

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

The Preparation of Some Protactinium Compounds and the Metal¹

BY PHILIP A. SELLERS, SHERMAN FRIED, ROBERT E. ELSON AND W. H. ZACHARIASEN

RECEIVED MARCH 24, 1954

Protactinium metal, monoxide, dioxide, pentoxide, trihydride, tetrafluoride, tetrachloride and oxysulfide (PaOS) have been prepared. The compounds were identified by X-ray analysis and most of them were found to be isostructural with the analogous compounds of uranium. Other protactinium compounds have been prepared but their compositions have not been established definitely. A preliminary study of the protactinium oxide system showed compounds of compositions varying from PaO_2 to Pa_2O_5 .

Protactinium was first discovered by Fajans and Gohring.² However, the isotope used in this work was discovered in 1917 by Hahn and Meitner³ and independently about the same time by Soddy and Cranston.⁴ It was not until 1928 that the first compound was prepared by A. V. Grosse⁵ who reported the preparation of protactinium pentoxide by heating either the hydrated oxide or the oxalate. (The formula of this compound was derived by analogy with niobium and tantalum; no experimental evidence was given to support this formula.) Grosse and Agruss⁶ claimed to have prepared the metal in 1934 and described two preparations; one from the oxide on a copper target by bombardment with 35 Kev. electrons in a high vacuum, and the other by the decomposition of the vapors of the chloride, bromide or iodide on a tungsten filament at elevated temperature and at a pressure of 10^{-5} to 10^{-6} mm.

Preparations of the dioxide, pentoxide, tetrachloride and pentachloride of protactinium were recently reported⁷ briefly.

It was the purpose of this work to investigate some of the simpler compounds of protactinium in order to elucidate the chemistry of this element. Special attention was given to the possibility of preparing compounds representing various oxidation states. It was also of interest to study the relationships of protactinium to the other 5f elements which are revealed by the chemical and physical properties of the element and its compounds.

The naturally occurring protactinium (mass 231) was the isotope used in this work. This isotope is an alpha emitter with an approximately 34,000 year half-life and several milligrams of this material was available for the work to be described in this paper. The purification⁸ of the protactinium has been described previously and spectrochemical analysis indicated its purity was greater than 99%.

In each case the formula of the compound was demonstrated from an analysis of its X-ray diffraction pattern. The technique of micro-preparation and X-ray diffraction analysis has been described before and has been applied successfully to the

study of the chemistry of the other heavy elements.⁹

Preparations of protactinium compounds were carried out on a 50–100 microgram scale in order to conserve material and minimize the health hazard.

Experimental

Hydrated Oxide.—The hydrated oxide was obtained by precipitation of protactinium from an acid solution by ammonium hydroxide. The precipitate was collected by centrifugation in a micro-centrifuge cone and the supernatant discarded. After being washed with water to remove soluble salts the precipitate was centrifuged again, the supernatant solution removed, and the resulting pellet dried at room temperature. The material prepared in this way is essentially amorphous. The product obtained by heating the hydrated oxide to 110° is the material used for the preparations described below, and is fairly reactive in contrast to oxides which have been prepared at higher temperatures. It usually is obtained as a single pellet which makes for ease of handling.

Cubic Protactinium Pentoxide and Dioxide.—An oxide of composition Pa_2O_5 was formed by heating the hydrated oxide to 500° in air. The compound is white. Protactinium dioxide has been prepared by reduction of Pa_2O_5 at 1550° with hydrogen. The apparatus, a modification of the one developed for the preparation of metals in micro-quantities, consisted of a resistance furnace mounted on electrodes passing through a ground glass joint so that the furnace could be operated in an enclosed system.^{9,10} About 0.1 mg. of Pa_2O_5 was placed in the crucible, the system evacuated and pure hydrogen admitted to a pressure of 10 mm. The furnace was gradually heated to 1550° for 15 minutes. The temperature was determined by means of an optical pyrometer. Protactinium dioxide is a black substance which is not readily soluble in either dilute or concentrated sulfuric, hydrochloric or nitric acids, but is easily soluble in hydrofluoric acid.

The two cubic face-centered oxides of protactinium, believed to be Pa_2O_5 and PaO_2 , have been repeatedly observed.

The white cubic oxide, presumed to be Pa_2O_5 , is always formed when the hydrated oxide is ignited in air at 500° . The unit cell constant of this substance is: $a = 5.455 \pm 0.007 \text{ \AA}$.¹¹ The X-ray diffraction lines are somewhat diffuse, indicating a crystallite size of about 150 Å.

Other supporting evidence for this formula is deduced from the fact that it is formed under oxidizing conditions and from the white color.

The black cubic oxide believed to be PaO_2 , is formed from the white oxide under extreme reducing conditions, namely, by heating in hydrogen at 1550° . The unit cell constant of this black oxide is $a = 5.505 \pm 0.001 \text{ \AA}$.¹² The assignment of the formula PaO_2 to this oxide is based upon the following arguments. In the first place, the a -value lies on the smooth curve which is obtained when the lattice con-

(1) This paper was presented in part at the XII International Congress of Pure and Applied Chemistry at New York City, September 5, 1951.

(2) K. Fajans and Gohring, *Physik. Z.*, **14**, 877 (1913).

(3) O. Hahn and L. Meitner, *Naturwissenschaften*, **6**, 324 (1918).

(4) F. Soddy and J. A. Cranston, *Proc. Roy. Soc. (London)*, **94A**, 384 (1918).

(5) A. V. Grosse, *Ber.*, **61**, 241 (1928).

(6) A. V. Grosse and M. Agruss, *THIS JOURNAL*, **56**, 2200 (1934).

(7) R. Elson, S. Fried, P. Sellers and W. H. Zachariassen, *ibid.*, **72**, 5791 (1950).

(8) R. Elson, G. Mason, D. Peppard, P. Sellers and M. Studier, *ibid.*, **73**, 4794 (1951).

(9) S. Fried and N. Davidson, *ibid.*, **70**, 3539 (1948). Descriptions of apparatus and techniques will be referred back to this reference for details.

(10) E. F. Westrum, Jr., Manhattan Project Report, CK-1586 (A-2251), May 1944, p. 20.

(11) The cubic Pa_2O_5 with $a = 5.416 \pm 0.001 \text{ \AA}$ reported in *THIS JOURNAL*, **72**, 5791 (1950), has since been found to be an impure substance. It is now clear that the composition of the white ignited (500°) protactinium oxide hydrate has the composition Pa_2O_5 with $a = 5.455 \pm 0.007 \text{ \AA}$. and not PaO_2 .

(12) This unit cell constant was misprinted as $5.05 \pm 0.001 \text{ \AA}$ in the earlier communications, *THIS JOURNAL*, **72**, 5791 (1950).

stants of the dioxides ThO_2 , UO_2 , NpO_2 , PuO_2 and AmO_2 are plotted against the atomic number. The a -values for the series of compounds are shown in Table I. Second, the black oxide may be used as a starting material for the successful preparation of the tetravalent compounds PaF_4 , PaCl_4 and PaOS .

TABLE I

UNIT CELL CONSTANTS FOR DIOXIDES	
Compound	a in Å.
ThO_2	5.597 ± 0.001
PaO_2	$5.505 \pm .001$
UO_2	$5.468 \pm .001$
NpO_2	$5.436 \pm .001$
PuO_2	$5.397 \pm .001$
AmO_2	$5.388 \pm .003$

The intensity distribution in the X-ray diffraction pattern of PaO_2 suggests the fluorite type of structure. In the case of Pa_2O_5 , the structure is that of fluorite with the excess oxygen atoms distributed at random over the available holes. Since density data are not available, it is impossible to tell whether or not there may be vacancies in the metal sites.

Orthorhombic Protactinium Pentoxide.—A second form of Pa_2O_5 , orthorhombic and isostructural with uranium, niobium and tantalum pentoxides, was obtained as a white solid in the course of an attempt to prepare a fluoride by action of bromine pentafluoride on the oxide at 500° . Hydrolysis (from traces of water) was probably responsible for the formation of the compound under these conditions.

In this instance the dimensions of the cell (probably a small pseudo-cell) containing two metal atoms were found to be $a_1 = 6.92 \pm 0.02$ Å., $a_2 = 4.02 \pm 0.01$ Å., $a_3 = 4.18 \pm 0.02$ Å. The diffraction pattern is very similar to that of Nb_2O_5 and Ta_2O_5 . This fact, and the white color, suggest that the oxide in question is a second form of Pa_2O_5 .

The cell dimensions for Nb_2O_5 and Ta_2O_5 are¹³

	a_1	a_2	a_3 in Å.
Nb_2O_5	6.17 ± 0.01	3.66 ± 0.01	3.94 ± 0.01
Ta_2O_5	6.19 ± 0.01	3.65 ± 0.01	3.91 ± 0.01

Other Oxides.—A sample of protactinium oxide whose composition was Pa_2O_5 was heated to 500° *in vacuo* and maintained at this temperature for ten minutes. The sample was cooled, removed from the vacuum system, and the composition and structure were determined by X-ray analysis. The process was repeated increasing the temperature 100° each time. The changes in composition and structure are described in Table II. The data indicated in the table with respect to the composition of the oxides are not to be regarded as accurate, but as indicating trends in the removal of oxygen.

TABLE II

THE EFFECT OF TEMPERATURE ON THE OXIDE WHEN HEATED *in vacuo*

Approx. temp., °C.	Composition	Crystal form	Color
500	Pa_2O_5	Cubic	White
1000	$\text{PaO}_{2.3}$	Tetragonal	Black
1500	$\text{PaO}_{2.3}$	Tetragonal	Black
1800	$\text{PaO}_{2.3}$	Cubic	Black

When the cubic Pa_2O_5 is heated *in vacuo* to a temperature in the range 1000 – 1500° and maintained at that tempera-

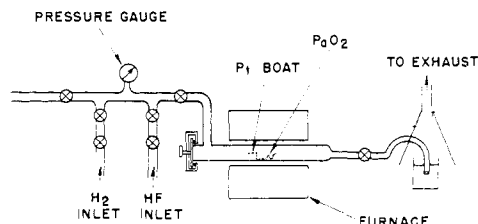


Fig. 1.—Fluorination apparatus (nickel).

(13) W. H. Zachariasen, Manhattan Project Report CF-2926, 13, 1945.

ture for ten minutes, the symmetry changes from cubic to tetragonal. The dimensions of the tetragonal unit cell containing two Pa atoms are $a_1 = 3.835 \pm 0.001$ Å., $a_3 = 5.573 \pm 0.001$ Å. The observed volume per metal atom corresponds to a composition $\text{PaO}_{2.3}$ if it is assumed that there is a linear change in volume with oxygen content in the range PaO_2 – $\text{PaO}_{2.8}$.

The sample heated to 1800° was found to be cubic face-centered with $a = 5.476 \pm 0.002$ Å. The volume per protactinium atom is the same as for the tetragonal form.

Protactinium Monoxide.¹⁴—This compound, which is cubic with the NaCl type of structure and $a = 4.961 \pm 0.003$ Å., is observed only as a coating on metal preparations. The evidence for the assigned formula is the similarity to the monoxides of thorium and of the elements U–Am and the fact the substance is slowly oxidized by air to the dioxide.

Protactinium "Pentafluoride."—A volatile compound of pentavalent protactinium containing fluorine may be prepared by the action of either bromine pentafluoride or bromine trifluoride on protactinium oxide. In a typical experiment, 0.1 mg. of the oxide was placed in a quartz capillary attached to a vacuum system and gaseous bromine trifluoride or pentafluoride was admitted. The temperature of the oxide in contact with the vapor was raised to 600° . A product of this reaction was volatile in vacuum at 150° . However, upon standing, it could not be revolatilized and X-ray analysis of this non-volatile substance proved it to be protactinium pentoxide having an orthorhombic crystal structure. From a consideration of the method of preparation and the volatility of the initial reaction product, it is assumed that protactinium pentafluoride or protactinium(V) oxyfluoride was formed and upon standing reacted with the quartz or with traces of water present in the system to form the pentoxide. The vigorous fluorinating action of bromine pentafluoride would favor the hypothesis that the fully fluorinated compound was formed.

Protactinium Tetrafluoride.—The apparatus shown in Fig. 1 was used to prepare this compound by the action of a hydrogen–hydrogen fluoride mixture on protactinium dioxide. A platinum boat containing the dioxide was placed in a nickel tube and the system was then evacuated. A mixture of five volumes of hydrogen and one of hydrogen fluoride was introduced slowly into the system. The system then was flushed with this mixture for one hour at room temperature. The temperature was gradually raised to 600° and maintained at this point for 15 minutes. The temperature was then allowed to fall slowly during which the flow of hydrogen fluoride was stopped but the flow of hydrogen was continued. It is very important to maintain a large excess of hydrogen during this reaction. Traces of oxygen result in the formation of the volatile higher fluoride of protactinium with attendant loss of the sample.

This reaction yielded protactinium tetrafluoride which has the zirconium tetrafluoride type of structure, isostructural with the tetrafluorides of thorium, uranium and plutonium. The compound is a reddish brown solid not readily reactive with air. It reacts when heated with moist oxygen to form an oxide and because of its physical characteristics is a suitable starting material for the preparation of the metal.

Protactinium "Pentachloride."—Protactinium pentachloride was prepared by the action of carbon tetrachloride on the oxide. The apparatus consisted of an X-ray capillary connected to a vacuum system so constructed that reactants could be admitted and removed (*cf.* ref. 10). About 0.1 mg. of the oxide was introduced into the capillary, the system assembled, and the capillary evacuated. The portion of the capillary containing the oxide was heated to 300° and carbon tetrachloride vapors admitted. The reaction was allowed to continue for ten minutes after which reaction products and excess carbon tetrachloride vapors were pumped off. This cycle was repeated until all the oxide had reacted.

The reaction yielded a white compound, volatile in vacuum at 150° . The X-ray diffraction pattern of this compound has not been interpreted. However, the method of preparation, the volatility, and the fact that the compound can be reduced to the tetrachloride with hydrogen indicates that it is the pentachloride and not an oxychloride.

Protactinium Tetrachloride.—This compound is prepared by reduction of the pentachloride with hydrogen. Protac-

(14) W. H. Zachariasen, *Acta Cryst.*, 5, 19 (1952).

tinium pentachloride was prepared as described above and was sublimed to a position one inch from the closed end of the capillary. The furnace was then cooled and placed above the compound. Hydrogen was admitted to the system and the temperature of the furnace raised to 800°. The furnace was then moved slowly down and toward the compound, eventually over it, thereby entrapping and forcing the highly volatile pentachloride to pass through a heated zone containing hydrogen.

Protactinium tetrachloride is a greenish-yellow compound that sublimes in vacuum at 400°. X-Ray analysis proved the compound to be protactinium tetrachloride with the tetragonal UCl_4 type of structure.

This compound may be directly prepared by the action of carbon tetrachloride vapor on PaO_2 at 500°.

The unit cell dimensions for the tetrachlorides with the UCl_4 type of structure¹⁵ are given in Table III.

TABLE III

UNIT CELL CONSTANTS FOR TETRACHLORIDES		
Compound	a_1 in Å.	a_2 in Å.
$ThCl_4$	8.490 ± 0.001	7.483 ± 0.001
$PaCl_4$	$8.377 \pm .004$	$7.482 \pm .004$
UCl_4	$8.303 \pm .001$	$7.483 \pm .001$
$NpCl_4$	$8.27 \pm .01$	$7.48 \pm .01$

Protactinium Bromides.—Protactinium bromides were prepared by reaction of the oxide with either aluminum bromide, hydrogen bromide, carbon tetrabromide or a mixture of hydrogen bromide and thionyl bromide. Volatile compounds also were obtained by reaction of the pentachloride with hydrogen bromide or thionyl bromide. The compositions or crystal structures of these compounds have not yet been established.

Protactinium Iodides.—These compounds have been prepared by the reaction of aluminum iodide or ammonium iodide with the oxide at elevated temperatures and by direct union of the elements at 600°. The composition of the products of these reactions has not been established.

Protactinium Metal.—The element was prepared by the reduction of approximately 0.1 mg. of protactinium tetrafluoride with barium metal at 1400°. The reduction was carried out using the "double crucible" system developed at this Laboratory (*cf.* ref. 9 and 10). The tetrafluoride and barium metal were charged into the crucibles which in turn were placed in the vacuum furnace. The system was evacuated to 10^{-6} mm. and the temperature raised to 1400° over a period of a few seconds. The temperature was kept at this point for about 50 seconds and the system was then allowed to cool. The reaction was found to have yielded shiny, malleable globules of protactinium metal.

The X-ray diffraction pattern of a flattened piece of metal showed it to be tetragonal body-centered with two atoms in a unit cell of dimensions $a_1 = 3.925 \pm 0.005$ Å., $a_2 = 3.238 \pm 0.007$ Å. The calculated density is 15.37 g./cm.³. The coordination number is ten, eight neighbors being at a distance of 3.212 Å. and two at 3.238 Å.

Protactinium Hydride.—This compound was prepared by heating protactinium metal in the presence of hydrogen. The apparatus consisted of an X-ray capillary connected to a ground joint, and was so constructed as to permit the capillary to be plugged by a droplet of mercury when the joint was turned through an angle (*cf.* ref. 10). The protactinium metal and mercury droplet were placed in the apparatus and the system evacuated. Pure hydrogen was admitted to a pressure of about 600 mm. The ground glass joint was then turned through an angle and the droplet of mercury formed a plug. Additional hydrogen was admitted to move the mercury plug some distance into the capillary and the joint was then returned to its original position. A furnace was then brought into position and the temperature gradually raised until the plug of mercury began to move toward the furnace, indicating an uptake of hydrogen by the metal. The hydride formed was a black flaky substance and the reaction occurred at about 250°. X-Ray analysis showed the product to be protactinium trihydride.

This compound is cubic and isostructural with UH_3 .¹⁶ The unit cell constant is $a = 6.648 \pm 0.005$ Å.

Protactinium Oxysulfide.—Protactinium(IV) oxysulfide was obtained from the reaction of protactinium pentachloride with a hydrogen sulfide-carbon disulfide mixture. The apparatus was similar to that used for the preparation of the chlorides. Hydrogen sulfide was bubbled through carbon disulfide and then through two cold traps at -50° . The mixture was admitted into the system to a pressure of 650 mm. and the temperature of the furnace was gradually raised so that it required one hour to reach 900°.

The light yellow non-volatile product thus obtained proved to be protactinium(IV) oxysulfide, $PaOS$, which is isostructural with uranium oxysulfide. Apparently the hydrogen sulfide reduced the $Pa(V)$ to $Pa(IV)$ under these conditions but the reduction was evidently not complete. X-Ray data indicated that the formula was approximately $Pa_{0.95}OS$. This product also was obtained by the reaction of the oxide with hydrogen sulfide and carbon disulfide at 1200°.

The unit cell dimensions for the oxysulfides¹⁷ with the $PbFCl$ type of structure are given in Table IV.

TABLE IV

UNIT CELL CONSTANTS FOR OXYSULFIDES		
Compound	a_1 in Å.	a_2 in Å.
$ThOS$	3.963 ± 0.002	6.746 ± 0.004
$PaOS$	$3.832 \pm .001$	$6.704 \pm .004$
UOS	$3.843 \pm .001$	$6.694 \pm .001$
$NpOS$	$3.825 \pm .002$	$6.654 \pm .010$

Protactinium Nitride.—Protactinium nitride was prepared by reaction of ammonia with either protactinium tetrachloride or pentachloride. Ammonia gas was admitted to a pressure of 540 mm. into a system containing the chloride. The temperature was raised at such a rate that it required one hour to reach 800°.

The product obtained was a bright yellow solid not volatile at 800° in vacuum.

Protactinium Carbide.—Protactinium monocarbide probably was prepared by the reduction of PaF_4 with barium in a carbon crucible at $\sim 1400^\circ$. An X-ray diffraction pattern of the product indicated that it probably was the compound PaC . However, X-ray diffraction data in this case do not distinguish the monocarbide from the monoxide. A consideration of the method of preparation (which in the case of neptunium yields carbides) suggests that the compound produced was indeed carbide.

Discussion

The preparation and identification of the dioxide, tetrachloride and tetrafluoride, of protactinium definitely demonstrate the existence of the IV state of protactinium. Likewise, the preparation and the identification of the pentoxide of protactinium demonstrate the existence of the V state. Haisinsky¹⁸ recently reported indication of the existence of $Pa(IV)$. The ease of reduction of the pentavalent protactinium to the tetravalent state has been shown by the reactions with hydrogen sulfide.

Observations during preparation of the oxides indicate the existence of cubic oxide phases PaO_2 and Pa_2O_5 . A preliminary study of the oxide system *in vacuo* over the temperature range 500–1800° indicates a loss of oxygen with increase in temperature. In the same temperature range a transition of crystal structure from cubic to tetragonal and back to cubic takes place. In addition to the changes described above, an orthorhombic structure has been observed.

The preparation of the metal reported here represents the first preparation which has yielded material suitable for making significant observations. It would be expected that the metal would melt

(17) W. H. Zachariassen, *Acta Cryst.*, **2**, 291 (1949).

(18) M. Haisinsky and G. Bouissières, *Bull. soc. chim. France*, 146 (1951).

(15) R. C. L. Mooney, *Acta Cryst.*, **2**, 189 (1949).

(16) R. E. Rundle, *THIS JOURNAL*, **73**, 4172 (1951).

at approximately 1300° by interpolation between the melting points of thorium and uranium. The metal, in common with other members of the 5f series, forms hydrides by direct union of the elements.

The compounds which were identified were found generally to be isostructural with the corresponding uranium compounds. However, the crystal structure of the metal was tetragonal and unlike any of the other 5f elements.

If an electron is added to an f-shell, there is a small contraction in metallic radius of 0.01–0.02 Å. as evidenced by the observed metallic radii for the 4f series of elements. The large decrease in metallic

radius from 1.79 Å. for thorium to 1.63 Å. for protactinium to 1.54 Å. for uranium is analogous to that in the series Zr–Nb–Mo rather than to that of the 4f-metals. Accordingly, it may be concluded that there are no 5f-electrons in the metal structures of the heavy elements thorium to uranium.

Acknowledgment.—The authors are grateful to Miss H. Anne Plettinger for her assistance with X-ray diffraction analyses reported in this paper. We would also like to thank Mr. Irving Sheft for his assistance in the early phases of the protactinium fluoride experiments, and Dr. Martin H. Studier for his help in many ways.

LEMONT, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, WAYNE UNIVERSITY]

The Solubility of Thorium Hydroxide in Solutions of Sodium Hydroxide and Perchloric Acid at 25°¹

BY K. H. GAYER AND H. LEIDER

RECEIVED JUNE 17, 1954

The solubility of thorium hydroxide has been studied in perchloric acid and sodium hydroxide solutions at 25°. The hydroxide reacts mainly as a base, the chief reaction in acid solution being $\text{Th}(\text{OH})_2 + 2\text{H}^+ \rightleftharpoons \text{ThO}^{++} + 2\text{H}_2\text{O}$. The reaction constant, K_s , is 5.5×10^4 and $\Delta F_s^\circ = -6500$ cal./mole. $K_{sp} = 5.5 \times 10^{-24}$ for the reaction $\text{ThO}(\text{OH})_2 \rightleftharpoons \text{ThO}^{++} + 2\text{OH}^-$.

The purpose of this investigation was to obtain information regarding the reactions of thorium hydroxide toward perchloric acid and sodium hydroxide solutions, to determine ionic species involved, and to evaluate free energies and equilibrium constants for such reactions. The results indicate that thorium hydroxide reacts predominantly as a base.

Procedure.—The general procedure is similar to that described by Garrett and Heiks.² An all-glass apparatus was used.

Water.—Conductivity water was prepared in a Barnstead conductivity still, degassed by boiling with nitrogen bubbling through it, and then stored under nitrogen.

Perchloric Acid Solutions.—Approximately one molar acid solutions were prepared from 70% G. F. Smith Chemical Co. purified perchloric acid with degassed conductivity water, and then stored under nitrogen. Standard acid solutions were also prepared with conductivity water and standardized against standard sodium hydroxide solution.

Sodium Hydroxide Solutions.—Approximately one molar solutions of bases were prepared under nitrogen by dissolving Baker and Adamson reagent pellets in degassed conductivity water in a paraffined flask. Barium hydroxide was added to just precipitate any carbonate. Following this, the solutions were stored under nitrogen. Standard base solutions were also prepared with conductivity water and standardized against potassium acid phthalate using phenolphthalein indicator.

Thorium Perchlorate Solutions.—Thorium hydroxide was precipitated from a solution of Baker and Adamson reagent grade thorium nitrate by addition of excess sodium hydroxide solution. The precipitate was washed by decantation with large volumes of conductivity water until the absence of a sodium flame test in the supernatant liquid was noted. The hydroxide was dissolved in perchloric acid, diluted to a final concentration of approximately one molar with degassed conductivity water, and stored under nitrogen.

Colorimetric Reagents.—A standard thorium solution was prepared by dissolving recrystallized J. T. Baker reagent

thorium nitrate in conductivity water. Aliquot portions of this solution were used to prepare the color standards. Eastman Kodak disodium salt of 1-(*o*-arsenophenylazo)-2-naphthol-3,6-disulfonic acid and Baker and Adamson A. C. S. standard hydrochloric acid were used to develop the color.

Thorium Hydroxide.—Thorium hydroxide was prepared by addition of excess sodium hydroxide solution to a solution of thorium perchlorate. The precipitate was washed with degassed conductivity water. Absence of the sodium flame test indicated completed washing. The solid phase was unchanged after equilibration with acid or base.

Equilibration.—Pairs of 100-ml. samples of the hydroxide in acid or base were collected in 125-ml. sample flasks under nitrogen. One of each pair was agitated in a 35° thermostat for five to seven days followed by agitation in a 25° thermostat for the same period of time. They were then allowed to settle for three to five days in the 25° thermostat. The other member of each pair was directly agitated in the 25° thermostat for at least seven days and allowed to settle for three to five days.

Determination of pH (–log A_{H^+}).—The flask necks were broken while enclosed in a rubber membrane and samples were taken using a Beckman 290–78 hypodermic type glass electrode. Measurements were made with a Beckman Model G meter which was calibrated at pH 4 with 0.05 *M* potassium acid phthalate buffer and at pH 7 with Beckman 3581 buffer.

Thorium Analysis.—The thorium analysis was made with a Beckman Model B spectrophotometer using the method of Thomason, Perry and Byerly.³

The Data.—The data are presented in Tables I, II and III and are represented graphically in Figs. 1 and 2. The slope of the curve of Fig. 1 is very nearly 0.5, indicating that a divalent ion is produced by the reaction

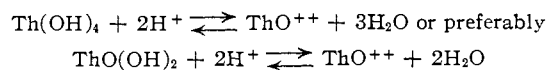


Figure 2, the solubility curve for $\text{ThO}(\text{OH})_2$ (or $\text{Th}(\text{OH})_4$) in base, does not seem to show a solubility minimum, but rather seems to extrapolate di-

(1) From a dissertation submitted by Herman Leider in partial fulfillment of the requirements for the Doctor of Philosophy degree at Wayne University.

(2) A. B. Garrett and R. E. Heiks, *THIS JOURNAL*, **63**, 562 (1941).

(3) P. F. Thomason, M. A. Perry and W. M. Byerly, *Anal. Chem.*, **21**, 1239 (1949).