Fluorine Bomb Calorimetry

Enthalpies of Formation of the Diborides of Niobium and Tantalum

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The energies of combustion in fluorine of nonstoichiometric specimens of the diborides of niobium and tantalum were measured in a bomb calorimeter. The standard enthalpies of formation, $\Delta Hf^{\circ}_{298.15}$, were $-58._6 \pm 1._6$ and $-43._9 \pm 1._2$ kcal. (g.f.m.)$^{-1}$ for $NbB_{1.875 \pm 0.006}$ and $TaB_{1.919 \pm 0.004}$, respectively.

THIS RESEARCH is part of a continuing program to obtain thermochemical data by fluorine bomb calorimetry. The enthalpy of formation of the diboride of niobium had not been previously determined; the present study was a natural extension of a similar study of the diborides of zirconium and hafnium (*20*).

EXPERIMENTAL

In general, the same experimental techniques were used in this work as in the previous study (*20*) of the diborides of zirconium and hafnium.

Calorimetric System. The calorimeters (*12*), laboratory designations ANL-R1 and ANL-R2, and the two-chambered reaction vessel (*24*), laboratory designation Ni-2-T-1, were similar to those described previously. The calorimetric systems were calibrated before and after the fluorine combustion runs by combustions of benzoic acid in oxygen. National Bureau of Standards benzoic acid, sample 39i whose certified energy of combustion under prescribed conditions is 26.434 ± 0.003 absolute kilojoules per gram, was used. For the niobium diboride series, eight calibration experiments performed with calorimeter ANL-R2 yielded an average value for $\mathcal{E}$(Calor.), the energy equivalent of the calorimetric system, of $3359.7_2 \pm 0.0_8$ cal. per degree. The tantalum diboride combustions were done as two series. Series A was carried out with calorimeter ANL-R2 with minor modifications from that used for the niobium diboride series, and Series B with ANL-R1. For series A, eight calibration experiments yielded the average value $\mathcal{E}$(Calor.) = $3360.0_5 \pm 0.1_9$ cal. per degree; for series B, 10 calibration experiments yielded the average value $\mathcal{E}$(Calor.) = $3399.5_1 \pm 0.1_6$ cal. per degree. The uncertainties given are the standard deviations of the mean.

Materials. Specimens of the diborides were supplied by ManLabs, Inc., in the form of zone-refined bars, designation numbers NbB_2–474 and TaB_2–677. The bars were lightly etched in aqueous HF–HNO_3 to remove surface contamination, then dried, pulverized, and sieved; the fractions between 100- and 325- mesh were used for the combustion experiments.

The results of analysis of representative samples of the specimens are given in Table I. Carbon, oxygen, nitrogen, and hydrogen were determined by vacuum fusion, the metal impurities by spectrographic methods. Boron was determined by the differential titration method of Frank (*9*) modified by the use of $BaCO_3$ instead of $CaCO_3$ in the separation procedure. The major components, niobium and tantalum, were assayed by the gravimetric method of Kriege (*21*) with the following results: Nb, 82.2%; Ta, 89.3%. However, because of large uncertainties (~0.6%) in these analyses, it was thought preferable to calculate the amount of the major component by difference.

Table I. Specimen Analysis

Impurity	Niobium Diboride, P.P.M.	Tantalum Diboride, P.P.M.
C	51	50
O	252	96
N	16	4
H	22	12
Ti	800	10
Zr	100	50
Cr	50	10
Fe	50	10
Mo	50	10
V	50	10
Mg	5	. . .
Si	5	. . .
Cu	50	5
W	. . .	15
Ta	500	. . .
Nb	. . .	250
	%	%
Total impurities	0.20 ± 0.10	0.05 ± 0.03
Boron	17.90 ± 0.04	10.28 ± 0.02
Nb or Ta (by difference)	81.90 ± 0.11	89.67 ± 0.04

X-ray powder diffraction patterns showed the specimens to have typical hexagonal structures with no extraneous lines. The lattice parameters were a_0 = 3.112 A. and c_0 = 3.264 A. for the niobium diboride specimen, and a_0 = 3.09 A. and c_0 = 3.25 A. for the tantalum diboride specimen.

The specimens were assumed to be diphasic and to contain a cubic (Nb,Ta)(O,C,N) impurity phase in the hexagonal diboride phase. Metallic impurities were assumed to be substitutional replacements for niobium or tantalum atoms in the diboride phases. After subtraction of the amounts of niobium and tantalum present in the cubic phases, the calculated atomic ratios of boron to total metal in the diboride phases were 1.875 ± 0.006 for the niobium diboride specimen and 1.919 ± 0.004 for the tantalum diboride specimen. These compositions, corresponding to 65.22 and 65.74 atomic % boron, respectively, are very close to the metal-rich boundaries of the homogeneity ranges given by Rudy and St. Windisch (*29*).

Sulfur, used as a kindler, was from the same lot that had been used to determine the enthalpy of formation of SF_6 (*26*).

Fluorine was obtained commercially from the General Chemical Co. with a purity of 99.8%, as determined by mercury titration.

Blank Experiments. Use of a two-chambered reaction vessel introduces two extraneous thermal effects: an endothermic effect due to expansion of fluorine into the bomb, and an exothermic effect due to reaction of fluorine with the bomb surfaces and/or adsorbed impurities. The combined thermal correction for these effects, ΔE_{blank}, was determined by blank experiments in which fluorine was expanded into a bomb in which no sample was present. All other procedures, however, were identical with those in a typical combustion.

Several blank experiments were interspersed among the niobium diboride and the series A tantalum diboride combustions. The technique was identical to that described earlier (*20*) and there was no significant change in the blank correction—namely, $12.5_8 \pm 1.0_3$ cal.

The series B tantalum diboride combustions were performed under conditions designed to passivate the bomb surfaces and to minimize the blank correction. At the start of the series, nickel fluoride was removed from the bomb surfaces by abrasion with nickel wool. Before each experiment the bomb was washed, dried, assembled, evacuated, filled with 2-atm. pressure of BF_3 for one hour, and then evacuated overnight. The combustion or the blank experiment was performed the following day. Values for ΔE_{blank} obtained by this method ranged from 0.34 cal. (endothermic) to 5.50 cal. (exothermic). In the series B tantalum diboride combustions, the value of ΔE_{blank} obtained immediately prior to each combustion was applied to the data for that combustion.

Experimental Procedure. The combustion procedure was similar to that previously described (*20*), except that after each combustion the bomb was opened in a glovebox to minimize hydrolytic formation of hydrogen fluoride and its subsequent reaction with the unburned diboride. In the B series of tantalum diboride combustions, the additional changes noted under Blank Experiments were made.

Table II. Results of Niobium Diboride Combustions

Combustion No.	2	3	4	6	7
Sample introduced, g.	0.73944	0.75335	0.74122	0.40339	0.40959
Unburned sample, g.	0.00188	0.00121	0.00345	0.00151	0.00099
m', sample reacted, g.	0.73756	0.75214	0.73777	0.40188	0.40860
m'', sulfur reacted, g.	0.06073	0.06167	0.06232	0.05721	0.05753
Δt_c, deg.	1.87599	1.91068	1.87888	1.08741	1.10418
$\mathcal{E}$(Calor.)($-\Delta t_c$), cal.	−6302.80	−6419.35	−6312.51	−3653.39	−3709.74
$\Delta E_{\text{contents}}$, cal.	−12.01	−12.10	−12.05	−6.93	−6.95
ΔE_{sulfur}, cal.	550.36	558.88	564.77	518.46	521.36
ΔE_{gas}, cal.	−0.15	−0.16	−0.14	−0.02	−0.03
ΔE_{blank}, cal.	12.58	12.58	12.58	12.58	12.58
$\Delta Ec^\circ/M$(sample), cal. $g.^{-1}$	−7798.71	−7791.30	−7790.16	−7786.65	−7789.48

Mean $\Delta Ec^\circ/M$(sample) $= -7791.3 \pm 2.0$ (s.d.) cal. $g.^{-1}$
Impurity correction $= -3.6 \pm 1.5$(s.d.) cal. $g.^{-1}$
$\Delta Ec^\circ/M(NbB_{1.875})$ $= -7794.9 \pm 2.5$ (s.d.) cal. $g.^{-1}$

Table III. Results of Series A Tantalum Diboride Combustions

Combustion No.	A-1	A-2	A-3	A-4	A-5	A-6	A-7
Sample introduced, g.	1.25201	1.24981	1.25322	1.25169	0.61004	0.61325	0.61490
Unburned sample, g.	0.00056	0.00111	0.00146	0.00107	0.00066	0.00080	0.00147
m', sample reacted, g.	1.25145	1.24870	1.25176	1.25062	0.60938	0.61245	0.61343
m'', sulfur reacted, g.	0.04947	0.04705	0.05110	0.04858	0.04947	0.05033	0.04841
Δt_c, deg.	1.85263	1.84104	1.85687	1.84823	0.97067	0.97790	0.97401
$\mathcal{E}$(Calor.)($-\Delta t_c$), cal.	−6224.93	−6185.99	−6239.18	−6210.15	−3261.50	−3285.79	−3272.72
$\Delta E_{\text{contents}}$, cal.	−11.86	−11.63	−11.88	−11.68	−6.17	−6.14	−6.19
ΔE_{sulfur}, cal.	448.32	426.39	463.09	440.25	448.32	456.11	438.71
ΔE_{gas}, cal.	−0.23	−0.23	−0.23	−0.23	−0.10	−0.10	−0.10
ΔE_{blank}, cal.	12.58	12.58	12.58	12.58	12.58	12.58	12.58
$\Delta Ec^\circ/M$(sample), cal. $g.^{-1}$	−4615.54	−4611.90	−4614.00	−4613.10	−4606.11	−4609.91	−4609.69

Mean $\Delta Ec^\circ/M$(sample) $= -4611.5 \pm 1.2$ (s.d.) cal. $g.^{-1}$

Table IV. Results of Series B Tantalum Diboride Combustions

Combustion No.	B-3	B-4	B-5	B-6	B-7
Sample introduced, g.	1.24705	1.25068	1.24902	0.61187	0.61106
Unburned sample, g.	0.00097	0.00251	0.00305	0.00089	0.00177
m', sample reacted, g.	1.24608	1.24817	1.24597	0.61098	0.60929
m'', sulfur reacted, g.	0.04756	0.04820	0.04935	0.04945	0.04938
Δt_c, deg.	1.81600	1.81840	1.81831	0.95944	0.95875
$\mathcal{E}$(Calor.)($-\Delta t_c$), cal.	−6173.51	−6181.67	−6181.36	−3261.63	−3259.28
$\Delta E_{\text{contents}}$, cal.	−11.41	−11.43	−11.43	−5.99	−5.99
ΔE_{sulfur}, cal.	431.01	436.81	447.23	448.14	447.50
ΔE_{gas}, cal.	−0.26	−0.26	−0.26	−0.13	−0.13
ΔE_{blank}, cal.	4.62	−0.34	0.31	3.71	5.50
$\Delta Ec^\circ/M$(sample), cal. $g.^{-1}$	−4614.11	−4612.26	−4611.27	−4608.83	−4615.86

Mean $\Delta Ec^\circ/M$(sample) $= -4612.5 \pm 1.2$ (s.d.) cal. $g.^{-1}$
Mean $\Delta Ec^\circ/M$(sample), series A and B $= -4611.9 \pm 0.8$ (s.d.) cal. $g.^{-1}$
Impurity correction $= -0.5 \pm 0.5$ (s.d.) cal. $g.^{-1}$
$\Delta Ec^\circ/M(TaB_{1.919})$ $= -4612.4 \pm 0.9$ (s.d.) cal. $g.^{-1}$

Postcombustion Examination. After representative experiments, portions of the combustion bomb gases were examined by infrared analysis in an 8-cm. nickel cell equipped with AgCl windows. The only significant bands observed in the infrared spectra were attributable to SF_6 from the kindler and to BF_3 and CF_4 from the sample. In other experiments the bomb was evacuated and then opened in an inert atmosphere. Portions of the white, partially sublimed, solid product were taken for x-ray powder diffraction analysis. The diffraction patterns were identical with those obtained from the pentafluorides produced in the calorimetric combustions of niobium (*11*) and tantalum (*11*) in fluorine.

The amount of unburned diboride remaining after combustion was determined in the manner previously described (*20*).

RESULTS

The results of five niobium diboride and 12 tantalum diboride combustion experiments (Tables II, III, and IV) are expressed in terms of the defined calorie equal to (exactly) 4.184 absolute joules. Corrections to standard state were applied in the usual manner (*14*). The entries in the tables are either self-explanatory or have been previously explained (*13, 14*). The auxiliary data needed for Tables II, III, and IV are given in Table V.

For the calculation of ΔE_{sulfur} a value of of −9.0624 cal. per mg. was used for the energy of combustion of the sulfur specimen (*26*).

For the calculation of ΔE_{gas} the coefficients μ [in the equation of state $PV = nRT\,(1 - \mu P)$] and $(\partial E/\partial P)_T$ were obtained from equations given previously (*20*) for a gaseous mixture of F_2, BF_3, and SF_6.

The mean values obtained from series A and B differed by 1.0 cal. per gram, or less than the uncertainty of either; for this reason the results of both series have been combined. The agreement between the series was taken as evidence that the blank corrections, which differed as much as 13 cal. per combustion, were not in serious error.

Corrections for the behavior of impurities in the combustion process were made on the basis of the assumptions already described plus the following: The enthalpy of reaction of the compounds to form the solid solution phase, M(C,O,N), was negligible; carbon, oxygen, and nitrogen formed CF_4, O_2, and N_2, respectively; hydrogen, present originally as H_2O, formed HF and O_2; trace metals substituted for niobium or tantalum without any thermal effect and formed their most stable fluorides.

DERIVED DATA

The derived data are presented in Table VI and refer to the following combustion and formation reactions:

$$NbB_{1.875}\,(c) + 5.312\,F_2(g) \rightarrow NbF_5(c) + 1.875\,BF_3(g) \tag{1}$$

$$TaB_{1.919}\,(c) + 5.378\,F_2(g) \rightarrow TaF_5(c) + 1.919\,BF_3(g) \tag{2}$$

$$Nb(c) + 1.875\,B(c) \rightarrow NbB_{1.875}(c) \tag{3}$$

$$Ta(c) + 1.919\,B(c) \rightarrow TaB_{1.919}(c) \tag{4}$$

The uncertainties in the derived data are uncertainty intervals (*27*) equal to twice the combined standard deviations arising from the following sources: $\Delta Ec^\circ/M$(sample), $\mathcal{E}$(Calor.), ΔE_{blank}, $\Delta E_{\text{impurities}}$, the mass of unburned sample, the auxiliary enthalpies of formation of niobium, tantalum, and boron fluorides, and the boron-to-metal ratios in the specimens. The uncertainty in the boron-to-metal ratio— ± 0.006 for the niobium diboride and ± 0.004 for the tantalum diboride—has a particularly strong effect on the uncertainty in the enthalpy of formation of the diborides, contributing about 50% of the total uncertainty in each case.

Table V. Auxiliary Data (25° C.)

		c_p°, Cal. Deg.$^{-1}$ Gram^{-1}
S	(*28*)	0.168
Zr	(*32*)	0.0659
NbB_2	(*37*)	0.100
NbF_5	(*2*)	0.172
TaB_2	(*36*)	0.058
TaF_5	[a]	0.122
		ΔHf°, Kcal. Mole^{-1}
NbC	(*22*)	−33.6
NbO	[a]	−96
NbN	(*23*)	−56.8
TaC	(*16*)	−34.6
TaN	(*23*)	−60.0
HF	(*35*)	−64.8
CF_4	(*6*)	−222.87
CuF_2	(*28*)	−126.9
CrF_3	(*28*)	−265.2
FeF_3	(*3*)	−235
TiF_4	(*13*)	−394.19
ZrF_4	(*12*)	−456.80
VF_5	(*3*)	−335
MoF_6	(*31*)	−372.35
WF_6	(*25*)	−411.5
BF_3	(*19*)	−271.65 ± 0.22
NbF_5	(*11*)	−433.50 ± 0.15
TaF_5	(*11*)	−454.97 ± 0.19
		C_p°, Cal. Deg.$^{-1}$ Mole^{-1}
F_2	(*8*)	5.50
BF_3	(*18*)	10.07
SF_6	(*26*)	21.144
		S°, Cal. Deg.$^{-1}$ Mole^{-1}
B	(*18*)	1.403
Nb	(*17*)	8.70
Ta	(*17*)	9.92
NbB_2	(*37*)	8.91
TaB_2	(*36*)	10.57
		ρ, Gram Cc.$^{-1}$
S	(*33*)	2.065
Zr	(*34*)	6.505
NbB_2	(*1*)	6.95
NbF_5	(*7*)	3.54
TaB_2	(*1*)	12.56
TaF_5	(*7*)	5.19
		Atomic Wt.
B	(*5*)	10.811
Nb	(*5*)	92.906
Ta	(*5*)	180.948

[a] Estimated value.

Table VI. Derived Data (25° C.)

	$NbB_{1.875}$	$TaB_{1.919}$
$\Delta Ec^\circ/M$, cal. g.$^{-1}$	-7794.9 ± 7.2	-4612.4 ± 3.4
ΔEc°, kcal. (g.f.m.)$^{-1}$	$-882.2_0 \pm 0.9_6$	$-930.2_9 \pm 0.7$
ΔHc°, kcal. (g.f.m.)$^{-1}$	$-884.2_3 \pm 0.9_6$	$-932.3_3 \pm 0.7$
ΔHf°, kcal. (g.f.m.)$^{-1}$	$-58._6 \pm 1._6$	$-43._9 \pm 1._2$
ΔSf°, cal. deg.$^{-1}$ (g.f.m.)$^{-1}$	$-2.4_2 \pm 0.1$	$-2.0_4 \pm 0.1$
ΔGf°, kcal. (g.f.m.)$^{-1}$	$-57._9 \pm 1._6$	$-43._3 \pm 1._2$

The value obtained for the enthalpy of formation of niobium diboride is the only experimental value reported. Attempts by Huber (*15*) to burn niobium diboride calorimetrically in oxygen were defeated by the formation of an undefined niobium oxyboride combustion product. The recent calorimetric combustion of tantalum diboride in chlorine by Galchenko *et al.* (*10*), yielded the value −46.3 ± 1.8 kcal. (g.f.m.)$^{-1}$ for $\Delta Hf°(TaB_{2.03 \pm 0.02})$. This value agrees with the result of this investigation. Various estimates for the enthalpies of formation of niobium and tantalum diborides are available and are compared below on a gram-atomic basis.

Brewer and Haraldsen based their estimates on phase equilibria; Samsonov on the gram-atomic volumes of formation. The estimated values do not agree very well with the experimental values, and in fact, predict an order of values which is opposite to that actually observed. Rudy and St. Windisch (*29*), however, also studied phase equilibria in these systems and predicted decreasing stability in the order VB_2, NbB_2, TaB_2, in agreement with the results of this study.

	$-\Delta Hf^0_{298.15}(NbB_2, c)$ Kcal. (Gram–Atom)$^{-1}$	$-\Delta Hf^0_{298.15}(TaB_2, c)$ Kcal. (Gram–Atom)$^{-1}$
Brewer and Haraldsen (*4*)	>12	>17.3
Samsonov (*30*)	19.7	21.0
Galchenko *et al.* (*10*)	. . .	$15.2_8 \pm 0.5_9$
This work	$20.3_8 \pm 0.5_6$	$15.0_4 \pm 0.4_1$

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