


AN ABSTRACT OF THE THESIS OF

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Title: ANALYTICAL UTILIZATION OF HAFNIUM AND ZIRCONIUM  
BOROHYDRIDES

Abstract approved:

  
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The borohydrides are the most volatile known compounds of hafnium and zirconium and consequently have potential analytical utility. The determination of hafnium and zirconium in the presence of each other has long been a difficult assignment and there are a limited number of good analytical methods. The borohydrides are reviewed and a study made of their analytical utility.

Apparatus has been devised to prepare and store the metal borohydrides.

Conventional thermal electron bombardment mass spectrometry is not satisfactory for zirconium borohydride because of the compounds' thermal instability.  $Zr^+$ ,  $ZrH^+$ , and various doubly charged species in the  $m/e$  60-70 region have been found.

Apparatus and methods are developed for the analytical hydrolysis of the metal borohydrides and their mixtures. Zirconium borohydride is quantitatively hydrolyzed ( $99.97 \pm 0.14\%$ ) and hafnium

borohydride incompletely hydrolyzed ( $97.80 \pm 0.68\%$ ) to hydrogen gas in aqueous 3 N hydrochloric acid. The formation of diborane observed in the incomplete hydrolysis of pure hafnium and zirconium borohydrides is indicative of at least a two step hydrolysis reaction: first a fast step producing diborane and hydrogen; secondly a slow hydrolysis of diborane. The hydrolysis method is applied to the analysis of hafnium/hafnium + zirconium ratios ( $\times 100$ ) in the range 1 to 11% with an accuracy of  $\pm 0.2\%$  absolute.

Analytical Utilization of Hafnium and Zirconium Borohydrides

by

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# ANALYTICAL UTILIZATION OF HAFNIUM AND ZIRCONIUM BOROHYDRIDES

## INTRODUCTION

The determination of hafnium and zirconium in the presence of each other has long been a difficult assignment. There are a limited number of good analytical methods.

The borohydrides are the most volatile known compounds of hafnium and zirconium and consequently have potential analytical utility. Very little work has been done with the borohydrides and no critical studies have been made of their analytical utilization.

Apparatus first had to be devised to prepare and store the metal borohydrides. The mass spectrometry of zirconium borohydride was then studied in the hope of finding an analytical method as well as structural information. Apparatus and methods were developed for a study of the analytical hydrolysis of the metal borohydrides and their mixtures. Application was then made to the analysis of hafnium zirconium ratios.

## BACKGROUND

Hafnium and Zirconium: Individual and Combined Determination

Zirconium is one of the more abundant metals on the surface of the earth. Almost all the known ores and compounds of zirconium contain 1 to 3% hafnium/hafnium + zirconium. The major use of zirconium metal is as a structural material for nuclear reactors. Zirconium is well suited for nuclear reactors because it has a low neutron (thermal) capture cross section and is nonreactive in corrosive nuclear reactor environments. Hafnium has a high neutron capture cross section and must be removed from reactor grade zirconium. The by-product hafnium finds use as control rods in nuclear reactors.

The determination of hafnium/hafnium + zirconium ratios is important in hafnium and zirconium separation procedures. Hafnium and zirconium have virtually identical chemical behaviors. There are almost no known qualitative differences in their chemical reactivity, and their quantitative separation is achieved with difficulty. The unusual similarity of the chemical behaviors of the two elements has not been completely explained, but is partially due to their similar peripheral electron configurations and virtually identical ionic radii.

The quantitative analysis of hafnium and zirconium is of particular interest to the present research. A brief critique of the nature and aspects of the methods is given below. Hahn (20), Elinson and Petrov (13), and Goward and Jacob (16) have published extensive reviews of the analytical chemistry of hafnium and zirconium.

Typically hafnium and zirconium are determined together because a distinction between them is not necessary. Hafnium is almost always in the 1 to 3% range of the total metal. These methods are considered semiquantitative and are not of especial interest.

Hafnium and zirconium are commonly separated from other elements by solvent extraction, ion exchange, and/or precipitation methods. Once hafnium and zirconium are separated from other elements they may be conveniently separated from each other by anion exchange. An excellent separation method of hafnium from zirconium by anion exchange was reported by Hague and Machlan (18). The methods considered semiquantitative above would be quantitative and perhaps of interest if only hafnium or zirconium were being dealt with.

The quantitative methods which deal with mixtures containing hafnium and zirconium (i. e., not separated) are generally divided into three categories: direct chemical methods; the physical property methods; the indirect methods. The direct chemical and physical property methods distinguish between hafnium and zirconium, whereas

the indirect methods give the ratio of hafnium to zirconium. These methods are described below.

### Xylenol Orange

Xylenol orange is a sensitive reagent for hafnium and zirconium in an acid medium, forming intensely red complexes. Hydrogen peroxide can completely mask the zirconium complex, but barely affects the hafnium complex. Hydrogen peroxide does not affect the xylenol orange complex of hafnium in the presence of sulfate. The spectrophotometric determination of 1  $\mu$ mole/25 mls of total hafnium and zirconium in 0.2 N  $\text{HClO}_4$  may be performed at 530  $\text{m}\mu$  using a 2:1 molar excess of xylenol orange. First the total absorbance of the xylenol orange complexes are determined without peroxide and sulfate, and secondly the absorbance of hafnium alone by the addition of both peroxide and sulfate. Zirconium is obtained by the difference in absorbance. The concentration of each metal is obtained from calibration standards run under the same conditions. This represents the first method whereby hafnium and zirconium can be chemically determined together in trace amounts without prior separation. This method should be reliable for the determination of hafnium or zirconium, or both in 5-95% mixtures of one in the other. This method can probably be improved upon by use of semixylenol orange (35), but

no data are yet available. The method has been criticized (35), but should not deter from its validity.

### Emission Spectroscopy

Fassel and Anderson (14) have developed a quantitative spectrographic method for the analysis of hafnium and zirconium mixtures where the hafnium/zirconium ratio varied from 0.001 to 100. The method depended on: careful selection of internal standard line pairs (only intensity ratios in the region 0.6 to 1.7 were measured to reduce experimental error); refined methods of photographic photometry; a controlled type discharge operated under conditions where extraneous influence and reversal effects are minimized. The use of pellets of powdered graphite and the mixed oxides (even prepared from oxides heated to 125 °C) as the matrix of excitation is emphasized. The results compare very favorably in accuracy and precision with the chemical selenite method.

Gray and Fassel (17) developed a spectroscopic method for 10-5000 ppm zirconium in hafnium where a direct carbon arc or a conducting briquette technique is used with the mixed oxides. Acceptable internal standardization was achieved by the proper choice of zirconium-hafnium line pairs. The precision and accuracy of the method was around 10%.

A method similar to that for low level zirconium in hafnium is

available for low level hafnium in zirconium.<sup>1</sup> A conducting briquette technique is used with the oxides. A high voltage AC spark excitation of the briquette allows a 10% accuracy and precision in the 25-1000 ppm hafnium in zirconium range.

#### X-ray Emission (Fluorescence)

Mortimore and Romans (33) have developed an x-ray spectroscopic method for the analysis of mixtures of hafnium and zirconium oxides now applied<sup>2</sup> in the range 0.1 to 99.9% hafnium/hafnium + zirconium. The method is based on two working curves. The first plots the logarithms of the intensity of the intensity ratios of ( $\text{HfL}_\beta$ , first order/ $\text{ZrK}_\beta$ , second order) against the logarithms of several standard samples and is useful in the range of hafnium/hafnium + zirconium ratios from 0.001 to 0.04. The second plots the logarithms of the intensity ratios of ( $\text{ZrK}_\alpha$ , first order/ $\text{HfL}_\beta$ , first order) against the logarithm of several standard samples and is useful in the range of zirconium/zirconium + hafnium ratios from 0.001-0.6. The method is rapid, requiring 5 to 10 minutes per oxide sample and is one of the most valuable analytical techniques for the analysis of

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<sup>1</sup>Personal communication. Mr. Gary Beck, Chief spectrographer, Wah Chang, Albany. Albany, Oregon.

<sup>2</sup>Ibid.



the hafnium and zirconium in the presence of each other. The method has an accuracy of 7% in the 0.001-0.01 ranges, 3% in the 0.01-0.2 ranges, and 5% in the 0.2-0.5 ranges. The precision is normally better than 2% over all ranges.

### Selenite Method

The determination of hafnium/hafnium + zirconium ratios may be made indirectly by igniting a weighed amount of hafnium and zirconium normal selenities ( $M(\text{SeO}_3)_2$ ) to hafnium and zirconium oxides. The oxides and normal selenities are both constant in composition and suitable for direct weighing. The ratio is obtained by a simultaneous solution based on the respective weights.

Hafnium and zirconium are precipitated as the basic selenities from a 0.6 N hydrochloric acid solution to which excess selenious acid had been added. The basic selenities are converted to normal selenities by heating at 100 °C for 15 hours. The well washed precipitates are then dried for 10 hours at 130 °C. The white powder is constant in composition. A weighed portion of this powder is then heated slowly to 900 °C. The resultant powder is a mixture of the oxides. The oxides are carefully weighed. The method is useful where the ratio of hafnium/hafnium + zirconium is between 0.1 and 0.9. The accuracy has been reported as accurate within 0.5% when the amount of  $\text{HfO}_2$  in the mixed oxides is 25%.

Mandelic Acid ( $\alpha$ -hydroxyphenylacetic acid) and Derivatives

Hafnium and zirconium are quantitatively precipitated as the tetramandelates ( $M(C_8H_7O_3)_4$ ) from a hot 6 N hydrochloric acid solution containing an excess of mandelic acid. (No other cations which might be in the solution are precipitated; some cations may be coprecipitated requiring dissolution of the mandelates in a dilute ammoniacal solution followed by reprecipitation of the mandelates with the addition of hydrochloric acid.) The mandelates are filtered and washed with a hydrochloric acid solution of dilute mandelic acid and then transferred to a crucible. The precipitate is dried at 120 °C and weighed. The precipitate is burned to the oxide at 900 °C. The oxides ( $MO_2$ ) are constant in composition and easily weighed. A simultaneous solution, based on the weight of the oxides and the tetramandelates, allows the hafnium/hafnium + zirconium ratio to be obtained. The procedure is recommended for samples of several hundred milligrams (20, p. 95-97, 124-125).

The tetrabromamandelates (19) ( $M(C_8H_6O_3Br)_4$ ) may be used in the same fashion as the tetramandelates with a slightly modified procedure. The bromomandelates are less soluble and provide a larger gravimetric factor than the mandelates. They may be used where the sample is about 100 mg. Both methods, are capable of a precision and accuracy within  $\pm 0.5\%$  absolute in samples containing 10-90%  $HfO_2$ .

EDTA (Ethylenediaminetetraacetic acid)

Sweetser and Bricker (50) have developed an indirect spectrophotometric titration method applicable and sensitive to both hafnium and zirconium in a pH 4 solution. Hafnium and zirconium form a very strong 1:1 complex with EDTA in a hydrochloric acid solution containing acetate. The method involves a back-titration of excess EDTA with iron (III). The iron (III)-salicylic acid end point at a wavelength of 520 to 525 m $\mu$  gives a very sharp break in the titration curve. The precision and relative error were better than 1% where the zirconium concentration was 50  $\mu$ g/ml. The method is applicable to the determination of hafnium/hafnium + zirconium ratios where the milliequivalents of combined hafnium and zirconium can be used with a weight of the pure oxides for a simultaneous solution of the ratio.

Alizarin Red (20, p. 100-101, 129-130)

A differential spectrophotometric method (15) has been developed which allows the determination of zirconium in the presence of hafnium. The absorbance of the colored chelates formed between alizarin red and hafnium and zirconium depends on the ratio of the elements when the combined weight of their oxides is constant. The method depends on a calibration curve of concentration (weight oxide/volume) against absorbance. The differential spectrophotometry is achieved by nulling out the absorbance of hafnium at 530 m $\mu$ .

with strips of colored cellophane in order to decrease the span of percent zirconium oxide covered by the instrument. The method uses final solutions of 0.1 mg/ml of solution. The average deviation of  $\pm 0.5\%$  (absolute) for the zirconium oxides compares favorably with gravimetric results and is useful in the range of zirconium/hafnium + zirconium ratios in the range 10-50%  $ZrO_2$ .

Chemical analyses, direct and indirect, demand careful attention to details and are time consuming; they become increasingly inaccurate as the hafnium/hafnium + zirconium ratio becomes very large or small. Further, pure mixtures of the two are required in order to obtain reliable results. The physical methods are rapid and reliable once they are set up, but the set up is very costly. Many commercial laboratories are equipped for the physical methods, while many academic laboratories are equipped only for the chemical methods.

#### General Background of Hafnium and Zirconium Borohydrides

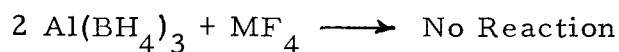
The chemistry division at Argonne National Laboratory was involved in the search for some volatile heavy metal compounds in the 1940's (22). The borohydrides<sup>3</sup> of aluminum (41, 42), beryllium (10),

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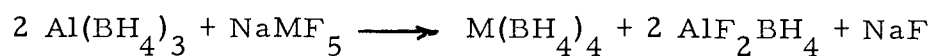
<sup>3</sup>The  $BH_4^-$  group was first called borohydride, but boronate (21) has been used and in 1961 Chemical Abstracts adopted tetrahydroborate.

and uranium(IV) (22, 45) had been prepared and were the most volatile known compounds of those elements (only the tetravalent state for uranium). The Argonne Laboratory synthesized hafnium, zirconium, and thorium borohydrides (22); these were also the most volatile known compounds of those elements. Hafnium and zirconium borohydrides are of special interest because of their volatility and a review of them is given below.

Hoekstra and Katz (22) tried unsuccessfully to prepare both hafnium and zirconium borohydrides by reacting the metal (M = Hf or Zr) tetrafluoride with an excess of aluminum borohydride.



They successfully prepared for the first time both the hafnium and zirconium borohydrides by reacting the respective sodium pentafluometallates with an excess of aluminum borohydride in an inert atmosphere at room temperature for several days.



The metal borohydride was isolated from the aluminum borohydride by fractionation. The hafnium and zirconium borohydrides are white solids melting at 29.0 and 28.7 °C, with vapor pressures of 14.9 and 15.0 mm at 25 °C respectively. They form beautiful transparent crystals and are easily sublimable in a vacuum at room temperature.

The empirical formulas are  $\text{Hf}(\text{BH}_4)_4$  and  $\text{Zr}(\text{BH}_4)_4$ .

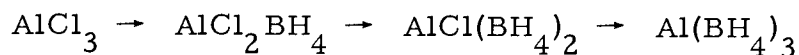
They prepared zirconium borohydride in a much shorter time by reacting zirconium tetrachloride with aluminum borohydride.



This method required several careful fractionation steps because of a complex mixture of aluminum chloroborohydrides. When an excess of aluminum borohydride was not used in the described preparations, the yields were reduced significantly. It was suggested that zirconium borohydride is formed in a series of steps



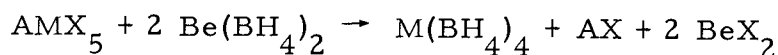
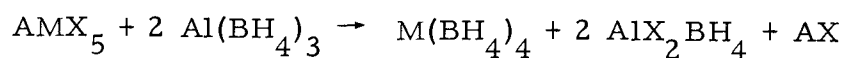
in a fashion similar to aluminum borohydride via chloroborohydrides (22)



Hafnium and zirconium borohydrides decomposed to hydrogen, diborane, and metallic borides (formulas not established) at elevated temperatures. They inflamed violently when exposed to dry air. They decompose very slowly at room temperature to form hydrogen and non-volatile compounds of indefinite composition (22).

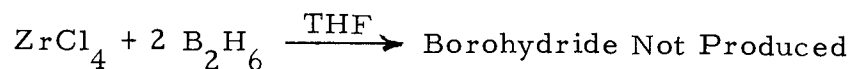
Further work by Hoekstra and Katz (23) established that the borohydrides of hafnium and zirconium may be obtained by the

reaction of a metal borohydride with an alkali metal group IV-B metal halide double salt:

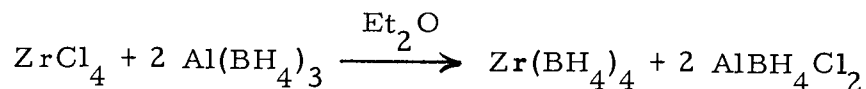


where A is sodium or potassium, M is hafnium or zirconium and X is fluoride or chloride.

A second group of workers at the National Bureau of Standards became interested in zirconium borohydride and several new zirconium borohydride preparation methods were developed (39). Zirconium tetrachloride and diborane in tetrahydrofuran did not react to produce the borohydride.

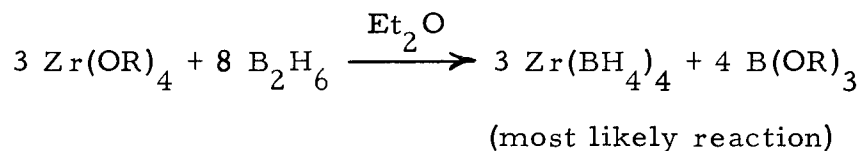


Zirconium tetrachloride and aluminum borohydride reacted in ethyl ether to produce zirconium borohydride and an aluminum chloroborohydride. The products were soluble in and difficult to separate from the ether.

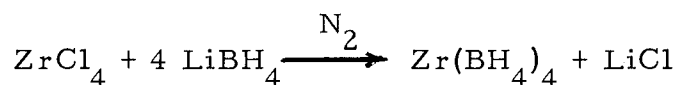


Zirconium borohydride was surprisingly soluble in ether, petroleum ether, and benzene. Diborane was mixed with a zirconium ester of

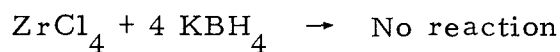
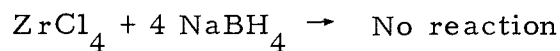
type  $\text{Zr(OR)}_4$  in ether to produce zirconium borohydride, but the products were difficult to separate.



Reid et al. (39) developed the most convenient method to the present time for preparing pure zirconium borohydride by the dry reaction of lithium borohydride and zirconium tetrachloride. The reaction is rapid and the yield as high as 90 percent with respect to both reactants.



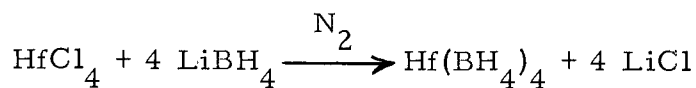
The volatile zirconium borohydride can be isolated very rapidly as the reactants, intermediates, and lithium chloride do not exhibit a noticeable pressure. Zirconium tetrachloride mixed dry with sodium or potassium borohydride did not produce zirconium borohydride.



James et al. (24), prepared hafnium borohydride by the dry reaction of lithium borohydride and hafnium tetrachloride, the



reaction proceeding in the same manner as that of Reid et al. (39).<sup>4</sup>

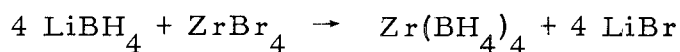


Mixed borohydride/halide compounds of zirconium (believed to be represented by the formula  $\text{ZrX}_n(\text{BH}_4)_{4-n}$  where X represents chloride or bromide and n is an integer 1 to 3) and zirconium borohydride have been used as catalysts in the polymerization of alpha-olefins (38). The borohydrides were dispersed in an inert liquid vehicle. Pentane, hexane, cyclohexane, tetrahydronaphthalene, decahydronaphthalene, benzene, xylene, o-dichlorobenzene, and chlorinated naphthalene were suitable. Aliphatic, cycloaliphatic, aromatic, and halogenated aromatic solvents in general were suggested as useful. Other catalyst systems were made by mixing lithium or aluminum borohydride with zirconium compounds such as chloride, bromide, oxychloride, freshly precipitated oxide or hydroxide, alcoholates, acetates, and benzoates.

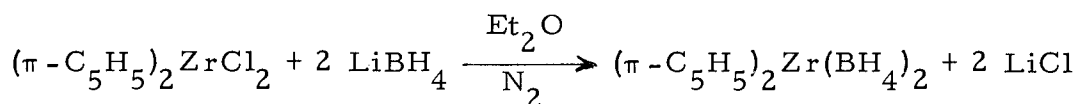
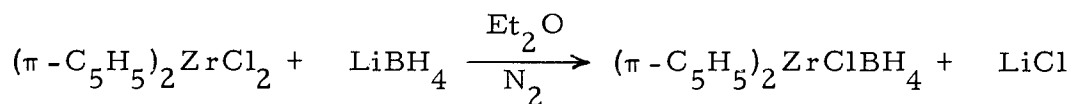
There are possibly several new methods of zirconium borohydride or borohydride derivative preparation suggested in these catalyst systems which have not yet been reported or investigated; for example:

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<sup>4</sup>Personal communication. B. D. James and M. G. H. Wallbridge, Staff, The University, Sheffield, England.



Further evidence for an addition of one borohydride group for each halide group in the preparation of hafnium and zirconium borohydrides was the recent preparation of dicyclopentadienyl zirconium chloroborohydride and dicyclopentadienyl zirconium dichloride first with a twofold molar excess and then over a threefold excess of lithium borohydride respectively:



Schrauzer (46) has classified the percentage ionic character of the borohydrides: sodium >45; potassium >45; lithium 37; magnesium 36.5; beryllium 27; aluminum 17; zirconium 12; and hafnium 12. Sodium and potassium borohydrides mixed with zirconium tetrachloride have not produced zirconium borohydride. Lithium, beryllium, and aluminum borohydrides mixed with zirconium tetrachloride have produced zirconium borohydride. Though the reaction of magnesium borohydride has not been reported, it can be speculated that their reaction would produce zirconium borohydride. Heal (21) discusses Schrauzer's work in an excellent review

of borohydrides through 1960.

The structures of aluminum and beryllium borohydrides have been studied and are of interest because projections can be made from them to hafnium and zirconium borohydrides. Electron diffraction studies of aluminum borohydride (1, 2) have shown that the boron atoms are planar with the aluminum atom and that each B-Al-B angle is  $120^\circ$ . Four hydrogens surround each boron atom in a tetrahedral fashion. There is some question over which of two dispositions of the bridging hydrogen atoms between the aluminum and the boron atom is correct. The  $\text{BH}_4$  tetrahedra may be oriented with a twofold axis or a threefold axis along the Al-B bond. Electron diffraction studies of beryllium borohydride (1, 49) indicate a linear B-Be-B bond and that four hydrogen atoms surround each boron in a tetrahedral fashion. There was greater evidence for a linear H-B-Be-B-H with three bridge hydrogens between each B and Be, but the orientation of the  $\text{BH}_4$  tetrahedra with a twofold axis along the Be-B bond was not eliminated. Price (36, 37) obtained the infrared spectra of aluminum and beryllium borohydrides and found strong evidence for bridged structures with protonated double bonds between the M (metal) and B as opposed to the girdle of three bridge hydrogens and one terminal hydrogen.

When one considers either hafnium or zirconium borohydride, it seems reasonable to assume tetrahedral disposition of the

hydrogens about each boron atom, but the number of bridge hydrogens and their disposition about the central metal atom, as well as the disposition of the boron atoms about the central metal atom are open to question. James et al. (24) have recently studied the infrared, proton and B<sup>11</sup> nuclear magnetic resonance spectra of zirconium and hafnium borohydrides. They interpreted their data in terms of two bridge hydrogens and two terminal hydrogens for each BH<sub>4</sub> group. They did not discuss directly the tetrahedral disposition of hydrogens in each BH<sub>4</sub> group, but implied it. They suggested a symmetry where the boron atoms have a square planar arrangement about the central metal atom. The N. M. R. data indicated equivalence of all hydrogens surrounding B<sup>11</sup>. Bird and Churchill (5) have determined the crystal structure of zirconium borohydride at -160°C. They found tetrahedral disposition of the boron atoms about the zirconium. The hydrogens are tetrahedrally disposed about each boron atom. There is one terminal hydrogen and three bridge hydrogens in each BH<sub>4</sub> group. The data of James et al. was taken around 25 °C. Hedberg<sup>5</sup> suggests that there is normally no difference between the molecular arrangement in the crystalline form and the molecular arrangement in the liquid or vapor. Hafnium borohydride almost

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<sup>5</sup>Private Communication. Professor Kenneth Hedberg, Dept. of Chemistry, Oregon State Univ., Corvallis, Oregon.

certainly has a structure similar to that of zirconium borohydride. Hedberg and coworkers are presently studying the structure of zirconium and hafnium borohydride by means of electron diffraction.

The density (51) of hafnium and zirconium borohydrides has recently been determined:  $\text{Zr}(\text{BH}_4)_4 - d^{30} 1.01 \pm 0.01$ ;  $\text{Hf}(\text{BH}_4)_4 - d^{30} 1.60 \pm 0.01$ . Information on the molecular volumes of hafnium and zirconium borohydrides can be obtained from the densities. The ratio of the formula weights and the ratio of the densities are the same implying very similar molecular volumes.

H. C. Brown has published Hydroboration (9) which has a chapter on borohydride chemistry. He shows further how many borohydrides have been extensively used in organic and inorganic syntheses. By analogy to Brown's discussion of aluminum borohydride one can see many possible uses for hafnium and zirconium borohydrides in synthesis work. Nothing has been published with regard to synthesis work utilizing them, however.

Blumenthal has stated (7; p. 7) that zirconium borohydride is a monomeric molecule. He bases his judgement on several things:<sup>6</sup>

1 The physical constants which have been reported offer no basis for polymerization; 2 No electrons appear available for

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<sup>6</sup> Personal communication. Warren B. Blumenthal, Chief, Chemical Division, Titanium Alloy Manufacturing Division, National Lead Company, Niagra Falls, New York.

donor-acceptor interaction, which would be necessary for polymerization; 3 For the second row elements capable of forming hydrided radicals,  $AH_n$ , where A is C, N, O, or F, association of molecules in which these radicals are bound to zirconium is characterized by formation of refractory substances distinguished from the easily fused and volatilized borohydrides. Association of zirconium borohydride molecules through formation of -B-Zr-B-Zr- linkages would tend toward the refractory structures found in zirconium borides, nitrides, etc., and in the associated and non-volatile amides, hydrous oxides, and their analogs. Association by hydrogen bonding would probably reduce the vapor pressure of the compound to a lower value than observed; 4 Zirconium methoxide, with some structural analogies to zirconium borohydride, is polymeric and solid at ordinary temperature, with a much lower vapor pressure than zirconium borohydride.

The above is, admittedly, all indirect evidence, but is felt to be reliable indirect evidence.

Hoekstra and Katz sublimed zirconium or hafnium borohydride into an evacuated bulb at  $-80^{\circ}C$ , distilled excess water into the bulb at  $-80^{\circ}C$ , and with the stopcock closed, warmed the bulb to room temperature. After completion of the vigorous reaction the stopcock was opened and the hydrogen pressure (corrected for water vapor) measured after equilibrium had been reached. The metal was

estimated gravimetrically as the oxide, the boron was determined by distillation as methyl borate and titration of the liberated boric acid. The empirical formulas obtained by hydrolysis and complete analysis were  $Zr_{1.04}B_{4.06}H_{16.00}$  ( $Zr(BH_4)_4$ ) and  $Hf_{1.03}B_{3.98}H_{16.00}$  ( $Hf(BH_4)_4$ ). It is suggested then, by the reliable indirect evidence cited by Blumenthal,<sup>7</sup> that the empirical formula is the molecular formula for hafnium and zirconium borohydrides.

Preparation of Hafnium and Zirconium Borohydrides  
by the Reid Method (24, 39)

The preparation of hafnium and zirconium borohydrides by the dry powder reaction of zirconium tetrachloride and excess lithium borohydride in an inert atmosphere will be called the method of Reid. The method is capable of 70 to 90%



yields of hafnium or zirconium borohydride in several hours. After a short induction period, followed by the evolution of heat, a moist product, hafnium and/or zirconium borohydride, is formed. This product can be isolated rapidly and easily in pure form from the reactants and other product/s.

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<sup>7</sup>Ibid.

The fact that 70 - 90% yields are obtained with either hafnium or zirconium borohydride, however, does not assure that an equal yield of hafnium and zirconium borohydrides would be obtained from a mixture of hafnium and zirconium tetrachlorides. It is reasonable to assume that equal yields of hafnium and zirconium borohydrides would be obtained from a mixture of hafnium and zirconium tetrachlorides because of the very great similarity of the chemical properties of hafnium and zirconium and their compounds.

Blumenthal has written on the similarity of the chemical properties of hafnium and zirconium:

This element (hafnium) is so extraordinarily like zirconium that no qualitative difference in chemical behavior between the two elements has been observed up to the present (1958). The unrecognized element (hafnium) had been following zirconium in all the processing of its ores and its subsequent handling as though it were a huge isotope of zirconium. . . .

. . . the zirconium metal and compounds of industry still usually contain the same concentration of hafnium as existed in the ores from which they were derived (6, p. 3-4).

Zirconium and hafnium tetrachlorides are seldom available in a pure form. The main use of the tetrachlorides and hence its importance as a starting material in the Reid method is in the production of hafnium and zirconium metals. Pure tetrachlorides may be obtained by chlorination of easily purified hafnium and zirconium oxides. A host of impurities may be found in the tetrachlorides (most at the trace level), but only a few might possibly cause



problems in the isolation of the borohydrides using the Reid method. Aluminum trichloride would react with lithium borohydride to form volatile aluminum borohydride and a complex mixture of volatile aluminum chloroborohydrides (44). Titanium tetrachloride reacts with lithium borohydride to form green volatile titanium (III) borohydride and volatile titanium (III) monochloroborohydride (22). Uranium (IV) chloride might possibly react with lithium borohydride to form dark green moderately volatile uranium (IV) borohydride (45). If the mentioned impurities would interfere in the isolation of hafnium and zirconium borohydrides, treatment of hafnium and zirconium tetrachlorides or preparation of them from the oxides would be necessary prior to the Reid method. Other impurities present in the tetrachlorides would not form stable or volatile borohydrides, and most probably no other volatile products which might interfere.

Lithium borohydride is commercially available in about 90% purity from 2 sources: Ventron Corporation, Beverly, Massachusetts; Foote Mineral Company, Exton, Pennsylvania. The most likely impurities are lithium halides (fluoride or chloride), the hydroxide, and metaborate. If these materials proved to be troublesome in the preparation or isolation of hafnium and zirconium borohydrides, then preliminary purification would be necessary. This purification should be relatively easy.

In summary, the interference in the isolation of hafnium and zirconium borohydrides of impurities in the starting materials and reaction products of the Reid method would have to be determined experimentally, but few interferences seem probable.

### The Mass Spectrometry of Hafnium and Zirconium Borohydrides and Their Mixtures

If a beam of electrons is passed through a gas at a very low pressure, positively charged ions of the gas are produced. The mass spectrometer is an analytical instrument which analyzes these positively charged ions according to their mass to charge ( $m/e$ ) ratio. The positive ions are linearly accelerated through a potential difference, and then angularly accelerated through a magnetic field. The  $m/e$  ratio is related to the potential difference  $V$  and the magnetic field intensity  $H$  in the following manner:  $m/e = r^2 H^2 / 2V$  where  $r$  is a fixed radius of curvature. For a particular instrument  $m/e = kH^2 / V$ . Through the use of the proper values of  $H$  and  $V$ , and the variance of either  $H$  or  $V$ , the various species are focused on an ion collector where their charge is given up. An electric current produced thereby is amplified and recorded. The mass spectrum is a fingerprint of the  $m/e$  ratios of the fragmentation pattern of the species originally present in the vapor. The mass spectrum of the vapor of a compound is unique, yields information regarding the

structure and molecular weight, and is useful in the qualitative and quantitative analysis of the compound. The theory and application of mass spectrometry have been discussed by several authors (4, 27, 29, 31).

The mass spectrum of methane at 70 ev should provide a good example.

<u>m/e</u>	<u>Recorder Peak Heights</u>	<u>Relative Intensity</u>	<u>Ionized Species</u>
2	9.5	0.57	$\text{H}_2^+$
12	23.2	1.39	$\text{C}^+$
13	51.4	3.08	$\text{CH}^+$ , $\text{C}^{13+}$
14	147	8.83	$\text{CH}_2^+$
15	1343	80.4	$\text{CH}_3^+$
16	1670	100.0	$\text{CH}_4^+$
17	17.9	1.07	$\text{C}^{13}\text{H}_4^+$

The pattern is unique and reproducible under rigidly controlled experimental conditions and very useful in qualitative analysis. The parent peak at m/e 16 is a good indication of the molecular weight. The peaks at 2 and 12 indicate hydrogen and carbon. The distribution of m/e 16 and 17 indicates  $\text{C}^{12}$  and  $\text{C}^{13}$  and it is obvious that the species are  $\text{CH}_4$  and  $\text{C}^{13}\text{H}_4$  or methane. High resolution of the m/e ratios leads to a splitting of the m/e ratios of a common low resolution spectrum, and helps to elucidate the particular ionic species contributing to the m/e ratio. The contribution of  $\text{C}^{12}\text{H}^+$  and  $\text{C}^{13+}$

to  $m/e$  13 can be found.

If a certain pressure of gas is introduced into the mass spectrometer and the mass spectrum indicates only the mass spectrum of methane, then the sample contained 100.0% methane, within detection limits. The instrumental sensitivity of methane would be the recorder deflection at a particular  $m/e$  divided by the sample pressure. For 90 microns of pressure and 1670 divisions of deflection at  $m/e$  16, the methane sensitivity would be 18.6 divs/micron. If methane was a constituent of a gas mixture, the pressure of methane in the mixture could be found from a mass spectrum of the gas and the total pressure of the gas.

The composition of a mixture of two gaseous components where the mass spectra completely overlap can be easily found by a simultaneous solution at two selected  $m/e$  values, provided the individual spectra and sensitivities of the constituents are known. A mixture of n-butane and i-butane is a good example of two isomers whose mass spectra completely overlap.

$m/e$	<u>Relative Intensity</u>	
	<u>n-C<sub>4</sub></u>	<u>i-C<sub>4</sub></u>
43	100.0	100.0
58	12.98	2.74

If  $X_1$  = division of  $m/e$  43 peak in the mixture spectrum due to n-butane and  $X_2$  = division of the  $m/e$  43 peak due to isobutane, then:

$$0.1298 X_1 + 0.02740 X_2 = \text{divisions at } m/e \text{ } 58$$

$$X_1 + X_2 = \text{divisions at } m/e \text{ } 43$$

Solving for  $X_1$  and  $X_2$  and knowing the sensitivities of the compounds leads to a quantitative analysis. Conventional mass spectrometers routinely analyze many mixtures even more complicated than the butane isomers, with very good results.

The mass spectra of hafnium and zirconium borohydrides have not been reported but would be of considerable interest for structural information, molecular weights, and qualitative analysis, but especially for quantitative analysis. Hafnium/hafnium + zirconium ratios are of considerable interest and a mass spectrometric method for the elucidation of them would be very valuable.

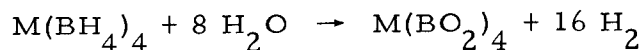
Hafnium and zirconium borohydrides are extremely strong reducing agents. Traces of residue on the surface of a mass spectrometer sample inlet system would be readily reduced. Many conventional inlet systems have greased stopcocks which would be unsuitable for quantitative analyses, but might prove suitable for qualitative analysis. For quantitative analysis a non-reactive sample inlet system would have to be utilized or designed.

Hafnium and zirconium borohydrides are thermally unstable, though they decompose very slowly at room temperature. The ionizing region of most mass spectrometers is maintained at a

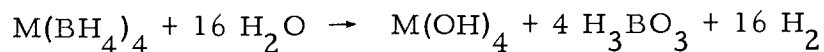
regulated elevated temperature, say 250 °C. The ionizing filament supplies some of the heat to maintain the elevated temperature, but is itself running at white heat (around 2000 °K). The sampling system and ionizing region are designed to eliminate thermal decomposition as much as possible, but many compounds which are normally thermally stable at room temperature experience some decomposition in the ionizing region. Though quantitative analysis of hafnium and zirconium borohydrides by conventional mass spectrometric analysis does not look especially promising, some useful information, perhaps pointing toward improvement and solution of the problems, might be found by its utilization.

The Hydrolysis of Hafnium and Zirconium  
Borohydrides and Their Mixtures

Hoekstra and Katz suggest the general hydrolysis equation



for hafnium and zirconium borohydrides. An alternate way of looking at the hydrolysis reaction is:



$M(\text{OH})_4$  is used for convenience rather than the mixtures of hydrous oxide species of the metals which actually exist in the solution.

If it is assumed that 1 mole of hafnium or zirconium borohydride or a mixture of hafnium and zirconium borohydrides produces 16 mole of hydrogen gas (quantitative conversion) through hydrolysis and the hydrogen follows the ideal gas law, then the ratio of the weight of the metal of interest compared to the combined weight of the metals may be found by knowing the weight of the total borohydride at the start, and the volume, temperature, and pressure of the hydrogen gas produced. Hydrogen gas is a convenient gas with which to work. It follows the well established ideal gas law very closely, and may be quantitatively isolated. A series of equations will clarify the situation.

Let

- $n_H$  = moles of hydrogen  
 $n_{TB}$  = moles of total borohydride  
 $n_{HfB}$  = moles of  $Hf(BH_4)_4$   
 $n_{ZrB}$  = moles of  $Zr(BH_4)_4$   
 $n_{MB}$  = moles of  $M(BH_4)_4$ ,  $M = Hf, Zr$   
 $W_{MB}$  = wt. of  $M(BH_4)_4$  in grams  
 $M_{MB}$  = Mol. wt. of  $M(BH_4)_4$  in grams  
 $P_H$  = pressure of  $H_2$  in mm  
 $V$  = volume of  $H_2$  in liters  
 $T$  = temperature in  $^{\circ}K$   
 $R$  =  $62.3637 \text{ l-mm-deg}^{-1}\text{-mole}^{-1}$

$$W_{\text{Hf}} = \text{wt. of Hf}$$

$$W_{\text{Zr}} = \text{wt. of Zr}$$

$$W_{\text{R}} = \text{weight ratio}$$

$$100W_{\text{R}} = \% \text{ Hf}$$

Then

$$(1) n_{\text{H}} = 16 n_{\text{TB}}$$

$$(2) n_{\text{TB}} = n_{\text{HfB}} + n_{\text{ZrB}}$$

$$(3) n_{\text{MB}} = \frac{W_{\text{MB}}}{M_{\text{MB}}}$$

$$(4) n_{\text{H}} = \frac{P_{\text{H}} V}{R T}$$

$$(5) n_{\text{TB}} = \frac{P_{\text{H}} V}{16 R T}$$

substituting (2) and (3) into (5)

$$(6) \frac{W_{\text{HfB}}}{M_{\text{HfB}}} + \frac{W_{\text{ZrB}}}{M_{\text{ZrB}}} = \frac{P_{\text{H}} V}{16 R T}$$

$$(7) W_{\text{TB}} = W_{\text{HfB}} + W_{\text{ZrB}}$$

substituting (7) into (6)

$$(8) \frac{W_{\text{HfB}}}{M_{\text{HfB}}} + \frac{W_{\text{TB}}}{M_{\text{ZrB}}} - \frac{W_{\text{HfB}}}{M_{\text{ZrB}}} = \frac{P_{\text{H}} V}{16 R T}$$

$$(9) W_{\text{HfB}} (M_{\text{HfB}}^{-1} - M_{\text{ZrB}}^{-1}) + \frac{W_{\text{TB}}}{M_{\text{ZrB}}} = \frac{P_{\text{H}} V}{16 R T}$$



$$(10) \quad W_{\text{HfB}} = \frac{\frac{P_{\text{H}} V}{16 R T} - \frac{W_{\text{TB}}}{M_{\text{ZrB}}}}{\frac{1}{M_{\text{HfB}}} - \frac{1}{M_{\text{ZrB}}}}$$

$$(11) \quad W_{\text{HfB}} = 2.7256 W_{\text{TB}} - 0.41135 \frac{P_{\text{H}} V}{T}$$

$$(12) \quad W_{\text{R}} = \frac{W_{\text{Hf}}}{W_{\text{Hf}} + W_{\text{Zr}}}$$

$$(13) \quad W_{\text{Hf}} = \frac{\text{Hf}}{\text{Hf}(\text{BH}_4)_4} \cdot W_{\text{HfB}} = \frac{178.49}{237.86} W_{\text{HfB}} = 0.75356 W_{\text{HfB}}$$

$$(14) \quad W_{\text{Zr}} = \frac{\text{Zr}}{\text{Zr}(\text{BH}_4)_4} \cdot W_{\text{ZrB}} = \frac{91.22}{150.59} W_{\text{ZrB}} = 0.60574 W_{\text{ZrB}}$$

$$(15) \quad W_{\text{R}} = \frac{0.75356 W_{\text{HfB}}}{0.75356 W_{\text{HfB}} + 0.60574 W_{\text{ZrB}}}$$

or alternately, by substituting (7) into (15)

$$(16) \quad W_{\text{R}} = \frac{0.75356 W_{\text{HfB}}}{0.14782 W_{\text{HfB}} + 0.60574 W_{\text{TB}}}$$

$$(17) \quad 100 W_{\text{R}} = \% \text{ Hf metal by weight}$$

The ratio  $W_{\text{R}}$  is simply a function of four parameters:

$$W_{\text{R}} = f(W_{\text{TB}}, P_{\text{H}}, V, T)$$

The performance of an analytical hydrolysis on hafnium and zirconium borohydrides would depend on the quality of measurement of the four parameters. The quality of measurement of the four parameters necessary for an accurate  $W_R$  with good precision must be determined experimentally, but a hypothetical consideration might prove valuable.

A 0.3500 gram sample of hafnium or zirconium borohydride or a mixture of them is hydrolyzed in a half liter hydrolysis flask. The hydrogen gas evolved is separated from the reaction mixture and collected in a 1.2200 liter bulb at 300.0 °K.  $100 W_R$  (% Hf by weight) is shown as a function of the hydrogen pressure in Figure I.

In the example there is a large difference, about 210 mm, between the hydrogen pressures due to pure hafnium and zirconium borohydrides. Since it is relatively easy to measure the pressure with an error no greater than 0.2 mm, it should be possible to distinguish a composition difference of about one part per thousand in various mixtures of hafnium and zirconium borohydrides, due to pressure differences alone. The other three parameters, however, would also influence the distinction. A brief theoretical look at all the factors and their influence in a typical case is given below.

The hydrogen from a hydrolyzed 0.3500 gram sample of a mixture of hafnium and zirconium borohydrides ( $W_R = 0.0194$ ) is collected in a 1.2200 liter bulb at 300.0 °K. The effects of small

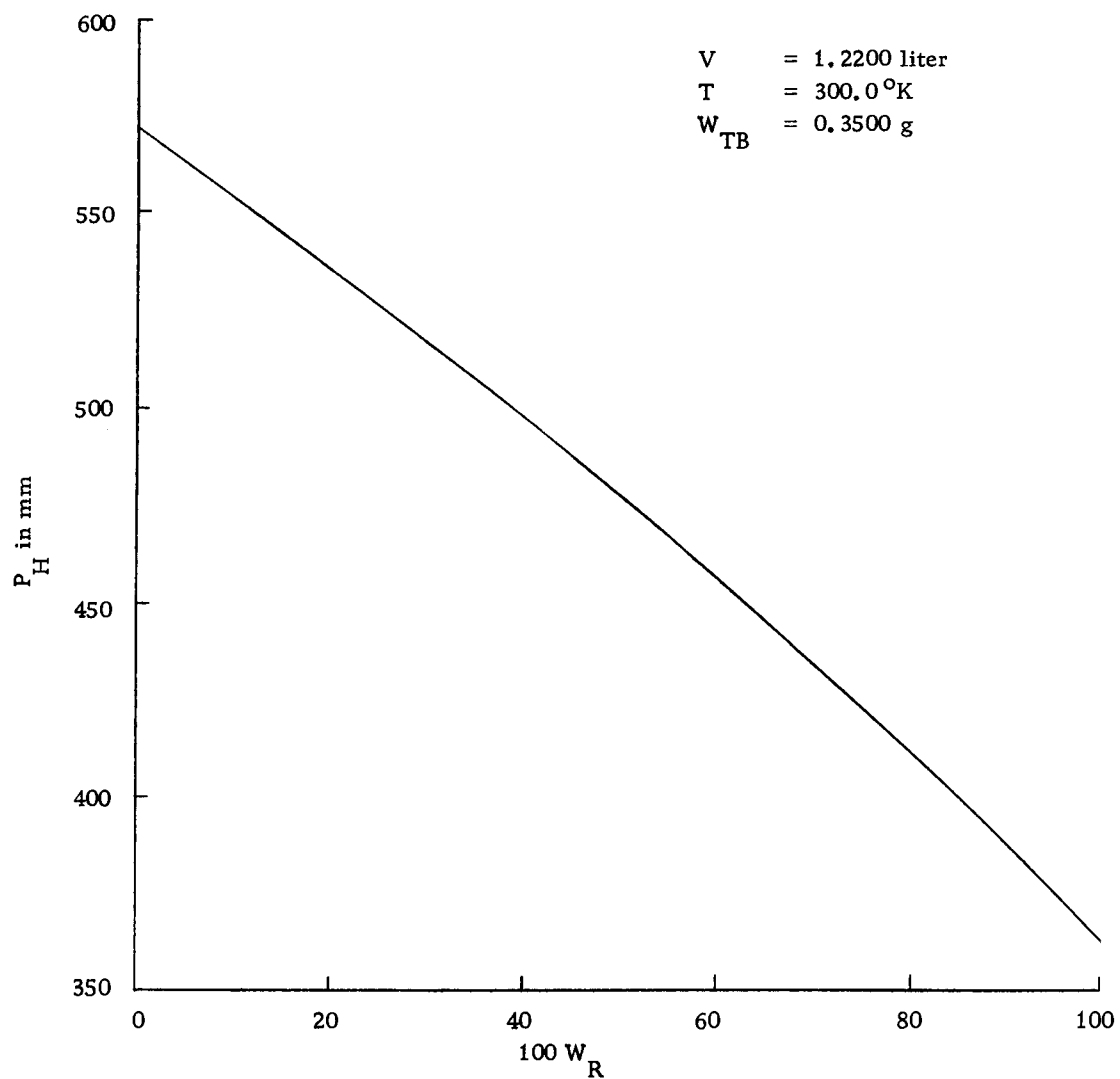


Figure I.  $W_R = f(P_H)$  at constant V, T,  $W_{TB}$

incremental changes in  $P_H$ ,  $T$ ,  $V$ , and  $W_{TB}$ , calculated from equations (11) and (16), are shown in Figures II - V below. The maximum error in the parameters to be expected under the given experimental conditions is of interest and a summary of them is given in Table I.

If the borohydrides can be quantitatively hydrolyzed, i. e. , 16 moles of hydrogen for each mole of borohydride, and the hydrogen quantitatively isolated from the reaction mixture, then a realistic evaluation of the maximum error expected is contained in Table I.

Figure VI displays  $W_{TB}$  v.  $P_H$  at a constant volume and temperature for all possible combinations of  $Hf(BH_4)_4$  and  $Zr(BH_4)_4$  where  $W_{TB}$  varies from 0 to 0.7 grams; for example the line connecting A and B contains all possible combinations of hafnium and zirconium borohydride where  $W_{TB}$  is .350 gram. If point B, .3500 g., is the largest convenient sample size manageable in a half-liter hydrolysis bulb for zirconium borohydride, then point C, .552 g., is the comparable sample size for hafnium borohydride under the same conditions.

When the equations for calculating the % Hf ( $100 W_R$ ) were derived, the behavior of the hydrogen gas was considered ideal. Hydrogen gas is nearly, but not quite ideal. Two equations of state have been derived which closely approximate the actual behavior in the vicinity of one atmosphere of pressure. The first is the equation

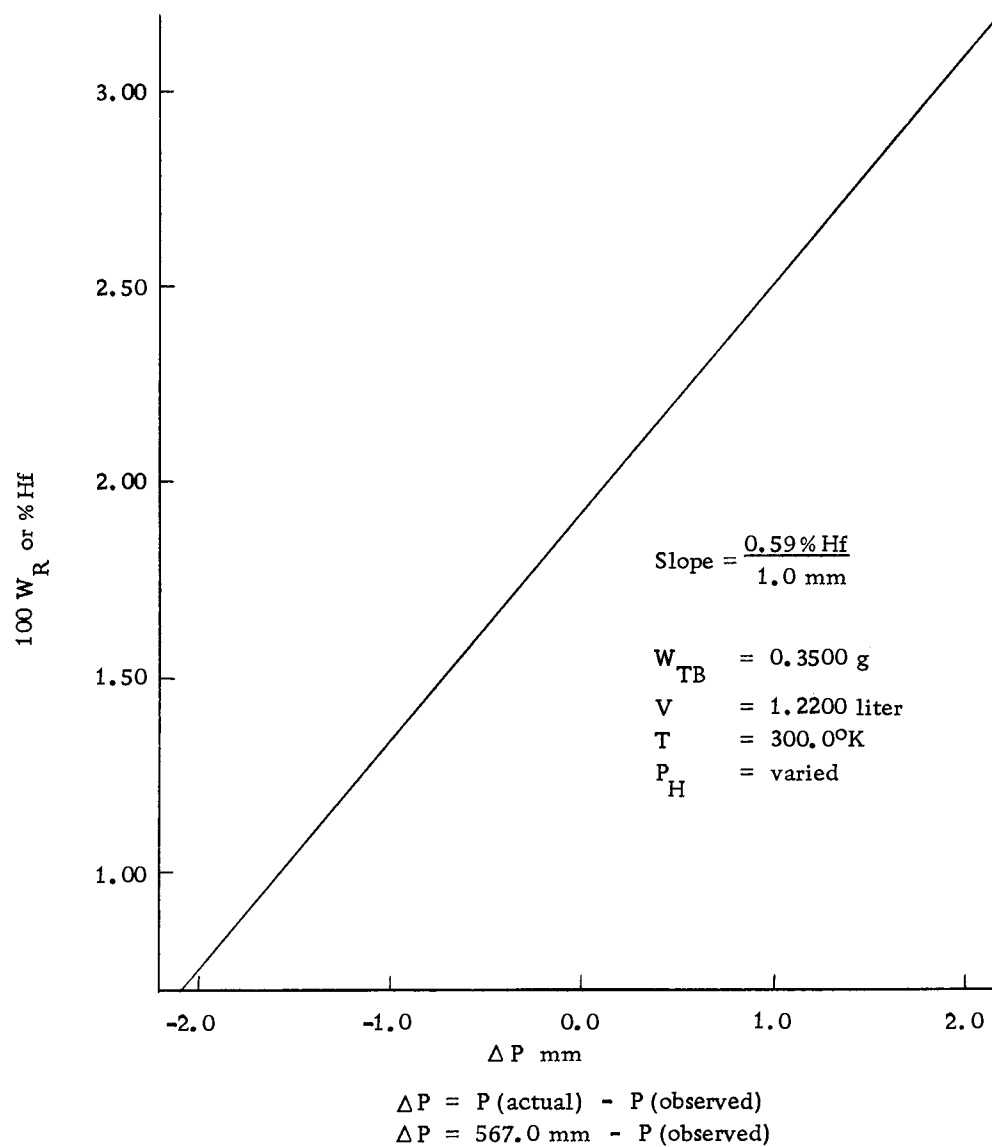


Figure II. The Calculated Effect of Small Pressure Changes on % Hf when the Actual % Hf is 1.94%

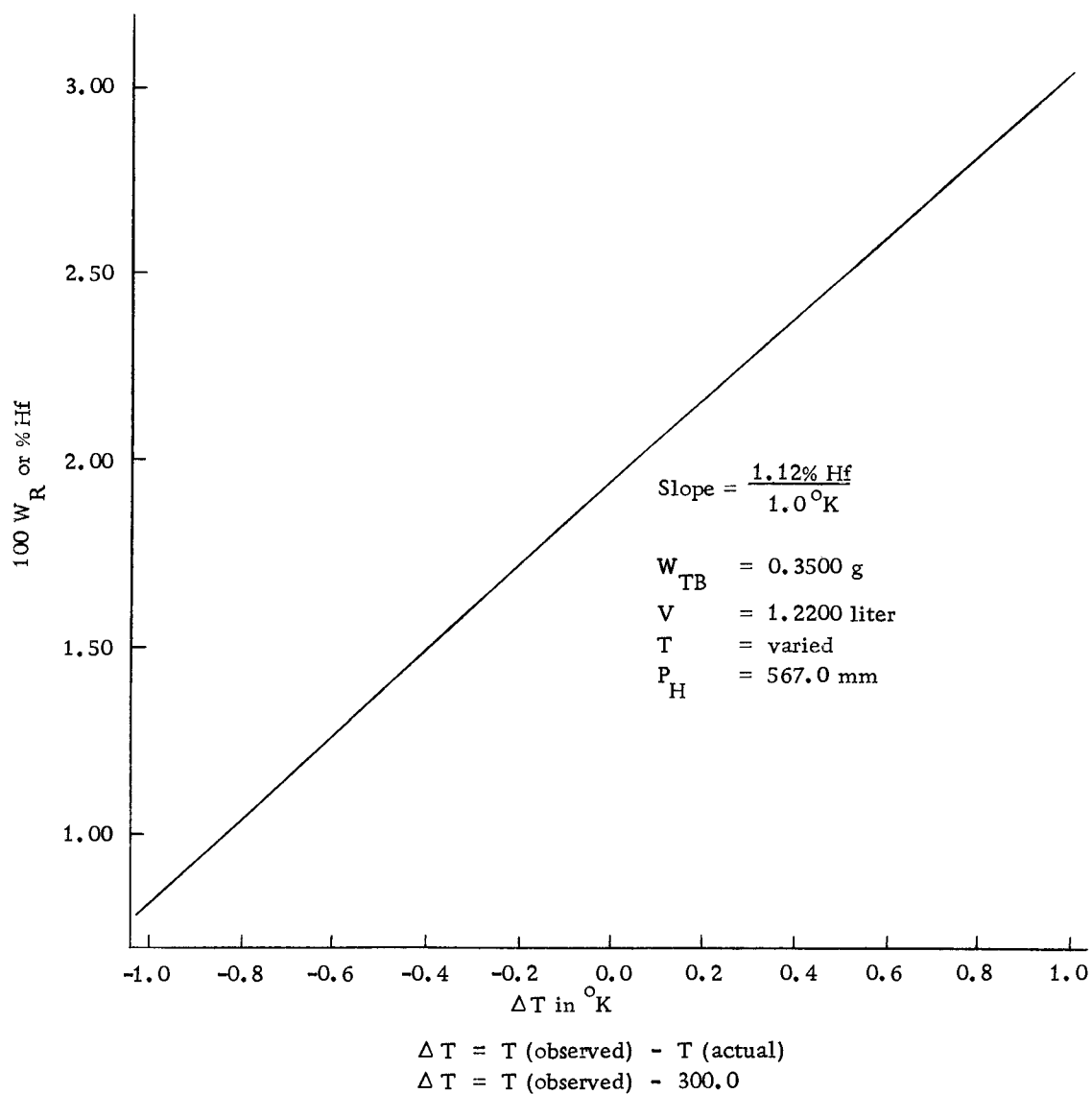


Figure III. The Calculated Effect of Small Temperature Changes on % Hf when the Actual % Hf is 1.94%

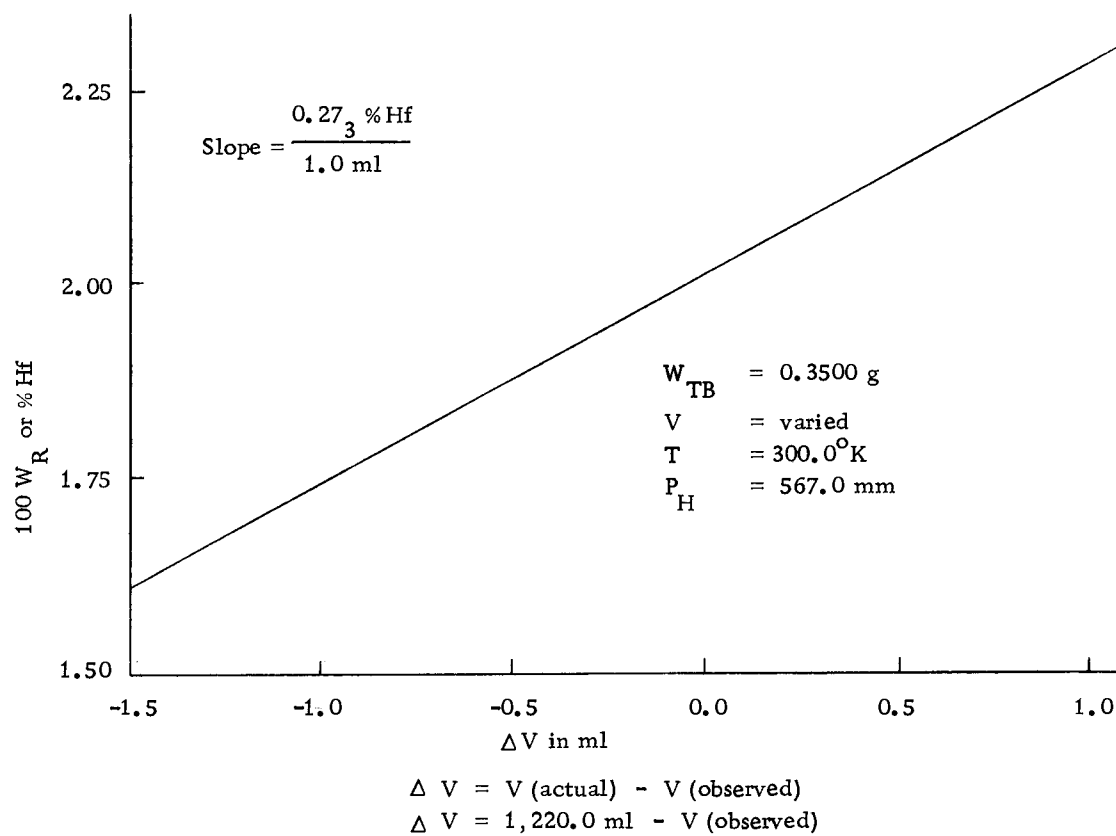


Figure IV. The Calculated Effect of Small Volume Changes on % Hf when the Actual % Hf is 1.94%

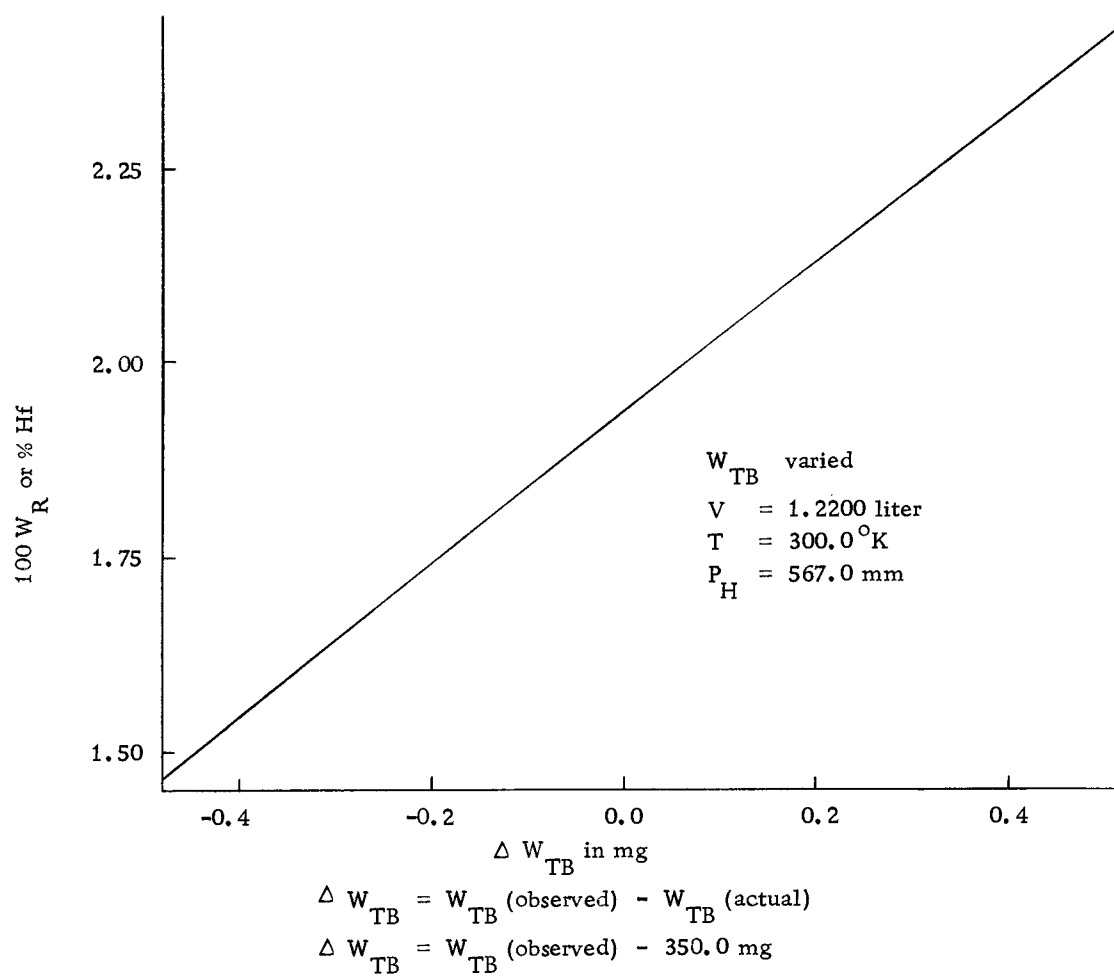


Figure V. The Calculated Effect of Small Total Borohydride Weight Changes on % Hf when the Actual % Hf is 1.94%



Table I. Summary of Parameter Error Calculations

Parameter	Magnitude of Parameter	Maximum Deviation Expected	Parameter Error (Figs. II-V)	100 W <sub>R</sub> or %Hf Error
W <sub>TB</sub>	.3500 g	± 0.1 mg	.96% Hf/mg	± 0.10
P <sub>H</sub>	567.0 mm	± 0.2 mm	.59% Hf/mm	± 0.12
V	1.2200 l	± 0.5 ml	.27% Hf/ml	± 0.14
T	300.0 °K	± 0.1 °K	1.12 % Hf/°K	± 0.11
W <sub>TB</sub>	.3501 g	+ 0.1 mg		+ 0.47
P <sub>H</sub>	566.8 mm	- 0.2 mm		
V	1.2195 l	- 0.5 ml		
T	300.1 °K	+ 0.1 °K		
W <sub>TB</sub>	.3499 g	- 0.1 mg		- 0.47
P <sub>H</sub>	567.2 mm	+ 0.2 mm		
V	1.2205 l	+ 0.5 ml		
T	299.9 °K	- 0.1 °K		

If  $W_{TB} = .3500$  g, and  $100 W_R = 1.940$ , then  $P_H = 567.0$  mm

when  $V = 1.2200$  l and  $T = 300.0$  °K

$$(11) W_{HfB} = 2.7256 W_{TB} - 0.41135 \frac{P_H V}{T}$$

$$(16) W_R = \frac{0.75356 W_{HfB}}{0.14782 W_{HfB} + 0.60574 W_{TB}}$$

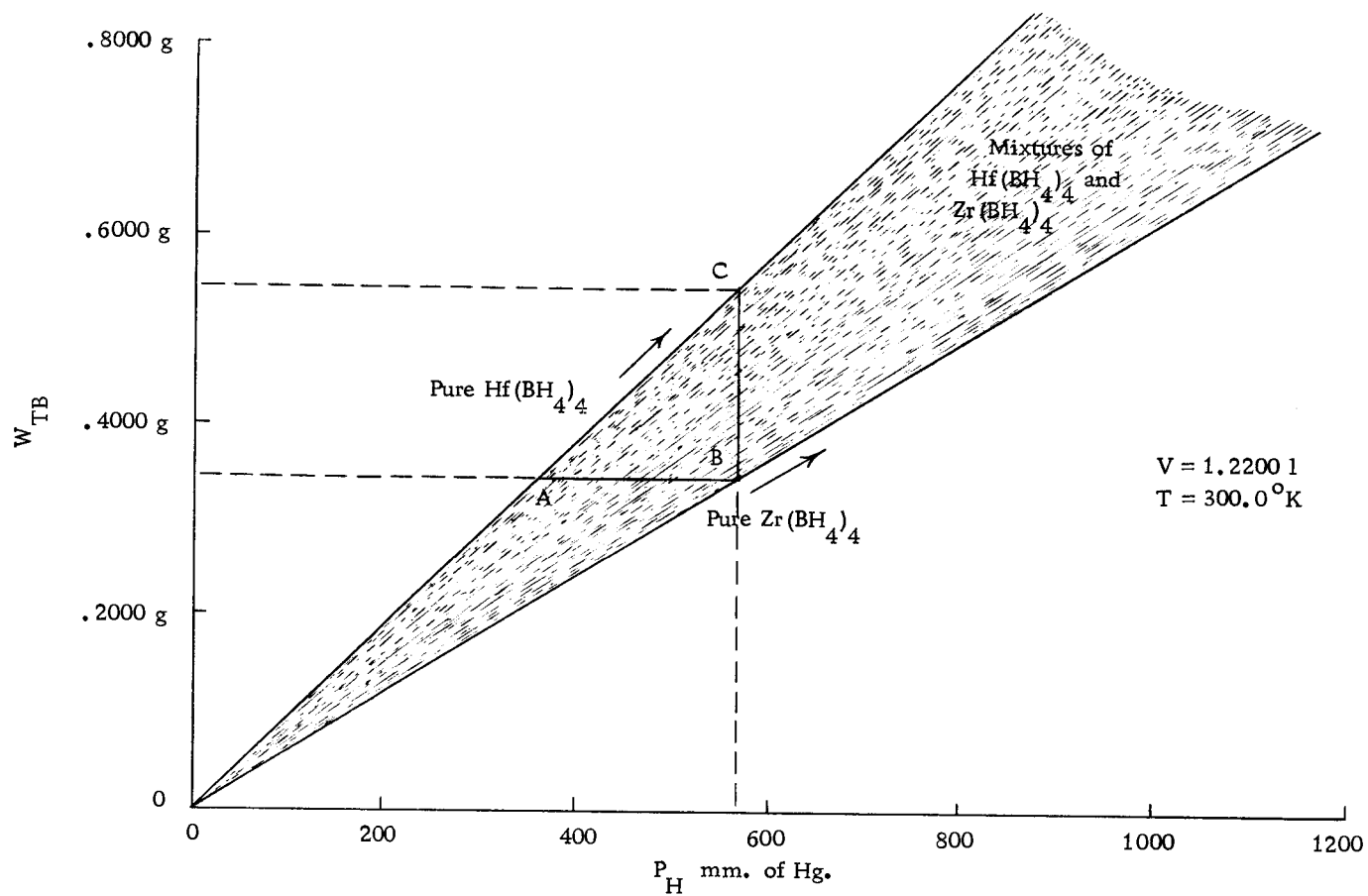


Figure VI.  $W_{TB}$  v.s.  $P_H$  at  $V_c, T_c$  for All Possible Combinations of Hafnium and Zirconium Borohydrides to 0.7 gram

of van der Waals and the second the equation of Berthelot (32, p. 18-23). The equations are given below:

IDEAL:  $PV = nRT$

VAN DER WAALS:  $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

BERTHELOT:  $\left(P + \frac{n^2A}{TV^2}\right)(V - nb) = nRT$

but more commonly

$$P_R V_R = nR'T_R \left[ 1 + \frac{9 P_R}{128 T_R} \left( 1 - \frac{6}{T_R} \right) \right]$$

where  $P_R = P/P_C$        $V_R = V/V_C$

$$T_R = T/T_C$$

$$R' = R \left( \frac{T_C}{V_C P_C} \right)$$

For the equations above the following constants are appropriate:

$$R = 0.082059$$

$$a = 0.2444 \text{ liter}^2 \text{-atm-mole}^{-2}$$

$$b = 0.02661 \text{ liter-mole}^{-2}$$

$$V_C = 57.6 \text{ cc-mole}^{-1}$$

$$P_C = 12.8 \text{ atm}$$

$$T_C = 33.0 \text{ }^\circ\text{K}$$

It is of considerable interest to compare the results of the three equations for the same data. Typical data might be:  $T = 300.0 \text{ }^\circ\text{K}$ ;

$V = 1.2200$  liters; the number of moles  $n$  is a variable function of the weight of total borohydride  $W_{TB}$ ; the resultant pressure  $P$  is to be calculated. The correction curves for the non-ideal behavior of hydrogen gas, calculated from the three equations of state, are shown in Figure VII from 200 to 800 mm.

The hydrogen pressure measured, even when corrected for non-ideality is not correct. The correlation (48, p. 215) between the observed and true pressures for hydrogen takes into account the density of the mercury in the manometer and the local acceleration due to gravity which effects the weight of mercury:

$$P_t = P_o \times \rho_{Hg, T} \times g \times 7.5006 \times 10^{-4} \text{ mm.}$$

where  $P_t$  = true pressure in mm.

$P_o$  = observed pressure in cm. (difference in height between mercury levels)

$\rho_{Hg, T}$  = density of mercury at temp.  $T$  in  $g/cm^3$   
 $7.5006 \times 10^{-4} = mm/dyne-cm^{-2}$

An example will clarify the situation. At  $300.0^\circ K$ ,  $P_o = 76.00$  cm.

The density of mercury at  $300.0^\circ K$  is 13.5294. The local acceleration due to gravity is 980.573 (3). The true pressure is:

$$P_t = 76.00 \times 13.5294 \times 980.573 \times 7.5006 \times 10^{-4} \text{ mm}$$

$$P_t = 756.3 \text{ mm}$$

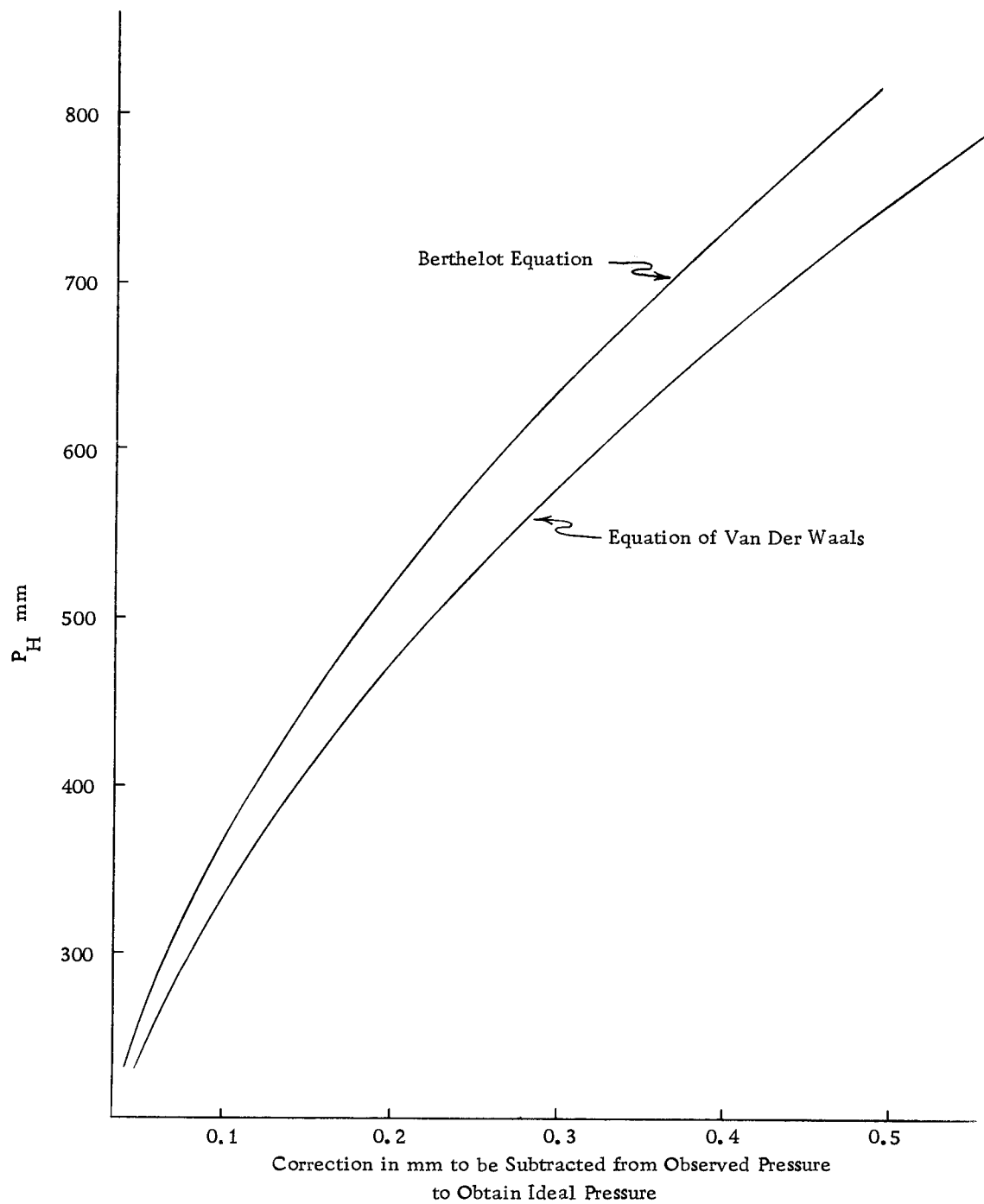


Figure VII. Pressure Correction Curves for Non-Ideal Behavior of Hydrogen Gas

Without the correction an error of 3.7 mm would have been incurred!

The construction and use of mercury barometers and manometers, including a discussion of factors effecting the observed pressure reading are effectively discussed in a recent monograph (8).

An attempt to develop a gasometric method for the measurement of hafnium/hafnium + zirconium ratios via hydrolysis of mixtures of hafnium and zirconium borohydrides would seem reasonable, then, if quantitative hydrolysis could be obtained. The experimental conditions given in the previous examples would be reasonable for a starting point.

## EXPERIMENTAL PROCEDURES AND RESULTS

### Sample Preparation and Storage

#### Apparatus for Preparation

The Reid method of preparation for hafnium and zirconium borohydrides requires an inert atmosphere; I<sup>2</sup>R, 108 Franklin Ave., Cheltenham, Pennsylvania, manufactures an inexpensive glove bag which is essentially an inflatable dry box. The bag is made of clear tough polyethylene and has integral gloves. The bags come in various sizes, the largest of which is 37" x 37" x 25". One of the glove bags, slightly modified, provides an excellent inert atmosphere chamber for the Reid preparation when incorporated into an inert gas drying system. The preparation system is shown in Figure VIII.

The mouth of the bag must be opened and closed for each preparation. A convenient way to seal the mouth is to line the inner and outer edges with electrical tape, and then seal the edges together by placing masking tape over the electrical tape. The masking tape is easily removed from the permanent electrical tape and inexpensively replaced. Masking tape was not used against the polyethylene because it cannot be replaced without tearing the glove bag. The sealed mouth is bent over and clamped to the plywood board by means of a strip of masonite. The masonite is secured with wing nuts. The bag is

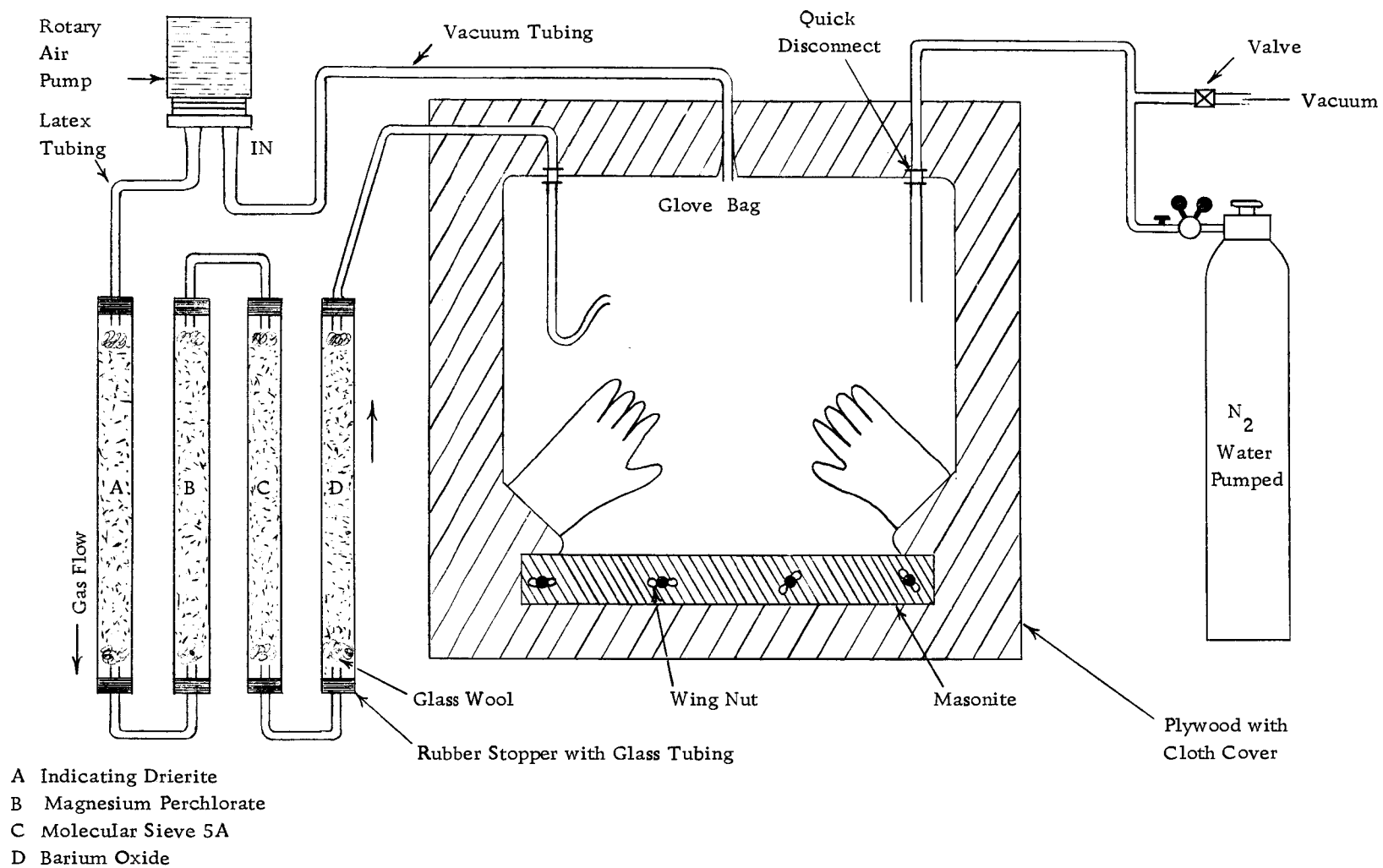


Figure VIII. Borohydride Preparation System



easily filled with nitrogen via the nitrogen tank regulator. A rotary air pump (Model 0211, Gast Mfg. Corporation, Benton Harbor, Michigan) conveniently circulates the nitrogen atmosphere through the drying train. The Drierite indicates when it should be regenerated. The Quick Disconnects are available from the Dynalab Corp., Rochester, New York.

The apparatus and material needed for a preparation are listed below:

1. single pan triple beam balance, 110 gram capacity
2. container of metallic tetrachloride
3. container of lithium borohydride
4. tube of Apiezon H Grease
5. dry 3 mm nickel balls
6. 2 ceramic spatulas
7. powder funnel
8. large stirring rod
9. preparation flask (see Figure IX), dry
10. 2 rectangular polyethylene mats, 24" x 18"

### The Inert Atmosphere

In order to test the composition of the atmosphere in the glove bag, the apparatus diagrammed in Figure X was designed and constructed. The bag was evacuated and filled with nitrogen several

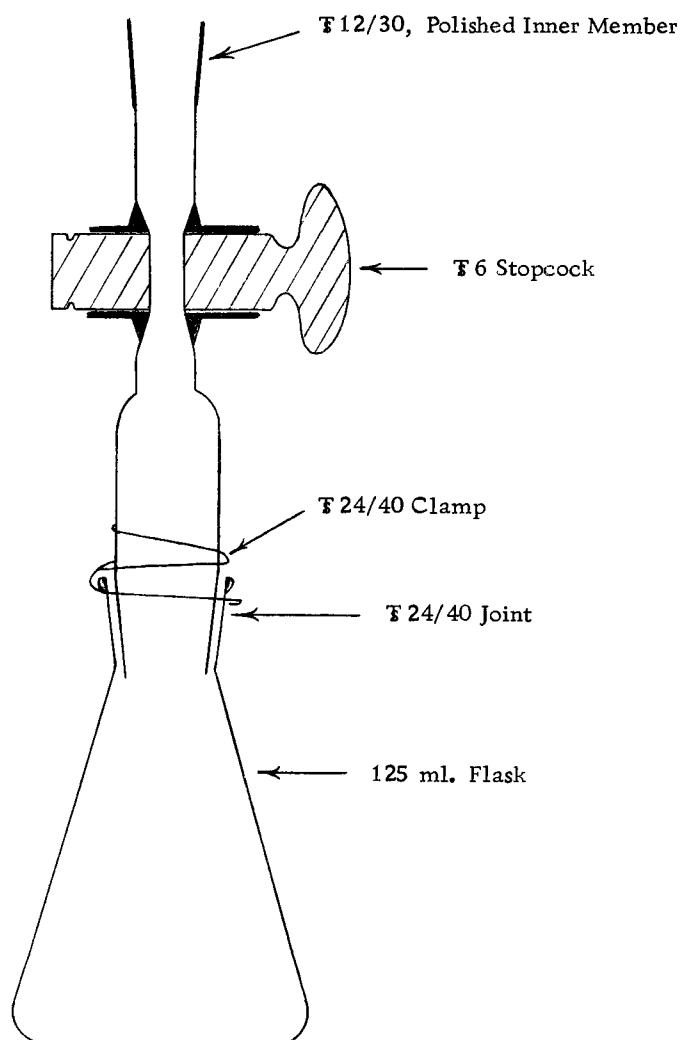


Figure IX. Borohydride Preparation Flask

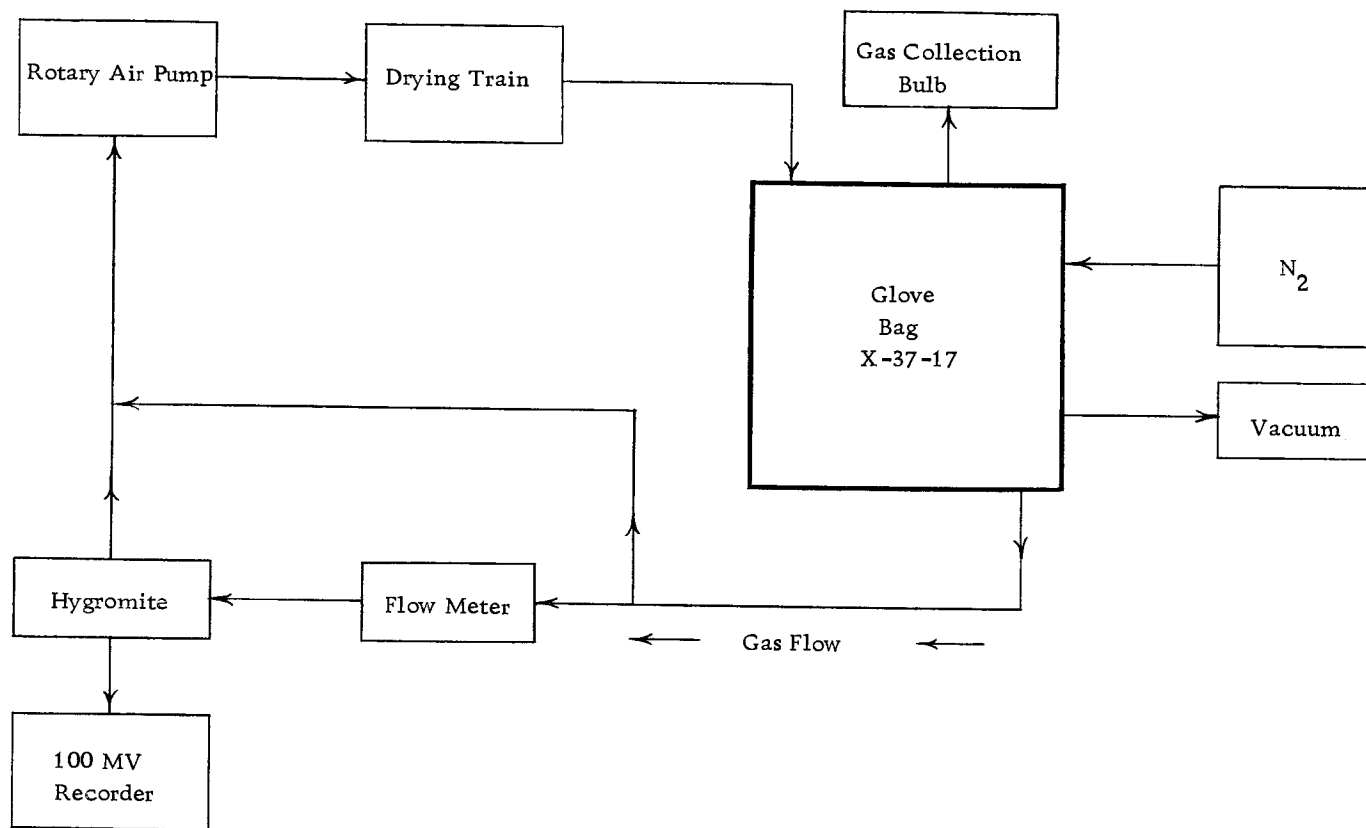


Figure X. System for Continuous Monitoring of Water in Glove Bag

times. The rotary air pump was actuated and approximately 100 cc/minute flowed through the Hygromite (an electrolytic hygrometer available from Beckman Instruments, Inc., Fullerton, California) which monitors water continuously in the 0-1000 ppm (v/v) range. The output of the Hygromite was monitored with a 100 mv recorder and a continuous record of the water level obtained. In ten minutes the water level had decreased to about 300 ppm, in forty minutes to about 100 ppm, and after one hour leveled off about 80 ppm. 100 ppm is comparable to about 80 micrograms  $H_2O$ /liter of nitrogen at atmospheric pressure, and in a large glove bag the total water would amount to only a few milligrams. A gas sample was collected in one run on a similar system and a mass spectrometric analysis indicated close agreement with the Hygromite result at the time of collection.

When the room atmosphere is removed from the glove bag by evacuation, oxygen, nitrogen, and water vapor are removed. Water vapor in particular is hard to eliminate because of surface adsorption, but oxygen and nitrogen are largely removed. Through several nitrogen purges the oxygen level is reduced to low levels. When the bag is filled with nitrogen and the gas circulated, small amounts of oxygen will seep continuously through the thin walls of the polyethylene glove bag. If the reaction is run shortly after a final evacuation of the bag and fresh nitrogen is placed in the bag, the oxygen level remains at levels which have not proved bothersome. This

method is justified over the conventional glove box because of its great convenience. Whereas a normal glove box occupies many cubic feet in a laboratory, a glove bag can be stored in a shoe box.

### Preparation Procedure

1. The apparatus and materials needed for a preparation are placed into the glove bag and the bag is sealed. Everything is placed between the two polyethylene sheets to prevent piercing the surface of the glove bag when a vacuum is applied.
2. A vacuum is applied to the bag until it is completely collapsed. The vacuum is shut off and nitrogen is introduced until the bag has billowed up. The nitrogen is evacuated from the bag, and then more nitrogen introduced to inflate it. This removes most of the water from the surfaces in the bag. The rotary air pump is actuated. The atmosphere is circulated through the drying train throughout the preparation, but in an hour the water level in the atmosphere is below 100 ppm. The bag is again evacuated and refilled with nitrogen.
3. The container of lithium borohydride is opened and a large stirring rod is used to crush lumps and produce a fine powder. The container is sealed.
4. The preweighed reaction flask is placed upright and a powder funnel put in the mouth.

5. The metallic tetrachloride container is opened. One ceramic spatula is used to transfer a previously determined weight of metallic tetrachloride to the flask. Intermittent weighings are necessary to determine how much has been transferred. When the right amount has been transferred the metallic tetrachloride container is closed.
6. The lithium borohydride container is opened. A second ceramic spatula is used to transfer a previously determined amount of lithium borohydride (5 moles of lithium borohydride/mole of metallic tetrachloride is quite sufficient) to the flask. Intermittent weighings are necessary. The transfer should be as rapid as possible.
7. A large stirring rod is used to crush and stir the mixture together. Several dozen nickel balls are then added for stirring purposes. The stopcock and the  $\text{F } 24/40$  joint are greased with Apiezon H grease. The stopcock is closed and the joint connected and clamped.
8. The rotary air pump is turned off, the glove bag is opened and the reaction vessel removed.
9. The reaction mixture is stirred vigorously. After about five minutes the powder becomes moist and then heat is evolved. The reaction mixture is stirred continuously until the mixture has cooled down. The heat will cause the evolution of some gas

(hydrogen and diborane). The resultant pressure may reduce itself by pushing the joint members slightly apart. A white smoke is formed when the gas contacts the air. If this takes place, the clamp will push the joint together again, but the greased seal should be manually adjusted for a leak free fit. The flask is placed in a dry-ice-acetone (DIAC) bath.

10. The reaction vessel is attached to the sample storage system for isolation of the metallic borohydride.

### Storage System

Initial storage of zirconium borohydride in a small vacuum manifold with greased joints and stopcocks revealed that the system was inadequate. Although Apiezon N grease (one of many tried) was seemingly reactive with the borohydride, it remained somewhat viscous and proved a good lubricant for several months. The grease eventually flowed into the storage and test cells, and into the bore of the stopcocks. Thereupon the grease layer in the joints and stopcocks became thinner and thinner with consequent channeling. With channeling the stopcocks began to freeze. The opening and closing of frozen stopcocks could lead to breakage of the vacuum system and possible exposure of the borohydrides to the air with a resulting explosion. Such a system was not amenable to unattended long term storage or short term handling without problems due to stopcock

grease.

Possible alternatives to the stopcock grease were examined. Mercury float valves would probably work well but are expensive. The borohydrides seem to wet mercury and mercury may cause the slow decomposition of the borohydride at room temperature. Teflon vacuum stopcocks were available and reasonably inexpensive, but the reactivity of Teflon with the borohydride was not known. It was anticipated and shown that Teflon was non-reactive with zirconium borohydride. Glass to metal vacuum valves with Teflon couplings, and Teflon sleeved standard taper joints were available. The Teflon valves, standard taper joints, and metal vacuum valves were obtained for testing.

The resultant borohydride storage system, shown in Figure XI, has been used successfully for one and a half years. Its construction is described below. The Teflon needle valve, #795-120, was obtained from Fisher and Porter Company, 3756 Grand Avenue, Oakland, California, 94610. It is claimed to hold a  $10^{-6}$  mm of mercury vacuum, and is sufficient for the  $10^{-2}$  mm of mercury vacuum necessary for the storage system. On prolonged use the Teflon stem may be stripped necessitating replacement. The Whitey ball valve, #43S4, with snug Teflon ferrules holds an excellent vacuum and was obtained from Portland Valve and Fitting Co., Suite A, Shanks Building, 936 S. E. Ankeny, Portland, Oregon,



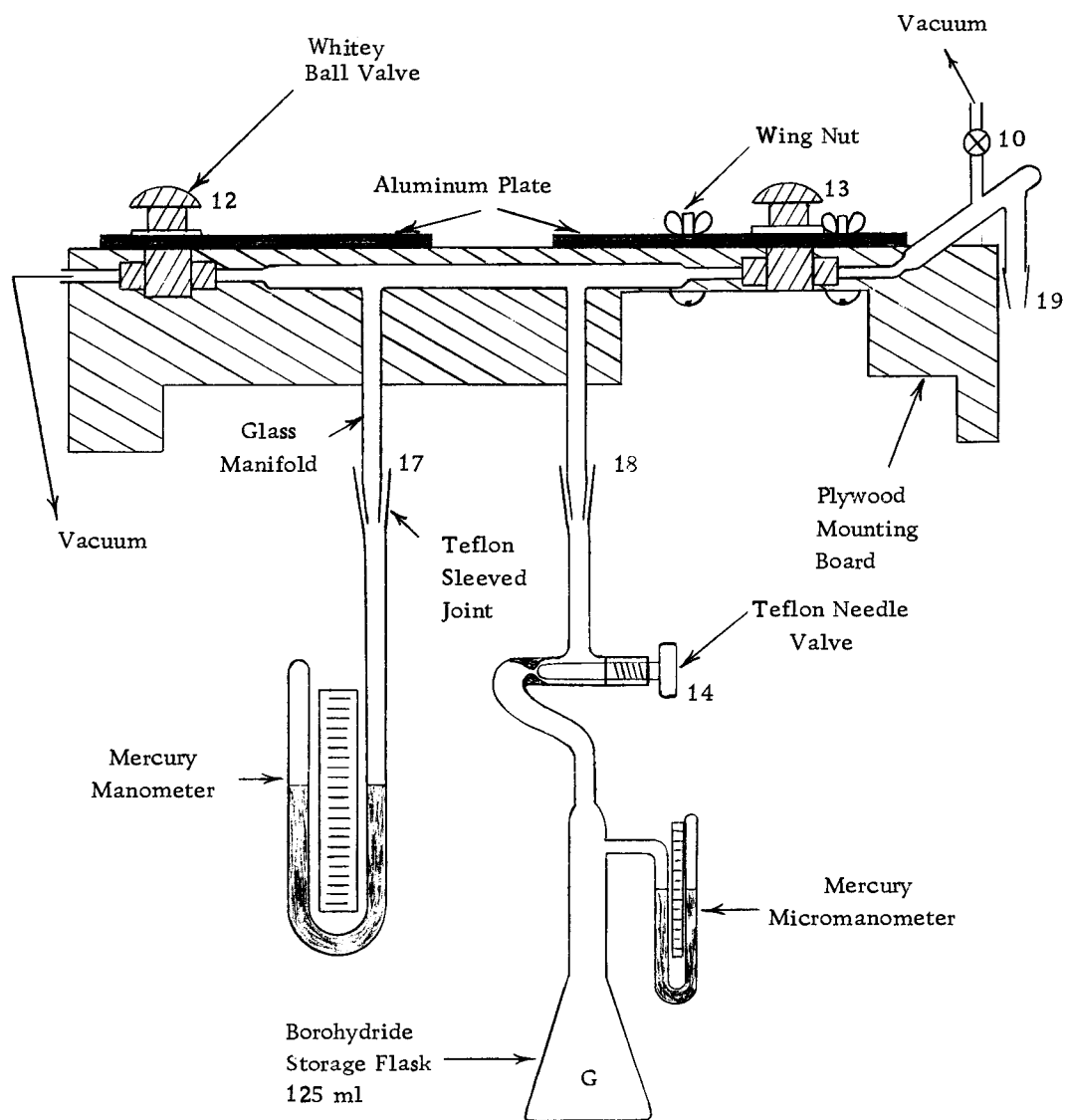


Figure XI. Borohydride Storage System

97214. The Teflon sleeved  $\frac{1}{2}$  12/30 joints, with polished outer members, were obtained from Ace Glass, Inc., P. O. Box 192, Vineland, New Jersey. These joints did not hold vacuum as well as hoped. When Apiezon N grease was applied to the outer lip of a joint it held an excellent vacuum. Over several hours, however, the leakage through a non-greased joint was inconsequential.

The storage system is suspended from the metal ball valves. Each ball valve is firmly attached to one aluminum plate, each aluminum plate is bolted to a plywood board, and the plywood board is mounted on a relay rack. The glass manifold is easily removed from between the metal ball valves by loosening the metal fittings holding it and then sliding the aluminum plate which is held by wing nuts away from it. The wing nuts loosen the plate and the plate has a straight slot cut in it in line with the two bolts which allows the plate to slide parallel to the glass manifold. The easy removal facilitates easy cleaning and maintenance. Further support for the manifold comes from clamps which are secured to ring stand rods built into the sides of the relay rack. The storage system is easily transportable if necessary.

The metallic borohydride from the reaction vessel is transferred to the storage flask in the following manner:

The reaction vessel is attached to the storage system at joint 19. The reaction flask is placed under a DIAC bath. The air

in the manifold between the ball valve and the  $\text{F } 6$  stopcock is removed by opening stopcock 10. After the air is removed the  $\text{F } 6$  stopcock is opened and all the non-condensable gas removed. Stopcock 10 is closed. The DIAC bath is removed. Valves 13 and 14 are opened and a DIAC bath is placed around the reaction vessel. A heating tape previously wound around the glass manifold is now held around  $40^\circ\text{C}$ . The metallic borohydride distills into G fairly rapidly. A gas pressure due to thermal decomposition of the metallic borohydride may eventually hinder rapid borohydride transfer, but it is easily removed by placing the reaction flask under a DIAC bath and evacuating the system. When the reaction mixture appears dry, the distillation is essentially complete. The removal of the water bath, followed by stirring of the mixture by moving the nickel balls with a magnet frees a small amount of entrapped borohydride. This metallic borohydride is distilled over and the reaction can be considered complete. Any residual gas pressure is pumped off. It should take about two hours to complete the isolation of the metallic borohydride. Valves 13 and 14 are closed. The  $\text{F } 6$  stopcock is closed, and the reaction vessel is removed from joint 19. The reaction vessel is dried and placed under a DIAC bath. The  $\text{F } 24/40$  joint is loosened and removed. The reaction mixture is poured into a

dry sink in a room with good ventilation and then destroyed by the application (from a safe distance) of a stream of water from a wash bottle. The reaction mixture inflames violently with orange and green flames. The nickel balls are salvaged.

The appearance, melting point, and vapor pressure have been used to characterize hafnium and zirconium borohydrides. Colorless zirconium borohydride melted between 28.5 and 28.8 °C. compared to the reported value of 28.7 °C. Colorless hafnium borohydride melts close to 29.0 °C as reported (22).

The vapor pressure of zirconium borohydride was very carefully observed. The storage cell was held under liquid nitrogen or a DIAC bath until a pressure measurement was to be made. All residual gas was previously removed. The storage flask was completely immersed in a water bath with good circulation. The temperature was observed, and the flask removed from the water bath and immersed in a cold bath. The residual pressure (a fraction of one millimeter) was measured and subtracted from the observed pressure. The experimental curve of  $\log P$  v.  $1/T$  agrees quite closely with the published curve (22) from 0 to 50 °C. Room temperature vapor pressure measurements on hafnium borohydride agree closely with the published values. By careful control of the temperature zirconium borohydride may be supercooled 3-4 °C.

During the winter months normal room temperature is around

22 °C. No significant thermal decomposition of hafnium and zirconium borohydrides was observed over several month periods when stored at room temperature. During the summer months normal room temperature varies between 27 and 33 °C, thermal decomposition of hafnium and zirconium borohydrides and their mixtures becomes more appreciable. The decomposition products are a non-volatile white powder (it is also violently inflammable on contact with water with green flames), hydrogen, and diborane. Accumulation of the white powder seems to increase the decomposition of the borohydrides. Sublimation of the borohydrides to a clean storage flask with subsequent storage below 0 °C is recommended if room temperature is a problem. Cold storage allows the borohydrides to be kept indefinitely.

#### Mass Spectrometry of Zirconium Borohydride

The first mass spectrum of zirconium borohydride was run on a Consolidated Engineering Corporation Model 21-401 mass spectrometer. The instrument is a direction focusing mass spectrometer with a range of  $m/e$  2-100 and a resolving power of 100 (largest mass number where ion beams differing by one mass number can be accurately separated, i. e., fringe intensity between beams of adjacent mass numbers decreases to 2% or less of the total intensity of both beams). The inlet system is designed for the introduction of

a measured amount of a gaseous sample. Gaseous samples are introduced to a 3 ml volume at pressures measured with a mercury manometer. They are expanded into a 3 liter volume for a thousand-fold pressure reduction. They are introduced into the high vacuum analyzer unit through a narrow leak where the sample is bombarded with a beam of 70 ev electrons. The stopcocks on the inlet system were lubricated with Dow Corning high vacuum grease (a silicone).

The instrument background was noted prior to introduction of the sample. A 9 mm sample of zirconium borohydride vapor was contained in a 200 ml mass spectrometer sample balloon. A portion of the sample was let into the manometer chamber and the pressure observed. The pressure dropped to 8 mm in 15 minutes. This was indicative of chemical or physical adsorption onto the surface of the silicone grease. The drop in pressure indicated that thermal decomposition into hydrogen was not a problem. A 500 micron sample was introduced into the 3 liter volume. This pressure was leaked into the analyzer unit and a mass spectrum obtained at  $m/e$  2 and from 10-97 (100 microamps ionizing current). The sample was evacuated from the inlet system. The intensities of the background and zirconium borohydride spectra are shown in Table II.

An examination of the spectrum revealed many things:

1. Hydrogen at  $m/e$  2 is the major constituent in the spectrum by at least an order of magnitude.

Table II. Mass Spectrum of Zirconium Borohydride (ZrB)

m/e	Bkg	Bkg + ZrB	ZrB	m/e	Bkg	Bkg + ZrB	ZrB
2	11.2	30,000 +	30,000 +	59	---	1.5	1.5
10	---	28.5	28.5	60	---	1.2	1.2
11	---	136	136	61	---	1.0	1.0
11 1/2	---	3.2	3.2	61 1/2	---	t	0.5
12	t	90	90	62	---	~3.0	~3.0
13	t	165	165	62 1/2	---	~5.0	~5.0
14	t	52.5	52.5	63	---	~7.0	~7.0
15	0.5	3.9	3.4	64	1.5	40	39
16	1.0	4.2	3.2	64 1/2	---	~1.0	~1.0
17	4.9	t		65	---	~3.5	~3.5
18	23.0	1.5		66	0.9	22.0	21.1
20	---	3.0	3.0	67	0.5	5.8	5.3
21	---	12.0	12.0	67 1/2	---	t	t
22	---	86.0	86.0	68	t	~20	~20
23	---	412	412	68 1/2	---	~5.0	~5.0
24	t	850	850	69	1.2	~7.0	~6.0
25	0.8	570	570	69 1/2	---	~3.0	~3.0
26	3.0	1020	1020	70	3.1	~8.0	~5.0
27	2.7	1060	1060	70 1/2	---	1.0	1.0
28	22.8	1540	1520	71	1.0	6.0	5.0
29	2.0	43.2	41.2	72	0.6	---	---
30	t	2.0	2.0	73	---	---	---
32	5.0	6.4	1.4	74	t	---	---
33	---	2.3	2.3	75	---	---	---
34	---	1.3	1.3	76	2.0	---	---
36	---	0.5	0.5	77	1.8	0.7	---
37	t	0.5	0.5	78	0.7	1.0	0.3
38	1.0	1.3	0.3	79	0.7	---	---
39	2.4	6.5	4.1	80	t	---	---
40	1.2	36.3	35.1	81	0.5	---	---
41	3.9	14.0	10.1	82	t	t	---
42	1.9	6.5	4.6	83	1.0	2.2	1.2
43	2.6	24.8	22.2	84	0.7	2.8	2.1
44	3.0	7.3	4.3	85	t	5.7	5.7
45	t	1.0	1.0	86	---	---	---
46	---	0.9	0.9	87	---	---	---
47	---	t	t	88	---	---	---
50	2.2	1.1	1.1	89	---	0.5	0.5
51	1.2	2.0	0.8	90	---	13.7	13.7
52	0.6	0.8	0.2	91	2.0	22.0	20.0
53	0.7	1.4	0.7	92	0.9	14.5	13.6
54	---	1.0	1.0	93	---	1.3	1.3
55	3.3	6.2	2.9	94	---	4.4	4.4
56	2.0	8.0	6.0	95	---	1.4	1.4
57	3.5	14.2	10.7	96	---	0.7	0.7
58	---	2.5	2.5	97	---	---	---

2. Boron is indicated by  $m/e$  10 and 11 and their relative intensities (1:4). Comparison with a published mass spectrum of diborane (30) conclusively indicated the presence of diborane.
3. Nitrogen was a constituent in the sample as indicated by  $m/e$  14, 28, and 29.
4. Air had obviously leaked into the sample bulb during transfer as evidenced not only by nitrogen, but argon (at 40), and carbon dioxide (at 44). Oxygen (at 32) was not present as would be expected and the water (at 17, 18) had disappeared from the instrument background.
5. There were definite doubly charged species at  $m/e$  61.5, 62.5, 68.5 and 69.5 and probably doubly charged species at 63.5, 64.5, 67.5, and 70.5. These are indicative of species at 123, 125, 137 and 139, and probably 127, 129, 135, and 141.
6. Peaks in the 90-96 range might possibly be due to isotopes of zirconium but the relative distribution and peaks at 93 and 95 would not be present.
7. Many minor peaks could not be explained and were perhaps due to residual material in the instrument which had been removed by introduction of the zirconium borohydride. No positive conclusion can be drawn on the origin of some of



the peaks.

8. There were prominent peaks at 64, 66, 68, 90, 91, and 92. Since air had leaked into the gas balloon, some of the peaks in the mass spectrum might be due to gaseous reaction products of air and zirconium borohydride. Previous to running the mass spectrum of zirconium borohydride the mass spectrum was obtained of gaseous products from the storage manifold where air, stopcock grease, and zirconium borohydride had reacted together (Figure XII). No zirconium borohydride was present in the sample. The spectrum indicated a large amount of hydrogen, diborane, and air. The significance of this spectrum was the close match in many of the relative intensities in the range  $m/e$  39-97 for the air and grease decomposition spectrum and the zirconium borohydride spectrum (Figure XII). Since air was found in the zirconium borohydride spectrum it is reasonably assumed that many of the unknown peaks in the spectrum are due to gaseous reaction products of air and stopcock grease, whatever they might be. The peaks in the 39 to 70 region would largely disappear. The doubly charged species in the 60-70 range would become particularly prominent if the reaction products peaks were subtracted out.
9. The definite doubly charged species at 61.5, 62.5, 68.5,

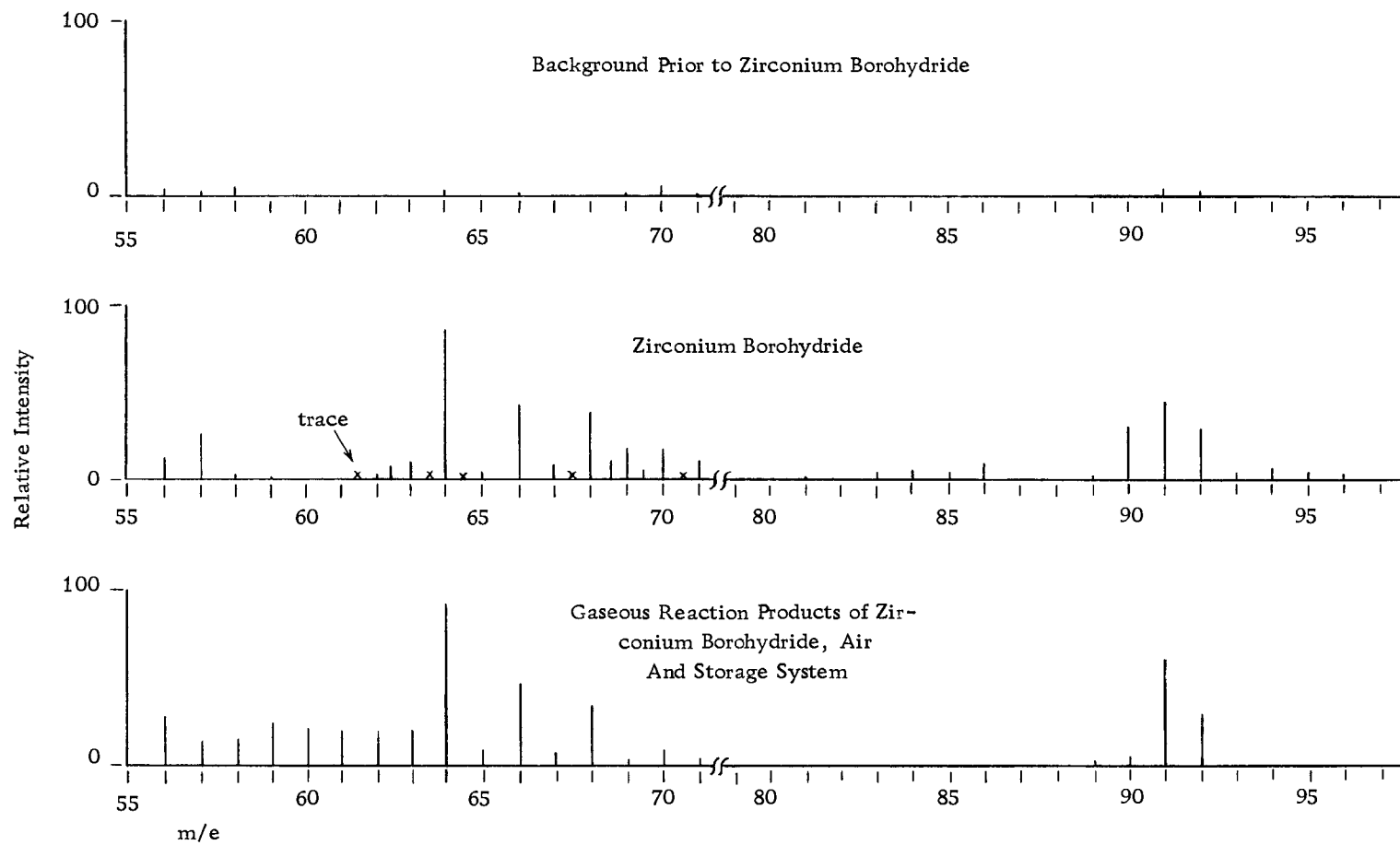


Figure XII. Mass Spectra of Zirconium Borohydride and Gaseous Reaction Products of Zirconium Borohydride, Air, and Storage System

and 69.5 are then prominent beyond the contribution due to reaction products and assignments are given to them in Figure XIII. There is a 0.038 amu difference between the proposed species at a given  $m/e$  which would be resolvable on a high resolution mass spectrometer.

10. It was suspected that the air and zirconium borohydride reaction products were hiding the zirconium isotopes in the vicinity of 90. The intensities of the peaks from both spectra are given in Table IIIa. The peaks at 93 and 95 in the zirconium borohydride spectrum could possibly be due to  $Zr^{92}H^+$  and  $Zr^{94}H^+$  and they are in the 1:1 proportion of the zirconium isotopes at 92 and 94. The peaks at 94 and 96 might be due to  $Zr^{94}$  and  $Zr^{96}$  as they are in the same proportion 6.1:1 and 6.3:1. The intensity of the 94 peak in the zirconium borohydride spectrum was used to subtract out the contribution of the zirconium isotopes (Table IIIb) in the spectrum (Table IIIc). The ratio of the intensity of the 95 to 94 peaks ( $1.4/4.4 = .32$ ) in the zirconium borohydride spectrum was used to subtract out the contribution of the  $ZrH^+$  species in the spectrum, assuming that the  $ZrH^+$  species followed the relative abundance of the zirconium isotopes (Table IIIc). The net relative intensity of the ZrB peaks in the zirconium borohydride spectrum (the

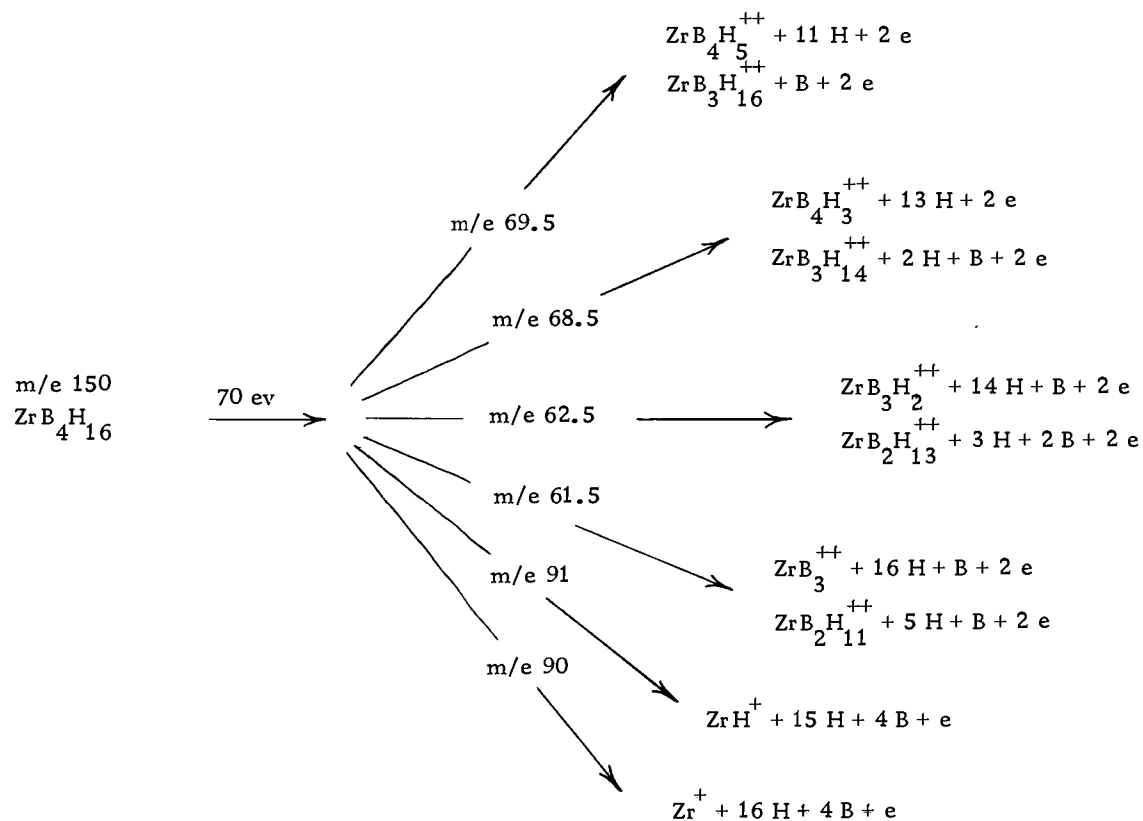


Figure XIII. Possible Species Detected in Mass Spectrum of Zirconium Borohydride

Table III. Comparison of the Mass Spectrum of Zirconium Borohydride (ZrB) and the Mass Spectrum of Gaseous Reaction Products of Air, Grease, and Zirconium Borohydride in the  $m/e$  90 Range.

a Intensities			b Abundance of Zirconium Isotopes		
$m/e$	Intensities		Mass	Percent Abundance	Relative Abundance
	Air-ZrB	ZrB			
89	6.5	0.5	90	51.46	100.0
90	8.1	13.7	91	11.23	21.82
91	100.	20.0	92	17.11	33.25
92	46.	13.6	94	17.40	33.81
93	--	1.3	96	2.8	5.44
94	--	4.4			
95	--	1.4			
96	--	0.7			
97	--	--			

c Contribution of $Zr^+$ and $ZrH^+$					
$m/e$	Intensity of ZrB	Contribution of Zr to ZrB based on 94	Contribution of ZrH to ZrB based on 95	Net Int. ZrB	Net Rel. Int. of ZrB
89	0.5	-	-	0.5	3.8
90	13.7	13.0	-	0.7	5.3
91	20.0	2.8	4.1	13.1	100.
92	13.6	4.3	0.9	8.4	64.
93	1.3	--	1.4	-0.1	
94	4.4	4.4			
95	1.4	-	1.4	-	
96	0.7	0.7	-	-	
97	-	-	0.1	0.1	

d Comparison of the Net Relative Intensities of the ZrB spectrum and Reaction Product Spectrum after Subtraction of Zr and ZrH from the ZrB Spectrum		
$m/e$	Relative Int. of Air-ZrB Reaction Prod.	Net Relative Int. of ZrB
89	6.5	3.8
90	8.1	5.3
91	100.	100.
92	46.	64.

relative abundance of the gaseous reaction products peaks which are present in the zirconium borohydride spectrum) is compared against the relative intensities of the air-grease-ZrB reaction product spectrum in Table IIIId. The comparison is good in terms of the relative magnitudes, though the numerical match is only fair. The comparison is good enough to justify the conclusion that  $Zr^+$  and  $ZrH^+$  species are present in the spectrum of zirconium borohydride. Further, since there is a good chance that the zirconium isotopes would be present, the evidence is virtual proof.

The next phase of the mass spectrometry study of zirconium borohydride was done on an Atlas Model CH 4 mass spectrometer. The CH 4 is a  $60^\circ$  sector instrument offering high accuracy, resolution, and sensitivity, and was equipped with a high speed galvanometric recording unit. The inlet system was all stainless steel and included a metal membrane micromanometer.

An inlet system background was taken at 70 ev with 60 microamps of ionizing current. The inlet system was running at  $50^\circ C$  and the ion source at  $250^\circ C$ . The electron multiplier (collector) voltage was 1.6 Kv. A 200 micron sample of zirconium borohydride was introduced to the 6 liter volume. The sample was scanned from  $m/e$  24-250. Air, diborane, and peaks from 50-58, 64-70, 77-78, and

91 were present, but no indication of a parent or species of zirconium borohydride. Additional sample pressure was introduced to 500 microns. This greatly increased the intensities of the peaks, but again nothing attributable to zirconium borohydride. The pattern looks like it originated from hydrocarbons and particularly aromatics.  $m/e$  64, 66, and 68 are split by about 0.1 amu. The electron multiplier voltage was increased to 1.85 Kv, and the next spectrum showed further increase in intensities, but mostly a hydrocarbon background.  $m/e$  64, 66, 67, and 68 were split by 0.1 amu. The inlet system was evacuated and a second sample let in. The sample pressure was off scale on the membrane micromanometer. The first spectrum showed many hydrocarbon peaks. There were traces of doubly charged species at 57.5, 62.5, 63.5, 64.5, 67.5, 68.5, 69.5, and 70.5. There were peaks at all the masses which would correspond to twice doubly charged species, but there was no means by which they could be distinguished from hydrocarbon species. Splitting in the 115-141 region was not observed. Hydrogen and diborane were present in large amounts. A second spectrum was run with the electron multiplier at 2.0 Kv. An extensive hydrocarbon background was found but the doubly-charged species at half-masses had disappeared. A third spectrum was run at 2.0 Kv on the electron multiplier and with a 20 ev ionizing energy in an attempt to increase parent ionization. A very prominent splitting of 64, 66, 67, and 68 was found, and a

very extensive hydrocarbon background which overwhelmed everything else. The sample was pumped out. The temperature of the inlet system was dropped by 37 °C and a third sample of 600 microns introduced into the sample system. An electron energy of 70 ev and 1.6 Kv on the electron multiplier were used. Several more spectra revealed nothing different than the other runs of zirconium borohydride: hydrogen, diborane, and hydrocarbons. The last spectrum was run at an electron energy of 10 ev. The hydrocarbon background was prominent again.

No evidence for zirconium borohydride could be found in the spectra. Even though the spectra were obtained by a fast scan and only semi-quantitative the evidence for the isotopes of zinc at 64, 66, 67, and 68 was strong.<sup>8</sup> A comparison of the relative intensities of the isotopes of zinc and the intensities of the masses approximately 0.1 amu lower than the respective hydrocarbon masses at 64, 66, 67, and 68 gave strong evidence for zinc (Table IV). The zinc isotopes would be 0.08 amu lower than the respective hydrocarbon species at 64, 66, 67, and 68. The origin of zinc is unknown.

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<sup>8</sup>Personal communication. Dr. R. M. Peekema, Assistant Professor, Dept. of Chemistry, Oregon State University. 1964.



Table IV. Comparison of the Intensities of the Isotopes of Zinc and the Intensities of the Masses 0.1 amu Lower than the Respective Hydrocarbon Masses at m/e 64, 66, 67, and 68.

Mass	Intensity	
	Zinc Isotopes	Spectrum
64	48.9	46.4
66	27.8	26.1
67	4.1	8.7
68	18.6	18.8

Several months after the first zirconium borohydride run on the CEC 21-401 and the second run on the Atlas CH 4, another sample was introduced into the 21-401 in an attempt to improve and reproduce the initial results found on that instrument. Apiezon N grease replaced the Dow Corning High Vacuum grease (silicone). The accelerating voltage and the ionizing current in the instrument became extremely erratic, fluctuation by tens of volts and microamps respectively. There was a close correlation between the entry of zirconium borohydride into the analyzer unit and the breakdown in the accelerating voltage and ionizing current. The small amount of interpretable data obtained gave no evidence of the species attributed to zirconium borohydride found in the first runs on the CEC 21-401. The 64, 66, and 68, and 91 and 92 peaks were prominent again in the same ratios as had been noted in the first runs. A small amount of

air was present. No assignment could be made for the species present but the zinc isotope characteristics were present. The zinc spectra from two different instruments points to the sample as its origin. No further study to find the source of zinc, if present, was made.

Further work with zirconium borohydride on the CEC 21-401 was curtailed as it might have proven detrimental to the instrument. The erratic behavior of the accelerating voltage and ionizing current was interpreted as a current leak across a deposited film of zirconium metal or a zirconium-boron mixture. When the filament assembly was examined a deposit was discovered, but a spectrographic study did not show zirconium (or zinc). The zirconium level in the sample may have been too low.

### Hydrolysis of Hafnium and Zirconium Borohydrides and Their Mixtures

#### Apparatus

The apparatus required for the determination of hafnium/hafnium + zirconium ratios by hydrolysis of hafnium and zirconium borohydrides and their mixtures is shown in Figure XIV. A key to the symbols is included on the following pages. A discussion of the calibration of the measurement system may be found in Appendix 3. Apiezon H was the stopcock grease used.

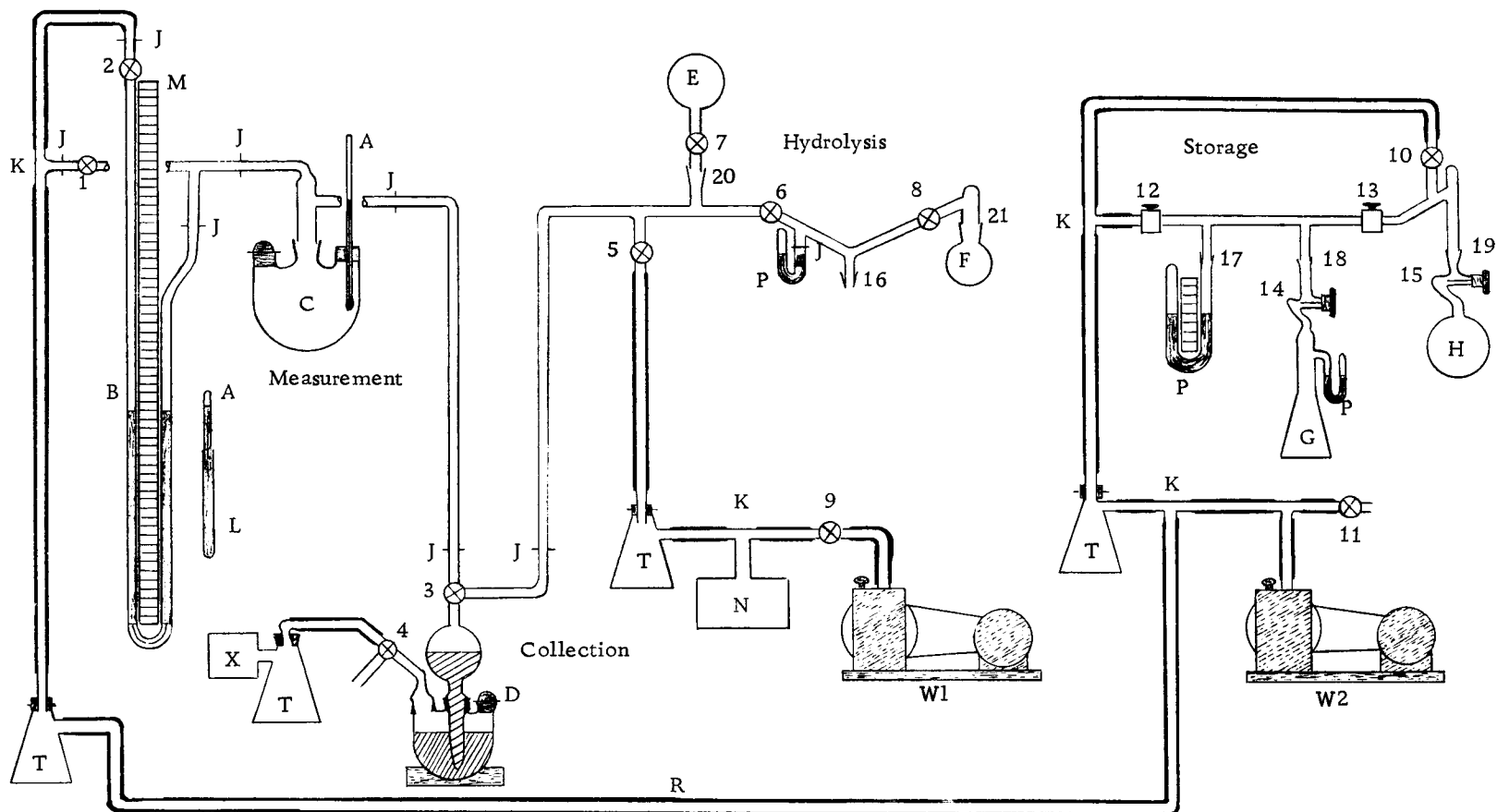


Figure XIV. Vacuum System for Borohydride Analysis

KEY TO VACUUM SYSTEM FOR BOROHYDRIDE ANALYSIS -  
(Figure XIV)

- A Mercury Thermometer
- B Mercury Manometer
- C 1 liter, 3-neck, Pyrex, round-bottom flask (Hydrogen  
Collection Flask)
- D Toepler Pump
- E Mass Spectrometer Sample Bulb
- F Water Storage Flask, 250 mls.
- G Borohydride Storage Flask
- H 500 ml Hydrolysis Bulb
- J 18/9
- K Pyrex Glass Tee
- L Mercury Temperature Tube
- M Meter Stick, Graduated in 0.1 cm
- N McLeod Gage
- P Mercury Micromanometer
- R Rubber Vacuum Tubing
- T Vacuum Traps, 500 or 1000 ml Pyrex Vacuum Filter Flask
- W Forepumps
- X Nash Vacuum System (25 cm Hg gas pressure turns ballast  
vacuum pump on)
- I Stockcock, 4 mm oblique bore, 2-way

- 2 Stopcock, 2 mm straight bore, 2-way
- 3 Stopcock, 2 mm straight bore, 3-way
- 4 Stopcock, 2 mm straight bore, 3-way
- 5 Stopcock, 4 mm oblique bore, 2-way
- 6 Stopcock, 6 mm straight bore, 2-way
- 7 Stopcock, 2 mm oblique bore, 2-way
- 8 Stopcock, 6 mm straight bore, 2-way
- 9 Stopcock, 6 mm straight bore, 2-way
- 10 Stopcock, 2 mm straight bore, 2-way
- 11 Stopcock, 2 mm straight bore, 2-way
- 12 Whitey Ball Valve with Teflon Ferrules, #43S4
- 13 Whitey Ball Valve with Teflon Ferrules, #43S4
- 14 Needle Valve, Glass with Teflon Stem, 4 mm i. e., Fisher and Porter Company
- 15 Needle Valve, Glass with Teflon Stem, 4 mm i. d., Fisher and Porter Company
- 16  $\text{F } 12/30$  joint: Teflon Clad Inner Member, Polished Outer Member. Ace Glass, Inc.
- 17  $\text{F } 12/30$  joint: Teflon Clad Inner Member, Polished Outer Member. Ace Glass, Inc.
18.  $\text{F } 12/30$  joint: Teflon Clad Inner Member, Polished Outer Member. Ace Glass, Inc.
- 19  $\text{F } 12/30$  joint: Teflon Clad Inner Member, Polished Outer Member. Ace Glass, Inc.
- 20 Joint,  $\text{F } 12/30$
- 21 Joint,  $\text{F } 24/40$

The borohydride was to be weighed and hydrolyzed in the same container. Too small a sample would decrease precision. The largest sample size which could be weighed depended on the weight of the hydrolysis bulb and the hydrogen pressure which could be safely accommodated in it. The size of the sample bulb was determined by the availability of an analytical balance on which it could be weighed. A half-liter hydrolysis bulb which weighed less than 200 grams was decided upon.

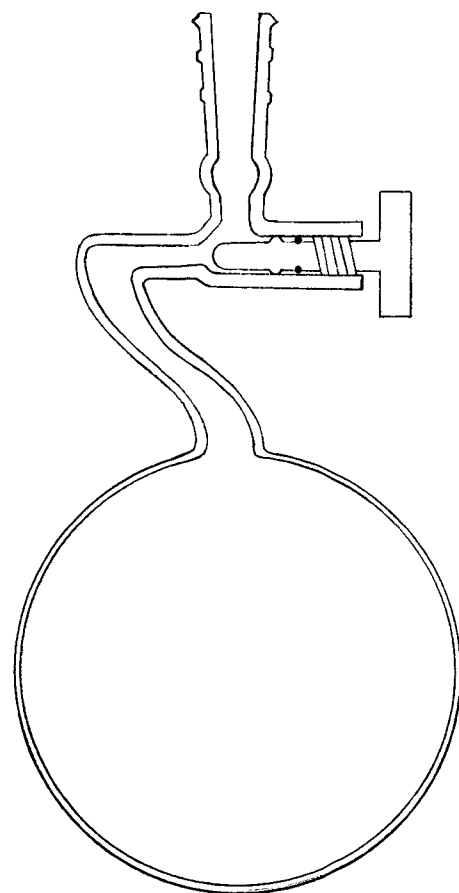
The stress in the walls of a perfect 500 milliliter bulb was calculated. The wall thickness was taken as 1 mm = 0.04". The inner radius was 1.90" and the outer radius 1.94". The stress area (cross sectional area of the glass at the radius) was 0.472 sq. in. The average tensile strength of Pyrex glass (a borosilicate glass) at room temperature is 10,000 lb/sq. in. (Perrys' Chemical Engineers' Handbook, 3d ed, p. 1548). The total force will be 10,000 lb./sq. in. x 0.472 sq. in. = 4720 lb; the equal but opposing force distributed on the surface area of the bulb (the area of the hemisphere) is 4720 lb./45.4 sq. in. = 104 lb./sq. in. or 104 lb./sq. in./14.7 lb./sq. in.-atm = 7 atmospheres. Imperfections may reduce the theoretical value. It was assumed and proven by use that the bulbs can safely hold two to three atmospheres of hydrogen pressure; this limit was never exceeded. About .35 grams of zirconium borohydride when hydrolyzed in a half liter bulb produces around 2 atmospheres of

hydrogen pressure and it is considered a reasonable working limit. The sample could be weighed to  $0.3500 \pm 0.0001$  gram without difficulty. Safety glasses should be worn for eye protection when working with the apparatus.

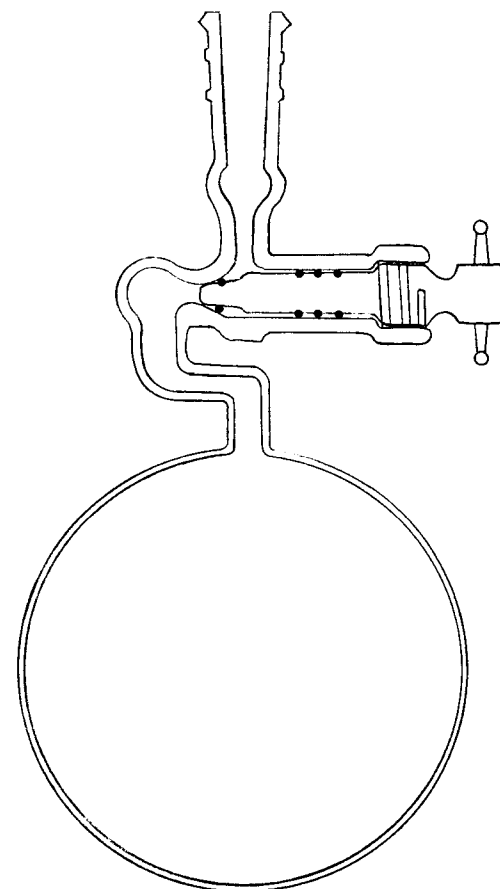
Each hydrolysis was performed in a half-liter round bottom distilling flask, the neck of which was replaced by a Teflon vacuum stopcock (valve) and a polished outer member  $\text{F } 12/30$  fitting (see Figure XV). A Fisher-Porter Corp. Teflon needle valve and a West-Glass Corp. vacuum stopcock were tried on the hydrolysis bulbs. The West-Glass vacuum stopcock was superior to the Fisher-Porter valve. Under heat from a heating tape the Fisher-Porter valve warped and would not seal. Upon long use the threads may be stripped necessitating replacement of the entire barrel. Under cold the seal must be closely watched because the Teflon barrel contracts. The West-Glass valve with O-ring seals, larger and sturdier barrel, and threads which cannot be stripped is very reliable and presented none of the problems encountered with the Fisher-Porter valve.

#### Distilled Water Hydrolysis

The hydrolysis study was initiated with a mixture of hafnium and zirconium borohydrides, about 2% hafnium, rather than pure hafnium or zirconium borohydride. If ratios by means of hydrolysis were not possible, then the method would not be practical. If



(a) with Fisher-Porter Valve



(b) with West-Glass Stopcock

Figure XV. Half-Liter Hydrolysis Bulbs



hydrolysis on a mixture was successful, then standards would need to be run. The % Hf in the starting material and in the hydrolysis residue was determined by X-ray fluorescence. The general evaluation of the method is outlined in Figure XVI.

The first hydrolysis solvent examined was distilled water. Initial experimentation led to the procedure which is, briefly, to take a carefully weighed sample of borohydride from the storage system, hydrolyze the sample, and collect the hydrogen gas given off. Measurement of the amount of hydrogen allows calculation of the ratio. The specific procedure is outlined below.

1. All the valves and stopcocks of the vacuum system are normally closed, except 9. Clean the hydrolysis bulb H - a 500 ml round bottom flask with neck replaced by a Fisher-Porter Teflon-stemmed valve - with dilute hydrofluoric acid and then rinse it well with distilled water. Drain the water from the flask. Attach H to joint 19. Open valve 15 and stopcock 10 in order to evacuate H. Place a heating mantle around the bottom of H and aluminum foil around the top. Adjust the variable transformer so the temperature inside H is about 130 °C. Bake the bulb out for one hour. The pressure should be below 0.02 mm Hg after one hour. The pressure may be read from the McLeod gage by opening stopcocks 1, 3, and 5.

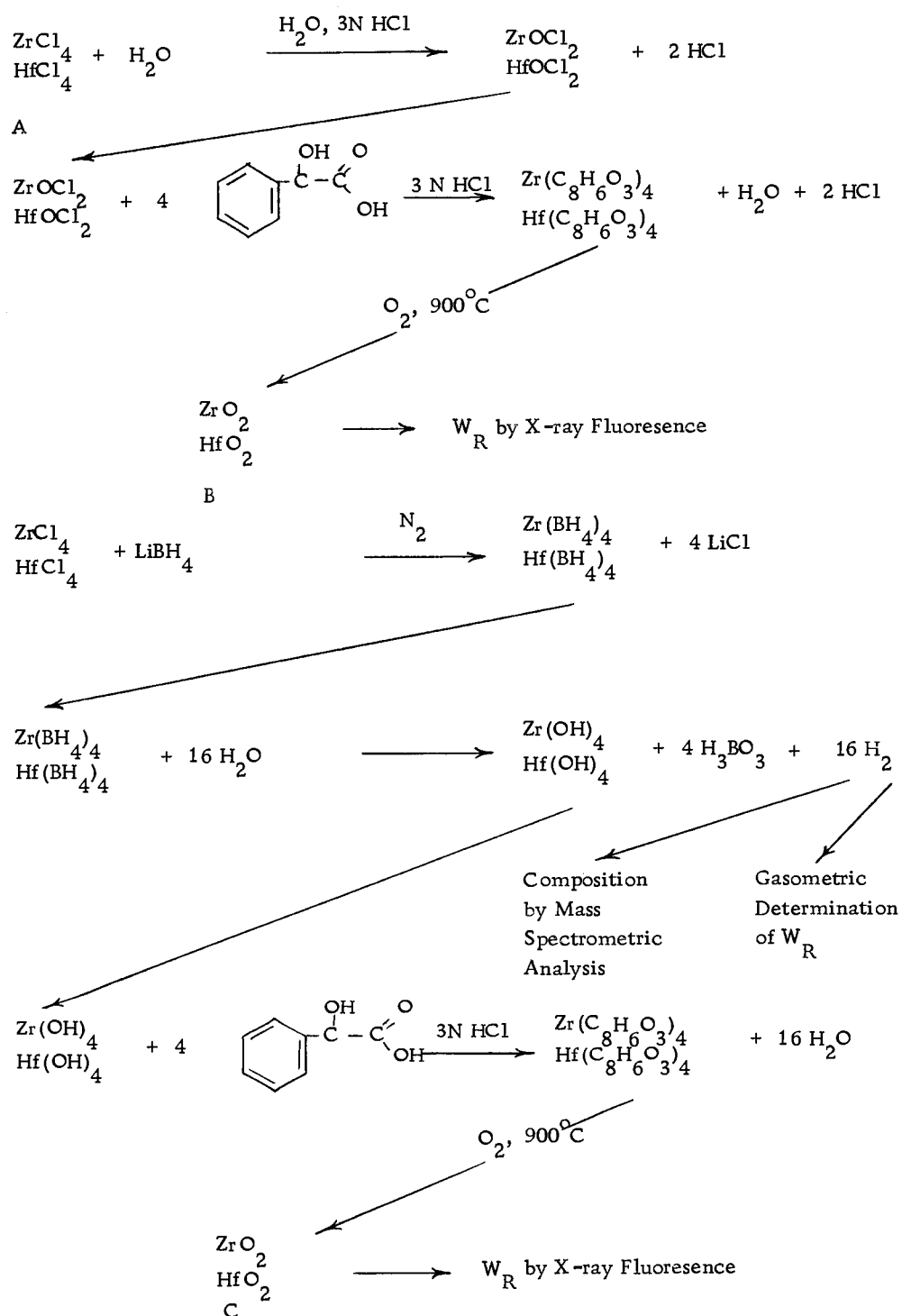


Figure XVI. Scheme for Evaluating the Gasometric Determination of Hafnium/Hafnium + Zirconium Ratios by Hydrolysis of the Metallic Borohydrides

2. Turn the heating mantle off and remove it from H. Close stopcock 10 and valve 15. Remove H from joint 19. Hang H on the suspension bar (see weighing method - Appendix 2) and allow it to equilibrate with the tare bulb for one hour. Wipe both bulbs clean with a silk cloth and wipe off the electrostatic charge with a clean dry hand. Equilibrate the bulbs for one hour. Do not allow any grease or dirt to contact the bulbs. Using a comparison weighing method, obtain the average weight difference between the tare bulb and the hydrolysis bulb. This should take about twenty minutes. This weight difference is the weight before borohydride condensation.
3. The borohydride storage bulb G is immersed in a dry ice-acetone (DIAC) bath and the pressure checked on the side arm micromanometer. If any pressure is noted, valves 12 and 14 are opened, G evacuated, and then valves 12 and 14 are closed. The DIAC bath is removed from G, and G is allowed to warm to room temperature.
4. Connect H to joint 19; use a  $\mathbb{F}$  clamp to secure the joint. Make sure that the joint is free of grease. Open stockcock 10 and evacuate the air in the inlet line. A heating tape will drive any significant water from the wall of the inlet line. Close stopcock 10, and open valves 13, 14, and 15. Spray

a stream of nitrogen gas, which has been cooled to about  $-20^{\circ}\text{C}$  by passing it through an aluminum coil immersed in a DIAC bath, around the bottom of H, condensing about .35 grams of borohydride. Close valve 15, immerse G in a DIAC bath, and when the borohydride has all condensed, close valves 13 and 14. Spray a stream of cold nitrogen on the tare weighing bulb for about the same length of time as on the hydrolysis bulb H.

5. Disconnect H from joint 19 and hang it from the weighing suspension bar. Allow H to equilibrate with the tare weighing bulb for one hour. Using the comparison weighing method obtain the average weight difference between the tare bulb and the hydrolysis bulb. This weight is the weight difference after borohydride condensation. The weight of total borohydride  $W_{\text{TB}}$  is the difference between the weight difference after borohydride condensation and the weight difference before borohydride condensation.
6. Transfer H to joint 16, apply some Apiezon N grease around the lip of the joint, and then secure the joint with a  $\text{F}$  clamp. Condense the borohydride in an approximate 5 cm diameter sector on the bottom of the bulb surface using a DIAC bath. When the borohydride has all condensed in the 5 cm sector, cover about half of the surface area of

bulb H with the DIAC bath.

7. Previous to or concurrent with step 6 above, a DIAC bath is placed around F, the water storage bulb, which contains 30 to 40 ml of water. When the water has equilibrated with the cold bath, stopcocks 5, 6, and 8 are opened and any air present pumped off. When the McLeod gage N indicates that the air has been removed, stopcocks 5, 6, and 8 are closed. F is warmed to room temperature with the aid of a warm water bath. Stopcocks 5, 6, and 8 are opened again for about 10 seconds to make sure any air trapped in the ice is pumped off. Close stopcocks 5 and 6, leave 8 open.
8. Open valve 15 and distill the 30 to 40 ml of water into H. A certain amount of gaseous pressure, beyond that due to water vapor, may build up in F and H. This pressure is due to a small initial hydrolysis reaction as a layer of ice and condensed water is being formed on the borohydride surface. The distillation is aided by a heating tape maintained at  $\sim 40$  to  $50^{\circ}\text{C}$ . When the distillation is complete, close valve 15 and stopcock 8. Tapping H during the condensation facilitates covering the borohydride with water, as discussed in step 9, below.
9. Begin warming the ice in the upper portion of H, condensing it to the bottom of the bulb. The intent is to form a pool of

ice water over the borohydride, but to do so while the borohydride is not too reactive. At least two hydrolytic reactions are possible, but the one which takes place in a large excess of water, producing a white hydrolysis product, not gray-black, is the one desired. If a small cloud of white material puffs up into the bulb before a pool of water has formed over the borohydride, quench the reaction with the cold bath. It is critically important that the reaction proceed smoothly. The ice will eventually melt as the upper portion of the bulb is warmed and the cold bath slowly removed. A white film may appear in the upper portion of the bulb when the ice melts; this film is due to hydrolysis products formed during the initial encounter of water and borohydride, as discussed in step 8. The borohydride hydrolyzes slowly in ice water, but as the water nears room temperature the reaction may become quite vigorous and exothermic and lead to poor results. Quenching the bulb with a cold bath decreases the reactivity. When bubbling ceases, within one hour most likely, a warm water bath may be placed around H, until no further reaction occurs.

10. Place a DIAC bath around H to freeze the water and hydrolysis products. Simultaneously place a DIAC bath

around F to freeze out any residual water. Open valve 15 and stopcock 6. Measure the capillary heights in manometer B. The hydrogen gas may be collected in the hydrogen collection bulb C by proper manipulation of stopcocks 3 and 4 of Toepler pump D. When the pressure in H is removed, close valve 15. Open stopcock 8 and Toepler pump any non-condensable gas from F into C. Close stopcock 8.

11. Remove the DIAC baths from F and H. During the hydrolysis reaction, some borohydride - on the order of one percent - has either not reacted or reacted incompletely (possibly encapsulation of some borohydride by the hydrolysis products). A heating mantle is placed around the lower half of H and aluminum foil around the top. A variable transformer is adjusted so that H is baking at approximately 100 to 120 °C. After two hours the heating mantle is turned off and removed from H. H is again immersed in a DIAC bath. Valve 15 is opened and all non-condensable gas Toepler pumped into C. Valve 15 and stopcock 6 are closed.
12. The pressure of the gas in C is measured several times. Refer to the section on pressure measurement for specific details.
13. A DIAC bath is placed around the bottom of C in order to

condense any condensible gases. Open stopcock 7. A portion of the non-condensable gas is Toepler pumped into the mass spectrometer sample bulb E. Stopcock 7 is closed. The non-condensable pressure is then removed from C and D by manipulation of stopcocks 1, 3, 4, and 5. When the gas pressure is gone, close stopcocks 1, 3, 4, and 5, if they are open.

14. Remove the DIAC bath from C and put a room temperature water bath around it for several minutes to help warm it up. After one hour measure the condensible pressure in bulb C. The condensible pressure is water vapor. Open stopcock 1 and pump off all pressure.
15. Concurrent with step 14 the mass spectra of the instrument background, the sample, and air (the only impurity possible) are obtained, respectively.
16. Remove H from joint 16. Open valve 15 and collect the water and hydrolysis products in a 150 ml beaker. Quantitative transfer is not necessary. The hydrolysis products are dissolved by dropwise addition of concentrated hydrochloric acid to the hot solution. When the sample is in solution, a mandelic acid precipitation of the hafnium and zirconium mandelates is performed to effect their complete separation from boron. The mandelates are collected on



Whatman #42 filter paper, washed, and transferred to ceramic crucibles. The mandelates are then burned to oxides in a muffle furnace at 900 °C. These oxides are ground, and an X-ray fluorescence analysis obtained, using appropriate standards.

17.  $P_H$ , V, T, and  $W_{TB}$  are used to calculate  $W_{HfB}$  and  $W_R$ .

#### Aqueous Hydrochloric Acid Hydrolysis

Low and erratic results were obtained with distilled water hydrolyses. 3 N hydrochloric acid was used as the next hydrolysis solution. The distilled water method was modified slightly for 3 N HCl and is described below.

Steps 1-8 are exactly the same except that 3 N HCl replaces water and ice. Step 9 holds true except that a pool of 3 N HCl forms at a much lower temperature than an ice-water equilibrium. The acid dissolves the reaction products. Step 10 is the same. Quantitative hydrolysis was obtained during the initial hydrolysis with the acid so step 11 is eliminated. Steps 12-14 are the same.

#### Partial Hydrolysis in 3 N Hydrochloric Acid

Partial 3 N HCl hydrolyses were run on hafnium and zirconium borohydrides in order to detect any gaseous intermediates. The

distilled water procedure was modified for 3 N HCl and is described below.

Step 1 is the same. Step 2 is eliminated because an analytical hydrolysis is not necessary. Steps 3 and 4 are the same except that H is transferred directly to step 6 eliminating step 5.

Step 6 is the same. In step 7 half a milliliter of 3 N HCl replaces 30-40 milliliters. In step 8 the small portion of acid is distilled into H. Step 9 is the key to an incomplete hydrolysis. After some reactivity is noted, H is quenched.

A sample of the non-condensable gas is taken into the mass spectrometer sample bulb by opening valve 15 and stopcock 7. Stopcock 7 and valve 15 are then closed. A mass spectrum of the non-condensable gas is obtained.

### Results

The distilled water hydrolyses of zirconium (2% hafnium) borohydride were low and erratic with respect to conversion to hydrogen gas, though they did approach completion. There was a close correlation between the degree of conversion to hydrogen gas and the amount of a black material produced during the hydrolysis reaction. The larger the amount of black material the more incomplete the total conversion to hydrogen gas. Better results were obtained when a black residue was not formed, but the results were

still low and erratic; the results given in Table V are for hydrolyses where black residue formation was not observed.

The aqueous 3 N hydrochloric acid hydrolyses for zirconium (2% and 11% hafnium) borohydride and zirconium borohydride were reliable if the outlined hydrolysis procedure was followed (See Table V). Black residue formation occurred when the reaction mixture was allowed to warm too quickly. The results reported are for hydrolyses where black residue formation was not observed.

The aqueous 3 N hydrochloric acid hydrolyses of pure hafnium borohydride were unreliable and erratic. The formation of a black residue was noted when the hydrolysis mixture was allowed to heat too rapidly. The experiments reported, however, did not exhibit a black reaction product, and the greatest care was taken to follow the procedure used successfully for pure zirconium borohydride and zirconium (2% and 10% hafnium) borohydride.

The hafnium/hafnium + zirconium ratio was determined by x-ray fluorescence of the metal oxides for the batch of zirconium (2% hafnium) tetrachloride used as a starting material for the Reid method. Three separate samples were run for the 2% Hf sample and their average was  $2.03 \pm 0.08\%$  Hf. This ratio compares favorably with the hafnium/hafnium + zirconium ratio of the metal oxides isolated from the metal borohydride hydrolysis products -  $2.01 \pm 0.23\%$  hafnium for eight samples. This implies that the

Table V. Results of the Evaluation of the Gasometric Determination of Hafnium/Hafnium + Zirconium Ratios by Hydrolysis of the Metallic Borohydrides

Borohydride Sample	Method of Hydrolysis	100 W <sub>R</sub> by Hydrolysis	% Hf by XR Fluorescence or Em. Spec. <sup>4</sup>	Percentage Conversion To Hydrogen	Analysis of Gas by Mass Spectrometry	n <sup>1</sup>
Zr w. 2% Hf	Aqueous	3.26 ± 0.93	{ 2.01 ± 0.23 }		Pure H <sub>2</sub>	3
Zr w. 2% Hf	Aqueous 3 N HCl	2.16 ± 0.19			Pure H <sub>2</sub>	2
Zr w. 11% Hf	Aqueous 3 N HCl	11.30 ± 0.21	11.65 ± 0.07		----	2
Pure Zr	Aqueous <sup>2</sup> 3 N HCl		40 ppm Hf	99.97 ± 0.14	Pure H <sub>2</sub>	3
Pure Hf	Aqueous 3 N HCl		295 ppm Zr	97.80 ± 0.68	Pure H <sub>2</sub>	5
Pure Zr	Aqueous 3 N HCl Incomplete		40 ppm Hf		H <sub>2</sub> , B <sub>2</sub> H <sub>6</sub>	1
Pure Hf	Aqueous 3 N HCl Incomplete		295 ppm Zr		H <sub>2</sub> , B <sub>2</sub> H <sub>6</sub>	1

<sup>1</sup> n = # of hydrolyses reported

<sup>2</sup> 1 run at 4.5 N HCl proceeded in same manner

<sup>3</sup> Pooled average (starting material was from same source of metal tetrachlorides) of eight samples

<sup>4</sup> Courteously supplied by Wah Chang, Albany.

hafnium/hafnium + zirconium ratio in the hafnium and zirconium borohydrides is the same as in the hafnium and zirconium tetrachlorides from which they were synthesized.

The zirconium (11% hafnium) borohydride was prepared from a synthetic sample: weighed portions of impure zirconium tetrachloride were intimately mixed together to form a 10% hafnium mixture. Two portions of the starting material were directly hydrolyzed and worked up to oxides for x-ray fluorescence analysis. The result was  $9.15 \pm 1.21\%$  Hf which compared poorly with the x-ray fluorescence value of  $11.65 \pm 0.07\%$  Hf obtained from the borohydride hydrolysis reaction products which were made into oxides. The poor input/output hafnium/hafnium + zirconium ratio is indicative of varying degrees of hydrolysis products present in the impure materials from which the synthetic sample was prepared.

## DISCUSSION

The Mass Spectrometry of Zirconium Borohydride

The results of the mass spectrometric study of zirconium borohydride indicate that analytical utilization, both qualitative and quantitative, is not possible with the instrumentation used. The reasons why analytical utilization is not possible and what directions should be pursued to make it possible are subject to interpretation.

Aside from reactivity with air and the sample inlet system in the CEC 21-401, a sufficient amount of zirconium borohydride reached the analyzer unit to give some evidence of singly charged species of the zirconium isotopes and zirconium isotopes with one hydrogen atom, and some doubly charged species, all produced with 70 ev electrons. The large amount of hydrogen and diborane in all the spectra is probably most indicative of thermal decomposition of zirconium borohydride prior to reaching the ionizing beam. Zirconium borohydride is thermally unstable above 30 °C and the rate of decomposition is directly related to the temperature. The ion source is normally running at 250 °C and most assuredly thermal decomposition occurs, and to a great extent. Most of the heat supplied to the ion source is from the filament itself which is running at white heat. Nothing can be done to significantly decrease the

temperature of the filament. The real problem is one of the mass spectrometry of thermally unstable zirconium borohydride (hafnium borohydride also) in particular and one of thermally unstable compounds in general. The likely explanation for the lack of evidence for zirconium borohydride in the spectra obtained on the Atlas CH 4 was prolonged passage through the heated inlet system. Design of any inlet system to the heated filament region is not likely to lead to quantitative spectra for hafnium and zirconium borohydrides, although some qualitative characteristics might be revealed. The breakdown of the accelerating voltage and ionizing current probably caused by deposits of zirconium metal in the filament assembly would lead to problems in further work.

The production of ions is not limited to bombardment with electrons from a heated filament. The production of ions of thermally unstable molecules must however be performed in an ion source which will not allow thermal decomposition of the molecules. The photo-ionization source and the field-emission source (4, p. 117-123) fulfill this requirement. The photo-ionization source employs a direct monochromatic radiation source (normally in the ultraviolet) for the ionization of molecules. It could be used above or below room temperature. Mass spectrometers with photoionization sources are not commercially available, although they may possibly be obtained on a contract basis. The field-emission source employs

strong electric fields ( $10^8$  volts/cm) in the vicinity of a fine metal point or fine wire to ionize a molecule by pulling an electron from it. Many of the spectra resulting from this source show intense parent ionization and a decreased amount of fragmentation in comparison with electron bombardment spectra. Field emission sources may be run above or below room temperature. Several manufacturers have recently made field-emission sources available for their mass spectrometers. The sources are still not especially dependable in their lifetime, but the outlook is promising. Regardless of the source lifetime, field emission mass spectrometry is the best direction to be pursued to obtain the mass spectra of hafnium and zirconium borohydrides and analytical uses of those spectra.

A non-reactive mass spectrometer sample inlet system will also be necessary for any quantitative work with hafnium and zirconium borohydrides. The West-Glass Corp. Teflon barreled vacuum stopcock should be invaluable in the design of a glass system, as no vacuum grease is required and it is capable of holding a high vacuum.

### Discussion of the Hydrolysis Results

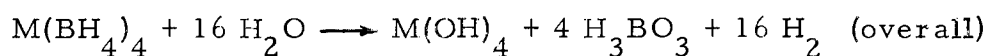
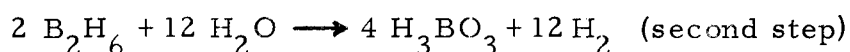
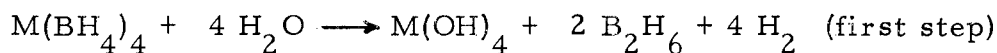
#### Incomplete Hydrolysis

The method for obtaining hafnium/hafnium + zirconium ratios by hydrolysis of a mixture of their borohydrides with the subsequent



measurement of the hydrogen gas evolved has not been entirely successful. The problem is the less than quantitative conversion of hafnium borohydride to hydrogen gas. Quantitative hydrolysis of zirconium borohydride but not hafnium borohydride can be achieved in aqueous 3 N hydrochloric acid. Conditions which might lead to incomplete hydrolysis of both hafnium and zirconium borohydrides and their mixtures must be considered.

The formation of diborane observed in the incomplete hydrolysis of pure hafnium or zirconium borohydride is indicative of at least a two step hydrolysis reaction. A proposed reaction scheme is shown below:



The distilled water hydrolyses of zirconium (2% hafnium) borohydride were incomplete because of an alternate path/s for hydrolysis. The samples were thoroughly hydrolyzed in all cases, but a quantitative conversion of the available hydrogen in the borohydrides to hydrogen gas was not achieved. The fact that nearly

all the hydrogen was converted to hydrogen gas is an argument for the hydrolysis proceeding almost entirely by the proposed route. The formation of a black hydrolysis product during vigorous side reaction was probably due to a localized temperature excursion from which the heat energy could not be dissipated quickly enough, leading to thermal decomposition of the borohydrides and/or a more energetic hydrolysis path/s.

A local temperature excursion might be due to the encapsulation of some unhydrolyzed borohydride with solid reaction products of some already hydrolyzed borohydride; when the water permeated the barrier the exothermic reaction began which could not dissipate its energy quickly enough causing a local temperature excursion. Alternately or in conjunction with the encapsulation, the evolving hydrogen gas may have separated the borohydride from an excess of water, leading to a local temperature excursion.

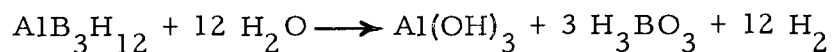
The role which the hydrochloric acid plays in the aqueous hydrolysis is, most likely, in the dissolution of the solid hydrolysis products as they form. The acid hydrolyses of zirconium borohydride were problematic only when the reaction mixture was heated too rapidly, allowing a black hydrolysis product/s to form. The zirconium and zirconium (2% hafnium) borohydride hydrolyses proceeded quantitatively and smoothly with a slow evolution of hydrogen gas and complete dissolution of the reaction products

when the temperature of the reaction bath was raised slowly. Hafnium borohydride hydrolyses may be described in the same manner except that they proceed nearly quantitatively. Somehow a side reaction takes place with hafnium borohydride that does not take place with zirconium borohydride. It is evident that hafnium borohydride cannot be quantitatively hydrolyzed under the present conditions which allow zirconium borohydride to be quantitatively hydrolyzed. The hydrogen not released in the hafnium borohydride hydrolysis must be chemically bound to a reaction product or products.

#### The Hydrolysis of Some Other Borohydrides and a Related Hydride

Aluminum and beryllium borohydrides are similar in nature to hafnium and zirconium borohydrides and their hydrolysis reactions are of interest. Hydrolysis studies of lithium borohydride and lithium aluminum hydride are also of interest.

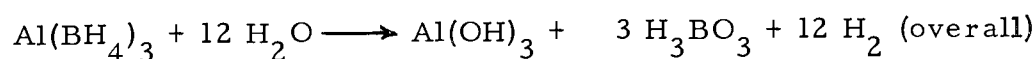
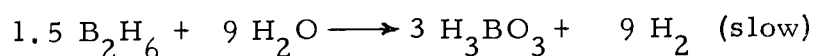
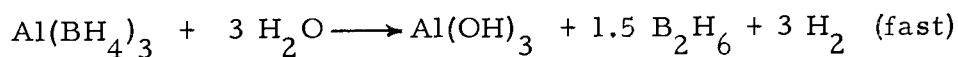
Schlesinger, Sanderson, and Burg (41, 42) studied aluminum borohydride and found hydrogen semi-quantitatively by aqueous hydrolysis in order to establish the empirical formula. They treated a portion of the compound with an excess of water and concluded that hydrogen, boric acid, and aluminum hydroxide were formed:



Schlesinger et al. did not report the details of their hydrolysis method.

Rulon and Mason (40) reported that direct hydrolysis of liquid aluminum borohydride with liquid water (in a bomb) produced dark colored residues, strong odors, and variation in the extent of completion of hydrolysis. Aluminum borohydride vapor reacted (in a bomb) with water vapor in the presence of a small excess of liquid water to give white reaction products and the absence of odor. Reasonably consistent results for calorimetric measurements were found for the reaction. There was an alternate reaction route which again produced dark residues and strong odors and gave erratic calorimetric measurements. There was no means of predicting the reaction route. Aluminum hydroxide and boric acid were positively identified in the reaction products from the consistent hydrolysis reactions.

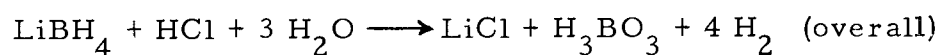
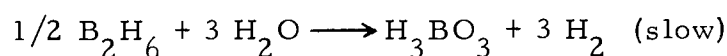
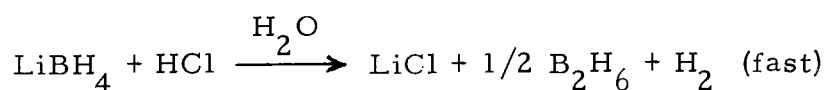
The hydrolysis of aluminum borohydride is achieved by two steps (26, 28).



(Kilpatrick et al. (28) claim that Schlesinger et al. (42) achieve

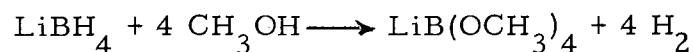
complete and quantitative hydrolysis if the reaction was carried out very slowly.) Approximately three normal aqueous hydrochloric and sulfuric (perchloric was also suggested as suitable) acid solutions were used for the hydrolyses. The quantitative conversion of the borohydride to hydrogen gas was not discussed.

Kilpatrick and McKinney (25) have shown that the aqueous acid hydrolysis of lithium borohydride also proceeds by a two step mechanism similar to aluminum borohydride:



The problem of incomplete reaction caused by residue formation in aqueous lithium aluminum hydride hydrolysis was solved by first adding ethyl ether, then ethanol for hydrolysis, then phosphoric acid to ensure complete hydrolysis. Hydrogen was produced to the extent of  $99.05 \pm 0.04\%$  (based on  $\text{LiAlH}_4$ ) (12).

Schlesinger and Brown (43) hydrolyzed lithium borohydride with methanol:

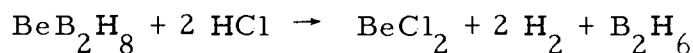


The purity of their material was not stated, so no evaluation can be

made with regard to quantitative hydrolysis. The procedure is of interest:

An excess of methyl alcohol was condensed in a reaction tube with a weighed sample of lithium borohydride. As the alcohol melted vigorous reaction occurred with evolution of hydrogen. After the reaction had stood for several hours at room temperature to ensure that the reaction had proceeded to completion, the hydrogen was removed and measured.

When beryllium borohydride (10) is treated with hydrogen chloride at  $-80^{\circ}\text{C}$  the following reaction occurs:



The reaction is somewhat incomplete because of a residue formed. By treating the residue with hydrogen chloride at elevated temperatures "an analytically adequate separation of boron from beryllium is obtained" (10, p. 3427). This suggests that the residue might contain either unreacted borohydride, or a boron-hydrogen containing reaction product which must somehow be released to assure adequate reaction. The hydrolysis of the residue and volatile products yield hydrogen quantitatively.

Lithium borohydride reacted with hydrogen chloride at  $-78^{\circ}\text{C}$  yielded mostly hydrogen and diboran, but also a small amount of chlorodiborane. Subsequent hydrolysis of diborane and

chlorodiborane yielded further hydrogen. The conversion of hydrogen was quantitative (43).

Aluminum borohydride reacted with hydrogen chloride (3) in a manner similar to lithium borohydride. The hydrogen conversion was quantitative.

In summary, the hydrolysis of various borohydrides and lithium aluminum hydride have been successfully carried out in many different ways.

#### Suggested New Methods for Hydrolyzing Hafnium and Zirconium Borohydrides

Several new methods which might be pursued for quantitatively hydrolyzing hafnium and zirconium borohydrides are suggested from the review of other hydrolysis reactions.

Zirconium (presumably hafnium) borohydride shows a surprising solubility in diethyl ether (also some saturated hydrocarbon solvents). A portion of diethyl ether could be used to disperse the metal borohydrides evenly throughout a solution prior to hydrolysis with methyl or ethyl alcohol.

Zirconium and hafnium borohydrides might be quantitatively converted to hydrogen by direct methyl or ethyl alcohol hydrolysis.

Treatment of zirconium and hafnium borohydrides with hydrogen chloride with subsequent aqueous hydrolysis of the mixture

and its reaction products might lead to quantitative conversion to hydrogen gas.

#### Applicability of the Method

The results of this initial study indicate that (hafnium/hafnium + zirconium ratios) ( $\times 100$ ) accurate to 0.2% absolute and 10% relative with a standard deviation of 0.2% (absolute) can be obtained from an impure sample of zirconium (2% hafnium) tetrachloride. The ratio method can be applied to samples where the ratio ( $\times 100$ ) is 1% if a 20% relative error is acceptable. Samples which contain a ratio ( $\times 100$ ) less than 0.1% can be considered pure zirconium borohydride; the hydrolysis method offers an excellent check for the purity of zirconium borohydride, but is meaningless with regard to its hafnium content.

Figure XVII indicates the reason why the hydrolysis method for obtaining ratios is meaningless for samples with a small weight percent of hafnium or zirconium. An absolute error of 0.2% was determined experimentally. When the weight percent of hafnium is 50.0, an absolute error of 0.2% is only a relative error of 0.4%. The relative error is a minimum at 50% hafnium or zirconium. The rate of increase of the relative error of the minor constituent increases as the percent of the minor constituent decreases. A relative error of 10% was found for the 2.0% hafnium sample.



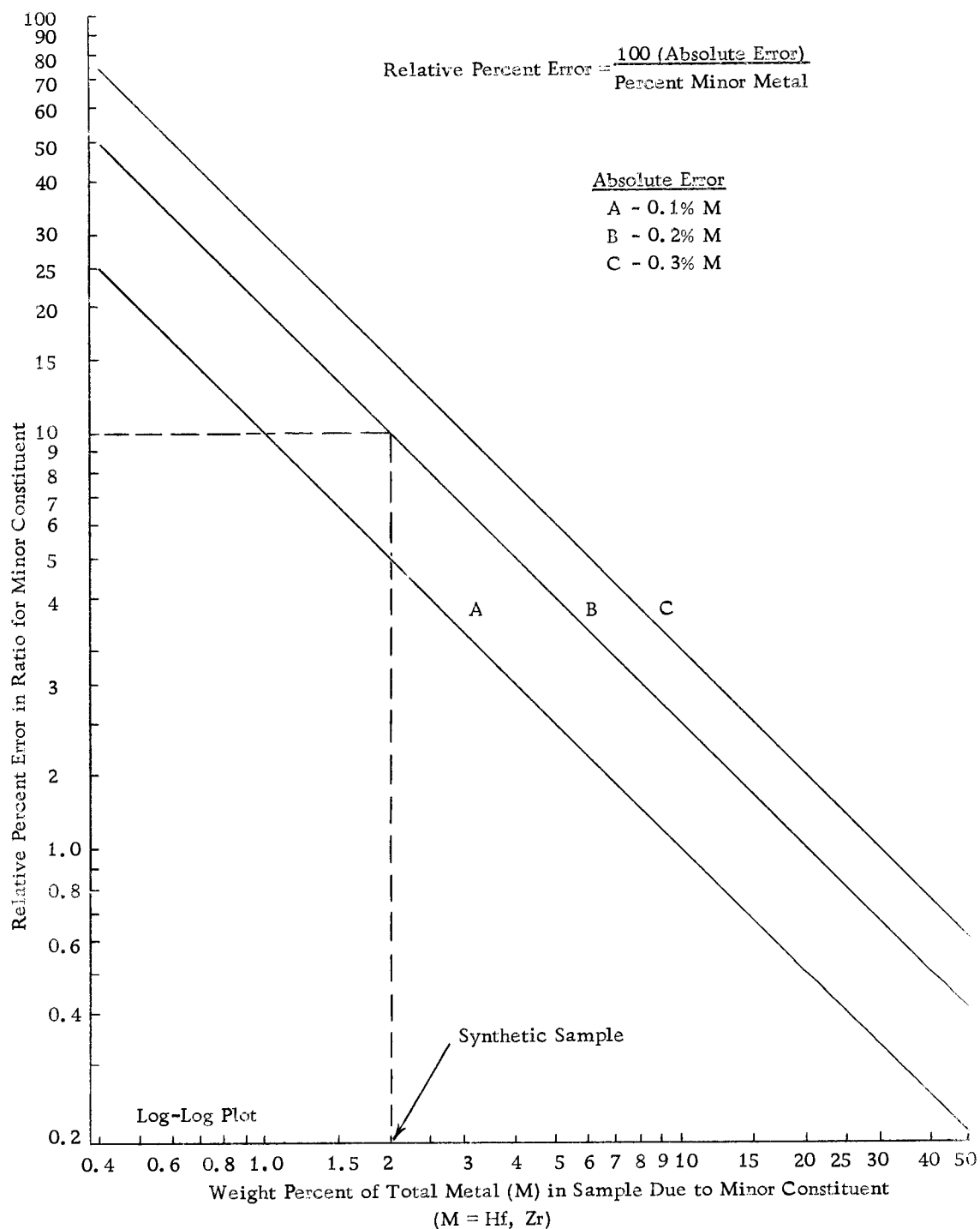


Figure XVII. Relationship Between Absolute and Relative Errors and the Weight Percent of the Total Metal in the Sample Due to the Minor Constituent for Quantitative Hydrolysis

Unfortunately hafnium borohydride has been found to hydrolyze neither quantitatively nor especially reproducibly and the relationship shown does not hold true over the entire range. Hafnium borohydride is hydrolyzed to the extent of 98% (within 1%) however. It has been demonstrated that the method can be applied at 2% and 11% hafnium with an approximate  $\pm 0.2\%$  hafnium error. Nearly all zirconium samples fall into this range.

The entire range of samples to which the present method is quantitatively applicable has not been established. It was felt that the 10% Hf sample would show an approximate 0.2% positive hafnium error (due to the 2% of the total hafnium borohydride present not hydrolyzed). In fact there was an error in the opposite direction. This can possibly be explained by assuming that hafnium borohydride cannot hydrolyze incompletely while diluted in a solid solution (crystal lattice) of zirconium borohydride. The incomplete hydrolysis of hafnium borohydride may become a factor only in high hafnium samples. The answers in the higher hafnium range would then be significant for semi-quantitative ratios.

Further work on this method for the higher hafnium ratios would be necessary to establish a calibration curve relating the observed ratio to the actual ratio. This approach is not recommended; the precedence to establish is a means for hydrolyzing both

hafnium and zirconium borohydrides quantitatively and then to apply the ratio method.

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## APPENDICES

## APPENDIX 1

The Infrared Spectra of the Vapor of Hafnium  
and Zirconium Borohydrides

James et al. (24) have recently published the infrared spectra of hafnium and zirconium borohydride vapors:

$\text{Zr}(\text{BH}_4)_4$	$\text{Hf}(\text{BH}_4)_4$
2584 s	2588 s
2575 s	2581 s
2568 ssh	
2497 w	2509 vw
2435 s	2447 vs
2198 s	2207 s
2135 s	2146 s
1295 vw	1300 vw
1223 vs	1228 vs
1165 vw	1140 vw
1040 vw	1120 vw
	493 ssh
509 vs	487 vs
505 ssh	

A tracing of the spectrum of zirconium borohydride vapor was kindly furnished by James and Wallbridge. They comment that the hafnium borohydride spectrum looks virtually identical apart from a few wavenumber shifts. The spectra were obtained using KBr windows and there was no attack on them during the time required to obtain the accurate data. The possible utility of the infrared method and a suggested sample cell are described below.

If equal molar concentration in the vapor state and equal molar absorptivities at their respective absorption maxima are assumed, a synthetic spectrum can be drawn for a gaseous sample of hafnium and zirconium borohydrides. This has been done and it appears that the only peaks useful for quantitative analysis lie in the  $500\text{ cm}^{-1}$  range. The synthetic spectrum in the  $500\text{ cm}^{-1}$  range is shown in Figure XVIII. Base lines were assumed around the 0.1 Absorbance line. The vapor pressures are considered equal at  $25.0^\circ\text{C}$  (15.0 mm each). The synthetic spectrum and calculation arising from it which would allow the determination of hafnium/hafnium + zirconium ratios are of interest and are reviewed below. It is also useful to relate the individual pressures, as they may be of interest in following thermal decomposition or reaction rates of the borohydrides.

The absorbance  $A$  of the vapor of a compound at a particular wavelength of infrared radiation  $\lambda$  is a function of the absorptivity  $a$  (strength of absorption in liter/mole-mm), the path length  $b$  of the cell containing the vapor, and the concentration  $c$  of the vapor in moles/liter.

$$1) \quad A_{\lambda} = abc$$

The concentration of the vapor in the sample cell in moles/liter is related by the general gas law:

$$2) \quad PV = nRT$$

$$3) \quad c = \frac{n}{V} = \frac{P}{RT}$$

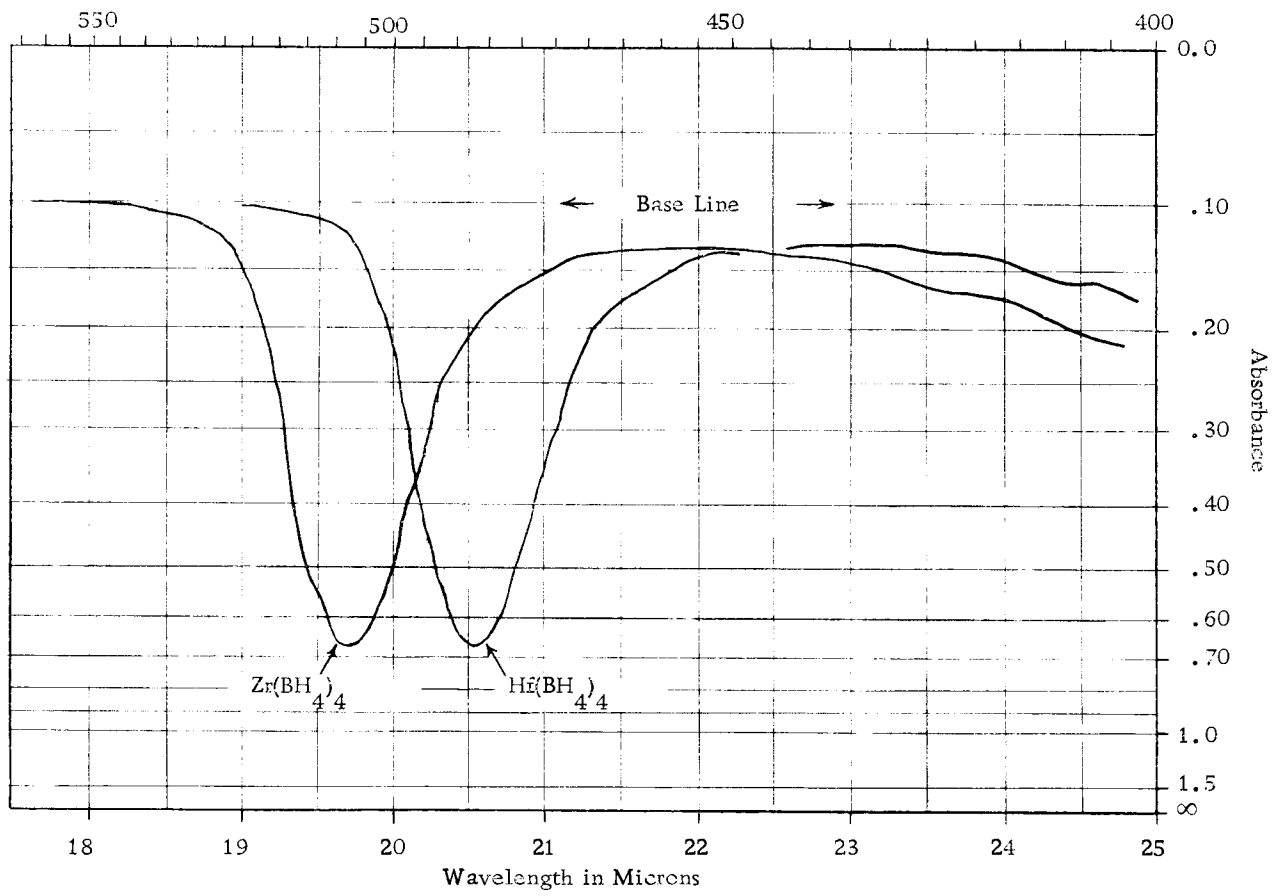


Figure XVIII. Synthetic Infrared Spectrum of Hafnium and Zirconium Borohydrides

$$4) \quad A_{\lambda} = ab \frac{P}{RT}$$

P = pressure in mm

V = volume in liters

n = moles of the vapor

R = 6.3184 (1-mm- $^{\circ}$ K $^{-1}$ -mole $^{-1}$ )

T =  $^{\circ}$ K

The absorbance due to 15.0 mm of zirconium borohydride vapor at 508  $\text{cm}^{-1}$  (from Figure XVIII) in a cell with a 100 mm path length is 0.570. The absorptivity of zirconium borohydride is a constant and can be calculated from 4).

$$a_{zb, 508} = A_{zb, 508} \frac{RT}{bP}$$

$$a_{zb, 508} = \frac{(0.570) (63.184) (1\text{-mm-}^{\circ}\text{K}^{-1}\text{-mole}^{-1}) (298.2^{\circ}\text{K})}{(100 \text{ mm}) (15.0 \text{ mm})}$$

$$a_{zb, 508} = 7.16 \frac{1}{\text{mm-mole}}$$

In a similar manner, other absorbancies were calculated:

$$a_{zb, 487} = A_{zb, 487} \frac{RT}{bP} = 0.955$$

$$a_{hb, 508} = A_{hb, 508} \frac{RT}{bP} = 0.0314$$

$$a_{hb, 487} = A_{hb, 487} \frac{RT}{bP} = 71.6$$

If the vapors of hafnium and zirconium borohydrides absorb radiation at the same wavelength, then the absorbance of the vapor

is an additive function of the individual absorbances.

$$5) A_{508} = \frac{a_{zb, 508} b P_{zb}}{RT} + \frac{a_{hb, 508} b P_{hb}}{RT}$$

$$6) A_{487} = \frac{a_{zb, 487} b P_{zb}}{RT} + \frac{a_{hb, 487} b P_{hb}}{RT}$$

Since the absorptivities are known, a simultaneous solution for the individual pressures is possible by noting the absorbance at two wavelengths. The pressures are given by:

$$7) P_{hb} = \frac{\begin{pmatrix} \frac{A_{508}}{a_{zb, 508}} & - & \frac{A_{487}}{a_{zb, 487}} \end{pmatrix}}{\begin{pmatrix} \frac{a_{hb, 508}}{a_{zb, 508}} & - & \frac{a_{hb, 487}}{a_{zb, 487}} \end{pmatrix}} \frac{RT}{b}$$

$$8) P_{zb} = \frac{\begin{pmatrix} \frac{A_{508}}{a_{hb, 508}} & - & \frac{A_{487}}{a_{hb, 487}} \end{pmatrix}}{\begin{pmatrix} \frac{a_{zb, 508}}{a_{hb, 508}} & - & \frac{a_{zb, 487}}{a_{hb, 487}} \end{pmatrix}} \frac{RT}{b}$$

The pressure terms may be reduced because the absorptivities, R, T, and b are all known. By substitution and solving:

$$9) P_{hb} = 26.3 A_{487} - 3.50 A_{508}$$

$$10) P_{zb} = 26.3 A_{508} - 0.15 A_{487}$$

The pressures are related to the hafnium/hafnium + zirconium

ratio ( $w/w$ ) of a sample. Let  $m = z$  (zirconium),  $h$  (hafnium)  
 $mb = zb, hb$ ;  $M_m$  = molecular weight of  $m$ ;  $M_{mb}$  = molecular weight  
of  $mb$ ;  $W_m$  = weight of  $m$ ;  $W_{mb}$  = weight of  $mb$ ;  $V_c$  and  $T_c$  be  
constant volume and temperature.

$$11) P_{mb} = \frac{W_{mb} RT_c}{M_{mb} V_c} = \frac{W_{mb} k}{M_{mb}}$$

$$12) W_{mb} = \frac{P_{mb} M_{mb}}{k}$$

$$13) W_m = \frac{M_m W_{mb}}{M_{mb}} = \frac{M_m P_{mb} M_{mb}}{M_{mb} k} = \frac{M_m P_{mb}}{k}$$

$$14) W_h = \frac{M_h P_{hb}}{k}; \quad W_z = \frac{M_z P_{zb}}{k}$$

The ratio  $R_w$  is then:

$$15) R_w = \frac{W_h}{W_h + W_z} = \frac{M_h P_h k^{-1}}{M_h P_h k^{-1} + M_z P_z k^{-1}}$$

$$16) R_w = \frac{M_h P_h}{M_h P_h + M_z P_z}$$

$$17) R_w = \frac{178.49 P_h}{178.49 P_h + 91.22 P_z}$$

Substituting 9) and 10) into 17) and solving:

$$18) R_w = \frac{4.69 A_{487} - 0.626 A_{508}}{4.68 A_{487} + 1.78 A_{508}}$$

Equation 18) has been derived for a specific set of conditions. It illustrates, however, that the hafnium/hafnium + zirconium ratios can be obtained from any mixture of metal borohydride vapors by using only two absorbance values, corrected for background. The method, of course, requires initial calibration.

A 10 cm gas sample cell would seem a reasonable starting point for experimental work. Commercially available gas cells have greased stopcocks and would be unsuitable for working with the borohydrides because of reactivity. A modified commercial cell with Teflon stopcocks and O-rings can be constructed. Beckman Instruments, Inc., 2500 Harbor Blvd., Fullerton, California, 92634, can provide a 10 cm Pyrex Infrared Gas Cell with straight side arms, KBr windows, and neoprene O-rings for \$67.50 (Quotation POR-0640 (F), July 11, 1966). Vacuum ( $10^{-6}$  mm Hg) Teflon stopcocks are available for the side arm/s of the gas cell from the West-Glass Corporation, 9822 Alpaca Street, South El Monte, California. Teflon O-rings (1.734"  $\pm$  .010 I.D. and .139"  $\pm$  .004 cross section) for the cell are available from Tetrafluor, 343 Hindry Avenue, Inglewood, California, 90301. Teflon sleeved standard taper joints, to connect the cell to a vacuum line, are available from Ace Glass Incorporated, Vineland, New Jersey.

The preceding discussion is an example of the attack necessary to develop an infrared quantitative analysis method for hafnium and



zirconium borohydrides. The accuracy and precision over the various sample compositions, and the range of compositions will have to be determined experimentally. The results depend highly on the competency of the operator and the quality and capability of the instrument. Instruments in the  $500\text{ cm}^{-1}$  range are quite expensive, if the instrument is to have general laboratory utility; a general laboratory instrument is a reasonable starting point.

## APPENDIX 2

Transfer and Weighing of BorohydridesAverage Weight Difference Weighing Method

The weighing of a half-liter glass bulb is affected by several factors which may cause the weight to drift several milligrams in the course of an hour. The drift is due to one or several of the following: adsorption or desorption of water, humidity changes, atmospheric temperature and pressure fluctuations, and electrostatic charge. A drift of over several tenths of a milligram is intolerable in the present work.

It would be both difficult and impractical to try to control the variables, but by comparing two similar bulbs which are subject to the same variations, the control might not be necessary, i. e., the difference in weight between the bulbs would be constant. The constancy of the weight difference must be determined. If the method proves successful, the weight difference must be examined when one bulb, the sample bulb, is subject to manipulations, while the tare bulb is not subject to manipulation. The constancy of the weight difference was determined experimentally.

Each bulb was equipped with a well secured piece of heavy gage copper wire with a hook on one end. The bulbs were wiped clean

with a silk cloth, discharged with a clean, dry hand, and suspended from a support rod (see Figure XIX). The balance is zeroed once. One bulb is weighed and then the next. This is repeated about ten times in the same order. The difference in weight between each pair of weights is noted.

It was found that the weight difference between two similar half-liter bulbs on a given day may vary as much as 0.7 milligrams over a short period of time, but the average difference over many short periods of time varies very little - less than 0.1 milligram. The average weight difference one hour after the sample bulb has been manipulated and had a cold stream of nitrogen gas passed over it (see part b) does not vary by more than 0.1 milligram. This comparison weighing method, using the average weight difference, is nearly two orders of magnitude better than weighing a single half-liter bulb in terms of reproducibility.

#### Cold Nitrogen Condensation Method for Transfer of Borohydrides

A unique method was developed for transferring small samples of hafnium and zirconium borohydrides from a storage vessel to a sample bulb. A stream of cold nitrogen gas is passed over the sample bulb whereby no liquid (e. g. , from a DIAC or ice-water bath) comes in contact with the bulb surface and no condensation of water

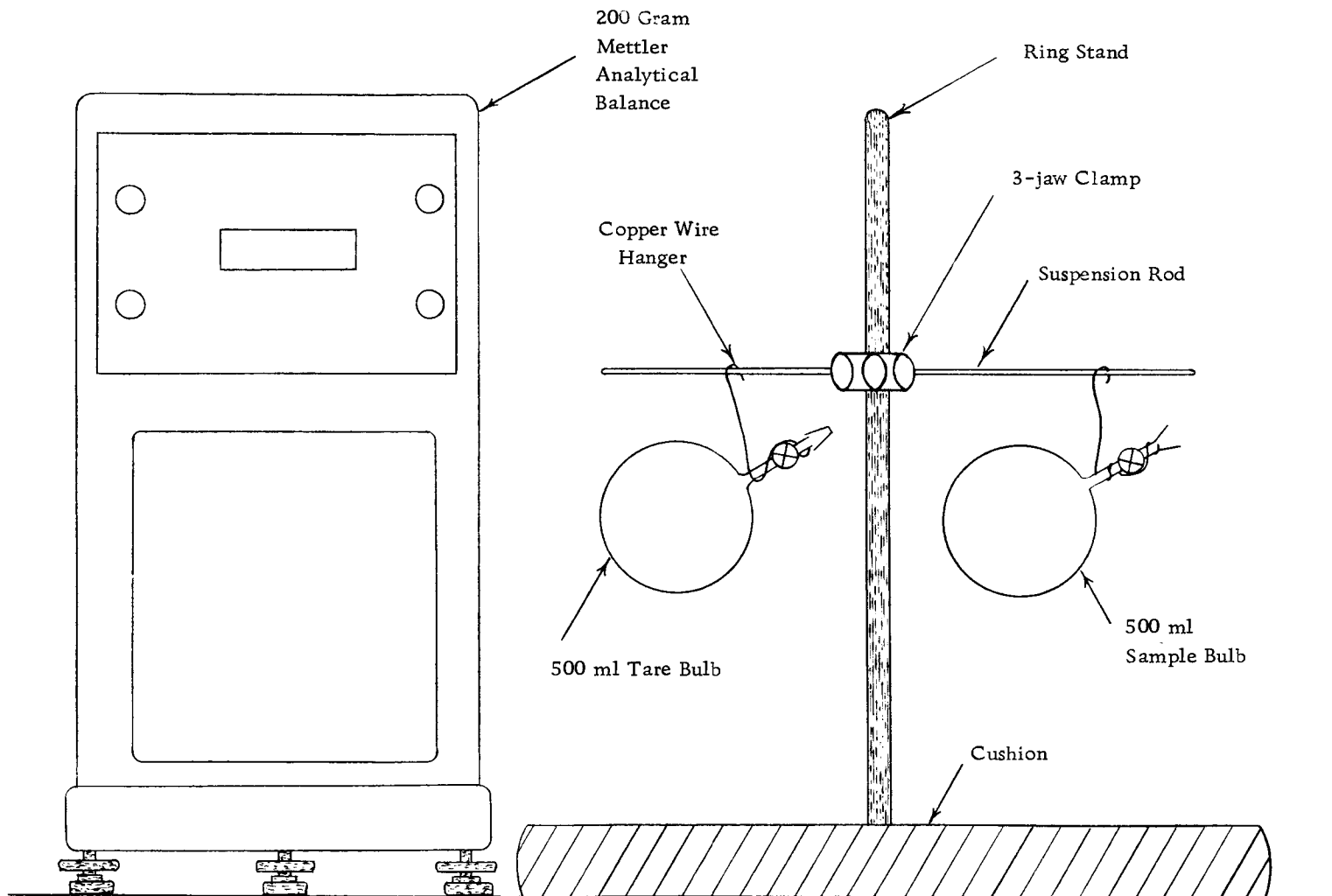


Figure XIX. Average Weight Difference Weighing Method Apparatus

vapor appears on the bulb surface. The apparatus is shown in Figure XX. The temperature of the gas is about  $-20^{\circ}\text{C}$  when measured with a thermometer at the exit of the latex rubber tubing. The general procedure is outlined below.

1. The sample bulb is unhooked from the support rod and connected to joint 19 (see Figures XI and XIV). A grease-free  $\text{E}$  clamp holds the bulb in place. The inlet line is evacuated and possible leakage noted on the micro-manometer.
2. The sample storage vessel is opened to the manifold, thereby letting borohydride into it. The borohydride will react with any residual material. The storage vessel is put under a DIAC bath to condense the borohydride. Any non-condensable pressure (normally none is found) is pumped off. The DIAC bath is removed.
3. The Teflon sample bulb stopcock is opened and the cold stream of nitrogen passed over the bulb until the approximate amount of borohydride needed has condensed. The sample bulb stopcock is closed.
4. The stream of cold nitrogen is sprayed over the tare bulb for about the same time as over the sample bulb (this speeds up the weight equilibration).
5. The borohydride in the manifold is condensed back into the

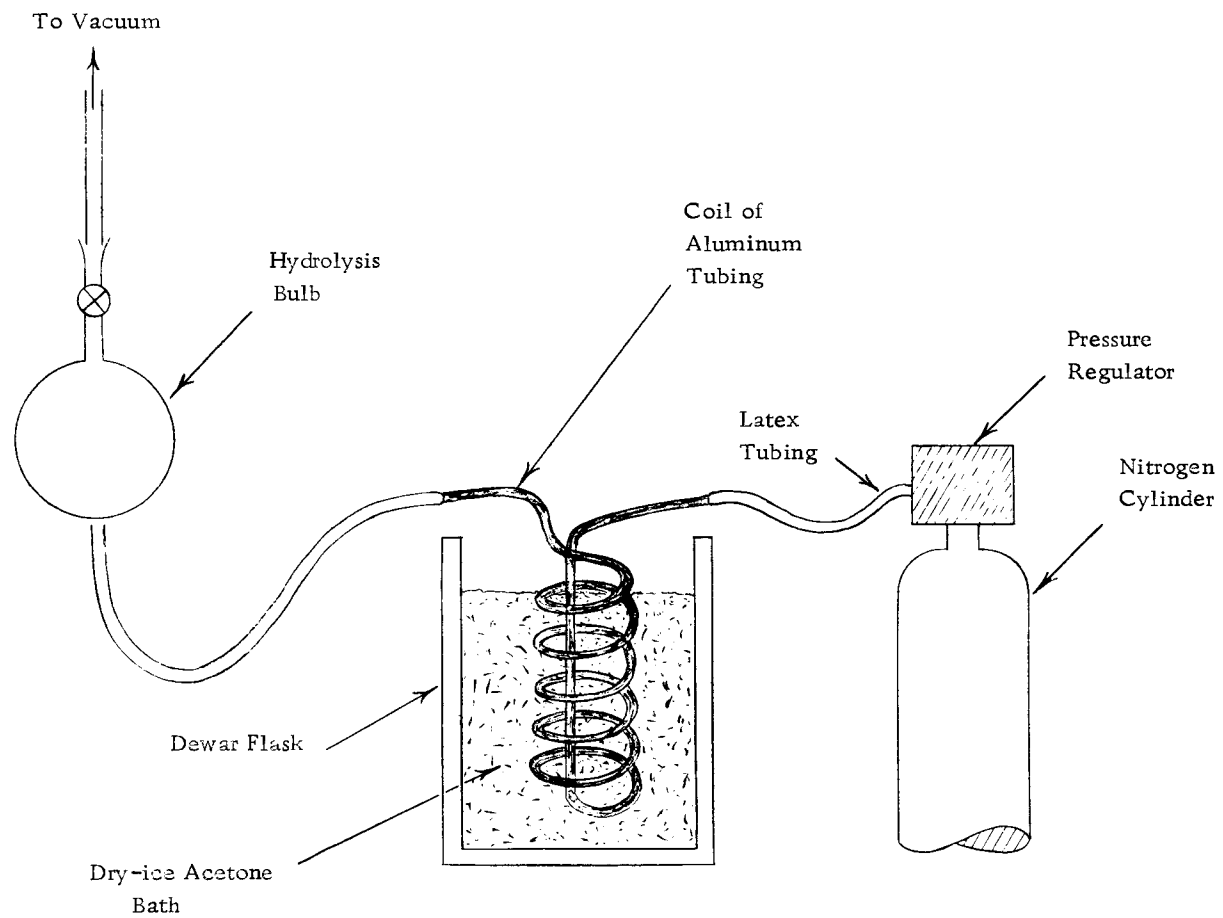


Figure XX. Apparatus for Cold Nitrogen Condensation Transfer Method

storage vessel for storage.

6. The sample bulb is removed and weighed. If there is too much borohydride, some must be condensed back to the storage vessel. If the sample is too small the above procedure is repeated. If the sample weight is correct the bulb is hung from the suspension rod and equilibrated with the tare bulb for one hour.

## APPENDIX 3

Calibration of the Hydrogen Collection VolumeBy Means of the General Gas Law

The hydrogen collection bulb volume can be calibrated by utilizing the general gas law  $PV = gRT/M$  or  $V = gRT/MP$  where  $P$  is the corrected pressure in atmospheres,  $V$  is the volume in liters,  $g$  is the gram weight of the gas,  $M$  is the gram molecular weight of the gas,  $R$  is the general gas constant in liter-atm- $^{\circ}\text{K}^{-1}$ -mole $^{-1}$ , and  $T$  is the absolute temperature in  $^{\circ}\text{K}$ .

Nitrogen gas was chosen because it follows closely the ideal gas law exactly in the range of interest and for its density, inertness, availability, purity and cost. The sampling procedure is described below.

A nitrogen tank was connected directly to the vacuum system at joint 19. The pressure regulator and the vacuum system were purged for several minutes with nitrogen to ensure that all residual air was removed. The collection bulb C, a precisely weighed half-liter hydrolysis bulb at joint 16 (greaseless connection), and fore-pump W2 were opened to the flowing nitrogen. The hose to the fore-pump was clamped lightly and the nitrogen pressure brought to about 900 mm absolute. The hydrolysis bulb stopcock was closed first and



then the nitrogen regulator turned off before the collection bulb and the vacuum system were evacuated. The half-liter bulb was then removed from the vacuum system to be weighed again (see Appendix 2a). The difference in the weight of the bulb with and without nitrogen determines the weight of nitrogen. The half-liter bulb is reattached to joint 16 after the final weighing. The inlet system is evacuated. The zero scale readings are taken on the manometer including capillary heights. The weighed amount of nitrogen gas is Toepler pumped from the half-liter bulb into the collection volume C. After equilibration the gas temperature, the mercury temperature, and the system pressure including capillary heights are carefully recorded. The measurements are repeated in one hour for a check. Factors affecting the measurements were taken into consideration.

A sample of the gas was taken for analysis by mass spectrometry to verify the assumption of pure nitrogen gas and an error of approximately one part of oxygen in 8000 parts of nitrogen (in terms of pressure) was found. This would be a positive weighing error of 0.2 parts in 8000 parts by weight, therefore negligible.

The distilled mercury obtained from the chemistry stockroom should be very pure, as the mercury is first cleaned quite well chemically (dropped through 25% nitric acid, washed with distilled water, and then dried; the exact procedure is outlined in any Chemical

Rubber Company Handbook of Chemistry and Physics) and then singly distilled under vacuum. An emission spectrograph was used to determine impurities in the mercury - 5 ppm copper and 5 ppm silicon were found. It was assumed that the density of mercury used in the manometer accurately reflects tabulated values.

The change in the volume of the collection bulb with changing temperature is insignificant. The mean coefficient of volume expansion for Pyrex chemical glassware is  $1.0 \times 10^{-5}/^{\circ}\text{C}$ . In 1.2 liters a nine degree change in temperature effects the volume by 0.1 milliliter.

To make the measurement of pressure more reliable, several steps were taken. A small light bulb can be placed near the meniscus of either leg of the manometer to illuminate it. A thin weighted string is used to plumb the meter stick. A mirror is placed behind the manometer when the meniscus is being read to avoid parallax error. The meter stick was checked against a good quality centimeter rule and the greatest error in reading would be 0.2 mm over the 800 mm used. The error in the mid-range was not measurable (less than 0.1 mm). The monograph (8) Mercury Barometers and Manometers is very useful in the discussion of pressure measurement. The thermometers used were calibrated against National Bureau of Standards calibrated thermometers.

The volume/unit length of the manometer leg exposed to

hydrogen was calibrated by using a piece of glass from the same four foot length of glass and weighing mercury between various lengths. All collection bulb volume readings were adjusted to a fixed manometer height - 23.35 cm - by means of the correction factor (.614 ml/cm).

The average collection bulb volume at 24 °C, calculated by the general gas law, was  $1.21955 \pm 0.00045$  liter (at 23.35 cm on the manometer). The reproducibility is good. The accuracy is questionable. Another means of calibrating the system was necessary to check the accuracy.

#### By Means of the Combined Charles-Boyle Law

The hydrogen collection bulb volume can be calibrated by utilizing the combined Boyle-Charles law  $P_1 V_1 / T_1 = P_2 V_2 / T_2$  where  $P$  is pressure,  $V$  volume, and  $T$  temperature. A hydrolysis bulb (Figure XV) volume was calibrated at 484.294 ml with distilled water and 484.203 ml with absolute ethanol - average 484.25 ml. The deviation is less than one part in 5000 parts. This bulb was attached to joint 16. Nitrogen gas was let into the hydrolysis bulb  $V_1$  and collection bulb  $V_2$  as described above until the pressure was about 780 mm. The temperature  $T_1$  and pressure  $P_1$  were noted. The hydrolysis bulb stopcock was closed. The collection bulb volume was evacuated. The nitrogen gas in the

hydrolysis bulb was Toepler pumped into the collection bulb volume. The pressure  $P_2$  and temperature  $T_2$  were noted. The collection bulb volume was calculated as 1.21981 liters.

Answers from the two methods agree with each other remarkably well. This offers a firm foundation for trusting the entire measurement system, as two independent methods of measuring the volume agreed.