

## The Pentavalent State of Americium

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In an earlier publication<sup>1a</sup> brief mention was made of experiments in which americium, subjected to sodium hypochlorite oxidation in carbonate solution, was converted from its normal trivalent state to an insoluble compound believed to contain americium(V). The principal pieces of evidence at hand at that time for americium(V) were its similarity in solubility properties to plutonium(V),<sup>2</sup> the differences in absorption spectrum upon oxidation and the reappearance of americium(III) upon addition of reducing agents. The present report describes the preparation and properties of americium(V) only mentioned previously and further work which proves its oxidation state.

The existence and stability of oxidation states of americium higher than the tripositive state are not only of intrinsic interest but also are of importance in relation to the oxidation states of neighboring elements according to the actinide concept of heavy element structure.<sup>3</sup> In addition, the existence of multiple oxidation states can often be exploited in effecting chemical separations of otherwise difficultly separable substances and this is of great practical importance for various nuclear chemical problems.

Although a number of early attempts<sup>4,5,6</sup> were made to oxidize americium(III) in aqueous solution, none of the results were unambiguous and insofar as the Am(III)-Am(IV) couple was concerned, it was deduced<sup>6</sup> that the potential was more negative than -2 volts. Judging by the disproportionation of plutonium(V) in acid solution,<sup>7</sup> it was considered profitable to consider the preparation of americium(V) at high pH and these experiments resulted in the discovery of this state.<sup>1a</sup> More recently, Asprey, Stephanou and Penneman<sup>8</sup> have been successful in preparing americium(VI) by treating americium(III) with ammonium peroxydisulfate in dilute acid solution.

### Experimental

It was considered convenient in attempting to oxidize americium(III) at high pH to work in carbonate solution because Am(III) is soluble as a complex ion giving the advantages of a homogeneous system. At least two of the possible oxidation products, Am(IV) and Am(VI), might also be expected to remain in solution so that there would be hope of observing an oxidation by following the absorption spectrum with a spectrophotometer. As it turned out,

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(1a) L. B. Werner and I. Perlman, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 22.5 (McGraw-Hill Book Co., Inc., New York, N. Y., 1949).

(2) G. E. Moore and D. E. Koshland, Jr., unpublished work, Clinton Laboratories, February, 1945.

(3) G. T. Seaborg, *Nucleonics*, **5**, no. 5, 16 (1949).

(4) G. T. Seaborg, R. A. James and L. O. Morgan, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 22.1 (McGraw-Hill Book Co., Inc., New York, N. Y., 1949).

(5) S. G. Thompson, L. O. Morgan, R. A. James and I. Perlman, *ibid.*, Paper No. 19.1.

(6) B. B. Cunningham, *ibid.*, Paper No. 19.2.

(7) R. E. Connick, M. Kasha, W. H. McVey and G. E. Sheline, *ibid.*, Paper No. 3.15.

(8) L. B. Asprey, S. E. Stephanou and R. A. Penneman, *This Journal*, **73**, 1425 (1950).

the only higher state formed was Am(V) which precipitated from the carbonate solution, and it became necessary to redissolve the insoluble compound in order to determine the absorption spectrum.

In using the spectrophotometer to follow the oxidation, the spectrum of Am(III) was first determined in carbonate solution. Quartz absorption microcells having a light path of 1 cm. were used in a Beckman spectrophotometer for the measurements. The range covered was 4000-11,000 Å. and the americium(III) concentration was 0.428 mg./ml. in a 40% potassium carbonate solution. The absorption spectrum, shown in Fig. 1a, has prominent absorption bands at 5080 and 8180 Å. Molar extinction coefficients calculated at these wave lengths were found to be  $\epsilon_{5080} = 270$  and  $\epsilon_{8180} = 44$ . For comparison, the absorption peaks of Am(III) in 1 M nitric acid solution are reported<sup>9</sup> to be at 5030 and 8100 Å. with molar extinction coefficients 295 and 41, respectively. This curve is reproduced as Fig. 1b.

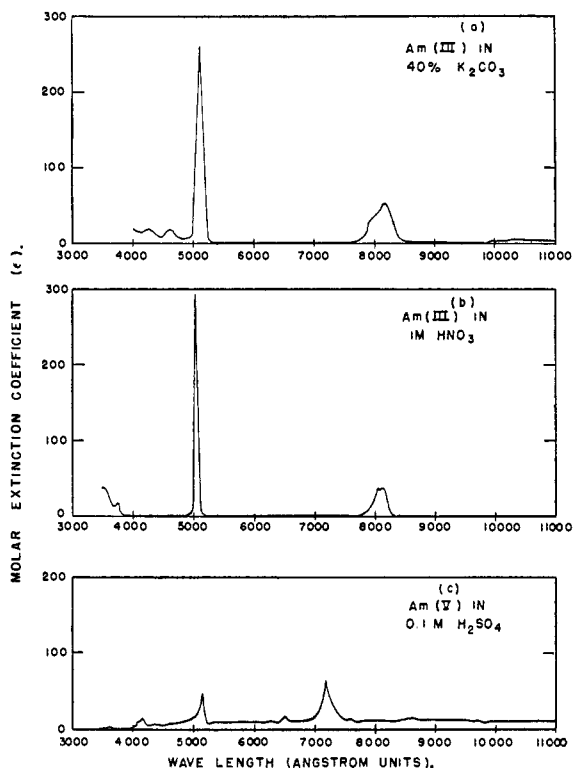


Fig. 1.—Absorption spectra of Am(III) and Am(V).

In an exploratory experiment, 0.185 ml. of a potassium carbonate solution containing 0.45 mg. Am/ml. and 0.05 M sodium hypochlorite was allowed to stand at room temperature in the absorption cell. The Am(III) absorption peaks decreased slowly with time, reaching a value of 35% of the initial values in 24 hours and a light colored precipitate was noted in the bottom of the absorption cell.

A series of further experiments established the following behavior: (1) Upon addition of sodium hypochlorite to a potassium carbonate-Am(III) solution at 95° and keeping it at this temperature for 10 min., the absorption peaks of Am(III) decreased to zero and a precipitate was in evidence. (2) Heating the potassium carbonate-Am(III) in the absence of sodium hypochlorite produced no change in Am(III). (3) Addition of a reducing agent, sodium hydrogensulfite ( $\text{Na}_2\text{S}_2\text{O}_4$ ), to a solution with precipitated americium caused a return of Am(III) absorption bands to their initial intensity.

This behavior strongly suggests the formation of a carbonate insoluble upper oxidation state of americium. Further work was then done on the precipitate itself and a few notes on the formation of the insoluble compound may be in order. The solubility of the compound was independent of the potassium carbonate concentration in the range

(9) B. B. Cunningham and L. B. Asprey, to be published.

0.4–3.0 *M*, radioactive assays after 6 days showing low solubilities of about 3 mg. Am/liter. However, the rate of precipitation after initial oxidation was dependent upon carbonate concentration. For example, 4.5 hours after oxidation in 0.4 *M* potassium carbonate solution, the americium concentration remaining in solution was ~60 mg./liter, while in 3.0 *M* potassium carbonate the unprecipitated americium was ~23 mg./liter.

It was found possible to dissolve quickly the insoluble americium compound in 0.1 *M* sulfuric acid after washing with distilled water. The solution appeared colorless and while being measured in the spectrophotometer, the absorption at 5030 Å. was checked at intervals as an index of the Am(III) present. During the course of the measurement (2.5 hours), the Am(III) increased from an initial concentration of 2% to a final value of 5%. By correcting the light absorption due to Am(III), the curve shown in Fig. 1c was obtained which is taken to be characteristic of Am(V) in 0.1 *M* sulfuric acid solution. The absorption bands are at 5150 and 7200 Å. with molar extinction coefficient 48 and 66, respectively.

Final proof of the oxidation state of the new form was obtained by titration with a reducing agent. In a typical experiment, americium was oxidized and precipitated as described, washed six times with distilled water, and dissolved in 0.1 *M* sulfuric acid. It was precipitated again by addition of potassium carbonate, washed four times again with water and dissolved in 0.1 *M* sulfuric acid. From this solution an aliquot of 0.100 ml. was removed and the concentration measured<sup>10</sup> as  $7.24 \pm 0.03$  millimolar. Measurement of the absorption spectrum showed 4% of the americium to be Am(III).

Exactly 0.030 ml. of 0.0502 *N* ferrous ion solution was added, and as well as could be told by spectral analysis, reduction to Am(III) was complete. The solution was transferred quantitatively to a micro titration dish and the excess ferrous ion titrated with standard ceric solution using ferrous phenanthroline as an indicator. It was found that 1.367 microequivalents of ferrous ion had been oxidized by the americium which upon calculation showed the oxidized state to have 1.96 equivalents/mole.

Since the forms of Pu(V) and Np(V) ions in acid solution have been shown<sup>11</sup> to be  $\text{PuO}_2^+$  and  $\text{NpO}_2^+$ , respectively, we may expect Am(V) to be  $\text{AmO}_2^+$  under similar conditions. No attempt has been made to identify the Am(V) compound which precipitates from carbonate solution.

This work was performed under the auspices of the U. S. AEC.

(10) Measured by  $\alpha$ -particle assay using a half-life of 475 years.

(11) K. A. Kraus and G. E. Moore, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 4.19 (McGraw-Hill Book Co., Inc., New York, N. Y., 1949); L. B. Magnusson, J. C. Hindman and T. J. LaChapelle, *ibid.*, Paper No. 15.4.

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## Oxygen Atom Transfer during the Oxidation of Aqueous Sodium Sulfite

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The very interesting communication of Halperin and Taube<sup>1</sup> on the above subject prompts us to put on record some experiments upon similar lines which were performed in 1939.<sup>2</sup> In this work we studied briefly the oxidation by normal oxygen gas and by normal hydrogen peroxide of normal sodium sulfite, dissolved in water containing  $\text{O}^{18}$  in excess of the normal abundance. In both cases the oxygen atom which was transferred to the sulfite ion came from the oxidizing agent, and not from the water.

The experiments upon oxygen oxidation were

(1) Halperin and Taube, *THIS JOURNAL*, **72**, 3319 (1950).

(2) Winter, Ph.D. Thesis, London University, 1942.

performed by dissolving 1.5 g. of Analar hydrated sodium sulfite ( $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ ) in 3 ml. of enriched water at room temperature ( $\approx 18^\circ$ ). This solution was exposed to oxygen, confined in a gas buret, until no further absorption of gas took place: in all cases the absorption was close to the theoretical requirements. That oxidation was complete was checked by titration with  $\text{KMnO}_4$  and also by gravimetric estimation of the sulfate formed. The  $\text{O}^{18}$  content of the water was measured before and after the oxidation by determination of the water density, after vigorous purification, by the semi-micro silica float method.<sup>3</sup> The results are summarized in Table I: it is clear from experiments 4 and 5, where the solution was left for some 72 hours at room temperature—a time longer than required for the completion of oxidation in experiments 1, 2, 3 and 6—that the exchange of the sulfite ion is negligible under these conditions, the observed decrease in water density in p.p.m.,  $\Delta\gamma d$ , being essentially that to be expected from dilution with the water of crystallization of the sodium sulfite. Experiments 1, 2, 3 and 6, show conclusively that the over-all reaction  $2\text{Na}_2\text{SO}_3 + \text{O}_2 \rightarrow 2\text{Na}_2\text{SO}_4$  proceeds without exchange of oxygen with the solvent water.

TABLE I

Expt.	Vol. of $\text{O}_2$ adsorbed, ml. N. T. P.	$\Delta\gamma d$ obs.	$\Delta\gamma d$ calcd. for $7\text{H}_2\text{O}$ from sulfite	Experimental conditions	
1	66.0	66.6	-79	-78	Oxygen from cylinder
2	66.2	66.6	-81	-78	
3	66.8	66.6	-80	-78	
4	..	..	-80	-78	In atmosphere of nitrogen
5	..	..	-79	-78	<i>In vacuo</i>
6	66.5	66.6	-80	-78	In oxygen, trace $\text{CuSO}_4$ added

$\Delta\gamma d$  calcd. for  $7\text{H}_2\text{O} + 0 = -91$ .

$\Delta\gamma d$  calcd. for  $7\text{H}_2\text{O} + 3.0 = -117$ .

$\Delta\gamma d$  calcd. for  $7\text{H}_2\text{O} + 4.0 = -130$ .

Examination of the various chain mechanisms which have been proposed for this reaction—involving, *e.g.*, either the radical  $\text{HSO}_5^4$  or the radical ion  $\text{SO}_5^{\cdot-}$  shows that on either hypothesis the above result might be expected, since oxygen transfer involving oxygen from the water molecules, would not be expected to occur. It is however unfortunate that our experiments were of necessity (because of the relatively small enrichments of  $\text{H}_2\text{O}^{18}$  available at the time) performed using solutions very much more concentrated than those which have been used in investigations of the chain reaction. It would be very interesting to know if these results are confirmed in more dilute solutions.

For experiments upon the oxidation of sodium sulfite with hydrogen peroxide, the exchange of hydrogen peroxide with water was first examined. Merck perhydrol (aqueous hydrogen peroxide containing 29%  $\text{H}_2\text{O}_2$  by analysis) was used as a source of hydrogen peroxide. It proved impossible

(3) Briscoe, *et al.*, *J. Chem. Soc.*, 1207, 1948 (1934); Spoor, Ph.D. Thesis, London, 1935.

(4) Franck and Haber, *Sitzungsber. Preuss. Akad.*, 50 (1931).

(5) Backstrom, *Z. physik. Chem.*, **25B**, 122 (1934).