TABLE IV

STANDARD HEATS OF FORMATION AND M–M BOND ENERGIES OF SOME GASEOUS HIGHER HYDRIDES OF THE GROUP IVB AND VB ELEMENTS

(in kcal./mole)

	Si_2H_6		Ge_2H_6		Ge_3H_8	Sn_2H_6	P_2H_4		As_2H_4	Sb_2H_4
	This work	Gunn and Green	This work	Gunn and Green	This work	This work	This work	Gunn and Green	This work	This work
$\Delta H_f^0(g)$	15.1	17.1	39.1	38.7	48.4	65.6	9.9	5.0	35.2	57.2
B.e.(M–M)	39.7	46.4	33.2	37.9	27.9	29.9	43.7	46.8	44.7	30.7

the assumed ion source reactions are correct. The poorest pair of values are those for $\Delta H_f^0(g)$ diphosphine but even these may be reconciled considering the fact that 1 e.v. is equivalent to 23.0 kcal. and our measuring uncertainties were slightly higher than usual when the work was done with this compound.

The trend of increasing ΔH_f^0 with increasing atomic number should be noted. A reverse trend is true for the M–M bond energies except for the (P–P) and (As–As) bonds, which are of equal strength. This is not entirely unexpected due to the other anomalous properties of the fourth row elements.

It is hoped that the problems pointed out in this paper indicate the need for improved methods of synthesizing some of these compounds so their thermochemical properties can be measured more accurately. At present, synthetic methods for all the compounds of this study are not adequate to allow for direct calorimetric measurements. However, any improvements in the syntheses will make it expedient that more refined mass spectrometric techniques be applied in the future. For the present, however, the results given in this paper can stand well alongside existing, comparable calorimetric results.

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The Kinetics of the Disproportionation of Americium(V)[1]

BY JAMES S. COLEMAN

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Use of the isotope Am^{243} ($T_{1/2}$ = 7951 years) has made possible the first observations of the disproportionation of Am(V) unobscured by the effects of radiolysis. The net reaction is: $3AmO_2^+ + 4H^+ \rightarrow 2AmO_2^{++} + Am^{+3} + 2H_2O$. The rate at 75.7° in perchlorate solutions of ionic strength 2 M is given by $-d(AmO_2^+)/dt = k_2(H^+)^2(AmO_2^+)^2 + k_3(H^+)^3(AmO_2^+)^2$, with k_2 and k_3 equal to $7.0 \times 10^{-4}\ M^{-3}\ sec.^{-1}$ and $4.6 \times 10^{-4}\ M^{-4}\ sec.^{-1}$, respectively. Estimation of the difference in the entropies of activation for the parallel paths suggested by this rate law combined with rate measurements at 60–85° gives $\Delta H_2^* = 16.5$ kcal./mole, $\Delta S_2^* = -26$ e.u., $\Delta H_3^* = 10.5$ kcal./mole, $\Delta S_3^* = -44$ e.u. At 75.7°, the rates in 2 N HNO_3, HCl, and H_2SO_4 are 4.0, 4.6, and 24 times as great as that in 2 N $HClO_4$. At room temperature, the reaction rate increases by a factor of 450 in going from 3 to 8 M perchloric acid. Observation of the oxidation of Am(III) by Am(VI), the reverse of the disproportionation reaction, is reported for the first time.

Introduction

The disproportionation of Am(V) has been observed in hydrochloric,[2] sulfuric,[3] nitric,[3] and perchloric[3–5] acids using the isotope Am^{241}. The α-decay of the Am^{241} led to radiolytic reduction of Am(VI) to Am(V) at a rate which, during most of the previous experiments, was roughly equal to that of the disproportionation reaction. This has resulted in disagreement regarding even the stoichiometry of the reaction. Hall and Markin[4b] and Stephanou, *et al.*,[4a] concluded that the reaction 2Am(V) → Am(VI) + Am(IV) is followed by immediate reduction of Am(IV) by water so that the apparent reaction is 2Am(V) → Am(VI) + Am(III). On the other hand, Zaitsev, *et al.*,[3] and Gunn and Cunningham[5] suggest the stoichiometry 3Am(V) → 2Am(VI) + Am(III) during which the average oxidation number of the americium is conserved.

Each study has confirmed that the rate of disproportionation is directly proportional to the square of the Am(V) concentration. Zaitsev, *et al.*,[3] reported specific rate constants in 4, 6, and 9 M perchloric acid and suggested that the rate is directly proportional to the fourth power of the hydrogen ion concentration. Similar results are reported in the earlier work of

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[1] This work was done under the auspices of the U. S. Atomic Energy Commission.

[2] G. R. Hall and P. D. Herniman, *J. Chem. Soc.*, 2214 (1954).

[3] A. A. Zaitsev, V. N. Kosyakov, A. G. Rykov, Yu. P. Sobolev, and G. N. Yakovlev, *Radiokhimiya*, **2**, 339 (1960).

[4] (a) S. E. Stephanou, L. B. Asprey, and R. A. Penneman, AECU-925 (1950); (b) G. R. Hall and T. L. Markin, *J. Inorg. Nucl. Chem.*, **4**, 296 (1957).

[5] S. R. Gunn and B. B. Cunningham, *J. Am. Chem. Soc.*, **79**, 1563 (1957).

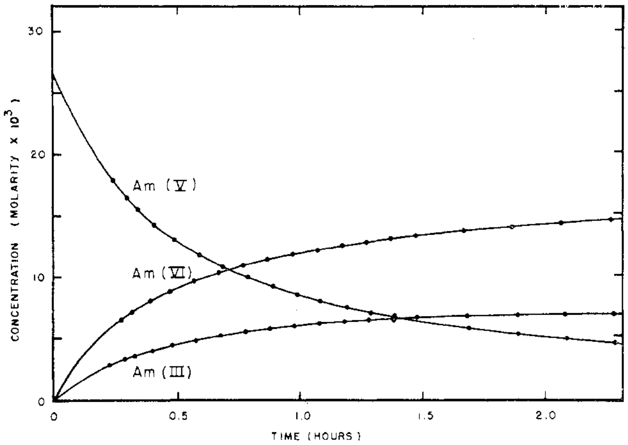

Fig. 1.—The disproportionation of Am(V) in 6 *M* perchloric acid at 25°.

Stephanou, *et al.*[4a] Such a high acid dependence is unexpected, particularly in view of the acid dependences found for analogous reactions of other actinides.[6]

The present study was undertaken when 6 mg. of americium became available containing 98% by weight Am^{243} and 2% Am^{241}. The specific activity of this material is only 0.089 times that of isotopically pure Am^{241}. Its use in the study of the kinetics of the reactions of americium has important advantages. For the first time, the disproportionation of Am(V) could be observed essentially free from the effects of radiolysis. The qualitative features of the reaction could be established unequivocally, and determination of the reaction rates could be made with greatly improved accuracy. This study also has emphasized measurements at lower acidities and lower ionic strengths than those previously used. For this purpose it has proved convenient to go to higher temperatures.

Experimental

The concentrations of Am(III), Am(V), and Am(VI) were followed spectrophotometrically throughout the course of each run using the absorption maxima which occur at 812, 717, and 995 mμ, respectively. The Cary Model 14M spectrophotometer employed for these measurements was equipped with a double-walled sample compartment maintained at 25°. The samples were contained in 0.6-ml. cells of 1 cm. path length fitted with double stoppers to avoid the spread of radioactive contamination. For the runs at 60–85°, the reaction was quenched before each spectrophotometric measurement by transferring the cell from a water bath held at the higher temperature to one held at 25°. Ordinarily, no correction was necessary for the extent of the reaction at the lower temperature. A layer of fluorocarbon oil (Fluorolube S-30, Hooker Electrochemical Co.) was floated above the sample in the neck of the cell during the runs at 60–85° to avoid evaporation. The fluorocarbon oil was found, in separate experiments, to have no detectable effect on the course of the reaction.

For each experiment the Am^{243} was recovered and converted to Am(V) by (1) ozone oxidation of Am(III) in 2 *M* sodium carbonate to a soluble Am(VI) carbonate complex at room temperature[7] and (2) heating this solution for 30 min. at 90° to precipitate sodium americyl(V) carbonate. When the latter salt was dissolved in acid, the resulting Am(V) solutions were essentially free of Am(VI) and Am(III). The concentration of acid was determined by addition of an excess of base to a portion of each sample and subsequent back-titration with acid to the brom phenol blue end point.

The lithium perchlorate used in maintaining constant ionic strength was the recrystallized product obtained by the neutralization of Mallinckrodt reagent grade lithium carbonate with this manufacturer's reagent grade 70% perchloric acid. The water was de-ionized using a commercial mixed bed unit. In some experiments the 70% perchloric acid was boiled and filtered and the water was redistilled from alkaline permanganate solution prior to use. These additional precautions had no observable effect.

Results and Discussion

Stoichiometry of Am(V) Disproportionation.—The concentrations of Am(III), (V), and (VI) during disproportionation of Am(V) in 6 *M* perchloric acid are shown in Fig. 1. During the period shown, the reaction became over 80% complete but the average oxidation number decreased less than 0.2%. The stoichiometry corresponds at all times to

$$3\mathrm{Am(V)} \longrightarrow 2\mathrm{Am(VI)} + \mathrm{Am(III)} \qquad (1)$$

The average oxidation number of the americium decreased linearly with time from 5.00 to 4.93 during continued observation over the next 20 hr. Such a decrease is characteristic of autoreduction. Further, this rate of decrease is about 0.1 that observed by Zaitsev, *et al.*, for the autoreduction of Am^{241}(VI) in 6 *M* perchloric acid,[8] just as expected from the lower specific activity of the americium used in this study.

The concentrations of americium in each of its oxidation states were similarly observed during each of the experiments described herein. The observed stoichiometry was consistent with reaction 1 throughout the ranges of perchloric acid concentration and temperature which were used. The same stoichiometry also was observed in nitric, sulfuric, and dibutylphosphoric acids. In hydrochloric acid no Am(VI) was detected since Am(VI) is rapidly reduced by chloride ion in acidic solution.

These results confirm the necessarily less direct conclusions of Gunn and Cunningham[5] and of Zaitsev, *et al.*[3] It has not been necessary to consider the reduction of the intermediate Am(IV) by water postulated by Stephanou, *et al.*,[4a] and Hall and Markin.[4b] The original results of Stephanou, *et al.*, have been reviewed in detail and the observed stoichiometry has been found consistent with that reported here if suitable account is taken of the rapid autoreduction caused by the Am^{241}.

The Effect of Am(V) Concentration on the Rate of its Disproportionation.—In each experiment, the rate of disproportionation was found to be proportional to the square of the Am(V) concentration as suggested by the previous work.[2–5] Under the conditions used, reaction 1 proceeds essentially to completion and, in fact, no indication of the back reaction was observed.

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(6) T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 365 (1959).

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

(8) A. A. Zaitsev, V. N. Kosyakov, A. G. Rykov, Yu. P. Sobolev, and G. N. Yakovlev, NP-7515; for English translation see AEC-tr-3985.

With Am^{243}, the plots of the reciprocal of the Am(V) concentration *vs.* time remained linear for as much as the first 80% of the reaction. As a result of autoreduction, some curvature became evident even with Am^{243} as the disproportionation reaction became very slow near its completion. In every case, the slight curvature was fully accounted for on the basis of the separately determined rate of the autoreduction. These results confirm that during the disproportionation reaction, two americyl(V) ions are used in forming each activated complex.

The rate-determining step may be represented by

$$\mathrm{Am(V)} + \mathrm{Am(V)} \xrightarrow{k} \mathrm{Am(VI)} + \mathrm{Am(IV)} \text{ (rate-determining)} \quad (2)$$

with k for this step defined by $-d[\mathrm{Am(V)}]/dt = 2k \cdot [\mathrm{Am(V)}]^2$. The Am(IV) produced in reaction 2 evidently appears only as an intermediate species of very low concentration. Material balance precluded the presence of more than 0.2% of the americium as Am(IV); further the spectra from 400 to 1200 mμ obtained during each experiment showed no absorption which could not be fully ascribed to the other americium species known to be present, and, in particular, gave no indication of the characteristic Am(IV) peak at 456 mμ.[9–10]

The Am(IV) may be consumed as a result of either of two reactions consistent with the observed stoichiometry,[11,12] Am(IV) disproportionation

$$2\mathrm{Am(IV)} \longrightarrow \mathrm{Am(V)} + \mathrm{Am(III)} \quad (3)$$

or reduction by Am(V)

$$\mathrm{Am(IV)} + \mathrm{Am(V)} \longrightarrow \mathrm{Am(III)} + \mathrm{Am(VI)} \quad (4)$$

Reaction 3 predominates during dissolution of americium(IV) hydroxide in perchloric acid, but reaction 4 makes an appreciable contribution even under these conditions.[11] At the very high Am(V)/Am(IV) ratios occurring during disproportionation of Am(V), neglect of Am(IV) disproportionation appears justified in comparison with reduction of Am(IV) by Am(V). With this plausible assumption, the rate law for the over-all change at constant acidity may be written $-d[\mathrm{Am(V)}]/dt = 3k[\mathrm{Am(V)}]^2$.

Disproportionation of Am(V) in $\mathrm{HClO_4}$ at 25°.—The rates of disproportionation of Am(V) in 3–8 *M* perchloric acid at 25° are shown in Fig. 2. These measurements cover the range of concentrations considered in several of the earlier studies.[4,5] The most extensive of the previous studies is that of Zaitsev, *et al.*,[3] and their results in perchloric acid also are shown in the figure. Their rate measurements depended on spectrophotometric determination of small Am(V) concentrations in the presence of Am(VI). In view of the difficulties such determinations impose, the agreement between the two sets of results appears reasonable.

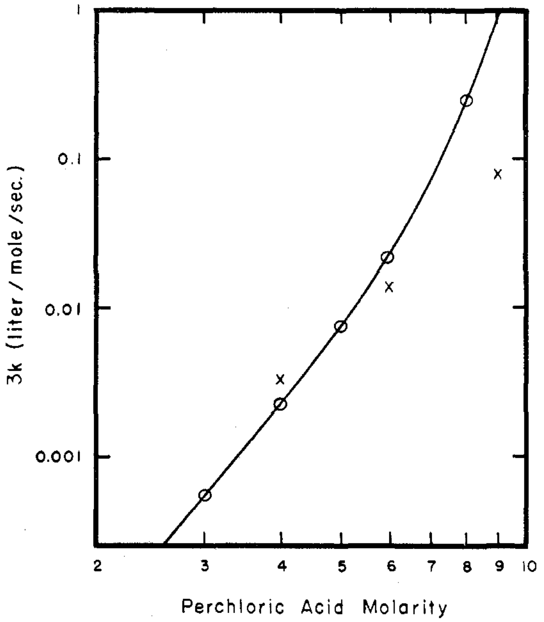

Fig. 2.—Rates of disproportionation of Am(V) in perchloric acid at 25°: O, this work; ×, Zaitsev, *et al.*, in ref. 3.

The solid curve in Fig. 2 corresponds to an empirical expression of the form $3k = aM^5 + bM^{13}$ in which M is the perchloric acid molarity and a and b are 2.25×10^{-6} and 3.3×10^{-13}, respectively. These results fail to confirm the previously suggested dependence of the rate on the fourth power of the perchloric acid molarity.[3,4a]

The measured rates probably reflect not only the changing acidity but also profound changes in the structure of the solutions. The effective acidity itself, at least as measured by the Hammett acidity function, varies from 17 *M* (at 3 *M* $\mathrm{HClO_4}$) to 21,400 *M* (at 8 *M* $\mathrm{HClO_4}$).[13] Rather than attempt deduction of the reaction mechanism in the face of such overwhelming medium effects, additional experiments were carried out as described in the next section to isolate the effects of changing acidity.

Disproportionation of Am(V) in 1–2 *M* $\mathrm{HClO_4}$ at 75.7°.—At higher temperatures, use of lower acidities and, hence, lower ionic strengths becomes feasible. The conditions become comparable to those under which many other oxidation–reduction reactions of actinide elements have been studied.[6] Accordingly, the measurements shown in Fig. 3 were carried out at 75.7° in lithium perchlorate–perchloric acid mixtures of ionic strength 2. The rate was found to be proportional to the 2.5 power of the perchloric acid molarity.

Two types of mechanism have been used for describing similar reactions with non-integral hydrogen ion dependences. Newton found that in the reaction between Pu(VI) and U(IV) the system passes consecutively through two activated complexes.[14] The results of Fig. 3 can be adequately represented by an analogous mechanism involving activated complexes

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(9) L. B. Asprey and T. K. Keenan, *J. Inorg. Nucl. Chem.*, **7**, 27 (1958).

(10) L. B. Asprey and R. A. Penneman, *J. Am. Chem. Soc.*, **83**, 2200 (1961).

(11) R. A. Penneman, J. S. Coleman, and T. K. Keenan, *J. Inorg. Nucl. Chem.*, **17**, 138 (1961).

(12) A. A. Zaitsev, V. N. Kosyakov, A. G. Rykov, Yu. P. Sobolev, and G. N. Yakovlev, NP-7517; for English translation see AEC-tr-3885.

(13) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

(14) T. W. Newton, *J. Phys. Chem.*, **62**, 943 (1958).

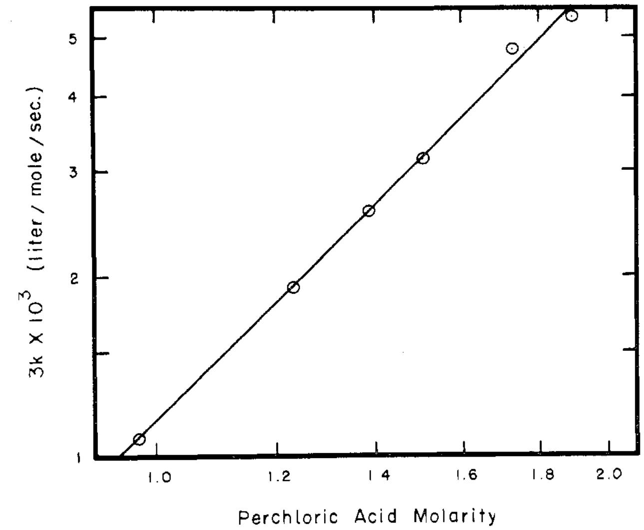

Fig. 3.—Rates of disproportionation of Am(V) in lithium perchlorate–perchloric acid mixtures at 75.7° and ionic strength 2 *M*.

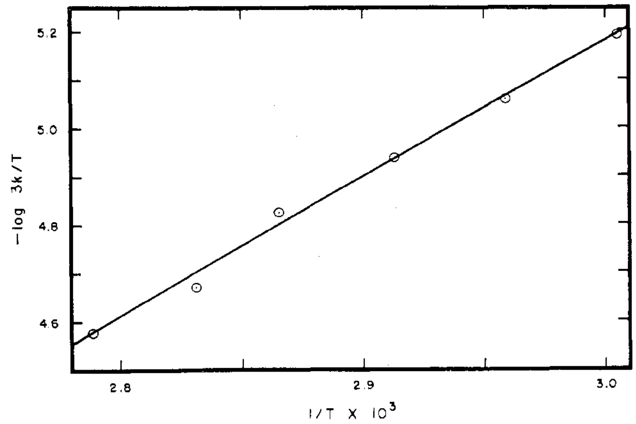

Fig. 4.—Rates of disproportionation of Am(V) in 1.92 *M* perchloric acid at 59.6–85.4°.

formed from two AmO_2^+ ions and, successively, two and three hydrogen ions. A detailed discussion of application of this type of mechanism to several reactions is given in reference 14 and will not be repeated here.

The alternative type of mechanism involves parallel paths with differing hydrogen ion dependences. For this case, the results in 1–2 *M* $HClO_4$ correspond to independent formation of activated complexes with two and with three hydrogen ions per pair of americyl(V) ions. The reaction rate is governed by eq. 5.

$$-d(AmO_2^+)/dt = 3k(AmO_2^+)^2 = k_2(H^+)^2(AmO_2^+)^2 + k_3(H^+)^3(AmO_2^+)^2 \quad (5)$$

The solid line in Fig. 3 corresponds to this equation with k_2 and k_3 equal to $7.0 \times 10^{-4}\ M^{-3}$ sec.$^{-1}$ and $4.6 \times 10^{-4}\ M^{-4}$ sec.$^{-1}$, respectively, and may be seen to fit the experimental points very adequately.

Although the acid dependence indicated by these results is lower than the previously suggested fourth power dependence, it remains higher than that observed for the disproportionation of either U(V)[15,16] or Pu(V).[17] The latter two reactions both have been reported to be first order in H^+. This difference is not unexpected, since Newton and Rabideau[6] have noted that many formally identical reactions among the actinides proceed by mechanisms with somewhat different hydrogen ion dependences. They conclude the observed paths are favored over other possible ones on the basis of relatively small differences in heat and entropy terms.

Temperature Dependence of Americium(V) Disproportionation.—Measurements of the rate of disproportionation of Am(V) in 1.92 *M* perchloric acid from 59.6 to 85.4° are shown in Fig. 4. These results may be shown to provide a direct estimate of the average enthalpy of activation for the parallel paths suggested by the observed acid dependence, and this mechanism will be assumed in the following discussion. The observed rate constants may be expressed in terms of

$$\overline{\Delta H^*} = {}^1/_2(\Delta H_2^* + \Delta H_3^*),\ \overline{\Delta S^*} = {}^1/_2(\Delta S_2^* + \Delta S_3^*),\ \delta H^* = {}^1/_2(\Delta H_2^* - \Delta H_3^*), \text{ and } \delta S^* = {}^1/_2(\Delta S_2^* - \Delta S_3^*)$$

where the subscripts 2 and 3 refer to the paths second and third order in hydrogen ion. Using eq. 5 and the equations of the transition state theory[18]

$$\ln 3k/T = \overline{\Delta S^*}/R - \overline{\Delta H^*}/RT + \ln\cosh\,[\delta H^*/RT - \delta S^*/R + {}^1/_2 \ln (H^+)] + {}^5/_2 \ln (H^+) + \ln 2k/h \quad (6)$$

The free energies of activation for the two paths are nearly equal so that $\delta H^*/RT - \delta S^*/R$ is very small. To an excellent approximation, the term in eq. 6 involving the hyperbolic cosine drops out and the slope d ln $(3k/T)/d(1/T)$ is equal to $-\overline{\Delta H^*}/R$.

A further step is made possible by the successful correlation by Newton and Rabideau[6] of the entropies of activation of twenty oxidation–reduction reactions of the actinides. On the basis of this correlation and its refinement by Masters[19] δS^* may be estimated to be 9 ± 2.5 entropy units. The values of ΔH^* and ΔS^* obtained in this fashion are shown in Table I. The uncertainties shown for the average values reflect the experimental error and correspond to one standard deviation. The uncertainties for the separate paths reflect, in addition, the asumed uncertainty in the estimate of δS^*.

Table I

Free Energy, Enthalpy, and Entropy of Activation for Disproportionation of Am(V)

	ΔF^*, kcal./mole at 75.7°	ΔH^*, kcal./mole	ΔS^*, e.u.
Average	25.70	13.5 ± 0.5	−35.0 ± 1.4
2nd order path	25.56	16.5 ± 1.5	−26.0 ± 3.9
3rd order path	25.85	10.5 ± 1.3	−44.0 ± 3.9

Observation of the Back Reaction.—Reaction 7,

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[15] D. M. H. Kern and E. F. Orleman, *J. Am. Chem. Soc.*, **71**, 2102 (1949).

[16] H. Imai, *Bull. Chem. Soc. Japan*, **30**, 873 (1957).

[17] S. W. Rabideau, *J. Am. Chem. Soc.*, **79**, 6350 (1957).

[18] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 196.

[19] B. J. Masters, Physical Paper No. 28, A.A.A.S. Meeting, Phoenix, 1961.

the reverse of the disproportionation reaction, was

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

observed upon addition of Am(III)–Am(VI) mixtures to aluminum perchlorate buffer at pH 4. It also was found to occur upon neutralization of Am(III)–Am(VI) mixtures with sodium bicarbonate, although in this case the acid produced rapidly quenched the reaction. These are the first observations of reaction 7 to be reported. Study of the kinetics of this reaction was not attempted, since the results were obscured by reduction of Am(VI) to Am(V) occurring at pH $\geqq$ 4 even in the absence of Am(III) and probably as a result of reaction of Am(VI) with water. At pH $\leqq$ 2.8 the Am(VI)–water reaction was suppressed. However, reaction 7 became too slow to detect even with the highest americium concentrations (0.02 M Am(VI) and 0.01 M Am(III)) found feasible in this study.

Autoreduction of Am^{243}(VI) at 75.7°.—To provide a basis for suitable correction of the disproportionation results at 75.7°, the autoreduction of Am^{243}(VI) was examined at this temperature in 2.18 M perchloric acid. The average oxidation number of the americium decreased linearly with time throughout the course of the experiment at a rate of 0.024/hr. This rate is about six times that observed at room temperature. The concentration of Am(V) reached a steady state in about 20 hr. The observed increase in Am(III) concentration equaled that computed from the known rate of disproportionation of Am(V), so that, just as at room temperature, autoreduction in the presence of Am(VI) proceeds by the reaction: Am(VI) + products of radiolysis → Am(V).

Effect of Other Anions.—The rate of disproportionation of Am(V) also has been studied in about 2 N hydrochloric, nitric, and sulfuric acids at 75.7°. In each of these media, the rate of reaction remains directly proportional to the second power of the Am(V) concentration. The results are given in Table II.

TABLE II

DISPROPORTIONATION OF Am(V) IN VARIOUS ACIDS AT 75.7°

Medium	d[1/Am(V)]/dt, l./mole/sec.
1.92 N $HClO_4$	5.20
1.86 N HCl	24
1.85 N HNO_3	21
1.81 N H_2SO_4	124

In hydrochloric acid no detectable amounts of Am(VI) were produced[2]; reaction 2 presumably is followed by rapid reduction by chloride ion of Am(VI) to Am(V) and, very likely, of Am(IV) to Am(III). In the other acids, the average oxidation number of the americium was found to be conserved within experimental error. The hydrogen ion concentration in the sulfuric acid experiment is about a factor of two less than that of the other acids used, although the rate constant is many times greater. The striking differences in rate of disproportionation due to the nature of the anion deserve further study. Such studies may indicate whether anions are included in the activated complex.

An attempt was made to stabilize the intermediate Am(IV) by carrying out the disproportionation of Am(V) in dibutylphosphoric acid. Potassium americyl(V) carbonate dissolved readily in this water-immiscible extractant, but disproportionation into Am(VI) and Am(III) was complete at room temperature within the few minutes elapsing before spectrophotometric examination of the sample.

Acknowledgments.—The author wishes to express his appreciation for helpful discussions with Drs. T. W. Newton and B. J. Masters and for the continued interest of Dr. R. A. Penneman, under whose general direction the work was performed. It is also a pleasure to acknowledge the assistance of Mr. Richard Chanda in carrying out many of the spectrophotometric measurements, and the help of Drs. W. M. Manning and P. Fields of Argonne National Laboratory in securing the Am^{243}.