magnitude that would have been expected before-hand. The other two values, especially that for sodium superoxide, are considerably larger than would have been predicted, which is partly attributable to the heat capacity maxima.

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High Temperature Heat Contents of Hafnium Dioxide and Hafnium Tetrachloride

BY RAYMOND L. ORR

High temperature heat contents of hafnium dioxide and hafnium tetrachloride were measured from 298.16°K. to 1804 and 486°K., respectively. A table of smooth heat content and entropy increment data above 298.16°K. was compiled, and heat content equations representing the data were derived.

Introduction

Recent progress in the large-scale separation and purification of zirconium and hafnium has led to the availability of hafnium and some of its compounds of sufficient purity and in adequate amounts for measuring thermodynamic properties. The present paper reports heat content measurements covering the range from 298.16°K. to 1804°K. for hafnium dioxide, and from 298.16°K. to 486°K. for hafnium tetrachloride. No high temperature heat content data have been reported previously for either substance.

Materials

The hafnium dioxide and hafnium tetrachloride were furnished by the Northwest Electrodevelopment Laboratory of the Bureau of Mines at Albany, Oregon, along with the results of chemical and spectrographic analyses.

The zirconium content of the dioxide is 1.45% of the total hafnium plus zirconium content. Other impurities amount to about 0.37%, being principally 0.21% iron, 0.08% silicon, 0.05% titanium, and about 0.005% each of lead, magnesium, zinc and nickel. An X-ray diffraction by R. E. Lorenson of this Laboratory showed the structure to be similar to that of the monoclinic variety of zirconium dioxide. In correcting the heat content measurements, the sample was considered as composed of 98.34% hafnium dioxide and 1.66% zirconium dioxide, in accordance with the above-designated zirconium content.

The zirconium content of the hafnium tetrachloride is 2.35% of the total hafnium plus zirconium content. Other impurities amount to about 0.08%, principally 0.03% iron, 0.01% silicon, 0.01% titanium, and about 0.005% each of zinc and nickel. Analysis for chlorine was made by K. R. Bonnickson of this Laboratory. The determined amount is 44.55%, as compared with the calculated 44.81% (allowance being made for the zirconium content). In correcting the heat content measurements, the sample was considered as composed of 96.69% hafnium tetrachloride and 3.31% zirconium tetrachloride.

Measurements and Results

The "dropping" method was used for the measurements, using apparatus and experimental procedures described previously.[1,2] The calorimeter was calibrated electrically, and during the course of the measurements the furnace thermocouple was calibrated frequently at the melting point of pure gold.

The samples were contained in platinum–rhodium alloy capsules, the heat contents of which were determined by separate experiments. The capsule containing the hafnium tetrachloride was sealed gas-tight by pinching the neck shut and soldering it with gold, after first evacuating of air and filling the pore space with helium. A correction was made for the heat content of the small amount of gold used. The

neck of the capsule containing the hafnium dioxide was merely pinched shut.

The measured heat content data, expressed in defined calories (1 cal. = 4.1840 abs. joules) per mole, are listed in Table I. Molal weights are computed according to the 1951 International Atomic Weights.[3]

TABLE I

MEASURED HEAT CONTENTS ABOVE 298.16°K. (CAL./MOLE)

T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$
HfO₂ (mol. wt. 210.60)					
382.7	1250	814.1	8,830	1283.9	17,880
388.6	1330	862.5	9,700	1383.4	19,870
481.5	2870	894.3	10,390	1488.6	21,980
593.7	4785	986.5	12,110	1591.2	24,080
673.3	6255	1088.0	14,050	1698.3	26,250
794.4	8460	1192.5	16,070	1803.6	28,470
HfCl₄ (mol. wt. 320.43)					
358.3	1750	426.5	3,800	459.8	4,810
393.1	2820	449.0	4,460	485.7	5,580
406.8	3230				

Corrections for the corresponding zirconium compounds contained by the two substances were made, using the data of Coughlin and King.[4]

TABLE II

HEAT CONTENTS (CAL./MOLE) AND ENTROPY VALUES (CAL./DEG. MOLE) ABOVE 298.16°K.

T, °K.	HfO₂ $H_T - H_{298.16}$	HfO₂ $S_T - S_{298.16}$	HfCl₄ $H_T - H_{298.16}$	HfCl₄ $S_T - S_{298.16}$
350	....	...	1520	4.69
400	1,540	4.43	3010	8.68
450	....	...	4510	12.21
500	3,170	8.06	6020	15.39
600	4,900	11.22		
700	6,710	14.01		
800	8,570	16.49		
900	10,450	18.71		
1000	12,350	20.71		
1100	14,280	22.55		
1200	16,230	24.24		
1300	18,200	25.82		
1400	20,200	27.30		
1500	22,220	28.69		
1600	24,260	30.01		
1700	26,320	31.26		
1800	28,400	32.45		

(1) J. C. Southard, THIS JOURNAL, 63, 3142 (1941).

(2) K. K. Kelley, B. F. Naylor and C. H. Shomate, Bureau Mines Tech. Paper 686 (1946).

(3) E. Wichers, THIS JOURNAL, 74, 2447 (1952).

(4) J. P. Coughlin and E. G. King, ibid., 72, 2262 (1950).

The results for both the hafnium dioxide and the hafnium tetrachloride are regular, no evidence of any anomaly in the heat capacity being found for either substance in the temperature range studied. Measurements for the tetrachloride above 486°K. were precluded because of excessive swelling of the capsule at that temperature, probably due to a very small amount of superficial moisture in the sample. Hafnium tetrachloride has been reported to develop a sublimation pressure of 1 atm. at about 590°K.[5]

Even temperature values of the heat contents above 298.16°K., obtained from smooth curves, are

(5) W. Fischer, R. Gewehr and H. Wingchen, Z. anorg. Chem.,'242, 161 (1939).

listed in Table II together with matching entropy increments calculated by the method of Kelley.[6]

The heat content data are represented by the following equations derived by the method of Shomate,[7] the temperature range of validity and the mean deviation from the data being given in parentheses

HfO_2: $H_T - H_{298.16} = 17.39T + 1.04 \times 10^{-3} T^2 + 3.48 \times 10^5 T^{-1} - 6445$ (298 – 1800°K; 0.3%)

$HfCl_4$ $H_T - H_{298.16} = 31.47T + 2.38 \times 10^5 T^{-1} - 10,181$ (298 – 485°K.; 0.2%)

(6) K. K. Kelley, U. S. Bur. Mines Bull. 476 (1949).

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

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The Heat Capacity, Heat of Fusion and Heat of Vaporization of Hydrogen Fluoride[1]

BY JIH-HENG HU, DAVID WHITE AND H. L. JOHNSTON

The heat capacity of 99.8% pure hydrogen fluoride has been measured between 15 and 300°K. No transitions were found, in the solid, as is the case in the other hydrogen halides; this is probably due to the existence of hydrogen bonding in hydrogen fluoride. The heat of fusion at the melting point, 189.79 ± 0.02°K., was found to be 46.93 ± 0.04 cal./g. The heat of vaporization at a pressure of 741.4 mm. and a temperature of 292.61 ± 0.1°K. was found to be 89.45 ± 0.20 cal./g. A comparison of the entropy at 741.4 mm. and 292.61 °K., calculated from the heat capacity data and the third law, with that of the spectroscopic value leads to a discrepancy of 17.53 e.u. This has been accounted for by assuming that gas at this temperature and pressure consists of an equilibrium mixture of the monomer, the dimer, the trimer, and so on, these polymers being a consequence of the hydrogen bonding.

Introduction

An examination of the literature on thermal data of hydrogen fluoride leads to the conclusion that a number of discrepancies exist. The heat capacity has been measured by Clusius, Hiller and Vaughan[2a] and by Dahmlos and Jung.[2b] Experiments of the former covered the region 15 to 75°K., while those of the latter covered the range 98 to 273°K. An examination of these experiments indicates that the two sets of data are not in agreement, and, in fact, at the point where the two sets of data should meet, there appears to be evidence of a transition in the solid. Furthermore, the values of the heat of fusion and vaporization determined in these early experiments[2b,3] are quite uncertain.

By analogy with the other halides one would expect, in hydrogen fluoride, the existence of what appears to be second order transitions in the solid, but this possibility is remote. Regardless of whether these transitions are due to rotational oscillation of the molecules below the transition temperature to a phase in which the molecules are freely rotating[4] or to one of order-disorder,[5,6] the existence of the high degree of hydrogen bonding in hydrogen fluoride makes such transitions in the solid improbable.

(1) This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

(2) (a) K. Clusius, K. Hiller and J. V. Vaughan, Z. physik. Chem., B8, 427 (1930); (b) J. Dahmlos and G. Jung, ibid., B21, 317 (1933).

(3) J. H. Simons and J. W. Bouknight, THIS JOURNAL, 54, 129 (1932).

(4) L. Pauling, Phys. Rev., 36, 430 (1930).

(5) L. Landau, Physik. Z. Sowjetunion, 11, 26, 545 (1937).

(6) N. L. Alpet, Phys. Rev., 75, 398 (1949).

Finally, the correlation of the spectroscopic data with that of the thermal data has not been settled. This problem is intimately connected with the manner in which these hydrogen bonds manifest themselves in the gas phase, since this ultimately reflects itself in the heat and entropy of dissociation to the ideal monomeric state. Two possibilities have been postulated: one by Hildebrand and Simons,[7a,b] assumed the formation of a six-membered ring, and the other by Briegleb,[8] which postulated the existence of monomer, dimer, trimer, etc., all being in equilibrium.

An attempt has been made in this paper to resolve these difficulties as well as to determine the thermodynamic properties which are important in the reaction: $H_2 + F_2 \rightarrow 2HF$. The work on thermal properties of fluorine, together with the thermodynamics of the reaction, will be reported in a subsequent paper.

Material.—The anhydrous hydrogen fluoride, having a purity of 99.8%, was obtained from the Harshaw Chemical Co. in Cleveland, Ohio. Their analysis indicated the following impurities: SO_2, 0.1%; as H_2SO_4, 0.06%; H_2SiF_6, 0.03%.

An attempt to further purify the material by distillation was made before using it in the calorimeter. Redetermination of the purity by the freezing point method indicated that the purity had not changed significantly. A description of the freezing point experiments are given in a later section of the text.

Apparatus.—The apparatus used in this research is shown schematically in Fig. 1. The calorimeter proper is a cylin-

(7) (a) J. H. Hildebrand, J. Chem. Phys., 15, 225 (1947); (b) J. Simons and J. H. Hildebrand, THIS JOURNAL, 46, 2183 (1924).

(8) G. Briegleb, Z. physik. Chem., B51, 9 (1941); B52, 368 (1942); B53, 225 (1943).