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The Effect of Thorium Oxide on Thorium–Hydrogen Equilibrium[1]

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The increase in hydrogen dissociation pressure with hydrogen content, at constant temperature, in the two phase thorium–thorium hydride region has been shown to be related to the dissolution of thorium oxide in thorium hydride. Thorium oxide does not change the equilibrium pressure over the solid solution of hydrogen in thorium nor does it change the hydrogen to free metal ratio in thorium hydride. Thorium hydride with 4.0% ThO_2 in solution was found to be face centered cubic rather than tetragonal. The volume per formula weight was nearly the same for both modifications so that this change probably does not indicate a significant change in the type of bonding.

Introduction

Pressure–composition isotherms for the thorium–hydrogen system have been reported by Mallett and Campbell[2] and by Nottorf.[3] An increase in the equilibrium hydrogen pressure at constant temperature in the composition region where thorium coexisted with thorium dihydride was found by both investigations. This increase in the observed hydrogen pressure is incompatible with the phase rule. Libowitz[4] has shown that such an increase could result from a temperature gradient in the sample. However, the magnitude of the increase was similar in both investigations, although the designs of the furnaces were different and the occurrence of identical temperature gradients was unlikely. An alternative explanation is the presence of a third component making a ternary system. The most abundant impurity in the thorium used in these investigations was thorium oxide, so the effect of thorium oxide on these pressure composition isotherms at 700° was investigated.

Experimental

Sample Preparation.—Samples about 6 mm. in diameter by 15 mm. long were cut from arc-melted thorium rods. The crystal bar thorium was obtained from Battelle Memorial Institute and a representative analysis is given in Table I. The calcium-reduced thorium was from a billet with the analysis given in Table I. Calcium-reduced thorium was arc-melted with weighed amounts of ThO_2 to make the samples with higher thorium oxide content. Carbon was determined by combustion in oxygen, nitrogen by the Kjeldahl method and thorium oxide by dissolving a sample in hydrochloric acid and weighing the insoluble residue. Iron and beryllium were determined spectrographically. The sample surface was cleaned by grinding on a water-cooled abrasive wheel and pickling in 1–4 nitric acid containing a small amount of Na_2SiF_6. The samples were washed with distilled water, dried with ethyl alcohol, and degassed at 850° for 3 hr. under a 1 micron vacuum before the first addition of hydrogen was made.

TABLE I

ANALYSIS OF THORIUM METAL

Element	Calcium-reduced thorium	Crystal bar thorium
Carbon	410 p.p.m.	170 p.p.m.
Nitrogen	121 p.p.m.	62 p.p.m.
ThO_2	1.1%	0.16%
Iron	130 p.p.m.	135 p.p.m.
Beryllium	170 p.p.m.	<20 p.p.m.
Hardness	64 DPH	43 DPH

The pressure–composition isotherms were measured in a Sievert's apparatus consisting of a quartz furnace tube which contained the sample, a mercury manometer, a calibrated volume for measuring the amount of hydrogen added and a McLeod gage to measure the pressure during degassing and to check for leaks. The pressure could be read to ±0.3 mm. on the manometer. The system was evacuated with a mechanical pump to about 1 micron. Pure hydrogen[5] was generated by the thermal decomposition of UH_3.

The heated zone of the furnace was 28 cm. long and 3.2 cm. in diameter. The sample tube, 8 mm. inside diameter, was inserted 18 cm. into the furnace and enclosed by a stain-

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[1] Contribution No. 725. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] M. W. Mallett and I. E. Campbell, THIS JOURNAL, **73**, 4850 (1951).

[3] R. W. Nottorf, Unpublished Ph.D. Thesis, Iowa State College Library, Ames, Iowa, 1945.

[4] G. G. Libowitz, *J. Phys. Chem.*, **62**, 296 (1958).

[5] F. H. Spedding, A. S. Newton, J. C. Wharf, O. Johnson, R. W. Nottorf, I. B. Johns and A. H. Daane, *Nucleonics*, **4**, 4 (1949).

less steel tube 10 cm. long, 30 mm. outside diameter and 15 mm. inside diameter. The bottom end of the furnace was closed with a 6 cm. plug of sintered MgO. A ceramic tube around the sample tube in the upper portion of the furnace reduced the heat loss in that direction. The temperature between the sample tube and the steel tube was measured with a thermocouple at points along the length of the tube. A zone 5 cm. long was found in which the temperature was uniform within one degree, and the sample was centered in this zone. The sample temperature during a run was measured by the thermocouple between the sample tube and the stainless steel tube. Since the sample was centered in a region of uniform temperature more than three times as long as the sample, a significant temperature gradient in the sample was unlikely. The furnace temperature was controlled by regulating the voltage output of a voltage stabilizer with an autotransformer and was constant to within two degrees.

After the sample had been degassed and the temperature stabilized at 700°, additions of hydrogen were made and the pressure measured after it had remained constant for 1 hr. This usually required several hours after each addition. Since previous work on this system had shown that the same pressure was observed on either adding or withdrawing hydrogen. the pressure–composition isotherms were determined by adding hydrogen only.

Samples with various hydrogen and thorium oxide contents were examined by X-ray diffraction after cooling to room temperature. Thorium dihydride was quite brittle and was easily pulverized to a powder which gave sharp diffraction lines without annealing. The diffraction patterns were obtained with a 11.46 cm. diameter Debye–Scherrer camera using filtered copper radiation. The lattice constants were plotted against $\sin^2\theta$ and extrapolated to eliminate systematic errors. Metallographic samples were mounted in bakelite, ground through 600 grit silicon carbide papers and polished with 0.5 micron diamond paste. The samples were examined in the as-polished condition.

Results and Discussion

The pressure–composition isotherms at 700° are shown in Fig. 1 for thorium containing varying amounts of thorium oxide. Thorium oxide does not affect the equilibrium hydrogen pressure below the solubility limit of thorium dihydride in thorium metal. Since thorium oxide is quite insoluble in thorium, it would not be expected to influence the equilibrium pressure in this range.

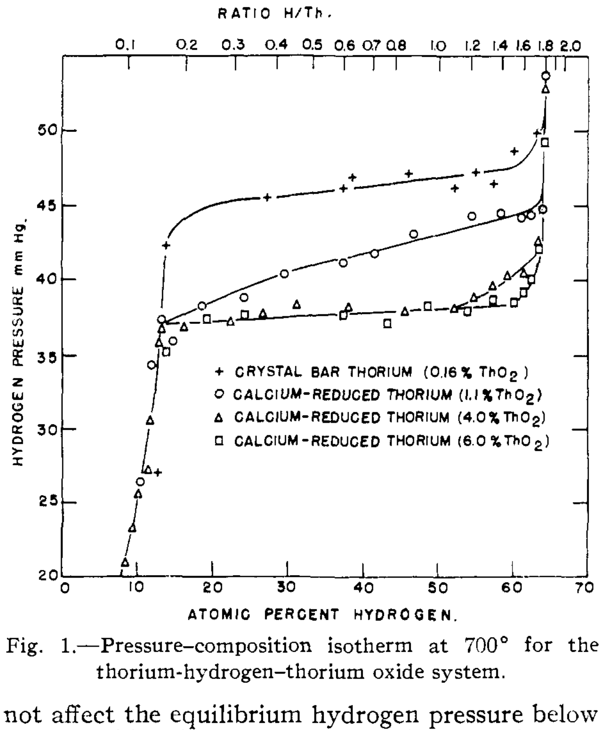

Fig. 1.—Pressure–composition isotherm at 700° for the thorium-hydrogen–thorium oxide system.

The dissociation pressure of thorium dihydride in the thorium–thorium dihydride region was reduced by thorium oxide. The crystal bar thorium sample had the highest dissociation pressure and only a slight variation of pressure with composition in this range. The pressure over the calcium-reduced thorium sample increased from 37 mm. at the lower composition limit to 44.5 at the upper composition limit. This is almost precisely the same pressure variation observed by Mallett and Campbell[2] at this temperature. The plateau for the samples containing 4.0 and 6.0% ThO_2 started at 37 mm. and did not increase significantly until the composition limit of thorium dihydride was reached. The explanation for this effect must be that thorium oxide dissolves in the thorium dihydride and thereby lowers the dissociation pressure. The increase in dissociation pressure for calcium-reduced thorium occurred because there was sufficient thorium oxide present to saturate the initial hydride which was formed. As additional thorium hydride was formed, the concentration of thorium oxide in the hydride phase decreased and the equilibrium hydrogen pressure increased. The thorium hydride in the sample containing 4.0% ThO_2 was saturated until almost all of the metal had been converted to hydride. As the 6.0% ThO_2 sample showed no increase in pressure in the plateau and hence was saturated with ThO_2 over the entire composition range, the solid solubility of ThO_2 in ThH_2 at 700° must be between 4 and 6%.

Microscopic examination of polished sections of thorium hydride containing up to 6% ThO_2 confirmed the solubility of ThO_2 in ThH_2. The gray globules of ThO_2 which were observed in the metal were not present in ThH_2 containing 4% ThO_2. ThH_2 containing 6.0% ThO_2 showed a few small globules of ThO_2. Decomposition of thorium hydride gave thorium metal in which the ThO_2 was present as a very fine precipitate, as contrasted with the large globules in the arc-melted metal.

Thorium oxide in solution did not change the hydrogen–metal ratio for thorium dihydride in equilibrium with thorium metal. The hydrogen-metal ratio and the atomic percentage hydrogen in Fig. 1 were calculated on the basis of the free thorium only. Apparently the ThO_2 dissolved in ThH_2 does not provide additional positions for hydrogen atoms. The hydrogen to free metal ratio for thorium dihydride at this temperature was 1.78 at 45 mm. pressure and increased slightly with hydrogen pressure.

X-Ray diffraction examination of thorium hydride containing 0.16 and 1.1% ThO_2 showed that it was body-centered tetragonal with lattice constants a_0 = 4.08 Å. and c_0 = 4.99 Å., in good agreement with the values of 4.10 and 5.03 Å. reported by Rundle.[6] The hydride containing 4.0 and 6.0% ThO_2 was face-centered cubic with a_0 = 5.492 A. The possibility that this change was due to variation in the hydrogen content was investigated by preparing samples of thorium hydride containing 0.16% ThO_2 which were in equilibrium with tho-

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[6] R. E. Rundle, C. G. Shull and E. O. Wollan, *Acta Cryst.*, **5**, 22 (1952).

rium metal and with Th_4H_{15}, respectively. These samples should represent the extreme composition limits of the lower hydride. Both samples had the tetragonal structure. The change from tetragonal to cubic lattice was caused by ThO_2 in solution. The structure of tetragonal ThH_2 is similar to the fluorite structure. This can be seen more easily by considering the alternate, face centered tetragonal unit cell with lattice constants a_0 = 5.73 Å. and c_0 = 4.99 Å. The volume of this cell is 163.8 Å.^{3} while the volume of the 5.492 Å. cubic cell is 165.6 Å.^{3}. The relatively small difference between these volumes indicates that bonding is quite similar in both, particularly as ThO_2 is somewhat larger than ThH_2 and in solution would tend to increase the lattice constant of ThH_2.

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[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY]

A Study of the Complexes of Curium(III) by Absorption Spectrometry[1]

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The absorption spectrum of Cm(III) in $HClO_4$, HCl, HNO_3 and H_2SO_4 in the region 220–1400 mμ has been studied. A number of new Cm(III) bands were found using larger amounts of curium than were available previously. The relative complexing of Cm(III) in HCl, HNO_3 and H_2SO_4 is indicated and these results are compared with those for Pu(III) and Am(III). Radiation decomposition of the solvent limited the study in concentrated acid solutions.

A recent communication[2] described the absorption spectrum of curium(III) in dilute $HClO_4$ and suggested reasons for its not being observed in earlier work. We have now extended this study to include the behavior of curium in HCl, HNO_3 and H_2SO_4 in order to determine whether known complexing, as demonstrated by its behavior in ion-exchange systems,[3-5] is reflected in spectral shifts or the formation of new bands which might aid in the elucidation of the species existing in solution. In addition, with the use of larger quantities of curium recently isolated at the Argonne National Laboratory, it has been possible to identify several new bands of low intensity characteristic of curium and of particular interest of the theoretical treatment of the spectrum. As in the earlier study the curium used was >95% by mass Cm^{244}, $t_{1/2}$ = 17.9 y.[6]

In each solvent system the intense α-activity limited the solvent concentration at which the complete spectrum of curium could be discerned by producing decomposition products whose absorption eventually obscured that of the curium.

Experimental

The Cm^{244} used in this work was produced by neutron bombardment of Pu^{239} in a high neutron flux reactor (Materials Testing Reactor, Arco, Idaho) and separated from fission products and other heavy elements by a series of steps involving ion exchange, solvent extraction and selective precipitation.[7] Much of the present work was carried out with the combined curium fractions from several different plutonium irradiations: a total of approximately 20 mg. of curium.

Spectrographic analysis of the curium showed calcium and aluminum to be the main impurities; no lanthanides were detected. Alpha pulse analysis indicated ≥98 α% Cm^{244}, <2 α% Cm^{242}; no other α-emitters were detected.

Solutions were prepared by precipitation of $Cm(OH)_3$ with NH_3 gas, washing and dissolution in the desired solvent. They were assayed radiometrically with a precision of ± 2%.

The measurements were made using either a Cary Model 12 or Model 14 Recording Spectrophotometer at 23 ± 2°. The reference cell contained the same solvent as the sample cell except for the HNO_3 system wherein H_2O was used. The base line was obtained by running pure solvent in the sample cell *versus* the reference cell.

Conventional fused silica spectrophotometer cells with 1 cm. path length equipped with a ground glass stopper were used; however, it was necessary to require actually *fused* joints instead of the usual fabrication with a low melting glass in order to prevent leakage of activity. These cells were placed in a special holder which could be sealed tightly to contain the activity in the event of cell rupture. When in the holder, the cells were so positioned and masked that a volume of 1 ml. was sufficient to load them.

Results and Discussion

$HClO_4$ System.—The spectrum of Cm(III) in $HClO_4$ is shown in Fig. 1. The trend in the earlier members of the actinide series as well as the negligible effect of increasing $HClO_4$ concentration on the extinction coefficient of the curium bands supports the view that the species present is the hydrated Cm(III) ion.[8]

A general increase in absorption in the far ultraviolet region with time has been attributed to the production of H_2O_2 by the intense α-activity of the sample[2]; consequently the curium bands in this region should be corrected for absorption due to H_2O_2. An exact correction is difficult because of problems in determining H_2O_2 concentration at any given time. As a first approximation a correction such as that indicated by the dashed line in Fig. 1 may be made. This correction curve is similar in shape to the absorption spectrum of H_2O_2, and the extent of the correction was consistent with the amount of H_2O_2 calculated as being produced during the interval between sample prepa-

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] W. T. Carnall, P. R. Fields, D. C. Stewart and T. K. Keenan, *J. Inorg. Nucl. Chem.*, **6**, 213 (1958).

[3] R. M. Diamond, K. Street, Jr., and G. T. Seaborg, THIS JOURNAL, **76**, 1461 (1954).

[4] M. Ward and G. A. Welch, *J. Inorg. Nucl. Chem.*, **2**, 395 (1956).

[5] S. G. Thompson, B. G. Harvey, G. R. Choppin and G. T. Seaborg, THIS JOURNAL, **76**, 6229 (1954).

[6] A half-life of 18.4 y., reported by Friedman, *et al.*, *Phys. Rev.*, **95**, 1501 (1954), was the weighted average of two determinations. It is now generally accepted that one of these, 17.9 y., is the more accurate.

[7] Bentley, *et al.*, "Proceedings of the International Conference on the Peaceful Uses of Atomic Energy," Vol. VII, United Nations, New York, N. Y., 1956, p. 261.

[8] K. A. Kraus, ref. 7, Vol. VII, p. 245.