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Title SOLID-VAPOR EQUILIBRIA OF HAFNIUM AND ZIRCONIUM
TETRACHLORIDES

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The chemically similar elements hafnium and zirconium occur together in nature. Because of their very dissimilar nuclear properties it is of commercial importance to separate them for use in the atomic energy field. One or more of the steps in the separation and purification processes presently used involve the volatile hafnium and zirconium tetrachlorides. It would be economically beneficial if a separation could be made by fractional sublimation of these tetrachlorides.

An experimental technique for determining solid-vapor equilibria of the hafnium tetrachloride-zirconium tetrachloride system was used to obtain basic data for such a fractionating system. Vapor and solid phases of the mixed tetrachlorides were brought to equilibrium at 315°C, separated and analyzed. Complete vaporization and recondensation of the solid assured equilibrium in this

phase. The data obtained, although somewhat scattered, followed a Raoult's law-type relationship in which the concentration of a component in the vapor phase is equal to the product of its mole fraction in the solid phase and its vapor pressure as a pure solid at the temperature considered.

SOLID-VAPOR EQUILIBRIA OF HAFNIUM
AND ZIRCONIUM TETRACHLORIDES

by

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TABLE OF CONTENTS

| | <u>Page</u> |
|------------------------|-------------|
| INTRODUCTION | 1 |
| EXPERIMENTAL | 6 |
| Experimental Criteria | 6 |
| Equipment | 7 |
| Materials | 16 |
| Procedure | 18 |
| RESULTS AND DISCUSSION | 22 |
| BIBLIOGRAPHY | 28 |

LIST OF FIGURES

| <u>Figure</u> | | <u>Page</u> |
|---------------|---|-------------|
| 1 | Original Apparatus | 8 |
| 2 | Tube Filling Apparatus | 11 |
| 3 | Cross-Section of Equilibrating Furnace | 13 |
| 4 | HfCl_4 - ZrCl_4 Solid-Vapor Equilibrium | 24 |

LIST OF TABLES

| <u>Table</u> | | <u>Page</u> |
|--------------|--|-------------|
| I | Results of Spectrographic Analysis of Hafnium and Zirconium | 16 |
| II | Gas Analysis | 17 |
| III | Experimental Data | 23 |
| IV | Data for Analytical Check Samples | 26 |

SOLID-VAPOR EQUILIBRIA OF HAFNIUM AND ZIRCONIUM TETRACHLORIDES

INTRODUCTION

Hafnium and zirconium present a clear example of the distinct separation of the chemical properties of an atom from its nuclear properties. In his treatise on zirconium, Blumenthal (2, p. 3) traces the recognition of the element in 1789 by Klaproth, through Berzelius' preparation of the metal in 1824, to the discovery in 1922 by deHevesy and Coster that so called pure zirconium had, until then, contained another element, which they called hafnium. For 133 years hafnium had gone undetected because of its chemical similarity to zirconium. deHevesy and Coster had made their discovery, not by chemical separation, but by spectroscopic analysis.

Surveys have shown that zirconium constitutes about 0.05 percent of the lithosphere (5), which is about the same as carbon, and that the hafnium/zirconium ratio in natural deposits has an average value of 0.02 (6, p. 1). Because of their abundance, these metals can be of commercial importance and, fortunately, it is not necessary to separate these homologues for most applications.

With the development of atomic energy, however, materials must be selected for their nuclear, as well as their chemical properties. The vast difference in nuclear properties of hafnium and

zirconium was illustrated by the decision in 1950 to use hafnium-free zirconium for the reactor core in the submarine Nautilus, and the choice, in the following year, of hafnium for control rods in the same reactor (23, p. 1). Indeed, the neutron cross-sections of these metals differ by a factor of 10^3 (9, p. 11 and 20). It has thus become an engineering problem to economically separate commercial quantities of hafnium and zirconium.

A comprehensive list of methods for separating hafnium from zirconium was given by Thomas and Hayes (23, p. 49). Aside from one notable exception these methods begin with the metal tetrachlorides, convert them into another chemical form for the separation step, and then back to the tetrachlorides for the removal of other impurities and the final reduction to the metal. The exception to this procedure is the direct distillation of the tetrachlorides under pressure. Palko, et al. (18) have shown that at their melting points hafnium tetrachloride and zirconium tetrachloride have vapor pressures of 14,500 mm Hg (at 434°C) and 24,700 mm Hg (at 437°C), respectively. This vapor pressure study, and observations by Friend, et al. (7) on zirconium tetrachloride, confirm the stability of the tetrachlorides above their melting points. Williams, et al. (25, p. 139), after preliminary investigations, have ruled out distillation of the tetrachlorides under pressure because of the difficulties presented by the required high temperatures and pressures.

A patent granted to Plucknett (19) claimed separation of hafnium and zirconium tetrachlorides by distillation from fused stannous chloride, but temperatures up to 450°C and severe corrosion were also noted. Gruen and Katz (8) have demonstrated a lower temperature distillation, but their process required forming the stable phosphorus oxychloride complexes of the tetrachlorides.

Two methods for hafnium-zirconium separation by differential dechlorination have been suggested. Newnham (17) proposed selective reaction of zirconium powder with the mixed tetrachloride vapors to give nonvolatile zirconium trichloride. This nonvolatile product would then have to be rechlorinated for further processing. Selective partial oxidation of mixed tetrachlorides, suggested by Prakash and Sundaram (20) would require several steps with rechlorination between each step.

Although gas-liquid partition chromatography has not yet been applied extensively to inorganic compounds, and present chromatographic technology permits only minute quantities of materials to be separated at one time, possibilities of commercial hafnium-zirconium separation by this method exist. Keller (11; 12) has separated volatile metal halides on columns having organic stationary phases. Juvet and Wachi (10) suggested fused salts as the stationary phase. These methods, however, are not yet applicable to large-scale production.

Fractional sublimation as a method of separating hafnium

from zirconium, as the tetrachloride, was first mentioned in a report by Wilhelm, et al. (24, p. 10). Such a process would have the advantages of lower operating temperature and pressure, and the separated products could go directly to the reduction step. In the past, sublimation, as a unit operation in chemical engineering, has been restricted to removing a volatile solid from a nonvolatile solid. In a review of industrial sublimation, Mullin (15) tells of the difficulty in fractional sublimation and discounts refluxing in such an operation. Gadgets for continuous fractional sublimation have been invented. The separation of benzene from cyclohexane from their mixed solids with such an apparatus has been demonstrated by Reid (21). One operation that could be adopted for continuous fractional sublimation is the fluidized bed. A fluidized, finely divided, inert solid could act as a very effective surface for condensation and sublimation. Even a refluxing action could be effected by partial condensation in the upper section of the equipment with condensed solid falling back into the bed.

Before separation operations can be designed solid-vapor equilibrium data for the hafnium tetrachloride-zirconium tetrachloride system must be obtained. Because of the extraordinary chemical similarity of hafnium and zirconium one would expect ideal behavior within the solid. Crystallographic data are not available for hafnium tetrachloride; however, the data given for the oxides,

carbides, nitrides and borides of hafnium and zirconium show that the interatomic distances for the pairs of similar compounds differ by less than three percent (22, p. 66-67 and 177). These data lend support to the assumption of ideality in the mixed solid. From vapor density measurements of zirconium tetrachloride, Friend, et al. (7) concluded that there was no evidence of association in the vapor. This behavior can be assumed for hafnium tetrachloride on the basis of its vapor pressure (18). Thus at equilibrium conditions a behavior following Raoult's law might be expected.

The only experimental determination of solid-vapor equilibria of a two component system known to the author was a study by Nelson (16) similar to the work reported here. Nelson, however, was unable to reach definite conclusions due to the scatter of his data caused by apparatus difficulties.

EXPERIMENTAL

Criteria

The following criteria were considered when planning the experimental apparatus and procedure. These criteria were necessary to insure that the data taken would have physical significance and be of use in engineering design.

1. The experimental apparatus should allow equilibrium to be obtained between a chamber containing a mixture of the solid chlorides and a chamber containing only the vapors.

2. These two chambers must be isolated from one another under equilibrium conditions, then cooled, and the condensed chlorides removed for hafnium-zirconium ratio analysis.

3. The solids chamber must not contain an amount of vapor sufficient to change the solid composition following total condensation.

4. The hafnium and zirconium tetrachlorides should be of high purity and be free of the oxides and oxychlorides which are nonvolatile at the temperatures used and which would, thus, give an erroneous solid composition.

5. The temperature and/or pressure of the system must be known accurately throughout each determination so that a decrease in temperature or pressure, resulting in a possible condensation in

the vapor chamber, could be detected.

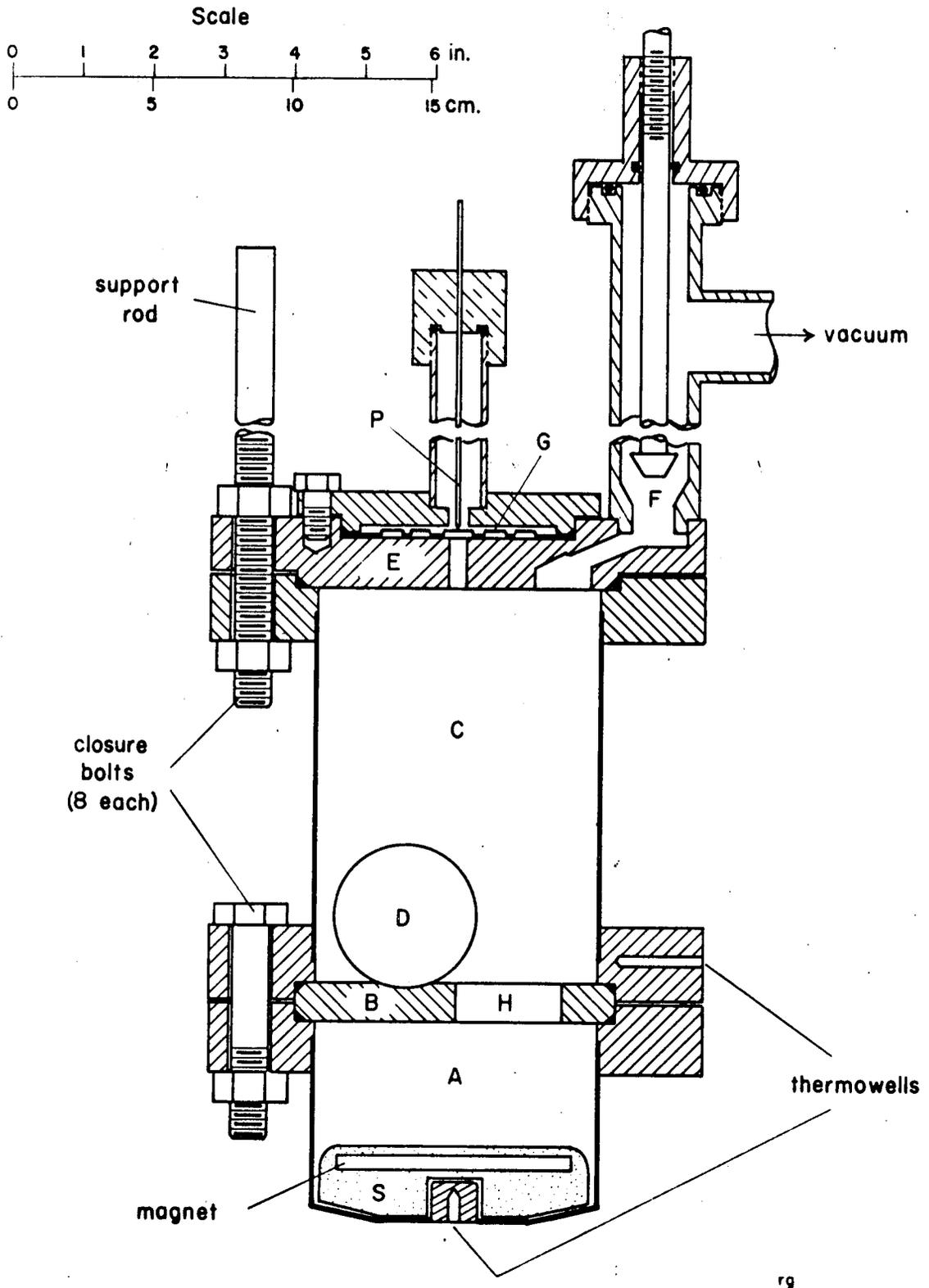
6. The vapor chamber must be at exactly the same or at a slightly higher temperature than the solids chamber to prevent condensation in, and hence material transport to, the vapor chamber.

Equipment

The original apparatus constructed for this work is shown in Figure 1. The lower section (A), the solids chamber, was fitted with a ceramic stirrer (S) containing a bar magnet allowing stirring with another outside magnet. Plate (B) separated the solids chamber from the vapor chamber (C); however, passage of vapor was allowed through a 1 1/2 inch hole (H). This hole could be closed by a large ball bearing (D) which otherwise rested in a slight depression on the plate. Lapping of the ball bearing into the hole provided a vapor-tight seal. Plate (E) covered the upper part of the vapor chamber. This plate was fitted with an evacuation valve (F) and pressure-sensing diaphragm mechanism (G). Internal pressure was equal to the external pressure applied when flexing of the diaphragm made or broke electrical contact with point (P). The chambers, plates, ball bearing and evacuation valve were made of inconel or stainless steel to reduce reaction with the volatile chlorides. The fired ceramic stirrer and bar magnet showed no visible reaction with the chloride vapors. The pressure-sensing diaphragm was

Figure 1

ORIGINAL APPARATUS



made from 0.005 inch tantalum sheet which required an oxygen-free gas in the pressure-measuring system; it was quite stable in chloride vapor at the temperatures used.

Operation began by subliming the appropriate quantities of hafnium and zirconium chlorides into the solids chamber. This chamber was then bolted in place and the entire apparatus was evacuated. With the apparatus evacuated and valve (F) closed the apparatus was placed in a specially constructed furnace and raised to a temperature giving an internal pressure of one atmosphere. The stirrer was then rotated by rotating a heavy U shaped magnet near the bottom of section (A). After time sufficient to establish equilibrium, the ball bearing was rolled into the hole (H) by slightly rocking the apparatus. With the solids and vapor chambers separated the apparatus was cooled to room temperature, dismantled, and the respective chambers washed to remove the solid and condensed vapor samples for analysis.

Two deficiencies in the operation of this equipment made it undesirable. First, the chlorides could not be introduced into the solids chamber without some exposure to the atmosphere and, hence, moisture. Second, because of its complexity, i. e., many gaskets and welds, the apparatus was not consistently leak free after assembling. For these reasons this original apparatus was abandoned and special glass tubes were used. These tubes permitted

direct chlorination of hafnium and zirconium into the apparatus without exposure to the atmosphere. Fusion sealing of the glass tubes provided vacuum tight chambers.

A typical equilibrium tube and the associated loading apparatus are shown schematically in Figure 2. The Pyrex tubes had five sections. Sections A and E, each 260 mm long were standard 10 mm tubing; solids chamber, B, 95 mm long was standard 20 mm tubing; vapor chamber, D, 245 mm long was standard 25 mm tubing; and section C, 40 mm long was slightly flattened 12 mm tubing. At points I and II the tube walls were made somewhat thicker (smaller inside diameter) to facilitate sealing.

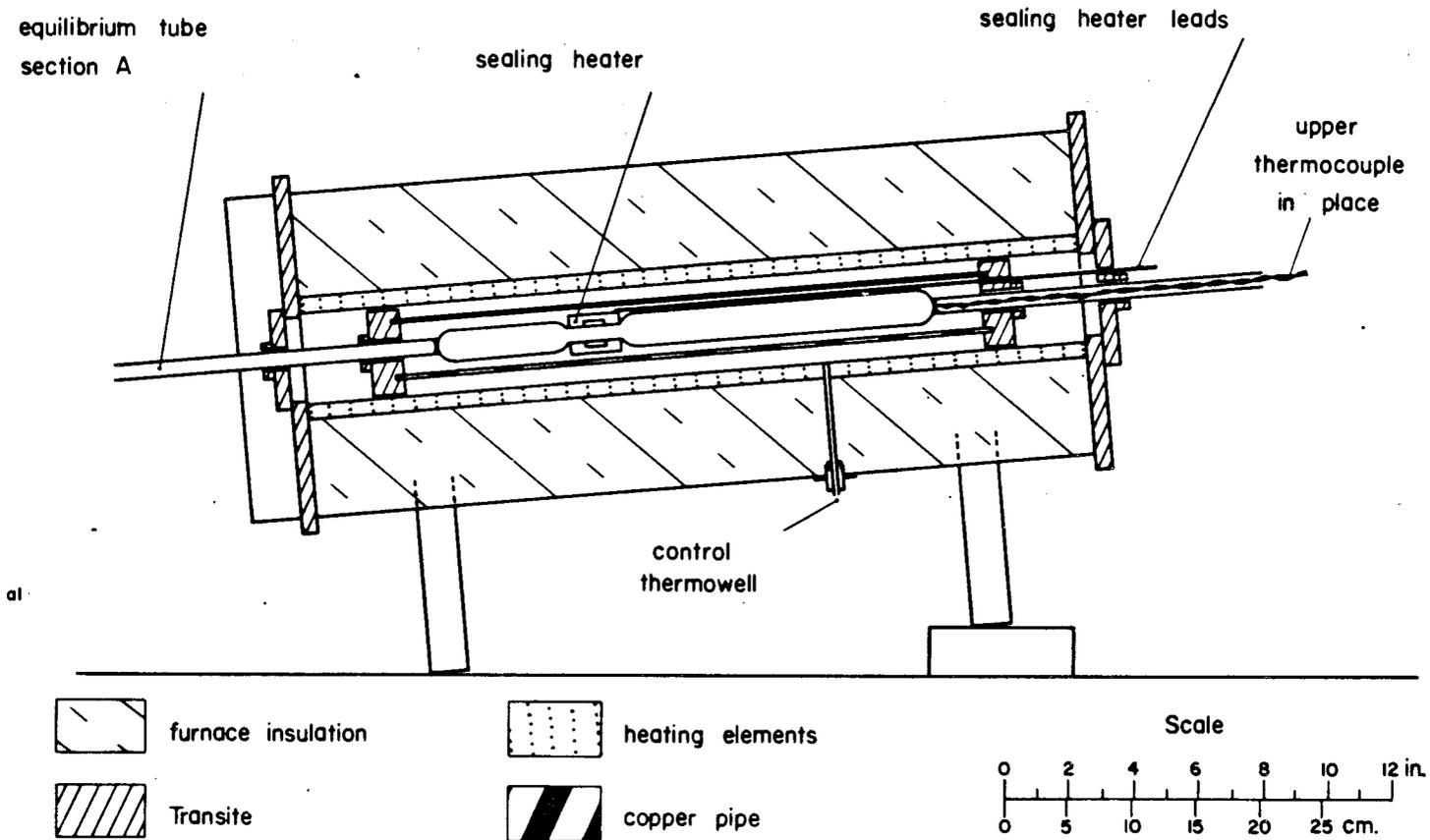
The filling apparatus is depicted in Figure 2. Polyethylene tubing connected pressure regulated chlorine and argon cylinders to a bubbler containing concentrated sulfuric acid. From this bubbler the flow was conducted through a drying tube filled with anhydrous calcium sulfate, through a 2 mm stopcock and into a 10 mm glass cross. On the opposite side of this cross was a three way 8 mm stopcock. One outlet of this stopcock vented to the atmosphere as a safety relief. The other outlet led through a dry ice-acetone cooled trap to the vacuum pump. Connected to the left arm of the cross by a short rubber tube was a tee constructed from nickel pipe and brass Swagelok fittings terminated with a compound gauge and a thermocouple gauge. The right arm of the cross was connected by a short

rubber tube to the equilibrium tube. The other end of the equilibrium tube was similarly connected through a 2 mm stopcock to a second sulfuric acid bubbler. The flow from this bubbler was exhausted from the laboratory. All stopcocks were lubricated with a fluorinated grease, and all glass-to-rubber connections were sealed with vacuum varnish.

The tube furnace (Hevi-Duty, 2 1/2 inch by 24 inch) in which the filled equilibrium tubes were heated is shown in Figure 3. The Transite ends of the furnace had been tapped to accommodate Transite end closures. Within the furnace was a 1 7/8 inch O.D. copper pipe with a 1/8 inch wall thickness. To prevent excessive oxidation at elevated temperatures this 18 1/2 inch length of pipe had been nickel-plated. Transite disks, slotted to fit the ends of the pipe, held it in the center of the furnace. The equilibrium tubes were held in place within the pipe and furnace by the extension of sections A and E through the Transite disks and end closures. Small circular Transite pieces held glass wool around the glass extensions where they passed through the Transite. A 1/8 inch nickel tube held to the outside of the furnace by a Swagelok fitting and extending to between two of the heating element wires served as a well for the control thermocouple. The entire furnace was slanted from the horizontal to establish a slight temperature gradient by convection along the length of the furnace.

Figure 3

CROSS-SECTION OF EQUILIBRATING FURNACE



Sealing section C of the equilibrium tube was accomplished by rapidly heating this section with a small nichrome wire heating coil and twisting the ends of sections A and E which extended from the furnace. The sealing heater consisted of about 15 cm of nichrome wire wound around the middle 15 mm of section C. To insulate sections B and D from this heater, asbestos paper strips were wound on either side of the coil. Several additional layers of asbestos paper encircled the heating coil. The asbestos paper, put in place while moist, formed a firm insulating enclosure around the heating coil when dried. The equilibrium tube could be rotated freely within this heater. The ends of the nichrome coil were crimped within 3/16 inch lengths of 1/8 inch nickel tubing to nickel plated copper wire leads. Ceramic thermocouple insulators protected the leads within the furnace. Each equilibrium tube was fitted with a new heater.

Temperatures were measured at points I and II by thermocouples which extended through equilibrium tube sections A and E that had been filled with glass wool. The outputs from the thermocouples were read on a Leeds and Northrup K-3 potentiometer or monitored continuously on a multipoint 0 to 1200°C Brown potentiometer. A water-ice cold junction was used when measuring with the K-3 potentiometer. The control thermocouple, connected to a 0 to 1200°C Brown circular scale potentiometric controller,

provided temperature control for the furnace. Electrical power was attenuated by a variable transformer between the controller and the furnace. Proper adjustment of the transformer reduced temperature cycling caused by the on-off control. The room in which the furnace was used was equipped with a thermostatically controlled heating system aiding in constant furnace temperature control over long periods.

Since pressure within the equilibrium tubes could not be measured the data were taken at a single temperature. This temperature (315°C) was chosen so that the total pressure within the tube was always less than one atmosphere. Sealing the tubes at section C was aided by this external pressure. The desired temperature of 315°C was maintained at point I in the tubes to within $\pm 1^\circ\text{C}$ on all runs. Slowly pulling a thermocouple through a glass wool-filled dummy tube which was at equilibrium within the furnace at 315°C showed a linear 2 to 3°C temperature rise from point I to point II. The two chromel-alumel thermocouples used in all measurements were calibrated at the melting point of potassium dichromate (397.5°C) and at the freezing points of tin (231.85°C) and lead (327.4°C). Calibrated values agreed to $\pm 1/4^\circ\text{C}$ (0.01 millivolt) with standard tables. Hence values from the tables were used.

Materials

The analysis and specifications for the hafnium, zirconium, chlorine and argon used are shown in Tables I and II. The hafnium, obtained from the Wah Chang Corporation, was in the form of finely broken metal sponge. Weighed samples of it were kept in stoppered sample bottles. The zirconium was obtained from the U. S. Bureau

Table I. Results of Spectrographic Analysis of Hafnium and Zirconium

| Impurity* | Hafnium | Zirconium |
|-----------|---------|-----------|
| Al | 30 | 30 |
| B | 0.4 | < 0.2 |
| Ca | 10 ** | 10 ** |
| Cd | 0.5 ** | 0.5 ** |
| Co | 0.5 ** | < 5 |
| Cr | 120 | <10 |
| Cu | 10 | 40 |
| Fe | 500 | 300 |
| Mg | >300 | 40 |
| Mn | 40 | <10 |
| Mo | 10 | <10 |
| Ni | 10 | 100 |
| Pb | 20 | <10 |
| Si | 40 | <20 |
| Sn | < 5 | < 5 |
| Ti | 20 | 20 ** |
| V | 20 ** | <20 |
| W | 40 ** | 500 |
| Zn | 50 ** | <50 |
| Zr | 2 to 5% | |

* Parts per million except where noted

** Not detected at this level

Table II. Gas Analysis

| Argon* | Results from two typical mass spectrographic analyses given by manufacturer. | |
|----------------|--|------|
| H ₂ | 0.5 ** | 1.0 |
| N ₂ | 5.0 | 15.0 |
| O ₂ | 9.0 | 2.0 |
| Hydrocarbons | 1.9 | 1.5 |
| Moisture | 1.6 | 1.0 |

* Supplied by Industrial Air Products Co.

** Parts per million

Chlorine*

Met Federal specifications BB-C-120, March 31, 1955,
99.5 percent Cl₂ by volume

One third of cylinder contents had been exhausted to remove
volatile impurities.

* Supplied by Pennsalt Corporation

of Mines in the form of a crystal bar. This bar was sawed into small pieces to facilitate eventual chlorination. To remove any contamination from the sawing, the small pieces were washed in approximately 1 N HCl, thoroughly rinsed in distilled water and dried. The dried pieces were weighed out and put with the hafnium to make up the desired samples.

Procedure

Preliminary tests were conducted to determine the experimental conditions and procedure (e.g., sample size, vacuum limits, tube size and equilibrium temperature) used in making the final runs, numbered 101 to 122. The following procedure was followed for each run.

Each equilibrium tube was immersed in a concentrated potassium dichromate-sulfuric acid bath for several hours, rinsed in distilled water and oven dried. A weighed sample of the hafnium and zirconium was placed in section A of the tube about one third of the way from point I, and the tube was sealed into the filling apparatus with vacuum varnish (see Figure 2). With stopcocks V_1 and V_3 closed and V_2 open, the tube was evacuated and checked for leaks. A leak rate of 0.5 micron per minute was the maximum allowed at a vacuum of five to ten microns. After closing stopcock V_2 the argon flow was started and stopcocks V_1 and V_3 were opened. When an argon flow of 50 to 100 cc per minute was established, the equilibrium tube was heated for 15 minutes with an oxyacetylene torch. After this the tube was again evacuated and heated. Finally, the argon flow was reestablished and chlorine was added. By carefully adjusting the two gas flow rates and heating section A the metal samples were slowly chlorinated, and the

chlorides condensed as a fluffy solid in chamber B. An excess of chlorine and low reaction rates were maintained to assure complete conversion to the volatile tetrachlorides. The greater part of the metal was chlorinated, but there always remained a very fragile oxide shell. Chlorine flow was then stopped, but the argon was allowed to purge for several minutes to remove any unreacted chlorine and, hence, protect the vacuum pump during the next step.

With the stopcocks appropriately adjusted the tube was again evacuated. Point II was fused with the gas torch, and sections C and D were gently heated while the tube was being evacuated. When a vacuum of five to ten microns was obtained point I was fused. The equilibrium tube, evacuated and sealed from point I to point II, contained pure hafnium and zirconium tetrachlorides in section B only.

When the filled equilibrium tube had been removed from the filling apparatus a sealing heater was assembled around it as has been already described. Being careful to keep all of the chlorides in section B the tube was placed in the equilibrating furnace as shown in Figure 3. The furnace was then heated slowly to 315°C as measured at point I. This heating was monitored with the K-3 potentiometer, and was conducted so that the temperature was never allowed to decrease from the highest attained value. This required a very slow rate of temperature increase when approaching 315°C.

Once the temperature reached 315°C the multipoint recorder was used to monitor both thermocouples. Checks were made at convenient times with the manual potentiometer. At these times the equilibrium tube was rotated in place ten to 20 revolutions to mix the solid phase.

After the equilibrium temperature had been maintained for the desired length of time (see Table III for the times used) the equilibrium tube was sealed at section C. This separated the solid section from the vapor section. This sealing operation began by applying 50 volts to the sealing heater and at the same time twisting and pulling equilibrium tube sections A and E where they extended from the furnace. A slight pull with three complete twists was sufficient to make the seal. Power to the sealing heater was shut off immediately after making the seal. The time required for the entire operation was less than 15 seconds.

Once the solid and vapor sections had been separated the furnace was cooled and the tube removed. Sections B and D were opened by breaking on either side of the seal in section C. Dilute hydrochloric acid was used to thoroughly wash the condensed chlorides from the two tube sections. It was added quite slowly to prevent overheating and splashing as the tetrachlorides dissolved. As much as 100 cc of the dilute acid was used for each chamber.

The individual solid and vapor samples were slowly evaporated to dryness as the oxychlorides.

Hafnium to zirconium ratios were determined on these samples by the analytical section of the U. S. Bureau of Mines Albany Station, using the method reported by Mortimore and Romans (14). As a check on the analytical results two special samples were submitted along with the experimental samples. These special samples were made by dissolving weighed amounts of the metals in a mixture of hydrofluoric and sulfuric acids. The volume of these acid solutions was reduced by evaporation, and ammonium hydroxide was added until the solutions were basic. After evaporating to dryness, these special samples were submitted as hydrolyzed tetrachlorides for analysis with the others.

RESULTS AND DISCUSSION

The experimental conditions and results are given in Table III. Of the twenty-one runs made, twelve were successfully completed. Difficulties were encountered when sealing the equilibrium tubes between the solid and vapor chambers at the end of a run. Six tubes were broken during sealing; two tubes were not completely sealed; and one tube was found not to have been completely closed when the tetrachlorides were put into it. Ten of the successful runs were held at 315°C for 48 hours or more. One tube was brought to 315°C from room temperature in about two hours and sealed immediately, and the last tube was held at 315°C for only six hours.

The data from the successful runs with the exception of run 120 are plotted in Figure 4, along with the theoretical curve.* Run 120 was sealed immediately upon reaching 315°C. The solid sample in this tube appeared much the same as it did before the tube had

* The theoretical curve was constructed from the equation:

$$(P_{\text{total}}) y_A = P_A x_A$$

where P_A is the vapor pressure of pure A at the given temperature

x_A is the mole fraction of A in the condensed phase

y_A is the concentration of A in the vapor phase

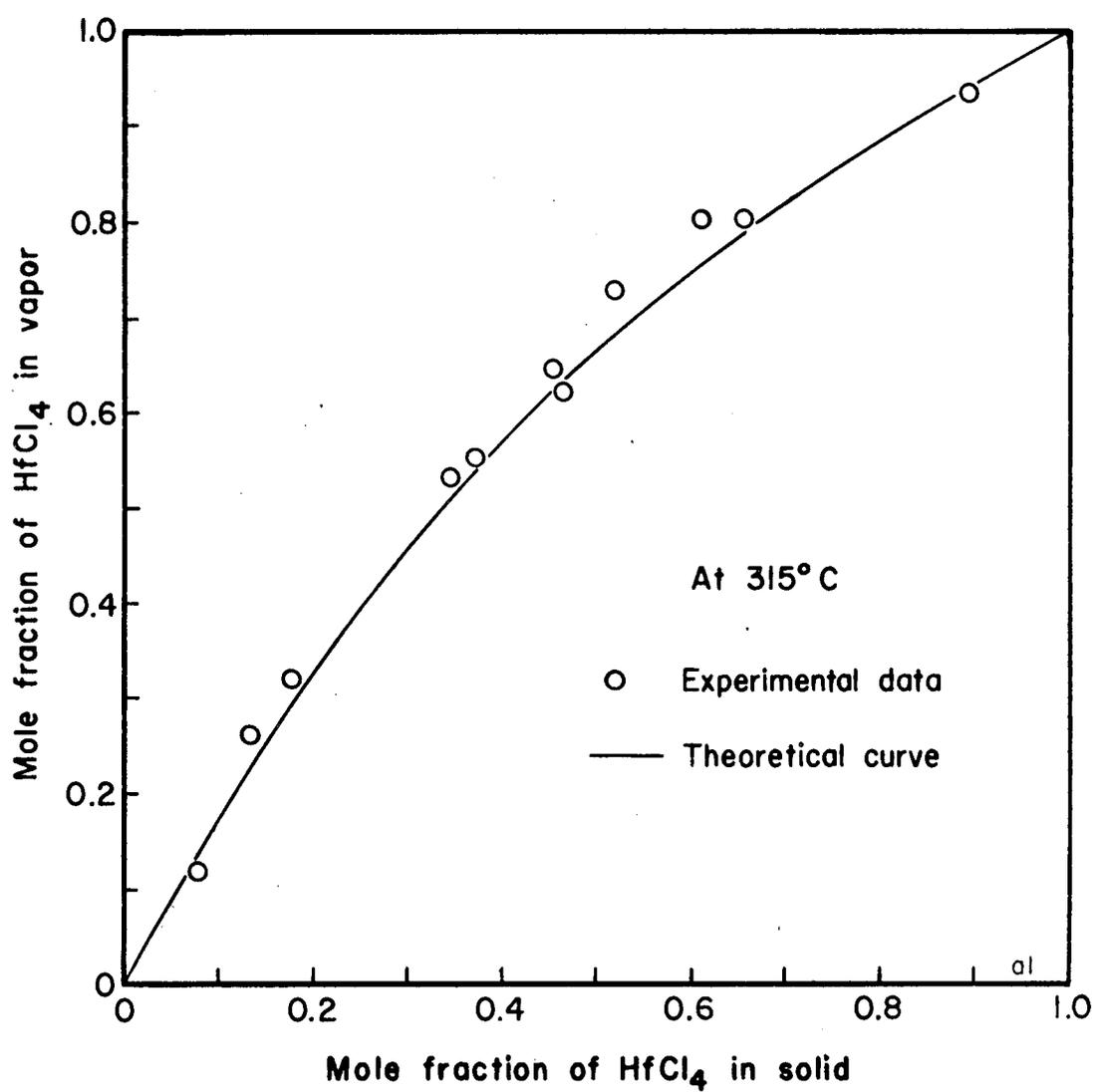
$$P_{\text{HfCl}_4} = 748 \text{ mm Hg and } P_{\text{ZrCl}_4} = 382 \text{ mm Hg at } 315^\circ\text{C (18).}$$

Table III. Experimental data

| Run No. | Original weight of metal (grams)* | | Solid sample | | Vapor sample | | Remarks |
|---------|-----------------------------------|------|--------------|------|--------------|------|--|
| | Hf | Zr | Analysis | Mole | Analysis | Mole | |
| | | | Hf/Hf+Zr | %Hf | Hf/Hf+Zr | %Hf | |
| 101 | 0.55 | 4.60 | | | | | tube broke upon sealing |
| 102 | 0.75 | 4.30 | | | | | tube broke upon sealing |
| 103 | 0.70 | 4.20 | 0.145 | 8.0 | 0.215 | 11.8 | 49 hours at 315°C |
| 104 | 1.20 | 4.00 | 0.233 | 13.5 | 0.410 | 26.2 | 50 hours at 315°C |
| 105 | 1.05 | 3.95 | | | | | seal not tight |
| 106 | 1.40 | 3.25 | 0.300 | 17.9 | 0.480 | 32.1 | 56 hours at 315°C |
| 107 | 1.50 | 3.55 | | | | | tube broke upon sealing |
| 108 | 2.50 | 2.45 | 0.510 | 34.7 | 0.690 | 53.2 | 54 hours at 315°C |
| 109 | 2.70 | 2.35 | 0.537 | 37.2 | 0.710 | 55.5 | 49 hours at 315°C |
| 110 | 3.10 | 1.80 | 0.630 | 46.5 | 0.763 | 62.2 | 48 hours at 315°C |
| 111 | 3.05 | 1.80 | | | | | seal not tight |
| 112 | 3.30 | 1.75 | | | | | leaking tube |
| 113 | 3.55 | 1.65 | 0.680 | 52.0 | 0.840 | 72.9 | 55 hours at 315°C |
| 114 | 3.95 | 1.00 | 0.810 | 61.2 | 0.904 | 82.8 | 50 hours at 315°C |
| 115 | 4.05 | 1.05 | 0.790 | 65.8 | 0.900 | 82.1 | 51 hours at 315°C |
| 116 | 4.10 | 0.95 | | | | | tube broke upon sealing |
| 117 | 4.00 | 0.85 | | | | | tube broke upon sealing |
| 118 | 4.55 | 0.60 | | | | | tube broke upon sealing |
| 119 | 4.65 | 0.30 | 0.945 | 89.8 | 0.965 | 93.5 | 55 hours at 315°C |
| 120 | 3.05 | 1.85 | 0.620 | 45.5 | 0.655 | 49.2 | tube sealed when temperature reached 315°C |
| 122 | 3.20 | 1.95 | 0.620 | 45.5 | 0.780 | 64.5 | 6 hours at 315°C |

* Determined to the nearest 0.05 gram

Figure 4
HfCl₄ - ZrCl₄
SOLID-VAPOR EQUILIBRIUM



been put into the equilibrating furnace. All of the solid samples in the other successful runs had migrated to the extreme lower end of the solid chamber and were more dense. From the appearance of this dense material it was evident that there had been a vapor transport of the solid during the equilibrating period and not just a sintering process. A complete vaporization and condensation of the solid due to the slight temperature gradient existing in the equilibrium tube would thus assure equilibrium. The results from run 120 differ from the theoretical curve by such an amount that it was not included in Figure 4 and it was assumed that the entire solid had not come to equilibrium with the vapor.

Data from the eleven meaningful runs show agreement with the theoretical curve. The data are, however, somewhat scattered. Results from the analytical check samples given in Table IV are within one percent of the calculated values if one assumes three percent zirconium in the hafnium. Similar accuracy for all the analyses would not account for most of the data scattering. Discrepancies in temperature measurement would not induce serious error because the ratio of the vapor pressures of the two chlorides is nearly independent of temperature near 315°C. Any change of composition of the solid phase due to the vapor contained in the solid chamber can be shown to be negligible when considering the solid sample size and the vapor density of zirconium tetrachloride (7).

One cause of experimental error could have occurred during the sealing operation. When section C of an equilibrium tube was heated for sealing, heat transfer to the solid sample could have produced some rapid vaporization. Such an effect had been reduced as much as possible by insulating the sealing heater and reducing the time necessary to make the seal. The actual sealing took no more than 15 seconds from the time the sealing heater was turned on, and it took from one to two minutes for a temperature rise due to sealing to be detected at point I by the lower thermocouple. Despite scatter in the data, the assumption of a Raoult's law-type behavior seems reasonable on the basis of the experimental results.

Table IV. Data for Analytical Check Samples

| Sample | Grams of metal used | | Analytical results Hf/Hf+Zr | Calculated values of Hf/Hf+Zr assuming 3% Zr in the Hf |
|--------|---------------------|-------|--------------------------------|--|
| | Hf | Zr | | |
| A | 0.871 | 0.758 | 0.515 | 0.519 |
| B | 1.167 | 0.304 | 0.768 | 0.765 |

The data obtained could be used for engineering design calculations for the separation of hafnium from zirconium by the

fractional sublimation of their tetrachlorides. However, in order to achieve equilibrium the solid phase must be completely vaporized and recondensed to overcome the slow mass transport in solids.

Such an operation might be carried out in a fluidized bed having a stepped configuration. The cross-sectional area of each stage would be larger than the one below. Inert bed particles would become segregated with the finer material in the upper sections. By carefully controlling the temperature at each stage, chloride vapor passing through a given section would partially condense on the bed particles. The increased weight of a particle due to condensation on it would cause the particle to fall to the next lower and hotter section where the condensate would be completely vaporized and the particle transported back to its originating stage. Although close temperature and flow control would be necessary, the fluid bed technique appears simpler than passing a train of material through alternating temperature areas. Finally, since there would be complete vaporization of the chlorides when going to a lower stage, each step would be an "ideal plate" and with a relative volatility of 1.9 (at 315°C) this separation scheme seems quite attractive.

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