the equivalent positions are filled). In both of the postulated structures, the apparent radius of the hydrogen atom is 0.39 Å. which is in the lower range of values obtained from calculations for previously reported hydrides. Postulated point positions for CrH and CrH_2 structures[6] are

CrH C_{6v}^4-*C*6mc. Wurtzite Hemihedral
Cr at 2(b) 00Z; $^1/_3$, $^2/_3$, $^1/_2 + Z$ where Z = 0
H at 2(b) 00Z; $^1/_3$, $^2/_3$, $^1/_2 + Z$ where Z = $^1/_6$

CrH_2 O_h^5-*F*m3m Fluorite–Holohedral
Cr at 4(a) 000; 0 $^1/_2$ $^1/_2$; $^1/_2$ 0 $^1/_2$; $^1/_2$ $^1/_2$ 0
H at 8(c) $^1/_4\,^1/_4\,^1/_4$; $^1/_4\,^3/_4\,^3/_4$; $^3/_4\,^1/_4\,^3/_4$; $^3/_4\,^3/_4\,^1/_4$
$^3/_4\,^3/_4\,^3/_4$; $^3/_4\,\overline{^1/_4}\,\overline{^1/_4}$; $\overline{^1/_4}\,^3/_4\,\overline{^1/_4}$; $\overline{^1/_4}\,\overline{^1/_4}\,^3/_4$

The important result of the discovery of these hydrides of chromium is that the radius of the chromium atom no longer constitutes an anomaly within the family of metals. Recent discussions of the chromium atom radius[7,8] have treated the hexagonal hydride as a normal H.C.P. allotropic form of the metal. A somewhat complicated postulate regarding behavior of the electrons in the outer rings was advanced to explain the very large apparent radius (1.35 Å.) of the atom in the H.C.P. arrangement. With the introduction of the hydride concept, the chromium atoms may be considered to undergo only the normal radius change of 3% in passing from the F.C.C or H.C.P. hydride phases to the B.C.C. metallic phase (r = 1.25 Å.). The interstitially placed hydrogen atoms expand the metal lattice in both hydride phases and the Goldschmidt correction[9] of 3% provides a radius value of 1.28 Å. which appears to satisfy the X-ray data for these phases.

Summary

1. A determination of the lattice parameter of F.C.C. chromium hydride is reported. The new value is a = 3.8605 ± 0.0005 Å.

2. Structures are postulated for the F.C.C. and H.C.P. chromium hydrides.

3. Argument is presented to refute the concept that chromium is allotropic.

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[6] International Tables for the Determination of Crystal Structures.

[7] Hume-Rothery, "The Structure of Metals and Alloys," 1936.

[8] Pauling, THIS JOURNAL, **69**, 542 (1947).

[9] Goldschmidt, *Z. physik. Chem.*, **133**, 397 (1928).

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

Heat Capacities at Low Temperatures and Entropies of Vanadium Carbide and Vanadium Nitride

BY C. H. SHOMATE[1] AND K. K. KELLEY[2]

In previous papers from this laboratory, Anderson[3] has reported low-temperature heat-capacity measurements of vanadium and three of its oxides and Shomate[4] has reported similar data for vanadium di- and trichlorides. The present paper reports heat capacity measurements throughout the temperature range 50.4 to 298.16°K. and entropies at 298.16°K. of vanadium carbide and vanadium nitride. No similar data for either of these substances are in the literature.

Materials.[5]—The starting material for the preparation of vanadium carbide was vanadium containing 8% carbon and only a trace of other impurities. An intimate mixture of this material was made with Norblack sufficient to comply with the formula VC. The mixture was heated in vacuum at 1300 to 1350° for a total of twenty-six hours. After twelve and twenty-two hours heating, the product was analyzed and reground, and minor adjustment was made in the composition. The final product was uniform and showed no signs of incomplete reaction, which also was confirmed by the X-ray diffraction pattern.[6] No free carbon was evident on solution in 1:3 nitric acid. The product was analyzed for vanadium by permanganate titration, after fusion in a mixture of sodium bisulfate and potassium nitrate, and for carbon by absorbing and weighing the carbon dioxide evolved on combustion in pure oxygen in the presence of red lead oxide. The results were 80.90% vanadium and 19.04% carbon, as compared with the theoretical 80.92% and 19.08%, respectively.

Vanadium containing carbon, as mentioned above, also was the source material for the preparation of vanadium nitride. A 5:1, by volume, mixture of purified nitrogen and hydrogen was passed over the finely ground carburized vanadium at 1200° for twenty-eight hours. This gas mixture slowly replaced carbon by nitrogen, the carbon being carried out of the hot zone evidently by free radical formation with hydrogen. At seven-hour intervals, the reaction mixture was cooled, removed from the furnace, and reground. After twenty-eight hours of treatment, the product contained 0.76% carbon and an excess of nitrogen. It then was heated for eight hours at 1100° in a stream of pure hydrogen. The final product was analyzed for vanadium by permanganate titration, after burning to oxide and fusing in sodium bisulfate. The average result was 78.24% vanadium, as compared with the theoretical 78.43%. Combustion analysis for residual carbon gave only 0.05%. The X-ray diffraction pattern showed no evidence of materials other than vanadium nitride.

Heat Capacities.—The heat capacities were measured with apparatus previously described.[7] The results, expressed in defined calories (1 cal. = 4.1833 int. joules) per mole, are listed in Table I and are plotted against temperature in Fig. 1.

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

[4] Shomate, *ibid.*, **69**, 220 (1947).

[5] The preparations and analyses of these substances were conducted by A. E. Salo, formerly chemist, Pacific Experiment Station, Bureau of Mines.

[6] X-Ray diffraction examinations of both substances were made by E. V. Potter, formerly physicist, Salt Lake City Station, Bureau of Mines.

[7] Kelley, Naylor and Shomate, Bureau of Mines Technical Paper 686, 1946, 34 pp.

The molecular weights accord with the 1947 International Atomic Weights. The samples of carbide and nitride weighed 284.19 g. and 351.29 g., respectively, corrected to vacuum.

The heat capacity curves follow a normal course, the nitride curve being higher at all temperatures. The difference in heat capacity ranges from 0.6 cal./deg./mole at 50°K. to 1.1 cal./deg./mole at 298.16°K. At the lowest points measured the heat capacity of the carbide is just on the verge of following the T^3-law, while an additional 20° lower temperature would be required to bring the nitride heat capacity to this region. Values of the heat capacities at 298.16°K., as read from smooth curves, also are included in Table I.

TABLE I

MOLAL HEAT CAPACITY OF VC (MOL. WT., 62.96)

T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.
52.5	0.5895	115.1	3.132	216.2	6.326
56.5	.7180	125.2	3.525	226.0	6.555
60.2	.8504	135.1	3.894	235.8	6.774
64.3	1.007	145.6	4.265	246.1	6.988
68.5	1.175	155.3	4.595	256.2	7.202
72.7	1.351	165.5	4.921	266.1	7.382
77.0	1.532	175.5	5.237	276.2	7.577
85.0	1.871	185.6	5.527	286.3	7.762
94.7	2.287	195.9	5.809	297.0	7.955
104.4	2.696	205.8	6.062	298.16	(7.970)

MOLAL HEAT CAPACITY OF VN (MOL. WT., 64.96)

T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.
52.6	1.272	115.1	4.255	216.1	7.483
56.7	1.484	125.1	4.649	226.1	7.727
60.9	1.702	135.0	5.036	235.8	7.925
65.1	1.925	145.6	5.413	246.1	8.159
69.4	2.150	155.5	5.759	256.1	8.379
73.5	2.365	165.4	6.085	266.0	8.546
80.0	2.688	175.3	6.415	276.0	8.727
84.8	2.917	185.6	6.700	286.1	8.899
94.7	3.376	195.9	6.980	296.3	9.053
104.5	3.809	205.8	7.244	298.16	(9.080)

Entropies.—The entropies were calculated in the usual manner, the portion between 52.00 and 298.16°K. being obtained by numerical integration of a plot of C_p against log T and the portion below 52.00°K. being obtained by extrapolation. The latter was accomplished by the empirical use of Debye functions, $D(476/T)$ and $D(351/T)$, respectively, for the carbide and nitride. These functions fit the measured data to within 0.02 cal./deg./mole, or better, at temperatures below 70 and 80°K., respectively. The results of the entropy calculations are in Table II. It is noteworthy that the extrapolated portions of the entropies are only 3.0 and 5.3% of the totals at 298.16°K.

TABLE II

ENTROPIES AT 298.16°K. (E. U./MOLE)

	VC	VN
0–52.00°K. (extrapolated)	0.20	0.47
52.00–298.16°K. (measured)	6.57	8.44
$S^\circ_{298.16}$	6.77 ± 0.03	8.91 ± 0.04

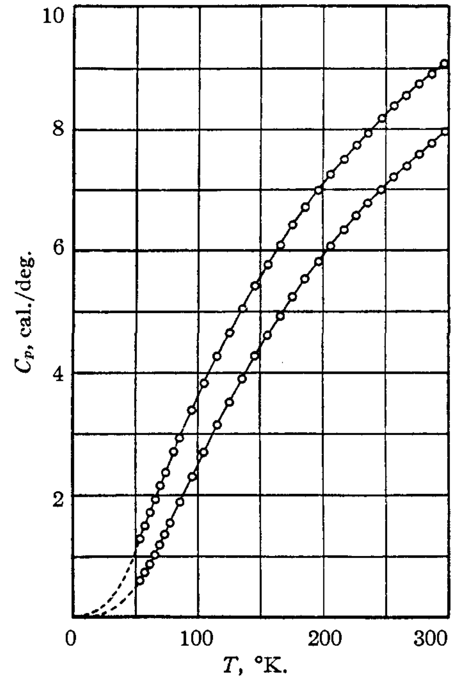

Fig. 1.—Molal heat capacities: upper curve, VN; lower curve, VC.

The results in Table II and the entropies of the elements[8] ($S^\circ_{298.16}$ = 7.0 ± 0.1 for V, $S^\circ_{298.16}$ = 1.36 ± 0.03 for C, and $S^\circ_{298.16}$ = 45.79 ± 0.01 for N_2) yield $\Delta S^\circ_{298.16} = -1.6 \pm 0.1$ for the entropy of formation of vanadium carbide from the elements and $\Delta S^\circ_{298.16} = -21.0 \pm 0.1$ for the entropy of formation of vanadium nitride from the elements.

Summary

The heat capacities of vanadium carbide and vanadium nitride were measured throughout the temperature range 50.4 to 298.16°K.

The entropies of vanadium carbide and nitride are, respectively, $S^\circ_{298.16} = 6.77 \pm 0.03$ and $S^\circ_{298.16} = 8.91 \pm 0.04$. The corresponding entropies of formation from the elements are $\Delta S^\circ_{298.16} = -1.6 \pm 0.1$ and $\Delta S_{298.16} = -21.0 \pm 0.1$.

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[8] Kelley, Bureau of Mines Bulletin 434, 1941, 115 pp.