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.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, WAYNE UNIVERSITY]

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

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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 $ThO(OH)_2 + 2H^+ \leftrightarrows ThO^{++} + 2H_2O$. The reaction constant, K_6, is 5.5×10^4 and $\Delta F_6^0 = -6500$ cal./mole. $K_{sp} = 5.5 \times 10^{-24}$ for the reaction $ThO(OH)_2 \leftrightarrows ThO^{++} + 2OH^-$.

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

$$Th(OH)_4 + 2H^+ \rightleftarrows ThO^{++} + 3H_2O \text{ or preferably}$$

$$ThO(OH)_2 + 2H^+ \rightleftarrows ThO^{++} + 2H_2O$$

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

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[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).

rectly to a water solubility of the order of 5 × 10^{-5} moles thorium/1000 g H_2O.

TABLE I

SOLUBILITY OF THORIUM HYDROXIDE IN NaOH SOLUTIONS AT 25°

Initial moles NaOH/1000 g. H_2O	Moles thorium/1000 g. H_2O	K_3	K_4
0.0098	1.08×10^{-5}	....	....
.0765	2.42	390×10^{-6}	3000×10^{-6}
.1595	8.85×10^{-6}	75	190
.2220	3.66	23	38
.3022	3.79	18	21
.3842	4.93×10^{-7}	1.3	1.6
.3950	5.94	1.5	1.9
.4342	13.8	3.2	3.5
.5081	9.88	1.9	1.8
.5257	4.93	0.9	0.9
.6307	8.92	1.4	1.1
.7023	9.86	1.4	0.9
.8650	12.9	1.5	0.8

TABLE II

SOLUBILITY OF THORIUM HYDROXIDE IN $HClO_4$ SOLUTIONS AT 25°

Initial moles $HClO_4$/1000 g. H_2O	Moles thorium/1000 g. H_2O
2.03×10^{-2}	6.48×10^{-3}
4.06×10^{-2}	1.48×10^{-2}
1.01×10^{-1}	4.04×10^{-2}
2.03×10^{-1}	9.80×10^{-2}
4.06×10^{-1}	2.00×10^{-1}
8.11×10^{-1}	3.62×10^{-1}

TABLE III

SOLUBILITY OF THORIUM HYDROXIDE IN $HClO_4$ SOLUTIONS AT 25°

Moles thorium/1000 g. H_2O	A_{H^+}	K_5	K_6
9.79×10^{-3}	3.63×10^{-4}	2.7×10^{1}	6.5×10^{4}
10.3×10^{-3}	3.89×10^{-4}	2.7×10^{1}	5.9×10^{4}
9.92×10^{-3}	3.98×10^{-4}	2.5×10^{1}	5.4×10^{4}
9.32×10^{-3}	4.17×10^{-4}	2.2×10^{1}	5.2×10^{4}
9.40×10^{-3}	4.47×10^{-4}	2.1×10^{1}	4.2×10^{4}
1.72×10^{-2}	5.13×10^{-4}	3.4×10^{1}	5.5×10^{4}
2.00×10^{-2}	5.62×10^{-4}	3.6×10^{1}	5.3×10^{4}
3.15×10^{-2}	6.61×10^{-4}	4.8×10^{1}	5.8×10^{4}
3.83×10^{-2}	7.59×10^{-4}	5.0×10^{1}	5.3×10^{4}

Chauvenet and Tonnet[4] reported that the hydrolysis of thorium proceeds by one of two mechanisms

$$Th^{+4} + 4H_2O \rightleftarrows Th(OH)_2^{++} + 3H_3O^+$$

$$\text{or } Th^{+4} + 3H_2O \rightleftarrows ThO^{++} + 2H_3O^+$$

A later work[5] supported this conclusion.

In more recent studies[6,7] it is reported that a $Th_4O_4^{+8}$, is formed over a considerable concentration range, and that there is no other simple species, but rather increasing polymerization occurs.[7]

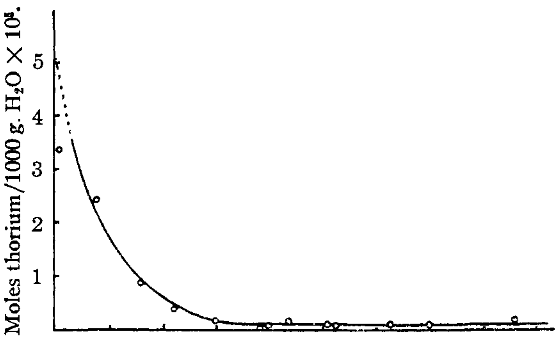

Fig. 1.—Solubility curve for thorium hydroxide in NaOH at 25°.

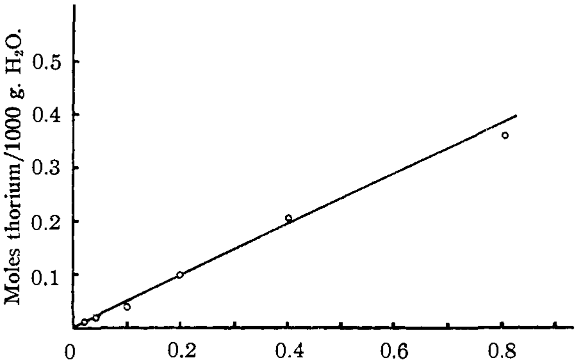

Fig. 2.—Solubility curve for thorium hydroxide in $HClO_4$ at 25°.

Kraus and Holmberg,[8] working with solutions of thorium perchlorate in excess perchloric acid at constant ionic strength (μ = 1.00), concluded that a monovalent hydrolysis product, $Th(OH)_3^+$, is unimportant and the reactions

$$Th^{+4} + 3H_2O \rightleftarrows ThO^{++} + 2H_3O^+ \text{ and}$$

$$2Th^{+4} + 3H_2O \rightleftarrows Th_2O^{+6} + 2H_3O^+$$

explained their hydrolysis data. Also, their reaction constants were given as $Km = mh^2/u = 3.1 \times 10^{-3}$ and $Kd = dh^2/u^2 = 2.7 \times 10^{-5}$, where

$u = Th^{+4}$
$m = ThO^{+2}$
$d = Th_2O^{+6}$
h = equilibrium acidity

Latimer[9] gives a solubility product for the reaction

$$Th(OH)_4 \rightleftarrows Th^{+4} + 4OH^-$$

$K = 1.0 \times 10^{-39}$, calculated from heats of formation and estimated entropy values. Latimer also gives values for titanium[10]

$$TiO(OH)_2 \rightleftarrows TiO^{++} + 2OH^- \quad K = ca.\ 10^{-29}$$

for zirconium[11]

$$ZrO(OH)_2 \rightleftarrows ZrO^{++} + 2OH^- \quad K = 3 \times 10^{-26}$$

and for hafnium[12]

$$HfO(OH)_2 \rightleftarrows HfO^{++} + 2OH^- \quad K = 4 \times 10^{-26}$$

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(4) E. Chauvenet and J. Tonnet, *Bull. soc. chim. France*, [4] **47**, 701 (1930).

(5) E. Chauvenet and Souteyrand-Franck, *ibid.*, **47**, 1128 (1930).

(6) P. Schall and J. Faucherre, *ibid.*, **14**, 937 (1947).

(7) P. Souchay, *ibid.*, **15**, 143 (1948).

(8) K. A. Kraus and R. W. Holmberg, A. E. C. D., 2919, August 29, 1950 (date declassified).

(9) W. M. Latimer, "Oxidation Potentials," Prentice-Hall Inc., New York, N. Y., 1952, p. 299.

(10) Ref. 9, p. 266.

(11) Ref. 9, p. 271.

(12) Ref. 9, p. 273.

The constant calculated in this work for the reaction

$$ThO(OH)_2(s) \rightleftharpoons ThO^{++} + 2OH^- \quad K_1 = 5.5 \times 10^{-24}$$

falls into correct sequence if thorium is considered to be a member of the titanium subgroup. This indicates that thorium is the most basic member of the subgroup, as would be expected.

General Equilibria.—The possible equilibria of $Th(OH)_4$ in acid, base and water solution may be represented by equations 1 to 8

$$ThO(OH)_2(s) \rightleftharpoons ThO^{++} + 2OH^- \qquad (1)$$

$$ThO(OH)_2(s) \rightleftharpoons ThO(OH)^+ + OH^- \qquad (2)$$

$$ThO(OH)_2(s) + OH^- \rightleftharpoons HThO_3^- + H_2O \qquad (3)$$

$$ThO(OH)_2(s) + 2OH^- \rightleftharpoons ThO_3^= + 2H_2O \qquad (4)$$

$$ThO(OH)_2(s) + H^+ \rightleftharpoons ThO(OH)^+ + H_2O \qquad (5)$$

$$ThO(OH)_2(s) + 2H^+ \rightleftharpoons ThO^{++} + 2H_2O \qquad (6)$$

$$ThO(OH)_2(s) \rightleftharpoons HThO_3^- + H^+ \qquad (7)$$

$$ThO(OH)_2(s) \rightleftharpoons ThO_3^= + 2H^+ \qquad (8)$$

Apparently, the reaction $ThO(OH)_2(s) \rightleftarrows ThO(OH)_2(aq)$ is unimportant, since the solubility curve does not show a solubility minimum but extrapolates upward to what can be assumed to be the water solubility. Direct measurement of the water solubility was not possible. Very erratic results were obtained.

Equilibria in Basic Solutions.—The values of K_3 and K_4 in Table I indicate that in concentrated base, above 0.38 molar sodium hydroxide, the important reactions of $Th(OH)_4$ are (3) and (4), and that these reactions occur to about the same extent. Reactions appear to be more involved in dilute sodium hydroxide. K_3 for reaction 3 was calculated

$$ThO(OH)_2(s) + OH^- \rightleftharpoons HThO_3^- + H_2O \qquad (3)$$

$$K_3 = \frac{M_{HThO_3^-}\gamma_{HThO_3^-}}{M_{OH^-}\gamma_{OH^-}} = 1.6 \times 10^{-6}$$

$$\Delta F_3^0 = 7900 \text{ cal./mole}$$

and K_4 for reaction 4

$$ThO(OH)_2(s) + 2OH^- \leftrightarrows Th_3O^= + H_2O \qquad (4)$$

$$K_4 = \frac{M_{ThO_3^=}\gamma_{ThO_3^=}}{M^2_{OH^-}\gamma^2_{OH^-}} = \frac{M_{ThO_3^=}}{M^2_{OH^-}}\gamma^2_{NaOH} = 1.6 \times 10^{-6}$$

$$\Delta F_4^0 = 7900 \text{ cal./mole}$$

In these calculations it is assumed that $\gamma_{HThO_3^-}/\gamma_{OH^-} = 1$, and $\gamma_{ThO_3^=}/\gamma^2_{OH^-} = \gamma^3_{Na_2ThO_3}/\gamma^4_{NaOH} = \gamma^6_{NaOH}/\gamma^4_{NaOH} = \gamma^2_{NaOH}$, from the Debye–Hückel theory. The values of γ_{NaOH} were interpolated from the data of Robinson and Stokes.[13]

Combining K_3 and the ionization constant for water K_w, K_7 was calculated for the reaction

$$ThO(OH)_2(s) \rightleftharpoons HThO_3^- + H^+ \qquad (7)$$

$$K_7 = K_3K_w = 1.6 \times 10^{-20}$$

$$\Delta F_7^0 = 27{,}000 \text{ cal./mole}$$

Similarly for K_8, using K_4 and K_w

$$ThO(OH)_2(s) \rightleftharpoons ThO_3^= + 2H^+ \qquad (8)$$

$$K_8 = K_4K_w^2 = 1.6 \times 10^{-34}$$

$$\Delta F_8^0 = 46{,}000 \text{ cal./mole}$$

Equilibrium in Acid Solutions.—The data presented in Table III indicate that the principal reaction of $Th(OH)_4$ in acid medium is given by equation 6. For reaction 6

$$ThO(OH)_2(s) + 2H^+ \rightleftharpoons ThO^{++} + 2H_2O$$

$$K_6 = \frac{M_{ThO^{++}}\gamma_{ThO^{++}}}{M^2_{H^+}\gamma^2_{H^+}} = 5.5 \times 10^4$$

$$\Delta F_6^0 = -6500 \text{ cal./mole}$$

The assumption was made that $\gamma_{ThO^{++}} = \gamma^2_{H^+}$, where γ_{H^+} was calculated from the Debye–Hückel equation.

For reaction 5

$$ThO(OH)_2(s) + H^+ \rightleftharpoons ThO(OH)^+ + H_2O \qquad (5)$$

$$K_5 = \frac{M_{ThO(OH)^+}\gamma_{ThO(OH)^+}}{M_{H^+}\gamma_{H^+}} = 3.2 \times 10^1$$

$$\Delta F_5^0 = -2100 \text{ cal./mole}$$

It has been assumed that $\gamma_{ThO(OH)^+}/\gamma_{H^+} = 1$.

Using K_5 and K_w, K_2 is evaluated for the reaction

$$ThO(OH)_2(s) = ThO(OH)^+ + OH^- \qquad (2)$$

$$K_2 = K_5K_w = 3.2 \times 10^{-13}$$

$$\Delta F_2^0 = 17{,}000 \text{ cal./mole}$$

Likewise, for the reaction

$$ThO(OH)_2(s) \rightleftharpoons ThO^{++} + 2OH^- \qquad (1)$$

$$K_1 = K_6K_w^2 = 5.5 \times 10^{-24}$$

$$\Delta F_1^0 = 32{,}000 \text{ cal./mole}$$

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DETROIT, MICHIGAN

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[13] R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).