represents the molar ratio of B:Me, Me is the considered metal and (s) denotes solid. The reacted boride pellets were reused in a subsequent set of measurements to determine their heat content:

$$\mathrm{MeB}_n\mathrm{(s,\ 298\ K)} = \mathrm{MeB}_n\mathrm{(s,\ 1473\ K)} \qquad (2)$$

The standard enthalpy of formation is given by

$$\Delta H_\mathrm{f}^\circ = \Delta H_\mathrm{m}(1) - \Delta H_\mathrm{m}(2) \qquad (3)$$

where $\Delta H_\mathrm{m}(1)$ and $\Delta H_\mathrm{m}(2)$ are the molar enthalpy changes associated with reactions (1) and (2) respectively.

To the best of our knowledge there are no verified experimental phase diagrams in the literature for Os + B and Ir + B. However, for both of these systems estimated and/or predicted diagrams were published by Spear [12, 13]. For Ir + B Spear's diagram shows two compounds, $\mathrm{IrB}_{1.1}$ and $\mathrm{IrB}_{1.35}$. Both compounds were estimated to have congruent melting points of the order of 1200 °C. Although our experiments showed that the melting points are significantly higher than 1200 °C, we performed direct synthesis experiments on boride samples with these two compositions. After the experiments the samples were subjected to scanning electron microscopy (SEM) and X-ray microanalysis and to X-ray powder diffraction. This examination confirmed that the $IrB_{1.35}$ sample was single phase; also, the X-ray diffraction pattern was consistent with that reported for this compound by Aronsson [14]. However, the $IrB_{1.1}$ sample showed the presence of more than one phase, namely $IrB_{0.9}$, $IrB_{1.15}$ and $IrB_{1.35}$ [15]. From these observations we have concluded that our calorimetric results for $IrB_{1.35}$ are fully valid but that the data for $IrB_{1.1}$ must be considered as approximate only. The relevant calorimetric data for these two borides are recorded in Tables 1 and 2.

For the system Os + B Spear's phase diagram suggests the existence of three boride phases with the approximate compositions OsB, $OsB_{1.5}$ and OsB_2. However, from other studies [16] it is known that an important compound in this system is $OsB_{2.5}$; Rogl *et al.* [17] also prepared $OsB_{1.2}$ at 1473 K.

In the course of our study of osmium borides we carried out calorimetric experiments on boride samples with the overall compositions OsB, $OsB_{1.1}$, $OsB_{1.2}$ and $OsB_{2.5}$. Among these compounds the SEM and X-ray microprobe analyses indicated that only $OsB_{2.5}$ was essentially single phase; the X-ray diffraction pattern for this compound was also in good agreement with the published pattern [16]. For this compound the calorimetric data are reported in Table 3.

For OsB, $OsB_{1.1}$ and $OsB_{1.2}$ the analyses all indicated the presence of at least two phases. Among these samples we completed the calorimetric

TABLE 1

Standard enthalpy of formation of $IrB_{1.35}$

Experiment no.	n(Ir) (mmol)	n(B) (mmol)	$n(IrB_{1.35})$ (mmol)	ΔH(obs) (J)	$\Delta H_m(1)$ (kJ mol^{-1})	$\Delta H_m(2)$ (kJ mol^{-1})
1-1	1.1190	1.5108		29.03	25.9	
1-2	1.1161	1.5069		30.43	27.3	
1-3	1.5852	2.1403		37.96	24.0	
1-4	0.9899	1.3365		21.86	22.1	
1-5	1.5155	2.0462		40.46	26.7	
1-6	0.8114	1.0956		18.90	23.3	
				Average	24.9 ± 2.1	
2-1			1.0997	79.18		72.0
2-2			1.1089	82.85		74.7
2-3			1.5765	118.19		75.0
2-4			0.9851	72.55		73.7
2-5			0.8071	60.18		74.6
				Average		74.0 ± 1.2

$\Delta H_f^\circ = 24.9 - 74.0 = -49.1 \pm 2.4$ kJ mol^{-1}

$\Delta H_f^\circ = -20.9 \pm 1.0$ kJ (g atom)$^{-1}$

TABLE 2

Standard enthalpy of formation of $IrB_{1.1}$

Experiment no.	n(Ir) (mmol)	n(B) (mmol)	$n(IrB_{1.1})$ (mmol)	ΔH(obs) (J)	$\Delta H_m(1)$ (kJ mol^{-1})	$\Delta H_m(2)$ (kJ mol^{-1})
1-1	1.0001	1.1000		18.08	18.1	
1-2	1.2416	1.3657		26.64	21.5	
1-3	1.1314	1.2444		23.72	21.0	
1-4	1.1216	1.2337		22.00	19.6	
1-5	1.1725	1.2897		26.06	22.2	
1-6	1.4185	1.5603		26.38	18.6	
				Average	20.2 ± 1.6	
2-1			1.1304	72.85		64.4
2-2			0.9550	62.00		64.9
2-3			1.1372	75.77		66.6
2-4			1.3945	95.98		68.8
2-5			1.2509	82.48		65.9
			1.2573	84.57		67.3
				Average		66.3 ± 1.6

$\Delta H_f^\circ = 20.2 - 66.3 = -46.1 \pm 2.3$ kJ mol^{-1}

$\Delta H_f^\circ = -22.0 \pm 1.1$ kJ (g $atom)^{-1}$

TABLE 3

Standard enthalpy of formation of $OsB_{2.5}$

Experiment no.	n(Os) (mmol)	n(B) (mmol)	$n(OsB_{2.5})$ (mmol)	ΔH(obs) (J)	$\Delta H_m(1)$ (kJ mol^{-1})	$\Delta H_m(2)$ (kJ mol^{-1})
1-1	0.9880	2.4689		58.82	59.5	
1-2	0.9102	2.2744		49.78	54.7	
1-3	0.9599	2.3987		56.12	58.5	
1-4	1.1555	2.8876		63.88	55.3	
1-5	1.2384	3.0947		72.58	58.6	
1-6	0.7509	1.8764		40.62	54.1	
1-7	0.7311	1.8269		39.69	54.3	
				Average	56.4 ± 2.3	
2-1			0.6873	64.68		94.1
2-2			0.6845	68.73		100.4
2-3			0.8558	81.34		95.1
2-4			1.2098	118.35		97.8
2-5			0.6753	63.69		94.3
				Average		96.3 ± 2.7

$\Delta H_f^\circ = 56.4 - 96.3 = -39.9 \pm 3.5$ kJ mol^{-1}

$\Delta H_f^\circ = -11.4 \pm 1.0$ kJ (g $atom)^{-1}$

TABLE 4

Standard enthalpy of formation of $OsB_{1.1}$

Experiment no.	n(Os) (mmol)	n(B) (mmol)	$n(OsB_{1.1})$ (mmol)	ΔH(obs) (J)	$\Delta H_m(1)$ (kJ mol^{-1})	$\Delta H_m(2)$ (kJ mol^{-1})
1-1	1.4541	1.6039		52.54	36.1	
1-2	1.0118	1.1160		36.86	36.4	
1-3	1.0152	1.1198		34.31	33.8	
1-4	0.9361	1.0325		32.76	35.0	
				Average	35.3 ± 1.2	
2-1			0.9615	58.69		61.0
2-2			1.0134	60.83		60.0
2-3			0.8991	50.04		55.7
2-4			0.9204	52.16		56.7
2-5			0.8956	51.00		56.9
2-6			1.0347	59.10		57.1
				Average		57.9 ± 2.1
				$\Delta H_f^\circ = 35.3 - 57.9 = -22.6 \pm 2.4$ kJ mol^{-1}		
				$\Delta H_f^\circ = -10.8 \pm 1.1$ kJ (g atom)$^{-1}$		

TABLE 5

Standard enthalpy of formation of $OsB_{1.2}$

Experiment no.	n(Os) (mmol)	n(B) (mmol)	$n(OsB_{1.2})$ (mmol)	ΔH(obs) (J)	$\Delta H_m(1)$ (kJ mol^{-1})	$\Delta H_m(2)$ (kJ mol^{-1})
1-1	1.2865	1.5441		55.06	42.8	
1-2	1.7639	2.1171		67.13	38.1	
1-3	1.5641	1.8773		58.08	37.1	
1-4	1.1349	1.3622		41.87	36.9	
1-5	1.0134	1.2163		36.56	36.1	
1-6	1.0636	1.2765		36.08	33.9	
				Average	37.6 ± 3.3	
2-1			1.2516	77.66		62.1
2-2			1.0179	63.47		62.4
2-3			1.1242	70.18		62.4
2-4			0.8894	52.42		58.9
2-5			1.4244	84.36		59.2
				Average		61.0 ± 1.8
				$\Delta H_f^\circ = 37.6 - 61.0 = -23.4 \pm 3.8$ kJ mol^{-1}		
				$\Delta H_f^\circ = -10.6 \pm 1.7$ kJ (g atom)$^{-1}$		

work on $OsB_{1.1}$ and $OsB_{1.2}$; the experimental results for these two borides, reported here as approximate only, are recorded in Tables 4 and 5.

3. Discussion

We give in Table 6 a summary of the measured molar enthalpies of formation of all the five boride samples covered in the present investigation. The data for $IrB_{1.35}$ and $OsB_{2.5}$ represent final values; the results for $IrB_{1.1}$, $OsB_{1.1}$ and $OsB_{1.2}$ are reported as approximate only. It will be noted that the measured enthalpies of formation per gramme atom do not seem to vary significantly with the molar ratio n. This is particularly interesting in view of the fact that the bonding character may change significantly in going from $n=1$ to $n=2.5$. $OsB_{1.1}$ and $IrB_{1.1}$ are considered to be compounds without significant B–B contacts. However, at higher B:Me ratios B–B chain formation may occur.

To the best of our knowledge there are no quantitative experimental data in the published literature for the enthalpies of formation of iridium or osmium borides. However, predictions of the enthalpies of formation for these compounds have been given by Niessen [8] and DeBoer *et al.* [9]. A comparison between our experimental results and their predicted values is presented in Table 7; the heat of formation of Pt_2B in this table was reported

TABLE 6

Comparison of enthalpies of formation at different molar ratios B:Me

n (B:Me)	Me	ΔH_f° (kJ (g atom)$^{-1}$)
1.1	Os	-10.8 ± 1.1
1.2	Os	-10.6 ± 1.7
2.5	Os	-11.4 ± 1.0
1.1	Ir	-22.0 ± 1.1
1.35	Ir	-20.9 ± 1.0

TABLE 7

Comparison of experimental and predicted enthalpies of formation

System	ΔH_f°(exp) (kJ (g atom)$^{-1}$)	ΔH_f°(pred) (kJ (g atom)$^{-1}$)
$IrB_{1.35}$	-20.9	-36 ($n=1.0$) -35 ($n=1.5$)
$OsB_{2.5}$	-11.4	-27 ($n=2$) -17 ($n=3$)
Pt_2B	-20	-29

by Kleppa and Topor [6]. Note that in all cases the experimental enthalpies of formation are considerably less exothermic than the predicted values.

Since we measure the heat contents of both iridium and osmium borides at several different molar ratios, it seemed that this study might provide a reasonable test of how well the Kopp–Neumann rule applies for the considered compounds. We recall that according to the Kopp–Neumann rule the heat content of a gramme atom of solid may be obtained as the weighted sum of the heat contents of its components. The results of this comparison are given in Table 8. Note that for the considered compounds the agreement is quite good. The observed deviations are both positive and negative and range in magnitude from 2.6% to 6.4%, *i.e.* they are roughly comparable to the experimental errors.

In earlier papers from this laboratory we reported enthalpies of formation for iron, cobalt and nickel borides [1, 2], for palladium and platinum borides [6] and most recently for $RuB_{1.1}$. and $RhB_{1.1}$ [7]. In Fig. 1 we present a

TABLE 8

Comparison of experimental and calculated heat contents

System	ΔH(calc)[a] (kJ (g atom)$^{-1}$)	ΔH(exp) (kJ (g atom)$^{-1}$)	Difference (%)
$IrB_{1.1}$	30.11	31.6 ± 1.1	+4.6
$IrB_{1.35}$	29.76	31.5 ± 1.0	+5.4
$OsB_{1.1}$	29.14	27.4 ± 1.2	−6.4
		27.6 ± 1.1	−5.7
$OsB_{1.2}$	29.04	27.7 ± 1.7	−4.7
$OsB_{2.5}$	28.22	27.5 ± 1.0	−2.6

[a] From data in ref. 11.

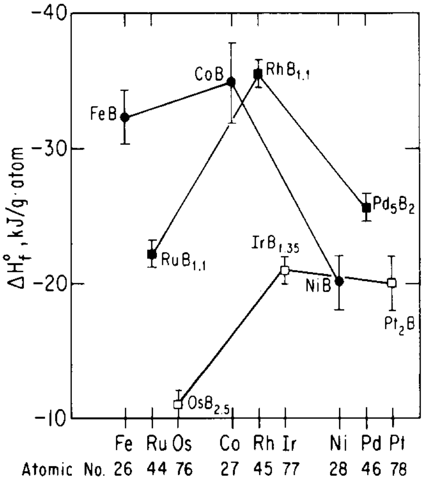

Fig. 1. Systematic plots of the enthalpies of formation per gramme atom for borides of iron, cobalt and nickel, of ruthenium, rhodium and palladium and of osmium, iridium and platinum.

comparison between our new results for $OsB_{2.5}$ and $IrB_{1.35}$ and the earlier data. The systematic trends of the three sets of 3d, 4d and 5d borides show some similarities. All three sets show an increase in magnitude of the enthalpy of formation on going from (Fe–Ru–Os) to (Co–Rh–Ir) and a reduction on going from the latter set to (Ni–Pd–Pt); however, the difference between the values for $IrB_{1.35}$ and Pt_2B is very small. There is also a systematic decrease from iron to ruthenium to osmium; however, this systematic trend is not present in the (Co–Rh–Ir) set or in the (Ni–Pd–Pt) set.

In general, the stability of the transition metal borides has been considered to be a function of two major factors: (a) the ratio B:Me of the components; (b) the number of d (or f) electrons of the metal component. On the basis of the limited amount of information we have presented for the considered borides, it is not possible to arrive at definite conclusions regarding these factors. However, the data in Fig. 1 give some indication of the effect of the number of d electrons on the enthalpy of formation.

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