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ALKALINE OXIDATION OF AMERICIUM; PREPARATION AND REACTIONS OF Am(IV) HYDROXIDE*

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Abstract—A pink slurry of $Am(OH)_3$ is converted quantitatively into the black hydroxide (or hydrous oxide) of tetravalent americium by hypochlorite oxidation in dilute base. Preparation of tetravalent americium from aqueous solution has not been previously reported. This material dissolves in nitric or perchloric acid and disproportionates according to the equation: 2Am(IV) = Am(V) + Am(III). It dissolves in sulphuric acid giving Am(VI) and Am(III), with a minimum of half of the Am(V) produced from the simple disproportionation of Am(IV) being consumed by a consecutive reaction:

Am(IV) + Am(V) - Am(VI) + Am(III).

Revision from + 0.4 to at least - 0.5 V is suggested for the value of the standard potential of the Am(OH)₃, Am(OH)₄ couple.

Oxidation of $Am(OH)_3$ past $Am(OH)_1$ is observed with both ozone and peroxydisulphate. Details are given for a new and convenient method for producing AmO_2^{2+} in dilute acid solution based on the ozone oxidation of $Am(OH)_a$. Ozone oxidizes $Am(OH)_a$ in 0.1 M NaOH to a soluble yellow complex of Am(VI).

THE aqueous oxidation states of americium include Am(111), Am(V) and Am(VI), but there is a significant vacancy; i.e., the lack of Am(IV).⁽¹⁻⁷⁾ Americium in the tetravalent state is known only in three compounds, AmO₂⁽⁸⁾, AmF₄ and KAmF₅⁽⁹⁾, which are prepared under anhydrous conditions. Pertinent to this fact are the potentials in aqueous acid solution^(7,10,11) relating Am³. AmO₂ and AmO₂², and including estimates for the hypothetical Am⁴.



- * This work was sponsored by the U.S. Atomic Energy Commission.
- ⁽¹⁾ R. A. PENNEMAN and T. K. KEENAN, *The Radiochemistry of Americium and Curium*, National Research Council Monograph NAS-NS-3006 (1960).
- (8) T. K. KEENAN, J. Chem. Ed. 36, 27 (1959).

- ⁽⁴⁾ J. K. KEENAN, J. Chem. Ed. 36, 27 (1959).
 ⁽³⁾ G. N. YAKOVLEV and V. N. KOSYAKOV, Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, 28, 373. United Nations (1959).
 ⁽⁴⁾ G. T. SEABORG, The Transuranium Elements. Yale University Press, New Haven (1958).
 ⁽⁵⁾ J. J. KATZ and G. T. SEABORG, The Chemistry of the Actinide Elements. John Wiley, New York (1957)
 ⁽⁶⁾ G. N. YAKOVLEV and V. N. KOSYAKOV, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955, 7, 363. United Nations (1956).
 ⁽¹⁾ P. A. PENISHAN and L. B. ASPERY Proceedings of the International Conference on the Peaceful Uses of the International Conference on the Peaceful Uses of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955, 7, 363. United Nations (1956).
- (1) R. A. PENNEMAN and L. B. ASPREY, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955, 7, 355. United Nations (1956).
- (8) B. B. CUNNINGHAM and L. B. ASPREY, AECD-2946 (1950).
- (19) L. B. ASPREY, J. Amer. Chem. Soc. 76, 2019 (1954).
 (10) S. R. GUNN. Thesis, University of California (1954); S. R. GUNN and B. B. CUNNINGHAM, J. Amer. Chem. Soc. 79, 1563 (1957).
- (11) L. EYRING, H. R. LOHR and B. B. CUNNINGHAM, J. Amer. Chem. Soc. 74, 1186 (1952).

Using these potentials as a basis for prediction, it is clear that Am⁴⁺ should be highly unstable in acid with respect to disproportionation into Am^{3+} and AmO_{2^+} . The reaction of Am^{4+} with AmO_2^+ to produce AmO_2^{2+} and Am^{3+} is predicted in molar acid. The reduction of Am(IV) to Am(III) by water is also energetically favourable.

In contrast to this, the situation in alkaline solution is much more favourable for stabilization of tetravalent americium. LATIMER⁽¹²⁾ outlined in detail the basis for his estimate of the $Am(OH)_3$, $Am(OH)_4$ couple in molar base and gave +0.4 V, which also has been listed in recent texts^(13,14). This value is apparently in error both in sign and magnitude and we are unable to obtain it on recomputation. For reasons which are developed later, we suggest -0.5 V as the value for the Am(OH)₃, Am(OH)₄ couple.

From a preparative chemist's point of view, it is very interesting that this potential is nearly 2 V more positive than the Am³⁺, Am⁴⁺ potential in acid solution, and should lie well within the range of chemical oxidizing agents. Two common oxidizing agents whose potentials in molar base exceed this value are hypochlorite and ozone:(15)

$$ClO^{-} + H_2O + 2e^{-} = Cl^{-} + 2OH^{-}; E_B^{\circ} = +0.89 V$$

 $O_3 + H_2O + 2e^{-} = O_2 + 2OH^{-}; E_B^{\circ} = +1.24 V.$

Tetravalent americium had not hitherto been prepared from aqueous solution and it was primarily to attempt its preparation that the present work was begun.

EXPERIMENTAL AND DISCUSSION

Oxidation of Am(OH)₃ to Am(OH)₄ with hypochlorite

Interestingly, hypochlorite oxidation was tried perhaps fifteen years ago in the early days of americium chemistry by CUNNINGHAM⁽¹⁸⁾. He reported a single experiment on a microgram scale in which Am(OH)₃ was precipitated by excess base containing ClO⁻ and a darkening of the precipitate was observed. We find that a light pink slurry of Am(OH)₃ turns brown-black when heated with NaOCl in the presence of NaOH. Presence of additional alkali is apparently necessary, since either 0.6 M NaOCl or 0.2 M NaOCl by itself produced less than 10 per cent oxidation to Am(OH)₄. With 0.2 M NaOH present, variation of NaOCI from 0.2 to 0.6 M seemed to produce $Am(OH)_4$ equally well.

In a typical experiment, 5 mg of freshly precipitated Am(OH)₃ was stirred with 2.5 ml of 0.2 M NaOCI-02 M NaOH in a boiling water-bath for 30 min. The dark precipitate which formed was centrifuged and heated again for 30 min with a second portion of 0.2 M NaOCI-0.2 M NaOH. The precipitate was centrifuged and washed twice in 2 ml portions of 0.001 M NaOH with warming to promote coagulation. After centrifugation, the material was then ready for subsequent experiments.

Oxidation of Am(OH)₃ using peroxydisulphate

Treatment of 5 mg of $Am(OH)_3$ in 0.1 M NaOH with excess solid K₂S₂O₈ for 2 hr in a boiling water bath yielded an olive-tan precipitate. Under these conditions, the average oxidation number of the americium was 4.53, showing that oxidation past Am(OH)₄ had occurred.

However, Am(OH)4 could be prepared using peroxydisulphate in very strong base. Americium was added to hot, 7 M potassium hydroxide saturated in potassium peroxydisulphate and the resulting

⁽¹²⁾ W. M. LATIMER, Oxidation Potentials (2nd Ed.) Chap. 21. Prentice-Hall, New York (1952).

⁽¹³⁾ Ref. 4, p. 129.

⁽¹⁴⁾ Ref. 5, p. 357. ⁽¹⁵⁾ Ref. 12, Table 85.

⁽¹⁶⁾ B. B. CUNNINGHAM, The Transuranium Elements, (Edited by G. T. SEABORG and J. J. KATZ) NNES, Plutonium Project Record, Div. IV, Vol. 14B, pp. 1363–1369. McGraw-Hill, New York (1949).

slurry was kept at 90° for 1 hr. The final precipitate was then washed carefully to remove excess reagent. The average oxidation number in the hydroxide was 4.0 ± 0.1 . Since the hypochlorite oxidation produces Am(OH), so conveniently, the variation in products of the peroxydisulphate oxidation was not investigated further.

Disproportionation of Am(IV) in H₂SO₄

As mentioned in connection with the americium potential diagram, Am⁴⁺ would be expected to undergo the following reactions in acid:

(1) simple disproportionation; 2Am(IV) = Am(V) + Am(III)

(2) redox reaction; Am(IV) + Am(V) = Am(VI) + Am(III).

There is some interesting work by ZAITSEV et al.^(3,17) in which AmO_2 (obtained by ignition of americium oxalate) was dissolved in H_2SO_4 . With 1 M H_2SO_4 they found

H₃SO₄ (M)	Temp	Valence s	Av. oxidation number in final		
	(M)	(°C)	III	v	VI
2	25	64.6	9.8	25.6	3.96
2	25	60·2	11.5	28.3	4∙08
1	25	67.6	5.4	27.0	3.92
1	25	65.3	4.8	29.8	3.99
1	0	67.1	3.5	29.4	3-95
0.1	25	58.4	24.7	16.9	4.00
0.1	25	57.9	23.4	18.7	4·03
0.05	25	63.5	14.1	22.4	3.95

TABLE	1.—DISSOLUTION	OF	Am(OH) ₄	IN H ₃ S	04
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* Final solution was 0.003-0.012 M in total americium.

Am(III) and Am(VI) in solution in proportions practically equivalent to the sum of reactions (1) and (2); i.e., 3Am(IV) = Am(VI) + 2Am(III). They did not work in other acids and thus were not able to isolate reaction (1).

Dissolution of our black hydroxide (prepared by hypochlorite oxidation) in sulphuric acid was also found to give Am(VI) and Am(III) with some Am(V). The concentrations of americium(III), (V) and (VI) were determined spectrophotometrically, using the Cary Recording Spectrophotometer, Model 14 M. In each experiment, the average oxidation number was found to be four within the accuracy of our spectrophotometric determinations. The results are shown in Table 1.

Since the average oxidation number remains four, it follows that Am(IV) must *not* have been reduced by water, and the observed products can be fully accounted for by reactions (1) and (2). This may be somewhat unexpected since the rapid reduction of Am(IV) by water is often postulated. Appreciable reduction of Am(IV) by water is found on dissolution of AmO_2 . ZAITSEV *et al.*⁽¹⁷⁾ found that the reduction of Am(IV) by water is of increasing importance when AmO_2 is dissolved in $> 1 M H_2SO_4$; e.g., 27 per cent reduction in 2 M H₂SO₄, and 64 per cent in 6 M H₂SO₄.

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⁽¹⁷⁾ A. A. ZAITSEV, V. N. KOSYAKOV, A. G. RYKOV, YU. P. SOBOLEV and G. N. YAKOVLEV, Institute of Atomic Energy, Academy of Sciences, Moscow, U.S.S.R. (1960); (NP-7518).

reduction of Am(IV) by water was also involved in the thermochemical work on the Am³⁺, Am⁴⁺ potential.⁽¹¹⁾

The data in Table 1 also show that variation in H_2SO_4 concentration changes the amount of reaction (2) significantly but do not allow the effects of hydrogen ion and sulphate (or bisulphate) ion to be separated. Therefore, we determined the effect of

H+ (M)	HSO ₄ ⁻ (M)	SO4 ² (M)	Am(VI)(%) (equals % Reaction 2)				
0.095*	0	0	3.2				
0.095	0.049	0.021	19.2				
0.094	0.37	0.38	27.3				

TABLE 2.—EFFECT OF SULPHATE CONCENTRATION ON REACTION (2) AT CONSTANT (H^+)

* Ionic strength was kept at 2.0. Li₂SO₄, LiClO₄ and HClO₄ were used.

sulphate at constant hydrogen ion. Table 2 shows these results. Since, from the stoichiometry, the Am(VI) produced cannot exceed one-third of the Am(IV) initially present, the approach to this figure shows that sulphate clearly promotes Am(IV) reacting with Am(V); i.e., reaction (2). Particularly noteworthy is the fact that in the absence of sulphate (i.e., in HClO₄) reaction (2) is almost completely suppressed.

Disproportionation of Am(IV) in HNO₃ and HClO₄

Observation of Am(IV) disproportionation in acids having weaker complexing anions than sulphate was desired. An additional series of experiments was performed

HNO ₃	Temp (°C)	Valence s	states after d (%)	Av. oxidation number in final	
(M)		III	v	VI	solution*
2	0	55.4	40.4	4.2	3.93
1	60	52-2	44.5	3.3	3.99
1	25	50.9	46.1	3.0	4.01
1	25	52.3	43 ⋅5	4·2	4.00
1	0	55.1	41.0	3.9	3.94
0.1	0	52.6	47.4	0-0	3.95
0.02	0	55· 0	45 ∙0	0.0	3.90

TABLE 3.—DISSOLUTION OF	Am(OH)	in HNO
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* Final solution was 0.005-0.008 M in total americium.

in which $Am(OH)_4$ was dissolved in various concentrations of nitric acid. Just as in the case of perchloric acid (see line 1, Table 2), only a few per cent reaction (2) was observed. Results are tabulated in Table 3.

In one case, an approximation to a minimum value for the rate of disproportionation of Am(IV) in 0.05 M HNO₃ at 0° could be made by noting the rate of change of the Am(III) and Am(V) absorption maxima. Under these conditions, and assuming a reaction second order in Am(IV), we estimate k_1 in the equation

$$-d[\operatorname{Am}(\operatorname{IV})]/dt = k_1[\operatorname{Am}(\operatorname{IV})]^2$$

to be > 3.7×10^4 l. mole⁻¹ hr⁻¹. In acidities > 0.1 M, dissolution of the Am(OH)₄ is too rapid to permit observation.

Proof of oxidation number in $Am(OH)_4$

(1) As can be seen from Tables 1 and 3, the average oxidation number in the solutions obtained by dissolution of the black hydroxide in acid was *four*. Although this information was noted with jubilation, one had to rule out that the black hydroxide was not just a fortuitous mixture of Am(III) and Am(V).

Media	% Reaction (2), no added Am(V)	% Reaction (2), with added Am(V)		
0·1 M HNO ₃	0	4.5		
0.1 M H ₂ SO ₄	18.2	28.7		
0.5 M H ₂ SO ₄	—	54.5		
1.0 M H ₂ SO ₄	27.4	44·0		

TABLE 4.—DISSOLUTION OF $Am(OH)_4$ in the presence of Am(V)

(2) The contrasting reactions of the black hydroxide on dissolution in HNO_3 and in H_2SO_4 provide convincing evidence that it is the hydroxide (or hydrous oxide) of tetravalent americium. Since Am(III), Am(V) and Am(VI) do not react with each other under the conditions of these experiments, the products obtained in the different acids can be fully accounted for only by assuming that all of the americium was originally in its tetravalent state.

(3) Tetravalency of americium in the new compound was also confirmed when the black hydroxide was dissolved in an acidic solution of Am(V). Decrease of the Am(V) concentration could only occur through oxidation by Am(IV). It was found that reaction (2) is still essentially negligible even when $Am(OH)_4$ is dissolved in HNO_3 containing an amount of Am(V) roughly equal to the amount of $Am(OH)_4$. As expected, reaction (2) is significantly increased in sulphuric acid when additional Am(V) is present. As a separate experiment, it was confirmed that the concentration of Am(V) in 0.5 M sulphuric acid is *not* changed when $Am(OH)_3$ is dissolved in it. Results are shown in Table 4.

(4) We had hoped that absorption lines characteristic of a new valence state would be observed. However, the absorption spectrum of the brown-black slurry gave only general absorption from 4500 to 10,000 Å with the Cary Recording Spectrophotometer. In contrast, the absorption spectrum of an $Am(OH)_3$ slurry gives sharp lines only slightly shifted from their characteristic positions in acid solution. The absorption spectra data thus rule out the presence of $Am(OH)_3$ in the black material even though no significant absorption from Am(IV) was found.

In very dilute HNO₃; e.g., 0.05 M, particularly at 0°C, $Am(OH)_4$ dissolves tantalizingly slowly and it was possible to examine this process in the spectrophotometer. A high general absorption was observed which diminished as the characteristic absorption peaks of Am(III) and Am(V) grew in. However, no discrete absorption lines were found which could be attributed to Am(IV).

Attempted dissolution of Am(OH)₄ in complexing media

Attempts were made to effect solution of Am(OH)₄ in various complexing media.

In acid solution, success would depend on the ability of a ligand to lower the activity of Am(IV) thus depressing the competing reaction of disproportionation. In basic media, the ligand must compete with the remarkable insolubility (K_{sp} ca. 10⁻⁵⁶) of Am(OH)₄.⁽¹²⁾ Americium tetrahydroxide was prepared by hypochlorite oxidation and was slurried with various complexing agents with the results shown in Table 5.

Reagent	Results				
2 M Li ₂ SO ₄ at pH 10	No dissolution, slow reduction to Am(III) only				
2 M Li ₂ SO ₄ at pH 10 - 0·1 M EDTA*	No dissolution, slow reduction to Am(III) only				
0-2 M DTPA† at pH 10	Only broad general continuum from 10,000–4,000 Å with Am(III) maxima slowly increasing				
0.2 M DTPA at pH 6	Only broad general continuum from 10,000–4,000 Å with Am(III) maxima slowly increasing				
0.2 M DTPA at pH 4	Only broad general continuum from 10,000–4,000 Å with Am(III) maxima slowly increasing				
0.2 M DTPA at pH 2	Only broad general continuum from 10,000–4,000 Å with Am(III) maxima slowly increasing				
Glacial acetic acid	Only broad general continuum from 10,000–4,000 Å with Am(III) maxima slowly increasing				
Glacial acetic acid + 0.001 M DTPA	Only broad general continuum from 10,000–4,000 Å with Am(III) maxima slowly increasing				
Dibutyl phosphoric acid	Continuum as above, with Am(III) slowly increasing; roughly 10% of Am appeared as Am(VI)				

Гавle 5.—.	Behaviour	OF	Am((OH)4	IN	VARIOUS	COMPLEXING	MEDIA
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* EDTA = ethylenediaminetetraacetic acid

† DTPA = diethylenetriaminepentaacetic acid

At pH 10 (even in DTPA), the black Am(IV) hydroxide precipitate appeared quite stable and the growth of Am(III) noted here is probably due only to slow reduction of the Am(IV) caused by the ²⁴¹Am α -radiation. From the Th(IV)-DTPA constant,⁽¹⁸⁾ one might predict the Am(IV)-DTPA complexity constant as ca. 10²⁸. Evidently, this is not sufficient to stabilize Am(IV). Dissolution in (undiluted) dibutyl phosphoric acid resulted in some Am(VI), presumably as a result of disproportionation of Am(IV) in this medium.

⁽¹⁰⁾ R. F. BOGUCKI and A. E. MARTELL, J. Amer. Chem. Soc. 80, 4170 (1958). 10

Oxidation of Am(OH)₃ with ozone

Ozone is one of the most powerful alkaline oxidizing agents, $E_{\rm B}^{\circ} = -1.24$ V. Its potential exceeds the value of not only the Am(OH)₃, Am(OH)₄ couple which we estimate at ca. -0.5 V, but exceeds the Am(OH)₄, AmO₂OH (-0.7 V) and the AmO₂OH, AmO₂(OH)₂ (-1.1 V) couples.⁽¹²⁾ Oxidation of Am(OH)₃ at least to AmO₂OH and possibly to AmO₂(OH)₂ is thus expected with ozone.

We find that ozone oxidizes $Am(OH)_3 past Am(OH)_4$ at all pH's from neutrality to 1 M NaOH. In 1 M NaOH, oxidation is very slow, requiring work at 0°C to increase the ozone solubility. Oxidation in 0.1 M NaOH at 25°C causes considerable oxidation to Am(VI), forming a soluble yellow complex.

Oxidation of a slurry of $Am(OH)_3$ in water with ozone occurs readily and was developed for the routine preparation of Am(VI) from Am(III). The following technique is recommended. Ozone is passed through a slurry of $Am(OH)_3$ in water at 90° for 1–2 hr, allowing the incoming ozone to stir the slurry vigorously. Dilute acid is then added dropwise to dissolve *part* of the oxidized material. The pH should not drop below 5 during this operation. If the slurry is made *too* acid (~0·1 M H⁺) at this time, any Am(III) (formed either from unoxidized Am(OH)₃ or from disproportionation of Am(IV)) cannot be oxidized further. Ozonization is continued for another hour. Additional acid is then slowly added to dissolve the remainder of the slurry and treatment with ozone is continued to oxidize any Am(V) to Am(VI).

Ozone oxidation of Am(OH)₃ to a hydroxy complex of Am(VI)

Evidence was obtained for the formation of a soluble hydroxide species of Am(VI). When $Am(OH)_3$ in 0.1 M NaOH was treated with O_3 , the supernatant liquid was yellow and contained considerable americium. The amount of soluble americium increased with time of ozonization. Spectral examination of this yellow solution indicated a continuum from 10,000 to 4,000 Å with no discernible maxima. After this yellow solution was slowly made acidic while being treated with ozone, the solution showed only the characteristic spectrum of hexavalent americium.

An attempt was made to produce this yellow hydroxide complex starting with an acidic solution of Am(VI): The experiment is complicated by the observation that, while AmO_2^{2+} is stable in acid solution at least up to pH 3, partial reduction to Am(V) occurs around neutrality. Therefore, ozone was bubbled through the Am(VI) solution while 2 M NaOH was added dropwise. A dark-brown precipitate formed at about pH 7 which *redissolved* to give a yellow solution at pH 13. The spectrum of this yellow solution was identical with that obtained previously.

When an acid solution containing Am(V) is made basic, a colourless supernatant is obtained although Am(V) is slightly soluble in base. Treatment with ozone produces the yellow colour of the hexavalent americium hydroxide complex. The spectrum of the hydroxide complex of Am(VI) was unaltered by addition of NaF or Na₂SO₄. These anions affect considerably the colour of Am(VI) in acidic media.

Remarks on the Am(OH)₃, Am(OH)₄ potential

LATIMER⁽¹²⁾ estimated K_{sp} for Am(OH)₄ as 10^{-56} based on the progression in hydroxide solubility products of Th(IV), U(IV), and Pu(IV). He estimated K_{sp} of Am(OH)₃ as 2.7×10^{-20} . The Am³⁺, Am⁴⁺ couple was taken as -2.18 V. For 1 M hydroxide, one estimates -0.02 V for the Am(OH)₃, Am(OH)₄ couple, not +0.4 V as given. Allowing for the latest value of the Am^{3+} , Am^{4+} couple $(-2.44 \text{ V})^{(11)}$ gives ca. -0.3 V for the $Am(OH)_3$, $Am(OH)_4$ couple in molar base. Several arguments suggest that this value is not sufficiently negative:

(1) Our experience at pH 7-8 is that K_{sp} of Am(OH)₃ is about 10⁻²⁴. This would make the Am(OH)₃, Am(OH)₄ potential more negative by ca. -0.24 V.

(2) Oxygen does not oxidize $Am(OH)_3$, although oxidation might be anticipated if the $Am(OH)_3$, $Am(OH)_4$ couple were less negative than the oxygen couple, $E_B^{\circ} = -0.4 \text{ V}$.

(3) Alkaline permanganate oxidizes $Am(OH)_3$ forming both manganate and MnO_2 as reduction products. The MnO_4^{2-} , MnO_4^{-} value of -0.56 V or the MnO_2 , MnO_4^{2-} value of -0.6 V may be controlling, although this is an insignificant difference for our purposes. (It might be mentioned here that bromate produced no oxidation of $Am(OH)_3$ although the bromide, bromate couple is -0.6 V in molar base. However, bromate is a notoriously slow oxidizing agent except in acid.)

We thus conclude that the $Am(OH)_3$, $Am(OH)_4$ potential in molar base is at least as negative as -0.5 V.

Since hypochlorite, $E_B^{\circ} = 0.89$ V, apparently does not oxidize Am(OH)₃ past Am(OH)₄, even after long treatment, LATIMER's estimate for the Am(OH)₄, AmO₂OH couple (-0.7 V) should perhaps be made more negative by a few tenths of a volt also.

Note added in proof—We are indebted to Prof. B. B. Cunningham, Univ. of Calif., Berkeley, for the following observation which he sent after reading a draft of our paper:

The published estimate of the value of the $Am^{+3} = Am^{+4} + e^{-}$ potential⁽¹¹⁾, was based on the assumption that the observed heat of reaction of AmO_2 with 6M $HNO_3 - 0.1$ M HBF₄ was due to the heat of solution of the dioxide plus the heat of reduction of Am(IV) by water. At the time this experimental work was done it was not known that the V and VI states of americum could be produced by dissolution of Am(IV) in acid solution.

It has since been found that in the solvent used in the calorimeter runs considerable amounts of Am(V) and Am(VI) are formed. Since the heats of formation of Am(V) and Am(VI) have been determined⁽¹⁰⁾, the old estimate of the potential of the $Am^{+3} = Am^{+4} + e^-$ couple may be corrected for disproportionation. The corrected value is about -2.6 to -2.9 V. However, this must be regarded as tentative until more extensive data are obtained.