High Temperature Enthalpy, Heat Capacity, Heat of Fusion, and Melting Point of Zirconium Tetrafluoride

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ZIRCONIUM tetrafluoride is of interest as a constituent of rocket exhausts as well as of importance in nuclear power plant processing and extractive metallurgy. Its heat of formation has recently been determined (2), and the low temperature heat capacity and entropy have been measured (5). The present article gives results of high temperature measurements, which completes data necessary to calculate thermodynamic properties of the condensed phase.

EXPERIMENTAL

Material. Hafnium-free zirconium metal was dissolved in 48% aqueous hydrofluoric acid, and the resulting solution was evaporated to dryness. The crystalline product was heated slowly to 500° C. in a platinum boat in a slow current of anhydrous hydrogen fluoride. X-ray diffraction showed only crystalline ZrF_4. Wet analysis indicated 54.6% Zr (theory 54.55) and 44.9% F (theory 45.45).

Enthalpy. The sample was sealed in a platinum-10% rhodium alloy capsule by arc welding under a helium pressure of 8 cm. mercury. The enthalpy, $H_T - H_{298.15}$, was determined in a copper block drop calorimeter previously described (3). The platinum *vs.* platinum-10% rhodium thermocouple used to measure the temperature of the capsule in the furnace was calibrated, just before the enthalpy measurements, against a similar couple standardized at the National Bureau of Standards.

Correction for enthalpy of the container and heat loss during the drop was obtained from previous empty capsule measurements. Above 1100° K., an additional correction was applied for heat of sublimation or vaporization. Vapor pressure and heat of sublimation data of Cantor, Newton, Grimes, and Blankenship (1) were used in determining this correction. It was about 0.1% of the enthalpy of the zirconium tetrafluoride at 1114° K. and about 0.3% at 1226° K.

RESULTS

The observed enthalpies are listed in Table I. The method of Shomate (4) was used to smooth the experimental data and to determine enthalpy and heat capacity equations for the solid.

$$H_T - H_{298.15} = 28.06\,T + 2.200 \times 10^{-3}T^2 + 4.116 \times 10^5 T^{-1} - 9942 \text{ cal. mole}^{-1}$$

$$C_p = 28.06 + 4.400 \times 10^{-3}\,T - 4.116 \times 10^5\,T^{-2} \text{ cal. mole}^{-1}\text{deg.}^{-1}$$

where H is enthalpy, T is absolute temperature, and C_p is molal heat capacity at constant pressure. The low temperature data of Westrum (5) were employed in smoothing the Shomate function curve. The value, $C_{p\ 298.15}$ = 24.74 cal. mole^{-1} deg.$^{-1}$, permitted a somewhat smoother joining of the low temperature and the high temperature Shomate functions than the given value of 24.79 cal. mole^{-1} deg.$^{-1}$. Smoothed enthalpy and heat capacity quantities are given in Table II.

Table I. Observed Enthalpy of ZrF_4

(Mole Wt. = 167.22 g. mole^{-1})

Temp., ° K.	$H_T - H_{298.15}$, Cal. Mole^{-1}	Temp., ° K.	$H_T - H_{298.15}$, Cal. Mole^{-1}
283.9	−372.4	838.5	15,586
366.2	1700.0	888.5	17,192
412.3	2959.1	909.0	17,839
432.2	3478.5	956.3	19,383
503.8	5518.1	1036.2	21,862
536.4	6515.4	1114.0	24,427[a]
573.3	7500.0	1165.1	26,604[a,b]
591.8	8184.4	1189.2	28,662[a,b]
616.4	8847.6	1199.6	34,339[a,b]
647.1	9839.6	1205.2	42,424[a,b]
728.2	12,239	1213.0	43,032[a]
758.7	13,197	1217.1	43,138[a]
804.6	14,406	1225.8	43,407[a]

[a] Corrected for heat of sublimation (vaporization). [b] Pre-melting.

Table II. Smoothed Enthalpy and Heat Capacity of ZrF_4

Temp., ° K.	$H_T - H_{298.15}$, Cal Mole^{-1}	C_p, Cal. Mole^{-1} Deg.$^{-1}$
300	45.8	24.81
400	2653.6	27.10
500	5444.4	28.58
600	8359.2	29.62
700	11,362	30.38
800	14,428	30.97
900	17,550	31.51
1000	20,728	32.03
1100	23,959	32.54
1200	27,239	33.04
1205(*s*)	27,415	33.07
1205(*l*)	42,765	Estd. value 29

Pre-melting is evident, starting between 1114° and 1165° K.; melting is complete at 1205° ± 2° K. The heat of fusion is 15,350 ± 100 cal. mole^{-1}.

Because the high vapor pressure of the sample deformed the capsule, only a few liquid enthalpy measurements were made. The heat capacity of the liquid is indicated to be about 29 cal. mole^{-1} deg.$^{-1}$, but not much confidence can be placed in this figure.

LITERATURE CITED

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