[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS EXPERIMENT STATION, REGION II, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heats of Formation of Niobium Nitride, Tantalum Nitride and Zirconium Nitride from Combustion Calorimetry

BY ALLA D. MAH AND NORMA L. GELLERT

RECEIVED MARCH 1, 1956

The energies of combustion of niobium nitride (NbN), tantalum nitride (TaN) and zirconium nitride (ZrN) were determined with a bomb calorimeter at 30 atm. pressure of oxygen and 303.15°K. as 1592.8, 943.0 and 1652.6 cal./g., respectively. These results, in conjunction with the heats of formation of the corresponding oxides, lead to the following values of the heats of formation of the nitrides (kcal./mole) at 298.15°K.: -56.8 ± 0.4 for NbN, -60.0 ± 0.6 for TaN and -87.3 ± 0.4 for ZrN.

Previous papers from this Laboratory have reported heats of formation of titanium nitride[1] and hafnium nitride.[2] Similar studies of other refractory nitrides are being conducted whenever suitable samples become available. The present paper describes measurements of the energies of combustion of niobium, tantalum and zirconium nitrides (containing 50 atomic % nitrogen), leading to the derivation of heats of formation of these nitrides from the elements.

Materials.—The nitrides were prepared by treating the metals with purified nitrogen at high temperatures.[3] Nitrogen was purified by passing it through concentrated sulfuric acid, over copper at 375° and then over magnesium perchlorate. The nitriding apparatus consisted of two concentrically mounted porcelain tubes heated by a tube furnace. Nitrogen was passed between the walls of the two tubes, as well as through the inner tube which contained the metal to be nitrided. The metal was held in an alundum boat and was protected by finely divided titanium which was placed upstream from the boat to act as a "getter."

The niobium metal was a Johnson, Matthey and Co. product containing 0.01% copper, 0.01% nickel and 0.01% silicon as the only significant metallic impurities. The metal, as received in powder form, was treated with nitrogen for about 35 hr. at 1200–1400°, the last several hours being at 1300°. Account was kept of the mass increase during nitriding and also portions of the product were tested to determine the mass increase upon conversion to niobium pentoxide. The results indicated the presence of 13.10% nitrogen, which fortuitously is virtually the theoretical amount for the composition NbN. The X-ray diffraction pattern agreed with that of Brauer and Jander.[4]

The preparation and testing of tantalum nitride gave considerable difficulty. Three batches were prepared, two from Fansteel Metallurgical Co., tantalum in bar form, and one from metal powder obtained from Johnson, Matthey and Co.

The Fansteel tantalum contained 0.01% iron, 0.08% niobium, 0.01% silicon, 0.005% titanium and no chromium, cobalt, molybdenum, nickel, tungsten or vanadium, according to spectrographic analysis. Lathe cuttings (0.002 in.), taken with a Carboloy tool, were treated with nitrogen for 20 hr. at 1200–1375°. The increase in mass during nitriding was determined and also the mass increase upon conversion of portions of the products to tantalum pentoxide. The results indicated a nitrogen content of 7.24% for batch A and 7.25% for batch B, as compared with the theoretical 7.19% for the composition TaN.

Johnson, Matthey and Co. tantalum powder was used as received in making batch C of the nitride. It was treated with nitrogen for 28 hr. at 1300–1350°. The nitrogen content of the product, determined by the Kjeldahl method, was 6.93%. From the nitrogen content and from the mass increase upon conversion to tantalum pentoxide, it was evident that this batch contained oxygen. The results accord with the assumption of 96.45% TaN and 3.55% TaO in crystalline solution.

The X-ray diffraction patterns of all three batches of tantalum nitride agreed with that of Brauer and Zopp.[5]

The zirconium was a portion of the low-hafnium containing metal used by Humphrey[6] in his heat of formation determinations of zirconium oxide. It contained less than 0.1% hafnium, 0.09% iron, 0.053% chlorine, 0.03% carbon, 0.011% magnesium, 0.009% aluminum, 0.009% lead, 0.007% nitrogen, 0.006% titanium, 0.002% chromium, 0.002% manganese, 0.001% silicon, 0.001% copper and less than 0.001% each of boron, molybdenum, nickel and tin. Fine lathe cuttings (0.002–0.003 in.), taken with a Carboloy tool, were treated with nitrogen for 5 hr. at 1300–1400°. Two batches of the nitride were made. The mass increase during nitriding and that upon conversion to zirconium dioxide indicated 13.35% nitrogen for batch A and for batch B, as compared with the theoretical 13.31% for the composition ZrN. The X-ray diffraction patterns agreed with that in the A.S.T.M. catalog.

Experimental Methods.—The heat of combustion measurements were made with previously described apparatus.[7] All weights were corrected to vacuum and all heat values are in terms of the defined calorie (1 cal. = 4.1840 abs. joules). The calorimeter was calibrated during each set of measurements by means of benzoic acid (National Bureau of Standards sample 39g). Two bombs were employed, the calibrations being 32480.6 (±0.02%) and 32435.7 (±0.02%) cal./ohm, respectively.

The combustions were conducted in oxygen at 30 atm. pressure. Ignition was accomplished by use of an electrically heated platinum spiral and a filter paper fuse for which proper corrections were made. The substances were tested for possible oxidation in the bomb prior to ignition. A weighed sample was placed in the bomb and all process steps conducted up to the point of ignition, after which the sample again was weighed. No significant weight increases were noted. The bomb gases after the combustions were tested for oxides of nitrogen. The amount present was negligible except in the zirconium nitride combustions for which a thermal correction of 0.006% was found necessary.

During the combustions, the samples of niobium nitride and tantalum nitride were held on disks of the respective pentoxides, about 4 cm. diameter and 3 mm. thick. The disks, formed from a heavy paste of the pentoxide and water and strongly ignited at 1100–1200°, were supported in the bomb by a heavy platinum sheet. The zirconium nitride was held in silica-glass crucibles that were heavily lined with zirconium dioxide and strongly ignited at 1050°.

In all cases, the bulk of the metal oxide from the combustion remained on the disk or in the crucible. A much smaller amount (averaging 7.2% in the niobium nitride combustions, 1.0% in the tantalum nitride combustions and only 0.2% in the zirconium nitride combustions) appeared as a deposit on the walls of the bomb. X-Ray examinations were made of the combustion products. The results were identical with those found by Humphrey[6] in burning the corresponding metals. The niobium pentoxide remaining on the disks was the same variety as employed in previous high temperature heat content measurements.[8] The wall deposit was a different crystalline modification. Likewise, the tan-

---

[1] G. L. Humphrey, THIS JOURNAL, **73**, 2261 (1951).

[2] G. L. Humphrey, *ibid.*, **75**, 2806 (1953).

[3] These preparations were conducted by C. J. O'Brien, except for one batch of tantalum nitride which was made by K. C. Conway.

[4] G. Brauer and J. Jander, *Z. anorg. allgem. Chem.*, **270**, 160 1952).

[5] G. Brauer and K. H. Zopp, *ibid.*, **277**, 129 (1954).

[6] G. L. Humphrey, THIS JOURNAL, **76**, 978 (1954).

[7] G. L. Humphrey, *ibid.*, **73**, 1587 (1951).

[8] R. L. Orr, *ibid.*, **75**, 2808 (1953).

TABLE I

ENERGY OF COMBUSTION AT 30°

Mass of substance, g.	Total energy evolved, cal.	Energy from Elt, fuse, N_2O_5, cal.	Cor. for incomplete comb., cal.	Total energy cor., cal.	$-\Delta U_B$, cal./g.
NbN					
1.38227	2213.65	12.52	..	2201.13	1592.4
1.38268	2214.24	12.13	..	2202.11	1592.6
1.38339	2214.08	9.44	..	2204.64	1593.6
1.38308	2212.25	8.97	..	2203.28	1593.0
1.38307	2216.01	13.37	..	2202.64	1592.6
1.38349	2215.93	12.39	..	2203.54	1592.7
1.38336	2213.08	9.22	..	2203.86	1593.1
				Mean	1592.9 ± 0.3
Cor. for impurities (−0.1 cal.)					1592.8
TaN (batch A)					
3.60254	3408.36	9.20	..	3399.16	943.5
3.60473	3413.25	8.57	..	3404.68	944.5
3.65006	3452.30	8.77	..	3443.53	943.4
3.70033	3502.80	8.90	..	3493.90	944.2
2.31017	2189.93	11.84	..	2178.09	942.8
				Mean	943.7 ± 0.6
Cor. for impurities (−3.9 cal.)					939.8
TaN (batch B)					
2.28696	2190.92	12.55	..	2178.37	952.5
2.30493	2204.71	8.92	..	2195.79	952.6
2.30999	2212.03	11.53	..	2200.50	952.6
2.30503	2207.25	11.82	..	2195.43	952.4
				Mean	952.5 ± 0.1
Cor. for impurities (−7.3 cal.)					945.2
TaN (batch C)					
2.49424	2350.69	9.33	..	2341.36	938.7
2.49785	2354.44	10.04	..	2344.40	938.6
2.49761	2353.96	10.32	..	2343.64	938.4
2.49631	2350.64	9.65	..	2340.99	937.8
2.49830	2354.62	10.10	..	2344.52	938.4
				Mean	938.4 ± 0.3
Cor. for impurities (+5.6 cal.)					944.0
ZrN (batch A)					
4.04990	6688.04	11.15	3.34	6680.23	1649.5
2.11998	3504.25	10.61	1.75	3495.39	1648.8
2.12021	3502.17	8.76	1.75	3495.16	1648.5
2.12066	3503.73	8.79	1.75	3496.69	1648.9
				Mean	1648.9 ± 0.4
Cor. for impurities (+1.6 cal.)					1650.5
ZrN (batch B)					
2.12046	3511.76	8.83	1.54	3504.47	1652.7
2.12054	3514.56	10.09	1.54	3506.01	1653.4
2.12041	3511.73	8.33	1.54	3504.94	1653.0
2.12025	3511.92	8.05	1.54	3505.41	1653.3
				Mean	1653.1 ± 0.3
Cor. for impurities (+1.6 cal.)					1654.7

talum pentoxide remaining on the disks was the same as used in previous low temperature heat capacity[9] and high temperature heat content[8] measurements. In the case of zirconium nitride, both the crucible contents and wall deposits were the same, being the monoclinic variety of zirconium dioxide.

Combustions of niobium and tantalum nitrides were 100% complete, according to visual observation. The combustion products were white and careful examination disclosed no dark particles or spots. The zirconium nitride combustion products showed visible traces of unburned material. The amount was determined for each run by noting the weight increase of the combustion product upon long ignition in air. Percentage completions of combustion were virtually constant for each batch of the nitride, being 99.950% for batch A and 99.956% for batch B.

Results

The experimental energy of combustion data are in Table I. Impurity corrections were calculated mainly from data in N. B. S. Circular 500[10] and previous results from this Laboratory.

In the case of niobium nitride, the net correction for the previously listed impurities amounts to only −0.1 cal./g. No correction was possible for the difference in crystal form of the portion of the combustion product deposited on the bomb walls.

For tantalum nitride, correction was made for 0.02% boron carbide in batch A and 0.05% in batch B, in addition to previously listed impurities. These two batches, made from tantalum cuttings, required grinding at intervals during the nitriding to obtain complete reaction. This grinding was done in a boron carbide mortar, resulting in boron carbide contamination which was estimated by a colorimeter (turmeric) method. The net impurity corrections for these two batches were −3.9 and −7.3 cal./g., respectively. Correction for boron carbide employed the data of Smith and co-workers.[11] Batch C, made from powdered metal, required no grinding during the nitriding. Batch C was assumed to contain the same metallic impurities as A and B, in addition to 3.55% tantalum oxide (as TaO). The molal heat of combustion of the latter was assumed to be 60% of that of tantalum metal. The net impurity correction for batch C is +5.6 cal./g. No allowance was made for the difference in structure of the 1% fraction of the combustion product that appeared as a deposit on the bomb walls.

The net impurity correction is the same for both batches of zirconium nitride, +1.6 cal./g.

The corrected energy of combustion value for niobium nitride corresponds to $\Delta E_{303.15} = -170.30$ kcal./mole for the combustion reaction under bomb conditions. Corrections to standard conditions (unit fugacity of oxygen and nitrogen, constant pressure process and 298.15°K.) need be made on this and on subsequent similar values. Reduction to unit fugacities was made by use of a pertinent modification of Washburn's[12] equation, which gave −71 cal./mole of nitride. Conversion to a constant pressure process involved the relationship $\Delta H = \Delta E + \Delta nRT$ and amounted to −452 cal./mole of nitride. The correction from 303.15 to 298.15°K. was estimated as −7 cal./mole of nitride. The net result of these corrections is

---

[9] K. K. Kelley, THIS JOURNAL, **62**, 818 (1940).

[10] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, Natl. Bur. Standards Circ., 500 (1952).

[11] D. Smith, A. S. Dworkin and E. R. Van Artsdalen, THIS JOURNAL, **77**, 2654 (1955).

[12] E. W. Washburn, *Natl. Bur. Standards J. Research*, **10**, 525 (1953) (eq. 43).

$\Delta H_{298.15} = -170.83$ kcal./mole of niobium nitride for the reaction

$$NbN(c) + 5/4\ O_2(g) = 1/2\ Nb_2O_5(c) + 1/2\ N_2(g)$$

From combination of the uncertainties in the calorimeter calibration, combustion of the nitride and impurity correction, it is estimated that the uncertainty in this result is ± 0.2 kcal./mole. Employing Humphrey's[6] heat of formation of niobium pentoxide ($\Delta H_{298.15} = -455.2 \pm 0.6$ kcal./mole), there is obtained $\Delta H_{298.15} = -56.8 \pm 0.4$ kcal./mole for the reaction

$$Nb(c) + 1/2\ N_2(g) = NbN(c)$$

that is, the standard heat of formation of niobium nitride.

The mean value of the energy of combustion of tantalum nitride, giving equal weight to the results for each batch, is 943.0 cal./g., corresponding to $\Delta E_{303.15} = -183.85$ kcal./mole. The correction to unit fugacities is -70 cal./mole, that to a constant pressure process is -452 cal./mole and that to 298.15°K. is estimated as -7 cal./mole. The net result is $\Delta H_{298.15} = -184.38$ kcal./mole for the standard heat of combustion of tantalum nitride

$$TaN(c) + 5/4\ O_2(g) = 1/2\ Ta_2O_5(c) + 1/2\ N_2(g)$$

This result is considered accurate to within ± 0.45 kcal. Upon combining with Humphrey's[6] heat of formation value for tantalum pentoxide ($\Delta H_{298.15} = -488.8 \pm 0.5$ kcal./mole), there is obtained $\Delta H_{298.15} = -60.0 \pm 0.6$ kcal./mole as the heat of formation of tantalum nitride from the elements.

The mean value of the energy of combustion of zirconium nitride, giving both batches equal weight, is 1652.6 cal./g., corresponding to $\Delta E_{303.15} = -173.90 \pm 0.30$ kcal. for the reaction

$$ZrN(c) + O_2(g) = ZrO_2(c) + 1/2\ N_2(g)$$

Correction to unit fugacity (-46 cal.), to a constant pressure process (-301 cal.), and to 298.15°K. (-1 cal.) leads to $\Delta H_{298.15} = -174.25 \pm 0.30$ kcal. for this reaction. Employing $\Delta H_{298.15} = -261.5 \pm 0.2$ kcal./mole as the heat of formation of zirconium dioxide,[6] there is obtained $\Delta H_{298.15} = -87.3 \pm 0.4$ kcal./mole as the heat of formation of zirconium nitride form the elements.

Discussion

Measurements in this Laboratory now have produced heat of formation values of the five refractory nitrides listed in Table II. Entropy data[13] at 298.15°K. are complete for titanium and zirconium nitrides and the requisite elements, giving $\Delta S^\circ_{298.15} = -22.9$ cal./deg. mole as the entropy of formation in each instance. It is reasonable to assume that the entropies of formation of the other three nitrides will not deviate much from this value. Using this assumption, their free energies of formation may be calculated as shown in Table II.

TABLE II

THERMAL DATA FOR NITRIDES

Substance	$\Delta H_{298.15}$, kcal./mole	$\Delta F^\circ_{298.15}$, kcal./mole
NbN	-56.8 ± 0.4	-50.0
TaN	$-60.0 \pm .6$	-53.2
ZrN	$-87.3 \pm .4$	-80.5
HfN[2]	$-88.2 \pm .3$	-81.4
TiN[1]	$-80.5 \pm .3$	-73.7

It appears from this table that hafnium nitride is slightly more stable than zirconium nitride and tantalum nitride is slightly more stable than niobium nitride.

(13) K. K. Kelley, U. S. Bur. Mines Bull., 477 (1950).

BERKELEY 4, CALIF.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY]

The Heat Capacity of Rhenium Heptoxide from 15 to 300° K. Entropy and Free Energy[1]

BY R. H. BUSEY

RECEIVED DECEMBER 12, 1955

Low temperature heat capacity data on rhenium heptoxide are presented and the thermodynamic functions for this heptoxide are tabulated. The entropy of Re_2O_7 at 298.16°K. is given as 49.54 ± 0.05 cal. deg.$^{-1}$ mole^{-1}. The following thermochemical values have been calculated: $S^\circ_{298.16}$ ($Re_2O_7(g)$, ideal gas at 1 atm.) $= 105.0 \pm 0.3$ cal. deg.$^{-1}$ mole^{-1}; $S^\circ_{298.16}$ ($HReO_4(c)$) $= 36.4 \pm 0.2$ cal. deg.$^{-1}$ mole^{-1}; ΔF°_f ($Re_2O_7(c)$) $= -255.0 \pm 2.0$ kcal. mole^{-1}; ΔF°_f ($HReO_4(c)$) $= -157.0 \pm 1.0$ kcal. mole^{-1}. Data obtained on a Calorimetry Conference standard sample of benzoic acid are compared with results obtained by National Bureau of Standards investigators. The agreement shown is quite satisfactory.

The low temperature heat capacity of rhenium heptoxide, Re_2O_7, reported here was measured to provide values of the entropy and free energy functions in connection with the study of the chemistry of technetium and rhenium being carried out in this Laboratory.[2] The entropy of the rhenium heptoxide when combined with other thermochemical and equilibrium data makes possible the computation of more reliable values for the free energy of formation of the heptoxide and perrhenic acid than heretofore possible.

No previous heat capacity data are available for this heptoxide.

Rhenium Heptoxide Sample.—The sample of rhenium heptoxide used was obtained on loan from the University of Tennessee rhenium project. The heptoxide was made from rhenium metal obtained from the reduction of purified $KReO_4$. The rhenium metal made in this manner usually contains a trace amount of potassium and only spectroscopic amounts of other elements. The rhenium heptoxide made by burning this metal in oxygen is resublimed at a lower temperature. This method of preparation should yield a product of high purity (>99.9%); consequently, the yellow, crystalline heptoxide was used without further purification. All handling of the sample was done in a vacuum type dry box. After the sample was placed in the calorimeter and the cap sealed on, the sample was evacuated (through the

---

(1) This work was performed for the Atomic Energy Commission.

(2) J. W. Cobble, G. D. Oliver and Wm. T. Smith, Jr., THIS JOURNAL, **75**, 5786 (1953) and preceding papers of this series.