CONCLUSIONS

These investigations have shown that particle size has little or no influence on the transformation temperature of monoclinic-tetragonal ZrO_2. The presence of metastable tetragonal ZrO_2, however, increased the transition range considerably. The thermal stability of the tetragonal phase present in the starting material seems to be related to the kinetics of the carbon arc preparation process and also may be due to impurities such as, primarily, carbon present. The 0.1% carbon present in the starting particles disappears gradually by heating them in air above 800° C., and it may be with this that the metastable tetragonal phase inverts back to the stable monoclinic phase of ZrO_2 upon cooling to room temperature.

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Vapor Pressure of Hafnium (IV) Iodide

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Vapor pressures of the hafnium (IV) iodide system were measured between 263 and 406° C. by a metal diaphragm technique. Three stable forms of the HfI_4 were identified (α, β, and γ modifications), in addition to a metastable form which transforms slowly at temperatures in the vicinity of 300° C. to the α-modification. Enthalpies of sublimation, ΔH°_T, were found to be 28.37 ± 0.04 (263 to 401° C.), 48.9 ± 1.3 (302 to 324° C.), 33.7 ± 0.6 (325 to 372° C.), and 28.2 ± 0.5 (375 to 405° C.) kcal./gram mole for the mestastable, α, β, and γ modifications, respectively. The transition temperatures were measured by thermal analysis to be 329 ± 3° C. and 375 ± 2° C. for the ($\alpha - \beta$) and ($\beta - \gamma$) transitions, respectively.

INTEREST in the separation of hafnium from zirconium and the subsequent purification of hafnium has stimulated a study of the thermodynamic properties of their halides. Hafnium (IV) iodide currently plays an intermediate role in the purification of hafnium by the van Arkel crystal bar method. Very little experimental data are available in the literature on the hafnium (IV) iodide system, and up to the present time no information on its vapor pressure. The heat and entropy of sublimation (ΔH° and ΔS°), however, were estimated by Brewer (*1*) to be on the order of 28 kcal./gram mole and 40 eu., respectively. Sublimation pressures and other thermodynamic properties are reported for HfI_4 (solid and gas), as estimated by Kelley and King (*7*) and are substantially based on Brewer's estimates. Krause and coworkers (*8*) isolated a small quantity of hafnium (IV) iodide in capillaries for study of the x-ray diffraction pattern. Hampel (*4*) gives a brief description of the preparation of pure hafnium by the iodide process. However, no data are given on the properties of hafnium (IV) iodide.

EXPERIMENTAL

Hafnium (IV) iodide was prepared by direct combination of the elements within an evacuated reaction tube at 400° to 500° C. Anhydrous iodine was supplied to the reaction zone by decomposition of chromium (III) iodide which had been prepared by the method of Gregory and Handy (*3*). These two steps are represented by Equations 1 and 2:

$$2CrI_3 \rightarrow 2CrI_2 + I_2 \qquad (1)$$

$$Hf + 2I_2 \rightarrow HfI_4 \qquad (2)$$

The vapor pressure sample was prepared by subliming the HfI_4 from the reaction tube to a sample capsule, which was afterwards sealed under vacuum. Details of the HfI_4 preparation have been given (*10*). Metallic impurities in the hafnium were in the p.p.m. range, except for zirconium which was 3.8% Zr/(Zr + Hf). The principal impurities were, by spectroanalysis: Al, 60 p.p.m.; B, 0.3 p.p.m.; Cd, < 0.5 p.p.m.; Cr, 10 p.p.m.; Cu, 15 p.p.m.; Fe, 10 to 50 p.p.m.; Mg, 5 to 80 p.p.m.; and Mo, 10 p.p.m. Chemical analysis indicated that the Zr iodated to ZrI_4 along with the Hf and remained with the HfI_4 sample. The absence

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of chromium in the HfI_4 (less than 100 p.p.m.) was verified by spectrographic analysis. The sample capsule was charged to the diaphragm apparatus, (*10, 11*), degassed under high vacuum, and fractured in the evacuated sample zone.

The vapor pressure measurements were made by heating the sample through the temperature range of interest in 5° to 10° C. intervals during a period of about 24 hours for Run 1 and about 20 hours for Run 2 (after transformation). Furnace temperatures were often maintained constant for several hours, until equilibrium conditions seemed to be established before stepping to the next temperature. Data points, taken at regular intervals, were consistent with those obtained as the temperature approached a constant value. The data points between temperature changes were therefore considered to approach reasonably close to equilibrium values. Sample temperatures were measured with a platinum *vs.* platinum-10% rhodium thermocouple, which was calibrated against a N.B.S. certified thermocouple. The thermocouple was positioned in the sample block near the sample.

The sample for the thermal analysis was prepared in the same way as the vapor pressure sample. The HfI_4 was sublimed within the closed, evacuated system to a glass sample capsule having a thin-walled glass thermocouple tube (approximately 4 inches long) sealed in one end. After the transfer, the sample capsule was sealed from the system and inserted into a copper block, which was specially drilled to receive the capsule. Thermal and differential thermal analyses were made by slowly heating the sample through the temperature ranges of the suspected transitions. Further details of the apparatus and procedure for the thermal analyses are given (*10, 11*).

RESULTS

The vapor pressure data obtained for HfI_4, a solid within the temperature range studied, and the thermal analysis results gave evidence for the existence of one metastable and three stable modifications. Vapor pressure data for the metastable HfI_4 were obtained during Run 1 for both increasing and decreasing temperatures and are represented in Figure 1. The constants for the vapor pressure equation were determined by least squares analysis and are given in Table I. The enthalpy of sublimation (ΔH_T°), obtained from a least squares analysis of log P_{mm} *vs.* $1/T$ (°K.) data, over the temperature interval of the measurements (263° to 401° C.) was 28.37 ± 0.04 kcal./gram mole.

Kelley's (*5*) estimated heat capacity data of $C_p(g) = 26.0$ cal./gram mole °C. and $C_p(c) = 32.27 + 7.46 \times 10^{-3}T$ cal./gram mole °C. for the vapor and solid, respectively, were used to calculate the enthalpy of sublimation at 298.15° K. The accuracy of these data were estimated by Kelley to be about ±3%(*6*). The enthalpy of sublimation ($\Delta H^\circ_{298.15}$) was obtained by first evaluating ΔH_o, a constant of integration, by a least squares analysis of the sigma function (Σ) *vs.* the reciprocal temperature, where sigma and ΔH_o are related by

$$\sum = I + \Delta H_o/T$$

Values of sigma were calculated for each vapor pressure point from the following equation:

$$\sum = -R\ln P + \Delta a \ln T + (\Delta b/2)\ T$$

Then from

$$\Delta H_T^\circ = \Delta H_o + \Delta a T + (\Delta b/2) T^2$$

the enthalpy of sublimation at 298.15 was calculated. A detailed description of the preceding calculation method is given by Darken and Garry (*2*).

The value of $\Delta H^\circ_{298.15}$ for the metastable HfI_4 was calculated by this procedure to be 31.34 kcal./gram mole with a standard deviation of 0.06 kcal./gram mole. This standard deviation, however, does not include the uncertainty of the heat capacity data. Using Kelley's uncertainty data of 3% for $C_p(g)$ and revising the 3 to 5% for $C_p(c)$ owing to the apparent existence of previously unknown solid phases, an uncertainty of $\Delta H^\circ_{298.15}$ was calculated to be ±0.6 kcal./gram mole. Values of $\Delta H^\circ_{298.15}$ were calculated for the α, β, and γ modifications to be 51.4 ± 1.4, 37.0 ± 0.9, and 31.5 ± 0.9 kcal./gram mole, respectively, where the standard deviations are based on 5% uncertainty in $C_p(c)$ and a 3% uncertainty in $C_p(g)$.

Early in Run 2, the hafnium (IV) iodide sample (same as used in Run 1) was observed to undergo a slow transformation -i.e., lowering of the vapor pressure—at about 300°C. to a more stable α-modification. This transformation is represented by A-A' in Figure 2. Though this transformation occurred slowly, it appeared to be complete within 24 hours. Figure 3, a plot of temperature and pressure *vs.* time, shows the initial course of the transformation. Subsequent vapor pressure measurements during Run 2 gave evidence of two phase transitions, one at about 325° C. and a second near 372° C. The vapor pressure data of these three solid phases are represented in Figure 2. The constants for the vapor pressure equations with their

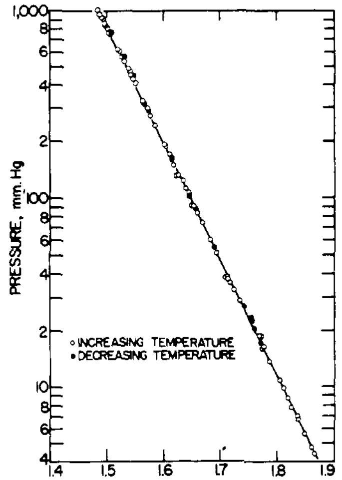

Figure 1. Vapor pressure of hafnium (IV) iodide, metastable

Table I. Thermodynamic Properties and Vapor Pressure Equations of HfI_4

$$\text{Log } P_{mm} = A - B/T$$

Form	Temp. Range, °C.	A ± σ_A	B ± σ_B	ΔH_T°, Kcal./Gram Mole	$\Delta H^\circ_{298.15}$, Kcal./Gram Mole
Metastable	263-401	12.235 ± 0.028	6,214 ± 17	28.37 ± 0.04	31.34 ± 0.6
α	302-324	19.46 ± 0.40	10,640 ± 230	48.9 ± 1.3	51.4 ± 1.4
β	325-372	13.99 ± 0.19	7,370 ± 120	33.7 ± 0.6	37.0 ± 0.9
γ	373-405	12.05 ± 0.13	6,125 ± 84	28.2 ± 0.5	31.5 ± 0.9

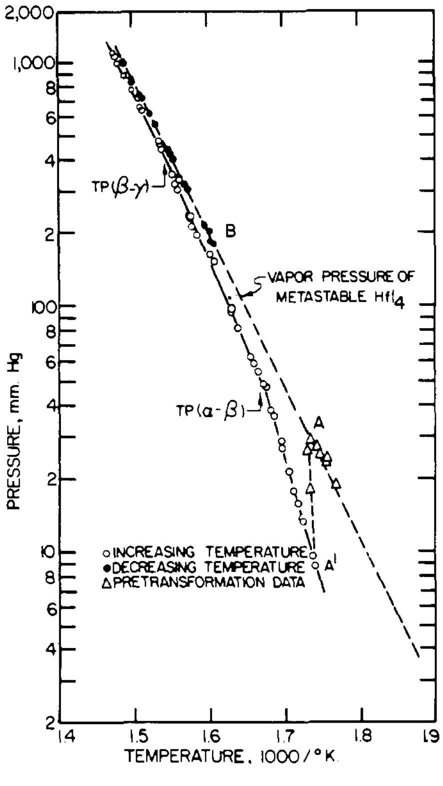

Figure 2. Vapor pressure of hafnium (IV) iodide, α, β, and γ modifications

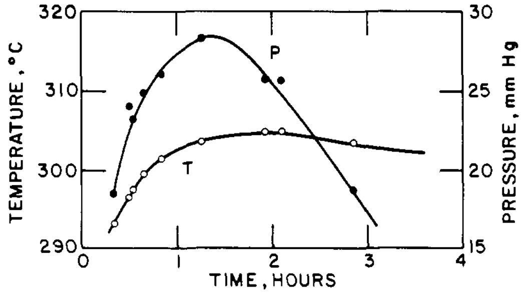

Figure 3. HfI_4 transformation, Run 2

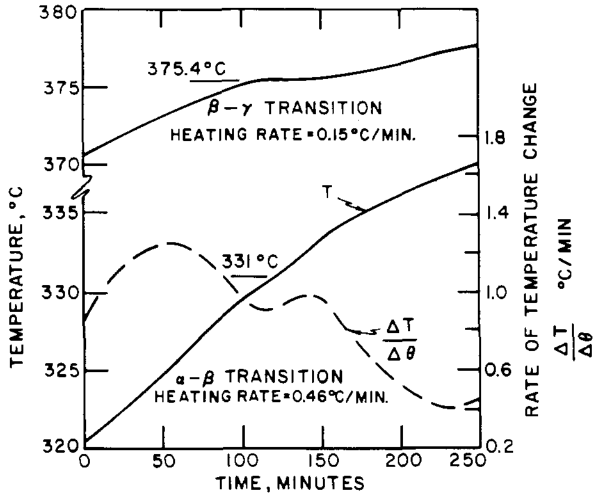

Figure 4. Thermal analyses of HfI_4

respective standard deviations for the hafnium (IV) iodide system are given in Table I along with enthalpies of sublimation.

From the heats of sublimation of the different phases at the transition temperatures, as calculated from the Clapeyron equation, the enthalpies of transition were estimated to be 14.4 ± 1.1 and 5.4 ± 0.6 kcal./gram mole for the ($\alpha - \beta$) and ($\beta - \gamma$) transitions, respectively. Both phase transitions were confirmed by thermal analysis of a sample which had been heat treated at 300° to 310° C. for an extended period of time to convert all HfI_4 to the α-modification. The respective transition temperatures, 329 ± 3° and 375 ± 2° C., were obtained only on heating the sample through the transition. No temperature halts were observed when cooling. The thermal arrests shown in Figure 4 are representative of those obtained during the thermal analyses. These results were considered primarily as indications of the transitions postulated rather than accurate transition temperature measurements, since these measurements were difficult to make owing to the inherent difficulty in measuring accurately the thermal arrests of hygroscopic inorganic salts. Table II gives other values obtained by thermal analysis. The transition temperatures from intersection of vapor pressure curves were 323° and 372° C. for the ($\alpha - \beta$) and ($\beta - \gamma$) transitions.

Table II. Thermal Analysis of Hafnium (IV) Iodide

Rate of Temp. Change, °C./Min.		Transition Temp., °C.
(α-β)	0.97	327–332[a]
(α-β)	0.46	327–332
(α-β)	0.12	327.5
(β-γ)	0.15	375.4
(β-γ)	0.77	372–377

[a] Differential thermal analysis.

Of particular interest were the vapor pressure data obtained for decreasing temperatures during Run 2. These data, instead of reproducing the data previously obtained (interpreted as γ, β, and α phases), duplicated the results obtained for the first run (interpreted as metastable HfI_4). In Figure 2, point *B* represents the temperature and pressure at which the vapor phase was degassed from the sample in the sample chamber; this step was taken intentionally to verify that the higher pressure was not a result of volatile impurities of decomposition products such as free iodine. In each case, the pressure returned to essentially the value of the metastable vapor pressure at that temperature. The last degassing, however, resulted in the loss of the sample from the chamber.

DISCUSSION

As no previous HfI_4 vapor pressure data have been reported, no comparison can be made to explain the peculiarities of this system. Krause and coworkers (*8*) did not allude to more than one HfI_4 modification in their reported x-ray data. The results of this work indicate that a metastable HfI_4 phase transforms to a more stable modification at temperatures near 300° C., though the metastable phase can exist up to at least 400° C. as evidenced by Run 1. It is possible that the transformation also takes place at higher temperatures, though this did not occur in this investigation. The occurrence of phase transitions from one stable form to another as the sample is heated is not unusual; however, the interesting result of obtaining metastable HfI_4 vapor pressures on cooling the system back down is somewhat atypical. This effect parallels, to some extent, the phosphorus system in which the white phosphorus transforms monotropically to the violet form and is converted back only by condensation from the vapor phase (*9*). To this extent, the HfI_4 system seems to behave monotropically. Conceivably, the zirconium iodide impurity in the sample could have influenced the phase transitions; however, the similarity of the hafnium and zirconium congeners makes this doubtful.

The zirconium iodide in the sample is not believed to affect the calculated enthalpies of vaporization considering the similarity of the reported enthalpies of vaporization of the other halides (*1*) (about 5% difference). The principal effect of the zirconium impurity is expected to be a net lowering of the magnitude of the vapor pressure. If Raoult's Law is assumed, the reported vapor pressure could be 3 to 4% lower than pure HfI_4.

The heats of sublimation, ΔH_T°, of the metastable (28.37 kcal./gram mole) and γ-modification (28.2 kcal./gram mole) are the same within experimental error, and both are in good agreement with the estimates of Brewer (28 kcal./gram mole). The vapor pressure of the metastable HfI_4 at 400° C. is approximately 9% higher than the vapor pressure of the γ-modification and nearly 40% higher than Brewer's estimate, which is based on a sublimation temperature of 700° K. Thermodynamic consistency of the data is confirmed by the temperature invarience of individual values of $\Delta H_{298.15}^\circ$ within a given phase. The respective entropies of sublimation (42.7 and 42.4 eu.) are in general agreement with the value of 40 eu. estimated by Brewer.

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