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

Heat Capacities at Low Temperatures of VCl_2 and VCl_3[1]

BY C. HOWARD SHOMATE[2]

Existing thermodynamic data for vanadium compounds are quite meager. In the low temperature field, heat capacity and entropy values have been reported only for V, V_2O_3, V_2O_4 and V_2O_5.[3] Recently, the Pacific Experiment Station of the Bureau of Mines has undertaken to supply such data for some of the vanadium compounds that are of metallurgical interest. This paper reports low temperature heat capacity and entropy data for vanadium dichloride and vanadium trichloride.

Materials[4]

Vanadium dichloride was prepared according to the reaction, $V + 2HCl \rightarrow VCl_2 + H_2$. Vanadium metal, containing no appreciable impurity other than carbon, ground to −20 mesh, was placed in an alundum boat inside a Vycor tube. Dry hydrogen chloride gas was passed through the tube and the temperature raised to 850°. Sublimed crystals of vanadium dichloride collected on the cooler portion of the tube. Analysis gave 42.09% V (theoretical, 41.81%) and 57.95% Cl (theoretical, 58.19%). The material was somewhat hygroscopic, and for the purpose of correcting the heat capacity results, it was assumed that the sample was 99.8% VCl_2 and 0.2% H_2O. The heat capacity determinations were made on a 119.09-g. sample.

Vanadium trichloride was prepared from freshly distilled vanadium tetrachloride which had been obtained by passing chlorine gas over ferrovanadium at 250°. The vanadium tetrachloride was refluxed in a dry atmosphere until conversion to vanadium trichloride was effected. The material was finally heated at 160° in a stream of dry carbon dioxide for twenty-four hours. Analysis gave 32.41% V (theoretical, 32.39%) and 67.45% Cl (theoretical, 67.61%). Because of the hygroscopic nature of the material, additional analyses were made after completion of the measurements and removal of the sample from the calorimeter. These showed 32.22% V and 67.19% Cl. On the basis of these analyses and of tests of the rate of moisture absorption on exposure to air, it was considered that the material as used in the measurements was 99.6% VCl_3 and 0.4% H_2O. The measurements were made on a 110.66-g. sample.

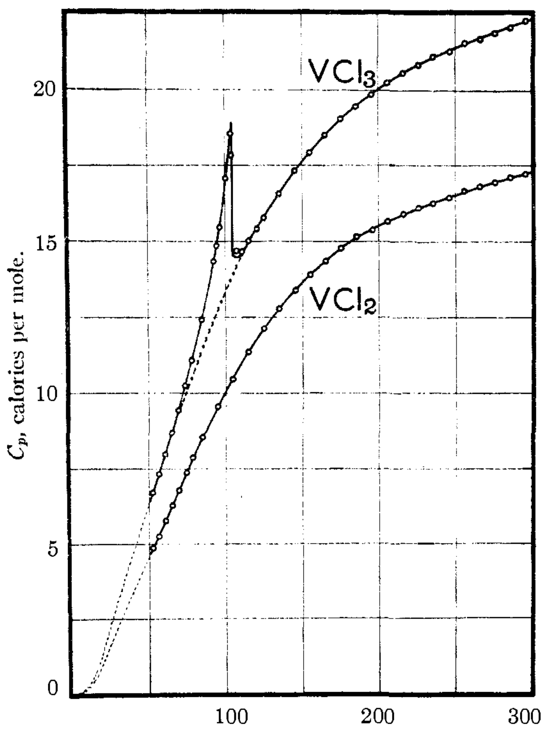

Fig. 1.—Low temperature heat capacities of vanadium dichloride and trichloride.

Heat Capacities

The method and apparatus used in the low temperature heat capacity measurements have been described previously.[5] The experimental results, expressed in defined calories (1 calorie = 4.1833 int. joules),[6] are listed in Table I and shown graphically in Fig. 1. The values of the heat capacities at 298.16°K., read from a smooth curve through the experimental points, also are included in Table I. The molecular weights are in accordance with the 1941 International Atomic Weights. The results for the dichloride and trichloride were corrected for 0.2 and 0.4% water impurity, respectively, using the data of Giauque and Stout.[7]

All weights were corrected to vacuum, using the following densities: vanadium dichloride, 3.23 and vanadium trichloride, 3.00 g./cc.

No anomalies appeared in the heat capacity curve of vanadium dichloride; however, vanadium trichloride has a marked "hump" in its heat capacity curve, the peak being at 104.9°K.

Entropies

Evaluation of the entropies at 298.16°K. is obtained from a plot of C_p against log T. This necessitates the extrapolation of the heat capacity curve from the temperature of the lowest measurement down to the absolute zero of temperature.

It was found that the function sum, $D(146/T) + 2E(351/T)$ fits the experimental results for vanadium dichloride within 1% in the temperature range 52–120°K. (The symbols D and E denote,

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

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

(4) Preparations and analyses of materials were made by R. J. O'Dea, chemist, and A. E. Salo, metallurgist, Pacific Experiment Station, Bureau of Mines.

(5) Kelley, Naylor and Shomate, Bur. Mines Tech. Paper 686 (1946).

(6) Mueller and Rossini, *Am. J. Phys.*, **12**, 1 (1944).

(7) Giauque and Stout, THIS JOURNAL, **58**, 1144 (1936).

TABLE I

MOLAL HEAT CAPACITIES

VCl_2 Mol. wt. = 121.864 T, °K.	C_p, cal./mole	VCl_3 Mol. wt. = 157.321 T, °K.	C_p, cal./mole
52.5	4.869	52.5	6.709
56.3	5.256	56.6	7.328
60.8	5.779	60.6	7.989
65.3	6.289	64.9	8.685
69.7	6.794	69.2	9.443
74.6	7.379	73.6	10.25
78.8	7.865	78.0	11.09
85.0	8.532	84.6	12.41
94.8	9.543	92.8	14.32
104.4	10.46	94.7	14.84
115.0	11.36	96.8	15.47
125.1	12.12	100.6	17.08
135.1	12.79	104.1	18.54
145.7	13.39	104.4	17.84
155.5	13.90	107.5	14.69
165.5	14.34	110.9	14.65
175.5	14.78	115.6	15.01
185.6	15.14	120.6	15.41
196.0	15.38	125.2	15.78
205.9	15.66	135.0	16.57
216.2	15.90	145.7	17.31
226.2	16.11	155.4	17.92
235.8	16.28	165.4	18.50
246.3	16.45	175.7	19.04
256.1	16.69	185.6	19.46
266.3	16.81	195.9	19.84
276.2	16.96	206.0	20.21
286.4	17.11	216.3	20.56
296.5	17.23	226.3	20.81
(298.16)	(17.26)	236.0	21.10
		246.6	21.27
		256.5	21.54
		266.5	21.68
		276.2	21.88
		286.3	22.06
		296.5	22.29
		(298.16)	(22.27)

respectively, Debye and Einstein functions.) Above 120°K. the deviation becomes much more marked. However, this is as good a fit as is reasonable to expect for an anhydrous chloride, since Kelley and Moore[8] were able to fit the heat capacity curves of the anhydrous chlorides of calcium, iron, magnesium and manganese with similar functions up to only 100 to 140°K. The above functions were used to extrapolate the heat capacity curve of vanadium dichloride to 0°K.

Extrapolation of the heat capacity curve of vanadium trichloride to absolute zero is difficult because of the presence of the "hump." However, the ratio of the molal heat capacity of the trichloride to that of the dichloride at the temperatures of the lowest measurements approaches the constant value of approximately 1.38. Therefore, the relationship, $C_{p,\ VCl_3} = 1.38\ C_{p,\ VCl_2}$, for the temperature range 0–52°K. was used to extrapolate the heat capacity curve of vanadium trichloride to 0°K.

The heat absorption in the region of the "hump" in vanadium trichloride was obtained by summing the energies of six successive heat capacity determinations in the manner described by Shomate.[9] The total heat absorption between 89.12 and 112.20°K. is 360.2 calories/mole, and the corresponding increase in entropy is 3.587 E. U./mole.

A "normal" curve was drawn through the region of the "hump" (broken line in Fig. 1) according to the relationship, $C_{p,\ VCl_3} = kC_{p,\ VCl_2}$ the factor k varying linearly with log T from a value of 1.38 at 55° to 1.29 at 140°K. (The ratio of the measured molal heat capacity of vanadium trichloride to that of vanadium dichloride is remarkably constant at 1.29 between 140° and 298.16°K.) The excess entropy in the "hump," above that calculated from this "normal" curve is 0.73 E.U./mole.

Table II summarizes the entropy calculations for the two chlorides.

TABLE II

ENTROPIES AT 298.16 °K. (E. U./MOLE)

	VCl_2	VCl_3
0–52.00 °K. (extrapolated)	2.93	4.04
52.00–298.16 °K. (measured)	20.30	27.29
$S^\circ_{298.16}$	23.2 ± 0.3	31.3 ± 0.4

The entropy values, of necessity, do not take account of the possibility of unextracted magnetic entropy at 52°K., and no allowance is made for this possibility in the assigned uncertainties. Otherwise, the uncertainties are larger than normally would be assigned because of uncertainties in the amounts of and corrections for the moisture contents of the samples.

Summary

The heat capacities of vanadium dichloride and vanadium trichloride were measured in the temperature range 52 to 298.16°K. Vanadium trichloride has a "hump" in its heat capacity curve, the maximum being at 104.9°K. There is approximately 0.73 unit of excess entropy in the "hump" above the "normal" curve.

The following molal entropies at 298.16°K. were computed: vanadium dichloride, 23.2 ± 0.3, and vanadium trichloride, 31.3 ± 0.4 E. U.

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(8) Kelley and Moore, THIS JOURNAL, **65**, 1264 (1943).

(9) Shomate, *Ind. Eng. Chem.*, **36**, 910 (1944).