The Separation and Purification of Americium-241 and the Absorption Spectra of Tervalent and Quinquevalent Americium Solutions.

By G. R. HALL and P. D. HERNIMAN.
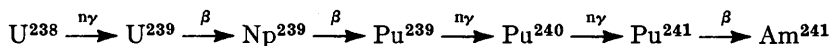
The separation and purification of americium-241 (25 mg.), produced by the β-decay of plutonium-241 in plutonium containing small amounts of the latter isotope, is described.

The absorption spectra of americium(III) in perchloric acid and in hydrochloric acid have been measured. The narrow 504-mμ peak does not obey either Beer's or Lambert's law; the 814-mμ peak obeys both.

By following changes in the absorption spectra the disproportionation and self-reduction of americium(V) in hydrochloric acid have been observed. Self-reduction is caused by reducing materials produced in solution by α-particle bombardment. In low acid concentrations only self-reduction occurs, but in more concentrated acid solutions disproportionation predominates.

The Separation and Purification of Americium by Carrier-free Methods.—Americium-241 is the β-decay product of plutonium-241, whose half life is $13 \cdot 0 \pm 0 \cdot 2$ years (MacKenzie, Lounsbury, and Boyd, *Phys. Review*, 1953, **90**, 327). Plutonium-241 is formed from uranium-238 in a nuclear reactor by the series of reactions :

$$U^{238} \xrightarrow{n\gamma} U^{239} \xrightarrow{\beta} Np^{239} \xrightarrow{\beta} Pu^{239} \xrightarrow{n\gamma} Pu^{240} \xrightarrow{n\gamma} Pu^{241} \xrightarrow{\beta} Am^{241}$$

As plutonium-241 is the product of three successive neutron captures, the quantity formed, compared with plutonium-239, is small except for long irradiations. The separation of americium from irradiated uranium would be extremely difficult because of the enormous activities of the fission products, especially as compounds of the stable valency, americium(III), are isomorphous with the corresponding rare-earth compounds which comprise an appreciable fraction of the total fission products. It is more convenient to start from partially purified plutonium, free from fission products, containing reasonable amounts of plutonium-241. If this is allowed to decay for a suitable period the americium can be extracted by using only glove-box handling techniques. Remote handling methods are necessary if fission products are present.

The 10 mg. of americium used for the absorption-spectra measurements were extracted from many grams of plutonium. Precipitation of the plutonium as plutonium(IV) peroxide separated most of the plutonium from the americium which is not precipitated (Milsted, 1953, H.M.S.O., A.E.R.E., report C/R 1102). The supernatant liquor contained small amounts of plutonium, uranium, and iron, and all the americium, and provided the starting material for the separations which are described.

Americium-241 is an α-emitter. Its half-life of 470 years (Harvey, *Phys. Review*, 1950, **85**, 482) corresponds to a specific activity of $7 \cdot 0 \times 10^6$ α-particles/min./μg. There are also some soft electromagnetic radiations (Beling, Newton, and Rose, *Phys. Review*, 1952, **86**, 797) with a particularly abundant 60 kev radiation (0·40 per α-particle).

Although the chemical properties of uranium, plutonium, and americium are similar there is an increasing tendency for lower valency states to become the most stable. In uranium the sexavalent state, the uranyl ion, is difficult to reduce whereas in plutonium each valency from three to six can readily be prepared. Plutonium(IV) disproportionates in solution at a rate inversely proportional to about the fourth power of the hydrogen-ion concentration (Connick and McVey, University of California Radiation Laboratory report UCRL 1687). Plutonium(III) is stable in non-oxidising acids but can be produced in dilute nitric acid solution only if a large excess of reducing agent is present. Plutonium(VI) is readily prepared by oxidation of plutonium(IV), *e.g.* with hot sodium dichromate solution. Americium(III) is stable in all acids and americium(VI) is produced only with great difficulty. Americium(V) is prepared by oxidation with sodium hypochlorite but disproportionates

in moderately strong acid. The transuranium elements can be separated by means of this gradation in valency stability. Thus, if a mixture of uranium, plutonium(III), and americium (III) is treated with hot sodium dichromate, the americium(III) can be precipitated as trifluoride, while the uranyl and plutonyl fluorides remain in solution.

The isolation and separation of americium as a tracer and on the microgram scale have been reported by Thompson, Morgan, James, and Perlman (" The Transuranium Elements," McGraw Hill, New York, 1949, Vol. II, p. 1339), by Cunningham (*ibid.*, p. 1363) and by Milsted (*loc. cit.*).

EXPERIMENTAL

Removal of Plutonium by Solvent Extraction.—After the peroxide precipitation, the stock solution contained plutonium (~2 g.), iron (500 mg.), uranium (500 mg.), americium (~25 mg.) in 100 ml. of 0·5M-nitric acid. Most of the plutonium was removed by the solvent extraction of plutonium-(IV) or -(VI); the solvents tributyl phosphate, " Dibutyl carbitol " (diethylene glycol di-*n*-butyl ether), or di*iso*butyl ketone are suitable. Some uranium is removed but americium(III) is not. The plutonium was extracted from the combined solvent phases by stirring with 5% hydroxylamine in 0·1M-nitric acid [to produce the solvent-insoluble tervalent plutonium(III)]. Counting sources were prepared from this solution and from the aqueous layer after the solvent extraction. These sources were examined in a pulse analyser (see p. 2216); the aqueous layer was found to contain ~23 mg. of americium together with 55 mg. of plutonium. The solvent retained 1·3 mg. of americium, carried over by poor separation of the solvent and aqueous phases.

Separation from Iron by Oxalate Precipitation.—Americium trioxalate is coprecipitated with plutonium tetraoxalate, whereas iron is soluble in oxalate solution (Milsted, *loc. cit.*). Accordingly, an excess of oxalic acid crystals was added to the aqueous layer and a brown precipitate of plutonium and americium oxalate was removed by centrifugation. The yellow supernatant liquid contained mainly iron, some uranium, and 0·25 mg. of americium. The oxalate precipitate was treated with hot concentrated sulphuric acid, a pink slurry of plutonium and americium sulphates being obtained which gradually dissolved on dilution with water. After the solution had cooled, ammonium hydroxide was slowly added, and americium trihydroxide and plutonium tetrahydroxide were coprecipitated. The supernatant liquid after centrifugation had high α-activity, but, as it showed only a low γ-activity, this was presumed to be due to plutonium in a soluble hydrolysed form.

Separation from Plutonium by " Oxidation and Fluoride Precipitation " Cycles.—The hydroxides were dissolved in nitric acid and the acidity adjusted to normality. Solid sodium dichromate was added, and the solution was heated at 90—95° for several hours. The solution, now containing americium(III) and plutonium(VI), was transferred to a nitrocellulose tube and treated with concentrated hydrofluoric acid. The resulting pink precipitate was washed with water and dissolved in concentrated nitric acid. Pulse analysis of a source prepared from this solution showed <3% of the α-activity to be due to plutonium. As the half life of plutonium-239, the principal isotope in this plutonium, is 2·44 × 10⁴ years, <40 mg. of plutonium were left; the dichromate oxidation of plutonium cannot have been complete. Spectrographic analysis of a solution containing 50 μg. of americium gave: chromium, 10; magnesium, 1; tin, <1 (limit); silicon, 10; iron, 0·8; aluminium, 100; calcium, 100 μg.

Final Purification.—The americium was precipitated as the pink gelatinous trihydroxide with a sufficient excess of potassium hydroxide solution to hold aluminium in solution as aluminate. The solubility of americium in the supernatant layer was <1 μg. per ml. The hydroxide was dissolved in hydrochloric acid and the precipitation repeated. The precipitate was again dissolved in hydrochloric acid and the pH of the solution was reduced to 2 by adding ammonium hydroxide. Solid ammonium sulphate was then added and a white precipitate of calcium sulphate was formed which was washed with dilute ammonium sulphate solution. The washings were added to the americium-containing layer, which was put through a final " oxidation–fluoride " cycle. Spectrographic analysis showed the calcium and aluminium impurities to be reduced to 10% (of the americium).

Final purification was achieved by an ion-exchange process described by Street and Seaborg (*J. Amer. Chem. Soc.*, 1950, 72, 2790) in which americium was eluted from a Dowex-50 column with concentrated hydrochloric acid. Spectrographic analysis of this product gave the result: chromium and manganese, undetectable; silicon, 8; iron, 0·2; aluminium, 1·6%; calcium, undetectable. The silicon figure is probably incorrect; no other elements were detected.

A yield of 25 mg. of americium was obtained.

Estimation of Americium.—Pure americium solutions were estimated by α-particle counting. Sources were prepared on platinium discs and for most accurate work were counted in a low-geometry proportional methane chamber (Hurst and Hall, *Analyst*, 1952, **77**, 790).

If other α-emitters were present, *e.g.* plutonium in the first stages of the above separations, the α-pulses from the counting chamber were fed into a pulse analyser. The discriminating bias of the analyser channels was suitably adjusted to cover, in this case, an α-particle energy range of 5—6 Mev. The mean energies and half lives of the plutonium isotopes and americium are as follows :

Isotope	Half-life, yr.	α-Particle energy, Mev	Isotope	Half-life, yr.	α-Particle energy, Mev
Plutonium-238	90·0	5·47	Plutonium-240	6000	5·15
Plutonium-239	24,400	5·14	Americium-241	470	5·47

The pulse analyser will not discriminate between the α-particles of plutonium-238 and americium or those of plutonium-239 and -240. Hence two peaks are observed in the curve of α-particle abundance against α-particle energy, and it is necessary to know the plutonium-238 content of the plutonium before the actual amount of americium can be calculated.

Although α-pulse analysis provides a convenient method of estimating americium in plutonium, it is difficult to measure less than a few units % by weight of plutonium in americium. This is because of the large difference in the half-lives of americium and plutonium. A better method is to oxidise the plutonium to plutonyl ion and measure the absorption of the 833-mμ plutonyl peak spectrophotometrically. As little as 0·5% of plutonium in 25 mg. of americium can thus be detected. It is possible that the plutonium in americium could be estimated by activation analysis, the fission cross-sections being 664 and 3 barns, respectively.

During each stage of the purification the americium was conveniently followed by means of its γ-radiation, a thin-window Geiger tube being used. After each precipitation, the solution was centrifuged and a little of the supernatant liquid was withdrawn in a fine glass tube and held near the Geiger tube. The monitor response gave an approximate figure for the americium in the solution.

Spectrophotometry of Americium Solutions.—Many workers have described the absorption spectra of americium in solution but most of the measurements have been made with very small quantities. Recently Stephanou, Nigon, and Penneman (*J. Chem. Phys.*, 1953, **21**, 42) have reported the absorption spectra of americium-(III), -(V), and -(VI) in 0·1M-perchloric acid with americium concentrations of 1—3 g./l. Asprey, Stephanou, and Penneman (*J. Amer. Chem. Soc.*, 1951, **73**, 5715) reported the preparation and absorption spectra of americium(VI) solutions at similar concentrations, and Werner and Perlman (U.S. Atomic Energy Commission Report A.E.C.D. 2898) that of americium(V) solutions.

The spectrum of each valency state possesses a few very sharp absorption bands. Stephanou *et al.* (*loc. cit.*) find that the 504-mμ band of americium(III) does not obey the Beer–Lambert laws at high optical densities.

Further results on americium absorption spectra are reported below.

Experimental. All the previous purifications and the preparation of the spectrophotometer solutions were carried out in a large laboratory glove box in which a pressure slightly lower than atmospheric was maintained, and the usual radiochemical precautions were observed. A complete " Uvispek " spectrophotometer was contained in a separate glove box and the cell compartment was maintained at 25°. The high γ-ray flux from the americium did not affect the stability of the spectrophotometer.

All chemicals were of " AnalaR " grade. Water was redistilled from alkaline permanganate solution. Solutions were centrifuged before measurement in the spectrophotometer.

It was necessary to recover the americium after each experiment, as only 10 mg. were available for the following measurements.

RESULTS AND DISCUSSION

Americium(III).—*Perchloric acid solutions.* Freshly precipitated americium trihydroxide was washed with water and dissolved in 0·1M-perchloric acid. The absorption spectrum was measured from 250 to 1000 mμ. Above 400 mμ the spectrum agreed well with those

reported by Stephanou *et al.* (*loc. cit.*) and by Stewart (AECD-3351).   Below 400 mμ the intensity of absorption was found to be considerably greater than that reported by these authors, although the peaks appear at the same wave-lengths.   It seems that the peaks are superimposed on a continuum of absorption increasing as the wave-length decreases. Stephanou found that absorption below 400 mμ gradually increased with time and suggested that this was due to the production of hydrogen peroxide by the reaction of α-particles with water.   We found that absorptions below 400 mμ gradually decreased with time

FIG. 1.   *Absorption spectra of* Am(III) *in* 0·1M-*perchloric acid.*
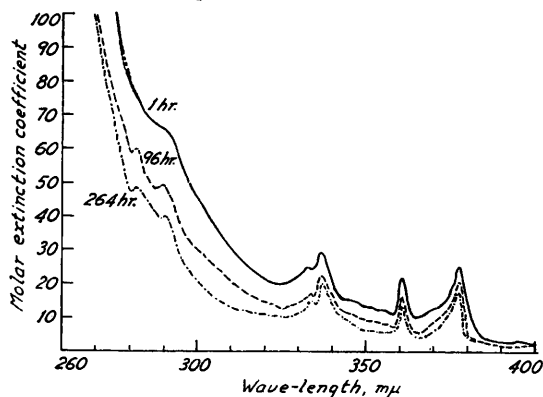
FIG. 2.   *Absorption spectra of* Am(III) *in hydrochloric acid at lower wave-lengths.*
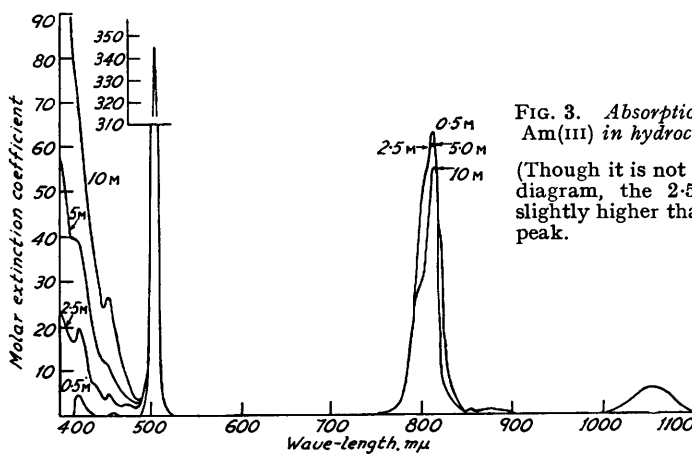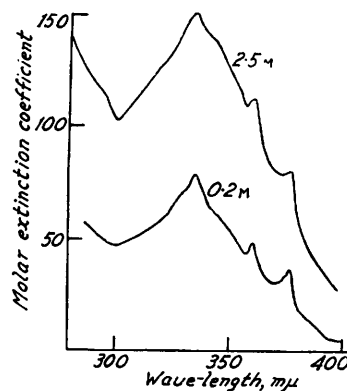

FIG. 3.   *Absorption spectra of* Am(III) *in hydrochloric acid.*

(Though it is not clear in the diagram, the 2·5M peak is slightly higher than the 5·0M peak.

(Fig. 1), although the general structure remained the same.   The absorption in the visible region at the two main peaks (504 and 814 mμ) remained unchanged during the 264 hr. in which the solution was examined, and hence no precipitation can have occurred.

The solution was made molar with respect to perchlorate ion by the addition of solid sodium perchlorate.   This produced a small decrease in absorption—about 3% for the 377-mμ peak and 20% at 290 mμ.   The spectrum of freshly-prepared americium(III) in M-perchloric acid is similar to that of the freshly prepared solution in 0·1M-acid but the absorption rises more steeply below 300 mμ.

This variable absorption at low wave-lengths is not due to hydrolysis, because the effect is enhanced by increasing the acidity both in perchloric acid and hydrochloric acid. There might be some impurity absorbing at lower wave-lengths, but it could not be detected.   It is thus inadvisable to use the absorption peaks below 400 mμ for the analysis of americium(III).

Hydrochloric acid solutions. In hydrochloric acid similar relatively high ultra-violet absorptions are observed. The absorption in 0·2M-hydrochloric acid is considerably higher than that in 0·1M-perchloric acid and the peaks are less well defined. In 2·5M-hydrochloric acid the structure almost disappears, and as the acidity is increased the absorption extends to higher wave-lengths and reaches 400 mμ in 10M-acid (Figs. 2 and 3). The spectrum in the visible region shows little change even in concentrated acid. Thus the 1050-mμ peak remains unchanged in height and position, the 814-mμ peak is reduced, and the 504-mμ peak decreased slightly, when allowance is made for the failure of Beer's law. The small changes are probably caused by small changes in the electronic transition probabilities produced by the great increase in ionic strength of the solution. It is difficult to explain the large changes below 450 mμ, which resemble the effect of increasing the hydrochloric acid concentration of plutonium(IV) solutions (Hindman, U.S. Atomic Energy Commission report, MDDC 1257) and which is explained by chloride complexing of the Pu^{4+} ion.

It is believed that the narrow bands in the absorption spectra of the transuranic

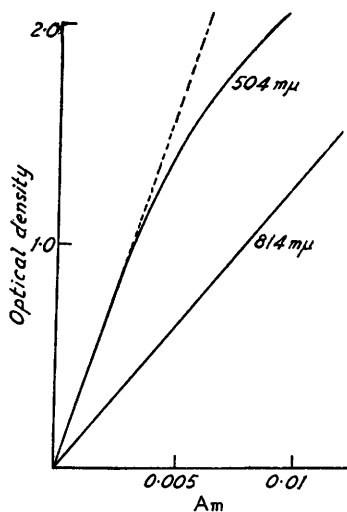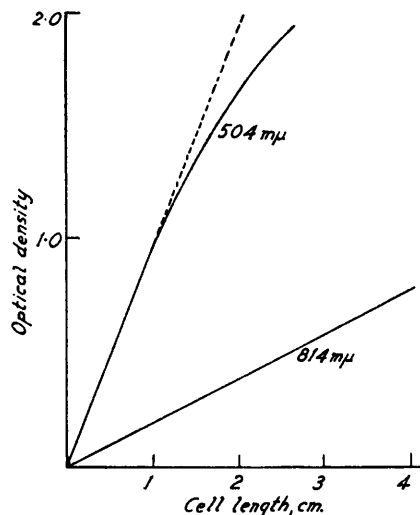FIG. 4. *Beer's law plot for* Am(III) *peaks.*   FIG. 5. *Lambert's law plot for* Am(III) *peaks.*

elements are due to the forbidden transitions of shielded $5f$ electrons. It may be that the ultra-violet absorptions result from some allowed transitions to an unshielded electronic state; such transitions would be susceptible to the changes in the electric field around the americium ions produced by chloride complexing.

Beer's and Lambert's law. The 504-mμ peak is extremely narrow, and Stephanou *et al.* (*loc. cit.*) find Beer's and Lambert's law to fail at high optical densities (>1·7). To obtain further information on this for analytical purposes the following measurements were made. A concentrated stock of americium(III) in M-hydrochloric acid was prepared. The optical densities of several dilutions of this stock at the 504- and 814-mμ peaks were measured. For one solution the absorptions in 0·5, 1·0, 2·0 and 4·0 cm. cells were also measured. The results are plotted in Figures 4 and 5. Neither Beer's nor Lambert's law is obeyed for the 504-mμ peak, but both are obeyed for the broader 814-mμ peak. The failure may be due to two instrumental effects—(*a*) the spectrophotometer-selected band-width is too large for the narrow 504-mμ peak and (*b*) there may be some stray light interference which would be more serious at high optical densities. A calibration curve of optical density plotted against concentration for the similar narrow 833-mμ plutonyl $(PuO_2)^{++}$ peak shows these combined effects. The curve obtained by using a glass prism shows less deviation from Beer's law at high optical densities than a similar curve obtained

by using the quartz prism, because the glass prism provides appreciably greater dispersion than the quartz prism at this wave-length.

The 504-mμ americium peak has been plotted for several slit widths for ranges of optical density which can be measured with good accuracy (Fig. 6). The observed peak height increases for smaller selected band widths. This shows that the normal slit width, corresponding to a dispersion of 10 Å (Hilger " Uvispek " handbook), is not sufficiently small to measure the actual peak top. It follows that as higher optical densities are measured for a given band width the peak heights will become increasingly smaller than the true heights. This occurs in the present study. If there were no stray light interference (this could not be checked because no suitable filters were available), the above deviations would not occur in an instrument of sufficiently high resolution.

FIG. 6. *Effect of slit width on* Am(III) *504* mμ *peak.*

Selected band widths
A   10Å
B   25Å
C   50Å
D   75Å

For estimations of americium(III) in solution the 504-mμ peak gives good results providing a Beer's law calibration is carried out at the slit width to be used.

Americium(v).—Americium(v) (AmO$_2^+$) solutions were prepared by Werner and Perlman's method (AECD 2898). Americium trihydroxide (10 mg.) was dissolved in 4M-potassium carbonate solution (2 ml.) and M-sodium hypochlorite solution (0·5 ml.) was added. The solution was heated at 95° for 1 hr. and then set aside overnight to ensure complete precipitation of the white americium carbonate which was washed and then dissolved in the desired acid.

The absorption spectrum of americium(v) in 0·5M-hydrochloric acid (Fig. 7) is very similar to that reported by Stephanou et al. (loc. cit.) for 0·1M-perchloric acid. The americium is slowly reduced, owing to the production of reducing species by the α-particle bombardment of the solution. The decrease in americium(v) and growth of americium(III), which were followed by measuring the absorptions at 715 and 514 mμ, respectively, were both linear with respect to time (Fig. 8), showing the reduction to be of zero order with respect to the individual ionic species. The slight curvature at zero time indicates an induction period while initial traces of oxidising impurities in the solution are destroyed. For a postulated rate law d[Amv]/dt = k[Am] where [Am] is the total concentration, k is found to be 0·0074 hr.$^{-1}$, similar to the value of 0·023 hr.$^{-1}$ obtained by Asprey and Stephanou (AECD 924) for americium(v) in M-perchloric acid. These workers find the reduction to be of first order with respect to the total americium concentration for a concentration range 0·009—0·033 M. The mass balances obtained in our calculations for americium-(III) and -(v) show that not more than 3% of a possible americium(IV) ion can be present. It appears that if any is formed it is immediately decomposed in solution to americium(III). At higher acidities the americium(v) concentration is expected to decrease because of both α-particle-induced self-reduction and disproportionation.

For studies on the disproportionation of americium(v) in hydrochloric acid, information on the change of molar extinction coefficients with acidity was required. Absorptions of solutions of americium(v) in 2·5M- and 5M-hydrochloric acid at 514 and 715 mμ [and also 504 and 814 mμ for americium(III) and 992 mμ for americium(VI)] were measured at suitable time intervals. Extrapolation of the optical densities to zero time gave values of the molar extinction coefficients for pure americium(v) solution. The values for 0·1M-perchloric acid are those reported by Stephanou et al. (loc. cit.).
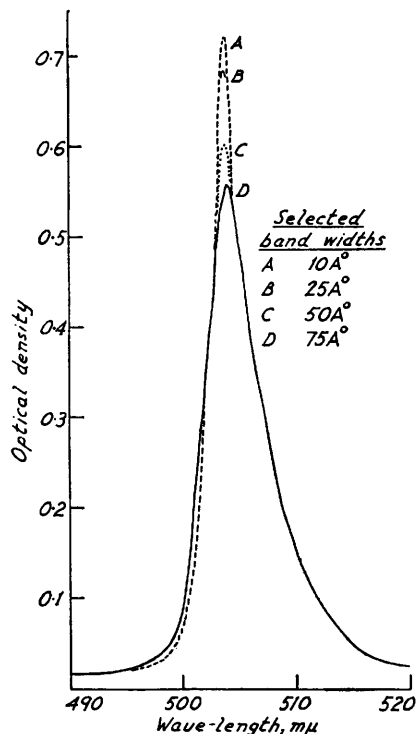
Absorption for both the americium(v) peaks drops considerably as the acidity is increased. The complete spectrum in 2·5m-hydrochloric acid (Fig. 7) shows a considerable increase in absorption from 400 to 450 mμ.

The change of americium valency with time in the 2·5m- and 5m-acid solutions has been calculated. Owing to insufficient readings at 992 mμ no americium(vi) was detected.
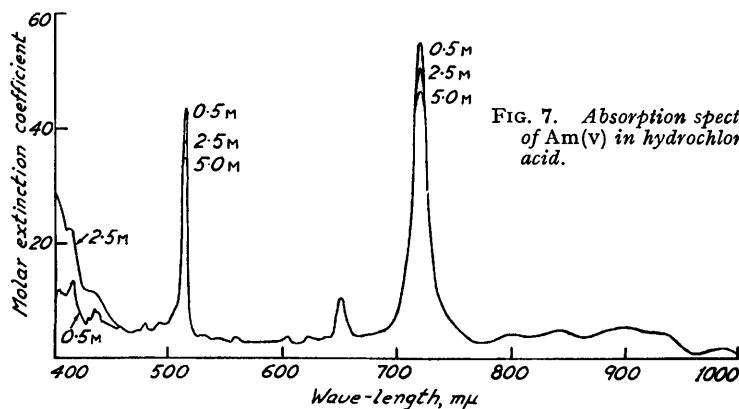

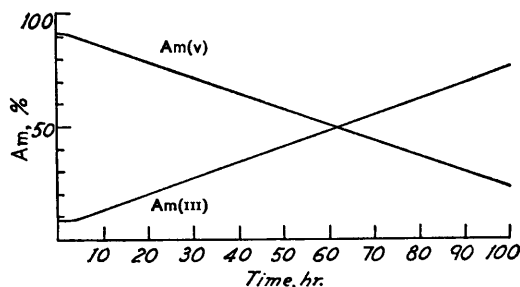Fig. 7. *Absorption spectra of* Am(v) *in hydrochloric acid.*

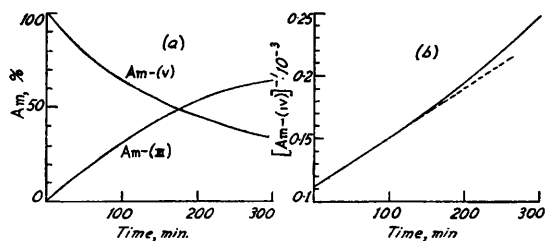Fig. 8. *Self reduction of* Am(v) *in* 0·5m-*hydrochloric acid.*

Fig. 9. *Reduction of* Am(v) *in* 5·0m-*hydrochloric acid.*

The mass balance between calculated quantities of americium-(v) and -(iii) and the total americium concentration is such that <5% of americium(vi) could have been formed, the

Molar extinction coefficients for americium(v).

| λ, mμ	0·1m-HClO$_4$	0·5m-HCl	2·5m-HCl	5m-HCl
514	45·6	44·4	39·1	35·7
715	59·3	56·4	51·9	47·4
814	—	~5	~4	~6

overall change being the conversion of americium-(v) into -(iii). The reduction of the americium(v) in 2·5m-acid was slower than in 0·5m-acid, whereas in 5·0m-acid the reduction was faster than in either 0·5m- or 2·5m-acid.

The change of valency with time for the 5·0m-acid solution is plotted in Figure 9a and 1/[Am(v)] is plotted against time in Figure 9b. The latter curve is approximately linear at the beginning, indicating a bimolecular reaction, but then deviates upwards possibly

because some americium(v) is also being self-reduced. Similar curves were obtained in 2·5M-hydrochloric acid. The initial rates of reduction of the americium(v) for these two acidities were approximately dependent on the fourth power of the hydrogen-ion concentration.

It appears that as the hydrochloric acid concentration is increased the rate of self reduction of americium(v) decreases. This may be due to the reducing species being less stable, or the americium(v) becoming more stable, in more concentrated acid because of chloride complex-formation. The progressive drop in the molar extinction coefficients in going from 0·1M-perchloric acid to 0·5, 2·5, and 5·0M-hydrochloric acid is evidence for complex-formation. Also the rate constant for self-reduction (k) in 0·5M-hydrochloric acid is one third of its value in 0·1M-perchloric acid.

In 2·5M- and 5·0M-acid reduction appears to be by disproportionation since the rate is bimolecular with respect to americium(v) and varies as the fourth power of the hydrogen-ion concentration. Disproportionation could be represented by

$$2AmO_2^+ + 4H^+ = AmO_2^{2+} + Am(IV) + 2H_2O$$
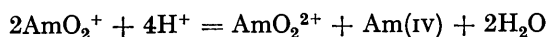
We did not observe any americium-(IV) or -(VI). Stephanou, Asprey, and Penneman (U.S. Atomic Energy Commission Report AECU-925) suggest that americium(VI) is reduced to americium-(V) and -(III) in strong acid, although they observed some americium(VI) in their experiments on the disproportionation of americium(v) in perchloric acid. In our experiments the quartz prism used in the " Uvispek " spectrophotometer made measurement of the americium(VI) peak at 992 mμ very insensitive. Our mass balances are such that <5% americium(VI) could have been present.

In order to understand the decomposition of americium(v) solutions it will be necessary to separate these two modes of reduction. More information about the stability of americium-(IV) and -(VI) is required before satisfactory rate equations can be deduced for the disproportionation process.