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Terbium Tetrafluoride: Preparation and Properties¹

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Solid terbium tetrafluoride has been prepared by the reaction: $\text{TbF}_3(\text{c}) + \frac{1}{2}\text{F}_2(\text{g}) \xrightarrow{320^\circ} \text{TbF}_4(\text{c})$. The crystalline tetrafluoride is monoclinic and isostructural with the tetrafluorides of cerium, uranium and thorium. The compound is inert to cold water but reacts fairly rapidly with acidified solutions of aluminum nitrate. No $\text{PrF}_4(\text{c})$ was formed under conditions suitable to the formation of $\text{TbF}_4(\text{c})$ and $\text{CeF}_4(\text{c})$.

The only anhydrous higher halide of a rare earth element described previously is cerium tetrafluoride, which was first prepared by Klemm and Henkel³ by treating the anhydrous trichloride with fluorine at room temperature. The identity of the product was established by a careful study of the stoichiometry of its conversion to: (a) cerium dioxide and (b) cerium trifluoride; and by an examination of its X-ray diffraction pattern and magnetic properties. Klemm and Henkel⁴ also reported that a reaction occurred between cerium dioxide and fluorine at 200°, but cerium tetrafluoride was not identified as a reaction product. No tetrafluoride was formed by the action of fluorine on the trichlorides of either praseodymium or neodymium.

Subsequent to the work of Klemm and Henkel, von Wartenberg⁵ demonstrated that cerium trifluoride could be converted quantitatively to the tetrafluoride by the action of fluorine at 500–650°.

Both von Wartenberg and Klemm and Henkel reported that cerium tetrafluoride is reduced to the trifluoride by hydrogen at 200–300°, and that the compound is relatively inert to cold water.

Recent attempts^{6,7} to prepare praseodymium tetrafluoride have been unsuccessful, in confirmation of the work of Klemm and Henkel. In contradiction to the experimental evidence, Perros, Munsen and Naeser⁸ have presented thermodynamic cal-

culations which purport to demonstrate the stability of praseodymium tetrafluoride even at moderately high temperature.

In connection with a program of investigating the analogies and differences between the 4f and 5f series of elements the present authors have made a brief study of the rare earth higher fluorides. The investigation led to the preparation of a new lanthanide higher fluoride, namely, TbF_4 .

Experimental

Apparatus.—Fluorinations were carried out with elemental fluorine in a tubular nickel reaction chamber heated to an appropriate temperature by a tube furnace.

Fluorine, obtained from a half-pound cylinder of the compressed gas, was passed through a double valved mixing chamber of copper provided with a side inlet for admitting dry argon and thence into an ice-cooled nickel trap, partially filled with solid potassium fluoride to remove hydrogen fluoride. Fluorine free of hydrogen fluoride was then passed into the tubular reaction chamber which could be heated by a surrounding tube furnace.

Temperatures were determined with an iron-constantan thermocouple, inserted near the center of the annular space between the chamber and furnace. In preliminary experiments the temperature of the interior of the reaction chamber was measured simultaneously with a second thermocouple, and a table of temperature correlations was prepared from the data. Reaction temperatures were uncertain by about $\pm 20^\circ$.

Samples to be fluorinated were contained in small barium fluoride crucibles (made from a paste of water and powdered fluoride, cast as short rods, dried, drilled and fired in air for 60 minutes at 1000°) supported in a short length of flattened and drilled nickel rod.

Materials.—The rare earths used in this work were obtained initially as oxides. Purities were determined by spectrographic analysis. Sources and purities were as follows: (1) cerium dioxide with less than 0.1% metallic impurities was purchased from Eimer and Amend, New York City; (2) praseodymium was obtained as " Pr_2O_3 " from Johnson, Matthey and Co., Ltd., of London, England, and was further purified at this Laboratory to less than 0.1% metallic impurities; (3) neodymium sesquioxide was obtained from Dr. F. H. Spedding at Iowa State College,

(1) This work was performed under the auspices of the Atomic Energy Commission.

(2) Part of the work described was done by D. C. Feay in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) W. Klemm and P. Henkel, *Z. anorg. allgem. Chem.*, **220**, 180 (1934).

(4) W. Klemm and P. Henkel, *op. cit.*

(5) H. von Wartenberg, *ibid.*, **244**, 339 (1940).

(6) A. I. Popov and G. Glockler, *THIS JOURNAL*, **74**, 1357 (1952).

(7) T. P. Perros and C. R. Naeser, *ibid.*, **74**, 3694 (1952).

(8) T. P. Perros, T. R. Munsen and Charles R. Naeser, *J. Chem. Ed.*, **30**, 402 (1953).

Ames, Iowa, and further purified at this Laboratory to less than 0.1% metallic impurities; (4) samarium sesquioxide with less than 1% metallic impurities was obtained from Dr. F. H. Spedding; (5) terbium oxide, "Tb₂O₇," as purchased from Johnson, Matthey and Co., contained less than 0.1% metallic impurities; and (6) dysprosium sesquioxide had been purified earlier at this Laboratory to less than 0.5% metallic impurities.

Samples of these oxides were converted to trifluorides as follows. Approximately one mg. of oxide was dissolved in about 100 μ l. of warm concentrated hydrochloric acid. In the case of cerium dioxide, hydrogen peroxide was added to increase the rate of solution as well as to reduce the tetravalent cerium ion to the trivalent state. The solution of the oxide was transferred to a Fluorothene⁹ cone.

To the solution was added one-tenth its volume of concentrated hydrofluoric acid. The precipitate was collected by centrifuging and washed once with distilled water and once with absolute alcohol. The trifluoride was then dried at 80° overnight.

The reagents used in these preparations were of analytical grade.

Fluorine at a pressure of 400 pounds per square inch was purchased in half-pound cylinders from the Pennsylvania Salt Manufacturing Co., Natrona, Pennsylvania. Since traces of hydrogen fluoride in the fluorine would suffice to convert our small samples of rare earth trifluorides to hydrogen fluoride addition compounds, tank fluorine was passed through a trap containing solid potassium fluoride before admission to the reaction chamber.

Argon, used to sweep the line before and after fluorination, was taken from a cylinder of the compressed gas and purified by passage over phosphorus pentoxide and over uranium metal turnings heated to 400°.

X-Ray Diffraction Studies.—Powder patterns of a number of our rare earth compounds were obtained by Mrs. Helena Ruben and Mrs. Carol Dauben, under the direction of Professor D. H. Templeton. These patterns were indexed and otherwise interpreted by this group.

Procedure.—At the beginning of a run the potassium fluoride trap was freshly charged with about one-half pound of the powdered salt and connected to the line. About 500 μ g. of the rare earth trifluoride under investigation was placed in a barium fluoride crucible, which was then inserted in its nickel rod holder into the reaction chamber. Assembly of the line was completed and it was then flushed thoroughly with dry argon. Fluorine was admitted slowly and the argon flow was discontinued. The chamber was heated to the desired temperature and fluorination continued for 40 to 60 minutes. The sample was allowed to cool in fluorine to about 100°, after which the flow of fluorine was discontinued and the apparatus flushed with dry argon, until it was near room temperature. Samples were removed after partial disassembly of the equipment, but without interruption of the flow of argon.

In practice, several samples of trifluoride were run simultaneously.

Results and Discussion

The results of X-ray examination of the products of fluorination are summarized in Table I.

TABLE I
EFFECT OF FLUORINE AT ATMOSPHERIC PRESSURE ON SOME RARE EARTH TRIFLUORIDES

| Tri-fluoride | Exposure time, min. | Approximate temp., °C. | Product Structure | Composition |
|--------------|---------------------|------------------------|-------------------------|------------------|
| Ce | 40-60 | 320 | Monoclinic ^a | CeF ₄ |
| Pr | 60 | 320 | Hexagonal | PrF ₃ |
| Nd | 40 | 320 | Hexagonal | NdF ₃ |
| Tb | 40-60 | 320 | Monoclinic ^a | TbF ₄ |
| Dy | 55 | 320 | Orthorhombic | DyF ₃ |
| Sm | 50 | 320 | Hexagonal | SmF ₃ |

^a CeF₄ and TbF₄ are isostructural with ZrF₄, ThF₄ and UF₄.

According to Zachariasen¹⁰ unit cell dimensions

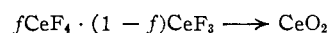
- (9) Fluorothene is the trade name for polyperfluorovinyl chloride.
(10) W. H. Zachariasen, *Acta Cryst.*, **2**, 388 (1949).

for CeF₄ are: $a = 12.6 \text{ \AA}$., $b = 10.6 \text{ \AA}$., $c = 8.3 \text{ \AA}$., and $\beta = 126^\circ$. For TbF₄, values found in this work were: $a = 12.1 \text{ \AA}$., $b = 10.3 \text{ \AA}$., $c = 7.9 \text{ \AA}$., and $\beta = 126^\circ$. Optical crystallographic work cited by Katz and Rabinowitch¹¹ has suggested a triclinic symmetry for UF₄.

We regard the crystallographic evidence as sufficient in itself to establish the identity of the reaction products CeF₄ and TbF₄. However, the tetrafluorides of cerium and terbium were subjected to additional investigation, as described below.

Samples of about 600 μ g. weight in tared platinum crucibles were heated in air at various temperatures, reweighed on a quartz fiber torsion balance^{12,13} and portions of the product taken for X-ray diffraction examination.

Three samples of CeF₄ heated in air at 600° to constant weight were converted to cerium dioxide (identified by X-ray diffraction) with the following weight losses in per cent.: 19.90, 20.11 and 20.65. The average weight loss corresponds to the conversion



with $f = 0.98$, or for a starting material consisting of 98 mole per cent. cerium tetrafluoride and 2 mole per cent. cerium trifluoride.

A similar investigation of two samples of TbF₄ indicated that the starting materials were 97 and 91 mole per cent. terbium tetrafluoride, respectively.

The product terbium oxides were identified by X-ray diffraction, and their compositions were calculated from the observed lattice dimensions by reference to the lattice parameter-composition data on the terbium-oxygen system reported by Gruen, Koehler and Katz.¹⁴

In the course of these investigations it was noted that when terbium tetrafluoride was heated in air for about 23 hours at 215-320°, the principal product was the trifluoride. Additional heating for 16 to 20 hours at 400-430° produced mainly terbium oxyfluoride (rhombohedral, $a = 6.689 \pm 0.007 \text{ \AA}$., $\beta = 33.40 \pm 0.2^\circ$) and further heating for several hours at 600° resulted in conversion to an oxide of somewhat variable composition, depending upon the time of heating and rate of cooling of the sample.

Because of our interest in a possible calorimetric study of cerium tetrafluoride and terbium tetrafluoride the action of several solvents on these compounds was tested. Neither compound appeared to be affected by a ten-minute exposure to either cold or hot water. Both dissolved slowly in 1 *M* hydrochloric or nitric acids, following an initial rapid change in appearance from opaque to nearly transparent materials. On treatment with 1 *M* potassium iodide solution the solid particles turned yellow. In 1 *M* aluminum nitrate solution terbium tetrafluoride dissolved slowly, with some gas evolution, but cerium tetrafluoride was unaffected.

(11) J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, National Nuclear Energy Series, Manhattan Project, Vol. VIII-5, p. 366.

(12) P. L. Kirk, Roderick Craig, J. E. Gullberg and R. Q. Boyer, *Anal. Chem.*, **19**, 420 (1947).

(13) B. B. Cunningham, *Nucleonics*, **5**, 62 (1949).

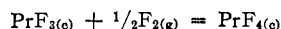
(14) D. M. Gruen, W. C. Koehler and J. J. Katz, *THIS JOURNAL*, **73** 1475 (1951).

Both compounds dissolved fairly rapidly in a solution that was about 1 *M* in both aluminum nitrate and nitric acid. Some gas evolution occurred in both cases. The gas may have been oxygen produced by the oxidation of water.

Efforts to determine the partial pressure of $F_{2(g)}$ in equilibrium with the solid tetrafluorides by an effusion technique were not successful, but it was noted that samples of cerium tetrafluoride heated in prefluorinated nickel crucibles in vacuum (10^{-6} mm.) were largely converted to the trifluorides at 230° in ten minutes. These results are not inconsistent with the work of Klemm and Henkel,⁴ who reported an equilibrium pressure of 2 mm. over cerium tetrafluoride at 400° . These workers, however, could not have observed a true pressure of $F_{2(g)}$ since their work was done in an apparatus of silica. In our own case, we cannot exclude the possibility that reduction to $CeF_{3(c)}$ of the small samples used was due to traces of reducing substances liberated in the vacuum line during the heating period.

Although it is thus not possible from present data to compute accurate free energy values for the trifluoride-fluorine reactions for cerium and terbium, we can conclude that the partial pressure of fluorine over the tetrafluorides of these elements is less than one atmosphere at about 320° . Since all other rare earths which might reasonably be expected to form simple tetrafluorides were examined in our study we also conclude that, except for cerium and terbium, the pressure of fluorine over all rare earth tetrafluorides exceeds one atmosphere at 320° .

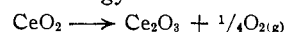
This last conclusion is inconsistent with the view of Perros, Munson and Naeser,⁸ who compute that the free energy of the reaction is negative to the extent of at least 48 kcal. mole⁻¹ at $298^\circ K$. From



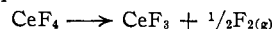
Latimer's¹⁵ rules ΔS for the reaction is about -16 e.u. and praseodymium tetrafluoride therefore should be stable in an atmosphere of fluorine even at very high temperatures. The fact that it was not formed under conditions which yielded CeF_4 and TbF_4 suggests that the data used by Perros, Munson and Naeser in their calculations may contain large errors.

If our view that PrF_4 is not thermodynamically stable with respect to PrF_3 and $F_{2(g)}$ is correct, the situation is unusual in that a higher oxide (PrO_2) is more stable than the corresponding higher fluoride (PrF_4). However, it is quite conceivable that a small highly charged cation (Pr^{+4}) with eight nearest neighbor O^{--} ions might form a more stable structure relative to the sesquioxide (coördination number 6) than does the tetrafluoride relative to the trifluoride. Crystal energy calculations on this point would be highly interesting, although the low symmetry of TbF_4 would make such calculations tedious.

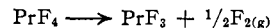
In any event, the extreme difficulty of reducing CeO_2 to Ce_2O_3 and the ready reduction of CeF_4 suggest that the free energy of the reaction



may be more positive than that for



Since PrO_2 is less stable than CeO_2 , the free energy of the reaction



may very well be negative.

Acknowledgment.—The authors take pleasure in expressing their gratitude to Dr. F. H. Spedding of Iowa State College for supplying certain of the rare earths used in this work.

(15) W. M. Latimer, "Oxidation Potentials," Second Edition, Prentice-Hall, Inc., New York, N. Y., 1952.
BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, REGION III, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heats of Formation of Chromium Oxide and Cadmium Oxide from Combustion Calorimetry

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Calorimetric combustions of pure chromium and cadmium metals were conducted at $303.16^\circ K$. under 30 atm. pressure of oxygen. The energies of combustion under these conditions are 2611.0 cal./g. of chromium and 541.5 cal./g. of cadmium. The corresponding standard heats of formation from the elements are $\Delta H_{298.16} = -272.7 \pm 0.4$ kcal./mole for chromic oxide and $\Delta H_{298.16} = -61.2 \pm 0.2$ kcal./mole for cadmium oxide.

Literature values^{1,2} of the heats of formation of both chromic oxide and cadmium oxide show variations and uncertainties that are large enough to warrant new determinations. New values, based upon combustion calorimetry, are reported in this paper, and it is believed that the uncertainties have been very significantly reduced.

(1) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffé, *Natl. Bur. Standards Circ.*, 500 (1952).

(2) L. Brewer, *Chem. Revs.*, 52, 1 (1953).

Materials.—The chromium was produced at the Albany, Oregon, Station of the Bureau of Mines and supplied by S. M. Shelton. The metal as received was in the form of a machined bar that had been produced by hydrogen purification of electrolytic chromium, followed by arc melting under helium and annealing for four hours at 1200° before machining. Spectrographic analysis showed 0.01% iron and 0.04% silicon; other impurity elements were not detected. Nitrogen was found to be 0.001% by chemical means, and hydrogen was 0.0005% by the vacuum fusion method. Fine lathe turnings (ca. 0.001 inch), cut with a Carboly tool, were used in the measurements.