repeat their work with HI, sp. gr. 1.60, 1.85 and 2.0, failed. At ordinary temperatures a yellow compound was formed which was not soluble in water but melted at about 165°. At high temperatures a lachrymator was formed. Attempts to extract the benzaldehyde with organic solvents gave no better success. (Extraction with alcohol is of course not feasible as it immediately precipitates hydrazine monoiodide.) This is the only hitherto undisputed method of preparation for this compound, and since it involves an aqueous medium it seems very unlikely that the compound they obtained was other than the compound we have now prepared below.

TABLE I

INFRARED ABSORPTION MAXIMA FOR SEVERAL HYDRAZINE HALIDES (CM.$^{-1}$)

$(N_2H_4)_3\cdot(HI)_2$	N_2H_5I	N_2H_5Br
941		
958	958	965
1098	1080	1095
1118		1100
	1236	1243
	1403	1410
	1493	1491
	1573	1568
2010		
2130		
	2556	2575
	2659	2690
2945		
3075	3037	
3300	3280	3250

In the light of our other work the m.p. of 220° looks unreasonable.

Hydrazine Diiodide Dihydrate.—Addition of fuming HI, sp. gr. 2.0, to a saturated water solution of hydrazine monoiodide with cooling resulted in the immediate formation of a white compound composed of small clear prisms, distinctly different from the needle-form of hydrazine monoiodide.[10] These crystals were collected on a fritted glass filter, and pressed with a rubber dam to remove as much liquid as possible. Washing with alcohol or water will remove the second molecule of HI leaving only hydrazine monoiodide. They were placed in a desiccator over KOH pellets for about 3–4 hours and analyzed. The material is extremely hygroscopic. In a sealed capillary the compound melts at 65–66°.

Anal. Calcd. for $N_2H_6I_2\cdot 2H_2O$: N_2H_4, 9.9; HI, 79.0; mol. wt., 324. Found: N_2H_4, 9.8, 10.6, 9.82; HI, 78.3, 81.2, 80.5; mol. wt. by titration with 0.02 *N* NaOH, 329, 332, 325.

For the determination of molecular weight, advantage was taken of the fact that in all hydrazine salts containing two equivalents of acid the second equivalent can be titrated to a neutral end-point with base.

This compound has not been reported previously in the literature but might be expected to exist by analogy to the hydrazine dibromide dihydrate.[11]

Standing for 24 hours over KOH removes both the water and second molecule of HI leaving hydrazine monoiodide.

The water of hydrazine dibromide dihydrate can be removed by standing over P_2O_5,[11] but unfortunately this is not true for the iodide. If an attempt is made to dehydrate the compound in this manner, HI and water are lost simultaneously. An anhydrous hydrazine diiodide is not obtained.

Dehydration cannot be effected with ethanol; dehydration with dioxane was also unsuccessful.

In a final attempt to synthesize anhydrous hydrazine diiodide two methods were used. (a) Gaseous dry HI was passed through a slurry of hydrazine monoiodide in benzene and also in chloroform. No formation of the diiodide took place. (b) Anhydrous HI was condensed on hydrazine monoiodide at the temperature of a Dry Ice–acetone bath. The temperature was then raised to −25° to remove excess HI. The residue proved to be unchanged hydrazine monoiodide.

---

[10] If anhydrous ether is added to a cold saturated solution of hydrazine monoiodide in 50% HI, it separates first into three layers. On scratching with a rod the material crystallizes but is unfortunately a mixture of the hydrated crystals with some hydrazine monoiodide. The mixture cannot be separated.

[11] E. C. Gilbert, THIS JOURNAL, **57**, 2611 (1935).

CORVALLIS, OREGON

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

Heats of Formation of Niobium Dioxide, Niobium Subnitride and Tantalum Subnitride

BY ALLA D. MAH[1]

RECEIVED FEBRUARY 8, 1958

The energies of combustion of niobium dioxide (NbO_2), niobium subnitride (Nb_2N) and, tentatively, tantalum subnitride (Ta_2N) were determined by bomb calorimetry. The results, in conjunction with the heats of formation of the corresponding pentoxides, lead to the following standard heats of formation at 298.15°K. (kcal./mole): NbO_2, -190.9 ± 0.4; Nb_2N, -61.1 ± 1.0; and Ta_2N, -64.7 ± 3.0 (tentative).

Previous papers from this Laboratory have dealt with heats of formation of the pentoxides[2] of niobium and tantalum and the nitrides[3] of composition NbN and TaN. The present paper reports energies of combustion and heats of formation of niobium dioxide and the subnitrides of composition Nb_2N and Ta_2N. As is usually the case with refractory nitrides, the purity of the available samples of these subnitrides leaves much to be desired. This is especially true of the tantalum compound for which only tentative values are reported. No previous similar measurements exist for any of these compounds.

Materials.—Niobium dioxide was prepared by K. C. Conway of this Laboratory from high purity niobium pentoxide obtained from Fansteel Metallurgical Corp. Small patches of the pentoxide were reduced in hydrogen at 950–1000° for 4 hours. These were combined and heated again in hydrogen for another 4 hours at the same temperature. Completion of the reactions was demonstrated by heating a portion of the product to 1450° in hydrogen and observing no weight change. Analysis by reconversion to the pentoxide indicated 99.90% niobium dioxide. Analysis by dissolving, precipitating the niobium as hydroxide and igniting to constant weight showed virtually 100.00% niobium dioxide. The X-ray diffraction pattern agreed with that of Brauer.[4]

---

[1] Bureau of Mines, U. S. Department of the Interior, Region II, Berkeley, California.

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

[3] A. D. Mah and N. L. Gellert, *ibid.*, **78**, 3261 (1956).

[4] G. Brauer, *Z. anorg. allgem. Chem.*, **248**, 1 (1941).

Niobium subnitride (prepared by K. R. Bonnickson, formerly of this Laboratory) was made from niobium metal (obtained from Johnson, Matthey and Co.) and purified nitrogen. After 6 hours of heating in a stream of nitrogen at 1150–1300°, the nitrogen content exceeded that for the subnitride. Niobium metal then was added in the correct proportion and the mixture was homogenized by heating for 9 days at 1120° *in vacuo*. The X-ray diffraction pattern of the product showed no niobium metal or other extraneous phase. Chemical analysis gave 92.81% niobium and 6.46% nitrogen (as compared with the theoretical 92.99 and 7.01%). The remainder was assumed to be oxygen. To correct the subsequently reported measurements, the material was treated as if it were a solid solution containing 92.33 mole % Nb_2N and 7.67 mole % Nb_2O, which is in line with the chemical analysis and with the single phase shown by X-ray diffraction.

Tantalum subnitride also was prepared by K. R. Bonnickson. Tantalum nitride (TaN), made by heating lathe cuttings from a Fansteel tantalum bar in purified nitrogen at 1300°, was combined with the stoichiometric amount of tantalum metal and homogenized by prolonged heating at 1120° *in vacuo*. The X-ray diffraction pattern of the product was sharp and gave no evidence of unreacted tantalum. The pattern checked that reported by Brauer and Zapp[5] for tantalum subnitride. The nitrogen content of this sample was not satisfactorily obtainable by the Kjeldahl method. Consequently, analysis was made by the vacuum fusion method at the Boulder City, Nev., Station of the Bureau of Mines. The results obtained were 3.48% nitrogen and 0.72% oxygen, the tantalum content by difference being 95.80%. (The theoretical analysis is 96.27% tantalum and 3.73% nitrogen.) To correct the subsequent measurements, the material was assumed to be 91.35 mole % Ta_2N, 5.34 mole % Ta and 3.31 mole % Ta_2O_5. As will be noted later, the uncertainty in composition of this sample permits obtaining only a tentative heat of formation value.

Experimental

The combustion calorimeter was described previously by Humphrey.[6] The mean calibration value obtained with National Bureau of Standards benzoic acid sample No. 39g was 32495.3 ± 0.01% cal./ohm. All weights are corrected to vacuum and heat values are in terms of the defined calories (1 cal. = 4.1840 abs. joules).

The combustions were conducted under 30 atm. pressure of oxygen. The combustion samples were held on disks of the corresponding pentoxide supported by a platinum sheet. The samples showed no weight increase upon standing in 30 atm. of oxygen for several hours. Ignition was by means of an electrically heated platinum spiral and a filter paper fuse. Oxygen deficiencies in the combustion products were calculated from the weight increases during combustion and proper corrections were made. The bomb gases after combustion contained only negligible amounts of oxides of nitrogen.

In the niobium dioxide experiments most of the combustion product remained on the disk; only about 0.08% was deposited on the bomb walls. X-Ray diffraction patterns showed that the combustion product on the disk and the disk material were the high temperature modification of niobium pentoxide listed in the ASTM catalog. The wall deposit appeared amorphous. No correction was made for this as the amount was so small.

The portion of combustion product remaining on the disk in the niobium subnitride experiments averaged 71%. X-Ray diffraction showed this to be the same high temperature modification as found in the dioxide combustions. The X-ray diffraction pattern of the wall deposit, however, agreed with a different modification of niobium pentoxide, also listed in the ASTM catalog. No correction was made for the difference in heat content between the two forms. However, the correction must be small as no trend in the heat of combustion was noted with amounts of wall deposit varying from 18 to 36%.

In the tantalum subnitride combustions, the amount of wall deposit ranged from 0.2 to 0.8%. X-Ray diffraction of the 99.2 to 99.8% portion remaining on the disk showed it to be the same form of pentoxide as that employed in previous low temperature heat capacity[7] and high temperature heat content[8] measurements.

Results

The experimental data for the niobium compounds are in Table I, in which the successive columns give the mass of substance burned, the total energy evolved, the energy of ignition, the oxygen deficiency of the combustion product, the correction for incompletion of combustion and finally the energy of combustion per gram.

TABLE I

ENERGY OF COMBUSTION AT 30°

Mass of substance, g.	Total energy evolved, cal.	Energy from Elt, fuse, cal.	O_2 deficiency, g.	Cor. for incomplete combustion, cal.	$-\Delta U_B$, cal./g.
			NbO_2		
4.99748	1434.30	10.68	0.00773	35.27	291.9
5.00551	1434.02	10.39	.00866	39.51	292.3
5.01532	1436.29	12.70	.00896	40.88	292.0
5.00882	1433.48	9.94	.00888	40.52	292.3
5.00694	1434.15	10.51	.00905	41.29	292.6
5.01178	1432.59	9.93	.00912	41.61	292.2
				Mean	292.2 ± 0.2
			Nb_2N		
1.00019	1950.73	11.69	0.00218	9.95	1948.6
1.00019	1948.75	10.05	.00218	9.95	1948.3
1.00010	1941.45	10.01	.00373	17.02	1948.3
1.00010	1937.33	10.14	.00448	20.44	1947.4
1.00048	1940.88	10.05	.00388	17.70	1947.6
1.00008	1940.08	10.94	.00451	20.58	1949.6
1.00017	1940.39	10.43	.00433	19.76	1949.4
1.00043	1940.42	10.65	.00426	19.44	1948.4
				Mean	1948.4 ± 0.6
			(Cor. for impurities)		16.7 ± 3.4
					1965.1 ± 3.5

The mean energy of combustion value for niobium dioxide corresponds to $\Delta E_{303.15} = -36.50$ kcal./mole under bomb conditions. Corrections to standard conditions of unit fugacity of oxygen (−23 cal.), a constant pressure process (−151 cal.), and 298.15°K. (−1 cal.) results in $\Delta H_{298.15} = -36.67 \pm 0.10$ kcal./mole for the standard heat of combustion of niobium dioxide. Employing Humphrey's[2] heat of formation of niobium pentoxide ($\Delta H_{298.15} = -455.2 \pm 0.6$ kcal./mole), there is obtained $\Delta H_{298.15} = -190.9 \pm 0.4$ kcal./mole as the standard heat of formation of niobium dioxide from the elements.

The literature contains no previous directly determined value of the heat of formation of niobium dioxide. The present result may be compared with −189.0 ± 1.0 kcal./mole calculated by Brewer[9] from hydrogen reduction equilibria of the pentoxide.

The mean value of the energy of combustion of niobium subnitride corresponds to $\Delta E_{303.15} = -392.7$ kcal./mole under bomb conditions. Corrections to unit fugacities of oxygen and nitrogen (−184 cal.) to a constant pressure process (−1205

---

(5) G. Brauer and K. H. Zapp, *Z. anorg. allgem. Chem.*, **277**, 129 (1954).

(6) G. L. Humphrey, THIS JOURNAL, **73**, 1587 (1951).

(7) K. K. Kelley, *ibid.*, **62**, 818 (1940).

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

(9) L. Brewer, *Chem. Revs.*, **52**, 1 (1953).

cal.) and to 298.15°K. (−10 cal.) leads to $\Delta H_{298.15} = -394.1 \pm 0.8$ kcal./mole for the standard heat of combustion. The estimated uncertainty takes into account the impurities in the sample as well as the uncertainties involved in the combustions and calibration. Again, combining with the heat of formation of niobium pentoxide gives $\Delta H_{298.15} = -61.1 \pm 1.0$ kcal./mole as the standard heat of formation of niobium subnitride from the elements.

No previous heat of formation value of niobium subnitride exists. The present result is 4.3 kcal./mole more negative than the heat of formation of NbN (−56.8 ± 0.4 kcal./mole).[3]

Because of uncertainty regarding the composition of the sample, only a tentative value is offered for tantalum subnitride. A tentative value appears justified as no previous value exists. Four combustions gave a mean of 1124.5 ± 2.0 cal./g., after correction for incompletion of combustion (average, 36.8 cal.) and for impurities (39.5 cal.). This corresponds to $\Delta E_{303.15} = -422.7$ kcal./mole for combustion under bomb conditions. Corrections to standard conditions gives $\Delta H_{298.15} = -424.1 \pm 2.9$ kcal./mole. Combining with Humphrey's[2] heat of formation of tantalum pentoxide (−488.8 ± 0.5 kcal./mole) gives $\Delta H_{298.15} = -64.7 \pm 3.0$ kcal./mole as the tentative heat of formation from the elements. This value appears reasonable in magnitude, being 4.7 kcal./mole more netative than the heat of formation of TaN (−60.0 ± 0.6 kcal./mole).[3]

BERKELEY 4, CALIFORNIA

[CONTRIBUTION NO. 1488 FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Tracer Studies on the Mechanism of Combustion of Carbon, Sulfur and Mercuric Sulfide[1]

BY JUI H. WANG AND EVERLY B. FLEISCHER

RECEIVED FEBRUARY 21, 1958

The mechanisms of the reactions $C + O_2 \rightarrow CO_2$ and $S + O_2 \rightarrow SO_2$, respectively, were studied with $O^{18}O^{18}$ as tracer. It was concluded that the two oxygen atoms in each CO_2 or SO_2 molecule produced came from different O_2 molecules.

The elucidation of the mechanism of combustion of solid fuels through kinetic studies is often hampered by the difficulty of reproducing the surface conditions. However, valuable information on the mechanism of combustion can sometimes be deduced from the result of tracer studies. For example, when solid carbon, sulfur and mercuric sulfide, respectively, are burned in excess of pure oxygen, the main over-all reactions are

$$C + O_2 \longrightarrow CO_2$$
$$S + O_2 \longrightarrow SO_2$$
$$HgS + O_2 \longrightarrow Hg + SO_2$$

One may ask, "Are the two oxygen atoms in each of the CO_2 or SO_2 molecules produced in the above reactions from the same oxygen molecule or from two different oxygen molecules?" The answer was deduced from the result of the present study with $O^{18}O^{18}$ as tracer.

The principle of our method, which has already been described,[2] is very simple. Suppose oxygen gas is prepared by the thermal decomposition of O^{18}-enriched silver oxide. If the isotopic atom-fraction of O^{18} in this oxygen gas is X, the mole-fraction of $O^{18}O^{18}$ must be approximately equal to X^2. (The small isotope effect due to the difference in zero point energies of light and heavy O-atoms in O_2 may be neglected for the present purpose.) When each mole of this O^{18}-enriched oxygen gas is blended with q moles of ordinary oxygen gas, the isotopic atom fraction of O^{18} and the mole fraction of $O^{18}O^{18}$ in the mixed O_2 become $[X + q(0.0020)]/(1 + q)$ and $[X^2 + q(0.0020)^2]/(1+q)$, respectively, where 0.0020 is the atom fraction of O^{18} in ordinary oxygen gas. The isotopic distribution in this blended oxygen gas is unnatural, because according to natural probabilities if the atom fraction of O^{18} is $[X + q(0.0020)]/(1 + q)$, the mole fraction of $O^{18}O^{18}$ should be approximately $[X + q(0.0020)]^2/(1 + q)^2$. Now if this O^{18}-enriched oxygen gas with unnatural isotopic distribution is used to burn solid carbon, sulfur and mercuric sulfide, respectively, the determination of O^{18}-distribution in the combustion product (CO_2 or SO_2) could lead to the answer of the above question. Thus if both O-atoms in each CO_2 (or SO_2) molecule produced are from the same O_2 molecule, the isotopic mole fraction of $CO^{18}O^{18}$ (or $SO^{18}O^{18}$) should still be approximately equal to $[X^2 + q(0.0020)^2]/(1 + q)$. But if the two O atoms in each CO_2(or SO_2) molecule are from different O_2 molecules, the reaction would involve a reshuffling of O-atoms and yield an isotopic mole fraction of $CO^{18}O^{18}$(or $SO^{18}O^{18}$) approximately equal to $[X + q(0.0020)]^2/(1 + q)^2$ in accordance with natural probabilities.

Experimental

Preparation of the Labeled Oxygen Gas.—Labeled oxygen gas was prepared by thermal decomposition of O^{18}-labeled silver oxide. The labeled silver oxide was precipitated from its saturated solution in O^{18}-enriched water (10.7 atom % in O^{18}) with a concentrated solution of KOH in O^{18}-enriched water. The precipitate, about 1.4 g., was washed with 20 ml. of ordinary water ten times, vacuum dried and then left in a drying oven at 105° for three days. It was stored in a desiccator before use. The oxygen gas so prepared contained 5.8 atom % O^{18} and 0.336 mole % of $O^{18}O^{18}$.

Combustion Experiments.—The combustion was carried out in an enclosed Pyrex tube which was approximately 25 cm. long and had a total inside volume of about 12.5 ml. In each experiment about 120 to 140 mg. of labeled silver oxide prepared above was weighed out and placed at one

---

(1) This work was supported in part by a research grant (USPHS-RG-4483) from the Division of Research Grants, Public Health Service.

(2) R. C. Jarnagin and J. H. Wang, THIS JOURNAL, **80**, 786 (1958).