Such studies are being undertaken in our laboratory.

The situation for corresponding technetium compounds is somewhat different. The lower stability of the pertechnetate ion causes TcO_3 to be unstable with respect to disproportionation in acid media, but the technitate ion, $TcO_4^=$ should be stable enough in basic media and even in very dilute acids to allow cell measurements to be made.

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The Heats of Formation of $AmO_2^+(aq)$ and $AmO_2^{++}(aq)$ in 1 M $HClO_4$[1]

BY S. R. GUNN[2] AND B. B. CUNNINGHAM

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The heats of reaction of $AmO_2^+(aq)$ and $AmO_2^{++}(aq)$ with $Fe^{++}(aq)$ in 1 M $HClO_4$ have been measured to be -72.2 ± 1.0 and -99.1 ± 0.2 kcal., respectively. From these and other thermodynamic data the heats of formation of $AmO_2^+(aq)$ and $AmO_2^{++}(aq)$ are calculated to be -207.7 ± 2.9 and -170.8 ± 2.7 kcal., respectively. The entropy difference $S_{AmO_2^{++}}(aq) - S_{AmO_2^+}(aq)$ is calculated to be -16 ± 4 e.u., and a self-consistent potential scheme for the various oxidation states of americium is given. A modified microcalorimeter used in the thermal measurements is described. The autoreduction of AmO_2^+ and AmO_2^{++} and the disproportionation of AmO_2^+ have been investigated.

Introduction

The present investigation was undertaken to secure thermodynamic and kinetic data on the aqueous ions of the higher oxidation states of americium. Estimates of the heats and free energies of the reactions

$$Am(c) + 3H^+(aq) = Am^{+3}(aq) + 3/2H_2(g) \quad (1)$$

and

$$Am^{+3}(aq) + H^+(aq) = Am^{+4}(aq) + 1/2H_2(g) \quad (2)$$

have been reported previously.[3,4]

All thermodynamic values calculated in this paper are for 298°K. and all values used in the calculations are taken from the National Bureau of Standards "Selected Values of Chemical Thermodynamic Properties" unless otherwise stated. The activity coefficients of the aqueous americium ions are not known; hence our heats of formation cannot be designated as $\Delta H°$ values, and the potential values are "formal" rather than "standard."

Experimental

Preparation of Americium Solutions.—The americium isotope used in this work was Am^{241}. Final purification was performed by oxidation-fluoride cycles.[5] Solutions of AmO_2^{++} were prepared by electrolytic oxidation in a cell consisting of three compartments separated by 1-cm. Pyrex "F" sintered discs. The anode and cathode were platinum wire spirals with surface areas of 3.0 and 0.3 cm.^{2}, respectively. The Am^{+3} in about 2 ml. of either 1 or 6 M $HClO_4$ was placed in the anode compartment and $HClO_4$ of the same concentration in the other two compartments. Electrolysis was performed at a current of 0.15 amp. with the cell immersed in an ice-bath; oxidation was 95% complete within 1 hour. For the calorimetric measurements the oxidized solution was then diluted to about 20 ml. with distilled water or dilute $HClO_4$ and used immediately for measurements of the heat of reduction of AmO_2^{++} or else was allowed to undergo autoreduction to AmO_2^+ for heat measurements on this species.

Autoreduction of AmO_2^+ and AmO_2^{++}.—Spectrophotometric observations of the autoreduction of AmO_2^+ and AmO_2^{++} were in reasonable agreement with the data reported by Asprey and Stephanou[6]; the rate laws are

$$-\frac{d(AmO_2^{++})}{dt} = \frac{d(AmO_2^+)}{dt} = 1.1 \times 10^{-5}(Am_{total})\ sec.^{-1} \quad (3)$$

and

$$-\frac{d(AmO_2^+)}{dt} = \frac{d(Am^{+3})}{dt} = 0.55 \times 10^{-5}(Am_{total})\ sec.^{-1} \quad (4)$$

The reduction is apparently effected mainly by hydrogen peroxide produced in the solution by the *alpha* radioactivity. An experiment in which extra hydrogen peroxide was added to a solution of AmO_2^+ showed the reaction to be first order with respect to (H_2O_2), the half-time being about 1 hour. The reaction of H_2O_2 with AmO_2^{++} was complete before spectra could be recorded, about 5 minutes after mixing.

Solutions of AmO_2^+ thus contain an appreciable steady-state concentration of hydrogen peroxide, but solutions of AmO_2^{++} contain very little peroxide. In freshly prepared solutions of AmO_2^+, the rate of autoreduction is initially zero and increases to the limiting value given by eq. 4 as the peroxide increases to its steady-state concentration. In mixed solutions of AmO_2^{++} and AmO_2^+, no AmO_2^+ is reduced to Am^{+3} until essentially all of the AmO_2^{++} has been reduced to AmO_2^+.

The Calorimeter.—A microcalorimeter previously used in this Laboratory[7] was extensively modified for the present work. The heater and thermometer consist of two coils of No. 42 B. and S. gage enameled copper wire of 40 and 25 ohms, respectively, wound bifilarly on a copper spool 0.010 inch thick, 0.56 inch in diameter and 0.65 inch long. The windings are enclosed by a 0.010 inch copper cover. The spool is centrally positioned in the reaction chamber and also

TABLE I

HEAT OF SOLUTION OF Mg IN 1.00 M HCl

Sample wt. (mg.)	Heat evolved, cal.	ΔH, kcal.
0.2280	1.039	-111.1
.1294	0.591	-111.4
.2192	1.002	-111.4

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[1] Abstracted in part from a dissertation submitted to the Graduate Division of the University of California by Stuart R. Gunn in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] University of California Radiation Laboratory, Livermore, California.

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[5] S. E. Stephanou and R. A. Penneman, *ibid.*, **74**, 3701 (1952).

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functions as a stirring well; it is supported from the copper chamber cap by four thin tubes through which the electrical leads are passed. All copper parts are gold plated; the chamber is tantalum. Because of the difficulty of soldering the cover over the heater-thermometer spool, the assembly was sealed by several baked coats of "Tygon" enamel.

The values agree well with that of −111.322 ± 0.041 determined by Shomate and Huffman.[8] The same correction for volatilized water has been applied.

The data are uncorrected for the heat of breakage of the small (~20-μl. volume) Pyrex bulbs used to hold the samples, since this heat was zero within the limits of sensitivity. The reductant solutions for the americium runs were contained in similar bulbs of 100-μl. volume; any heat of breakage would be eliminated from the final result on correction for the apparent heat of dilution of the reductant in blank runs.

Heat of Formation of AmO_2^{++}.—Two equal aliquots of the AmO_2^{++} solution were taken, one being treated in the calorimeter and the other titrated to determine the AmO_2^{++} concentration. The reducing solutions were weighed samples of 75 to 100 μl. of 0.88 *M* $Fe(ClO_4)_2$ in 1.00 *M* $HClO_4$; the correction for the heat of dilution was about 0.03 cal. Analysis of the americium solutions for AmO_2^+ or AmO_2^{++} consisted of addition of a slight excess of 0.1 *N* $Fe(ClO_4)_2$ from a gravimetrically calibrated micropipet followed by back-titration with 0.1 *N* $KMnO_4$ from a microburet, using 5 μl. of 0.025 *M* orthophenanthroline ferrous sulfate. This titration was performed as close to the time of the calorimetric reaction as possible, and the $(AmO_2^{++}):(AmO_2^+)$ ratio was measured spectrophotometrically at about the same time. Appropriate corrections were made for the AmO_2^+ present. The results of the measurements of the heat of the reaction

$$AmO_2^{++}(aq) + 3Fe^{++}(aq) + 4H^+(aq) = Am^{+3}(aq) + 3Fe^{+3}(aq) + 2H_2O(l) \quad (5)$$

are given in Table II.

TABLE II

HEAT OF REDUCTION OF AmO_2^{++} BY Fe^{++}

Run	AmO_2^+, μmoles	AmO_2^{++} μmoles	$HClO_4$, *M*	Heat evolved, cal.	−Δ*H*, kcal.
1[a]	1.08	14.16	1.30	1.436	95.9
2	.49	8.06	0.42	0.832	98.9
3	.38	6.42	1.15	.664	99.3
4	.58	9.31	1.28	.967	99.0

[a] Run No. 1 is rejected from the series to give an average value of Δ*H* = −99.1 ± 0.2 kcal.

Heat of Formation of AmO_2^+.—The heat of reduction measurements were performed in the same manner as the preceding series except that the AmO_2^{++} solution was allowed to undergo autoreduction until it was about 90% AmO_2^+. The data are presented in Table III.

TABLE III

HEAT OF REDUCTION OF AmO_2^+ BY Fe^{++}

Run	AmO_2^+, μmoles	AmO_2^{++}, μmoles	$HClO_4$, *M*	Heat evolved, cal.	−Δ*H*, kcal.
1	9.09	0.98	1.19	0.7507	71.9
2	9.33	.96	.84	.7719	72.5
3	9.21	.90	.9	.7673	73.6
4	9.58	.82	.92	.7621	71.0

The average value of Δ*H* for the reduction

$$AmO_2^+ + 2Fe^{++} + 4H^+ = Am^{+3} + 2Fe^{+3} + 2H_2O \quad (6)$$

is −72.2 ± 1.0 kcal.

The method of analysis eliminates errors from chemical impurities except for substances such as Cr or Mn which would be oxidized with the americium and reduced by Fe^{++}, and these would be effective only so far as their heats of reduction per equivalent differed from that of AmO_2^{++} or AmO_2^+. Spectrographic analysis of the americium gave upper limits of 0.2 wt. % each of Cr and Mn.

The spectrophotometric determination of the $(AmO_2^{++}):(AmO_2^+)$ ratio is accurate only to about 3%, but the error introduced is small since the heats of reduction per equivalent of the two species differ by only 10%.

Disproportionation of AmO_2^+.—The estimated potentials derived from thermal data indicate that AmO_2^+ should disproportionate in 1 *M* $HClO_4$ according to the reaction

$$3AmO_2^+ + 4H^+ = 2AmO_2^{++} + Am^{+3} + 2H_2O \quad (7)$$

This disproportionation of AmO_2^+ has been observed previously in 6 and 3 *M* $HClO_4$,[9] but is not seen in 1 *M* $HClO_4$. In the present work two series of spectrophotometric observations of the disproportionation of solutions of AmO_2^+ in 5.70 and 5.97 *M* $HClO_4$ gave data in agreement with the earlier measurements by Stephenou, Asprey and Penneman.[9] The combined data of the two investigations give the rate law

$$\frac{d(AmO_2^+)}{dt} = -1.1 \times 10^{-5}(AmO_2^+)^2(HClO_4)^4 \text{ moles l.}^{-1}\text{ sec.}^{-1} \quad (8)$$

The data indicate that the disproportionation follows the stoichiometry of reaction 7 within the limits of experimental error. The most probable mechanism would seem to be the rate-determining step

$$2AmO_2^+ + 4H^+ = AmO_2^{++} + Am(IV) + 2H_2O \quad (9)$$

followed by the rapid reaction

$$AmO_2^+ + Am(IV) = AmO_2^{++} + Am^{+3} \quad (10)$$

Detectable amounts of Am(IV) have not been found in aqueous solution.

In an initially pure solution of AmO_2^+, no appreciable concentration of AmO_2^{++} will appear unless the concentration of AmO_2^+ is greater than approximately 1.5 $(H^+)^{-4}$ mole liter^{-1}, since the AmO_2^{++} formed by reaction 7 will be reduced by the radiation-produced hydrogen peroxide.

Discussion

Using the value of Δ*H* = +9.95 kcal.[10] for the heat of oxidation of Fe^{++}

$$Fe^{++}(aq) + H^+(aq) = Fe^{+3}(aq) + 1/2H_2(g) \quad (11)$$

the heats of oxidation of Am(III) to Am(V) and Am(VI) may be calculated

$$Am^{+3}(aq) + 2H_2O(l) = AmO_2^+(aq) + 2H^+(aq) + H_2(g) \quad (12)$$

$$\Delta H = +92.1 \pm 1.0 \text{ kcal.}$$

$$Am^{+3}(aq) + 2H_2O(l) = AmO_2^{++}(aq) + H^+(aq) + 3/2H_2(g) \quad (13)$$

$$\Delta H = +129.0 \pm 0.3 \text{ kcal.}$$

These data, in combination with earlier values for the heats of reactions 1 and 2 (Δ*H* = −163.2 ± 2.7 kcal. and Δ*H* = +47 kcal., respectively), give the heats of formation summarized in Table IV.

TABLE IV

HEATS OF FORMATION OF THE AQUEOUS IONS OF AMERICIUM, KCAL.

Am^{+3}	−163.2 ± 2.7
Am^{+4}	−116 ± 6
AmO_2^+	−207.7 ± 2.9
AmO_2^{++}	−170.8 ± 2.7

The free energies and oxidation potentials of the various couples may be calculated from the data of Table IV by making use of estimated entropies; however, in view of the large discrepancies between the entropies given by Latimer[11] for the MO_2^+ type of actinide ion and the values found by Cohen and

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[8] C. H. Shomate and E. H. Huffman, THIS JOURNAL, **65**, 1625 (1943).

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[10] R. E. Connick and W. H. McVey, THIS JOURNAL, **73**, 1798 (1951).

[11] W. M. Latimer, "Oxidation Potentials," second edition, Prentice-Hall, Inc., New York, N. Y., 1952, pp. 302–306.

Hindman[12] for the corresponding neptunium ion, we shall use our value of $\Delta H = +36.9 \pm 1.0$ kcal. for the reaction

$$AmO^{+}_{2}(aq) + H^{+}(aq) = AmO_2^{+}(aq) + 1/2H_2(g) \quad (14)$$

in combination with the value of −1.60 v. reported by Penneman and Asprey[13] for this couple, to calculate $S_{AmO_2}{}^{++}(aq) - S_{AmO_2}{}^{+}(aq)$. Straight forward manipulation of the data yields −16 ± 4 e. u. for this difference. We then adopt, for the entropy of $AmO_2^{++}(aq)$, −18 e.u., the value given by Connick and McVey[10] for PuO_2^{++}, to obtain −2 for the entropy of $AmO_2^{+}(aq)$. We also adopt for $Am^{+4}(aq)$ the entropy of −77 e.u., given by Connick and McVey for $Pu^{+4}(aq)$ and take the difference in entropy $S_{Am}{}^{+4}(aq) - S_{Am}{}^{+3}(aq)$ to be −47 e.u., the same value as for $S_{Np}{}^{+4}(aq) - S_{Np}{}^{+3}(aq)$ found by Cohen and Hindman.[12] Finally the entropy of Am^0 is assumed to be 12 e.u., the same as that of U^0.

These entropy values in combination with the heat data of Table IV yield the following self-consistent potential scheme:

$$\begin{tikzcd}
Am^0 \arrow[r, dash, "+2.38\text{ v.}"] & Am^{+3}(aq) \arrow[r, dash, "-2.4\text{ v.}"] \arrow[rr, bend left, dash, "-1.83\text{ v.}"] \arrow[rrr, bend right, dash] & Am^{+4}(aq) \arrow[r, dash, "-1.2\text{ v.}", "-1.75\text{ v.}"'] & AmO_2^{+}(aq) \arrow[r, dash, "-1.60\text{ v.}"] & AmO_2^{++}(aq)
\end{tikzcd}$$

The more reliable values are given to the nearest 0.01 v. and the less reliable to 0.1 v. At best, however, the potentials are uncertain by 0.05 v. and those involving $Am^{+4}(aq)$ by 0.2 v.

It is recognized that differences in ground-state multiplicities of analogous actinide ions will lead to variations in entropy of 1 to 2 entropy units, and that the contraction in ionic radius with increasing atomic number will cause the entropies to become more negative along the series. At present, however, it is not possible to evaluate these effects adequately. It does seem most probable, however, that the entropy values assigned by Latimer to the MO_2^{+} type of actinide ions are too positive by some 15 to 20 entropy units. The linear structure and high formal charge on the MO_2^{+} type of ion should permit close approach and marked ordering of water of hydration, as compared with the large alkali cations, to which Latimer's entropy values correspond.

Use of the longer-lived isotope Am^{243} in studies on the disproportionation of AmO_2^{+} in 1 *M* H^{+} may yield equilibrium values that will define the ratio of the potentials of the 3–5 and 3–6 couples more precisely than is possible from the present data. In solutions of Am^{241} of conveniently realizable concentrations the disproportionation in 1 *M* acid is completely masked by autoreduction.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BROOKHAVEN NATIONAL LABORATORY]

Radiation Chemistry Studies with Cyclotron Beams of Variable Energy: Yields in Aerated Ferrous Sulfate Solution[1]

BY ROBERT H. SCHULER[2] AND AUGUSTINE O. ALLEN

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Yields of ferrous ion oxidation and of hydrogen gas evolution in air- or oxygen-saturated solutions of ferrous sulfate in 0.8 *N* sulfuric acid have been determined for beams of helium ions and deuterons of various energies. From the results, the yields of total net water decomposed and of hydrogen atoms produced are found. The results are compared with those reported in the literature for various types of radiation, and are discussed in terms of the free radical model of water radiolysis.

A key phenomenon in the radiolysis of water and aqueous solutions is the variation of yields with the type of radiation. Ferrous sulfate solution is advantageously used for such studies, since the reaction mechanism is believed to be well understood[3-5] and precise measurements of the yield are made with relative ease. A considerable number of reports have appeared on yields found on irradiation of ferrous sulfate solutions with a wide variety of types of radiation. The cyclotron is one of the most useful radiation sources for studies of this kind, in that it provides beams of charged particles of precisely known initial speed which can be varied at will over a considerable range. Preliminary data on the effect of deuteron and helium ion beams on ferrous sulfate solutions have been published by the present authors[6] and further work has been performed with proton and deuteron beams by Hart, Ramler and Rocklin.[7] This paper

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[1] Research carried out under the auspices of the U. S. Atomic Energy Commission.

[2] Department of Radiation Research, Mellon Institute, Pittsburgh 13, Pa.

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