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Abstract

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ENTHALPY AND HEAT CAPACITY OF TUNGSTEN IN THE TEMPERATURE RANGE 0–2400°C

Owing to the wide use of tungsten in electrovacuum technology, at the beginning of the twentieth century numerous works appeared ([1–7]), etc., in which its heat capacity was determined up to very high temperatures (2250° ([1])) by the incandescent-filament method and its variants. The value of most of these works is substantially reduced because of the insufficient accuracy of the results, due mainly to the difficulty of allowing for heat losses by radiation. In these investigations a considerable scatter of experimental points is observed, and the results of different authors are in poor agreement. Experimental data on the enthalpy and heat capacity of tungsten obtained by the mixing method were limited to temperatures of 1500–1600° ([8–10,16,17]). Meanwhile, in the region of very high temperatures this method can give the most accurate results in comparison with other methods.

In order to refine the available experimental data, and also to extend investigations into the high-temperature region, work was carried out on the experimental determination of the enthalpy and heat capacity of tungsten in the temperature range 350–2000° ([11]). The investigations were carried out by the mixing method ([12,13]).

In the present work, by the same method, the enthalpy and heat capacity of tungsten have for the first time been determined at still higher temperatures, reaching

Table 1

Experimental data on the enthalpy of tungsten

Sample No.	Medium	t, °C	$i_t - i_0$, $\frac{\text{kcal}}{\text{kg}}$	t'_n, °C	$i_t - i'_n$, $\frac{\text{kcal}}{\text{kg}}$
1	Vacuum	2006	75.44	30.55	74.27
2	Argon	2070	78.37	28.54	77.23
3	Argon	2155	81.80	27.97	80.61

Sample No.	Medium	t, °C	$i_t{-}i_0$, $\frac{\text{kcal}}{\text{kg}}$	t'_n, °C	$i_t -$ i'_n, $\frac{\text{kcal}}{\text{kg}}$
3	Vacuum	2169	82.52	28.60	81.22
3	Argon	2223	85.16	28.78	83.92
3	Argon	2247	86.92	28.48	85.65
4	Argon	2254	86.15	28.39	84.89
4	Argon	2340	90.29	28.76	88.95

Note. t is the temperature of the specimen in the furnace; t'_n is the final temperature of the calorimeter, taking into account the heat-exchange correction; $i_t - i_0$ is the change in enthalpy from 0° to temperature t; $i_t - i_{t'_n}$ is the change in enthalpy from temperature t'_n to t. The change in enthalpy from 0° to t'_n was taken from the data of Kelley ([15]).

2340°. The results of these experiments are presented in Table 1. Owing to the use of a high-temperature furnace with a tungsten heater, more favorable conditions were created for protecting the specimens from contamination than in the case of using a graphite heater. The magni-

the amount of impurities in the samples studied did not exceed 0.05%. The samples were turned from tungsten rods prepared by powder metallurgy. To account for heat losses by the samples when they fell into the calorimeter, a correction was introduced, calculated from the known coefficients of total radiation of tungsten (19, 20). The surface of the samples in all experiments was kept polished. Four samples were used to determine the enthalpy (see Table 1).

The experimental apparatus was leak-tight, which made it possible to carry out experiments in a vacuum of the order of 10^{-2}–10^{-3} mm Hg or in an argon atmosphere at a pressure of 1.05 ata (see Table 1).

The temperature of the sample in the furnace was measured with an optical disappearing-filament pyrometer through a glass prism of total internal reflection. The error in measuring temperature with the pyrometer in the interval 2000–2400° is estimated at ±0.7%. To obtain more accurate results, the temperature was measured with the aid of a blackbody model formed by a cavity in the sample. From above the cavity was closed by a tungsten disk with a central aperture 2.3 mm in diameter for sighting the pyrometer. A fine tungsten powder was poured onto the bottom of the cavity for diffuse reflection of radiation. In contrast to earlier work (11-13), in this series of experiments, when measuring temperatures above 2000°, the space between the sample and the pyrometer was purged with a weak stream of argon in order to disperse vapors and gases which sometimes accumulated in small amounts in the upper part of the heater and entered the field of view of the pyrometer. The effectiveness of such purging was checked repeatedly by experiments in vacuum both in the study of tungsten (see Table 1) and of other materials (14).

On the basis of the experimental data (11) and the results of the experimental determination of enthalpy in the present work, empirical equations were obtained for calculating the enthalpy and heat capacity of tungsten:

$$i_t - i_{0^\circ} = 0.03170t + 2.75 \cdot 10^{-6}t^2 + 8.1 \cdot 10^{-11}t^3; \quad (1)$$

$$c_p = 0.03170 + 5.50 \cdot 10^{-6}t + 2.43 \cdot 10^{-10}t^2; \quad (2)$$

$$\mu c_p = 5.828 + 10.11 \cdot 10^{-4}t + 4.47 \cdot 10^{-8}t^2, \quad (3)$$

where t is the temperature (°C); $i_t - i_{0^\circ}$ is the change in enthalpy from 0° to temperature t (kcal/kg); c_p is the true specific heat capacity (kcal/kg • deg); μc_p is the true atomic heat capacity (cal/g-atom • deg). The atomic weight of tungsten in the calculation formulas was taken as 183.86, and the relation between the calorie and the absolute joule as 1 cal = 4.1840 abs. J.

Empirical formula (1) gives a good average of the experimental data (11) and the experiments listed in Table 1. The greatest deviation of the experimental points from the curve obtained from equation (1) does not exceed 0.4% when the temperature is measured by thermocouple in the interval 357–1200° and does not exceed 0.56 and 1% when the temperature is measured by pyrometer, respectively in the intervals 1000–2000 and 2000–2400°. These deviations are in good agreement with the calculated maximum relative random errors of the experimental determination of enthalpy, which for the same temperature intervals are estimated as: ±0.6, ±0.9, and ±1.2%.

The empirical formulas obtained may be recommended for use in the temperature interval 0–2400°. It should be noted that these formulas are consistent with the data on the true heat capacity at 0° of other investigators (1, 8-10, 16-18).

Table 2 gives smoothed values of enthalpy and heat capacity calculated by formulas (1), (2), (3).

Of the known works in which the hot-filament method was used, the most reliable results were obtained by Zwikker (1). His experiments were distinguish –

are distinguished by the thoroughness of the measurement procedure and by the wide temperature range of the investigation. In the high-temperature region (370-2250°), Zwikker used two indirect, mutually independent methods for the experimental determination of the true heat capacity of tungsten. The maximum scatter of the experimental points obtained by the two methods, relative to the smoothing curve proposed by the author for the temperature interval 0-2300°, does not exceed ±(4-5)%. This smoothing curve agrees well with his own low-temperature investigations of heat capacity by the method of direct heating at temperatures of 90-290° K. The curves of true heat capacity according to Zwikker and according to equation (3) at the beginning of the temperature interval 0-2300° C differ from one another within about 1%, coinciding at higher temperatures.

Table 2

Smoothed values of enthalpy and heat capacity

t, °C	$i_t - i_0$, kcal/kg	c_p, kcal/(kg· deg)	μc_p, cal/(g-atom · deg)	t, °C	$i_t - i_0$, kcal/kg	c_p, kcal/(kg· deg)	μc_p, cal/(g-atom · deg)
0	0	0.03170	5.828	1300	46.03	0.03926	7.218
100	3.197	0.03225	5.930	1400	49.99	0.03988	7.331
200	6.451	0.03281	6.032	1500	54.01	0.04050	7.445
300	9.759	0.03337	6.135	1600	58.09	0.04112	7.560
400	13.12	0.03394	6.240	1700	62.23	0.04175	7.676
500	16.55	0.03451	6.345	1800	66.44	0.04239	7.793
600	20.03	0.03509	6.451	1900	70.71	0.04303	7.910
700	23.56	0.03567	6.558	2000	75.05	0.04367	8.029
800	27.16	0.03625	6.665	2100	79.45	0.04432	8.148
900	30.82	0.03685	6.774	2200	83.91	0.04498	8.269
1000	34.53	0.03744	6.884	2300	88.44	0.04563	8.390
1100	38.30	0.03804	6.994	2400	93.04	0.04630	8.512
1200	42.14	0.03865	7.106				

In the second, less accurate but noteworthy work ([2]), carried out by the incandescent-filament method, the temperature interval 927-2127° is covered. In this work, only the experimental points obtained during heating of the filament are used, since experiments during cooling of the filament have lower accuracy. The scatter of the experimental points relative to the averaging straight line proposed by the author reaches about $±6^{2}$).

The experimental points for the enthalpy of Jaeger and Rosenbohm ([9], [10]), obtained by the mixing method in the temperature interval 327-1604°, deviate most from our calculated curve (1) at 1600°, lying below it by 1.5%. With decreasing temperature the discrepancy diminishes to complete agreement at 600-800°, and then increases again, so that the extreme points at a temperature of 300° lie 0.5% above our curve.

The results of work ([8]), obtained in the temperature interval 0-1500° on an ice calorimeter, seem to us insufficiently accurate because of methodological errors and possible contamination of the tungsten samples, the amount of impurities in which is not reported by the authors. The discrepancy between the curve calculated from equation (1) and the data of work ([8]) is greatest at the ends of the overlapping temperature interval and reaches 3-5%.

Magnus and Holtzmann ([16]) determined the enthalpy of tungsten at temperatures of 100-900°. Their experimental points differ from our curve within 0.6-0.9%. In work ([17]) the experimental data were obtained for temperatures

−20 to 500°. In the temperature interval 100-500° they agree well with the curve calculated from equation (1).

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Note: Figure translations are in progress. See original paper for figures.