He^3 due to disintegration and an increase in protium content due to exchange with stopcock grease was evident. These impurities interfered with condensation of the T-D mixture when attempts were made to make measurements in the temperature region above 24.5°K. Only results from freshly prepared mixtures are reported here. Earlier experiments on material in which the impurity buildup had been excessive were discarded. A correction for the small amount of impurities present in the original deuterium and tritium was applied on the assumption of a linear relationship between the mole fraction and the molar volume. For this purpose, the molar volume of HT was assumed to be the same as that of deuterium.

Results

A. Deuterium.—The molar volumes of deuterium in the temperature range 19.5 to 24.2°K. are shown in Table I. The five experimental values of this research were combined with the eight measurements of Clusius and Bartholemé by the least squares method to obtain the equation

$$V_M(\text{cm.}^3/\text{mole}) = 20.188 + 0.03587T + 0.006565T^2$$

The maximum deviation of the experimental points from this equation is 0.025 cm.^{3}/mole (or 0.1%) and the standard deviation is 0.01 cm.^{3}/mole (or 0.04%)

B. Deuterium–Tritium Mixture.—A mixture containing 49.7 mole per cent. tritium and 50.3 mole per cent. deuterium was used in these measurements. Since T_2 and D_2 equilibrate rapidly even at room temperatures, the mixture was actually a three component one containing approximately 50% TD as shown by mass spectrometric analysis.

The ten experimental points are shown in Table II and can be represented by the equation

$$V_M(\text{cm.}^3/\text{mole}) = 18.555 + 0.1294T + 0.004203T^2$$

with a maximum deviation of 0.08 cm.^{3}/mole (or 0.35%) and a standard deviation of 0.05 cm.^{3}/mole (or 0.2%)

A comparison of these results with similar data on pure tritium[4] shows a small positive deviation in the molar volume of the mixture over the mean molar volumes of the components. This volume increase on mixing is a linear function of temperature, varying from 0.7% at 21°K. to 0.2% at 26°K.

TABLE I

MOLAR VOLUME OF DEUTERIUM

T, °K.	V_M (cm.^{3}/mole)	Dev. (calcd. − obsd.)
24.205	24.905	−0.003
23.41	24.620	+ .006
22.375	24.281	− .004
21.14	23.889	− .009
19.51	23.411	+ .025

TABLE II

MOLAR VOLUME OF A 50:50 ATOM PER CENT. TRITIUM–DEUTERIUM MIXTURE

T, °K.	V_M (cm.^{3}/mole)	Dev. (calcd. − obsd.)
24.06	24.11	−0.01
23.28	23.79	+ .06
22.64	23.68	− .04
22.56	23.695	− .08
22.46	23.53	+ .05
21.75	23.39	− .03
21.12	23.09	+ .07
20.73	23.05	− .01
19.56	22.66	+ .04
19.55	22.74	− .05

---

[4] E. R. Grilly, THIS JOURNAL, **73**, 5307 (1951).

LOS ALAMOS, NEW MEXICO RECEIVED AUGUST 20, 1951

[CONTRIBUTION NO. 167 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMICAL ENGINEERING, IOWA STATE COLLEGE]

Production of a Hafnium Concentrate by Adsorption[1,2]

BY GERHARD H. BEYER, ALFRED JACOBS AND RICHARD D. MASTELLER

A process has been developed for concentrating hafnium from a naturally-occurring feed material containing 2 wt. % hafnium oxide (based on hafnium and zirconium content) to an approximately 90 wt. % hafnium oxide in two cycles, involving adsorption and differential stripping with mineral acids at room temperature. Each cycle consists of the adsorption of hafnium and zirconium tetrachlorides in methanol solution on activated silica gel, and the subsequent stripping of the gel using a methanol-hydrogen chloride strip solution and, finally, a sulfuric acid strip solution. Approximately 70% of the original hafnium adsorbed can be recovered as high-hafnium concentrate.

Introduction

The quantity of hafnium occurring with zirconium in common American ore varies from about 0.020 to 0.025 hafnium to zirconium weight ratio. Because of their chemical similarity, hafnium and zirconium are difficult to separate, most of the proposed separation methods being quite laborious and expensive. The limited industrial use of hafnium in the preparation of certain lamp filaments and photoelectric cells,[3] reflects its high cost. Experimentally, it has been used in the making of X-ray photographs, in special glasses, and in television tubes. There is reason to believe that the development of efficient processes for removing hafnium from zirconium may make hafnium available as a by-product at greatly reduced cost.

An adsorption method for the separation of hafnium from zirconium was recently reported.[4] Separation was effected by preferential adsorption of hafnium on activated silica gel from a methanol solution of hafnium and zirconium tetrachlorides. Later results[5] indicated further concentration of the

---

[1] From the M.S. Thesis of Alfred Jacobs, Iowa State College 1951.

[2] This work was performed in the Ames Laboratory of the Atomic Energy Commission.

[3] A. G. Arend, *Chem. Products*, **11**, 30 (1948).

[4] R. S. Hansen and K. Gunnar, THIS JOURNAL, **71**, 4158 (1949).

[5] R. S. Hansen, K. Gunnar, A. Jacobs and C. R. Simmons, *ibid.*, **72**, 5043 (1950).

hafnium adsorbed on the silica gel as a result of differential stripping with acid solutions. This paper discusses a process which has been developed in this Laboratory to produce a mixture of hafnium and zirconium oxides containing more than 90 wt. % hafnium oxide.

Experimental

A 20 wt. % solution of hafnium and zirconium tetrachlorides in methanol was passed upward through a 6-inch diameter Pyrex column, 60 inches high, containing 40 lb. of 28–200 mesh activated silica gel. The gel was activated two hours at 300°, bringing its moisture content in the range of 3.20 to 3.35 wt. %. Subsequent contacting of the gel and adsorbate with solutions of 1.9 *N* anhydrous hydrogen chloride in methanol, and 7 *N* aqueous sulfuric acid, was accomplished by introducing the appropriate solution into the bottom of the column. Aliquots of column effluent were precipitated with ammonium hydroxide, filtered, and ignited. The oxides obtained were analyzed spectrographically for weight ratio of hafnium to zirconium. Concentrations expressed as wt. % hafnium oxide refer to the quantity of hafnium oxide relative to the total weight of hafnium and zirconium oxide, obtained upon precipitation from acid solution and ignition to the oxide.

To prepare the enriched feed for the second process cycle, selected increments of the hafnium-rich sulfuric strip were precipitated, ignited and then converted to the tetrachloride. The hot, powdered oxide was fluidized and chlorinated by passing a mixture of helium and carbon tetrachloride vapor through the bed, and collecting the sublimed tetrachlorides on a cold finger at the top of the apparatus. The three steps of adsorption on activated gel, contacting with methanol-hydrogen chloride strip solution, and, finally contacting with sulfuric acid strip solution were then repeated using feed made up of tetrachlorides from the first cycle, which were enriched in hafnium. Neither the adsorption nor the stripping operation is instantaneous; flow rates were so chosen that the solution was in contact with gel 10 hours for adsorption and 5 hours for stripping.

Discussion

The activated silica gel was found to adsorb from 0.075 to 0.085 g. of mixed hafnium and zirconium oxides per gram of gel, when the occluded feed from the adsorption step was removed by an unacidified methanol wash. The amount of hafnium adsorbed on the gel was, of course, dependent on the quantity of feed solution put through the column. After contacting 35 gallons of feed, the column of gel was still found to be capable of removing hafnium, while 50 gallons of feed completely dissipated gel activity. Complete use of gel activity is desirable from the viewpoint of hafnium production, since saturation with respect to hafnium affords a richer sulfuric strip product for carrying out a second adsorption. Using 35 gallons of feed, the wt. % hafnium oxide on the gel prior to stripping was found to be 18, while 50 gallons of feed increased this to 24.

By stripping a column of gel through which 35 gallons of feed had passed, with a 1.9 *N* anhydrous solution of hydrogen chloride in methanol, the curves shown in Figs. 1 and 2 were obtained. Although this strip solution removed two-thirds of the total oxide, the strong preference for zirconium is evident from Fig. 1. Only 14% of the adsorbed hafnium was removed, compared to 77% of the zirconium. A significant decrease in the quantity of material being removed indicated when this strip solution was no longer effective.

Subsequent contacting of the gel with 7 *N* sulfuric acid removed the remaining adsorbate. The data are shown in Figs. 3 and 4. Approximately 86% of the hafnium originally adsorbed was found in the sulfuric strip as 42 wt. % hafnium oxide. A similar experiment in which the adsorptive capacity of the gel was completely utilized

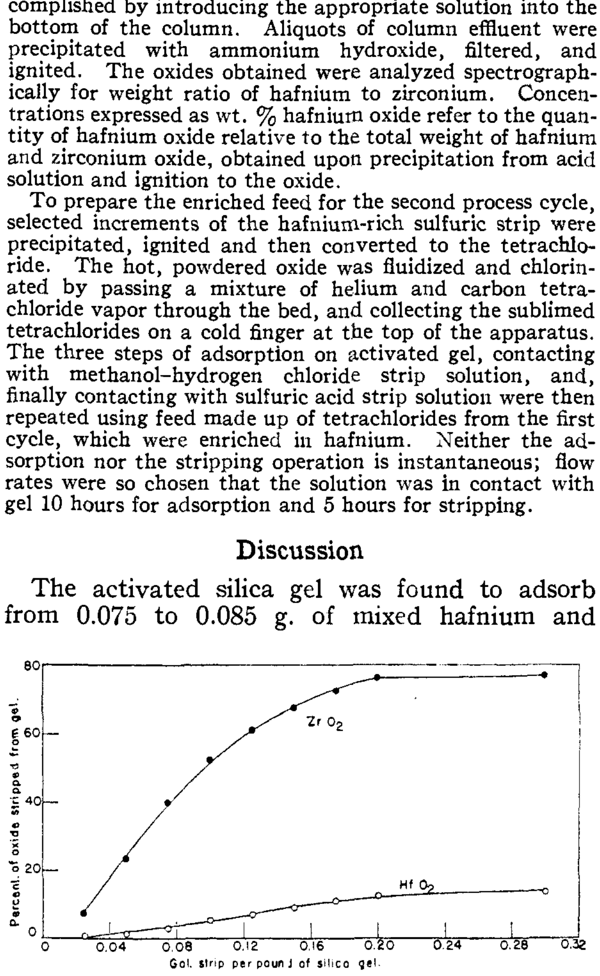

Fig. 1.—Methanol-hydrogen chloride stripping of silica gel.

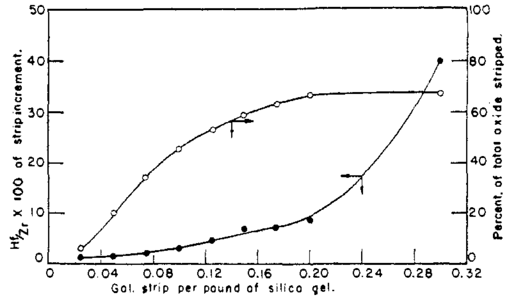

Fig. 2.—Characteristics of the hydrogen chloride-methanol stripping of silica gel.

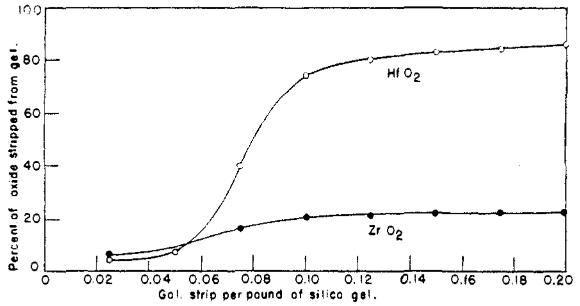

Fig. 3.—Final stripping of silica gel with 7 *N* sulfuric acid.

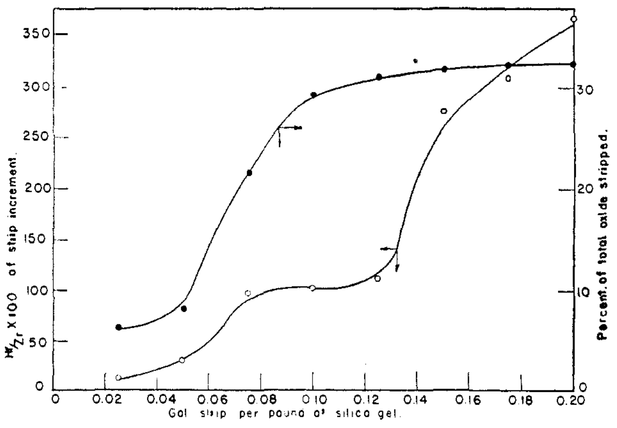

Fig. 4.—Characteristics of the sulfuric acid stripping of silica gel.

(50 gallons of feed) showed 83% of the adsorbed hafnium in the sulfuric strip as 50 wt. % hafnium oxide.

After conversion to the tetrachloride, the enriched hafnium made available by the first process cycle was further concentrated in a second similar cycle to 90 wt. % hafnium oxide. The over-all yield for the entire operation averaged 70%. Further concentration of hafnium by adsorption would probably require a zirconium-selective adsorbent.

Acknowledgment.—The authors are indebted to Olaf A. Runquist and Wendell Van Horn of the spectrographic section of the Ames Laboratory, Atomic Energy Commission, for their coöperation in analyzing the many samples submitted in this investigation.

AMES, IOWA RECEIVED JUNE 11, 1951

NOTES

Carbohydrate Thioacetals. I. Lead Tetraacetate Oxidation of D-Arabinose Derivatives

BY S. B. BAKER

Sugar thioacetals are important intermediates in carbohydrate syntheses and the oxidation of these sulfur-containing derivatives by means of glycol-cleaving oxidants should yield valuable intermediates. However, divalent sulfur atoms readily oxidize to form sulfones.[1] Some work has been done[2,3] on the periodate and lead tetraacetate oxidations of sugar thioacetals. The relative position of a glycol group to a thioacetal group may have some effect on the mode of oxidation and the present paper shows that this apparently occurs with arabinose thioacetal derivatives.

Two derivatives of D-arabinose dibenzyl thioacetal were prepared to determine what effect the position of a glycol had on the mode of oxidation of a thioacetal by lead tetraacetate. The first derivative, 4,5-isopropylidene-D-arabinose dibenzyl thioacetal, on reaction with one molecular equivalent of lead tetraacetate was oxidized in the normal manner, as shown by the isolation of isopropylidene-D-glyceraldehyde in good yield. The second derivative, 2,3-dibenzoyl-D-arabinose dibenzyl thioacetal did not yield formaldehyde on reaction with one molecular equivalent of lead tetraacetate, because the oxidant was apparently consumed in the oxidation of a sulfur atom.[3] On addition of a second equivalent of oxidant, the latter was consumed and approximately one equivalent of formaldehyde was produced as determined by the formation and isolation of formaldimethone.

Thus it seems that oxidation of arabinose thioacetal derivatives containing a glycol group in different positions relative to the thioacetal group can follow two paths and the point of reaction is apparently dependent on these relative spacial positions of the two groups.

Experimental

D-Arabinose Dibenzyl Thioacetal.—D-Arabinose (100 g.) was dissolved in cold concentrated hydrochloric acid (200 cc.). Benzyl mercaptan (200 cc.) was added and the mixture was vigorously agitated. After about 30 min. the mixture, which had become homogeneous with evolution of heat, began to cool and solidify. The hard reaction mixture was broken up, filtered and washed with water (6000 cc.), dilute ammonium hydroxide (400 cc.) and finally with water again. The crude air-dried material was recrystallized from 1-propanol-petroleum ether (3:1). The yield was 215 g. (80%) and melted at 148–149°; $[\alpha]^{22}\mathrm{D}$ +18.3 (*c* 2.6, pyridine). Pacsu[4] reported a melting point of 144° and $[\alpha]^{20}\mathrm{D}$ −18.86 for the L-isomer.

4,5-Isopropylidene-D-Arabinose Dibenzyl Thioacetal.—D-Arabinose dibenzyl thioacetal (70 g.) and anhydrous cupric sulfate (350 g.) were suspended in anhydrous acetone (1750 cc.) in a 5 l. round-bottomed flask. The mixture was vigorously agitated for 7 days on a shaking machine. The reaction mixture was filtered and the partially hydrated copper sulfate washed with chloroform. The filtrates were combined and concentrated to dryness at 50° *in vacuo*. The crystalline residue was dissolved in chloroform (100 cc.), the solution decolorized with charcoal and then filtered. The colorless filtrate was treated with low-boiling petroleum ether until turbid. Crystallization commenced immediately and the mixture was then cooled at −15° overnight for maximum crystallization; yield 70 g. (90%). A portion was twice recrystallized from boiling petroleum ether (65–110°) and dried at 65° *in vacuo*, melted at 100–100.5° and $[\alpha]^{24}\mathrm{D}$ −56.5° (*c* 1.7, chloroform).

Anal. Calcd. for $C_{22}H_{28}S_2O_4$; C, 62.85; H, 6.66; S, 15.2. Found: C, 62.7; H, 6.9; S, 15.2.

Lead Tetraacetate Oxidation of 4,5-Isopropylidene-D-Arabinose Dibenzyl Thioacetal.—The presumed 4,5-isopropylidene derivative (6.07 g.) was dissolved in thoroughly dried benzene (150 cc.). Twice recrystallized lead tetraacetate (6.4 g., 1 mole) was added rapidly and the mixture was agitated for 30 min. with occasional cooling. The mixture was then allowed to stand for 2 hr. and a 1-ml. aliquot showed that all the lead tetraacetate was consumed. The mixture was filtered through a sintered glass filter and the filter washed well with two portions of anhydrous benzene (25 cc.). The combined filtrates were then distilled through a 30-cm. column to remove the benzene and the residue slowly distilled under reduced pressure. A fraction (1.6 g.) was obtained, boiling at 42–44° (13 mm.), $n^{21}\mathrm{D}$ 1.4559; $[\alpha]^{22}\mathrm{D}$ +68.1 (*c* 0.45, benzene). These constants were in agreement with those found by Baer and Fischer[5] for isopropylidene-L-glyceraldehyde except for the direction of rotation.

A fraction (0.5 g.) was dissolved in saturated 2,4-dinitrophenylhydrazine hydrochloride and the solution after stand-

---

(1) W. A. Bonner and R. W. Drisko, THIS JOURNAL, **73**, 3699 (1951).

(2) B. H. Nicolet and L. A. Shinn, *ibid.*, **61**, 1615 (1939).

(3) C. F. Huebner , R. A. Pankratz and K. P. Link, *ibid.*, **72**, 4811 (1950).

(4) Pacsu and Ticharich, *Ber.*, **62**, 3008 (1929).

(5) E. Baer and H. O. L. Fischer, THIS JOURNAL, **61**, 764 (1939).