[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, REGION III, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

High-temperature Heat Contents of Tantalum and Niobium Oxides

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High-temperature heat content measurements of tantalum oxide (Ta_2O_5) and niobium oxide (Nb_2O_5) were conducted from 298° to temperatures slightly above 1800°K. A table of values of heat content and entropy increments above 298.16°K. and equations representing the heat content results are included.

This paper reports high-temperature heat content data for tantalum and niobium oxides from room temperature to temperatures above 1800°K. No previous similar data exist for tantalum oxide, and the only values for niobium oxide are the over 60-year old, rather uncertain results of Krüss and Nilson[1] at four temperatures between 273 and 713°K.

Materials

The tantalum oxide, purchased several years ago from Fansteel Products Co., was identical with that used by Kelley[2] in low-temperature heat capacity measurements. The sample was heated at 1200° before the present measurements. The X-ray diffraction pattern was similar to that of the low-temperature variety of niobium oxide described by Brauer,[3] the two substances evidently being isomorphous.

The niobium oxide was purchased from Fansteel Metallurgical Corp. Spectrographic analysis showed 0.03% silicon, < 0.05% magnesium and < 0.01% titanium. Tantalum, tungsten, nickel, zirconium, aluminum and calcium were not detected. The sample was heated to 1050° before use in the measurements. The X-ray diffraction pattern agreed with that of the high-temperature variety reported by Brauer.[3]

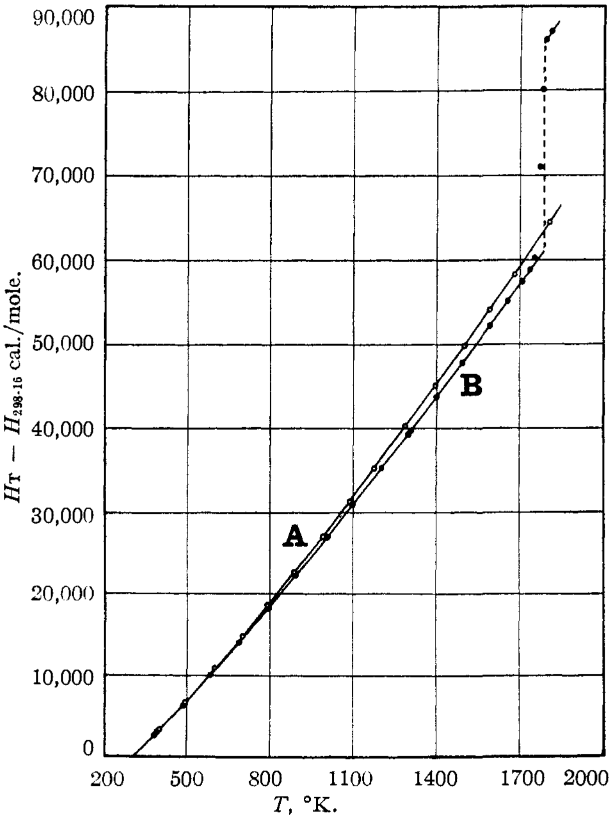

Fig. 1.—Heat contents above 298.16°K.: A, Ta_2O_5; B, Nb_2O_5.

Measurements and Results

The high temperature heat content measurements were made with previously described apparatus.[4] The results are reported in terms of defined calories (1 cal. = 4.1840 abs. joules) per mole. Molecular weights accord with the 1951 International Atomic Weights,[5] and all weighings were reduced to vacuum. During the measurements, the substances were enclosed in platinum–rhodium capsules, the heat contents of which were determined in separate experiments. The furnace thermocouple was calibrated at frequent intervals against the melting point of pure gold.

The experimental results are listed in Table I and plotted in Fig. 1. In the crystalline state both substances have similar, regular heat content curves. Crystalline niobium oxide has the lower heat content, and consequently the lower heat capacity, at all temperatures below the range where premelting is observed (1750–1785°K.). The average difference between 298 and 1700°K. is 3.69%.

TABLE I

EXPERIMENTAL HEAT CONTENTS ABOVE 298.16°K. (CAL./MOLE)

T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$
		Ta_2O_5 (mol. wt., 441.76)			
395.6	3,270	884.9	22,650	1394.2	45,090
488.4	6,590	988.8	27,150	1497.8	49,860
596.5	10,850	1083.6	31,310	1590.3	54,060
693.6	14,750	1173.7	35,260	1678.2	58,340
787.9	18,620	1285.2	40,250	1802.6	64,440
		Nb_2O_5 (mol. wt., 265.82)			
381.4	2,720	1097.4	30,960	1706.4	57,500
390.4	3,040	1199.7	35,290	1731.8	58,910
484.1	6,370	1295.4	39,280	1750.6	60,360[a]
582.2	10,050	1306.1	39,800	1769.1	71,000[a]
686.7	14,130	1396.6	43,720	1779.9	81,170[a]
791.2	18,250	1491.3	47,810	1792.8	86,130
890.8	22,320	1589.4	52,190	1809.2	87,080
1004.5	27,060	1653.7	55,150		

[a] In premelting range.

Niobium oxide melts at 1785°K. The heat of fusion is 24,590 cal./mole, giving an entropy of fusion of 13.77 cal./deg. mole. Three determinations (labeled (*a*) in Table I) show premelting effects.

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(1) G. Krüss and L. F. Nilson, *Z. physik. Chem.*, **1**, 391 (1887).

(2) K. K. Kelley, THIS JOURNAL, **62**, 818 (1940).

(3) G. Brauer, *Z. anorg. Chem.*, **248**, 1 (1941).

(4) K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).

(5) E. Wichers, THIS JOURNAL, **74**, 2447 (1952).

However, the amount of premelting is small at 1750°K. (*i.e.*, at 98% of the absolute melting point), which is confirmation of the high purity of the substance. Because of the temperature limitation of the equipment, only two measurements were obtained in the liquid range, at 1792.8 and 1809.2° K. These two measurements indicate a normal magnitude for the heat capacity of the liquid, 57.9 cal./deg. mole or 8.27 cal./deg./mean gram atom.

TABLE II

HEAT CONTENTS (CAL./MOLE) AND ENTROPIES (CAL./DEG. MOLE) ABOVE 298.16°K.

	Ta_2O_5		Nb_2O_5	
T, °K.	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$
400	3,430	9.87	3,410	9.82
500	7,070	17.98	6,970	17.75
600	10,950	25.05	10,730	24.60
700	14,990	31.28	14,630	30.62
800	19,130	36.81	18,630	35.95
900	23,340	41.76	22,710	40.76
1000	27,630	46.29	26,860	45.13
1100	31,990	50.44	31,050	49.13
1200	36,410	54.29	35,280	52.80
1300	40,880	57.86	39,550	56.22
1400	45,390	61.20	43,860	59.42
1500	49,970	64.36	48,230	62.43
1600	54,630	67.37	52,670	65.30
1700	59,380	70.25	57,190	68.04
1785	....	...	61,090(c)	70.28
1785	....	...	85,680(l)	84.05
1800	64,220	73.01	86,550	84.53

Table II contains smooth values of the heat contents to 1800°K. and the corresponding entropy increments, computed to match the heat contents by the method of Kelley.[6]

The following relationships, which represent the heat content values to within the average limits shown in parentheses, were derived for use by those who make thermodynamic calculations by means of equations.

Ta_2O_5(c)

$$H_T - H_{298.16} = 37.00T + 3.28 \times 10^{-3}T^2 + 5.92 \times 10^5 T^{-1} - 13{,}309;\ (0.4\%,\ 298\text{–}1800°\text{K.})$$

Nb_2O_5(c)

$$H_T - H_{298.16} = 36.23T + 2.77 \times 10^{-3}T^{-2} + 4.88 \times 10^5 T^{-1} - 12{,}685;\ (0.5\%,\ 298\text{–}1785°\text{K.})$$

Nb_2O_5(l)

$$H_T - H_{298.16} = 57.90T - 17{,}672;\ (0.1\%;\ 1785\text{–}1810°\text{K.})$$

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(6) K. K. Kelley, U. S. Bur. Mines Bulletin 476 (1949).

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The Heat and Entropy of Ionization of Hydrofluoric Acid. The Entropy of Bifluoride Ion

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The heats of solution of sodium fluoride in water and in aqueous perchloric acid have been measured. These values are used to calculate the heat of ionization of hydrofluoric acid. By combining this heat with the free energy of ionization, we have calculated the entropy of ionization. We found $\Delta H^0 = -3180$ cal./mole and $\Delta S^0 = -25.2$ e.u. This value is used in calculating the entropy of bifluoride ion which is found to be 26 e.u.

Because of the unusual structure of bifluoride ion, FHF^-, a value for its entropy in aqueous solution is of considerable interest. This work was undertaken to obtain this value and also to clear up uncertainties in the heat and entropy of ionization of aqueous HF.

The equilibrium constants for the dissociation of hydrofluoric acid and for the formation of HF_2^- have been determined by Broene and DeVries.[1] Hence measurement of the heat of solution of sodium fluoride in water and in acid enables one to calculate the heat and entropy of ionization of aqueous hydrofluoric acid and the HF_2^- entropy.

Experimental Procedures

The calorimeter used in this investigation has been described in detail elsewhere.[2,3] For the runs involving acid solutions, the glass surfaces of the calorimeter were coated with a thin layer of Tygon Paint (Series K, White, U. S. Stoneware). Samples of sodium fluoride were contained in small thin glass bulbs and were introduced into the calorimetric solution by breaking the bulbs against the bottom of the dewar. The sample bulbs were coated with paraffin wax for the runs using acid solutions. All heats were measured at 25 ± 1° and are reported in terms of the defined calorie.

C.P. sodium fluoride was dried for two hours at 150° and then stored in a desiccator until used.

Double vacuum-distilled 72% perchloric acid was diluted with distilled water to make a stock solution which was standardized against mercuric oxide. Concentration expressed in moles of acid/liter was converted to molality by using the relation due to Stonehill.[4]

The Heat of Solution of Sodium Fluoride in Water.—One measurement of the heat of solution of sodium fluoride in water was made. The result of this experiment is in agreement with the values obtained by Latimer and Jolly.[5] The details are given in Table I, where the most recent determination is designated as Run 3.

TABLE I

Run	NaF, g.	H_2O, g.	ΔH, cal./mole
1[5]	1.063	1064	291
2[5]	1.759	1042	297
3	1.598	1060	290

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(1) H. Broene and T. DeVries, THIS JOURNAL, **69**, 1644 (1947).

(2) B. J. Fontana, "National Nuclear Energy Series IV-19B," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 321.

(3) H. W. Zimmermann and W. M. Latimer, THIS JOURNAL, **61**, 1550 (1939).

(4) H. Stonehill, *Trans. Faraday Soc.*, **36**, 76 (1943).

(5) W. M. Latimer and W. L. Jolly, THIS JOURNAL, **75**, 1548 (1953).