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RECENT DEVELOPMENTS IN THE CHEMISTRY OF AMERICIUM AND CURIUM*

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A resumè of a talk presented by Thomas K. Keenan**
at the Argonne Hot Lab Conference, Argonne National Laboratory, May 22 - 24, 1963

In this paper, a brief summary of recent developments in the inorganic chemistry of americium and curium will be presented. Since these elements have been known for some 17 - 18 years, much historical and classical information is omitted. Standard references(1, 2) may be consulted if such information is desired.

Most of the recent advances in the chemistry of these elements have involved the use of the two isotopes Am^{243} of 7951 year half-life and Cm^{244} of 17.9 year half-life. Increasing amounts of these isotopes became available during the late 1950's and their longer half-lives enabled several discoveries which probably would not have been possible using the more readily obtained (but more intensely radioactive) Am^{241} or Cm^{242}.

As an example, a thorough study of the kinetics of the disproportionation of Am(V) was recently announced.(3) There had been several conflicting pieces of information in the literature concerning this reaction, but careful experiments (using Am^{243}) were able to establish the competative paths as indicated in Figure 1.

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1. Joseph J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements", John Wiley and Sons, Inc., New York, New York, 1957.
2. R. A. Penneman and T. K. Keenan, "The Radiochemistry of Americium and Curium", National Academy of Sciences Nuclear Science Series, NAS-NS-3006, 1960.
3. J. S. Coleman, Inorg. Chem., 2, 53 (1963) This paper contains an excellent bibliography of previous studies on the disproportionation.

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DEPENDENCE OF RATE ON ACID CONCENTRATION

(1) OBSERVED RATE LAW

$$d\left[\mathrm{Am}(\mathrm{V})\right]/dt = k'\left[\mathrm{H}^{+}\right]^{2.5}\left[\mathrm{Am}(\mathrm{V})\right]^{2}$$

$$= \left\{k_{2}\left[\mathrm{H}^{+}\right]^{2} + k_{3}\left[\mathrm{H}^{+}\right]^{3}\right\}\left[\mathrm{Am}\ \mathrm{V}\right]^{2}$$

(2) FAST EQUILIBRIA PRECEDING SLOW REACTIONS

(A) $\mathrm{AmO_2^{+}} + \mathrm{H^{+}} \rightleftharpoons \mathrm{AmO(OH)^{++}}$

(B) $\mathrm{AmO_2^{+}} + 2\mathrm{H^{+}} \rightleftharpoons \mathrm{Am(OH)_2^{+3}}$

FIGURE 1

Note that both paths involve a second order term in Am(V); however, because of the hydrogen ion effect observed, there are postulated two fast equilibria prior to the rate determining step. These two reactions involve either two or three hydrogen ions in equilibrium with a pentavalent americium prior to the rate-determining step. The actual rate-determining step, therefore, is a reaction of two of the first or one each of the first and second Am(V) species with each other to give the final products. Figure 2 shows a plot of the observed rate using the indicated rate constants to calculate the line. The experimental points fit the line quite well.

It should be pointed out that these experiments were carried out at temperatures of 70° so that low hydrogen-ion concentrations might be used while maintaining a convenient experimental rate. Most of the early workers used room temperature with correspondingly higher hydrogen-ion concentrations. In the present work, the total ionic strength never exceeded 2.0.

Some results have been reported in the last few years concerning the behavior of hexavalent americium in carbonate or bicarbonate solutions.(4) Rather striking differences in behavior of americium in sodium or potassium carbonate or bicarbonate were observed. Figure 3 shows several examples of such behavior. For example, when trivalent americium is slurried with sodium bicarbonate and treated with ozone, quantitative oxidation of a soluble Am(VI) species takes place under almost any conditions. Conversely, subjecting a slurry of trivalent americium hydroxide in potassium bicarbonate to ozone does indeed oxidize the americium but the oxidation stops at an insoluble compound $KAmO_2CO_3$ of hexagonal symmetry. In sodium or potassium carbonates, the initial trivalent americium is no longer a slurry, it forms a soluble complex. Treating this complex in sodium carbonate with ozone will oxidize the americium to the soluble Am(VI) species (as was obtained with bicarbonate) *only if the temperature is* maintained at 25° or below. Oxidation at higher temperatures forms an insoluble monoclinic sodium americyl (V) carbonate. The exact

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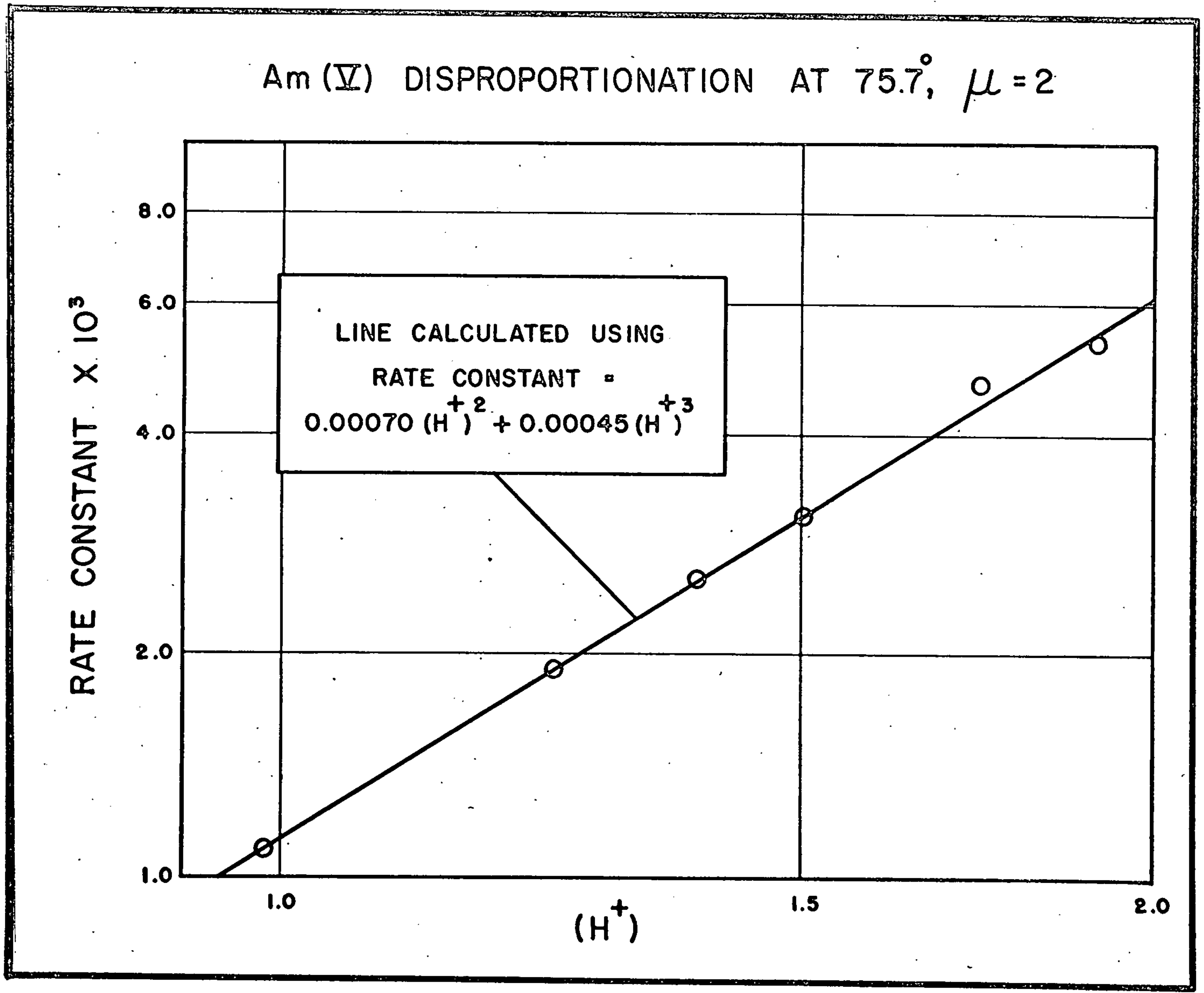
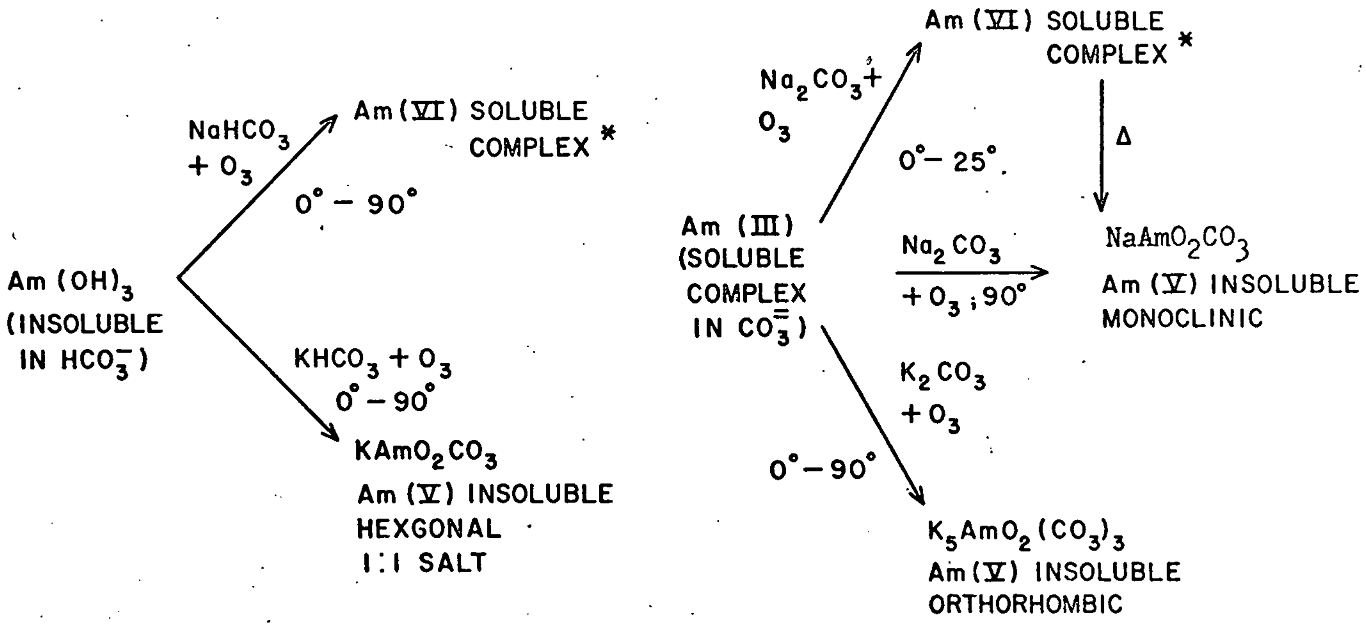
4. J. S. Coleman, T. K. Keenan, L. H. Jones, W. T. Carnall, and R. A. Penneman, Inorg. Chem., 2, 58 (1963).


Am (V) DISPROPORTIONATION AT 75.7°, $\mu = 2$

LINE CALCULATED USING RATE CONSTANT = $0.00070 (H^+)^2 + 0.00045 (H^+)^3$

FIGURE 2

THE BEHAVIOR OF AMERICUM HYDROXIDE IN CARBONATE – BICARBONATE MEDIA



* NOTE: Am (VI) SOLUBLE COMPLEX + Na_2CO_3 + $NaHCO_3$ GIVES PRECIPITATE NOT ISOSTRUCTURAL WITH $Na_4UO_2(CO_3)_2$.

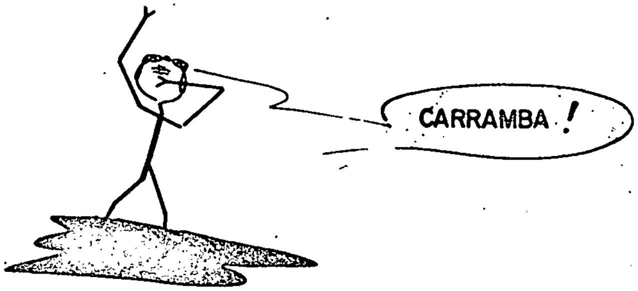


FIGURE 3

stoichiometry of this compound is not yet known, it is shown in the figure as $NaAmO_2CO_3$ for simplicity. In fact, if a sodium carbonate solution containing the soluble Am(VI) species (prepared at 25°) is heated, the hexavalent americium is reduced (by water ?) to Am(V) and the corresponding monoclinic sodium americyl (V) compound precipitates.

With potassium carbonate containing soluble trivalent americium, oxidation with ozone proceeds as far as an insoluble orthorhombic potassium americyl (V) carbonate, $K_5AmO_2(CO_3)_3$. No oxidation to Am(VI) is ordinarily obtained in potassium carbonate.

The nature of the soluble complex species of hexavalent americium prepared in sodium bicarbonate (or carbonate) is not well understood. Qualitative behavior generally follows the analogous uranium carbonate species. A sodium americyl (VI) carbonate compound may be precipitated from such solutions by addition of sodium bicarbonate and sodium carbonate; however, the X-ray pattern of this salt is not isostructural with the known $Na_4UO_2(CO_3)_3$.

Although there may be some doubt concerning the exact nature of the americium species present in carbonate-bicarbonate solutions, there have been several studies of complex ion constants for americium with common inorganic ligands. Several of these are shown in Table I. In addition to the

Table I

Complex-Ion Constants for Americium

1)	Am^{+++}	+	Cl^-	⇄	$AmCl^{++}$	K = 1.7(5); 1.4(6); 0.9(7)
2)	$AmCl^{++}$	+	Cl^-	⇄	$AmCl_2^+$	K = 0.4(6)
3)	Am^{+++}	+	$C_2O_4^=$	⇄	$AmC_2O_4^+$	$K = 9.8 \times 10^5$ (8)
4)	$AmC_2O_4^+$	+	$C_2O_4^=$	⇄	$Am(C_2O_4)_2^-$	$K = 1.4 \times 10^4$ (8)
5)	$Am(C_2O_4)^-$	+	$C_2O_4^=$	⇄	$Am(C_2O_4)_3^{\equiv}$	K = 6.2(9)
6)	Am^{+++}	+	NO_3^-	⇄	$AmNO_3^{++}$	K = 4.0(8); 1.8(7)
7)	Am^{+++}	+	$SO_4^=$	⇄	$AmSO_4^+$	K = 60(6)
8)	$AmSO_4^+$	+	$SO_4^=$	⇄	$Am(SO_4)_2^-$	K = 2.2(6)

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5. M. Ward and G. A. Welch, J. Inorg. Nucl. Chem., 2, 395 (1956)
6. I. Grenthe, Acta Chem. Scand., 16, 2300 (1962)

inorganic ligand constants shown in Table I, many others involving the common organic ligands such as glycolate, alphahydroxyisobutrate, etc., have been measured. The indicated references of Table I include the values for the organic ligands.

A perpetual problem in americium chemistry is its separation from common contaminants. The scope of these remarks does not permit a listing of all of the separations methods which have been announced in the last few years. A certain amount of chemical intuition is the best guide in selecting one method (or combination of methods) as compared to others. One recent paper gives one scheme,(10) others may be found in references 1 and 2.

Generally speaking, if the fission-product (and gamma radiation) level is not too high and the americium is present in macro amounts, some combination of oxidation-reduction cycling is usually the most efficient. If, however, the gamma radiation is excessive, some ion-exchange or solvent extraction technique is advised since these are more adaptable to remote control. A new ion-exchange system involves the use of lithium nitrate (low pH) eluant from anion resin.(11) This system apparently gives high separation factors (≥ 2) between americium and curium.

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7. D. F. Peppard, G. W. Mason and I. Hurcher, USAEC Report TID-14716, see Nucl. Sci. Abs., 17, 1044 (1963), Abs. Number 8004.
8. I. A. Lebeduv, S. V. Pirozhkov and G. N. Yakovlev, Radiokhimiya 2, 549 (1960): See Chemical Abstracts, 58, 3083g (1963)
9. I. A. Lebedev, S. V. Pirozhkov, V. M. Razbitnoi and G. N. Yakovlev, "Study of Complex Formation of Am^{+3} With Oxalate Ions" This was a "preprint" of an unpublished paper which was sent personally to R. A. Penneman of the Los Alamos Laboratory. This paper apparently has not appeared in the Russian literature; however, it may have been superceded by the paper in Ref. 8.
10. T. K. Keenan, J. Inorg. Nucl. Chem., 20, 185 (1961)
11. S. Adar, R. K. Sjoblom, R. F. Barnes, P. R. Fields, E. K. Hulet and H. D. Wilson, submitted to J. Inorg. Nucl. Chem. for publication.

Perhaps the most significant advance that has been made in the chemistry of americium in the last several years was the attainment of tetravalent americium in aqueous solution.(12) It was found that tetravalent americium hydroxide could be dissolved in saturated ammonium, potassium or rubidium fluorides without disproportionation. The spectrum of the soluble Am(IV) is shown in Figure 4. Various reasons suggest the species AmF_8^{-4} as the soluble tetravalent americium species.

In spite of the discoveries that have been made in the last few years, there are still several gaps in americium chemistry that have not been satisfactorily explained. The lack of a hexafluoride of americium is somewhat puzzling, certainly it does not form under conditions where the corresponding hexafluorides of plutonium or platinum have been synthesized.(13) In addition, one should not rule out the possibility of a pentavalent fluoride such as AmF_5. Perhaps some high-pressure micro-fluorination technique may be employed in the future to prepare these compounds. Some initial structure studies have been carried out on the double fluoride salts of the alkali metals and tetravalent americium. However, since many analogous compounds are known for U(IV) and Pu(IV), one would predict an equally large number for americium. Much the same could be said regarding the complicated system involving the carbonates of pentavalent and hexavalent americium with the alkali metals. Further research is certainly indicated in these areas.

Perhaps the most perplexing void in the chemistry of americium has been the non-attainment of a divalent state. Since the $7s^25f^7$ ground state electronic configuration of americium seems so well established, the apparent non-existence of Am(II) has remained a mystery.

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12. L. B. Asprey and R. A. Penneman, Inorg. Chem. 1, 134 (1962)

13. S. Tsujimura, D. Cohen, C. L. Chernick and B. Weinstock, J. Inorg. Nucl. Chem., 25, 226 (1963)

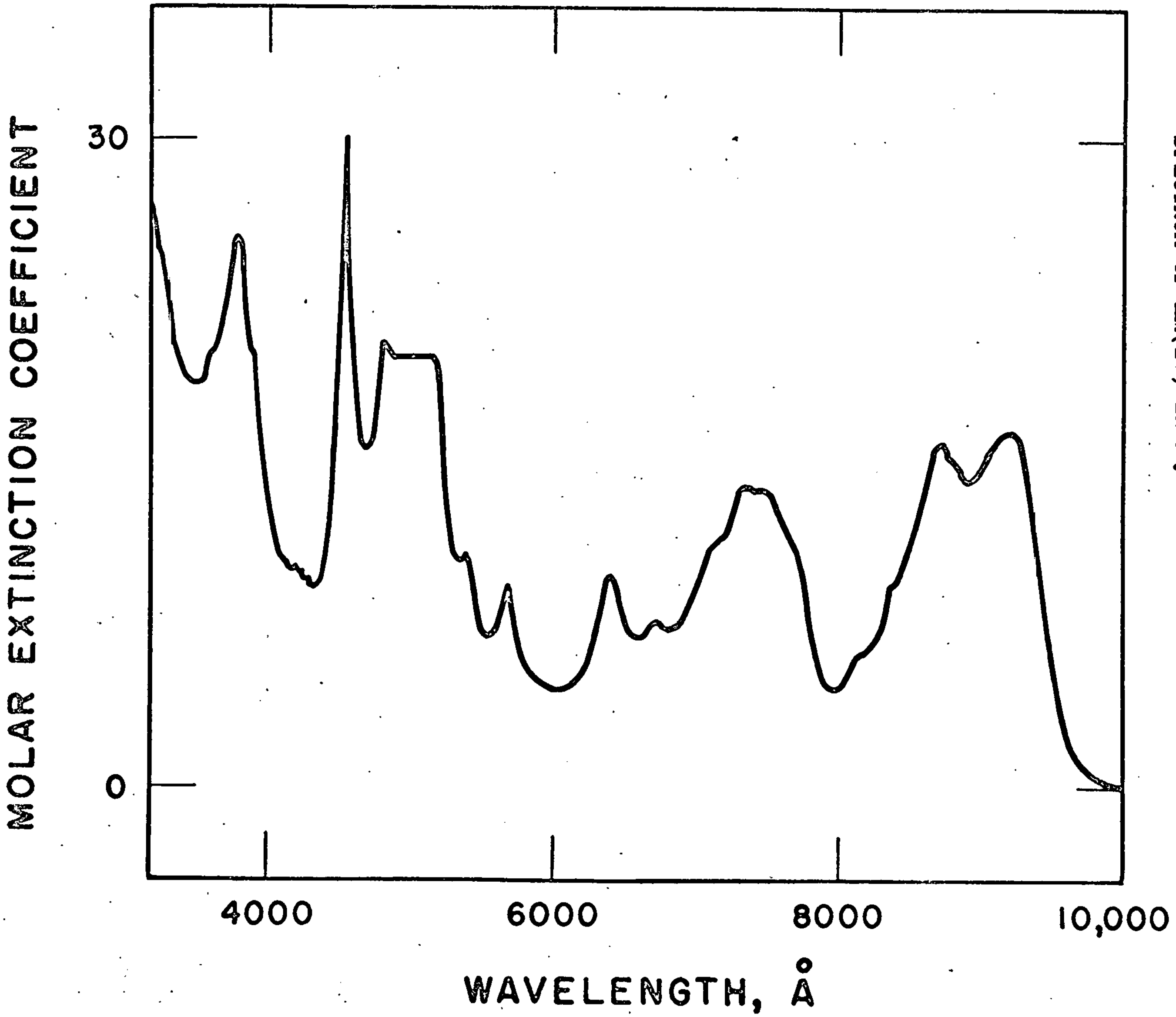

FIGURE 4

SPECTRUM OF Am(IV) IN AQUEOUS AMMONIUM FLUORIDE

Turning now to curium, the tetravalent state of this element has also been isolated in a soluble form in aqueous solution.(14) As with americium, high concentrations of fluoride ion were necessary to stabilize the tetravalent state but two important experimental differences should be noted when comparing with americium. First, it was necessary to prepare CmF_4 as starting material for the dissolution; this involved the reaction of elemental fluoride with CmF_3. Secondly, ammonium fluoride, (which dissolved $Am(OH)_4$) led only to rapid reduction of CmF_4 to CmF_3. It was necessary to treat CmF_4 with saturated (15 M) cesium fluoride to form a soluble species. The spectrum of soluble Cm(IV) is shown in Figure 5. The general features of this spectrum agree well with that previously determined for solid CmF_4.

These studies on the tetravalent state of curium required the use of Cm^{244}. Even with this isotope, a self-reduction rate of ca. -1.3%/minute was observed for the solutions of tetravalent curium which is about the rate one would estimate from the half-life.

As with americium, several equilibrium constants have been measured for curium with common inorganic ligands. Several of these are shown in Figure 6. References 5 - 9 may be consulted for experimental procedures for the curium values; in addition, these references list other appropriate constants for some common organic ligands.

Analogous to americium, one would predict the existence of several double salt fluorides with Cm(IV) and the alkali metals.

To sum up, several significant advances have been made in studies on americium and curium chemistry in the past several years. These, in turn, have suggested other paths to be explored. Perhaps, considering the increasing amounts of Am^{243} and Cm^{244} which will become available during the next few years, some of these intriguing problems may be solved in the near future.

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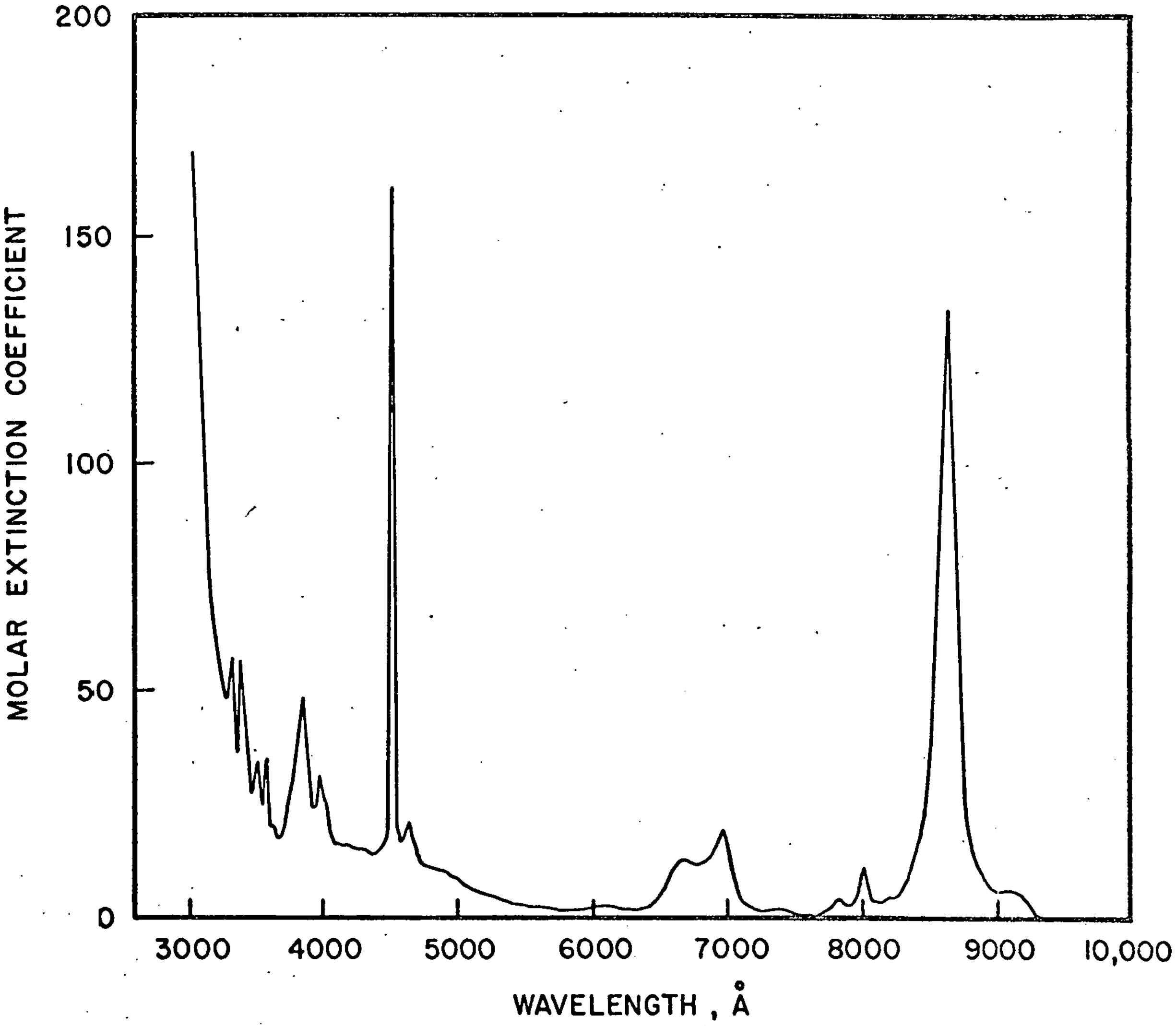
14. T. K. Keenan, J. Am. Chem. Soc., 83, 3719 (1961)

FIGURE 5



ABSORPTION SPECTRUM OF AQUEOUS Cm (IV)
IN 15M CsF AT 10.5°

COMPLEX ION EQUILIBRIA FOR CURIUM

$$Cm^{+++} + Cl^{-} \rightleftharpoons CmCl^{++} \qquad K = 1.5$$

$$Cm^{+++} + C_2O_4^{=} \rightleftharpoons CmC_2O_4^{+} \qquad K = 9.1 \times 10^{5}$$

$$CmC_2O_4^{+} + C_2O_4^{=} \rightleftharpoons Cm(C_2O_4)_2^{-} \qquad K = 1.5 \times 10^{4}$$

$$Cm^{+++} + NO_3^{-} \rightleftharpoons CmNO_3^{++} \qquad K = 3.7$$

$$Cm^{+++} + SO_4^{=} \rightleftharpoons CmSO_4^{+} \qquad K = 56$$

$$Cm(SO_4)^{+} + SO_4^{=} \rightleftharpoons Cm(SO_4)_2^{-} \qquad K = 1.5$$

FIGURE 6