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

High Temperature Heat Contents of Vanadium Carbide and Vanadium Nitride

BY E. G. KING[1]

In a recent paper, Shomate and Kelley[2] reported low temperature heat capacity data for vanadium carbide and vanadium nitride, but with the exception of three measurements of vanadium nitride between 273 and 732°K. by Sato,[3] no high temperature heat content values have been available for these substances. This paper reports the results of high temperature heat content measurements covering the temperature range from 298 to 1611°K.

Materials and Method

The materials used in the present work were identical with those employed by Shomate and Kelley.[2] Reference is made to their paper for the description of methods of preparation, chemical analyses and X-ray examinations.

The heat content measurements were made by the "drop" method, for which apparatus and experimental procedure have been described[4] previously. The calorimeter was calibrated electrically in terms of international joules and conversion to calories was made by the relation, 1 cal. = 4.1833 int. joules.

During the measurements the samples were contained in platinum-rhodium alloy capsules, the heat contents of which were determined by separate experiments. The capsules, after being filled with sample, were evacuated of air, filled with helium, and then quickly sealed gas-tight by platinum welding.

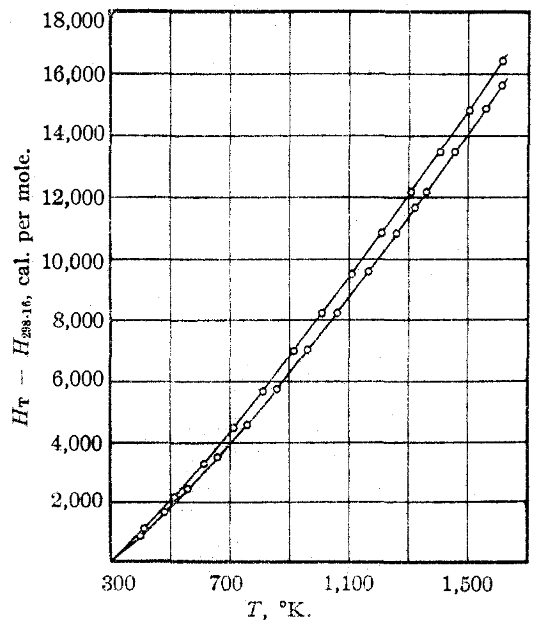

Fig. 1.—High temperature heat contents: upper curve, VN; lower curve, VC.

The weights of materials used in the measurements were 17.1426 g. of vanadium carbide and 19.3105 g. of vanadium nitride, corrected to vacuum by means of the densities, 5.93 g./cc. and 6.21 g./cc., respectively. The heat content of the empty capsule averaged about 12% of the total heat content in each instance.

Results

The experimental results, covering the temperature range 298° to 1611°K., are listed in Table I and shown plotted against temperature in Fig. 1. In Table I, T, °K., is the temperature of the sample immediately before dropping into the calorimeter, and $H_T - H_{298.16}$ is the heat liberated per gram mole in cooling from this temperature to 298.16°K. The molecular weights are in accord with the 1947 International Atomic Weights.

TABLE I

HEAT CONTENTS ABOVE 298.16°K. (EXPERIMENTAL VALUES)

VC (mol. wt. = 62.96)		VN (mol. wt. = 64.96)	
T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole
397.2	855	408.1	1,105
476.9	1,660	511.0	2,195
557.2	2,435	609.6	3,310
657.4	3,500	709.8	4,475
756.4	4,570	807.7	5,685
858.1	5,765	910.0	6,970
958.1	7,000	1006.8	8,220
1057.0	8,220	1106.6	9,520
1162.9	9,580	1206.6	10,840
1258.1	10,810	1306	12,170
1319	11,620	1406	13,490
1359	12,150	1503	14,830
1458	13,470	1611	16,400
1558	14,870		
1611	15,620		

Measurements at temperatures above 1611°K. were invalidated by the progressive development of embrittlement, which finally produced leaks in the platinum-rhodium alloy capsules. The occurrence of a leak was readily detectable by weighing the capsule and contents after each of the higher temperature determinations, because of resulting oxidation of the sample. The capsules remained gas-tight for all determinations listed in Table I.

It is evident from Fig. 1 that the behavior of these substances is normal in all respects. The heat content of vanadium nitride is the higher throughout the measured temperature range, thus extending the similar observation of Shomate and Kelley[2] for low temperatures. The three previous determinations of Sato[3] for vanadium nitride deviate from the present work and merit no weight in comparison. The deviations are, respectively,

(1) Chemist, Pacific Experimental Station, Bureau of Mines.

(2) Shomate and Kelley, THIS JOURNAL, 71, 314 (1949).

(3) Sato, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 34, 241 (1938).

(4) (a) Southard, THIS JOURNAL, 63, 3142 (1941); (b) Kelley, Naylor and Shomate, U. S. Bureau of Mines Technical Paper 686, 1946.

−1.4% at 373°K., +2.2% at 578°K., and +4.9% at 732°K., the temperatures being those reported by Sato.

Table II gives heat content values read from smooth curves at 100° intervals, together with the corresponding entropy increments above 298.16°K. The latter were computed from and exactly match the former.

TABLE II

HEAT CONTENTS AND ENTROPIES ABOVE 298.16°K. (SMOOTH VALUES)

	VC		VN	
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
400	890	2.55	1,010	2.91
500	1,850	4.70	2,080	5.30
600	2,870	6.55	3,200	7.34
700	3,950	8.22	4,370	9.14
800	5,090	9.74	5,590	10.76
900	6,280	11.14	6,850	12.25
1000	7,510	12.43	8,130	13.60
1100	8,770	13.64	9,430	14.84
1200	10,060	14.76	10,750	15.99
1300	11,380	15.81	12,090	17.06
1400	12,720	16.80	13,450	18.07
1500	14,080	17.74	14,820	19.01
1600	15,450	18.63	16,200	19.90

High temperature heat content equations were derived by the method of Shomate[5]; using all the data of Table I and the molal heat capacities[2] at 298.16°K., $C_{p,\ 298.16} = 7.970$ for vanadium carbide and $C_{p,298.16} = 9.080$ for vanadium nitride. The resulting equations, which follow, fit the measured data to within an average deviation of 0.3% in each instance.

VC: $H_T - H_{298.16} = 9.18T + 1.65 \times 10^{-3}T^2 + 1.95 \times 10^5T^{-1} - 3538$

VN: $H_T - H_{298.16} = 10.94T + 1.05 \times 10^{-3}T^2 + 2.21 \times 10^5T^{-1} - 4096$

The corresponding molar heat capacity equations are:

VC: $C_p = 9.18 + 3.30 \times 10^{-3}T - 1.95 \times 10^5T^{-2}$

VN: $C_p = 10.94 + 2.10 \times 10^{-3}T - 2.21 \times 10^5T^{-2}$

Summary

High temperature heat contents above 298.16°K. of vanadium carbide and vanadium nitride were measured from about 400° to 1611°K. A table of heat content and entropy increments above 298.16°K. is reported, and heat content and heat capacity equations are derived.

(5) Shomate, THIS JOURNAL, **66**, 928 (1944).

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Low-Temperature Heat Capacity and High-Temperature Heat Content of Ammonium Vanadate

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Ammonium vanadate is the commercially most readily obtainable, substantially pure, vanadium-containing substance and frequently is the source material in the preparation of other vanadium compounds. Consequently, considerable interest attaches to its properties. This paper reports the results of low temperature heat capacity measurements in the temperature range 51.4 to 298.16°K. and of high temperature heat content measurements in the temperature range 298.16 to 550°K. No previous similar data are available for this substance.

Material.—Ammonium vanadate of 96.7% purity was dissolved in hot concentrated hydrochloric acid until saturation, diluted by two volumes of distilled water, and filtered. The filtrate was heated to boiling, oxidized with ammonium persulfate in the presence of a small amount of nitric acid, and again filtered. The oxidized solution was neutralized with ammonium hydroxide in the presence of an excess of ammonium chloride. The precipitated ammonium vanadate was filtered off, washed several times with 1:40 ammonium hydroxide and once with distilled water, and finally dried for twenty-four hours at 75 to 80°. The product was analyzed by dissolving in 10% sulfuric acid, reducing the vanadium with sulfur dioxide, expelling excess sulfur dioxide by bubbling with a stream of carbon dioxide, and titrating with 0.1 N potassium permanganate. The analysis gave 43.55% vanadium content, which is the theoretical value for ammonium vanadate.

Measurements and Results

Both the low temperature heat capacity and high temperature heat content measurements were made by means of previously described[2] apparatus and methods. The defined calorie (1 cal. = 4.1833 int. joules) is used throughout. All weighings were corrected to vacuum and the molecular weight of ammonium vanadate is taken as 116.99 in accordance with the 1947 International Atomic Weights. The ice point is taken as 273.16°K.

A 41.810 g. sample was employed in the low temperature heat capacity measurements. The measured results are given in Table I and are plotted against temperature in Fig. 1. The heat capacity curve is normal, there being no indication whatever of the transition encountered in similar measurements of the ammonium halides[3,4,5] and

(1) Chemist, Pacific Experiment Station, Bureau of Mines.

(2) Kelley, Naylor and Shomate, U. S. Bureau of Mines, Tech. Paper 686, 1946, 34 pp.

(3) Simon, *Ann. Physik* (4), **68**, 241 (1922).

(4) Simon Simson, and Ruhemann, *Z. physik. Chem.*, **129**, 344 (1927).

(5) Extermann and Weigle, *Helv. Phys. Acta*, **15**, 455 (1942).