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.

AMES, IOWA

[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY]

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

BY W. T. CARNALL AND P. R. FIELDS

RECEIVED MARCH 6, 1959

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 $\geq 98\ \alpha\%\ Cm^{244}$, $<2\ \alpha\%\ Cm^{242}$; 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.

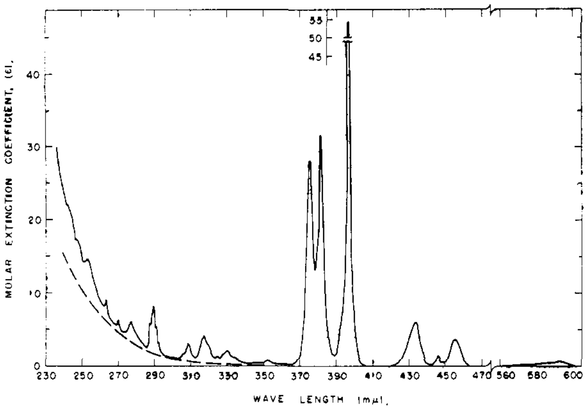

Fig. 1.—Absorption spectrum of Cm(III) in 1.0 M $HClO_4$.

ration and running of the spectrum on the assumption that $GH_2O_2 = 1$. Similar corrections were found necessary when the molar extinction coefficients were calculated for americium from a spectrum obtained by the use of the Am^{241} isotope.[9] Increasing the $HClO_4$ concentration to 5.5 M did not significantly change the characteristics of the curium absorption bands; however, this did result in increasing the rate of solvent decomposition. It was found that Beer's law was obeyed by the 375.4 and 381.1 mμ bands up to the highest concentrations attained, *ca.* 0.06 M, corresponding to optical density (O.D.) ≅ 1.8; however, deviations of a few per cent. were observed in the 396.4 mμ band at this same O.D.

The broad band centered near 594 mμ was observed in both fused silica and Corex cells, and its intensity varied directly with the curium concentration, indicating that it was characteristic of curium.

In dilute $HClO_4$ the only important product of radiolysis which absorbed appreciably in the region 220–500 mμ was H_2O_2. Upon increasing the acid concentration products of the decomposition of perchlorate ion were observed. It has been shown that both Cl_2 and ClO_2 are produced in the Co^{60} γ-decomposition of 5.9 M $HClO_4$.[10] The α-decomposition of 5.5 M $HClO_4$ gave rise to a broad absorption centered near 350 mμ which may have been due to ClO_2.

HCl System.—Hydrochloric acid as well as chloride salt solutions have been widely used in the separation both of actinides from lanthanides and of actinides from one another.[4,11] The absorption of curium relative to lanthanides on ion-exchange resins as a function of increasing HCl concentration makes it clear that chloride complexing does occur; however, the complexes are weak even in concentrated HCl.

A study of the chloride complexing of tri-positive Pu, Am and Cm by ion-exchange methods has indicated practically identical stability constants for the monochloro complexes in dilute HCl for the three elements, while in concentrated HCl solution the relative complexing ability is in the order Pu >> Am ≅ Cm.[4] It was thus of interest to determine whether this observed complexing sufficiently altered the electric field of the curium ions to induce significant changes in the curium spectrum.

The principal effect of increasing HCl concentration on the Pu(III) spectrum at wave lengths greater than 400 mμ is in general to decrease the extinction coefficient of a given band, without appreciably shifting the wave length of its maximum. Some of the peaks that are broad in dilute HCl appear to sharpen and show some structure in 11.6 M HCl, but no new bands develop.[12]

The spectrum of Am(III) at wave lengths greater than 400 mμ shows little change as the concentration of HCl is increased to 10 M. However, at wave lengths less than 400 mμ there is a general increase in the background upon which the americium bands are superimposed with increasing HCl concentration. This results in the loss of some of the far ultraviolet bands, but those that remain discernible do not appear to change their structure.[13]

In the present investigation the range of HCl concentrations in which quantitative data on the curium absorption bands could be obtained was severely limited by absorption due to radiation decomposition products. The results are illustrated in Fig. 2. Two effects can be discerned: (1) on increasing the HCl concentration several of the curium bands split and new bands are formed, particularly in the region near 380 mμ. (2) These changes, and others such as variation of molar extinction coefficient with HCl concentration for a given band, are superimposed on a general absorption which is broad relative to the individual curium bands. This absorption increases both with time and solvent concentration and is due to radiation decomposition of the solvent.

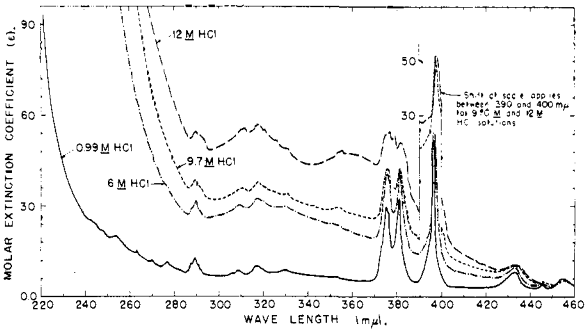

Fig. 2.—Absorption spectrum of Cm(III) in HCl.

For each of the samples shown in Fig. 2, the time lapse between dissolution of the $Cm(OH)_3$ and measurement in the spectrophotometer was approximately the same, of the order of 20 minutes. However, the difficulty of separating the two effects referred to above permits only a qualitative comparison of the curves.

In comparing the behavior of Pu, Am and Cm in HCl solution, it is seen that only with curium does

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[9] S. E. Stephanou, J. P. Nigon and R. A. Penneman, *J. Chem. Phys.*, **21**, 42 (1953).

[10] M. Cottin, *J. chim. phys.*, **53**, 903 (1956).

[11] J. S. Coleman, C. Hecht, R. A. Penneman, quoted in J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," John Wiley and Sons, Inc., New York, N. Y., 1957, pg. 363.

[12] J. C. Hindman and D. P. Ames, "The Transuranium Elements, National Nuclear Energy Series," Vol. 14-B, Part 1, McGraw-Hill Book Co., New York, N. Y., 1949, p. 348.

[13] G. R. Hall and P. D. Herniman, *J. Chem. Soc.*, 2214 (1954).

a significant modification of absorption bands occur at high HCl concentrations. Both $AmCl_3$ and $CmCl_3$ solutions give rise to a general absorption in the ultraviolet region that increases with increasing HCl concentration; however, it is not clear that the reasons for this are the same in the two cases. In the $CmCl_3$ system the main radiation decomposition product at high HCl concentration is Cl_2, which gives rise to two relatively broad bands in the ultraviolet, one centered near 320 mμ, and the other more intense band centered near 220 mμ. The absorbing species is Cl_3^-.[14] Figure 3 shows the growth of Cl_2 in a $CmCl_3$ solution over a period of 14 hr.; this type of structure was not discerned in the ultraviolet spectrum of americium in concentrated HCl.[13] It also should be noted that less radiation decomposition would be expected in the $AmCl_3$ solutions used by Hall and Herniman than in comparable concentrations of the $CmCl_3$ solutions used in the present investigation since the former were a factor of 25 less in specific activity.

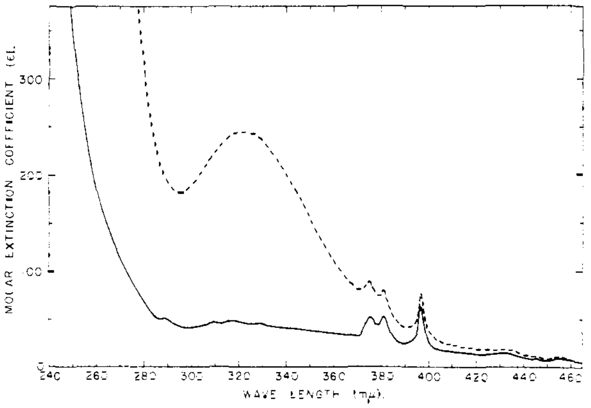

Fig. 3.—Effect of radiation decomposition on the spectrum of Cm(III) in 8.0 *M* HCl: ———, immediately following sample preparation; – – – –, 14.75 hours after sample preparation.

If one assumes that each of the curves of Fig. 2 is superimposed on a general absorption that is principally due to Cl_2, it follows that the principal band in curium at 396 mμ undergoes a decrease in molar extinction coefficient with increasing HCl concentration and simultaneously a shift toward the infrared. Under similar conditions the bands at 375 and 381 mμ do not appear to shift position appreciably or to undergo large changes in molar extinction coefficients.

HNO_3 System.—While nitrate complexes of many of the actinide elements have been shown to exist, the HNO_3 system has not been utilized analytically to the extent of the chloride system, in part because of its oxidizing properties. Since NO_3^- absorbs appreciably in the ultraviolet region, spectral studies in HNO_3 media are essentially limited to wave lengths > 350 mμ.[15] Studies of the complexing of Pu(III) by NO_3^- in HNO_3 are restricted to the concentration range 1–5 *M* since Pu(III) is oxidized to Pu(IV) in higher HNO_3 concentrations. Within this range relatively small changes were observed in the molar extinction coefficients of the principal bands, with only slight shifts of wave length.[12]

The complexing of Am(III) by NO_3^- has been demonstrated by several methods; the principal effect on the spectrum is the decrease in molar extinction coefficient of the two main bands with increasing HNO_3 concentration without shifting the bands appreciably or giving rise to new ones.[16]

In 0.1 *M* HNO_3 the spectrum of curium approaches that in $HClO_4$; however there is a marked decrease in molar extinction coefficients for the principal bands with increasing HNO_3 concentration. The shift in band position at higher HNO_3 concentrations was small, and no new bands were found to develop. An increase in HNO_3 concentration also increased the rate of solvent decomposition, as is shown in Fig. 4 where preparation time for each sample was the same. Molar extinction coefficients for the curium bands were corrected for the absorption due to solvent decomposition by assuming them to be superimposed on a smooth curve which increased rapidly near 350 mμ. At high HNO_3 concentrations corrections for solvent decomposition were so large as to render the corrected results highly uncertain.

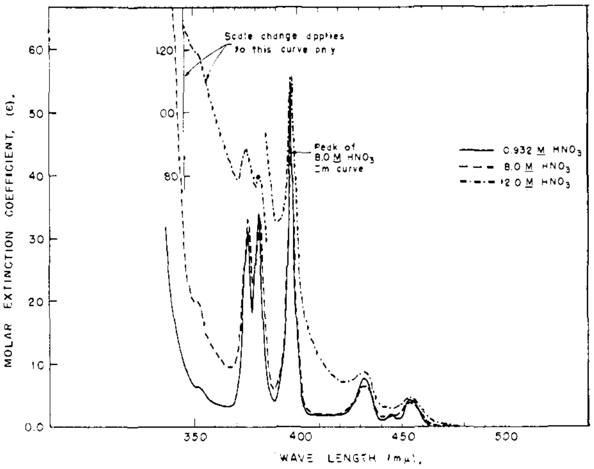

Fig. 4.—Absorption spectrum of Cm(III) in HNO_3.

H_2SO_4 System.—The effect of increasing H_2SO_4 concentration on the spectra of both Pu(III) and Am(III) reportedly follows the same pattern as in the HCl and HNO_3 systems. Relatively small changes take place in band position, and no new bands appear except in the ultraviolet region of Am(III) where there is a general increase in absorption as the concentration of H_2SO_4 is increased.[12,16] The spectrum of curium in H_2SO_4 does not exactly parallel that of Pu(III) and Am(III); with curium new band formation was observed, as shown in Fig. 5. In the concentration range 0–4 *M* H_2SO_4, the spectrum differs only slightly from that in $HClO_4$; however, there was observed a progressive decrease in intensity of the principal bands at H_2SO_4 concentrations above 4 *M*.

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(14) G. Zimmerman and F. C. Strong, THIS JOURNAL, **79**, 2063 (1957).

(15) H. v. Halban and J. Eisenbrand, *Z. physik. Chem.*, **132**, 401 (1928).

(16) G. N. Yakovlev and V. N. Kosyakov, "Proceedings of the International Conference on the Peaceful Uses of Atomic Energy," Vol. VII, United Nations, New York, N. Y., 1956, p. 363.

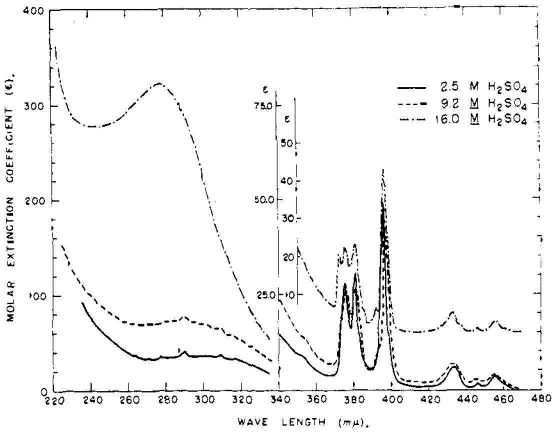

Fig. 5.—Absorption spectrum of Cm(III) in H_2SO_4.

New band formation near 375 mμ began to become apparent in 9 *M* H_2SO_4; it was not identical with that observed in concentrated HCl, but did occur in the same region. In 16 *M* H_2SO_4 it was noted that the ratio of extinction coefficients, $\epsilon_{381}/\epsilon_{375}$, was essentially the same as in $HClO_4$, whereas the ratio $\epsilon_{396}/\epsilon_{375}$ was considerably greater than in $HClO_4$, showing a disproportionate effect of $SO_4^=$ complexing on the 375 and 381 mμ bands as compared to the more intense band at 396 mμ.

The effect of γ-radiation on H_2SO_4 has been studied.[17] It was shown that SO_2 was produced at a rate which increased with increasing acid concentration. Sulfur dioxide absorbs in the ultraviolet with a maximum near 280 mμ.[18] Similar results were obtained in the present investigation with α-induced decomposition of H_2SO_4.

The alterations in the absorption spectrum of curium induced by increasing the concentration of the anions studied were in general relatively small, in most cases involving a decrease in intensity of a given band with essentially no shift in band position. However, in concentrated solutions of HCl and H_2SO_4 band splitting and weak new band formation was observed.

These results are consistent with similar studies of Am(III) and Pu(III). While some complexing is indicated in the NO_3^-, $SO_4^=$ and Cl^- systems of all three cations, the small spectral changes suggest the absence of a simple relationship between the degree of complexing and the change in molar extraction coefficients. The order of decreasing perturbing effect on the curium spectrum appears to be $NO_3^- > SO_4^= > Cl^- > ClO_4^-$.

Beer's law is valid for the three principal bands up to O.D. values of *ca.* 1.3 in dilute solutions of all four acids studied. However, variations in the correction for background due to species produced by radiation decomposition make it difficult to appraise the validity of this law over a similar range of O.D. values in solutions of higher acid concentration. One of the complicating factors is that radiation decomposition is not a linear function of increasing acidity, particularly with HCl and HNO_3.

Several experiments in salt solutions of high chloride concentration but low acidity have shown that here, too, a correlation between anion concentration and apparent complexing is subject to large errors because of background absorption due to radiation decomposition.

The tripositive lanthanides and tripositive actinides whose absorption spectra are known are characterized by a migration of the principal bands toward the ultraviolet as the half-filled 4f or 5f shell is approached; the half-filled shell representing a particularly stable configuration. In the case of gadolinium this stability is reflected in the exclusive existence of the tripositive oxidation state. In curium, the tripositive state is the most stable but not the exclusive oxidation state.[19-21] Stewart has pointed out that there is also a progression in the ultraviolet spectra of tripositive uranium, neptunium, plutonium, americium not observed in the lanthanides.[22] The intensity of absorption decreases at shorter wave lengths (above 220 mμ) with increasing atomic number. The spectrum of curium is consistent with this progression to the extent that an upper limit on the extinction coefficient for any peak at wave lengths $\geq$ 220 mμ can be set at $\epsilon = 90$.

In comparing their absorption spectra one observes that, unlike curium, gadolinium bands are restricted to the ultraviolet region; the principal bands in curium are located in the same region as those of Eu(III) and Tb(III) which again emphasizes the fact that the 5f shell is relatively more loosely bound than the 4f shell. However direct comparison of the spectra of tripositive lanthanides with their uranium and transuranium analogs shows in general only superficial resemblances, primarily emphasizing the infrared shift of the 5f series.

The absorptions involved here arise from transitions between quantum states within the 4f or 5f electron shells and thus are in the class of forbidden transitions. The fact that transitions in the 5f series are less forbidden, by a factor of 10–100 than in the 4f series, may possibly be due to the lower shielding of the outer electrons of the 5f shell, making the effect of external environment more important.

Attempts have been made by Jorgensen to identify the energy levels in the absorption spectra of these two groups of elements.[23] This theoretical treatment correctly interpreted the early curium spectra as masked by solvent decomposition products such that the narrow bands of $(Rn)5f^7$ were not detected. One can calculate approximate values for the band positions in curium by use of the expressions given by Jorgensen, based on the fact that the term values for f^7-systems are roughly the opposite in value to those same terms in f^2-systems; there is reasonable agreement with the

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[21] L. B. Asprey and T. K. Keenan, *J. Inorg. Nucl. Chem.*, **7**, 27 (1958).

[22] D. C. Stewart, ANL-4812 (Feb. 1952).

[23] C. K. Jorgensen, *Kgl. Danske Videnskab. Selskab Mat-fys. Medd.*, **29**, No. 7 and 11 (1955).

TABLE I

COMPARISON OF SOME OF THE CURIUM BANDS IN SOLIDS WITH THOSE IN SOLUTION

1.3 *M* $HClO_4$[a]		Solid[21] CmF_3		Solid[b] CmF_3		(Absorption)[25] $CmCl_3$ in $LaCl_3$	(Fluorescence)[25] $CmCl_3$ in $LaCl_3$
λ(mμ)	ε	λ(mμ)	Relative intensity[c]	λ(mμ)	Relative intensity	λ(mμ)	λ(mμ)
454.3	3.8	449.0	w				460.6
433.2	6.3						460.3
396.4	55.2	395.0	s				458.8
381.1	32.7	378.0	m			383.5	400.1
375.4	28.9	374.0	m			383.0	399.5
287.5	3.4			282.6	2	378.7	399.0
277.0	2.5			277.4	10	377.6	398.4
270.2	1.4			268.0	6		
				236.8	4		

[a] Present study. [b] D. C. Feay, UCRL-2547 (April 12, 1954). [c] W = weak or broad peak; m = moderately sharp peak; s = sharp peak.

band positions found. Using the same assumptions which gave good agreement between calculated and observed data for U(IV) indicates that the ^6I and ^6P levels should be the lowest excited levels over the ^8S ground state, with ^6I lying below ^6P. Calculations for Gd(III) result in the same relationships; however, evidence from the crystal absorption spectra of $Gd_2(SO_4)_3$ and $GdAc_3$ indicates that the ^6P state lies lowest over the ground level.[24] Similar considerations appear to apply to Cm(III), although there is presently no conclusive evidence.

Table I summarizes most of the presently available data on the curium absorption bands. A study of the fluorescence spectra of $CmCl_3$ in $LaCl_3$ has confirmed the presence of curium bands near 450 and 400 mμ, and they were ascribed to transitions between ^6P and the ^8S ground level.[25] A recent study of the absorption spectrum of CmF_3 gave good agreement with the results obtained in solution.[21]

(24) S. P. Cook and G. H. Dieke, *J. Chem. Phys.*, **27**, 1213 (1957).

(25) J. G. Conway, J. C. Wallman, B. B. Cunningham and G. V. Shalimoff, *ibid.*, **27**, 1416 (1957).

LEMONT, ILLINOIS

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY DIVISION, BATTELLE MEMORIAL INSTITUTE]

Preparation of Anhydrous Rare Earth Chlorides for Physicochemical Studies[1]

BY J. F. MILLER, S. E. MILLER AND R. C. HIMES

RECEIVED MARCH 21, 1959

A method for synthesizing anhydrous rare earth chlorides is presented and discussed. This method, which is based on conversion of the oxides or mixtures of oxides by reaction with carbon tetrachloride vapor at elevated temperatures, yields chlorides which appear to be superior in quality to those prepared by several other methods which have been described in the literature and were investigated in this research.

Introduction

In precise studies of the physicochemical properties of materials, composition and purity of the samples to be studied are, obviously, of primary importance. Halides of the higher-valent metals such as U, W, Mo, Co, Fe, Al and the rare earth elements, present a special problem in this area. Because of the ease with which they hydrolyze, obtaining the anhydrous compounds, making up samples to a definite size or composition and preserving purity through any required sample transfers are very difficult. In the course of a recent investigation dealing with physical properties of the chlorides of the rare earth elements and yttrium, these difficulties were circumvented by devising a preparative method by which the required samples could be synthesized *in situ* (*i.e.*, within the containers in which they were to be studied). Details of this method, which is based on conversion of the oxide or mixture of oxides by reaction with carbon tetrachloride vapor at elevated temperatures, are discussed in this paper.

The method described here is suited to the preparation of either an individual rare earth chloride or mixtures of rare earth chlorides of predetermined compositions. The method is convenient; the necessary reaction can be carried out in a single small container (only about double the volume required to contain the sample in powder form), and the chlorides obtained appear to be superior to those prepared by the several other methods tested.

Discussion

Numerous methods of preparing anhydrous rare earth chlorides are described in the literature.[2] In the course of work which preceded development of the subject method, a number of these methods were investigated. Chlorination of oxides with ammonium chloride[3] and dehydration of the hydrated chlorides in dry HCl[4] proved to be cumbersome and failed to give complete conversion to the chlorides. The latter observation is in agreement with that of Harrison.[5] Further, serious sample losses occur as ammonium chloride or water is removed.

Chlorination of the oxides with HCl alone[6] or HCl in combination with a reducing agent[7] are reported as methods for preparing rare earth

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(1) Appreciation is expressed to Grace Research and Development Division, W. R. Grace and Company, for support of the work described in this paper and for permission to publish the results.

(2) See J. B. Reed, B. S. Hopkins and L. F. Audrieth, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, pp. 28–33.

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(6) C. Matignon, *Ann. chim. phys.*, [8] **8**, 364 (1906).

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