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# The Separation of Zirconium and Hafnium by Differential Reduction of their Tetrachlorides

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If crude zirconium tetrachloride, containing hafnium tetrachloride, is heated with zirconium powder *in vacuo* at 400–450°, most of the zirconium chloride is reduced to the comparatively involatile trichloride. The hafnium tetrachloride is not reduced and, together with any unreduced zirconium chloride, can be recovered by sublimation as a hafnium concentrate with a Hf/Zr ratio higher than 10%. The residual zirconium trichloride, in which the original Hf/Zr ratio of the crude chloride has been reduced from 2% to less than 0.05%, can be disproportionated at 550° to give zirconium tetrachloride with a correspondingly low hafnium content. Factors controlling the reduction process are discussed and a separation technique is outlined.

Interest in the lower halides of zirconium has been only spasmodically maintained since Ruff and Wallstein[1] published the first paper on the reduction of zirconium tetrachloride. Young[2] developed a method for preparing the anhydrous lower bromides of zirconium and he, like Ruff, used aluminum as the reducing agent. Although de Boer and Fast[3] indicated that zirconium could probably be used to reduce its own halides it was left to Fast[4] to give the first demonstration of the reduction of zirconium tetraiodide to the triiodide by zirconium.

Schumb and Morehouse[5] employed Young's technique[2] to produce hafnium tribromide but the reaction temperature of 600° which they used was 150° higher than that which Young recommended for the reduction of zirconium tetrabromide. This temperature difference was not commented upon although it may have constituted the first published clue to a possible method of separating zirconium and hafnium by a chemical process. The compounds of these two metals are normally regarded as having almost identical chemical properties, but the purpose of this paper is to show that the difference in reducibility of their tetrahalides can provide the basis of a new method for separating zirconium and hafnium. In particular the reduction of zirconium tetrachloride to the di- or trichloride and the subsequent separation of unreduced hafnium chloride is described.

## Experimental

**Materials and Analysis.**—Zirconium powder was prepared by heating commercial grade zirconium hydride at 900° in a continuously evacuated silica bulb for six hours and allowing the product to cool in argon. Zirconium chloride was obtained from Australian zircon sand by a modified Kroll technique.[6] Zirconium oxide was prepared by dissolving the chloride in water and adding ammonia to precipitate the hydroxide, which was subsequently filtered and ignited.

In all cases where it was necessary to determine the hafnium content of chloride samples radioactive $Hf^{181}$ was used as a tracer. A small quantity of irradiated hafnium oxide was mixed with zirconium oxide which was converted to carbide by reduction with graphite at 1600°. Small samples of this active carbide were then chlorinated as required for each experiment.

The mandelic acid method of Kumins[7] was employed for all zirconium analyses; chloride determinations were made using the Caldwell modification[8] of the Volhard process.

**Apparatus.**—Zirconium chloride, prepared by heating the carbide in a stream of chlorine, was sublimed *in vacuo* into a reaction bulb containing zirconium powder which had been thoroughly out-gassed. The bulb was then evacuated to $10^{-5}$ mm. and sealed off ready for heating.

For experiments on the critical pressure of $ZrCl_4$ vapor in equilibrium with the lower halides, the bulb was replaced by a thin tube which was subsequently heated in furnaces similar to those used by Schäfer[9] in his investigation of the niobium chlorides.

**Procedure.**—Two series of experiments with different sized reaction bulbs were carried out. In the first, 2 g. of chloride and 1 g. of zirconium reacted in 50-ml. bulbs; in the other 40 g. of chloride and 80 g. of zirconium were heated in 250-ml. bulbs. The first series covered the temperature range of 330–530°; the range of the larger bulbs was more limited owing to their tendency to explode at temperatures above 440°. Later experiments showed that these explosions were due to the exothermic nature of the reaction and to an excessive hydrogen chloride pressure resulting from hydrolysis of the tetrachloride.

For the investigation of the $ZrCl_2$–$ZrCl_3$–$ZrCl_4$ system 0.1 g. of zirconium was allowed to react with 0.25 g. of zirconium chloride in 4-cc. tubes which were heated in a vertical position in two aluminum block furnaces. These furnaces were mounted one on top of the other in such a way that the temperatures of the upper and lower halves of the tubes could be controlled independently.[9] The zirconium powder collected in the lower end of the tube and hence the temperature of the bottom furnace determined the reaction temperature of the experiment. So long as the temperature of the top furnace was kept below that of the bottom furnace, the $ZrCl_4$ reaction pressure could be controlled by varying the temperature of the upper part of the tube. The equilibrium pressure of the chloride corresponding to the temperature of the top furnace was obtained from the report of Kuhn, Ryon and Palko.[10]

The technique used to recover pure hafnium oxide from the sublimate by using Dowex 50 already has been described.[11]

## Results

**Zirconium Chloride–Zirconium Reaction.**—When zirconium powder was heated in an atmosphere of zirconium chloride vapor no reaction was apparent below 330°. Above this temperature the grey powder darkened and a hard cake formed in the bottom of the reaction bulb. From 330 to 460° this cake was greenish-black in color and consisted

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[1] O. Ruff and R. Wallstein, *Z. anorg. allgem. Chem.*, **128**, 96 (1923).

[2] R. C. Young, THIS JOURNAL, **53**, 2148 (1931).

[3] J. H. de Boer and J. D. Fast. *Z. anorg. allgem. Chem.*, **187**, 177 (1930).

[4] J. D. Fast, *ibid.*, **239**, 145 (1938).

[5] W. C. Schumb and C. K. Morehouse, THIS JOURNAL, **69**, 2696 (1947).

[6] I. E. Newnham, Eleanor Rutherford and A. G. Turnbull, *Aust. J. Appl. Sci.*, **6**, 218 (1955).

[7] C. A. Kumins, *Ind. Eng. Chem., Anal. Ed.*, **19**, 376 (1947).

[8] J. R. Caldwell and H. V. Mayer, *ibid.*, **7**, 38 (1935).

[9] H. Schäfer, C. Göser and L. Bayer, *Z. anorg. allgem. Chem.*, **265**, 258 (1951).

[10] D. W. Kuhn, A. D. Ryon, A. A. Palko (Union Carbide and Carbon Corporation), Report No. Y-552 (1950).

[11] I. E. Newnham, THIS JOURNAL, **73**, 5899 (1951).

of zirconium trichloride and unreacted zirconium. It dissolved in water with vigorous evolution of hydrogen, yielding a brownish-yellow solution and a black sediment of zirconium powder. The color of the solution was due to the presence of trivalent zirconium and its exposure to air resulted in oxidation to the tetravalent state and consequent fading of the brown color. Between 460 and 580° the walls of the bulb were covered with a thin black film which became increasingly dense as the reaction temperature rose. At the same time the green color disappeared from the cake, which dissolved in water with decreasing vigor. The aqueous solution varied in composition from $ZrCl_3$ (460°) to $ZrCl_2$ (580°) and in color from reddish-brown to deep chocolate, but these colors faded on standing and a residue of colloidal zirconium remained suspended in the solution. Above 580° the cake was replaced by black granules containing pyrophoric zirconium which ignited spontaneously in air.

**Differential Reduction of the Chlorides of Hafnium and Zirconium.**—All the experiments in the 50-ml. and 250-ml. bulbs showed that hafnium chloride was not reduced by powdered zirconium. The reduced cake consisted of zirconium trichloride and excess zirconium powder, and the trichloride was found to contain in all cases less than 0.1%, and in most cases less than 0.05%, hafnium. (The starting material contained 1.5% hafnium, all hafnium contents being expressed as percentage $HfO_2$ in the mixed oxides of zirconium and hafnium.)

The relationship between the hafnium content of the sublimate and the reaction temperature is shown in Fig. 1. This curve represents the results of the 50-ml. bulb experiments but the existence of the sharp peak at 420° was confirmed by the reactions in the 250-ml. bulbs. It was found that the formation of a solid cake in the smaller bulbs seriously retarded the progress of the reduction and the larger bulbs were therefore shaken vigorously in order to break up the cake. By alternately heating and shaking the bulb several times the hafnium content of the sublimate from the larger bulb rose to 29.4% as compared with 5.7% in the sublimate from the smaller bulb. In both cases the reaction temperature was 420° and the reaction time 8 hours. The effectiveness of the separation was indicated by the fact that, in the larger scale experiment, 95% of the original $ZrCl_4$ was reduced to $ZrCl_3$ containing 0.5% Hf, and 95% of the original $HfCl_4$ impurity was recovered as a concentrate containing 30% Hf.

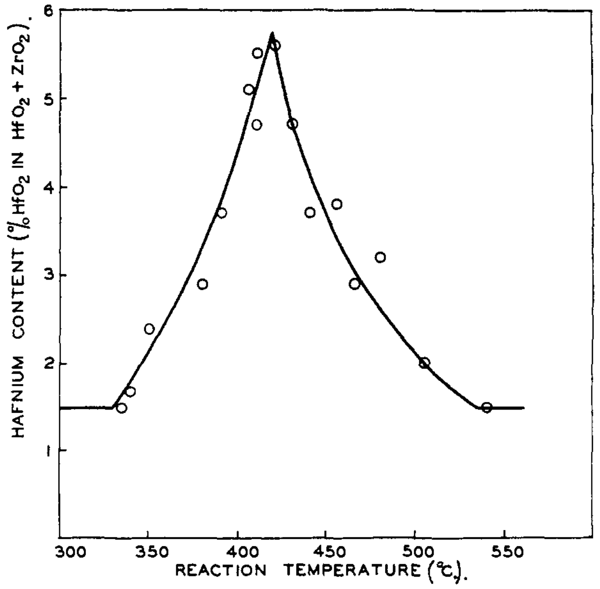

Fig. 1.—Hafnium content of unreduced $ZrCl_4$ sublimate.

**The Separation of Hafnium and Zirconium.**—The non-reduction of hafnium chloride by zirconium made possible the recovery of a low-hafnium zirconium compound from the reduced zirconium chloride either by dissolving the trichloride in water or by heating it *in vacuo* to disproportionate it

$$2ZrCl_3 \longrightarrow ZrCl_2 + ZrCl_4 \qquad (1)$$

$$2ZrCl_2 \longrightarrow Zr + ZrCl_4 \qquad (2)$$

The trichloride disproportionated completely at 540° but more than half the resultant dichloride remained unchanged even after heating for several hours at 650°.

Since the disproportionation of zirconium trichloride has been shown to be reversible[1] it was found possible to use it as a basis for a semi-continuous process[12] for removing the hafnium from crude zirconium chloride. This involved reducing the tetrachloride to the trichloride by heating it *in vacuo* with powdered zirconium, subliming off the hafnium chloride and any unreduced zirconium chloride, and finally disproportionating the trichloride to give the di- and tetrachloride. The dichloride was then available as a reducing agent for the next batch of tetrachloride.

For reasons outlined in the following paragraph the hafnium-containing sublimate was considerably diluted with unreduced zirconium chloride but the concentration of hafnium was sufficiently high to make its recovery by ion-exchange[11] or solvent extraction methods a simple matter.

**Incomplete Reduction of Zirconium Chloride.**—Because zirconium trichloride commenced to disproportionate into the tetra- and dichlorides at 300° it was found that, in any reduction of zirconium chloride by zirconium, some dilution of the hafnium chloride sublimate by unreduced zirconium chloride was unavoidable. The actual amount of unreduced chloride depended on the volume of the reaction vessel, the physical state of the reducing agent and the reaction temperature and pressure. It was found that, for any given reaction temperature, there was a critical tetrachloride vapor pressure below which reduction to the trichloride would not take place, and this critical reaction pressure increased with rising temperature (Fig. 2).

## Discussion

The foregoing results demonstrate that there is a marked difference in the ease with which $ZrCl_4$ and $HfCl_4$ can be reduced to $ZrCl_3$ and $HfCl_3$. The fact

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(12) I. E. Newnham, Australian Patents 167,210, 167,211; U. S. Patent 2,791,485.

that $HfCl_4$ can be sublimed *in vacuo* at 200° makes its separation from the involatile $ZrCl_3$ comparatively simple. Over the temperature range investigated (330–550°) the hafnium content of the reduced chloride was always less than 0.1% and, by eliminating all hydrolysis of the initial $ZrCl_4$ charge, it was possible to reduce the hafnium content of the lower chloride well below this level. By careful attention to technique the $ZrCl_3$ produced in the small-scale tube experiments contained only 0.01% Hf.

The extent to which the $HfCl_4$ can be concentrated by this process depends on the amount of $ZrCl_4$ which remains unreduced at the conclusion of the reaction. By keeping the bulb volume small, by using a large excess of zirconium and by constantly exposing a fresh zirconium surface to the chloride vapors, it was possible to reduce 95% of a 40 gram charge of $ZrCl_4$ at 420° after 8 hours heating. Up to this temperature disproportionation of the $ZrCl_3$ played little part in the reaction but above this point the degree of disproportionation increased rapidly. It is obviously this disproportionation effect which is responsible for the sudden change in slope of the curve in Fig. 2.

The peak in the curve in Fig. 1 is also obviously due to this disproportionation effect though the sharp increase in the vapor density of $ZrCl_4$ at this temperature[10] must also result in an increase in the weight of $ZrCl_4$ vapor in equilibrium with the lower chloride.

One of the big advantages of the foregoing method for separating hafnium and zirconium is that the zirconium can be introduced as the chloride and recovered as the chloride, thus making possible a process for removing the hafnium impurity from zirconium chloride which is free from solution chemistry. In this way the uneconomical steps, which are a feature of ion-exchange or solvent extraction methods, of dissolving the chloride in a suitable solvent and subsequently recovering the zirconium by precipitation and re-chlorination, can be eliminated. However several points require close attention if the process is to be used on a large scale, and one of the main ones is the undesirable caking of the zirconium powder. This can be overcome by spreading out the powder in thin layers so as to expose as large a surface area as possible. This tends to add to the volume of the reaction vessel which must be kept to a minimum in order to reduce the dilution of the hafnium chloride with unreduced zirconium chloride. An alternative solution may lie in the use of a more porous reducing agent such as zirconium carbide, although experiments with this compound have indicated that a higher reaction temperature would be necessary. This is undesirable since a high reaction temperature results in a raised equilibrium vapor pressure, thus leading to further dilution of the hafnium chloride sublimate.

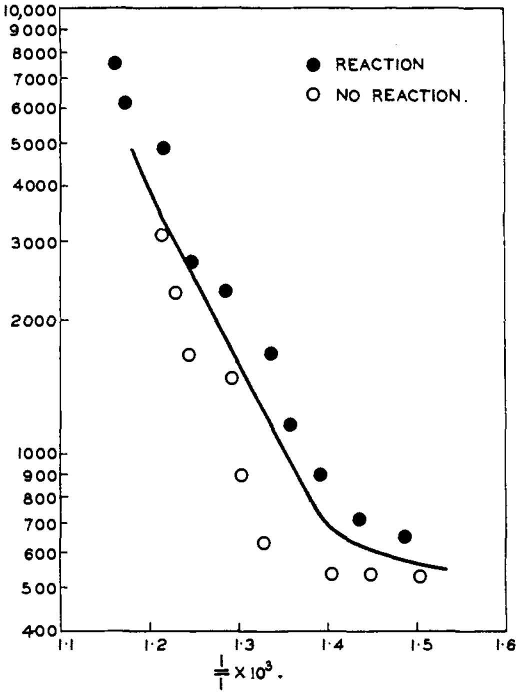

Fig. 2.—Relationship between critical pressure and reaction temp. ($T$, °A.).

A more profitable field of investigation has been found to lie in the use of aluminum powder which will reduce zirconium chloride to the trichloride at 300°. Not only does this eliminate the disproportionation effect but it also has the added advantage of forming an aluminum chloride melt in which zirconium trichloride will dissolve. This would appear to be one of the best ways of overcoming caking although it has the disadvantage of contaminating the hafnium chloride sublimate with aluminum chloride.

The complete separation process has been tested on a pound-scale in a mild steel reaction vessel and details of this work will be published in a subsequent paper.

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