contrast to the precipitation of the di-potassium salt of tetrahydroxyquinone from carbonate buffers, when the nitric acid oxidation products of inositol are oxidized by a stream of air in such solutions.[3] The usual pathway of oxidation of hexahydroxybenzene to rhodizonic acid is stepwise through tetrahydroxyquinone, but in acetate buffers rhodizonic acid is formed also by the dismutation of tetrahydroxyquinone into hexahydroxybenzene and rhodizonate. In carbonate buffers, the di-potassium salt of tetrahydroxyquinone does not dismute into rhodizonate and hexahydroxybenzene but precipitates out as formed, thus preventing further oxidation to rhodizonate. The ionization constants of the two substances are such that precipitation of the di-potassium rhodizonate would be favored in acetate buffers.

The potential of these systems in the normal *p*H range of living cells is such that when present they might take part in the oxidation–reduction processes as catalysts offering more rapid di-valent pathways or acting as mediators between tetravalent and di-valent steps according to the "equivalence change principle."[10]

Summary

The oxidation–reduction potentials of the several equilibria involved in the reversible systems composed of hexahydroxybenzene, tetrahydroxyquinone and rhodizonic acid have been measured at various *p*H. From these the E_0 of the systems and the *pK* of the components have been estimated. Equations are presented which apply to this complex relationship involving one tetravalent system and two di-valent systems in equilibrium.

---

[10] P. A. Shaffer, *Cold Spring Harbor Symposia on Quant. Biol.*, **7**, 50 (1939); *J. Phys. Chem.*, **40**, 1021 (1936); THIS JOURNAL, **55**, 2169 (1933)..

ST. LOUIS, MO. RECEIVED AUGUST 15, 1946

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Heat of Combustion of Tungsten Carbide, WC[1]

BY L. D. MCGRAW,[2] HARRY SELTZ AND PAUL E. SNYDER

The heat of combustion of tungsten carbide, WC, has not been reported in the literature, and this paper describes measurements of this thermal value, as carried out in a precision bomb calorimeter which has been described previously.[3]

The heat of formation of WC has been calculated from these results, but this calculation is subject to the uncertainties in the reported values for the heat of formation of tungstic oxide. Further measurements, in these laboratories, on the heat of combustion of tungsten are contemplated in the near future.

Experimental

Material.—The tungsten carbide used in these measurements was supplied by the McKenna Metals Company. It was reported to have been prepared by dissolving tungsten in molten aluminum and heating to about 2000° in a graphite crucible.[4] The aluminum carbide formed was dissolved from the solidified mass with nitric acid, which does not attack WC. This carbide remains as a shiny macro-crystalline material. Spectroscopic analysis showed it to contain an appreciable amount of nickel, along with several hundreths per cent of molybdenum and columbium, and with lesser amounts of titanium, silicon, calcium, iron, aluminum, magnesium and copper decreasing in this order to less than 0.001%. These results are only roughly quantitative since no adequate standard of this material was available for comparison. Purification of the carbide was effected by passing dry chlorine over it as the temperature was raised slowly to 630°. It has been shown[5] that WC is not affected by such treatment, while any lower carbides and tungsten metal are volatilized. An appreciable amount of volatilizate was obtained by this treatment, and analysis showed it to contain nickel chloride corresponding to 0.17 per cent. of nickel in the original carbide. The residual material was thoroughly washed with ammonia, dilute acid, water, alcohol and ether and then dried. The appearance of the carbide was unchanged and chemical and spectroscopic analysis gave the following results

Chemical analysis	Spectroscopic
Cb, trace	Less than 0.05%
Ni, trace	Less than 0.05%
Fe, trace	Trace
Mo, 0.04%	Less than 0.05%

Combustion analysis for carbon gave 6.128 ± 0.006 per cent., compared to the theoretical value of 6.130 per cent.

The Calorimeter.—In this study the precision bomb calorimeter described by Snyder and Seltz[6] was used. The resistance thermometer was recalibrated and found to have changed inappreciably. The procedure and precautions followed those previously described except that in these measurements it was not necessary to use the large protecting zircon crucible required for the combustion of aluminum. Small fused silica dishes satisfactorily withstood the combustion and the fused tungstic oxide showed no slaging action on the silica.

Calibration of the Calorimeter.—To obtain the heat capacity of the calorimeter benzoic acid was used as a calibrating substance. Standard sample No. 39f was obtained from the Bureau of Standards. Its heat of combustion was reported by R. S. Jessup[7] to be Q (under standard conditions) = 26,428.4 ± 2.6 international

---

(1) Abstracted from a thesis presented by L. D. McGraw to the Committee on Graduate Instruction of the Carnegie Institute of Technology, in partial fulfillment of the requirements for the degree degree of Doctor of Science, February, 1946.

(2) Present address: Dept. of Chem., Webster College, Webster Groves, Missouri.

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

(4) R. Mitsche, *Berg huttenmann. Jahrb. montan. Hochschule Leoben*, **87** 135–187 (1939).

(5) Iitaka and Aoki, *Bull. Chem. Soc. Japan*, **7**, 108 (1932); *C. A.*, **26**, 3743 (1932).

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

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

joules per gram mass. The weights of the several samples were adjusted to values between 1.63 and 1.64 g. so that the shape of the heating curve would be the same for all experiments. Under this condition Dickinson's graphical method could be used to determine the thermal leakage correction. The total firing energy had been determined by a series of experiments with only the iron fuse wire in the calorimeter. The observed heat capacity of the calorimeter was corrected to the standard bomb conditions as given by Jessup. Table I presents the results of fifteen calibration experiments.

Table I

Results of Calibration Experiments

Expt.	Mass of sample, g.	Energy equivalent cor. to stand. cal. int. joules/ohm	Deviations from mean
15	1.63258 to	138,985 to	−51 to
	1.63790	139,078	+42

Mean[a] = 139,036 ± 14 int. joules/ohm.

[a] Uncertainty interval of calibration defined as $c = 2\sqrt{\Sigma\Delta^2/n(n-1)}$.

In Table I the energy equivalent of the calorimeter is given in international joules per ohm, that is, in terms of the change of resistance of the platinum resistance thermometer. From the results given in Table I the energy equivalent of the calorimeter was assigned the value of 139,036 international joules per ohm, referred to the average final temperature of the calibration experiments, 30.23°.

Combustion of Tungsten Carbide.—By using iron fuse wire, sufficient heat was developed to ignite the carbide without the use of ignition aids. About 6 g. of the carbide were used in each measurement and combustion was very nearly complete if the carbide was piled in the center of the flat fused-silica dish so that the molten combustion product would flow away from the carbide and permit easy access of oxygen to the burning sample. The amount of unburned carbide was determined by measuring the increase in weight of the combustion product when ignited in an electric muffle furnace at 750°. This never exceeded 35 mg. and in most experiments was less than 10 mg. The tungstic oxide was never seen to flux with the crucible material. Since the weight of the crucible was different in each experiment, the mean observed energy equivalent of the calorimeter was corrected for these small weight differences. These corrected values are listed in column 3 of Table II.

The temperature rise in the combustion experiments was only 85% of the rise in the calibration experiments and the heating time was somewhat lengthened. This may introduce a small indeterminable error in the value of the effective heat capacity of the calorimeter.

The results of ten combustion experiments are given in Table II. This shows the mean heat of combustion of the tungsten carbide to be 6,079.92 ± 1.64 international joules per gram for the sample burning at a constant volume and at an initial pressure of 35 atmospheres of oxygen. This value is calculated to a mean initial temperature of 27.29°. The experimental value of the effective heat capacity of the calorimeter was for 30.23°. This figure was used in the calculations without correction to 27.29°. This is in accord with the work of Jessup and Green[8] who state that the rate of change with temperature of the energy equivalent of the calorimetric system is negligibly small at this temperature.

Table II

Results of WC Combustion

Expt.	Mass of WC burned, g.	Actual value of energy equivalent used, int. joules/ohm	Heat of combustion int. joules/g.	Deviations from mean
11	5.93771 to	139,108 to	6,076.84 to	−3.08 to
	6.00229	139,173	6,083.06	+3.14

Mean = 6,079.92 ± 1.64 int. joules/g.

Calculations

Using 195.93 as the molecular weight of tungsten carbide, there is obtained from the heat of combustion per gram, the value of the energy change for the formation of one mole of the oxide under the conditions prevailing in the bomb. Thus for the reaction

$$\text{WC(s)} + 5/2\text{O}_2(\text{g}, 300.45\,^\circ\text{K.}, 35 \text{ atm.}) = \text{WO}_3(\text{s}) + \text{CO}_2(\text{g}, 300.45\,^\circ\text{K.}, 2.15 \text{ atm.})$$

$$\Delta E = -1{,}191.239 \text{ international kilojoules} \quad (1)$$

In order to obtain ΔE at unit fugacity of oxygen the following equation is added to (1)

$$5/2\text{O}_2\ (\text{g}, 300.45\,^\circ\text{K.}, 35 \text{ atm.}) = 5/2\text{O}_2(\text{g}, 300.45\,^\circ\text{K.}, \text{unit fugacity}) \quad (2)$$

From work done at the Bureau of Standards,[9] it has been found that $\delta E/\delta P_{301\,^\circ\text{K.}}$ for oxygen is −6.51 joules per atmosphere per mole. Since the correction to change this value to 300.45°K. is negligible then for equation (2)

$$\Delta E = 569.6 \text{ joules}$$

Combining (1) and (2) gives

$$\text{WC(s)} + 5/2\text{O}_2(\text{g}, 300.45\,^\circ\text{K.}, \text{unit fugacity}) = \text{WO}_3(\text{s}) + \text{CO}_2(\text{g}, 300.45\,^\circ\text{K.}, 2.15 \text{ atm.}) \quad (3)$$

$$\Delta E_c = -1{,}191.81 \text{ int. kilojoules}$$

For the process

$$\text{CO}_2(\text{g}, 300.45\,^\circ\text{K.}, 2.15 \text{ atm.}) = \text{CO}_2(\text{g}, 300.45\,^\circ\text{K. unit fugacity}) \quad (4)$$

Washburn[10] has accepted the value of $\delta E/\delta P_T$ for carbon dioxide calculated from the Beattie–Bridgeman equation of state. Evaluated at 20° $(\Delta E)_0^p = -0.287 \times p$ liter atm./mole, or $-29.26 \times P$ joules per mole. The temperature coefficient of $\delta E/\delta P_T$ is −0.4% giving $(\Delta E)_0^p = -28.4$ joules per atmosphere per mole at 27.29°. For equation (4) then, $\Delta E_d = 61.1$ joules. Combining (3) and (4) gives

$$\text{WC(s)} + 5/2\text{O}_2(\text{g}, 300.45\,^\circ\text{K.}, \text{unit fugacity}) = \text{WO}_3(\text{s}) + \text{CO}_2(\text{g}, 300.45\,^\circ\text{K.}, \text{unit fugacity}) \quad (5)$$

$$\Delta E_e = -1{,}191.75 \pm 0.32 \text{ kilojoules}$$

To change to ΔH for this reaction use is made of

$$\Delta H = \Delta E + RT\Delta n$$

Then for reaction (5), $\Delta H_e = -1{,}195.50$ int. kilojoules. To correct (5) to standard temperature, use is made of the equation $\delta\Delta H/\delta T_p = \Delta C_p$, using for O_2(g); $C_p = 6.95$, for WO_3(s)[11]; $C_p = 19.55$, for WC(s)[12]; $C_p = 8.63$, giving for the reaction under standard conditions

$$\text{WC(s)} + 5/2\text{O}+(\text{g}, 298.16\,^\circ\text{K.}, \text{unit fugacity}) = \text{WO}_3(\text{s}) + \text{CO}_2(\text{g}, 298.16\,^\circ\text{K.}, \text{unit fugacity}) \quad (6)$$

$$\Delta H_f = -285.80 \text{ kcal./mole}$$

---

(8) Jessup and Green, *J. Research Natl. Bur. Standards*, **13**, 477 (1936).

(9) Rossini and Frandsen, *ibid.*, **9**, 733 (1932).

(10) Washburn, *ibid.*, **19**, 525 (1932).

(11) Seltz, Dunkerley and DeWitt, This Journal, **65**, 600 (1943).

(12) From unpublished value in this Laboratory.

(The conversion to kcal. is based on the defined calorie equal to 4.1833 int. joules.) This is the heat of combustion of tungsten carbide under standard conditions and the following values of precision are obtained

"e" error assigned to the benzoic acid = ±0.010% (Bureau of Standards)
"c" (calibration error) = ±0.010%
"b" (reaction error) = ±0.023%

The precision error is

$$p.e. = \sqrt{e^2 + c^2 + b^2} = \pm 0.027\%$$

ΔH of Formation of WC.—A calculation of the heat of tungsten carbide involves the heat of combustion of carbon and of tungsten. For carbon the value is known to a high precision.[13]

$$\text{C(graphite)} + \text{O}_2\text{(g)} = \text{CO}_2\text{(g)}: \Delta H_{298\cdot16} = -94{,}051.8 \pm 10.8 \text{ cal./mole} \quad (7)$$

The value available for the heat of formation of tungstic oxide is from the measurements of Moose and Parr,[14] for which, however, we estimate an uncertainty of ±900 cal.

$$\text{W(s)} + 3/2\text{O}_2\text{(g)} = \text{WO}_3\text{(s)}: \Delta H_{298\cdot16} = -195{,}700 \pm 900 \text{ cal./mole} \quad (8)$$

Combining equations (6), (7) and (8) we obtain for the heat of formation of the carbide

$$\text{W(s)} + \text{C(graphite)} = \text{WC(s)}: \Delta H_{298\cdot16} = -3.92 \pm 0.9 \text{ kcal./mole} \quad (9)$$

Summary

1. The heat of combustion, $\Delta H_{298\cdot16}$, of tungsten carbide under standard conditions has been found to be -285.80 ± 0.07 kcal./mole.

2. The heat of formation, $\Delta H_{298\cdot16}$, of the carbide, subject to the uncertainty in the value for the heat of combustion of tungsten, is calculated to be -3.92 ± 0.90 kcal./mole.

---

[13] Prosen, Jessup and Rossini, *J. Research Natl. Bur. Standards*, **33**, 447 (1944).

[14] Moose and Parr, THIS JOURNAL, **46**, 2656 (1924).

RECEIVED SEPTEMBER 20, 1946

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

High-Temperature Heat Contents of V_2O_3, V_2O_4 and V_2O_5[1]

BY O. A. COOK[2]

Thermodynamic data of any type are available only in rare instances for vanadium compounds and, in particular, high-temperature heat content data are entirely lacking. This Station has begun to secure such data for the more metallurgically important vanadium compounds. The present paper contains high-temperature heat content values for V_2O_3, V_2O_4 and V_2O_5, three of the substances for which no previous similar data exist, although heat capacities at low temperatures (56–298°K.) and entropies at 298.16°K. were reported several years ago by Anderson.[3]

Experimental

Materials

The preparations and analyses of the vanadium oxides were conducted by A. E. Salo.[4]

The original source material was commercial ammonium vanadate (96.7% pure). This material was purified by the following procedure: Concentrated hydrochloric acid was saturated with ammonium vanadate at about 100° and the resulting solution was diluted 3:1 with distilled water and filtered. The filtrate was heated to boiling and oxidized with ammonium persulfate in the presence of a small amount of nitric acid. Reprecipitation of ammonium vanadate was obtained on neutralizing with ammonium hydroxide in the presence of an excess of ammonium chloride. The precipitate was filtered, washed repeatedly with 1:40 ammonium hydroxide and once with distilled water, and finally dried twenty-four hours at 75–80°. Analysis gave 43.55% vanadium, which is the theoretical value.

Vanadium pentoxide was prepared from the purified ammonium vanadate by heating in a platinum vessel in a stream of pure oxygen at 440–460° for seven days. Analysis for vanadium gave 55.96%, as compared with the theoretical 56.02%.

To prepare vanadium trioxide, pure vanadium pentoxide was heated in a silica flask at 800° in a stream of pure hydrogen until no further water vapor was evolved. Analysis of the product gave 67.89% vanadium, as compared with the theoretical 67.98%.

Vanadium tetroxide was prepared from pure vanadium trioxide by controlled oxidation with air, in a platinum vessel, starting at 300°. At this temperature combustion became self-supporting and additional heat was not required. The blue-black product was removed, placed in a silica flask, evacuated at room temperature, and given a prolonged heat treatment at temperatures below 600° to assure uniformity of composition. Analysis gave 61.45% vanadium, as compared with the theoretical 61.42%.

Analyses of ammonium vanadate and vanadium pentoxide were made by dissolving samples in 10% sulfuric acid, reducing with sulfur dioxide, expelling the excess sulfur dioxide with carbon dioxide, and titrating against potassium permanganate. Analyses of vanadium trioxide and tetroxide were made similarly except that fusion with sodium bisulfate was required before dissolving in 10% sulfuric acid.

Measurements and Results

The high-temperature heat content measurements were made using apparatus and methods described in detail by Kelley, Naylor and Shomate.[5] The calibrator was calibrated electrically in terms of the defined calorie, 1 cal. = 4.1833

---

[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

[2] Chemist, Pacific Experiment Station, Bureau of Mines.

[3] Anderson, THIS JOURNAL, **58**, 564 (1936).

[4] Formerly metallurgist, Pacific Experiment Station, Bureau of Mines.

[5] Kelley, Naylor and Shomate, Bureau of Mines Technical Paper 686, 34 (1946).