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A. N. Kornilov, V. Ya. Leonidov, and S. M. Skuratov

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Abstract

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A. N. Kornilov, V. Ya. Leonidov, and S. M. Skuratov

Standard Heats of Formation of Niobium Pentoxide and Tantalum Pentoxide

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In recent years there has been intensive development of the chemistry of niobium and tantalum, since these metals and their compounds have found wide application in important areas of modern technology.

In the thermochemistry of niobium and tantalum, fundamentally important quantities are the standard heats of formation of the higher oxides Nb_2O_5 and Ta_2O_5, since their values must be used in calculating the heats of formation of other compounds of these elements. The problem of establishing accurate values of ΔH^0_{form} Nb_2O_5 and ΔH^0_{form} Ta_2O_5 cannot yet be regarded as solved, since the data available in the literature are not mutually consistent. Thus, for ΔH^0_{form} Nb_2O_5 the following values are given in the literature: −442.8 (1), −463.1 ± 0.7 (2); −455.2 ± 0.6 (3); −472.6 ± 1.0 (4); −458.6 ± 5.0 (5); −455.1 ± 0.5 (6); −473.2 ± 0.8; −454.8 ± 0.8 (7)*; −456.9 (8) and −454.4 ± 1.6 kcal/mol (9). All these data were obtained by a single method—combustion of metallic niobium in oxygen in a calorimetric bomb; the exception is work (8), in which a noncalorimetric method was used. Although the degree of reliability of the above values of ΔH^0_{form} Nb_2O_5 varies, and therefore they are difficult to compare with one another, nevertheless, in our opinion, there is reason to believe that the main cause of the discrepancy between the data obtained by different authors is the insufficient purity of the niobium preparations used for the calorimetric determinations. Indeed, even in Humphrey' s most carefully performed and thoroughly described work (3), the information on the niobium sample used is insufficient, since the amounts of oxygen and nitrogen impurities that could have been present in the niobium sample and could have appreciably distorted its heat of combustion are not indicated.

For ΔH^0_{form} Ta_2O_5 the literature contains the following values: −309.5 (1); −498.3 (10); −480.5 (11); −486.0 ± 0.5 (2); −499.9 ± 1.0 (12); −488.8 ± 0.5 (3); and 480.0 ± 0.8 kcal/mol (13). The main cause of the discrepancy among the reported values of ΔH^0_{form} Ta_2O_5, apparently, in this case also is the presence of impurities not detected by the authors in the tantalum samples, since in none of the works was the tantalum preparation burned characterized sufficiently completely.

In the present work we report new experimental determinations of the heats of formation of Nb_2O_5 and Ta_2O_5. Particular attention was paid to the purity of the initial niobium and tantalum preparations and to the accurate determination of small amounts of impurities in them. To achieve this aim, impurity determinations were carried out independently in two different laboratories. The absence in the preparations of impurities other than those found by analysis was checked by the fact that calorimetric determinations were performed with preparations obtained at different times in different institutions. In developing the procedure for determining the heats of combustion of metallic niobium and tantalum, we tried to avoid the shortcomings that we had found in previous works.

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* In work (^{7}), two values are given for ΔH^0_{form} Nb_2O_5.

Experimental Part

1. Heat of combustion of niobium. For the calorimetric determinations, two samples of metallic niobium (in the form of ingots) were used, in which the following impurities were found (wt. %):

	O	N	H	C	Ta	Fe	Ti	Si
Sample No. 1	0.03	0.03	0.004	0.02	0.30	0.09	0.12	0.06
Sample No. 2	0.015	0.01	–	0.005	1.27	0.07	0.12	0.04

In addition, it was established that in both samples impurities of Al, Mg, Mo, Mn, Ni, P, Pb, and Sn could not be present in amounts greater than 0.01% each.

On igniting a weighed portion of sample No. 1 in oxygen, its weight increased by 42.95% (theoretical 42.93%). An analogous determination for sample No. 2 could not be carried out because of the insufficient amount of this sample available to us. The calorimetric measurements were performed in the same calorimeter as in work $^{(14)}$. The heat value of the calorimeter ($\sim$ 2600 cal/deg) was determined with an accuracy of $\pm 0.02\%$ by combustion of standard benzoic acid. In experiments to determine the heat of combustion of metallic niobium, niobium shavings obtained on a drilling machine were used. (It was established that during this treatment the niobium sample was not contaminated.) Combustion of niobium ($\sim$ 0.5 g) was carried out in a quartz cup at an oxygen pressure in the bomb of 30 atm. The oxygen used to fill the bomb was purified from combustible impurities, water vapor, and CO_2. Ignition of the niobium was accomplished with a nitrocellulose thread ($\sim$ 10 mg) ignited by a platinum wire heated by an electric current. The percentage combustion of niobium in the experiments was 99.48-99.96% and was determined from the amount of oxygen that combined with the niobium combustion products on igniting them in oxygen (900°, 2 hours).

As Humphrey (3) noted, niobium pentoxide is somewhat hygroscopic. In this connection, in the present work the procedure for determining the percentage combustion of niobium was developed so as to exclude the influence of the hygroscopicity of Nb_2O_5 on the measurement results. The major part of the niobium combustion products ($\sim 99.5\%$) remained in the quartz cup in which the combustion was carried out. X-ray analysis of this portion of the combustion products established that, when both niobium samples are burned in the bomb, the β-modification of Nb_2O_5 is formed, as described, for example, in work (15). The results of the calorimetric determinations are presented in Table 1.

Table 1

	Heat of combustion of the niobium sample $-\Delta U_B(24.3^{\circ})$, cal/g sample	Correction for impurities, cal/g sample	Heat of combustion of pure niobium $-\Delta U_B(24.3^{\circ})$, cal/g niobium
Sample No. 1	$2433.9 \pm 1.6^*$(from 8 experiments)	$+0.1 \pm 2.8$	2434.0 ± 4.4
Sample No. 2	$2421.0 \pm 1.6^*$(from 5 experiments)	$+10.5 \pm 0.7$	2431.5 ± 2.3
Weighted mean:			2432.0 ± 2.0

* The error is twice the quadratic error of the mean result.

In calculating the correction for impurities (see Table 1), two assumptions were made concerning the state of the impurities in the niobium samples: 1) impurities O, N,

H and C form the compounds Nb_2O_5, NbN, NbH, and NbC with niobium; the other impurities do not form chemical compounds with niobium, and 2) all impurities, including O, N, H, and C, do not form compounds with niobium. The values of the correction for impurities given in Table 1 were calculated as the averages of the values of this correction calculated in accordance with the two assumptions regarding the state of the impurities.

The error in determining the correction for impurities indicated in Table 1 for each niobium specimen characterizes the actual uncertainty of this correction, since under any assumptions concerning the state of the impurities in the niobium specimen, the magnitude of the correction for impurities does not go beyond the limits of this error.

Thus, finally we have:

$$2\text{Nb(solid)} + {}^5/_2\text{O}_2\text{(g)} = \text{Nb}_2\text{O}_5\ (\beta\text{-modification});$$

$$\Delta H^0_{298} = -453.5 \pm 0.4 \text{ kcal/mole} \quad (1 \text{ cal} = 4.1840 \text{ abs. J.; at. wt. Nb } 92.91)$$

2. Heats of combustion of tantalum. For the calorimetric determinations two specimens of metallic tantalum (in the form of ingots) were used, in which the following impurities were found (in wt.%):

	O	N	H	C	Nb	Ti	Fe	Si	W	Mo
Specimen No. 1	$6 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	$3 \cdot 10^{-4}$	$2 \cdot 10^{-2}$	0.12	0.11	$3 \cdot 10^{-2}$	$< 4 \cdot 10^{-3}$	$4 \cdot 10^{-2}$	$1 \cdot 10^{-2}$
Specimen No. 2	$4 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	0.80	$< 5 \cdot 10^{-3}$	$< 2 \cdot 10^{-3}$	$< 3 \cdot 10^{-3}$	$< 1 \cdot 10^{-2}$	$< 1 \cdot 10^{-2}$

In addition, it was established that the content of the impurities Al, Ni, and Mg was less than $1 \cdot 10^{-3}$% of each in both tantalum specimens; the impurities Pb, Bi, Sn, Sb, and Cd—less than $1 \cdot 10^{-3}$% each in specimen No. 1 and less than $1 \cdot 10^{-4}$% in specimen No. 2; the impurities S and P—less than $2 \cdot 10^{-3}$% each in specimen No. 2.

When weighed portions of tantalum specimens Nos. 1 and 2 were ignited in oxygen, their weight increased by 22.18% (theoretical 22.16%) and 22.31% (theoretical 22.27%), respectively.

The method for determining the heat of combustion of tantalum was analogous to that used in determining the heat of combustion of niobium. The tantalum charge for an experiment (chips from a drilling or lathe machine were used) was about 0.85 g. The combustion of tantalum was carried out in a quartz cup at an oxygen pressure in the bomb equal to 10 atm. The lowering of the oxygen pressure made it possible (as had already been noted by Smirnova and Ormont ([13])) to achieve more complete combustion of tantalum. The percentage of tantalum burned was 99.5-99.9% and was determined by two methods: 1) from the amount of oxygen combined with the tantalum in the bomb, and 2) from the amount of oxygen combined with the tantalum combustion products when they were ignited in oxygen. Both methods gave coincident results (within the limits of experimental error). It was noted that tantalum pentoxide, like niobium pentoxide, is somewhat hygroscopic. Both methods for determining the percentage of tantalum burned were developed so as to exclude the influence of the hygroscopicity of Ta_2O_5 on the measurement results. The principal part of the tantalum combustion products ($ $99.9%) remained in the quartz cup in which the combustion was carried out. X-ray analysis of this part of the combustion products established that, when both tantalum specimens were burned in the bomb, the high-temperature α-modification of Ta_2O_5, described in reference (^{16}), was formed. (It should be noted that in reference (^{3}), another modification of Ta_2O_5 was found in the tantalum combustion products in the bomb; the reason for this discrepancy is not clear to us. Comparison with data from other works devoted to determining the heat of combustion of tantalum cannot be made, since in them the modification of tantalum pentoxide formed in the bomb was not identified.)

The results of the calorimetric determinations are presented in Table 2.

Table 2

	Heat of combustion of the tantalum specimen $-\Delta U_B$ (24.3°),cal/g specimen	Correction for impurities,cal/g specimen	Heat of combustion of pure tantalum $-\Delta U_B$ (24.3°),cal/g tantalum
Specimen No. 1	1352.1 ± 0.8 *(from 8 experiments)	-5.1 ± 0.8	1347.0 ± 1.6
Specimen No. 2	1357.7 ± 0.8 *(from 7 experiments)	-9.3 ± 0.5	1348.4 ± 1.3
Weighted mean:			1347.8 ± 1.0

* The error is twice the quadratic error of the mean result.

The calculation of the correction for impurities and the determination of the error of this correction were carried out in the same way as for niobium.

Finally, we have:

$$2\text{Ta (solid)} + {}^{5}/{}_{2}O_2(g) = Ta_2O_5\ (\alpha\text{-modification});$$

$$\Delta H^0_{298} = -489.3 \pm 0.4\ \text{kcal/mole} \quad (1\ \text{cal} = 4.1840\ \text{abs. J.; at. wt. Ta } 180.95)$$

Thus, in the present work, consistent results have been obtained for the heat of combustion of niobium (and the heat of combustion of tantalum) using specimens of different origin, in which the impurity content was small and accurately established. On the basis of these measurements, the following values of the heats of formation of the higher oxides of niobium and tantalum were found:

$$\Delta H^0_{\text{form}}\ \mathrm{Nb_2O_5}\ (\beta\text{-modification}) = -453.5 \pm 0.4\ \text{kcal/mole};$$

$$\Delta H^0_{\text{form}}\ \mathrm{Ta_2O_5}\ (\alpha\text{-modification}) = -489.3 \pm 0.4\ \text{kcal/mole}.$$

In conclusion, we consider it our duty to express our deep gratitude to A. I. Vaisenberg and V. I. Konstantinov for providing pure niobium and tantalum specimens and for their assistance in carrying out the analyses.

Moscow State University
named after M. V. Lomonosov

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