the neighborhood of the critical region, but accurately represents the remaining vapor pressure data above the boiling point. It is evident that an equation obtained by a least squares solution in which all the vapor pressure points are weighted equally does not lead to a satisfactory solution in the neighborhood of the critical temperature. Heavy weighting of the vapor pressure data in the neighborhood of the critical point, however, would tend to give poorer agreement near the boiling point.

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[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

Hexavalent Americium[1]

BY L. B. ASPREY, S. E. STEPHANOU AND R. A. PENNEMAN

Americium in the formal oxidation state of plus six has been prepared by the oxidation of Am(III) and Am(V) in acid solution. Various methods of obtaining Am(VI) are described, including the disproportionation of Am(V). Sodium americyl acetate, $NaAmO_2(OOCCH_3)_3$, was prepared and identified by optical crystallography and X-ray analysis. From its crystal and chemical similarity to uranyl, neptunyl and plutonyl ions, americyl ion is assigned the formula, AmO_2^{++}. The absorption spectrum of Am(VI) in perchloric acid solution shows a narrow absorption peak at 992 mμ, a minor peak at 666 mμ and ultraviolet absorption. The potential of the Am(III)-Am(VI) couple is estimated to be −1.8 ± 0.15 volts.

Introduction

In the 5f- series of elements, the hexavalent oxidation state is well known for uranium, neptunium and plutonium, but was discovered only recently for americium.[2] Previous work on oxidation states of americium higher than (III) had demonstrated the existence of Am(IV) (only as the oxide, AmO_2), and of Am(V).[3,4,5] Evidence has been obtained at this laboratory characterizing Am(VI). Methods of preparation, identification, absorption spectrum and other properties of this new oxidation state are discussed.

Materials.—The chemicals used were all of reagent grade. The isotope of americium employed was Am^{241}, an alpha emitter of 475 years half-life.[6] In all experiments, carrier-free americium exceeding 95% purity was used. The americium had been purified originally in coöperation with S. G. Thompson of the Berkeley Radiation Laboratory using methods previously reported.[3,5,7,8] The total americium concentration was determined by radiometric methods, while the concentration of Am(III), Am(V) and Am(VI) were measured spectrophotometrically. Due to the quantity of alpha emission from this element, it was necessary to carry out all the work in gloved boxes through which a current of air was drawn.[5]

Preparation of Am(VI).—In the following oxidation experiments, the concentrations of americium varied from 0.002 to 0.035 *M*.

Oxidation to Am(VI) was achieved by the addition of solid ammonium peroxydisulfate (in excess of the stoichiometric amount) to Am(III) in 0.2 *M* nitric, perchloric or sulfuric acids, and heating in a water-bath at about 85°. In approximately ten minutes the characteristic pink color of Am(III) was replaced by a straw-yellow color which changed to a reddish-brown. In stronger acid, *e.g.*, 2 *M*, the oxidation did not occur.

Addition of solid argentic oxide to a solution of Am(III) in 0.3 *M* perchloric acid gave complete oxidation to Am(VI). Argentic oxide added to Am(V) in perchloric acid solution also yielded Am(VI). An experiment with cerium (at a IV/III ratio of 12/1) gave only 5% oxidation of Am(III) to Am(VI) in hot 6 *M* perchloric acid. Cerium(IV) added to Am(V) caused oxidation to Am(VI) in 1 *M* perchloric acid. Periodic acid and hypochlorous acid both failed to oxidize Am(III) in dilute acid solution.

The anodic oxidation of Am(III) in various concentrations of perchloric acid was studied. A single compartment cell was used with platinum electrodes having an anode to cathode surface ratio of about 200:1 and a current density of *ca.* 0.025 amp./sq. cm. at the anode. The maximum yield (*ca.* 80%) of Am(VI) was obtained in 6 *M* perchloric acid after an hour of electrolysis. At lower acidities, no measurable oxidation occurred.

The acidification of a dilute acid solution of Am(V) to 3 *M* hydrogen ion concentration or greater was found to cause rapid disappearance of Am(V) with corresponding growth of Am(VI) and Am(III). Preliminary experiments show that the disproportionation reaction is second order with respect to Am(V) and has a fourth order hydrogen ion dependence.

Identification of Am(VI). (1) **Sodium Americyl Acetate.**—A 0.02 *M* solution of Am(VI) in 0.3 *M* perchloric acid was made 2 *M* in sodium acetate. A lemon-yellow precipitate formed which was centrifuged and dried with acetone. Under the microscope, the precipitate was found to consist of isotropic crystals with tetrahedral habit, similar, except for color, to the sodium uranyl and sodium plutonyl acetates. The index of refraction of the crystals was in the range expected for sodium americyl acetate. No Am(III) or Am(V) absorption lines were observed in the compound. (The refractive index of sodium neptunyl acetate also was measured in this study.) Comparison of refractive index values for the $NaMO_2(OOCCH_3)_3$ compounds are given in Table I.

TABLE I

REFRACTIVE INDICES OF $NaMO_2(OOCCH_3)_3$ n_D

Compound	Refractive index
$NaUO_2(OOCCH_3)_3$[9]	1.5015 ± 0.0005
$NaNpO_2(OOCCH_3)_3$	1.5105 ± .0005
$NaPuO_2(OOCCH_3)_3$[9]	1.518 ± .001
$NaAmO_2(OOCCH_3)_3$	1.528 ± .002

X-Ray diffraction patterns revealed a cubic structure with a lattice constant a_0 = 10.6 Å., the same as that of the uranyl, neptunyl and plutonyl analogs.

Further proof of the existence of Am(VI) in this com-

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[1] Presented in part before the Division of Physical and Inorganic Chemistry at the Chicago Meeting of the American Chemical Society in September, 1950. This work sponsored by the A.E.C.

[2] L. B. Asprey, S. E. Stephanou and R. A. Penneman, THIS JOURNAL, **72**, 1425 (1950).

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[4] S. G. Thompson, L. O. Morgan, R. A. James and I. Perlman, *ibid.*, p. 1339.

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[6] B. B. Cunningham, private communication.

[7] S. G. Thompson, B. B. Cunningham and G. T. Seaborg, THIS JOURNAL, **72**, 2798 (1950).

[8] K. Street, Jr., and G. T. Seaborg, *ibid.*, **72**, 2790 (1950).

[9] E. Staritzky, unpublished work.

pound was obtained in the following manner: Sodium americyl acetate was reduced with excess ferrous ammonium sulfate and the excess was titrated with ceric sulfate using ferroin as the indicator. The solution was maintained at 50° and the reagents were added from weight burets. The amount of americium was determined radiometrically. The results showed that 6.0 micromoles of Am(VI) in $NaAmO_2(OOCCH_3)_3$ were reduced to Am(III) by 17.34 micromoles of Fe(II), yielding a value of 2.9 equivalents for this three-electron reduction.

(2) **Solvent Extraction of Am(VI).**—A solution containing Am(VI) (prepared by peroxydisulfate oxidation) was treated with barium nitrate to remove sulfate. It was saturated with ammonium nitrate, made 1 M in HNO_3, and extracted with ethyl ether. Three extractions with ether removed a total of 95% of the americium present in the original aqueous solution. The volume ratio of ether to aqueous solution was maintained at *ca.* 3:1, and the distribution coefficient, K_d, (ether)/(H_2O), was calculated to have a value of 0.6. Some americium not extracted by ether was found occluded in the $BaSO_4$ precipitate. Repetition of the experiment with hexone (methyl isobutyl ketone) gave incomplete extraction, apparently due to reduction, since the pink color of Am(III) appeared.

(3) **Absorption Spectrum of Am(VI).**—Absorption spectrum measurements were made with a Beckman model DU spectrophotometer using quartz microcells of 1 cm. path length containing about 100 microliters of solution. The instrument was operated using the 0.1 sensitivity scale at a minimum slit width. The wave length scale was calibrated with the hydrogen arc lamp. For three of the hydrogen emission lines, 486.13, 656.28 and 434.05 mμ, agreement within 0.5 mμ was obtained. Readings were made at 5 millimicron intervals, except in the vicinity of absorption bands where readings at 1 millimicron intervals or less were made. Peak maxima were located by slowly rotating the wave length drum until maximum deflection of the galvanometer was obtained. The americium concentrations ranged from 0.002 to 0.025 molar.

A solution of 6 M $HClO_4$, containing Am(VI) (sulfate-free), gave a spectrum which was marked by a strong absorption band having a sharp peak at 992 mμ, a minor peak at 666 mμ and general ultraviolet absorption (Fig. 1). The characteristic Am(III) peaks[3,10] at 504 and 811 mμ and the Am(V) peaks[5] at 514 and 715 mμ were absent. The spectra of Am(III) and Am(V) shown in Fig. 1 were obtained on the same instrument for comparison with the spectrum of Am(VI). The Am(VI) peak at 992 mμ was found to obey Beer's law and was used successfully as a quantitative method for Am(VI) in the range studied.

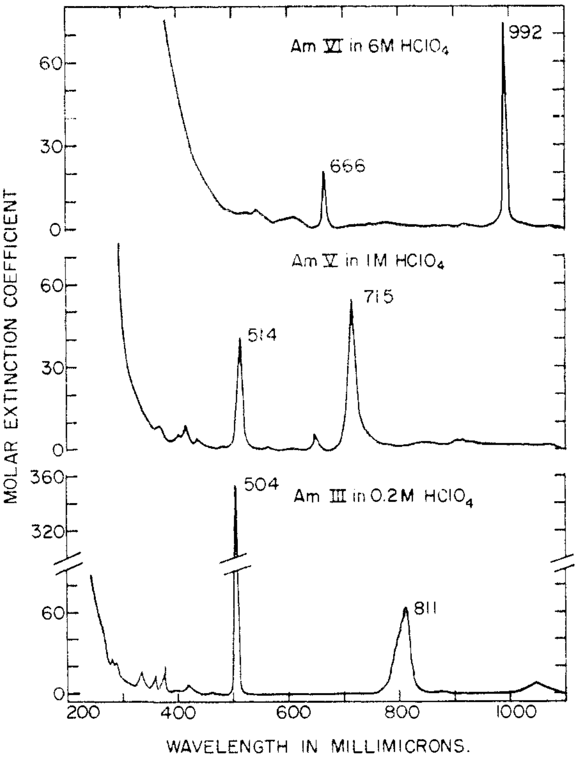

Fig. 1.—Absorption spectra of the Am(III), Am(V) and Am(VI) ions in $HClO_4$.

The change in color of an Am(VI) solution from pale yellow to red-brown when sulfate was added indicated the formation of a complex ion. In 1 M ammonium sulfate, the molar extinction coefficient of the 992 mμ Am(VI) peak was not appreciably changed but the peak itself was displaced to 996 mμ. The sulfate solution gave relatively greater ultraviolet absorption than did the sulfate-free Am(VI) solution.

(4) **Stability of Am(VI).**—Observation of the 992, 715 and 811 mμ absorption peaks of Am(VI), Am(V) and Am(III), respectively, showed that Am(VI) reduced to Am(V) in dilute acid without growth of Am(III). In dilute acid (0.1 M) the reduction of Am(VI) to Am(V) is zero order with respect to Am(VI), and first order with respect to the total americium. A solution of 1 M $HClO_4$ containing only Am(VI) initially will reduce to Am(V) at the rate of about 5% per hour.

(5) **Separation of Am(III) and Am(VI) Using Hydrogen Fluoride.**—A solution of Am(VI) gave no precipitate when treated with hydrofluoric acid. A solution containing both Am(III) and Am(VI) precipitated Am(III) fluoride when treated with hydrofluoric acid, leaving Am(VI) in solution.

(6) **Behavior of Am(VI) in Alkaline Media.**—Treatment of pure Am(VI) in dilute nitric acid with gaseous ammonia, gave a precipitate containing only Am(V), although transient formation of a dark precipitate was observed. Addition of potassium hydroxide gave the same result. Injection of a dilute acid solution of Am(VI) into excess sodium carbonate at 0° gave an intense red-brown solution, indicating a carbonate complex of Am(VI). Upon standing, the solution decolorized gradually, yielding an Am(V) precipitate.

Discussion

From consideration of the experimental results, it is seen that the general chemistry of Am(VI) is similar to that of U(VI), Np(VI) and Pu(VI). The absorption spectrum of Am(VI) resembles that of Pu(VI), both species having an extremely sharp absorption band in the near infrared.[11]

From the chemical behavior, X-ray and crystallographic evidence, americyl ion is analogous to uranyl, neptunyl and plutonyl ions and is assigned the formula, AmO_2^{++}.

The oxidation potential of the Am(III)–Am(VI) couple can be estimated within certain limits. Since both of the following reagents will oxidize

$$2SO_4^{--} = S_2O_8^{--} + 2e^- \qquad E^0 = -2.05 \text{ volts}^{12}$$

$$Ag^+ = Ag^{++} + e^- \qquad E^0 = -1.98 \text{ volts}^{12}$$

Am(III) to Am(VI) essentially completely, this places the maximum negative value of about −2 volts on the potential. Partial oxidation using Ce(IV) in 6 M $HClO_4$ gave a value of approximately −1.8 volts.[13] The oxidation of Am(III) to Am(VI) has a strong hydrogen ion dependence and cannot be accomplished by peroxydisulfate in acidity as high as 2 M.[14] It is estimated that the potential for

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(10) B. M. Jones and B. B. Cunningham, "The Absorption Spectrum of the Aqueous Tripositive Ion of Americium." Presented before the Division of Physical and Inorganic Chemistry at the Chicago meeting of the American Chemical Society in September, 1950.

(11) G. E. Moore and K. A. Kraus, "Spectrophotometry of Plutonium(VI) in Perchlorate Solutions," MonC-204, January, 1948.

(12) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938, p. 298.

(13) The value of the Ce(III)–Ce(IV) couple was taken from the data of G. F. Smith, "Cerate Oxidimetry," The G. F. Smith Chemical Co., Columbus, Ohio, 1942, p. 22.

(14) Unpublished.

the following half-cell reaction

$$Am^{+++} + 2H_2O = AmO_2^{++} + 4H^+ + 3e^-$$

is in the range -1.8 ± 0.15 volts.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

The Ternary System Potassium Bromide–Potassium Chloride–50% Aqueous Ethanol

BY EDWARD L. SIMONS[1] AND SAMUEL E. BLUM

The distribution of the isomorphous salts potassium bromide and potassium chloride in solubility equilibrium between liquid and solid solutions has been studied in 50% aqueous ethanol. As in water, the system belongs to Roozeboom Type II, but the solvent change shifts the crystallization end-point from 65.5 mole per cent. KBr to 83.5 mole per cent. The solvent change leaves unaltered the slope of the Hill, Durham and Ricci distribution plot. From the Yutzy and Kolthoff distribution equation heats of formation of the solid solutions have been calculated and compared with calorimetric and theoretical values.

The distribution of the isomorphous salts potassium bromide and potassium chloride in solubility equilibrium between solid and aqueous solutions has been studied at 25° by Amadori and Pampanini[2] and by Flatt and Burkhardt[3] and at 35° by Shlezinger and Zorkin.[4] All three reports are in qualitative agreement in classifying the distribution as Roozeboom Type II,[5] although the data of Amadori and Pampanini indicate a congruent crystallization end-point at 61.0 mole per cent. potassium bromide, while those of the latter two investigations indicate a value of 65.5%.

The data may also be compared in terms of the distribution equation 1[6] in which R_l and R_s represent

$$\log R_l = \log K + m \log R_s \qquad (1)$$

the mole ratios of bromide to chloride in the liquid and solid phases, K represents the ratio of the activity product constants of potassium bromide and chloride, and m is a constant assumed to be characteristic of the solid phase. In the range of $\log R_s$ values between +1 and −1, where equation 1 has previously been shown to be applicable,[6–9] all three sets of data can be represented by this equation with the following K and m values:

Investigators	m	log K (obsd.)	log K (calcd.)	Sat. solns. of pure salts: molality mKBr	$\gamma_\pm$KBr[10]	molality mKCl	$\gamma_\pm$KCl[10]
Ref. 2	0.38	0.14_5	0.227	5.753	0.655	4.845	0.599
Ref. 3	.47	$.16_5$	.223	5.764	.655	4.869	.600
Ref. 4	.45	$.16_5$	.244	6.222[11]	.683	5.164[12]	.608

The discrepancy between the two investigations at 25° lies in the solid phase compositions, since the liquid phase solubility curves are identical over most of the composition range. In view of the special techniques employed by Flatt and Burkhardt to assure equilibrium it is felt that their data are the more reliable. The results of Shlezinger and Zorkin indicate that the distribution is essentially the same at 35° as at 25°.

It was the purpose of this investigation to observe the effect of solvent on the distribution by studying the ternary system potassium bromide–potassium chloride–50% aqueous ethanol at 35°.

Materials.—C.P. grade potassium bromide and potassium chloride were used without recrystallization. The potassium bromide was found to contain 0.10% potassium chloride, and this was taken into account in the preparation of complexes. After three days of drying at 190°, the salts were stored until used in a calcium chloride desiccator. The solvent was prepared from redistilled ethanol by dilution with distilled water. The resulting solution had a density of $0.91130\,^{25}_{4}$, which corresponds to 49.35 weight per cent. ethanol.[13,14]

Solubility Determinations.—The solubility determinations were made according to the usual procedure described in similar investigations in so far as method of stirring, sampling, filtering and temperature control are concerned. The constant temperature bath was maintained at 34.95 ± 0.05°. The solid phases were determined by algebraic extrapolation[15] of the tie lines connecting the known complexes with the resulting saturated solutions. The constancy of successive analyses indicated that two weeks of stirring were sufficient for equilibration.

The analytical method used was that of Andrews,[16] which involves the Volhard determination of total halide on one sample and the Volhard determination of chloride on a second sample from which the bromide has been removed by oxidation to bromine with iodate followed by boiling. In applying Caldwell and Moyer's[17] Volhard procedure to the chloride determination, it was found necessary to add the indicator before adding the standard silver nitrate solution. When the order was reversed, unsatisfactory end-points were obtained.

Results.—The solubility data are shown in Table I. The change in the distribution between

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[1] Research Laboratory, General Electric Co., Schenectady, N. Y.

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