[CONTRIBUTION FROM THE METALLURGICAL FUNDAMENTALS SECTION, METALLURGICAL DIVISION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

The Specific Heats at Low Temperatures of Tantalum Oxide and Tantalum Carbide[1]

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The measurement of specific heats, at low temperatures, of metallurgically important substances has been one of the programs of study of the Metallurgical Division of the Bureau of Mines for the past several years. This paper presents results for tantalum oxide and tantalum carbide for which no low-temperature specific heat or entropy data have been available heretofore. The results for tantalum carbide may be of special interest in that they are the first adequate set of low-temperature true specific-heat measurements to be obtained for a metal carbide, the only other pertinent data being those of Nernst and Schwers[3] and Günther[4] for silicon carbide in the temperature range 22 to 97°K.

Materials

The tantalum oxide was a product of the Fansteel Products Co., purchased several years ago. It was stated to be of virtually atomic weight purity. Because of its low apparent density, it was compressed into pellets and the pellets broken into sizes below 2 mm. for filling the calorimeter. A 210.5-g. sample was used.

The tantalum carbide was loaned for this work by the Fansteel Metallurgical Co. through the courtesy of Mr. J. H. Harper and Mr. F. L. Hunter. This material was in powder form and according to the manufacturers contained 4.26% carbon compared with 4.23%, the theoretical figure for TaC. Impurities other than the excess carbon were stated to be of the order of 0.02%. It required 803.5 g. to fill the calorimeter.

Results

Specific Heats.—The method and apparatus have been described previously.[5]

The results, expressed in defined calories (1 calorie = 4.1833 int. joules), are given in Table I and shown graphically in Fig. 1. The values for tantalum carbide have been corrected for the 0.03% excess carbon on the assumption that it is present as graphite. The correction increases with the temperature and ranges from 0.02 to 0.09%.

TABLE I

SPECIFIC HEAT OF Ta_2O_5 (441.76 G.)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
53.4	5.872	115.7	16.19	214.2	26.88
57.6	6.623	124.9	17.49	224.5	27.71
62.1	7.480	134.9	18.86	234.7	28.54
66.6	8.353	145.0	20.10	245.2	29.34
70.9	9.142	154.7	21.23	255.8	30.15
75.4	9.971	165.0	22.33	265.8	30.63
81.5	10.93	174.6	23.34	275.5	31.14
86.2	11.70	184.4	24.29	285.0	31.76
95.6	13.12	194.5	25.20	294.2	32.10
105.3	14.70	203.4	26.04		

SPECIFIC HEAT OF TaC (192.89)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
54.6	2.275	104.3	4.583	214.6	7.292
58.1	2.505	114.7	4.876	224.5	7.514
62.1	2.759	124.8	5.149	234.5	7.713
66.5	3.032	134.8	5.415	244.7	7.912
71.1	3.298	144.8	5.661	255.1	8.109
75.6	3.525	154.5	5.900	265.3	8.280
80.2	3.735	164.6	6.141	275.1	8.424
80.6	3.752	174.2	6.377	284.6	8.559
84.4	3.903	184.5	6.614	293.9	8.741
84.9	3.924	194.3	6.843	294.5	8.764
94.5	4.271	204.5	7.078		

The tantalum oxide results appear normal and require no discussion. There are, however, two items of interest to be mentioned concerning the measurements for tantalum carbide. Comparison of the results for this substance with those for pure tantalum[6] shows that at temperatures below 125°K. the former has the lower specific heat per gram formula mass, the difference at 54°K. being 0.59 calorie. Also, if C_p for tantalum carbide is plotted against log T, an inflection point in the neighborhood of 100–110°K. is readily apparent. This is caused by the carbon skeleton, the vibrations of which contribute only a very minor portion of the specific heat at the lowest temperatures studied, beginning to take up vibrational energy. Such an inflection is not usual in low temperature specific-heat curves but has been observed in other instances in which the constituent atoms differ widely in atomic mass, as, for example, hydrogen chloride.[7]

The results for tantalum oxide may be adequately represented throughout the entire temperature range studied by the function combination

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(3) Nernst and Schwers, *Sitzber. Kgl. Preuss. Akad. Wiss.*, 355 (1914).

(4) Günther, *Ann. Physik*, [4] **51**, 828 (1916).

(5) Millar, THIS JOURNAL, **50**, 1875 (1928); Anderson, *ibid.*, **52**, 2296 (1930).

(6) Kelley, unpublished data.

(7) Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928).

$$D\left(\frac{170}{T}\right) + 2E\left(\frac{265}{T}\right) + 2E\left(\frac{528}{T}\right) + 2E\left(\frac{880}{T}\right)$$

In the case of tantalum carbide

$$D\left(\frac{268}{T}\right) + E\left(\frac{861}{T}\right)$$

represents the data adequately except in the region near the inflection point, where the function sum is somewhat low (at worst 0.1 calorie). Below 72°K., however, the Debye function alone is adequate.

Entropy Calculations.—The entropies at 298.1°K. were calculated in the usual manner. The extrapolated portions below 53.1°K. were obtained from the functions given above. Only the Debye function and first pair of Einstein functions for tantalum oxide need be considered at 53.1°K. while for tantalum carbide only the Debye function is significant at this temperature. The results are given in Table II.

There are no other values for these substances with which to compare the present results. It may be of interest to note, however, that the figure for tantalum carbide is only 0.2 unit higher than the entropy at 298.1°K. of pure tantalum.[6]

Related Thermal Data.—The heat of formation of tantalum carbide never has been determined. Several values exist for tantalum oxide: −498,400, Moose and Parr[8]; −480,500, Sieverts, Gotta and Halberstadt[9]; −486,000 ± 500, Becker and Roth[10]; and −499,900 ± 1000, Neumann, Kröger and Kunz.[11]

TABLE II

ENTROPIES AT 298.1°K.

	Ta_2O_5	TaC
0–53.1°K. (extrapolation)	2.83	0.95
53.1–298.1°K. (graphical)	31.36	9.16
$S_{298.1}$	34.2±0.4	10.1±0.1

The spread in these values probably may be attributed to the presence of different amounts of hydrogen in the samples of metal burned to oxide. For the present purpose the result of Becker and Roth is adopted. From this value and the entropies of the oxide, metal (9.9 ± 0.1)[6] and oxygen (49.03)[12] there is computed $\Delta F^0_{298.1} = -453{,}700$ as the free energy of formation of tantalum oxide from the elements.

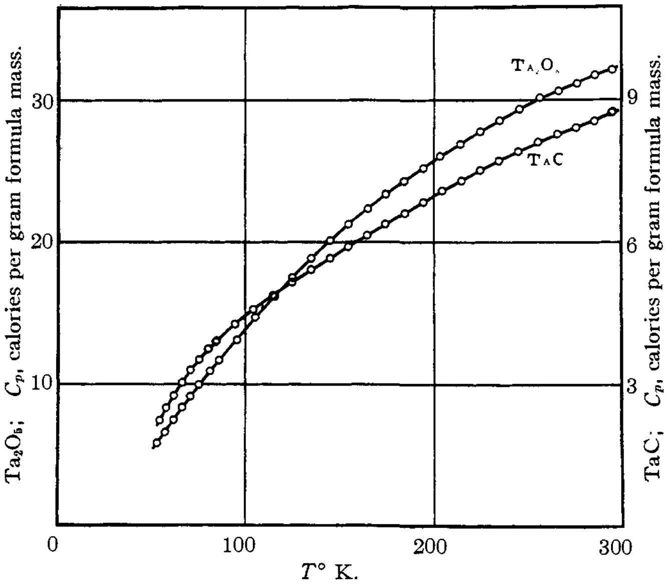

Fig. 1.—Specific heats of Ta_2O_5 and TaC.

Summary

Specific heat measurements of tantalum oxide and tantalum carbide were made in the temperature range 53 to 298.1°K.

The entropies are $S_{298.1} = 34.2 \pm 0.4$ for tantalum oxide and $S_{298.1} = 10.1 \pm 0.1$ for tantalum carbide.

The free energy of formation of tantalum oxide from the elements has been computed as $\Delta F^0_{298.1}$ −453,700.

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[8] Landolt-Börnstein, "Physikalisch-chemische Tabellen," Julius Springer, Berlin, 1st Suppl., 1927, p. 838.

[9] *Ibid.*, 2nd Suppl., Vol. 2, 1931, p. 1515.

[10] Becker and Roth, *Z. physik. Chem.*, **A167**, 16 (1933).

[11] Neumann, Kröger and Kunz, *Z. anorg. Chem.*, **218**, 395 (1934).

[12] Giauque and Johnston, THIS JOURNAL, **51**, 2300 (1929).