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SOME CHEMICAL PROPERTIES OF CURIUM

Darrell Charles Feay

April 12, 1954

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SOME CHEMICAL PROPERTIES OF CURIUM

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April 12, 1954

ABSTRACT

A procedure for separating curium from americium utilizing the oxidation of americium by peroxydisulfate in very dilute solutions of acid is outlined. The equilibrium constants for the solution of curium trifluoride as a neutral trifluoride complex in dilute hydrofluoric acid at a constant ionic strength of 0.102 N are as follows: $(6.0 \pm 0.2) \times 10^{-6}$ at 0° C, $(1.223 \pm 0.02) \times 10^{-5}$ at 23° C, and $(1.77 \pm 0.4) \times 10^{-5}$ at 47° C. The first dissociation constants at the same temperatures are $(1.36 \pm 0.2) \times 10^{-4}$, $(1.250 \pm 0.02) \times 10^{-4}$, and $(4.31 \pm 0.8) \times 10^{-5}$, respectively. The ΔS° solution and ΔS° dissociation were calculated from the equilibrium constants at different temperatures.

There was no evidence of the oxidation of curium under conditions suitable for the preparation of americium dioxide and tetrafluoride. A simple spectroscope suitable for the qualitative study of the absorption spectrum of about 10 micrograms of solid compounds was developed. The preparation of terbium tetrafluoride which constituted its discovery is described.

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SOME CHEMICAL PROPERTIES OF CURIUM

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April 12, 1954

I. INTRODUCTION

The first production of curium was accomplished by G. T. Seaborg, R. A. James and A. Ghiorso[1] in 1945. Isotopes of mass 242, 241 and 240 were produced by (α, xn) reactions on Pu^{239}. The two larger masses were formed by using 32 Mev alpha particles, but Cm^{240} was identified in bombardments with 40 Mev alpha particles. At that time S. G. Thompson, L. O. Morgan, R. A. James and I. Perlman[2] used standard tracer techniques to establish the tripositive state of curium as the most stable oxidation state. They were unable to oxidize curium (III) with various oxidizing agents or to reduce it with sodium amalgam and barium metal in hydrochloric acid. Also the attempts to oxidize curium oxide were ineffective.

The only isotope of curium that has been available in amounts large enough to allow the study of its chemistry beyond the tracer scale was the relatively short-lived Cm^{242}. Hundreds of micrograms of Cm^{242} were produced by the irradiation of Am^{241} with thermal neutrons[3] according to the reactions below:

$$Am^{241}(n, \gamma)Am^{242m} \xrightarrow[16\ hr]{\beta^-} Cm^{242}.$$

Although a considerable amount of Cm^{242} was available for study, the amount and type of work that could be done was limited by the very high specific activity of the isotope. G. C. Hanna, B. G. Harvey and N. Moss[4] determined the half-life as 162.5 ± 2 days which corresponds

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to the production of 7.12×10^9 alpha particles per minute by each microgram. F. Asaro, F. Reynolds and I. Perlman[5] found energies of 6.110 Mev (73.7 percent), 6.066 Mev (26.3 percent) and 5.965 Mev (0.035 percent). The emission of the shorter range particles was followed by the emission of gamma rays as determined by O'Kelley[6] and F. Asaro.[7] Altogether the decay of Cm^{242} liberated approximately 1.23×10^{-3} watts per microgram. Consequently curium samples underwent considerable self-heating, especially when the samples were thermally isolated. In connection with this factor the magnetic susceptibility results of W. Crane[8] on 25 micrograms of curium trifluoride at low pressures indicated that the sample temperature was on the order of 800° C. In addition, J. C. Wallmann, W. Crane and B. B. Cunningham[9] observed that metallic curium corroded rapidly as compared to the other actinide metals and concluded that it was probably due to this self-heating effect. Another result of the decay was the rapid production of hydrogen peroxide in aqueous solutions. In fact Cm^{242} concentrations of 0.00015 M prevented the oxidation of Am(III) to Am(VI) by peroxydisulfate.[8]

L. Werner and I. Perlman[10] were the first to prepare pure compounds of curium. A few micrograms of curium were separated using a column packed with Dowex-50 cation resin and eluting at room temperature with 0.25 M citrate solution at pH 3.05. J. G. Conway, L. Werner and I. Perlman[11] determined the absorption and emission spectra of curium.

Later W. Crane[8] and B. B. Cunningham improved the separation of curium from americium using cation exchange resins and eluting at

elevated temperatures. The method was first developed by S. G Thompson, B. B. Cunningham and G. T. Seaborg.[12] At the same time W. Crane[8] redetermined the absorption spectrum and J. G. Conway, M. F. Moore and W. Crane[13] also redetermined the emission spectrum of curium.

J. C. Wallmann, W. Crane and B. B. Cunningham[9] prepared metallic curium and determined the density of the metal as approximately 7 but thought that the unexpected low value might be due to voids in the metal.

W. Crane[8] measured the magnetic susceptibility of pure curium trifluoride and of the trifluoride in solid solution in lanthanum trifluoride. The observed molar susceptibility in lanthanum trifluoride (26, 500 ± 700 cgs) agreed well with that expected theoretically for an $^8S_{7/2}$ ground state of tripositive curium identical with the ground state of tripositive gadolinium. Apparently both elements possess just half-filled f-shells.

Although the measurements of L. Werner[10] and W. Crane[8] of the absorption spectrum of curium showed the absence of absorption in the visible region (as with tripositive gadolinium), the determinations did not take into account the absorption by hydrogen peroxide in the ultraviolet region. Consequently it was felt that this spectrum should be redetermined. Since no data on the solubility of curium compounds was available, it was desired that these data be obtained as they would be useful in learning more about the complex ions of curium. In line with the general interest in the chemical properties of curium, especially in comparison to the other

actinides, the oxidation and reduction of tripositive curium in dry compounds was attempted.

II. PURIFICATION OF CURIUM

Curium used in these experiments was produced by the thermal neutron irradiation of americium according to the following equations:

$$Am^{241}(n, \gamma)Am^{242m} \xrightarrow[16\ hr]{\beta^-} Cm^{242}.$$

Inasmuch as the americium dioxide was pressed into an aluminum slug, the curium had to be separated from gross amounts of aluminum and americium as well as fission products.

A. Separation of Americium and Curium from Aluminum and Fission Products

The aluminum slug was dissolved in concentrated potassium hydroxide solution, leaving the actinide and lanthanide elements as a hydroxide or unconverted oxide precipitate. Then the precipitate was dissolved with anhydrous hydrogen chloride gas. After adding a trace of nitric acid, the dissolved precipitates were placed on top of a water cooled column packed with Dowex-I Anion resin (Dow Chemical Company, Midland, Michigan). A solution of 10 N hydrochloric acid containing a trace of nitric acid was used as the eluant. Curium, americium and some fission products passed through the column, while iron, etc., remained on the column.

The solution containing curium and americium was reduced in volume to less than 30 milliliters. Subsequently that solution was chilled and anhydrous hydrogen chloride gas was passed through the solution until it was about 13 N in hydrochloric acid. The solution was placed on top of a water-cooled column packed with Dowex-50X4-cation

resin[14] (Dow Chemical Company, Midland, Michigan). The designation X4 indicates that 4 percent of the linkages in the resin were cross-linkages between straight polymer chains. Americium and curium were eluted ahead of most of the fission products with 13 N hydrochloric acid using a flow rate of about 0.96 milliliters per minute per square centimeter of cross sectional area of the resin bed. Some yttrium remained with the americium and curium but was removed later in corresponding experiments.

The eluate containing americium and curium was reduced in volume and hydrochloric acid content by evaporation. Precipitation of the fluoride was accomplished by making the solution 2 N in hydrofluoric acid. After digesting for ten minutes, the fluorides were washed with water and centrifuged. Any alpha particle activity in the fluoride supernatant solution was removed by adding a solution of lanthanum which precipitated as lanthanum trifluoride. The combined fluoride precipitates were dissolved in approximately 1 N nitric acid saturated with boric acid.

B. Separation of Curium from Americium

First anhydrous ammonia gas was bubbled through the solution and the hydroxide precipitate was centrifuged and washed with water. Then the hydroxide precipitate was dissolved in the minimum amount of 30 percent citric acid solution at pH 3. Next, that solution was placed on top of a heated column packed with Dowex-50X12 resin.[14] Elution of the americium and curium was done at 87° C with a citrate solution at pH 3.50 using a flow rate of 0.46 milliliters per minute per square centimeter of cross sectional area of resin bed. The citrate solution was prepared by dissolving 50 grams of citric acid in one liter of hot

water. After cooling to about 25° C, the pH of the solution was adjusted to 3.50 with concentrated ammonium hydroxide. Inasmuch as the column was very short compared to its diameter (10 cm x 35 mm), almost no separation was accomplished and this method of separation was abandoned.

Approximately 30 microliters of concentrated HCl were added for each milliliter of citrate solution containing americium and curium. At that time the resulting solution was absorbed in a column packed with Dowex-50X4 resin.[14] The americium and curium were eluted with concentrated hydrochloric acid at room temperature. The purpose of this experiment was to remove the americium and curium from the citric acid solution which complexed them very strongly and to place them in a hydrochloric acid solution. Removal of hydrochloric acid was accomplished by evaporation to dryness. Subsequently, the residue was dissolved in dilute nitric acid. For ease in manipulation, the nitric acid solution was split into four sections.

The oxidation procedure described below, developed primarily by R. A. Penneman and S. E. Stephanou,[15] was used to separate americium and curium. S. G. Thompson[16] suggested the addition of silver ion. The argentous-argentic couple appeared to catalyze the reaction and about 85 percent of the americium present could be removed in one oxidation cycle. A total of five oxidation steps reduced the americium to curium ratio from 36 to 1 to less than 0.05 to 100 which gave an average purification factor of 6 for each step.

Details of the oxidation procedure are as follows:

1. The hydroxides were precipitated with ammonia gas, centrifuged and washed with dilute ammonium hydroxide solution.

2. Lanthanum hydroxide was used as a carrier to remove all the americium and curium from the supernate of step 1, if necessary. About 2 mg of lanthanum was used prior to the first oxidation in order to have sufficient mass to precipitate the curium from the oxidation solution in a very short time.

3. The combined precipitates from steps 1 and 2 were dissolved with a minimal amount of concentrated nitric acid solution.

4. Silver nitrate solution was added to remove any remaining chloride ions and to add silver ions for the oxidation step. The solution was centrifuged and transferred to a clean cone. Any precipitate present was washed with water, and the water was added to the original solution.

5. The solution from step 4 was diluted until the acid concentration was about 0.1 N and the curium concentration was approximately 100 μg per ml.

6. Excess solid ammonium peroxydisulfate was added to the solution as the solution was heated for twenty minutes at nearly 90° C. Both the argentic ion and the americyl ion (AmO_2^{++}) have a brown color in solution.

7. Following this the solution was removed from the hot bath and cooled for approximately one minute. About one ml of HF that had been pre-oxidized with potassium permanganate at room temperature for one hour was added to the cooled solution. The fluoride precipitates were allowed to digest for nearly one minute.

8. Next the supernatant solution was saved for the recovery of americium and any unprecipitated curium.

9. Immediately the precipitate from step 7 was washed with hot peroxydisulfate solution that was around 0.1 N in nitric acid and about 3 N in hydrofluoric acid. The precipitate was centrifuged and the supernatant solution was added to that from step 8.

10. Later the precipitate was dissolved in 1 N nitric acid saturated with boric acid.

11. Steps 1 through 10 were repeated until spectrographic analysis indicated that the curium was sufficiently separated from americium.

The separation of americium and curium was followed at first by comparing the intensity of the 40 kev gamma ray arising from the decay of Cm^{242} with the intensity of the 60 kev arising from the decay of Am^{241}. Final analysis for americium and all other impurities was done by the spectrographic group under John Conway.

G. Higgins and W. Crane later attempted to separate americium and curium by ion exchange technique using a lactic acid solution as the elutant.[17] Approximately 2 mg of curium and 15 mg of americium in 3 ml of dilute HCl were placed on the top of a heated column packed with Dowex-50X12 cation resin (Dow Chemical Company, Midland, Michigan). The column bed was 1 cm in diameter and nearly 20 cm long and was heated to about 87° C with trichloroethylene vapor. After the solution had been absorbed by the column, the curium was eluted slightly ahead of the americium with 0.4 M lactic acid solution at pH 3.52 using a flow rate of approximately 0.35 ml per minute per cm^2 of cross sectional area of the resin bed. The elution is independent of pH in the range 3.50 to 3.60, but a trace of phenol is needed to prevent

mold formation in the lactic acid solution. As only 15 percent of the curium contained 0.5 percent or less of americium, this method of separation was not repeated. This curium contained no lanthanum so the ion exchange column separation from lanthanum using concentrated hydrochloric acid was not repeated on this material, but it was otherwise treated as described in the next section.

C. Final Purification of Curium

Because spectrographic analysis of the curium indicated that it contained approximately 20 percent aluminum, the solution was treated with sodium hydroxide to precipitate the lanthanum and curium hydroxides while aluminum remained in solution. The precipitate was centrifuged and washed with distilled water.

Just enough concentrated HCl was added to dissolve the hydroxide precipitate, and half of the solution was placed on top of a column packed with Dowex-50X4 resin.[14] The curium was eluted considerably ahead of the lanthanum with 13 N hydrochloric acid. Subsequently the solution containing curium was evaporated to dryness and dissolved in a minimum amount of dilute hydrochloric acid. Curium hydroxide was precipitated with a freshly prepared sodium hydroxide solution in an attempt to remove aluminum. After the precipitate was centrifuged, and washed with water, it was dissolved in a minimal amount of concentrated nitric acid. It was necessary to recentrifuge all supernatant solutions to recover the curium precipitates completely as the precipitates were stirred by the formation and decomposition of hydrogen peroxide. The solution was made about 2 N in hydrofluoric acid. Following this the fluoride precipitate was centrifuged, washed with water and dissolved in 1 N nitric acid saturated with boric acid. Curium hydroxide was

precipitated by passing anhydrous ammonia gas over the solution. The hydroxide precipitate was centrifuged and washed with water and dissolved in a minimum amount of nitric acid. The remaining half of the solution was treated similarly. Typical spectrographic analyses of the final curium nitrate solution are given in Table 1.

During subsequent repurifications, approximately twenty mole percent of aluminum and calcium were detected by spectrographic analysis. A nitric acid solution of curium was evaporated to dryness in a platinum dish. Afterwards it was dissolved in concentrated sulfuric acid and again evaporated to dryness. The sulfuric acid treatment was repeated once more. Subsequently the remaining solid was slurried with 0.02 N sulfuric acid and transferred to a clean microcone and heated in a water bath for two hours. The undissolved solid (mainly calcium sulfate) was removed by centrifuging and then washed with 0.02 N sulfuric acid. The hydroxides were precipitated by using freshly prepared 2 N sodium hydroxide solution. After washing, the hydroxide precipitate was dissolved in dilute acid. The hydroxide was reprecipitated twice with anhydrous ammonia. The last precipitate was dissolved in 0.01 N nitric acid to prepare the stock solution of curium.

Table 1
Spectrographic Analysis of the Curium Stock Solution

Impurity	Percent present by weight
Am	0.5
La	0.2
Fe	0.1
Al	0.4

III. GAMMA RADIATION FROM Cm^{242}

A sample of curium (see Table 1) was prepared for the investigation of the electron spectra from gamma radiation using a double-focusing beta ray spectrometer. These measurements were carried out in collaboration with T. O. Passell.[18] The energies and $L_I + L_{II}:L_{III}$ conversion ratios were determined for the two most abundant transitions of 44.1 and 102.0 kev, respectively. Previous work by F. Asaro[7] on total conversion coefficients gave strong evidence that both are of E2 character. Since the $L_I + L_{II}:L_{III}$ ratio narrows the possibilities to E1 or E2 for the 44.1 kev gamma ray and to E2 only for the 102.0 kev gamma ray, we may consider their E2 character confirmed. Thus, the decay scheme of Cm^{242} is as shown in Fig. 1. Some hint of the previously reported 157 kev radiation in this decay was found but remains to be confirmed with a sample of greater intensity.

IV. SOLUBILITY OF CURIUM TRIFLUORIDE

In the study of the chemistry of the actinide elements, some knowledge of the various complexes that form in solution was wanted. Since only small amounts of curium were available at this time, the solubility approach was chosen. It was adaptable to very small samples, even as little as 0.1 μg.

The trifluorides were selected as they had a low solubility and had a known crystal structure which was identified as hexagonal by W. Zachariasen.[19] By measuring the solubility at constant ionic strength as a function of fluoride ion concentration, the species present in solution were identified. Then from determination of the equilibrium

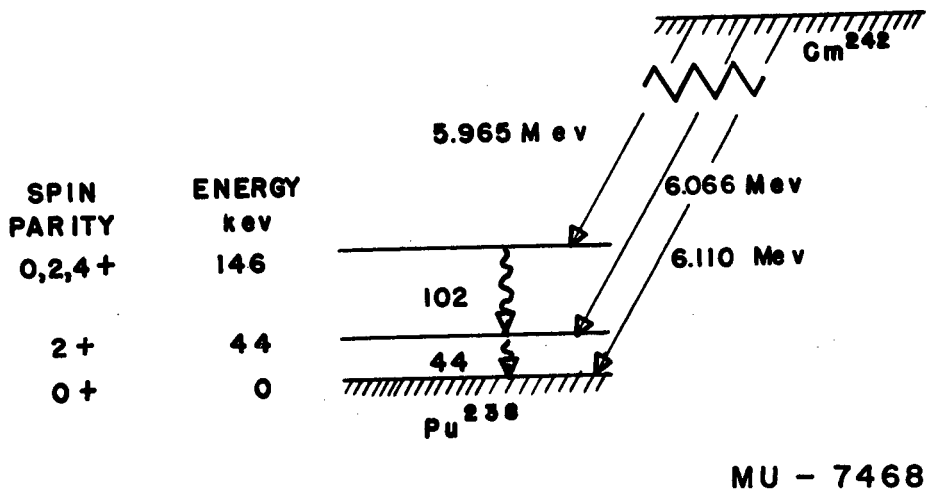


Fig. 1. Decay scheme of Cm^{242}.

constants at various temperatures, the entropy changes were calculated.

Measurement of the solubility of curium trifluoride at constant ionic strength and fixed acid concentration was done at three temperatures as a function of hydrofluoric acid concentration. Curium in solution was determined by counting the alpha particles from a small aliquot of the solution. Determinations were made over a period of several days until solubility equilibrium was reached. The results are summarized in Table 2.

A. Experimental Details of the Solubility Measurements

A stock solution of hydrofluoric acid was prepared by diluting 27 N hydrofluoric acid (Baker and Adamson, Analytical Reagent) with conductivity water. Determination of the total hydrogen ion present was done by titrating with a standardized sodium hydroxide solution. The solution was 0.580 ± 0.006 N in hydrogen ion. This was assumed to be the total concentration of hydrofluoric acid as it was the only added source of hydrogen ion. Later the solutions listed in Tables 2 and 3 were prepared by diluting a measured volume of the stock solution with the required volume of 0.102 N perchloric acid. Perchloric acid was chosen to maintain the ionic strength constant as it forms almost no complexes.

Approximately 2 μg of curium trifluoride was precipitated in each of four fluorothene cones. For mechanical support during centrifuging, the cones had to be mounted in one ml Pyrex centrifuge cones. Afterwards the precipitates were washed four times with the solution with which they were to be equilibrated. Twenty μl of one of the solutions was left in each cone. Self stirring of the samples

Table 2
Solubility Data for CmF_3 in Various Concentrations of Hydrofluoric Acid
at a Constant Ionic Strength of 0.102

Initial N of HF	T, °C	mg Cm / L	Calculated Final Activities				K_{sol}	K_{diss}
			F^- (x 10^5)	HF_2 (x 10^2)	H^+ (x 10^2)	HF_2^-		
1.015×10^{-1}	0	1.651	129.2	9.83	8.44	4.45×10^{-4}		
1.015×10^{-2}	0	3.655	13.40	1.002	8.28	4.70×10^{-6}	6.03×10^{-6}	1.36×10^{-4}
1.015×10^{-3}	0	15.29	0.1394	0.1038	8.26	5.07×10^{-8}		
1.00×10^{-1}	23	3.515	83.6	9.85	8.31	3.20×10^{-4}		
1.10×10^{-2}	23	7.887	9.28	1.008	8.21	3.98×10^{-6}	1.223×10^{-5}	1.250×10^{-4}
1.00×10^{-2}	23	8.348	8.47	0.993	8.21	3.29×10^{-6}		
1.00×10^{-3}	23	51.40	0.985	0.1151	8.18	4.44×10^{-8}		
1.015×10^{-1}	47	4.77	54.3	9.95	8.18	2.37×10^{-4}	1.773×10^{-5}	4.31×10^{-5}
1.015×10^{-2}	47	8.47	5.57	1.012	8.10	2.48×10^{-6}		

occurred due to gas evolution. Between measurements this self stirring was augmented by frequent agitation with a small platinum stirring wire.

All solutions were stirred prior to centrifuging and duplicate samples of two microliters were taken for analysis. To insure the complete recovery of the sample from the pipets, the pipets were coated with a monomolecular, water repellent film (Desicote, Beckman Instruments Company, Inc., South Pasadena, California). The half-life used to calculate the concentration of curium was 162.5 ± 2 days.[4] After ignition on a platinum disk, the samples were counted using a low geometry alpha particle counter as described by E. H. Fleming, Jr.[20] The probable error of this measurement was about ±2 percent for the measurements at 23° C and ±10 percent for the measurements at 0 and 47° C.

An ice-water bath was used to obtain solubility measurements at 0° C. Due to the lack of space inside the Berkeley glove boxes used to contain the radioactive samples, it was possible to use only a very simple hot bath that maintained the samples at 47 ± 2° C. Temperatures were kept constant during centrifuging by placing the cones in small Dewar flasks which were filled with water at the appropriate temperature.

The measurements on curium were preceded by a similar set of solubility determinations on americium trifluoride.

About 8 μg of the solid trifluoride was equilibrated with the 0.001 N hydrofluoric acid solution. In addition these samples were stirred by rotating the tubes with an electric motor. The results are summarized in Table 3.

Table 3
Solubility Data for AmF_3 in Various Concentrations of Hydrofluoric Acid
at a Constant Ionic Strength of 0.102

Initial N of HF^-	T, °C	$\frac{mg\ Am}{L}$	Calculated Final Activities				K_{sol}	K_{diss}
			F^- (x 10^4)	HF (x 10^2)	H^+ (x 10^2)	HF_2^-		
1.015×10^{-2}	0	34.15	13.65	1.012	8.26	4.80×10^{-6}	8.21×10^{-6}	1.81×10^{-3}
1.015×10^{-3}	0	199.5	2.24	0.1660	8.20	1.32×10^{-7}		
1.00×10^{-1}	23	6.947	83.0	9.86	8.31	3.20×10^{-4}		
1.10×10^{-2}	23	35.78	9.37	1.098	8.20	4.05×10^{-6}	1.363×10^{-5}	7.44×10^{-5}
1.00×10^{-2}	23	38.73	8.56	1.003	8.20	3.27×10^{-6}		
1.00×10^{-3}	23	212.6	1.449	0.1683	8.13	9.59×10^{-8}		
1.015×10^{-1}	47	10.39	54.4	9.96	8.17	1.90×10^{-4}	2.11×10^{-5}	4.51×10^{-5}
1.015×10^{-2}	47	56.00	5.67	1.027	8.08	2.53×10^{-6}		

B. Calculations and Results

The two reactions used in calculating the concentration of fluoride ion in the solutions are given below:

$$HF = H^+ + F^-,$$

$$HF + F^- = HF_2^-.$$

Equilibrium constants are those of H. H. Broene and T. DeVries,[21] corrected to the various temperatures according to the data of L. G. Hepler, W. L. Jolly and W. M. Latimer.[22] The equilibrium constants are summarized in Table 4.

Activity coefficients of all neutral species were considered to be unity. Activity coefficients of the singly charged ions were considered to be equal to the mean activity coefficient of perchloric acid. The value of $\gamma = 0.803$ for 0.1 N perchloric acid at 25° C is that of R. A. Robinson and R. H. Stokes.[23] Temperature corrections were made according to the Debye-Hückel theory. These are also listed in Table 4.

Table 4

Constants Used in Calculations

T, °C	K_{HF}	$K_{HF_2^-}$	γ
0	1.108×10^{-3}	3.50	0.810
23	7.00×10^{-4}	3.92	0.804
47	4.46×10^{-4}	4.39	0.794

A first approximation to the fluoride ion concentration was calculated by assuming that only the metal bifluoride complex ion was formed in solution and then solving the equilibrium constant equations by successive approximations.

$$K_{HF} = \frac{A_{H^+}A_{F^-}}{A_{HF}} = \frac{(H^+ + X)(F^- + X - Y)}{(HF - X - Y)\,\gamma^2}$$

$$K_{HF_2^-} = \frac{A_{HF_2^-}}{A_{HF}A_{F^-}} = \frac{Y}{(HF - X - Y)(F^- + X - Y)} \; .$$

In the above equations, X is the difference between the analytical concentration of hydrofluoric acid and its actual concentration due to dissociation or association, and Y is the concentration of bifluoride, HF_2^-, formed.

Using these fluoride ion concentrations in the content equation for each fluoride ion concentration, the two equilibrium constants were calculated.

$$K_{soln} = \frac{A_{MF_3^o(aq)}}{A_{MF_3(c)}} = MF^o_{3(aq)}$$

$$K_{diss} = \frac{A_{MF_2^+}A_{F^-}}{A_{MF_3^o(aq)}} = \frac{(MF_2^+)(F^-)}{MF^o_{3(aq)}\,\gamma^2}$$

$$\Sigma M = MF^o_{3(aq)} + MF_2^+ = K_1 + \frac{K_1K_2}{\gamma A_{F^-}} \; .$$

Since this reduced the amount of fluoride ion produced during the solution of the trifluoride, the activities of the fluoride ion were recalculated. Using these new values the final values of the two constants were recalculated. The largest variation was on the order of 1 percent for the 0.001 N hydrofluoric acid solutions.

From the equilibrium constants at the various temperatures, the entropy changes, heats of solution and heats of dissociation were calculated. The results are summarized in Table 5.

Table 5

Thermodynamic Constants from the Solubility of MF_3

$$MF_{3(s)} = MF_{3(aq)} \text{ (solution)}$$

$$MF_{3(aq)} = MF^{+}_{2(aq)} + F^{-}_{(aq)} \text{ (dissociation)}$$

Constant	Americium	Curium
$\Delta F_{296,\ soln}$	6.59 ± 0.1 kcal	6.66 ± 0.1 kcal
ΔH_{soln}	+3.48 ± 0.5 kcal	+3.99 ± 0.5 kcal
ΔS_{soln}	-10.5 ± 4 eu	-9.2 ± 4 eu
$\Delta F_{296,\ diss}$	4.24 ± 0.1 kcal	5.29 ± 0.1 kcal
ΔH_{diss}	-5.23 ± 0.5 kcal	-4.28 ± 0.5 kcal
ΔS_{diss}	-31.8 ± 4 eu	-33.3 ± 4 eu

From the ΔS values listed in Table 5 and estimating a value of 28.1 eu for the entropy of the solid trifluorides from W. Latimer's[24] figures, entropies were calculated for the complex ions. It was ascertained that S^o equaled 18.9 ± 4 eu for $CmF^o_{3(aq)}$, -11.7 ± 4 for CmF^-_2, +17.6 ± 4 for $AmF^o_{3\ (aq)}$ and -11.9 ± 4 for AmF^-_2.

J. Cobble's[25] equations for estimating the entropy of inorganic complex ions in aqueous solutions are as follows:

for neutral species, $\bar{S}' = 132 - (354/r_{12})$,

for charged species, $\bar{S}' = 49 - (99Z/r_{12})$,

where $\bar{S}' = \bar{S}^o - \bar{S}^o_{H_2O}$.

In the above equations r_{12} is the sum of the radii of the atoms in the complex ion, Z is the charge on the complex ion, and n represents the number of water molecules replaced from the normal coordinated

aquated ion by the complexing agent; n is 3 for MF_3^o and 2 for MF_2^+. By using a radius of 1.33 Å [30] for fluoride ion, and the radius of tripositive americium (1.00 Å [38]) as the radius of the metal portion of the complex, the entropies of the complex ions were calculated. Since the radius of tripositive curium has been estimated as 0.99 Å, [30] the calculated entropies of the curium complex ions were the same as those of the americium complexes within the accuracy of the method. The value calculated for $\bar{S}^o$ of the MF_2^+ ions was 40 eu which was not in agreement with the experimental value. However, J. Cobble[25] indicated that the bifluoride complex ions did not fit the proposed method of estimating entropies. W. Latimer and W. Jolly[39] determined $\bar{S}^o$ of AlF_2^+ as -21.5 eu which was in reasonable agreement with the values determined in this experiment for the larger metal ions. The value of 27 eu for the neutral trifluoride complex was somewhat larger than either of the experimental values. However, this could be due to the fact that it was not possible to determine if there were any hydration effects. Nevertheless the estimated value is within an order of magnitude of the experimental result which substantiates the assumed formulas of the species in solution.

V. THE ABSORPTION SPECTRUM OF CURIUM TRIFLUORIDE

The curium solutions used in obtaining the absorption spectrum of tripositive curium reported earlier contained an undetermined concentration of hydrogen peroxide, probably in the range 0.05-0.2 M. Solutions containing hydrogen peroxide have a very large extinction coefficient below 2800 Å, and thus the accuracy of the data reported previously for the absorption of curium at the shorter wave lengths is

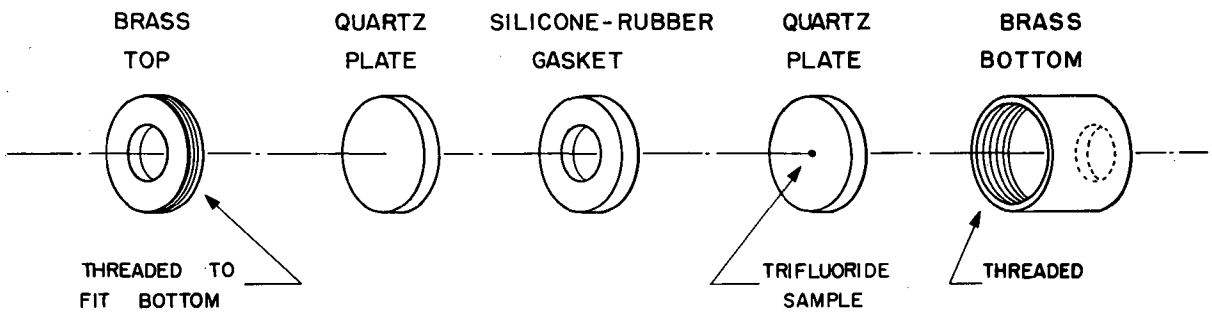
questionable. To avoid the production of hydrogen peroxide, solid dry curium trifluoride was used as the absorber rather than an aqueous solution of curium.

A. Experimental Details

The trifluoride was precipitated from aqueous solution and washed with dilute hydrofluoric acid. After forming a slurry with concentrated hydrofluoric acid the trifluoride was transferred into a small platinum dish where it was dried and then heated at approximately 200° C for a few minutes. The sample was placed in the cell shown in Fig. 2 immediately after the last heating was finished. The kind and amount of impurities in the curium stock solution are listed in Table 1.

J. G. Conway photographed the absorption spectrum on a 21 foot Wadsworth mount Jarrell-Ash spectrograph in the first order using 3 1/2 in. of a grating with 15,000 lines per inch. The optical system was composed entirely of quartz with a hydrogen discharge lamp as the light source. Eastman Kodak 103a0 ultraviolet sensitive film was used. Several exposures of various times were made on two plates. Three or four densitometer tracings were made of each plate. The first plate was exposed within 1 1/2 hours after preparation of the sample. The second plate required another two hours. All photographs were taken at room temperature.

A sample of gadolinium trifluoride was prepared in the same manner, and its absorption spectrum was also photographed.



THE CELL IS ASSEMBLED IN THE ORDER SHOWN ABOVE. THE TOP AND BOTTOM HOLD THE QUARTZ PLATES AND THE GASKET TOGETHER. THE BRASS PARTS AND GASKET HAVE HOLES IN THEM FOR A LIGHT PATH.

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Fig. 2. Cell used in absorption spectroscopy of solid trifluorides.

B. Results and Discussion

The observed lines and their relative intensities are given in Table 6. A tracing of the absorption spectrum of CmF_3 is shown in Figs. 3a and 3b. Relative intensities are only approximate and the absorption by curium trifluoride is greater than by gadolinium trifluoride. No attempt was made to calculate extinction coefficients since the path lengths of the light through the trifluoride samples were not known.

Table 6

Ultraviolet Absorption Spectra of Curium and Gadolinium in the Solid Trifluorides

CmF_3 λ	Relative intensity	GdF_3 λ	Relative intensity
2826 Å	2	2834 Å	4
2774	10	2759	10
2680	6	2666	4
2368	4	2334	4

Note: The wavelengths are good to about 3 Å; the intensities are only relative, and the absorption in the curium is stronger than in gadolinium.

The lines at the shortest wavelengths (2368 and 2334 Å) are both very broad (see Fig. 3b). The line at 2680 Å in curium trifluoride appears to be at least double, but the spectrum must be photographed at lower temperatures to verify this indication. No absorption at wavelengths longer than 2850 Å was found in either curium trifluoride or gadolinium trifluoride. This is in sharp contrast to the absorption spectra of the other lanthanides and pre-curium actinides. While all

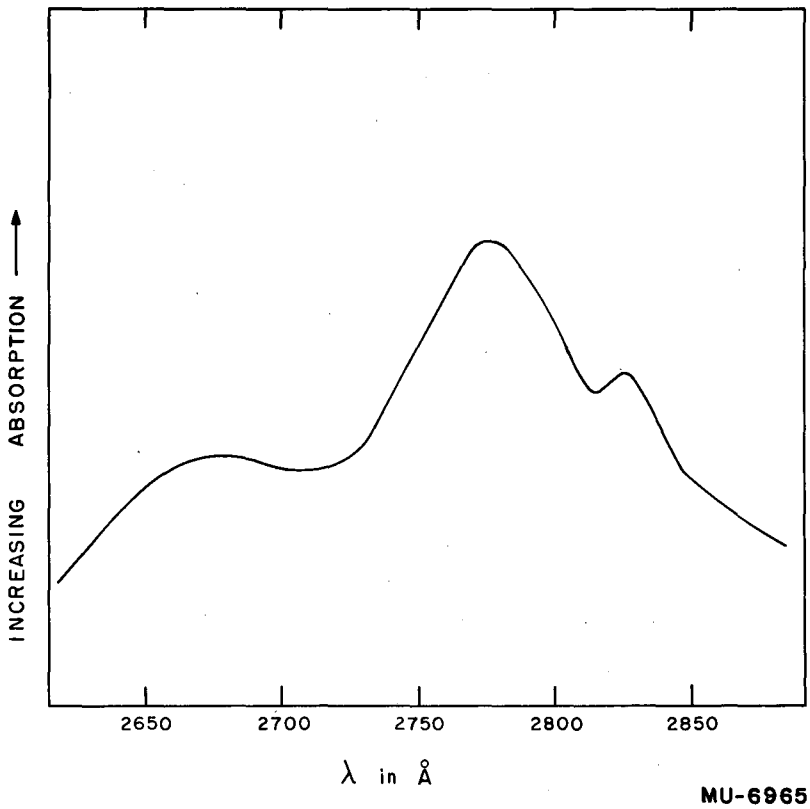

Fig. 3a. Absorption spectrum of curium trifluoride from 2650 to 2850 Å.

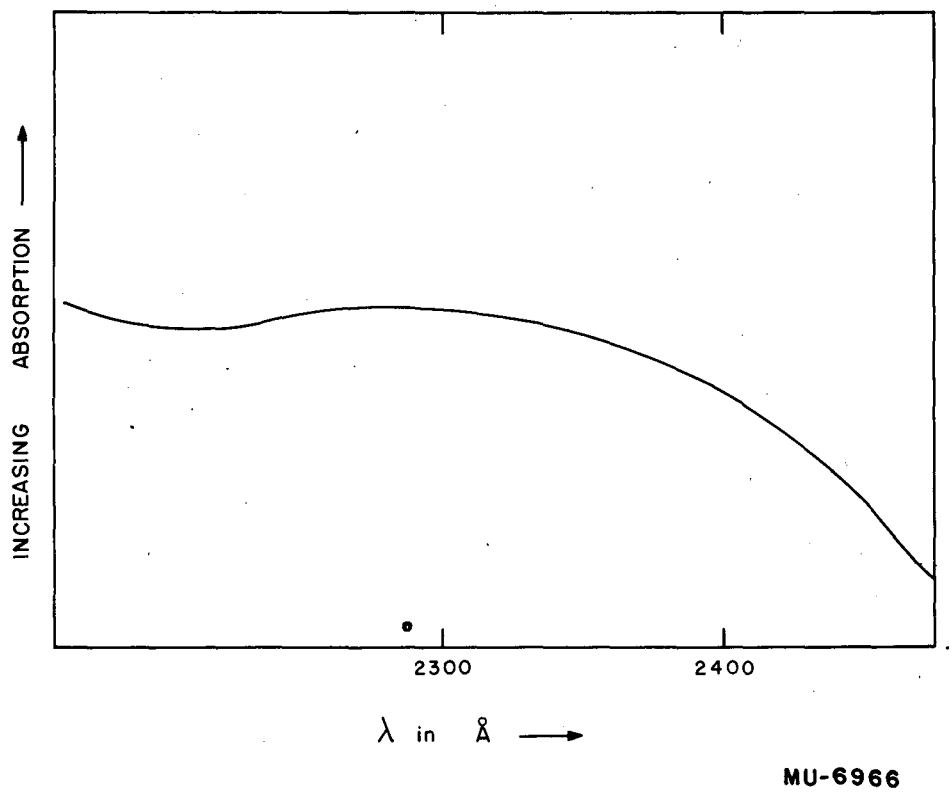

Fig. 3b. Absorption spectrum of curium trifluoride near 2370 Å.

the absorption lines that are present in the absorption spectrum of aqueous solutions of tripositive gadolinium were not found, there is still considerable similarity between the two absorption spectra in the grouping and relative intensities of the absorption peaks. This would seem to indicate that the lines arise from corresponding transitions. The magnetic evidence suggests that the tripositive ions of gadolinium and curium have the same ground state, $^8S_{7/2}$. Thus the ground state configuration is that expected from the actinide hypothesis.

VI. ATTEMPTED PREPARATION OF HIGHER OXIDATION STATES OF CURIUM

A. Preliminary Discussion

If the 5f electrons were as strongly bound as the 4f electrons, one would expect curium to exhibit only a tripositive oxidation state. However, since it has been observed that this is not the case in pre-curium actinides, the possibility of preparing a higher oxidation state compound of curium is not excluded. Data on the rare earth oxides and tetrafluorides suggest that the fluoride type dioxide would be the most stable oxidized compound, followed by the tetrafluoride. Tetrapositive curium would be isoelectronic with tripositive americium. Therefore, it might be expected that the absorption spectrum of the two ions would be similar. B. J. Stover, J. G. Conway and B. B. Cunningham[26] have reported that the solution absorption spectrum of tripositive americium has a very strong, persistent peak at 502 mμ. Therefore tetrapositive curium might have an absorption peak near this region, although some isoelectronic rare earth ions (La^{+3}, Ce^{+4}; Sm^{+3}, Eu^{+2}) do not show the expected optical resemblance.

Some experiments with gadolinium and americium as well as curium are described in the following sections, in order to facilitate the discussion of results.

B. Absorption Spectroscope

The absorption spectroscope was assembled by replacing one of the oculars of a Spencer standard binocular microscope with a Bausch and Lomb direct vision pocket spectroscope with a calibrating prism. A 130 volt, 100 watt tungsten lamp was used as the light source, and a Spencer condensing lens was mounted on the microscope. Radioactive samples were mounted in a sealed capillary. Before examining the spectrum the capillary was placed in a slot cut through a glass microscope slide and held in position by glass cover slips cemented on each side of the slide. Focusing of the microscope on the sample was accomplished by using the remaining ocular, then the absorption spectrum was observed through the spectroscope. In addition the samples could be examined by reflected light if the remaining ocular was used.

Unknown wavelengths were approximated by comparing them with known cut off frequencies of some Corning glass filter slides, and emission lines of various elements, (mercury, neon and argon). Probable error in the wavelength estimations was about ±10 mμ.

Excellent absorption spectra were visible if the samples were mounted in capillaries with two flat, parallel walls about half a millimeter apart. However, nearly all the absorption peaks were detected when round capillaries with about a 0.3 mm diameter were used.

Preliminary experiments indicated that it was possible to recognize from the absorption bands various rare earths and actinide elements in their oxides, fluorides, nitrates, sulfates and oxalates. It was also possible to differentiate between oxidation states in compounds of uranium and neptunium.

Attempts were made to photograph the spectra, but no 35 mm film suitable for spectrographic purposes was readily available. The results with a Kodak panchromatic film emulsion indicated that photographing the absorption spectrum is both possible and of considerable use in studying the spectra.

C. Absorption Spectra of the Compounds

A sample of americium trifluoride that had been identified by its X-ray diffraction pattern was examined. Its absorption spectrum had medium broad peaks at 505 and 515 mμ and a narrow peak at 520 mμ. All wavelengths are ±10 mμ. They are in good agreement with the values reported by E. Staritzky[27] for a trivalent compound that was prepared by the reduction in air of americium tetrafluoride.

The absorption spectra of curium trifluoride and gadolinium trifluoride had four peaks in the ultraviolet but none in the visible portion of the spectrum as reported in a previous section.

As might be expected from its very weak absorption in solutions, the absorption spectrum of solid terbium trifluoride had no peaks in the visible portion of the spectrum that were discernible with the spectroscope.

The absorption of americium tetrafluoride has been reported by E. Staritzky[27] as containing peaks at 641, 568, 538, 517, 502 and

453 mμ. The relative intensities varied in the two samples examined, but the peak at 517 mμ was the weakest peak. The color of their tetrafluoride was tan.

No data were available about the absorption spectra of any of the oxides used in these experiments. However, it was expected that the spectra would be similar to those of the corresponding fluorides.

D. Preparation of the Oxides

1. Preparation of americium oxides. -- Approximately 10 μg of americium hydroxide were precipitated from solution with anhydrous ammonia. After washing with water and drying under a heat lamp, the sample was loaded in a quartz capillary. A wire wound microfurnace was used to heat the oxide in air for one hour at 700° C. After cooling the capillary was sealed and cleaned of any radioactivity on its outer walls by washing with hot nitric acid. The product was the black oxide previously identified as the dioxide by W. Zachariasen.[19] No absorption peaks were detected; only a general absorption due to reflections from crystal faces and imperfections was seen.

Later the capillary was opened at one end and inserted in a second quartz capillary which was drawn from a standard taper ground joint. Afterwards the capillary was connected to a system which could alternately be filled with hydrogen and evacuated to approximately 100 microns pressure, (Duo-Seal Vacuum Pump, W. M. Welch Manufacturing Company, Chicago, Illinois). The hydrogen was dried over phosphorus pentoxide after having

been purified of oxygen by passing through a liquid nitrogen cooled trap packed with Pyrex wool. After several flushings the oxide was heated for one hour at 700° C. Both the reddish orange hexagonal and tan cubic forms (D. Templeton and C. Dauben)[28] of the sesquioxide were present in the product. A broad moderately intense peak from 500 to 520 mμ was detected in the absorption spectrum in good agreement with the absorption spectrum of americium trifluoride reported in an earlier section.

2. Preparation of gadolinium sesquioxide with various impurities. -- All samples were heated in air as described previously. Examination of a sample of pure gadolinium sesquioxide detected no absorption bands in the visible region of the spectrum and the crystals were white. Gadolinium sesquioxide with about 2 percent iron as an impurity was brownish but had no sharp absorption peaks in the visible region. A general absorption may be present in the far blue. A sample containing 10 percent plutonium as an impurity is light green, and its absorption spectrum contained a broad, weak peak from approximately 480 to 500 mμ. In addition, the absorption spectrum of a sample with 2 percent americium was examined. Although the sample was white, the absorption spectrum had peaks at 520, 528 and 535 mμ. They are grouped similarly as the peaks in americium trifluoride but are shifted to longer wavelengths.

3. Preparation of curium oxides. -- Two samples of approximately 10 μg of curium hydroxide were prepared and heated in air at 700° C as was americium hydroxide. See Table 1 for the analysis of the curium solution. Sample A had a very broad, weak absorption band

from 480 to 500 mμ and was brownish in color. Treatment of the stock solution to remove any daughter plutonium was completed before sample B was prepared. Although the product was a mixture of white crystals and some brownish ones, the absorption spectrum contained no peaks in the visible region.

Both samples of ignited curium oxide were heated in one atmosphere of hydrogen at 700° C as was the americium dioxide. Sample A was destroyed before it could be examined with the spectroscope, but it showed no change to the unaided eye. After reduction, Sample B was carefully examined, the white and brownish crystals were still present, and their relative amounts did not appear to have changed. Also the absorption spectrum still did not contain any peaks in the visible region of the spectrum; therefore, no positive evidence for the oxidation or reduction of curium oxide was found.

E. Preparation of the Tetrafluorides

1. Preparation of terbium tetrafluoride. -- Because of the danger involved in treating curium with elemental fluorine, a solid fluorinating agent was used. Discovery of the compound terbium tetrafluoride and the indication that it would readily decompose to terbium trifluoride and fluorine suggested its use as a fluorinating agent. The method used to prepare terbium tetrafluoride is described below.

The apparatus was made primarily of nickel and is diagrammed in Figs. 4a, b, c. The design of the apparatus was similar to one used by A. E. Florin.[29]

Fluorine from a half-pound cylinder of the compressed gas passed through a double valved mixing chamber of copper provided

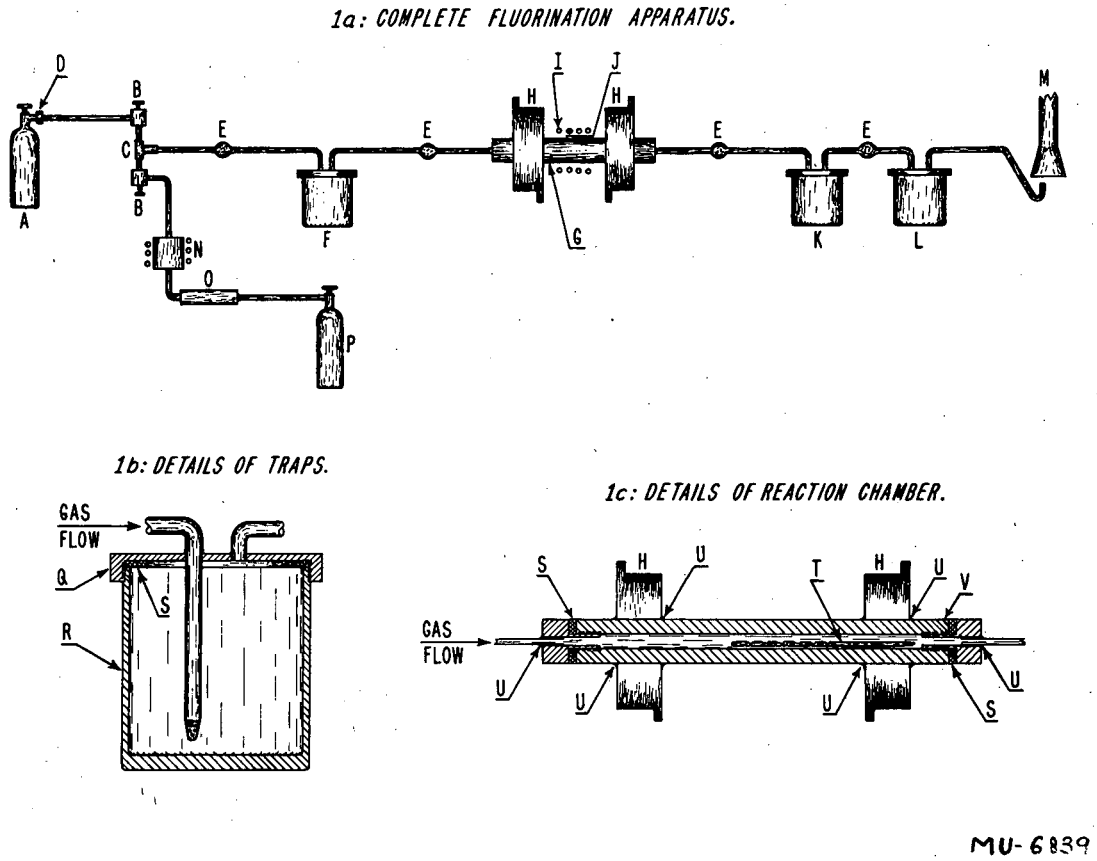

Fig. 4. Complete fluorination apparatus.

Legend: A, fluoride cylinder; B, kerotest valves; C, copper mixing chamber; D, fitting for fluorine cylinder; E, brass flare fittings; F, potassium fluoride trap (ice cooled); G, tubular reaction chamber; H, water cooling jackets; I, electric tube furnace; J, iron-constantan thermocouple; K, calcium bromide trap (ice cooled); L, bromine trap, (cooled with solid carbon dioxide; M, fume hood; N, heated tube of uranium fillings; O, phosphorous pentoxide drying tube; P, argon cylinder; Q, nickel top of traps; R, nickel bottom of traps; S, Teflon gaskets; T, flattened rod drilled to hold barium fluoride crucibles; U, hard soldered joints.

with an inlet for admitting dried argon. Kerotest Valves (Mueller Brass Company, Port Huron, Michigan) were used. These brass angle valves were packed with Teflon turnings. From the mixing chamber the fluorine, with or without admixed argon, passed into an ice cooled trap containing solid potassium fluoride to remove hydrogen fluoride and then into the tubular reaction chamber. The chamber could be heated by a surrounding tube furnace.

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

Samples to be fluorinated were placed in small barium fluoride crucibles supported in a short length of flattened and drilled nickel rod (T of Fig. 4c). The crucibles were prepared from a paste of water and powdered fluoride, slip cast as short lengths of rod, dried, drilled and fired in air for one hour at 1000° C. For easy removal of the rod, a small copper wire (long enough to extend out of the reaction chamber when one end was removed) was connected to the nickel rod.

Excess fluorine passed out of the reaction chamber into an ice cooled trap containing solid calcium bromide. Bromine formed in the reaction between fluorine and the bromide was condensed in a final nickel trap cooled with solid carbon dioxide. Threaded sections of the flared joints (E of Fig. 4a) were coated with Permatex 2

(Permatex Company, Inc., Brooklyn, New York) as recommended by A. E. Florin.[29] Teflon (tetrafluoroethylene polymer) was used as a gasketing material between cap and lip of the nickel traps, and at the ends of the reaction chamber.

It was not possible to use Teflon gaskets between the fluorine cylinder and the fitting connected to it, (D of Fig. 4a). Although Teflon is inert to fluorine at room temperature and atmospheric pressure, it reacts readily with the compressed gas. A soft copper gasket was satisfactory.

Terbium was obtained as the oxide, Tb_4O_7, from Johnson, Matthey and Company, Ltd., of London, England ("Specpure" Catalog No. J. M. 314) and contained less than 0.1 percent metallic impurities. Merck and Company, Inc., reagent grade concentrated hydrochloric acid was used. Hydrofluoric acid, barium fluoride, potassium fluoride and calcium bromide were Baker and Adamson, analytical grade reagents. Fluorine at a pressure of 400 psi was purchased in half-pound cylinders from the Pennsylvania Salt Manufacturing Company, Natrona, Pennsylvania. Argon was taken from a cylinder of the compressed gas (Linde Air Products, Inc.,) and purified by passing over phosphorus pentoxide and over uranium metal turnings heated to 400° C.

Terbium oxide dissolved rapidly in concentrated hydrochloric acid with mild heating. The solution was made 2 N in hydrofluoric acid. Later the precipitate was separated by centrifuging and washed with distilled water and anhydrous alcohol. After drying the precipitate at 80° C for one day, it was identified as the trifluoride by its X-ray diffraction pattern.

Diffraction studies were carried out by the powder method by Mrs. Helena Ruben and Mrs. Carol Dauben, under the direction of Dr. D. H. Templeton.[30] These patterns were indexed and otherwise interpreted by this group.

The nickel traps (K and F of Fig. 4a) were freshly charged with about one-half pound of powdered potassium fluoride and calcium bromide, respectively. The line was then assembled as far as point V, Fig. 4c. Approximately 500 μg of terbium trifluoride were placed in a barium fluoride crucible which was inserted in its nickel rod holder into the reaction chamber. The line then was completely assembled and flushed thoroughly with dry argon. Fluorine was admitted slowly and the temperature raised to about 320° C and maintained there for about sixty minutes. The sample was allowed to cool in fluorine to about 100° C. Then the fluorine flow was stopped, and the system was flushed with dry argon until the sample was near room temperature. Samples were removed after partial disassembly of the line, but without interruption of the flow of argon.

The product was a white powder, which was identified as terbium tetrafluoride by its X-ray diffraction pattern. Terbium tetrafluoride is isostructural with the tetrafluorides of zirconium, thorium, uranium and cerium. W. H. Zahariasen[19] identified the structure of uranium tetrafluoride as monoclinic from powder diffraction patterns. However, optical crystallographic data cited by J. J. Katz and E. Rabinowitch[31] for uranium tetrafluoride suggest that this compound is triclinic. Unit cell dimensions for the monoclinic cell of terbium tetrafluoride are as follows:

$$a = 12.14 \pm 0.06 \text{ Å}$$

$$b = 10.19 \pm 0.05 \text{ Å}$$

$$c = 7.91 \pm 0.04 \text{ Å}$$

$$\beta = 126.2 \pm 0.5^{\circ}.$$

This information was considered sufficient to identify the cation: anion ratio as 1:4.

The tetrafluoride was subjected to additional investigation as described below.

Samples of about 500 μg weight in tared platinum crucibles were heated in air at various temperatures, reweighed on quartz torsion balances and portions of the product taken for X-ray diffraction examination. The terbium oxides were identified by X-ray diffraction, and their compositions calculated from the observed lattice dimensions by reference to the lattice paramater-composition data reported by D. M. Gruen, W. C. Koehler and J. J. Katz.[32] The data are summarized in Table 7.

Table 7

Thermal Conversion of TbF_4 to TbO_x at 600° C in Air

Sample number	% weight lost in heating	Product	Theoretical weight loss	Mole % TbF_4
88	20.75	$TbO_{1.675 \pm 0.01}$	20.87	97
91	20.31	$TbO_{1.68 \pm 0.1}$	20.88	91

Since spectrographic analysis had indicated that no metallic impurities greater than 0.1 percent were present, any impurity present was assumed to be terbium trifluoride.

In the course of these investigations it was noted that when terbium tetrafluoride was heated in air for about 23 hours at 215-320° C, the principal product was the trifluoride. Additional heating for 20 hours at 400-430° C produced mainly terbium oxyfluoride (rhombohedral, $a = 6.676 \pm 0.007$ Å, $\beta = 33.40 \pm 0.2°$).

As would be expected from the absorption spectrum of the isoelectronic tripositive gadolinium, no sharp bands were detected in the visible region of the absorption spectrum of terbium tetrafluoride.

As a preliminary to the attempted oxidation of curium trifluoride, the decomposition of terbium tetrafluoride was studied as described below.

Decomposition of terbium tetrafluoride was attempted by heating for 15 minutes at 230° C in high vacuum, 5×10^{-6} mm Hg. However, X-ray diffraction analysis of the product indicated that it was pure terbium tetrafluoride. As described previously, the absorption spectrum of terbium tetrafluoride contained no sharp peaks in the visible region.

Heating of the terbium tetrafluoride at 450° C in high vacuum liberated sufficient fluorine to etch the inside of the glass capillary containing the sample. The sample was destroyed prior to X-ray analysis. However, some decomposition was assumed to have occurred because of the etching mentioned above. No evidence for decomposition could be obtained from the absorption spectrum as it contained no sharp peaks in the visible region, and the product's color was white. Both the tetrafluoride and trifluoride were white and neither had any

absorption in the visible region.

2. Preparation of americium tetrafluoride. -- Two attempts were made at oxidizing americium trifluoride to the tetrafluoride by heating with an excess of solid terbium tetrafluoride. Approximately 30 μg of the trifluoride that had been precipitated from aqueous solution and dried at 110° C were mixed with approximately tenfold mole excess of terbium tetrafluoride. At this time the mixture was put in a glass capillary. Because of the radioactivity involved, this work had to be done in an enclosed space. This capillary was transferred out of the dry box and inserted inside a second capillary which was connected to a high speed mercury vacuum pump system and evacuated to about 5×10^{-6} mm Hg. The temperature was raised to the desired value and held there for 15 minutes. After cooling both capillaries were sealed.

If the second capillary had been placed inside the box and loaded directly, its outer surface would have been excessively contaminated with radioactivity. However, the use of the inner capillary prevented this contamination. By this method the capillaries could be sealed, and the absorption spectrum examined through both layers of glass without radioactive contamination of equipment or personnel.

As expected, the sample heated at 230° C had only the absorption spectrum of americium trifluoride. However, some of the crystals had a tan color which faded slightly in two days, but there was no conclusive evidence for the formation of americium tetrafluoride.

Three different crystals were present as the product of the oxidation at 450° C. Some white crystals of terbium fluoride, pink crystals of americium trifluoride and tan crystals were visible under the microscope. The tan crystals appeared to be more intimately mixed with the terbium fluoride than was the americium trifluoride. As expected, the crystals of terbium fluoride had no sharp absorption bands in the visible portion of the spectrum. Americium trifluoride exhibited the absorption spectrum typical of tripositive americium. However, the absorption spectrum of these tannish crystals had weak peaks at about 570, 540, 500 and 450 mμ. These are in excellent agreement with four of the six lines seen by E. Staritzky[27] for americium tetrafluoride. Lines at about 650 mμ (red) are difficult to see in our simple spectroscope, and the other line was very weak. Therefore it was assumed that the presence of these four lines in the absorption spectrum was proof of the conversion of some of the sample to americium tetrafluoride.

3. Attempted preparation of curium tetrafluoride. -- Two attempts were made at preparing curium tetrafluoride under conditions that had been used previously to prepare americium tetrafluoride. Approximately 10 μg of curium trifluoride were used in each experiment.

Treatment of the mixture of curium trifluoride and terbium tetrafluoride at 230° C resulted in a white product. As expected from the data on the decomposition of terbium tetrafluoride, there was no evidence of decomposition of terbium tetrafluoride or for the oxidation of curium. There were no sharp peaks in the visible region of the absorption spectrum of the product. Heating the second mixture at 450° C also produced no evidence for the formation of curium

tetrafluoride as the sample still had no sharp absorption peaks in the visible region.

F. Results

There was no evidence for the oxidation of curium under conditions suitable for the preparation of americium dioxide or tetrafluoride.

Although it is not possible to compute accurate free energy values from these experiments, a few rather qualitative conclusions can be drawn. It was estimated that about one-third (10 μg) of the americium trifluoride had been converted to the tetrafluoride. The area of the trifluoride was estimated at 6×10^{-3} cm^2 by arbitrarily multiplying the area of a cube of 10 μg of americium trifluoride by 10. The only loss of fluorine from the atmosphere over terbium tetrafluoride was assumed to be by transport to the surface of the americium trifluoride where it reacted to form americium tetrafluoride. Then the following effusion equation was used:

$$P_{atm} = \frac{Z(MT)^{1/2}}{44.4},$$

where Z was the moles lost per second per cm^2 of effusing area, M was the molecular weight of effusing molecule, T was the temperature on the Kelvin scale and 44.4 was the value of some collected constants. By this method the pressure of fluorine over terbium tetrafluoride was calculated to be approximately 1.2×10^{-7} mm Hg. Therefore the ΔF_{723} was about 11.4 kcal/mole of terbium tetrafluoride for the reaction below:

$$MF_4 \rightarrow MF_3 + 1/2F_2.$$

By estimating a ΔS of 16 from Latimer's[24] figures, the ΔF_{298} was 18.2 kcal/mole. This is somewhat more positive than the value for the decomposition of americium tetrafluoride estimated by L. Eyring, H. R. Lohr and B. B. Cunningham.[33] The discrepancy probably is due to loss of fluorine by reaction with the glass walls during the decomposition of terbium tetrafluoride.

L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren[40] have estimated the $\Delta F_{F,298}$ of terbium trifluoride as -382 kcal/mole. Then using the value estimated above for the ΔF of the decomposition of terbium tetrafluoride at 298° C, a value of -400 kcal/mole was calculated for the $\Delta F_{F,298}$ of terbium tetrafluoride. This corresponded to a $\Delta H_{F,298}$ of -405 kcal/mole.

In estimating the ΔF_{298} for praseodymium and americium in the reaction below:

$$MO_2 \rightarrow 1/2M_2O_3 + 1/4O_2.$$

The following values were used:

$$AmO_2,\ \Delta H_{F,298} = -239.9 \text{ kcal/mole},$$
$$PrO_2,\ \Delta H_{F,298} = -232.9,$$
$$Pr_2O_3,\ \Delta H_{F,298} = -444.5,$$
$$Am_2O_3,\ \Delta H_{F,298} = -442.4,$$
$$\Delta S_{298} = 11 \text{ eu.}$$

The dioxide values are those of L. Eyring, H. R. Lohr and B. B. Cunningham.[33] The ΔS value was estimated from the figures given by W. Latimer[24] and the $\Delta H_{F,Pr_2O_3}$ was from the same source. The data of H. R. Lohr and B. B. Cunningham[41] indicated that the $\Delta H_{F,298}$ of $Am^{+3}_{(aq)}$ was 2.1 kcal/mole more positive than the $\Delta H_{F,298}$ of $Pr^{+3}_{(aq)}$. Therefore, it was assumed that the $\Delta H_{F,298}$

of a tripositive americium compound would be 2.1 kcal more positive than the value for the corresponding praseodymium compound. Consequently $\Delta H_{F,298}$ of americium sesquioxide was estimated as -444.2 kcal/mole. Consequently the ΔF_{298} for the decomposition of americium dioxide and praseodymium dioxide was calculated as 15.4 and 7.4 kcal/mole, respectively. From these values plus the knowledge that both AmO_2 and Pr_6O_{11}[33] were produced by ignition in air at 700° C of a tripositive compound, the ΔF_{298} for curium dioxide decomposition was less positive than 7.5 kcal/mole. In fact it could have been negative. Thus the stability of the dioxides decreased in the order americium, praseodymium and then curium.

Praseodymium tetrafluoride was not formed in experiments by D. C. Feay, M. A. Rollier and B. B. Cunningham[34] by treating the trifluoride in one atmosphere of fluorine at 350° C. Although americium tetrafluoride has been prepared by L. Asprey and R. A. Penneman,[35] the ΔF_{298} for the decomposition to the trifluoride and fluorine has been estimated as 10.5 kcal/mole.[33] Thus it was assumed that the stability of the tetrafluorides decreased in the same order as that of the dioxides. Consequently the fact that curium tetrafluoride was not prepared was consistent with already known information. Thus the ΔF_{298} for the decomposition of curium tetrafluoride to fluorine and the trifluoride was less positive than 10.5 kcal/mole and could have been negative.

VII. CONCLUSIONS

The similarity of the absorption spectra of curium and gadolinium trifluoride suggested that corresponding transitions

were involved. Also, as previously reported, the magnetic evidence indicated that the two tripositive ions have the same ground state $^8S_{7/2}$. So it appears that gadolinium and curium occupy analogous positions in the lanthanide and actinide series, respectively. In addition the similarity of the entropies of the aqueous fluoride complexes of americium and curium suggested that they were members of a transition series of elements. Also, the fact that in contrast to the pre-curium actinides the oxidation states of curium higher than three were not prepared could have been expected from an analogy with gadolinium. In conclusion, all the data obtained in this series of experiments were as predicted by the actinide theory.

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