Systematic extinctions:

hkl appears only when all odd or all even
0*kl* appears only with $k = 2n$ and $l = 2n$
*h*0*l* appears only with $h = 2n$, $l = 2n$ and $h + l = 4n$
*hk*0 appears only with $h = 2n$, $k = 2n$ and $h + k = 4n$
Space group: F d d

The number of molecules per unit cell is 8 and the "ideal" density of the crystal is 1.478 g./ml. The compound is unusually interesting because of the very small *a* spacing in comparison with *b* and *c*, probably indicating very flat molecules lying extended in the *bc* plane, also probably with hydrogen bonding. Hence this offers an excellent opportunity for a two-dimensional Fourier analysis of electron densities which is now being carried out.

Summary

1. A new simple procedure for single crystal analysis by the combination of the equi-inclination Weissenberg and the Buerger precession methods has been investigated and its application has been illustrated with practical problems. This new procedure provides a simple solution for needle crystals the orientation of which, along the crystallographic axes other than needle axis, is extraordinarily difficult.

2. Determinations were made of crystal habits, densities, lattice constants and probable space-groups of four compounds, for which no previous X-ray and crystallographical data are available, as tabulated on the preceding page.

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

Heat Contents at High Temperatures of Vanadium Dichloride and Vanadium Trichloride[1]

BY E. G. KING[2]

In continuation of a program of study of the thermodynamic properties of vanadium compounds, high-temperature heat contents of vanadium dichloride and vanadium trichloride were measured. No previous similar values exist for these substances, but low temperature heat capacity and entropy data have been reported by Shomate.[3]

Materials

The samples used in this work were portions of the materials prepared for previous low temperature heat capacity measurements, and the methods of preparation and the analyses were described by Shomate.[3] Before the present measurements were begun, both compounds were given a preliminary heating in vacuum, the dichloride to 850° and the trichloride to 150°.

Measurements and Results

The high temperature heat content measurements were made by the "dropping" method with previously described[4,5] apparatus. Frequent calibrations of the furnace thermocouple at the gold point were made by the method described by Southard.[4]

The samples were contained in platinum–rhodium alloy capsules. Two capsules were employed for the dichloride, containing, respectively, 8.9608 and 8.6643 g. (corrected to vacuum) of sample. These capsules were sealed by platinum welding after replacing air in the pore space by helium. One capsule, containing 7.4429 g. (corrected to vacuum) of sample was used for the trichloride. It was sealed by gold soldering, after the pore space was filled with helium. Corrections for the capsules were made by means of separate measurements of the platinum–rhodium alloy and the known heat contents of gold and platinum. These corrections amounted to 25% of the total measured heats for the dichloride and 28% for the trichloride.

The experimental results, expressed in defined calories[6] (1 cal. = 4.1833 int. joules), are in Table

TABLE I

HIGH-TEMPERATURE HEAT CONTENT OF VCl_2
(Mol. wt. = 121.86)

T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole
339.9	760	875.9	10,730
389.0	1670	971.3	12,620
393.9	1745	1029.5	13,850
471.7	3125	1072.7	14,640
570.4	4895	1172.9	16,660
673.8	6830	1272.5	18,740
773.8	8740		

HIGH-TEMPERATURE HEAT CONTENT OF VCl_3
(Mol. wt. = 157.32)

T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole
343.1	1070	704.9	9,875
400.3	2405	803.8	12,420
502.2	4775	902.5	14,870
601.9	7225		

(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) Shomate, THIS JOURNAL, **69**, 220 (1947).
(4) Southard, *ibid.*, **63**, 3142 (1941).
(5) Kelley, Naylor and Shomate, *Bur. Mines Tech. Paper*, 686, 1946, 34 pp.
(6) Mueller and Rossini, *Am. J. Phys.*, **12**, 1 (1944).

I. Molal weights accord with the 1947 International Atomic Weights.

Measurements of the dichloride could not be extended beyond 1272°K. because of swelling of the capsule from vapor pressure of the substance. Pressure of tetrachloride from the disproportionation reaction of the trichloride precluded obtaining results above 902°K. for the latter substance.

The heat content curves are shown in Fig. 1. No anomalous behavior of either substance was observed.

Smooth curve values of the heat contents and entropy increments calculated from them are in Table II. The average deviation of experimental points from the smooth curves is 0.15% for the dichloride and 0.3% for the trichloride.

TABLE II

HEAT CONTENTS AND ENTROPIES ABOVE 298.16°K.

	VCl_2		VCl_3	
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	1,840	5.30	2,360	6.80
500	3,620	9.27	4,730	12.09
600	5,450	12.61	7,180	16.55
700	7,330	15.50	9,700	20.43
800	9,250	18.07	12,270	23.85
900	11,200	20.36	14,860	26.90
1000	13,180	22.45		
1100	15,190	24.36		
1200	17,220	26.13		
1300	19,270	27.77		

Heat content equations, representing the data, were derived by the method of Shomate,[7] use being made of his values[3] of the heat capacities at 298.16°K. The average deviations from smooth values and temperature ranges of validity are given in parentheses. Corresponding molal heat capacity equations also are listed.

For VCl_2

$$H_T - H_{298.16} = 17.25T + 1.36 \times 10^{-3}T^2 + 0.71 \times 10^5T^{-1} - 5502$$

(298–1200°K.; 0.3%)

$$C_p = 17.25 + 2.72 \times 10^{-3}T - 0.71 \times 10^5T^{-2}$$

(7) Shomate, THIS JOURNAL, 66, 928 (1944).

For VCl_3

$$H_T - H_{298.16} = 22.99T + 1.96 \times 10^{-3}T^2 + 1.68 \times 10^5T^{-1} - 7592$$

(298–900°K.; 0.2%)

$$C_p = 22.99 + 3.92 \times 10^{-3}T - 1.68 \times 10^5T^{-2}$$

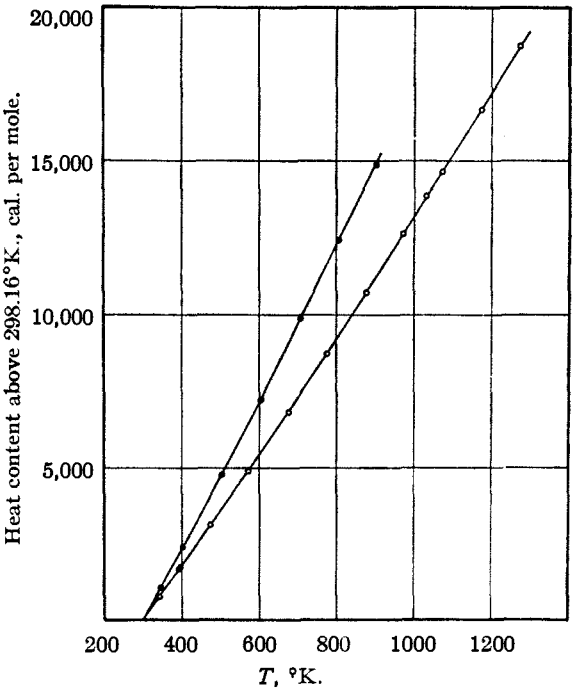

Fig. 1.—High temperature heat content of vanadium chlorides: upper curve, VCl_3; lower curve, VCl_2.

Summary

High-temperature heat contents of vanadium dichloride and vanadium trichloride were measured from 298.16°K. to 1272°K. and 902°K., respectively.

Tables of heat contents and entropy increments above 298.16°K. are assembled and heat content and heat capacity equations are derived.

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