(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]

$$\text{C(graphite)} + \text{O}_2\text{(g)} = \text{CO}_2\text{(g)}: \ \Delta H_{298.16} = -94{,}051.8 \pm 10.8 \text{ cal./mole} \quad (7)$$

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.

$$\text{W(s)} + 3/2\text{O}_2\text{(g)} = \text{WO}_3\text{(s)}: \ \Delta H_{298.16} = -195{,}700 \pm 900 \text{ cal./mole} \quad (8)$$

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

$$\text{W(s)} + \text{C(graphite)} = \text{WC(s)}: \ \Delta H_{298.16} = -3.92 \pm 0.9 \text{ kcal./mole} \quad (9)$$

Summary

1. The heat of combustion, $\Delta H_{298.16}$, of tungsten carbide under standard conditions has been found to be −285.80 ± 0.07 kcal./mole.

2. The heat of formation, $\Delta H_{298.16}$, 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.

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

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

[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 calorimeter was calibrated electrically in terms of the defined calorie, 1 cal. = 4.1833

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(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).

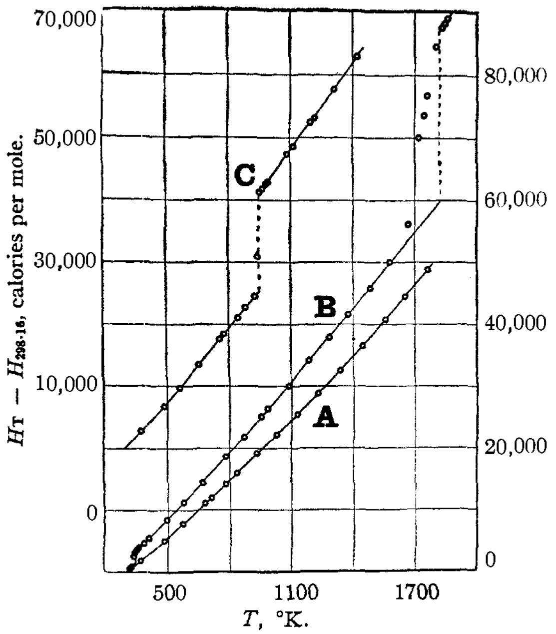

Fig. 1.—Heat contents above 298.16°K. of vanadium oxides: Curve A, V_2O_3; curve B, V_2O_4; curve C, V_2O_5 (curves A and B, scale at right; curve C, scale at left).

Table I

Heat Contents above 298.16°K. (Cal./Mole)

V_2O_3 (mol. wt. = 149.90)

T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$
369.1	1,845	831.8	15,940	1331.3	32,415
478.8	5,000	929.3	19,120	1441.4	36,425
569.1	7,695	1021.7	22,060	1552.4	40,715
676.3	10,985	1122.8	25,410	1650.2	44,420
707.7	11,940	1223.2	28,730	1760.0	48,800
775.5	14,115				

V_2O_4 (mol. wt. = 165.90)

T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$
315.5	535	574.6	11,110	1481.0	45,775
322.8	730	667.2	14,375	1577.9	50,020
323.0	740	780.0	18,625	1667.3	56,050[b]
335.1	2,425[a]	866.6	21,675	1719.9	70,090[b]
340.7	2,985[a]	949.5	25,020	1742.1	73,640[b]
350.5	3,645	979.9	26,420	1757.5	76,750[b]
357.1	3,895	1081.2	29,995	1802.9	84,470[b]
380.6	4,610	1182.4	34,040	1829.7	87,410
405.4	5,405	1280.6	37,870	1844.0	88,070
492.3	8,360	1373.9	41,640	1856.8	88,850

V_2O_5 (mol. wt. = 181.90)

T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$
371.6	2,650	877.3	22,670	984.0	42,910
482.7	6,715	921.1	24,495	1080.7	47,340
558.3	9,645	937.7	30,900[c]	1111.4	48,580
651.8	13,400	946.1	41,130	1211.3	53,080
754.4	17,495	960.2	41,760	1309.1	57,650
771.1	18,335	975.9	42,470	1419.7	62,820
840.2	21,005			1513.2	66,960

int. joules (NBS).[6] Frequent calibrations of the furnace thermocouple were made at the gold and palladium points as described by Southard.[7] Sample weights were corrected to vacuum by means of the following densities: 4.87 g./ml. for V_2O_3; 4.40 g./ml. for V_2O_4 and 3.36 g./ml. for V_2O_5.

During the measurements the materials were contained in platinum-rhodium alloy capsules. These capsules were filled through small necks that subsequently were pinched shut and sealed by platinum welding. The heat contents of the empty capsules had been determined separately and only a small correction was required for platinum used in sealing.

The measured heat contents of V_2O_3, V_2O_4 and V_2O_5 are listed in Table I and shown graphically in Fig. 1. The columns labeled T, °K., give the temperature of the sample just before dropping into the calorimeter, and the columns labeled $H_T - H_{298.16}$ give the heat liberated per gram mole in cooling from T to 298.16°K.

Considerable difficulty was encountered with minute pin holes that appeared in the walls of the capsules at high temperatures (1,300 to 1,370°K. for V_2O_3 and V_2O_4 and 1,190 to 1,210°K. for V_2O_5). Similar occurrence of such pin holes was noted by Naylor[8] in his study of the sodium titanates. Whether this is attributable to the substances contained or is merely accidentally defective capsules is not known, but it does not generally occur. For vanadium trioxide and tetroxide, no measurements were made after the weight of capsule and contents had changed by as much as 0.1% of the weight of the sample; when this point was reached a new capsule and a new portion of substance were used. Three capsules and three separate portions of substance were required to obtain the results for each of the substances vanadium trioxide and tetroxide. In the case of vanadium pentoxide, it was necessary to allow greater tolerance, and measurements beyond 1,210°K. were made with over-all weight decreases that reached 1.0% of the sample weight for the highest temperature determination. In this instance, correction was made on the reasonable assumption that oxygen had been lost and vanadium tetroxide formed. The maximum net correction was 0.9% of the value reported at 1,513.2°K. At lower temperatures the correction was progressively smaller, being 0.3% of the value at 1,419.7°K., 0.2% of the value at 1,309.1°K. and 0.1% of the value at 1,211.3°K. Two capsules and two portions of substance were used in obtaining the results for vanadium pentoxide.

The content curve of vanadium trioxide is regular and requires no discussion.

Vanadium tetroxide exhibits a fairly sharp transition at 345°K., with a heat absorption of 2,050 cal. per mole. Determinations marked (a)

[6] Mueller and Rossini, *Am. J. Physics*, **12**, 1 (1944).

[7] Southard, This Journal, **63**, 3142 (1941).

[8] Naylor, *ibid.*, **67**, 2120 (1945).

TABLE II

HEAT CONTENTS AND ENTROPIES ABOVE 298.16°K.

	V_2O_3		V_2O_4		V_2O_5	
T, °K.	$H_T - H_{298.16}$, (cal./mole)	$S_T - S_{298.16}$, (cal./deg./mole)	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, (cal./deg./mole)	$H_T - H_{298.16}$, (cal./mole)	$S_T - S_{298.16}$, (cal./deg./mole)
345			1,400(α)	4.36		
345			3,450(β)	10.30		
400	2,720	7.83	5,270	15.20	3,650	10.50
500	5,590	14.23	8,600	22.62	7,400	18.86
600	8,600	19.72	12,000	28.80	11,290	25.95
700	11,700	24.49	15,560	34.29	15,290	32.11
800	14,870	28.72	19,230	39.19	19,390	37.58
900	18,100	32.53	22,990	43.62	23,590	42.52
943					25,420(s)	44.51
943					40,980(l)	61.01
1000	21,370	35.97	26,830	47.67	43,580	63.69
1100	24,660	39.11	30,730	51.38	48,140	68.04
1200	27,960	41.98	34,670	54.81	52,700	72.00
1300	31,360	44 70	38,630	57.98	57,260	75.65
1400	34,940	47.35	42,600	60.92	61,820	79.03
1500	38,670	49.92	46,590	63.68	66,380	82.18
1600	42,480	52.38	50,620	66.27		
1700	46,370	54.73	54,710	68.75		
1800	50,350	57.01	58,850	71.12		
1818			59,600(β)	71.54		
1818			86,810(l)	86.51		
1900			90,990	88.76		

in Table I show pretransition effects. The melting point of vanadium tetroxide was difficult to fix accurately because of premelting phenomena (runs marked (b) in Table I). The value selected is 1,818°K., and the heat of fusion was evaluated as 27,210 cal. per mole.

The vanadium pentoxide sample melted rather sharply at 943°K. as is evident in Fig. 1. The heat of fusion is 15,560 cal. per mole. The determination marked (c) in Table I is high because of premelting.

The following equations were derived to represent the molal heat content results. The temperature range of validity and average deviation from the experimental results are shown in parentheses in each instance. The equations for V_2O_3(s) and V_2O_5(s) were made to conform with the true heat capacities at 298.16°K., 24.67 and 30.51 cal. per mole,[9] respectively. Because of the transition in V_2O_4 at 345°K., it appeared expedient to use only the simplest possible equation for $V_2O_4(\alpha)$.

V_2O_3(s): $H_T - H_{298.16} = 29.35T + 2.38 \times 10^{-3}T^2 + 5.42 \times 10^5T^{-1} - 10{,}780$ (298 – 1800°K.; 0.6%)

$V_2O_4(\alpha)$: $H_T - H_{298.16} = 29.91T - 8{,}918$ (298 – 345°; 1.1%)

$V_2O_4(\beta)$: $H_T - H_{298.16} = 35.70T + 1.70 \times 10^{-3}T^2 + 7.89 \times 10^5T^{-1} - 11{,}355$ (345 – 1818°K.; 0.4%)

V_2O_4(l): $H_T - H_{298.16} = 51.00T - 5{,}910$ (1818 – 1900°K.; 0.1%)

V_2O_5(s): $H_T - H_{298.16} = 46.54T - 1.95 \times 10^{-3}T^2 + 13.22 \times 10^5T^{-1} - 18{,}137$ (298 – 943°K.; 1.3%)

V_2O_5(l): $H_T - H_{298.16} = 45.60T - 2{,}020$ (943 – 1500°K.; 0.1%)

The corresponding heat capacity equations, obtained by differentiation, are

V_2O_3(s): $C_p = 29.35 + 4.76 \times 10^{-3}T - 5.42 \times 10^5T^{-2}$

$V_2O_4(\alpha)$: $C_p = 29.91$

$V_2O_4(\beta)$: $C_p = 35.70 + 3.40 \times 10^{-3}T - 7.89 \times 10^5T^{-2}$

V_2O_4(l): $C_p = 51.00$

V_2O_5(s): $C_p = 46.54T - 3.90 \times 10^{-3}T - 13.22 \times 10^5T^{-2}$

V_2O_5(l): $C_p = 45.60$

It should be noted that the heat content measurements of vanadium tetroxide cover only 39° of the liquid range; consequently, the specific heat equation for V_2O_4(l) can be considered only as a rough approximation.

Taple II gives heat content and entropy values above 298.16°K. at even values of temperature and at transition and melting points. The heat contents were read from smooth curves drawn through the experimental data. The entropy values were obtained from the relationship

$$S_T - S_{298.16} = \frac{H_T - H_{298.16}}{T} + \int_{298.16}^{T} \frac{H_T - H_{298.16}}{T^2}\, dT$$

the last term being evaluated by numerical integration of a plot of $(H_T - H_{298.16})/T$ against log T.

Summary

Heat content measurements of V_2O_3, V_2O_4 and V_2O_5 were made from 298.16°K. to the respective temperatures, 1760, 1857 and 1513°K. The data include the temperatures and heats of fusion of vanadium tetroxide and pentoxide and the temperature and heat of transition of vanadium tetroxide.

The results are summarized by means of algebraic equations relating heat content to temperature. A table of smooth values of heat content and entropy increments above 298.16°K. is included.

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[9] Kelley, Bureau of Mines Bull. 434, 1941, 115 pp.