~~SECRET~~

~~CONFIDENTIAL~~

ANL-4269

Chemistry-General

This document consists of 26 pages.

No. 18 of 121 copies, Series A.

ARGONNE NATIONAL LABORATORY

P. O. Box 5207

Chicago 80, Illinois

CLASSIFICATION CANCELLED

DATE 12-11-52

For The Atomic Energy Commission

H. F. Darnell

Chief, Declassification Branch ser

THE SEPARATION OF ZIRCONIUM AND HAFNIUM
BY A FRACTIONAL DISTILLATION METHOD

By

D. M. Gruen and J. J. Katz

Chemistry Division

W. M. Manning, Director

March 22, 1949

Operated by the University of Chicago
under

Contract W-31-109-eng-38

~~CONFIDENTIAL~~

THIS DOCUMENT CONTAINS
NEITHER RECOMMENDATIONS
NOR CONCLUSIONS OF THE
ATOMIC ENERGY COMMISSION

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Chemistry-General

<u>Distribution</u>	<u>Copy No.</u>
Argonne National Laboratory	1-21
Armed Forces Special Weapons Project	22
Atomic Energy Commission, Washington	23-24
Battelle Memorial Institute	25
Brookhaven National Laboratory	26-35
Bureau of Ships	36
Carbide and Carbon Chemicals Corporation (K-25)	37-40
Carbide and Carbon Chemicals Corporation (Y-12)	41-44
Columbia University (Failla)	45
General Electric Company, Richland	46-51
Hanford Operations Office	52
Iowa State College	53
Kellex Corporation	54-55
Knolls Atomic Power Laboratory	56-59
Los Alamos	60-62
Massachusetts Institute of Technology (Kaufmann)	63
Massachusetts Institute of Technology (Gaudin)	64
Mound Laboratory	65-66
National Bureau of Standards	67-68
Naval Radiological Defense Laboratory	69
NEPA Project	70
New York Operations Office	71-72
North American Aviation, Incorporated	73
Oak Ridge National Laboratory	74-85
Patent Branch, Washington	86
Sylvania Electric Products, Incorporated	87
Technical Information Division, ORE	88-102
UCLA Medical Research Laboratory (Warren)	103
University of California Radiation Laboratory	104-108
University of Rochester	109-110
Western Reserve University (Friedell)	111
Argonne National Laboratory, Inventory Unit	112-121

THE SEPARATION OF ZIRCONIUM AND HAFNIUM BY A FRACTIONAL DISTILLATION METHOD

D. M. Gruen and J. J. Katz

1. Introduction

Efficient separation of hafnium and zirconium has been a troublesome problem in inorganic chemistry since the discovery of hafnium. These two elements resemble each other as closely as two adjacent rare earth elements, and the differences in the chemical and physical properties of their compounds are in general so slight as to make separation difficult. The procedures which have received attention are largely analogous to those used for rare earth separations. Gmelin,¹ for example, lists fractional crystallization and precipitation methods; thermal decomposition of the fluorides; fractional distillation, sublimation or diffusion of the chlorides; and fractionation based on differences in ionic mobility as possible methods for obtaining separation. Recently two other processes have been proposed. The first involves ion exchange;² and the other solvent extraction with thenoyltrifluoroacetone as a chelating agent.³ A rather comprehensive literature survey of proposed methods has recently been prepared by E. Charney.⁴ No attempt will be made here to discuss the various procedures critically; however, it is felt that the method to be discussed here compares favorably with any described so far.

In 1924, van Arkel and DeBoer^{5,6} separated zirconium and hafnium by the fractional distillation of the complex compounds of zirconium tetrachloride and hafnium tetrachloride with phosphorus pentachloride or phosphorus oxychloride. The compounds in question were formulated by these workers as $2MCl_4 \cdot PCl_5$ and $2MCl_4 \cdot POCl_3$, where "M" is either Zr or Hf, the formulas being based on zirconium and chlorine analyses of the complexes. The preparation of the phosphorus pentachloride complex as described by van Arkel and DeBoer consisted in heating crude zirconium tetrachloride with approximately half its weight of phosphorus pentachloride at 200°C; the mixture fuses, and on heating to 300°C, a homogeneous brown or dark green melt was obtained. The $ZrCl_4 \cdot PCl_5$ complex as obtained after distillation is a colorless liquid boiling at 416°C without decomposition. This complex is reported to melt at 164.5°C; the solid forms a white, easily crystallizable mass. The phosphorus oxychloride complex was prepared in similar fashion by heating crude $ZrCl_4$ with $POCl_3$. This was described as a light green glass, melting to a transparent light green liquid which boils at 363-368°C.

Distillation experiments were carried out by van Arkel and DeBoer in a pyrex flask to which was sealed a 15 cm length of 4 cm tubing packed

with glass fragments. A series of fractions were collected and analyzed for hafnium both by the ultraviolet arc spectrum (in a vacuum spectrograph) and by the x-ray spectrum. Table 1 summarizes their results on the distillation of the phosphorus pentachloride compounds.

Table 1
Distillation Data of van Arkel and DeBoer
on $\text{MCl}_4\text{-PCl}_5$ Complex

Description of Sample	Temperature Range in which collected	% Hf
(Run 1. 1 Kg ZrCl_4 , 1/2 Kg PCl_5)		
Starting Material		1%
Vapor Fraction (a_1)	to 400°C	
Vapor Fraction (a_2)	to 414°C	
Residue (a_3)		
Vapor Fraction (b_1) from (a_1)	to 345°C	2%
Vapor Fraction (b_2) from (a_1)	345°-360°C	
Vapor Fraction (b_3) from (a_3) + (a_2)	361°-364°C (mostly POCl_3 complex)	
Vapor Fraction (b_4) from (a_3) + (a_2)	410°-415°C (no distillate between 364°-410°C)	
Vapor Fraction (b_5) from (a_3) + (a_2)	416°C	no Hf
Residue (b_6)		no Hf
Vapor Fraction (c_1) from (b_2) + (b_3) + (b_4)	345°-360°C	< 2%
Vapor Fraction (c_2) from (b_2) + (b_3) + (b_4)	363°-364°C	no Hf
(Run 2. (100 g ZrCl_4 (from Zirkit) + 200 g PCl_5)		
Fraction under 414°C		4%
Fraction above 414°C		< 2%

Table 1 (continued)

Description of Sample	Temperature Range in which collected	% Hf
(Run 3. 200 g $ZrCl_4$ (from Alvit) + 130 g $POCl_3$)		
Starting Material		10%
Vapor Fraction (a_1)	to 366°C	
Vapor Fraction (a_2)	366°-419°C	
Residue (a_3) (containing Fe)		<3%
Vapor Fraction after 4 further fractionations		20%

These experiments indicate that extensive separation of zirconium and hafnium can be achieved by this means. However, it is at once evident that the data are too scanty to permit even rough calculations of separation coefficients. Moreover, all of their experiments were carried out using mixtures of the oxychloride and pentachloride complexes. In view of the interesting results of van Arkel and DeBoer it appeared desirable to obtain more precise data on systems of known composition. Preliminary experiments showed that the phosphorus pentachloride complexes were much more difficult to work with than the oxychloride complexes. In the first place, the boiling points of the pentachloride complexes are 50° higher than the corresponding oxychlorides, secondly the pentachloride complexes appear to undergo slow decomposition on boiling contrary to the observation of van Arkel and DeBoer. It was decided, therefore, to concentrate on the more stable $POCl_3$ complexes and the work to be reported here concerns itself with these compounds.

2. Preparation and Vapor Pressures of $ZrCl_4$ - $POCl_3$ and $HfCl_4$ - $POCl_3$ Complexes

Preparation: - The reactants used in the preparation of the complexes were (a) sublimed zirconium tetrachloride (containing 2.5% hafnium based on the weight of zirconium) obtained from the Bureau of Mines; (b) reagent grade phosphorus oxychloride ($d = 1.675$); (c) hafnium oxide (99.9%) obtained from Chemical Commerce Co., Newark, N. J.; (d) reagent grade phosphorus pentachloride.

A. ZrCl₄-POCl₃ and ZrCl₄-PCl₅ Complexes.

To prepare the ZrCl₄-POCl₃ complex, a weighed, dried flask was placed in a dry box and the approximate amount of pulverized ZrCl₄ added. After removing the flask from the dry box it was weighed and enough POCl₃ was added to give a mole ratio of 1:1. A reflux condenser was affixed to the flask. Entry of moisture into the apparatus was prevented by a drierite-filled drying tube. After the short initial evolution of hydrogen chloride due to adsorbed moisture subsided, the mixture was heated until the excess POCl₃ refluxed. After refluxing for one-half hour the reaction was usually complete as evidenced by the formation of a homogeneous, dark-brown liquid phase. Excess POCl₃ was then removed by distillation; to insure complete removal of POCl₃, a vacuum was applied to the flask through a solid CO₂-acetone cooled trap while the complex was still molten. After cooling, the flask and complex were weighed, as well as the recovered POCl₃. Data on some typical runs are given in Table 2.

Table 2

Composition of ZrCl₄-POCl₃ Complex

Sample	ZrCl ₄ (g)	POCl ₃ (g)	Mole Ratio ZrCl ₄ /POCl ₃
1	40	20	1.3/1
2	80	40	1.3/1
3	428	197	1.4/1

The preparation of the PCl₅ complexes for preliminary experiments was carried out in an analogous way. Phosphorus pentachloride was added to ZrCl₄ until a 1:1 mole ratio was attained. The mixture was heated until a dark-brown liquid phase resulted. Meanwhile, excess PCl₅ sublimed and was trapped in an air condenser. No analytical weight data for this system are available at the present time.

B. HfCl₄-POCl₃ Complex.

This complex was prepared by heating hafnium dioxide with phosphorus pentachloride under pressure. The reaction in question is:

Into a piece of pyrex tubing (7 mm I.D., 12 mm O.D., 25 cm in length) were placed 1.85 g of HfO_2 and 4.10 g of PCl_5 , giving an oxide to chloride mole ratio of 1:3. The glass tube was sealed off under vacuum, placed in a stainless steel jacket and heated to 250°C in a furnace for 16 hours. At the end of this time, the contents of the tube were transferred to a distilling flask. The mixture was refluxed with 3 cc of POCl_3 for several minutes. Excess POCl_3 , as well as PCl_5 , were then removed by distillation. When the temperature rose to 350°C , the vessel to be used in the vapor pressure measurements was made the receiver of the distillation flask. About 2.9 g of complex were distilled, representing a yield of 65% based on the amount of HfO_2 used.

Vapor Pressure Measurements: - Vapor pressure measurements were made on the $\text{ZrCl}_4\text{-POCl}_3$ and $\text{HfCl}_4\text{-POCl}_3$ complexes in the apparatus shown in Fig. 1. The apparatus consisted of a 5 ml round bottom flask to which was attached a 15/30 standard taper female joint. A 15/30 standard taper running seal held a 2 mm glass finger extending 15 cm down the tube. The finger was closed at the bottom and served as a thermocouple well. Near the top of the tube were two side arms. One was connected to a U-type manometer and a nitrogen inlet. The other arm led to a vacuum pump through a trap. The measurements were made by refluxing about 3 grams of the complex and noting the reflux temperature. The apparatus was first swept with nitrogen. Next, the stopcock leading to the pump was opened and then quickly closed again. Refluxing was continued until the manometer remained constant. The new refluxing temperature and pressure were noted, and in this way, values of the boiling point at various pressures were obtained. These are summarized in Table 3. The plot of $\log P$ vs. $\frac{1}{T}$ is given in Fig. 2. Straight lines are obtained as demanded by the Clausius-Clapeyron equation. The heat of vaporization for both complexes is, therefore, calculated to be 20 ± 0.5 kcal; and Trouton's constant is 33. The boiling points at 760 mm are 355°C for the hafnium complex and 360°C for the zirconium complex. The measurement seems to be reproducible to $\pm 1^\circ\text{C}$. Since both the zirconium and the hafnium compound were measured in the same apparatus, the difference in boiling point is probably more significant than the absolute values.

FIG. 1. APPARATUS FOR MEASURING VAPOR PRESSURE OF HfCl_4 -
 POCl_3 AND ZrCl_4 - POCl_3 .

FIG. 2. VAPOR PRESSURE OF $\text{HfCl}_4\text{-POCl}_3$ AND $\text{ZrCl}_4\text{-POCl}_3$ COMPLEXES.

Table 3

Vapor Pressure Data for $\text{ZrCl}_4\text{-POCl}_3$
and $\text{HfCl}_4\text{-POCl}_3$ Complexes

P (atm.)	$\text{ZrCl}_4\text{-POCl}_3^*$		$\frac{1}{T^\circ\text{K}}$
	$^\circ\text{C}$	log P (atm.)	
0.990	360	-0.005	0.00158
0.899	356	-0.047	0.00159
0.707	347	-0.150	0.00161
0.512	334	-0.290	0.00165
0.278	313	-0.558	0.00171
0.171	298	-0.767	0.00175
0.092	281	-1.036	0.00181
	$\text{HfCl}_4\text{-POCl}_3$		
	$^\circ\text{C}$	log P (atm.)	
0.990	355	-0.005	0.00159
0.935	354	-0.030	0.00159
0.675	342	-0.172	0.00163
0.572	335	-0.243	0.00165
0.366	319	-0.438	0.00169
0.268	308	-0.572	0.00172
0.137	291	-0.864	0.00177
0.109	282	-0.962	0.00180

*These values are for $\text{ZrCl}_4\text{-POCl}_3$ containing 2.5 % Hf. They are, however, essentially the same for the pure complex, since this amount of hafnium impurity would lower the boiling point 0.1° , which is within the experimental error of the measurements.

3. Distillation Columns

Several different types of distillation columns were used, varying in complexity from a simple Claisen flask to a well-insulated, fifty unit Oldershaw column. The first experiments were conducted to determine roughly the separation coefficients of the complexes in various columns.

Unpacked Distillation Column: - This column (Fig. 3) consisted of a straight piece of 24 mm O.D. pyrex tubing of 55 cm overall length, with a male 29/42 standard taper joint at the top. About 30 cm from the top, an internal flanged piece of glass with slant edge served as a return spout. To the cap was fastened a thermocouple finger carrying at its lower end a small pyrex cup (10 mm O.D., 30 mm long), into which a funnel dipped to within about 2 mm from the bottom of the cup. During the distillation, the funnel was placed just below the return spout so that the new condensate went to the bottom of the cup, thereby displacing material from the top. It was possible in this way to collect equilibrium fractions. The column was heated by means of heating coils wound directly on it and it was found that the complex condensed in a region 5-10 cm above the return spout. Nitrogen was swept in a slow stream through the two sidearms near the top of the column during the distillation. The results of the distillation are discussed in the next section.

Helix Packed Column: - A more elaborate column consisting of a glass tube (30 mm O.D.) 30" long packed with 1/8" glass helices (Fig. 4) was also investigated. In filling the column, care was taken to separate the helices from each other so as to prepare a loose, pocketfree packing. A 100 ml round-bottom flask served as a boiler which was heated with nichrome heating elements. The head of the column was similar to that used in the differential distillation, with a cup and funnel arrangement placed below the return spout. The distillate was condensed in a 2' long glass section provided with nitrogen inlet and outlet tubes. The column was wrapped with nichrome ribbon (1/8" x .022", ca. 0.2 ohms/ft) encased in glass sleeving. Without insulation, refluxing conditions could be established only by heating the column; however, when the column was surrounded with a layer of magnesia pipe lagging, no external heating was necessary.

Oldershaw Column: - The last two columns to be tested were Oldershaw Bubble Plate Columns^{7, 8} made by the H. S. Martin Co., Evanston, Illinois. These columns consist of a series of perforated glass plates sealed into a tube at 1" intervals. Each plate is equipped with a baffle to direct the flow of liquid, a weir to maintain the proper liquid level on the plate, and a reflux return tube. The inner diameter of the column is 28 mm. There are 82 holes (0.9 mm) in each plate arranged in three concentric circles, through which ascending vapor must flow.

FIG. 3. DIFFERENTIAL DISTILLATION APPARATUS. FIG. 4. HELIX PACKED COLUMN.

thus bubbling through the liquid reflux. The first plate in the column serves as a small reservoir to maintain a liquid seal for the drain tube from the first regular distillation plate. Construction details have been described by Oldershaw.⁷

(a) The first Oldershaw column tested was a 10 plate section identical in every way with the helix packed column except for the nature of the distilling path.

(b) The second Oldershaw column had 50 physical plates with an actual distilling path of 55". Special care was taken in preparing it for operation and a detailed description of this column is given here. A cross-section through the completed column is shown in Fig. 5. The boiler consisted of a 500 cc round-bottom flask sealed to the lower end of the column; the flask was fitted with a male ball joint for introducing material into the column, withdrawing samples, and as a thermometer well during distillation. The condenser consisted of a 2' length of 1" tubing sealed at an angle of 135° to the barrel of the column. A thermocouple well could be inserted into the condenser through the 29/42 standard taper joint. Nitrogen inlet and outlet tubes were provided near the top of the condenser. For takeoff, a 5" length of 1 mm capillary fitted with a 12/30 running seal was sealed to the underside of the condenser. This takeoff device was adopted in view of the lubrication problems posed by conventional stopcocks and joints. For total reflux, it was necessary simply to freeze a solid plug of the complex in the capillary by directing a jet of air against it. When a sample was to be taken, the plug was melted with an infrared heat lamp. Condensate then dripped into the receiving flask. The rate of collection could be controlled after a fashion by regulating the power supplied to the heat lamp. Alternatively, smaller capillaries may be used. The column itself was supported on a metal rack by a heating mantle in which the boiler rested, and a three-prong clamp fastened to the middle of the condenser. The boiler heating-jacket was a Quartz Hemispherical Glas-Col Mantle with a maximum temperature rating of 650°C. At the first and every tenth succeeding plate were placed iron constantan thermocouples (No. 30, B and S gauge, glass covered Duplex) by tying them with asbestos string to the barrel of the column. The barrel was then wrapped with a layer of 0.1 mm aluminum foil. Next, 1" I.D. corrugated asbestos pipe covering (Air Cell) was cut into 15" lengths. Each length was threaded along the middle corrugation with 1/8" x .022" nichrome ribbon (~0.2 ohms/ft). Approximately 7' of ribbon were used per section. Four such sections were placed on the column after having been previously baked out. The current leads were insulated by covering them with glass sleeving to prevent shorts. The first section rested on a small transite platform placed about 4" above the boiler. The succeeding sections rested on the lower ones with a sheet of asbestos paper between each. A layer of aluminum foil (0.05 mm) was wrapped around the pipe

FIG. 5
DISTILLATION COLUMN FOR ZIRCONIUM-HAFNIUM SEPARATIONS.

covering. Next, 3" I.D. half-cylinders of 85% magnesia pipe covering were encased in 12" wide aluminum foil (Reynold's household variety). Two lengths of lagging were used to enclose completely the asbestos covering. The slits in the magnesia pipe were covered with a strip of asbestos tape. The thermocouple leads were soldered to a double pole multiple throw switch, with common leads to a Rubicon potentiometer. The leads from each of the four heater sections along the column were connected to separate variacs as were also the leads from the quartz mantle, the infrared lamps and an air-blower used to cool the condenser. The very top and bottom of the columns were insulated with glass wool and covered with aluminum foil.

4. Distillation Results

In order to indicate the degree of separation effected by distillation, data are given here for each of the columns tested. Table 4 summarizes results obtained with the three short columns described above. In all of these experiments, the vapor fractions were collected in an internal cup under approximate equilibrium conditions; at intervals samples were taken from the boilers. Because of their preliminary nature, these runs are not further discussed.

Table 4

Distillation Data for Various Short Columns

Per Cent Hafnium in Zirconium						
Per Cent Complex Distilled	1 Unpacked Column		2 Ten Plate Oldershaw		3 Helix Packed Column	
	Vapor	Residue	Vapor	Residue	Vapor	Residue
0		2.5		2.5		2.5
5		2.5	4.4		4.9	
15					3.1	
25			3.7			
35		2.0	2.3	1.4	2.4	1.2
40						
50		1.6				
95		1.2				

Distillation in the Fifty-plate Oldershaw Column: - A more extended description of distillation in this column is in order. The column was prepared for use by washing it with 2 liters of Barnstead distilled water. The water was siphoned off at the bottom and the column pumped out under vacuum. Nitrogen was then blown through for several hours while the column was being heated to 65°C. The 500 ml flask in which 625 grams of complex had been prepared was attached to the column boiler flask by means of an adaptor and 600 grams of complex distilled into the reservoir through the sidearm. The transfer was completed in 30 minutes. A thermocouple was then placed in the well which in turn rested in the molten complex. During this run the column heater units were not utilized. The rise of the refluxing zone in the column was noted by means of the thermocouples along the barrel of the column. With the variac controlling the boiler heating mantle at 125 units (130 units = full scale), it took one hour for complex to distill to the top of the column. The temperature of the boiling liquid was 362°C, that of the refluxing zone, 359°C. Refluxing was continued for two hours before taking a sample. The temperatures of all thermocouples remained sensibly constant during the entire run. It may be pointed out that a temperature gradient of 300° existed between the inside of the column and the outer insulation. By using the heaters to compensate for heat losses, more efficient fractionation would probably be realized.

The first sample was collected by unfreezing the solid plug in the capillary and allowing complex to drip into a weighed 25 ml flask. Collection of a sample took from 15-30 minutes, and the column was operated at total reflux for 45-90 minutes between each sample. Eight vapor fractions were collected in this way. The boiler content was sampled after the 4th and the 8th fractions. (A density determination on the last fraction was made by collecting about 15 cc in a graduate. A value of 2.1 was obtained for the density of the liquid complex.) Table 4 gives the pertinent data regarding this run. An examination of Table 4 reveals that the hafnium content of zirconium may be reduced from 2.5% to 0.12% by distilling 40% of the complex through a 50 plate Oldershaw column. About 70% of the original hafnium content is found in the first 10% of distillate. It is of interest to follow the change in the hafnium content of the residue as a function of the percentage of complex distilled. For this purpose, one may calculate the composition of the residue from the amount of hafnium originally present and that found in the distillate. The results of such a calculation appear in the last column of Table 5 and graphically in Fig. 6.

Calculation of Hafnium Content of Residues: - The validity of the calculation is based on a hafnium mass balance of 99%. A few words about the mass balance calculations are desirable since the calculation is indirect. The pile method of analysis (Section 6) yields results of per cent by weight of hafnium in zirconium on the basis of the elements. To find

Table 5

Fractionation of $ZrCl_4$ - $POCl_3$ Complex
in a Fifty-plate Oldershaw Column

Fraction	Per Cent Distilled	Weight of Fraction (g)	Per Cent Hafnium in Fraction ^{a)}	Weight of Hafnium in Fraction ^{b)} (g)	Per Cent Hafnium in Residue ^{a),c)}
1	5.5	33.6	18.9 (17.1)	1.74	1.44
2	11.5	35.9	10.4	1.01	0.77
3	17.5	35.0	5.2	0.48	0.36
4	23.5	37.2	1.7	0.12	0.29
Residue 4A	23.5				0.13 (0.24) ^{d)}
5	26.8	18.5	1.0	0.05	0.26
6	31.8	30.7	1.4	0.12	0.17
7	35.3	19.9	0.94	0.05	0.13
8	41.7	39.0	0.25	0.02	0.12
Residue 8A	41.7	350		0.12	0.11 (0.12) ^{d)}
Total Grams of Hafnium Found in Vapor Fractions and Residue				3.71	
Original Charge	0	600	2.5 (1.5)	3.77	

a) Based on weight of zirconium. Figures in parentheses are by spectrographic analysis.

b) Calculation in text.

c) Calculated from composition of vapor fractions.

d) Direct analysis of residue in boiler.

FIG. 6. ZIRCONIUM PURIFICATION CURVE.

FIG. 7. VALUES OF RAYLEIGH " α 's"
I UNPACKED COLUMN; II HELIX-PACKED COLUMN; III 10-PLATE OLDERSHAW; IV 50-PLATE OLDERSHAW.

the grams of hafnium in a given weight of complex, the following method has been used. Let X and Y be the grams of zirconium and hafnium as elements in a given weight of complex. Assuming a formula $1.5 \text{ MCl}_4 \cdot \text{POCl}_3$ (see Table 2) for the pure complex compounds, the zirconium complex contains 27% zirconium and the hafnium complex 42% hafnium. Then,

$$(1) \frac{X}{0.27} + \frac{Y}{0.42} = \text{weight of a mixture of the two complexes.}$$

$$(2) \frac{Y}{X + Y} \cdot 100 = \% \text{ Hf as metal in a mixture of complexes.}$$

Solving these equations for Y gives the weights of zirconium and hafnium as metal in a given weight of complex when the hafnium-zirconium ratio is known.

5. Separation Coefficients and Theoretical Plates

An analysis of the $\text{ZrCl}_4 \cdot \text{POCl}_3$ distillations on the basis of the results given in the previous sections may now be made.

The quantities that are of particular interest are the separation coefficients and the number of theoretical plates found in each column. The overall separation coefficient, " α ", may be calculated by means of the Rayleigh equation:⁹

$$\ln \frac{M_1}{M_2} = \frac{1}{\alpha - 1} \ln \frac{x_1(1-x_2)}{x_2(1-x_1)} + \ln \frac{(1-x_2)}{(1-x_1)}$$

where M is the moles of liquid remaining in the still at any given time during the distillation; x is the mole fraction of one of the components. This equation reduces to

$$\ln \frac{M_1}{M_2} = \frac{1}{\alpha - 1} \ln \frac{x_1}{x_2}$$

without introducing appreciable errors, since in this case if x_1 and x_2 are the mole fractions of hafnium in the residue at different times during the distillation, the fractions $\frac{1-x_2}{1-x_1}$ are never far from unity. It is also seen that before the introduction of limits the equation is simply

$$\ln M = \frac{1}{\alpha - 1} \ln x + C.$$

A plot of $\ln M$ vs. $\ln x$ should, therefore, give a straight line of slope $\frac{1}{\alpha - 1}$. Graphs of this type are given in Fig. 7 for the various distillations. The composition of the residues was determined in some instances by direct sampling, and in the majority of cases by mass balance calculations (see previous section) based on the amounts of hafnium initially present and the amount in the distillate. The α 's determined in this way are given in Table 6.

Table 6

Values for the Separation Factor α in Different Distillations*

Experiment	α	Number Theoretical Plates	T.P.-1	Length of Distillation Path	H.E.T.P. (cm)
Unpacked Column	1.6	3.7	2.7	25 cm	9.3
Ten-plate Oldershaw	2.6	7.5	6.5	28 cm	4.3
Helix Packed Column	2.9	8.4	7.4	75 cm	10
50-plate Oldershaw: Overall	9.0	17.3	16.3	138 cm	8.5
In range 2.5-0.25% Hf	10	18.2	17.2	138 cm	8.0
In range 0.25-0.10% Hf	8.0	16.4	15.4	138 cm	8.9

* The α 's determined in this way are approximate only since column hold-up was not taken into consideration. It is felt that they are within 20% of the actual values. Similar considerations apply to the calculations based on the α -values.

The separation coefficient for a single plate, " α_0 ", is defined as the ratio of the vapor pressures of the pure hafnium and zirconium complexes at the boiling point of the mixture. This ratio may be calculated by means of the Clausius-Clapeyron equation by using the vapor pressure data previously obtained. (Sec. 2.) The value for " α_0 " thus calculated is 1.14. One may now calculate the number of theoretical plates in the various columns by the formula:

$$\alpha = \alpha_0^n$$

$$n = \text{No. of theoretical plates} = \frac{\log \alpha}{\log \alpha_0} = \frac{\log \alpha}{0.055}$$

The values obtained from this expression are given in row 3 of Table 6. The H.E.T.P. for these columns may be obtained by dividing the length of the distillation path by the number of theoretical plates minus one in the column, or

$$\text{H.E.T.P.} = \frac{\text{Length of distn. path}}{\text{No. theor. plates} - 1}$$

Row 4 of Table 6 gives the theoretical plates minus one (i.e., not counting the vapor-liquid boundary in the boiler) in the column, and row 5 of Table 6 gives H.E.T.P.'s of each column. The H.E.T.P. of the Oldershaw Column is about 4.2 cm for ordinary organic liquids.⁸

The fractional distillation procedure offers an opportunity to prepare not only pure zirconium, but pure hafnium as well. When one is interested in operating the column as an enriching rather than a stripping column, the separation coefficient " α " is related to the concentrations of hafnium in boiler and distillate by the formula:

$$\frac{(X_d)(Y_b)}{(X_b)(Y_d)} = \alpha$$

where X_d and X_b are the mol fractions of the hafnium complex in distillate and boiler respectively; Y_d and Y_b are the corresponding mol fractions of zirconium complex. This equation may be derived from Raoult's Law. When actual values are substituted into the above equation, a curve shown in Figure 8 results. The " α " was assumed to be 10, the value obtained for the 50-plate Oldershaw column used in this distillation. Inspection of the curve shows that a mixture of 2.5% hafnium in zirconium should yield a distillate containing 17% hafnium; a mixture containing 17% hafnium should yield a distillate containing 72% hafnium, etc. Thus, by repeated distillations of enriched fractions, essentially pure hafnium may be obtained.

6. Conversion of Complex and Some General Observations

It has been the usual practice to convert the oxychloride complexes to oxide by hydrolysis with sodium hydroxide. No systematic data on the phosphorus content of the oxide have been obtained, and in general no detailed study of the hydrolysis has been made. According to van Arkel and DeBoer, zirconium oxide essentially free of phosphate can be obtained, and the present work indicates that this may be so. Further, we have observed that the complexes dissolve in absolute ethyl alcohol with the evolution of heat. Addition of water results in a clear solution from which a flocculant precipitate separates on addition of ammonium hydroxide. This precipitate dissolves completely in HCl or HNO₃, the latter solution giving no test for phosphate with molybdate reagent. A heavy phosphate precipitate, however, is obtained when the supernatant liquid is treated with ammonium molybdate after boiling with concentrated H₂SO₄ and HNO₃. This procedure may be useful for converting the complexes to oxide.

It is well known that phosphorus pentachloride is a powerful chlorinating agent for metal oxides. This suggests the possibility of using it to open zirconium ores such as zirkite or baddeleyite.

FIG. 8. HAFNIUM ENRICHMENT CURVE FOR A COLUMN WITH " α " = 10.

This reaction would yield the oxychloride complex directly which could then be purified by distillation. If a convenient method for decomposing the complex to $ZrCl_4$ or $ZrCl_3$ is discovered, this sequence might have a number of advantages compared to the present Bureau of Mines process. Work along these lines is contemplated.

7. Methods of Analysis

Two methods of analysis were used. The first depends upon a 19 sec hafnium activity induced by thermal neutrons,¹⁰ the other on the ratio of intensities of certain lines in the emission spectra¹¹ of zirconium and hafnium.

Approximately one-milliliter samples of the melted complex were hydrolyzed with 20% sodium hydroxide. After the initial reaction subsided, the mixture was heated on a hot plate for 20 minutes, and the slurries transferred to 15 ml centrifuge cones. The supernatant liquid was discarded after centrifugation, and the precipitates were washed with distilled water and re-centrifuged. About 7 cc of concentrated hydrochloric acid was added to each tube, the precipitates stirred and heated for 15 minutes. Any insoluble material remaining was separated from the acid solution by centrifugation. The hydrochloric acid solutions were treated with concentrated ammonia until a permanent precipitate appeared. This was centrifuged, washed twice with water, and dried in an oven at 110° for 2 hours. Samples of the dried material were submitted for spectroscopic analysis and the results reported in terms of (grams Hf/grams Zr) x 100.

In order to prepare the samples for pile analysis, the dried precipitates were ignited in porcelain crucibles at 1100° for 15 minutes to yield the mixed dioxides. The ignited oxides were ground in a mullite mortar, and 2-milligram samples were weighed on to a clean, dry Puron iron disk. The solid was spread uniformly over the disk by stirring with 2 drops of Zapon, using a pointed probe. The samples were irradiated in the rabbit of the Argonne Pile for 10 seconds at 250 Kw power level. The induced activity on the bombarded disk was determined by an ionization chamber, usually not later than 10-15 seconds after removal from the flux field. The decay curve was followed for about two minutes with a strip-chart recorder. Logarithmic plots extrapolated to zero time gave the initial activity of each sample, and this can be compared with the activity of standards. Hafnium concentrations were based on the value 133 relative "ionization current" units per milligram Zr at zero time for zirconium containing one per cent hafnium by weight as element. Some analytical results are listed in Table 7.

Table 9

Pile Analyses for Hafnium in Zirconium
for Distillation in Fifty-plate Oldershaw

(1% Hf in 1 mg Zr = 133 relative "ionization current" units)

Sample	Weight of Sample (mg)	Relative Units Zero Time	Relative Units per mg	Per Cent Hf in Zr
Initial Material	2.13	700	329	2.5
Vapor Fractions				
1	2.50	6000	2400	18.9
2	2.27	3100	1368	10.4
3	2.21	1500	680	5.2
4	2.58	560	217	1.7
5	0.75	100	133	1.0
6	2.32	440	190	1.4
7	2.18	270	123	0.94
8	2.47	85	34	0.25
Residue after 4th Fraction	2.93	50	17	0.13
Residue after 8th Fraction	2.63	42	16	0.12
	2.63	42	16	0.12
	2.63	35	13.7	0.10
				0.11 av.

Acknowledgment: - Our thanks are due to E. der Mateosian for his cooperation in obtaining the pile analyses, and to S. Untermyer for bringing this problem to our attention.

Summary

1. It has been shown that the hafnium content of zirconium may be decreased from ~2.5 per cent to ~0.11 per cent by fractional distillation of 40 per cent of a mixture of complexes of the type $MCl_4 \cdot POCl_3$ (where M is either Hf or Zr) in a 1" Oldershaw Column containing 50 physical plates. Structural details for a suitable column are given.
2. The vapor pressures of the $ZrCl_4 \cdot POCl_3$ and $HfCl_4 \cdot POCl_3$ complexes have been measured in the range 1.0-0.1 atm, and 20.5 ± 0.5 Kcal has been calculated for the heats of vaporization of the complexes. The boiling points at 760 mm are 355 and 360°C for the hafnium and zirconium complexes respectively.
3. A separation factor " α " of 1.14 has been calculated for the zirconium and hafnium complexes on the basis of the vapor pressure data.
4. On the basis of gravimetric data, the literature formula $2MCl_4 \cdot POCl_3$ for the complexes has been rendered doubtful.
5. Four distillation columns have been compared with regard to efficiency of separation by calculating separation coefficients, numbers of theoretical plates and H.E.T.P.'s for each.
6. The possibility of preparing pure hafnium compounds by repeated distillation of enriched fractions has been indicated.
7. A proposed process for zirconium-hafnium separation starting with ore is briefly discussed.

References

1. Gmelins Handbuch der Anorganischen Chemie. System No. 43, 1941.
2. K. Street and G. T. Seaborg, J. Am. Chem. Soc. 70, 4268 (1948).
3. E. H. Huffmann and L. I. Beaufait, UCRL-194, Oct. 7, 1948.
4. E. Charney, N.Y.D.O. 36.
5. A. E. van Arkel, J. H. DeBoer, Z. anorg. chem. 141, 289-296 (1924).
6. A. E. van Arkel, J. H. DeBoer, U. S. Patent 1,582,860. April 27, 1926.
7. C. F. Oldershaw, Ind. Eng. Chem. Anal. Ed. 13, 265 (1941).
8. F. C. Collins and V. Lantz, Ind. Eng. Chem. Anal. Ed. 18, 673 (1946).
9. Walker, Lewis, McAdams and Gilliland, "Principles of Chemical Engineering," p. 533. The equation holds for binary mixtures obeying Raoult's Law.
10. E. der Mateosian, private communication.
11. C. Feldman, AECD-2342.