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The Heat of Formation of Tungstic Oxide, WO_3[1]

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In common with many other older values of thermal data involving inorganic compounds, the heat of formation of tungstic oxide, WO_3, has been subject to a considerable amount of uncertainty. With this in mind the measurements described in this publication were undertaken in order that a more certain and precise value for the above quantity be obtained.

The several values obtained in the past are given in Table I.

TABLE I

Investigators	Date	ΔH, kcal./mole	Estimated precision, %
Delépine and Hallopean[2]	1899	−196.3	±2.5
Mixter[3]	1908	−195.8	±0.6
Weiss, Martin, and Stimmelmayer[4]	1910	−192.7	±0.9
van Liempt[5]	1923	−194.2	±0.8
Moose and Parr[6]	1924	−195.7	±0.4
Z. Shibata[7][a]	1929	−199.9	....
This work	1947	−200.2	±0.05

[a] This value resulted from equilibrium studies.

In these investigations the tungsten used was in the form of powder. Combustion in practically every case was reported to be complete.

Experimental

Apparatus.—In this study the calorimeter and auxiliary equipment used previously[8,9] were employed. Recalibration of both bridge and thermometer was made, yielding results that were little changed from the previous work.

Material.—The tungsten used in this investigation was obtained from a commercial supplier in the form of 20 mil. wire whose purity was reported to be in excess of 99%. This type of wire is normally supplied for use as filaments in electronic tubes of the highest grade. In view of the fact that the purity was not sufficient for combustion work, a method of purification was worked out. The wire was wound into a coil using a mandrel $^3/_{16}$ inches in diameter. After stretching the coil to about three times its original length, a suitable portion was spot-welded onto two heavy nickel wires connected to seal-in wires in a glass seal. By means of a ground-glass joint the entire unit was then suspended inside of a round glass flask. The assembly was then evacuated, and about fifteen amperes was passed through the tungsten coil for ten hours. This treatment resulted in most of the impurities being evaporated out of the tungsten, yielding material of exceptional purity. Spectrographic analysis[10] of the wire so treated gave these results

Ca	<0.001%
Fe	0.003
Mo	0.04
Purity by difference	99.95%

Calibration of the Calorimeter.—In line with the usual calibration procedure in inorganic combustion work, benzoic acid was used as the calibrating substance. For this purpose standard sample No. 39f was obtained from the Bureau of Standards. Its heat of combustion under standard conditions as reported by R. S. Jessup[11] (modified by using the newer value for the density of benzoic acid) is Q = 26,429.4 international joules per gram mass. In both the calibration experiments and the combustion runs use was made of Dickinson's graphical method[12] in order to obtain the corrected temperature rise of the calorimeter. In view of the fact that the same fuse was used in both types of determinations, the energy supplied by the fuse was not treated explicitly. The results of the calibration experiments are given in Table II. In this table the extremes of the several quantities are given.

TABLE II

RESULTS OF CALIBRATION EXPERIMENTS

Number of experiments (n)	Mass of sample, g.	Energy equivalent Corrected to standard calorimeter, Int. joules/ohm	Deviations from mean (Δ)
12	1.61735	139,310	−64
	to	to	to
	1.67032	139,414	+40

Mean = 139,374. ± 22.0 international joules/ohm.

The precision of the above mean value was obtained by the method recommended by Rossini and Deming.[13] The calibration error is defined as $C = 2\sqrt{\Sigma\Delta^2/n(n-1)}$. From the results shown, the assigned energy equivalent of the calorimeter in terms of the change in resistance of the resistance thermometer was 139,374 international joules per ohm.

Combustion of Tungsten.—In order to insure complete combustion of the tungsten, a special arrangement of the wire and crucibles had to be made. The purified coils were cut into lengths about 3 cm. long. These were loosely interleaved and stacked vertically in a fused silica combustion crucible 16 mm. high and 32 mm. in diameter. A hole about 6 mm. in diameter was cut in the bottom of the crucible. One centimeter below the crucible was placed a silica dish 50 mm. in diameter and 13 mm. high. The iron fuse wire was placed at the bottom of the tungsten pile. Upon ignition the tungsten at the bottom started burning while at the same time the molten oxide flowed from the crucible into the dish below. In this manner no tungsten was trapped by the molten oxide. To prove this, chemical tests were made on the melt, and at no time was unburned tungsten detected. Furthermore, the molten oxide showed no tendency to slag with the silica crucibles.

In consideration of the conditions necessary for combustion, a new set of silica ware had to be used for each experiment, thus necessitating the obtaining of a different

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(1) This work was performed under Office of Naval Research Contract.

(2) Delépine and Hallopean, *Compt. rend.*, **129**, 600 (1899).

(3) Mixter, *Am. J. Sci.*, **26**, 125 (1908).

(4) Weiss, Martin and Stimmelmayer, *Z. anorg. allgem. Chem.*, **65**, 279 (1910).

(5) van Liempt, *ibid.*, **129**, 263 (1923).

(6) Moose and Parr, THIS JOURNAL, **46**, 2656 (1924).

(7) Z. Shibata, *Tech. Repts. Tôhoku Imp. Univ.*, **8**, 129 (1929); **8**, 145 (1929).

(8) Snyder and Seltz, THIS JOURNAL, **67**, 683 (1945).

(9) McGraw, Seltz and Snyder, *ibid.*, **69**, 329 (1947).

(10) This analysis was obtained through the courtesy of Mr. A. Poritsky of the General Electric Company.

(11) Jessup, *J. Research Natl. Bur. Standards*, **29**, 247 (1942).

(12) Dickinson, *Bur. Standards J. Research*, **11**, 189 (1915).

(13) Rossini and Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

heat capacity for the calorimeter for each combustion. The error caused by this was negligible since practically the same weight of silica was used each time. The results of the combustion experiments are given in Table III.

TABLE III

RESULTS OF TUNGSTEN COMBUSTION

Number of experiments (n)	Mass of sample, g.	Heat of combustion, Int. joules/g.	Deviations from mean (Δ)
11	9.58862	4541.77	−4.39
	to	to	to
	9.60625	4553.37	+7.23

Mean = 4546.13 ± 2.36 international joules/g.

Thus for tungsten burning in oxygen at 30 atmospheres initial pressure and at constant volume, the heat of combustion was found to be 4546.13 int. joules per gram mass at a mean temperature of 27.20°. In order to obtain the true mass of tungsten *in vacuo*, it was assumed that the density of tungsten is 19.3 g. per cc. at 25°. The air temperature and density were such that the mass correction multiplier averaged 0.999922 within very close limits.

In view of the fact that tungsten is multi-valent, it is necessary to investigate the assumption that the product of combustion is actually tungstic oxide within the limit of precision obtained. This investigation proceeded along two lines. The first involved an attempt to prove experimentally that no lower oxides were present; the second involved the calculation of equilibrium conditions.

A weighed sample of oxide from each combustion was dissolved in concentrated sodium hydroxide solution. It has been shown[14] that the lower oxides of tungsten are unstable with respect to the +5 state in the presence of hydroxyl ion. However, when such an oxidation occurs, one of the products is metallic tungsten. At no time was the element found after solution of the oxide. In addition the solution was acidified and titrated with potassium permanganate. Here again no evidence of lower valence states was obtained at any time.

The other course of investigation involved the equilibrium data obtained by Alterthum and Koref.[15] From these data it is found that the degree of dissociation of WO_2, W_2O_5, and WO_3 is approximately 10^{-9}, 0.85 and $10^{-4.6}$, respectively. These values refer to the gas-phase equilibrium at 3000°K. and 1 atm. total pressure. A decrease in temperature would decrease the dissociation. The dissociation pressure of each of the above solid oxides at 1800°K. is about $10^{-7.5}$ atmospheres. Combining the necessary data, it is found that for the reaction $4WO_3 = 4WO_2 + 2O_2$ at a total oxygen pressure of 30 atm. and 2000°K. the ratio P_{WO_3}/P_{WO_2} has a value of 24000. Thus it can be concluded that the only oxide formed in the combustion is WO_3.

Calculations

Assuming the atomic weight of tungsten to be 183.92, and using the above value for the heat of combustion, the change in internal energy for the formation of a mole of WO_3 is obtained. There is obtained for the reaction

$$W(s) + 3/2O_2(g,\ 300.36°K.,\ 30\ atm.) = WO_3(s)$$
$$\Delta E = -836.124 \text{ int. kilojoules}$$

To change ΔE to unit fugacity, use is made of the data of Rossini and Frandsen.[16] Making the usual ΔE to ΔH correction and changing to standard temperature, gives the following reaction taking place under standard conditions

$$W(s) + 3/2O_2(g,\ 298.16°K.\ \text{unit fugacity}) = WO_3(s)$$
$$\Delta H = -837.3_4 \pm 0.4_4 \text{ international kilojoules}$$

or, in terms of the defined calorie

$$\Delta H = -200.1_6 \pm 0.1_0 \text{ kilocalorie}$$

The limits given in the above value for ΔH represent the mathematical value of the random errors obtained in the usual manner as recommended by Rossini and Deming.[13]

The oxide, WO_3, formed by combustion was examined by means of X-ray powder photographs and found to be the usual crystalline form exhibited by this compound, namely, a close approximation to the tetragonal. In this crystal the angles are 90°, but the edges of the cell differ slightly from the usual 1, 1, 0.5 ratio.

ΔH of Formation of WC.—In a previous publication a calculation was made of the ΔH of formation of WC, using the best value then available for WO_3. This calculation can now be modified making use of the data obtained in this investigation. In addition to the equation above, use is made of the following

$$C(graphite) + O_2(g) = CO_2(g):$$
$$\Delta H_{298.16} = -94.052 \pm 0.011 \text{ kilocal.}$$
$$WC(s) + 5/2O_2(g) = WO_3(s) + CO_2(g):$$
$$\Delta H_{298.16} = -285.80 \pm 0.077 \text{ kilocal.}$$

Combining these equations properly, gives for the heat of formation of the carbide

$$W(s) + C(graphite) = WC(s)$$
$$\Delta H_{298.16} = -8.4_1 \pm 0.1_9 \text{ kilocalorie}$$

Summary

1. The heat of formation of tungstic oxide, WO_3, under standard conditions has been found to be −200.16 ± 0.10 kcal. per mole.

2. The heat of formation of tungsten carbide, WC, under standard conditions has been recalculated and found to be −8.41 ± 0.19 kcal. per mole.

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[14] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., p. 237.

[15] Alterthum and Koref, *Z. Elektrochem.*, **31**, 508 (1925).

[16] Rossini and Frandsen, *J. Research Natl. Bur. Standards*, **9**, 733 (1932).