188. *The Chemistry of Plutonium.*

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A survey of some of the chemical and electrochemical properties of plutonium has been made. Valency states of 3, 4, and 6 have been established.

Oxidation and reduction reactions between the different valency states have been investigated. The reactions of plutonium ions with some of the commoner organic reagents are described.

PLUTONIUM was discovered late in 1940 by Seaborg, McMillan, Kennedy, and Wahl (*Physical Rev.*, 1946, **69**, 366; see also Seaborg, Wahl, and Kennedy, *ibid.*, p. 367). The investigations now reported were carried out with about 5 mg. of ^{239}Pu extracted from neutron-irradiated uranium. Experiments were carried out either with the plutonium in tracer concentrations, or else, by microchemical methods, with plutonium concentrations of the order of 1 mg. per ml.

^{239}Pu is an α-active nucleus with a half-life of $2·4 \times 10^4$ years (Seaborg, *Chem. Eng. News*, 1945, **23**, 2190).

I. *The Valencies of Plutonium.*—Plutonium was investigated in each of three well-defined valency states. It appears to be more stable to both mild oxidation and reduction when it is in the middle valency state of the three; in this condition, it was shown to be quadrivalent (see Experimental, A).

Polarographic experiments in plutonium solutions showed the presence of a wave at a half-wave potential of + 0·7 volt on the hydrogen scale. It was already known that plutonium could be oxidised to a valency state higher than 4, but the observed wave did not appear to be sufficiently positive to correspond to this process. It was therefore suspected that the wave corresponded to the reduction of plutonium to a state with a valency lower than 4. The existence of such a state was immediately confirmed chemically, and its valency was shown to be 3 by two methods (Experimental, B, i and ii), and that of plutonium in its highest oxidation state was shown to be 6 by the experiment described under B, iii.

II. *The Electrochemistry of Plutonium.*—Plutonium, like uranium, is a base metal and a transition element. Electrochemical studies were therefore mainly concerned with the processes of oxidation and reduction between the various valency states, and with complex formation. Evidence for complex formation is presented elsewhere (Sect. IV).

The potential of the Pu–Pu(III) *couple.* No indication of the potential of this couple has been obtained. The corresponding couple U–U(III) has a potential which has been estimated at − 1·5 volts (European sign convention) (Heal, unpublished work), and it is probable that the value for plutonium is not very different from this.

The potential of the couple Pu(III)–Pu(IV). The potential was determined both by direct measurement and polarographically (see C and D). The best characterised waves obtained are shown in Figs. 3a, 3b, and 3c. In all cases the diffusion current was lower for Pu(IV) than for Pu(III) solutions. The explanation of this phenomenon remains obscure.

The estimates of the molal oxidation–reduction potential given below were taken from the

direct determination in the case of sulphuric acid, and from the half-wave potentials in the other two cases :

In $1N$-H_2SO_4, $+ 0.72$ volt at $23°$.　In $1N$-HCl, $+ 0.99$ volt at $30°$.　In $1N$-$HClO_4$, $+ 0.86$ volt at $23°$.

These results show that the tervalent plutonium ion is a much less powerful reducing agent than the tervalent uranium ion (which liberates hydrogen from water). Indeed, the quadrivalent plutonium ion may be reduced to the tervalent state by the quadrivalent uranium ion. This reaction was studied polarographically at $30°$, with the results recorded in E (Experimental).

III. *The Reactions of Plutonium.*—(a) *Oxidation–reduction reactions.* (i) In aqueous solutions, Pu(IV) may be reduced to Pu(III) by sulphur dioxide, hydroxylamine hydrochloride, the uranous ion, hydrazine hydrochloride, the iodide ion, electrolytically at a platinum cathode, or by shaking with mercury in chloride solutions.

The reaction with sulphur dioxide is slow at room temperature, but in hot solutions it goes to completion in about 5 minutes. The reduction of Pu(IV) by the iodide ion is also somewhat slow at room temperature in both sulphate and chloride solutions. The titration of the liberated iodine does not appear to be a useful method for the routine determination of plutonium.

(ii) Oxidation of Pu(III) by atmospheric oxygen is fairly rapid, and solutions of Pu(III) salts are completely oxidised to Pu(IV) on two or three evaporations to dryness in an open vessel in air. However, Pu(III) solutions are stable in an inert atmosphere. Permanganate oxidises Pu(III) quantitatively to Pu(IV) at room temperature in acid solutions. At $60°$, the plutonium is oxidised to the sexavalent state.

(iii) In tracer concentrations of plutonium, the following oxidising agents were found to oxidise the Pu(IV) ion to the sexavalent state : hot potassium permanganate, potassium dichromate, argentic salts (including sodium perdisulphate in the presence of silver ions), and ceric ions. The conditions found to give satisfactory oxidation with perdisulphate and silver ions in these experiments are set out in section F (Experimental).

In concentrations of about 1 mg. per ml., Pu(IV) was oxidised to the sexavalent state by the following reagents : potassium permanganate in hot acid solution, hot sodium perdisulphate, argentic nitrate at room temperature, or hot bromate solutions containing nitric acid.

(iv) Pu(VI) is reduced to the ter- or quadri-valent state by sulphur dioxide, ferrocyanide ions, and hydrogen peroxide. The last reaction is complicated by a subsequent reaction between the hydrogen peroxide and the Pu(IV) ion to give a precipitate of a plutonium peroxide (see p. 1012).

(b) *Compounds of tervalent plutonium.* Solutions of tervalent plutonium salts are bright blue. The sulphate, chloride, and perchlorate are readily soluble in dilute acids. On addition of an excess of ammonium hydroxide a dirty blue precipitate of plutonium hydroxide is obtained. It may readily be redissolved in dilute acids to give solutions of Pu(III) salts.

The fluoride is insoluble in dilute acids, and tracer amounts of tervalent plutonium may be removed from solution by coprecipitation with lanthanum fluoride in the presence of hydrofluoric acid.

In the presence of hydroxylamine hydrochloride (to keep the plutonium in the reduced state), Pu(III) can be precipitated on a carrier of lanthanum oxalate. The removal of plutonium from the solution, however, was only 75% complete. The plutonium could be removed from the lanthanum oxalate carrier by washing with hot ammonium oxalate solution. It was not removed by ammonium oxalate solution at room temperature.

In acetate buffers at pH's of 3.6 and 5.6 it was found that Pu(IV) was much more completely removed from solution on a precipitate of bismuth oxychloride than was Pu(III) ; Pu(IV) ions therefore appear to be much more readily hydrolysed in solution than Pu(III) ions. To prevent losses of plutonium by adsorption on to glass, it is always necessary to work in acid solutions : pH < 1 is normally safe.

Pu(III) cannot be removed from acid solutions by coprecipitation with zirconium and one of the typical reagents for quadrivalent ions such as phenylarsonic acid or *m*-nitrobenzoic acid. Since Pu(IV) may readily be precipitated under these conditions, this enables a separation of Pu(III) from Pu(IV) to be carried out (see p. 1013).

(c) *Compounds of quadrivalent plutonium.* Solutions of the quadrivalent salts of plutonium are pale pink, with the exception of the nitrate, whose solutions are green.

Oxide, PuO_2. Ignition of the nitrate, iodate, or hydroxide of quadrivalent plutonium at about 500—$600°$ yields a dark brown oxide PuO_2. In thin layers, the oxide appears to be yellow. If prepared by gentle ignition, it may easily be redissolved in hot concentrated

sulphuric or nitric acid. If ignited to a bright red heat, it dissolves readily only in potassium hydrogen sulphate at a dull red heat.

Hydroxide. The hydroxide is precipitated on the addition of ammonium hydroxide to solutions of Pu(IV) salts. It is a pale green gelatinous substance which can be centrifuged very readily. Precipitation of this hydroxide is one of the most convenient ways of removing plutonium from solution.

After being washed with dilute ammonium hydroxide and dried at 100°, the hydroxide dissolves readily in 1N-mineral acids, but decidedly more readily in nitric than in sulphuric or hydrochloric acid.

Peroxide. When hydrogen peroxide is added to an acid solution of a quadrivalent plutonium salt, a red-brown colour develops, and a bulky green precipitate of doubtful composition is slowly deposited. Precipitation of the plutonium is most complete in the pH range 3—4·5. The presence of sulphate ion appears to favour the reaction.

A precipitate of the same nature is obtained by adding hydrogen peroxide to solutions containing sexavalent plutonium, but it is formed less readily than from Pu(IV) solutions. It is therefore probable that the peroxide is a compound of quadrivalent plutonium, and that hydrogen peroxide reduces Pu(VI) to Pu(IV). The peroxide of plutonium is therefore quite different from uranium peroxide (peruranic acid). It is insoluble in sodium hydroxide solutions, and is presumably not a per-acid.

The peroxide dissolves in concentrated nitric acid with evolution of oxygen, to give a bright blue solution. When this solution is warmed, more oxygen is lost, and the blue solution fades to the pale green of Pu(IV) nitrate solutions. The peroxide may also be dissolved in 6% sulphurous acid solution.

The ratio of plutonium to peroxidic oxygen in the peroxide was determined by permanganate titration as described in the Experimental (G, i); if the permanganate reacted with the peroxidic oxygen in the same way as it does with hydrogen peroxide, the titration indicates that the ratio of atoms plutonium to atoms peroxidic oxygen is 2 to 3 (see G, ii). If the 0·335 mg. not accounted for is expressed as oxygen, the data give the following atomic ratios : Pu, 1; SO_4, 0·30; O (peroxidic and non-peroxidic), 2·93. The peroxide could therefore be written as $PuO_3, \frac{1}{3}SO_4$. It is possible that the dried peroxide is different in composition from the original precipitate. Thorium, for example, forms two peroxides, Th_2O_7 (or Th_2O_7, SO_4) and ThO_3. The latter form is more stable than the former, and is obtained when the former is allowed to decompose (Pascal, " Traité de Chimie Minérale," Vol. 11, p. 289).

Fluoride. The fluoride of Pu(IV) coprecipitates very well with lanthanum fluoride. Experiments (see H) were carried out to determine the weight of lanthanum which must be precipitated as fluoride in order to obtain efficient carrying of the plutonium. Precipitation of plutonium on a lanthanum fluoride carrier under these conditions appears to be substantially complete when the weight of lanthanum precipitated is greater than about 0·1 mg. per ml. of plutonium solution.

The precipitation of plutonium fluoride in the absence of a carrier was uncertain : 0·35 mg. of Pu(IV) in 2 ml. of 1N-perchloric acid was not precipitated by the addition of 48% hydrofluoric acid. In higher concentrations of plutonium, a gelatinous precipitate was obtained which quickly collapsed to a dense yellowish powder, difficult to centrifuge off on account of its lack of coherence. The precipitation of an equal weight of lanthanum fluoride was found to bind the precipitate and eliminate this difficulty.

Sulphate, $Pu(SO_4)_2$. Evaporation of Pu(IV) solutions, prepared from the hydroxide and sulphuric acid or from the peroxide and sulphurous acid in the presence of sulphuric acid, followed by gentle ignition to remove the sulphuric acid, gives anhydrous *plutonium sulphate* as a light pink powder. The same compound is obtained when the oxide PuO_2 is fumed down to dryness with sulphuric acid. The anydrous salt may be weighed in air. It is soluble in dilute mineral acids to give pale pink solutions. Dilute sulphuric acid solutions appear to be metastable, and sometimes a deposit of red-brown crystals is obtained on standing (Experimental, I).

Nitrate. Solutions of the nitrate in nitric acid are green. A sample of the hydrated solid nitrate was readily soluble in nitromethane.

Iodate, $Pu(IO_3)_4$. The iodate is obtained as a voluminous, very pale pink precipitate on addition of iodic acid or an iodate solution to solutions of Pu(IV) salts. It dissolves readily in 6% sulphurous acid solution, giving a solution containing tervalent plutonium.

Phenylarsonate. Pu(IV) is coprecipitated very efficiently from acid solutions on a precipitate of zirconium phenylarsonate, and the best pH range for this coprecipitation was investigated (Experimental, J), even strongly acid solutions being suitable.

In the presence of reducing agents (SO_2 or hydroxylamine hydrochloride), it was found that plutonium was not carried down at all by zirconium phenylarsonate. It was therefore concluded that the phenylarsonate of Pu(III) is soluble.

m-Nitrobenzoate. Pu(IV) may be precipitated on zirconium *m*-nitrobenzoate. The effect of pH on the completeness of the precipitation was investigated in the same way as with phenylarsonic acid (Experimental, K). In the presence of reducing agents, plutonium was not carried down on the precipitate of zirconium *m*-nitrobenzoate. It was therefore concluded that the *m*-nitrobenzoate of Pu(III) is soluble.

(d) *Compounds of sexavalent plutonium.* Ammonium plutonate. This salt may be prepared by adding ammonium hydroxide to a hot solution of a plutonium salt which has been oxidised to the sexavalent state with argentic nitrate; it is thereby obtained as a brownish-yellow precipitate which may be filtered off after it has cooled and stood until coagulated. The composition of ammonium plutonate has not been determined.
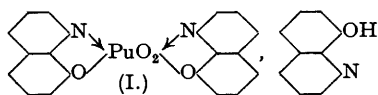
On account of the similarity between the chemistry of uranium and of plutonium in their sexavalent states, the terms " plutonate " and " plutonyl " have been used in the present paper to describe the sexavalent compounds of plutonium.

Plutonyl fluoride. Sexavalent plutonium is not precipitated on a lanthanum fluoride carrier in the presence of an excess of hydrofluoric acid. By this method, plutonium can readily be separated from lanthanum.

Plutonyl nitrate. Ammonium plutonate dissolves readily in nitric acid to give an orange solution, which, by analogy with uranium, is believed to contain plutonyl nitrate, $PuO_2(NO_3)_2$. At low pH values, the solution appears pink, and as the pH is increased, the colour becomes progressively more orange.

Ethyl ether and nitromethane extracted plutonyl nitrate from its aqueous solutions saturated with ammonium nitrate.

Sodium plutonyl acetate. Addition of sodium acetate solutions to a mixed plutonyl and ammonium nitrate solution (prepared by dissolving ammonium plutonate in nitric acid) slowly precipitates crystals similar in appearance to those of sodium uranyl acetate, but pale mauve in colour. The compound is presumably sodium plutonyl acetate.

Plutonyl " oxinate." 8-Hydroxyquinoline (" oxine ") precipitates plutonyl ions quantitatively in the pH range 3·5—9. The plutonium content of this *oxinate* was determined as described in Experimental (L). The weight of the complex obtained agreed with the structure (I) for the oxinate, which therefore appears to be the analogue of the corresponding uranyl complex.

IV. *Complex Formation by Plutonium.*—(a) *Inorganic complex ions.* The oxidation–reduction potentials for the Pu(III)–Pu(IV) couple are about + 0·72 volt in 1N-sulphuric acid, + 0·99 volt in 1N-hydrochloric acid, and + 0·86 volt in 1N-perchloric acid. This variation indicates that there must be a tendency towards complex formation with the anion in at least two of the three acids, but the electrochemical evidence does not indicate in which acids this occurs. The presence of a high concentration of chloride ions inhibited the coprecipitation of Pu(III) on a lanthanum fluoride carrier, whereas the sulphate ion showed no real effect. This indicates that Pu(III) ions probably form complexes in chloride solutions. Similarly, ammonium thiocyanate completely inhibited the coprecipitation of Pu(IV) on a carrier of zirconium phenylarsonate or *m*-nitrobenzoate, thus indicating that Pu(IV) ions probably form complexes with the thiocyanate ion.

The presence of alkali carbonates interfered with the extraction of the acetylacetone complex of Pu(IV) into benzene. Experiments with visible quantities of plutonium showed that Pu(IV) salts, including the fluoride, dissolve completely in excess of ammonium carbonate.

Experiments with tracer amounts of plutonium showed that Pu(IV) coprecipitated with lanthanum oxalate could be washed off the lanthanum precipitate with hot or cold ammonium oxalate solution much more readily than could Pu(III). The solubility of Pu(IV) oxalate in ammonium oxalate was confirmed by using visible quantities of plutonium. Pu(IV) fluoride was also found to be readily soluble in ammonium oxalate solution.

(b) *Organic complexes of plutonium.* A brief survey of the behaviour of Pu(III), Pu(IV), and Pu(VI) towards some of the commoner organic complexing reagents was made. The results are contained in Experimental (M). In some cases, the reaction between the plutonium ion and the organic reagent was studied in more detail, using tracer concentrations of plutonium.

Diketone complexes. The extraction coefficient (defined as the ratio of the concentrations

3 U

of plutonium in the solvent and the aqueous layer) was measured at various pH's for the systems Pu(IV), water, benzene, and acetylacetone, trifluoroacetylacetone, or benzoylacetone. With the first two diketones, the extraction coefficient rose from 0·5 at pH 1 to an almost constant value of 80 at pH's of greater than 5 for acetylacetone and greater than 4 for trifluoroacetyl-acetone. The benzoylacetonate gave a maximum extraction coefficient of 8 at a pH of 4. At higher pH's, the extraction coefficient decreased.

Salicylate complex. The extraction coefficient was measured for the system Pu(IV), amyl acetate, salicylic acid, and water at different concentrations of salicylic acid and at two different pH's. The detailed results are given in Experimental (N). In general, the extraction coefficient increased with increasing salicylate concentration in the aqueous layer, but at the higher pH, it was lower for a given salicylate concentration than for the same salicylate concentration at the lower pH. The irregularity of some of the results is believed to be due to the fact that a considerable proportion of the plutonium adhered to the glass walls of the vessels at the pH's used.

EXPERIMENTAL.

General Methods.—(a) *Preparation and purification of plutonium compounds.* During the present work, several methods were used for the initial purification of plutonium and for its recovery from the residues of previous experiments. The most useful method was found to be the one already described by Seaborg *et al.* (*loc. cit.*, p. 367) in which plutonium is precipitated with a carrier of lanthanum fluoride, and then separated from the lanthanum fluoride by making use of the solubility of the fluoride of sexavalent plutonium.

The plutonium in the ter- or quadri-valent state is precipitated on a carrier of lanthanum fluoride by the method described above. The precipitate is then dissolved by fuming with sulphuric or per-chloric acid, and the solution is diluted with water. The plutonium is then oxidised to the sexavalent state : potassium permanganate in hot solution was found to be the most convenient oxidising agent for this purpose. The lanthanum is then precipitated by the addition of hydrofluoric acid, leaving the plutonium in solution.

The final purification of the plutonium may be carried out by evaporating the solution to fuming to eliminate the excess of hydrofluoric acid, reducing the plutonium to the tervalent state by warming with an excess of 6% sulphurous acid solution, and then precipitating the plutonium as $Pu(OH)_3$ by the addition of ammonium hydroxide.

The $Pu(OH)_3$ may then be dissolved in sulphuric acid, the plutonium converted to the quadrivalent state by evaporating the solution to dryness in air, and then successively precipitated as peroxide and iodate until the desired degree of purity has been reached.

(b) *Methods of determining plutonium.* Counting of α-particles provides a rapid method for carrying out determinations of relative amounts of plutonium when working with tracer quantities of the element. The half-life of ^{239}Pu is $2·4 \times 10^4$ years (Seaborg, *loc. cit.*). This corresponds to the production of 138×10^6 α-particles/min./mg. Pu.

Plutonium may be weighed as $Pu(SO_4)_2$, PuO_2, or $Pu(IO_3)_4$. The sulphate is particularly convenient, since it may be prepared by fuming many plutonium compounds to dryness with sulphuric acid. The iodate is a useful form in which to weigh small amounts of Pu since it contains only 25·46% of Pu.

It has already been mentioned that permanganate titration of Pu(III) or Pu(IV) may be carried out in hot acid solutions. Titration of the iodine liberated in sulphate solution by the oxidation of iodide ions by Pu(IV) ions is not a convenient method for routine estimation of plutonium because the reaction is rather slow. In chloride solutions, the reaction is faster, but the titration is still not satisfactory.

(A) About 1 mg. of plutonium was purified and precipitated from sulphate solution as its insoluble iodate by addition of a solution of iodic acid. The precipitate was dried at 100° and weighed in a platinum crucible. It was then ignited to constant weight at a dull red heat in air. 3·532 Mg. of iodate gave a plutonium compound weighing 1·021 mg. after ignition. The loss of weight agrees well with the reaction $Pu(IO_3)_4 \longrightarrow PuO_2 + 5O_2 + 2I_2$. The weights of iodate and oxide correspond to a valency of 3·92 for the middle oxidation state of plutonium. The 1·021 mg. of dioxide formed in this experiment was converted into sulphate by fuming to dryness three times with sulphuric acid. The *sulphate* weighed 1·616 mg. ; *i.e.*, the sulphate contains 63·2% of PuO_2 [$Pu(SO_4)_2$ requires PuO_2, 62·9%].

(B) (i) During a determination of the oxidation–reduction potential of the Pu(IV)–Pu(IV−*n*) couple, it was found that a plot of the potential of a platinum electrode against the logarithm of the concentration ratio of Pu(IV) to Pu(IV−*n*) gave a straight line of slope 0·048 volt at 23°. This corresponds most nearly to the theoretical value of 0·059 volt for a single-electron transfer.
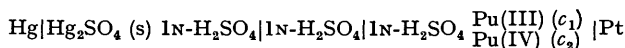
(ii) It was found that in sulphate solutions, the Pu(IV) ion will oxidise the iodide ion to iodine. The iodine which was liberated by 2·206 mg. of $Pu(SO_4)_2$ gave a titre of 0·47 ml. of 0·0103N-sodium thiosulphate. This corresponds to a valency difference of 0·95 between the middle and the lower state of plutonium.

(iii) 0·814 Mg. of $Pu(SO_4)_2$ was titrated in 1N-sulphuric acid solution with approximately 0·005N-potassium permanganate. Reaction was very slow at room temperature, but proceeded rapidly at 60°. After completion of the titration, the plutonium was reduced to the tervalent state by warming with sulphurous acid solution. The excess of sulphur dioxide was driven off by evaporating the solution to a very small volume in a stream of purified carbon dioxide. The tervalent plutonium was then titrated at room temperature to the quadrivalent state with the same permanganate solution. The end-point was quite definite and stable. On warming the solution to 60°, the pink colour of the end-

point faded, and a further quantity of permanganate reacted as the plutonium was oxidised to the highest valency state.

In four such cycles, the average volume of permanganate required to oxidise the Pu(III) to Pu(IV) was 0·37 ml. The volume required to oxidise the Pu(IV) to the highest valency state was almost exactly twice as much, *viz.*, 0·72 ml.

(C) Potentials of the cell

$$\text{Hg|Hg}_2\text{SO}_4 \text{ (s) } 1\text{N-H}_2\text{SO}_4|1\text{N-H}_2\text{SO}_4|1\text{N-H}_2\text{SO}_4 \begin{array}{cc} \text{Pu(III)} & (c_1) \\ \text{Pu(IV)} & (c_2) \end{array} |\text{Pt}$$

were measured. The cell is shown in Fig. 1.

The ratio of c_1 to c_2 was varied by mixing in various proportions stock solutions of Pu(IV) sulphate and of Pu(III) sulphate, both in $1\text{N-H}_2\text{SO}_4$. The Pu(III) solution was made as and when required by both electrolytic reduction at a platinum cathode of a Pu(IV) solution.

FIG. 1.

Cell used for polarography and for E_0 *measurements (half actual size).*
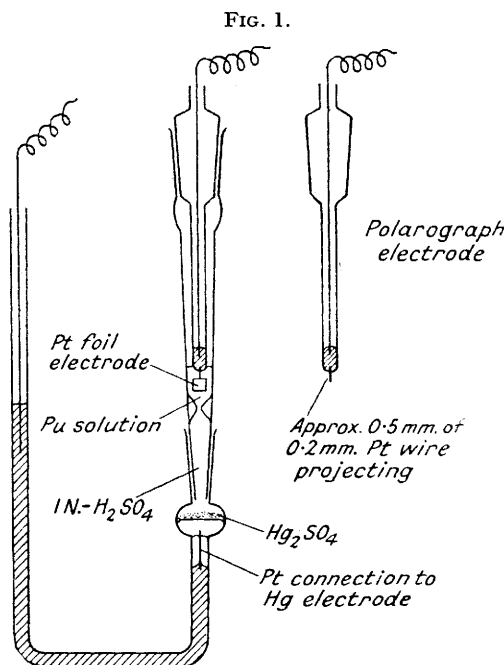
The potentials were determined at 23°. They became steady within 5 mins. after insertion of the platinum electrode into the cell. The values are recorded below :

Potentials of the couple Pu(III)–Pu(IV).

| Concn. of Pu(III) in solution, M.	Concn. of Pu(IV) in solution, M.	Potential, volt.	Concn. of Pu(III) in solution, M.	Concn. of Pu(IV) in solution, M.	Potential, volt.
0·00404	0·00058	0·0289	0·00152	0·00354	0·0825
0·00354	0·00118	0·0420	0·00101	0·00412	0·0931
0·00304	0·00177	0·0548	0·00051	0·00471	0·1050
0·00227	0·00265	0·0581			

The molar concentrations were estimated by diluting a small volume of each of the stock solutions, and α-counting aliquots of the dilute solutions. There may thus be errors of up to 15% in the absolute concentration values, but as the same counter and counting technique were used for both of the solutions, the relative concentrations are believed to be correct to ± 5%.

Fig. 2 shows the linear variation of the potential with $\log_{10} c_2/c_1$. The potential when $c_2 = c_1$ was + 0·064 volt, with the platinum electrode positive. Assuming that the potential of the mercurous sulphate electrode is + 0·66 volt on the hydrogen scale, this gives a value of + 0·72 volt for the couple with equal concentrations. The molal standard potential is therefore in the region of + 0·72 volt.

Similar experiments designed to measure the potential of the same couple in 1N-hydrochloric acid and 1N-perchloric acid failed, because in several trials with different lots of plutonium the potentials drifted badly. However, the observed values of the equimolar potentials were always close to the potentials of the polarographic waves in the same solutions (see p. 1018).

(D) Polarographic experiments were carried out in 1N-sulphuric, -perchloric, and -hydrochloric acids (see Figs. 3, *a*, *b*, and *c*).

FIG. 2.
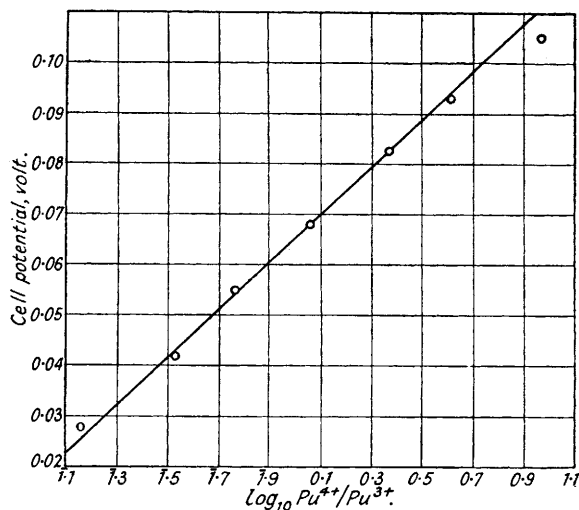
A small platinum wire micro-electrode replaced the foil electrode of the cell in Fig. 1, and a sintered-glass plug was substituted for the constriction. A dropping-mercury electrode could not be used because mercury dissolves anodically in the range of potentials studied. For polarograms in hydrochloric acid, a normal calomel reference electrode was used. For perchloric acid solutions, the reference electrode was $Hg|Hg_2Cl_2$ (s) $+$ $0.1N$-HCl $+$ $1N$-HClO$_4|$ with a bridge solution of $1N$-HClO$_4$. In sulphuric acid, the reference electrode was $Hg|Hg_2SO_4$ (s) $+$ $1N$-H$_2$SO$_4|$.

FIG. 3 (*a*).

FIG. 3 (*b*).

Potential of platinum electrode.
vs. Hg, Hg₂SO₄, 1N-H₂SO₄ electrode.

FIG. 3 (*c*).
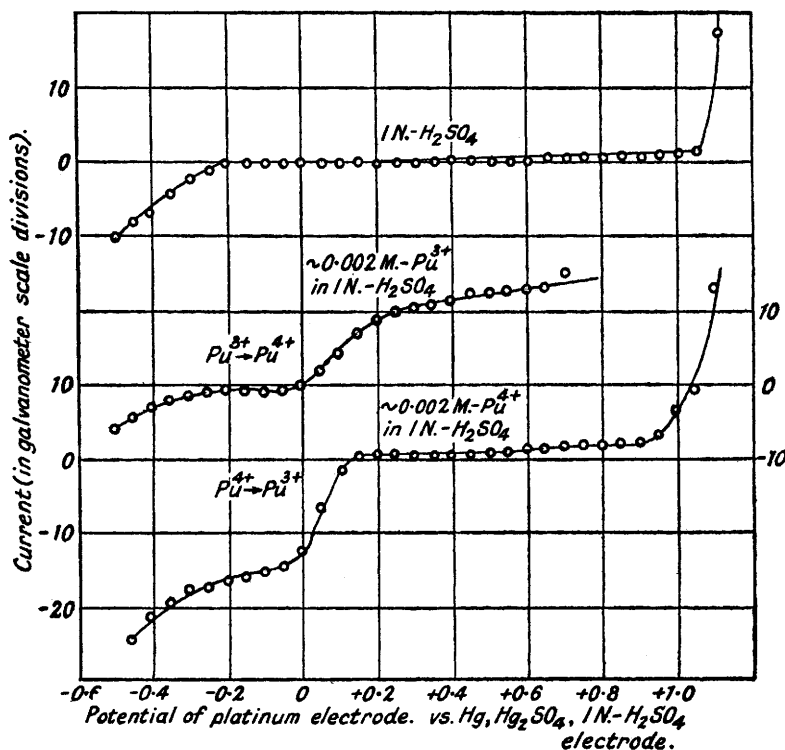

Potential of platinum electrode.   vs. Hg, Hg₂SO₄, 1N.-H₂SO₄
electrode.
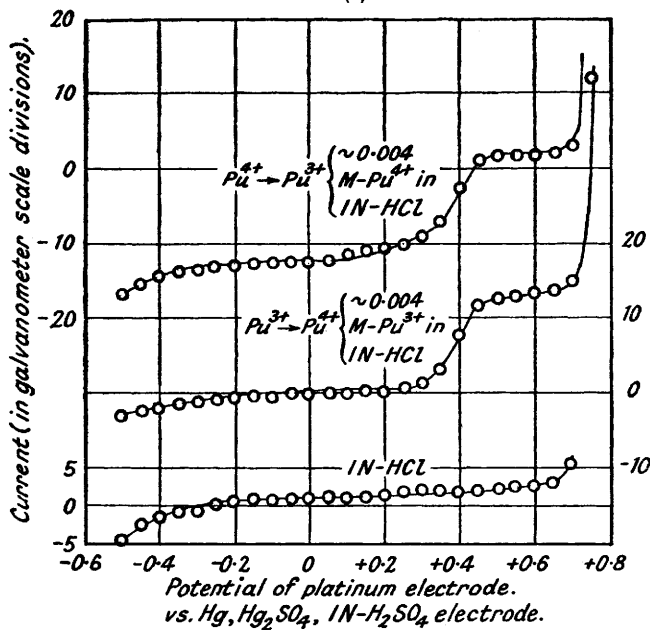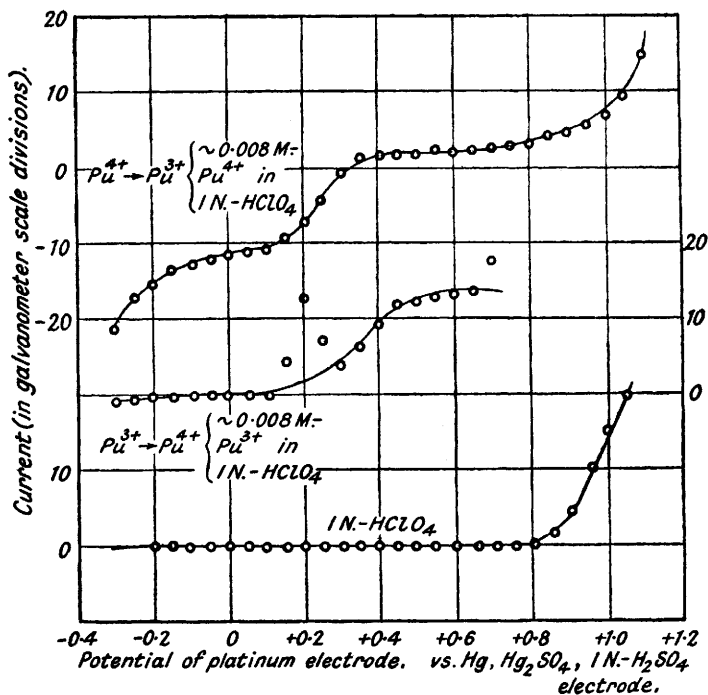
The polarograms in perchloric acid solution were carried out at 23°. In all other cases, the cell was held at 30° in a vibration-free thermostat.

(E) Small volumes of concentrated uranous sulphate and uranous chloride in their respective 1N-acids were added to solutions of Pu(IV) in 1N-sulphuric and hydrochloric acids. In both cases the Pu(IV) reduction wave disappeared within 2 or 3 minutes of the addition and was replaced by a wave starting

in the same place as the Pu(III) wave in the same solution (Figs. 4 and 5). The concentrations of Pu(IV) in these experiments were chosen so that after addition of the U(IV) solution, the Pu concentrations were equal to those used in plotting the polarograms for pure Pu(III) solutions given in the same diagram.

U(IV) in sulphuric and hydrochloric acids does not give an oxidation wave in this range of potentials. The great height of the oxidation wave in the Pu–U mixtures must be due to the oxidation of U(IV) at the electrodes in the presence of Pu(III), which acts as an electron carrier. (The uranium concentration was about 5 times the plutonium concentration.)

FIG. 4.
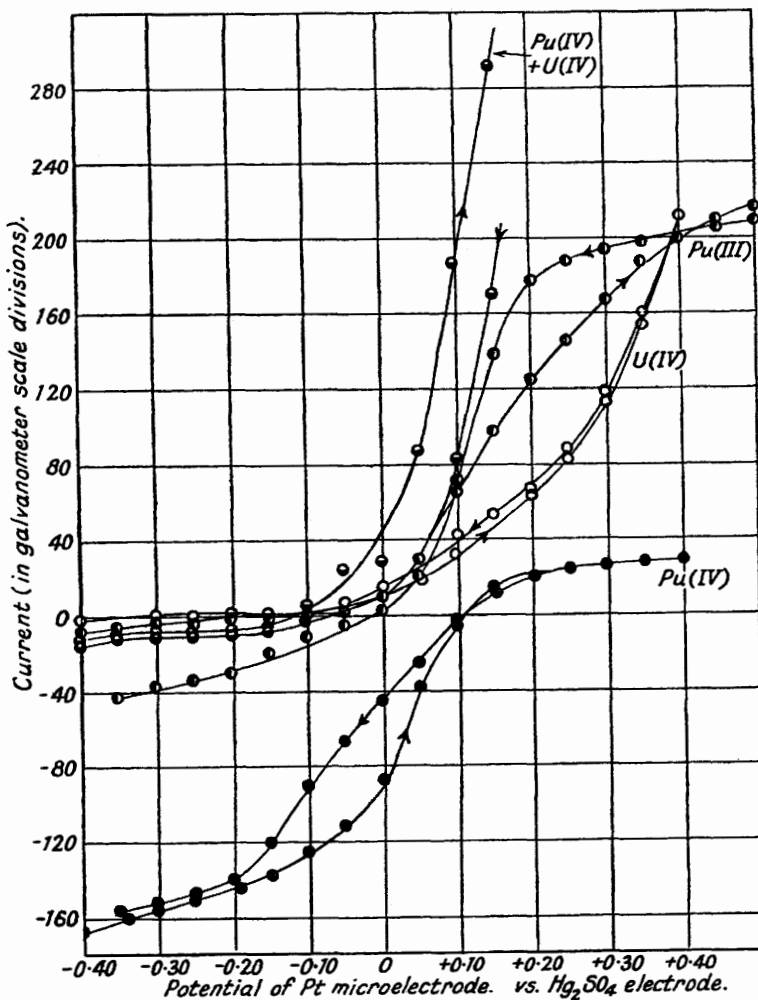
Polarograms in $1N-H_2SO_4$.

(F) Experiments were carried out in which the Pu(IV) ion was oxidised by the perdisulphate ion in the presence of silver ions. Different concentrations of reagents were tried, and the fraction of the plutonium which had been oxidised in the experiment was estimated by precipitating the remaining Pu(IV) on a carrier of lanthanum fluoride (the fluoride of sexavalent plutonium remains in solution under these conditions). The plutonium on the lanthanum fluoride carrier was then estimated by α-counting.

Concentrations of 0·2 mg. per ml. of silver ion and 2 mg. per ml. of perdisulphate ion were found to be sufficient. Oxidation of the plutonium took place when the solutions were heated to 80° and then allowed to cool and stand for 20 minutes. The presence of nitrate ions (about 0·5M) appeared to be advantageous. Perchloric acid up to 2M was without influence of the reaction.

(G) (i) A sample of plutonium peroxide precipitated from sulphate solution was washed free from excess of hydrogen peroxide, suspended in 1N-sulphuric acid, and titrated with potassium permanganate. It was found that on warming the solution very slightly, a reaction took place and the per-

oxide went into solution. After 0·71 ml. of permanganate had been used, the peroxide appeared to have dissolved completely, and further permanganate only reacted at a somewhat higher temperature. The volume of permanganate required at this higher temperature was 0·47 ml.

The second half of this titration was believed to represent the oxidation of Pu(IV) to Pu(VI). This was confirmed by reducing the plutonium to Pu(III) with sulphur dioxide, and evaporating the solution to fuming in air to remove the excess sulphur dioxide and convert the Pu(III) into Pu(IV). The same volume (0·47 ml.) of permanganate was used when the Pu(IV) obtained in this way was titrated to Pu(VI).

Fig. 5.
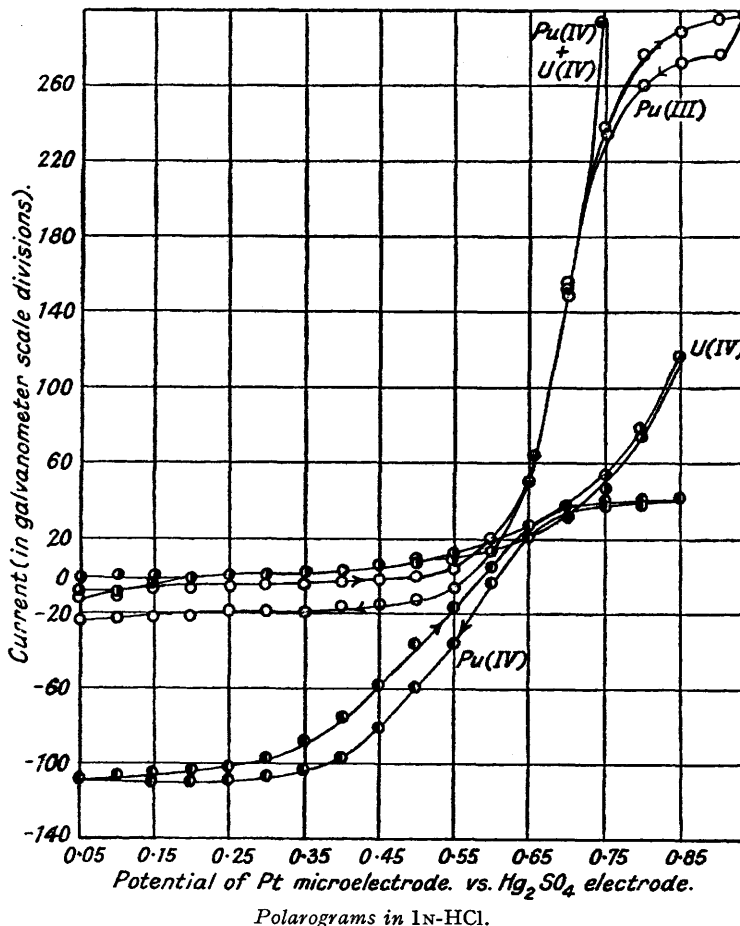
Polarograms in 1N-HCl.

(ii) A second sample of the peroxide, precipitated from sulphuric acid solution, washed three times with water, and dried to constant weight over silica gel at room temperature, was dissolved in concentrated nitric acid. The sulphate ion present in the solution was determined by precipitating it as barium sulphate. The plutonium was then precipitated from the solution as hydroxide and weighed as PuO_2. The following results were obtained :

Wt. of peroxide, mg.	2·255
Wt. SO_4, mg.	0·216
Wt. Pu, mg.	1·704
Total, mg.	1·920
Remainder, mg.	0·335

(H) A small weight of lanthanum nitrate in aqueous solution was added to a dilute perchloric acid solution containing a tracer quantity of quadrivalent plutonium; 48% hydrofluoric acid was then added until its concentration in the Pu–La solution was 12%. The precipitate of lanthanum fluoride was allowed to settle, and a further quantity of lanthanum nitrate, equal to the first amount, was then slowly added with good stirring.

After standing for about 30 minutes with occasional stirring, the solution was centrifuged to separate the fluoride precipitate. The supernatant solution was removed, and the precipitate washed several times with dilute hydrofluoric acid. The lanthanum fluoride was then spread on a sample tray, and the plutonium estimated by α-counting. The results are given below :

Precipitation of Pu(IV) *on lanthanum fluoride.*

Total wt. of La used, mg./ml. of Pu soln. .... 0·35	0·093	0·034	0·017
% Pu remaining in solution .... 1·49	1·94	6·11	10·4

(I) A sample of sulphate crystals (see p. 1012) was separated from the solution, washed with acetone, dried at room temperature and weighed. The sample was then converted into the anhydrous salt by fuming to dryness with sulphuric acid. The crystals were found to be the *tetrahydrate* [Found : Pu$(SO_4)_2$, 85·8. Pu$(SO_4)_2$,4H$_2$O requires Pu$(SO_4)_2$, 85·6%].

(J) Experiments were carried out to discover over what pH range zirconium phenylarsonate could be used as a carrier for tracer quantities of plutonium. Zirconyl nitrate solutions were added to dilute perchloric acid solutions containing tracer quantities of plutonium. The pH's of the solutions were then adjusted to various values by the addition of either more perchloric acid or ammonia. An excess of saturated aqueous phenylarsonic acid solution was then added, and the precipitate of zirconium phenylarsonate was removed by centrifuging, and its plutonium content estimated by α-counting. The results are shown herewith.

The precipitation of Pu(IV) *on zirconium phenylarsonate.*

pH .... 0·1	0·19	0·33	1·45	1·90	3·95
% Pu precipitated by 0·2mg./ml. of Zr .... 87·6	88·5	93·9	93·7	90·0	93·2

(K) *Precipitation of* Pu(IV) *on zirconium* m-*nitrobenzoate.*

pH .... 0·39	1·46	1·88	3·80
% Pu precipitated by 0·2 mg./ml. of Zr .... 5·1 *	91·0	95·4	93·3

* Zr not completely precipitated.

(L) 9·457 Mg. of Pu$(SO_4)_2$ were dissolved in sulphuric acid and oxidised by heating for several hours at 90° on a steam-bath with an excess of sodium perdisulphate. The pH of the solution was then adjusted to about 5, and about 5 equivs. of oxine dissolved in acetic acid were added. The precipitate was coagulated by heating on the steam-bath, filtered off, washed with hot water, dried at 130°, and weighed. The *oxinate* weighed 15·713 mg. [Found : Pu, 33·4. PuO$_2$(C$_9$H$_6$ON)$_2$,C$_9$H$_7$OH requires Pu, 33·9%].

(M) *Reaction of plutonium with organic complexing reagents.*

Ion.	Reagent.	pH range.	Reaction.
Pu(IV)	Acetylacetone	2—10	Complex extractable in benzene
Pu(IV)	Benzoylacetone	3	Complex extractable in benzene
Pu(IV)	Monofluoroacetylacetone	3	Complex extractable in benzene
Pu(IV)	Trifluoroacetylacetone	2—4	Complex extractable in benzene
Pu(IV)	*p*-Dimethylaminobenzeneazophenyl-arsonic acid	4	Orange precipitate
Pu(III)	*p*-Dimethylaminobenzeneazophenyl-arsonic acid	4	No precipitate
Pu(IV)	*p*-Dimethylaminobenzeneazophenyl-arsinic acid	4	Orange-red precipitate
Pu(III)	*p*-Dimethylaminobenzeneazophenyl-arsinic acid	4	No precipitate
Pu(IV)	3-Nitro-4-hydroxyphenylarsonic acid	2·5	Pale greenish-buff precipitate, Pu carried down on Zr salt
Pu(III)	3-Nitro-4-hydroxyphenylarsonic acid	2·5	No ppt. Pu not carried down on Zr salt
Pu(IV)	*m*-Nitrophenylarsonic acid	2·5	Pale greenish-buff ppt. Pu carried down on Zr salt
Pu(III)	*m*-Nitrophenylarsonic acid	2·5	No ppt. Pu not carried down on Zr salt
Pu(IV)	Phenylarsonic acid	2	Pale greenish-buff ppt. Pu carried down on Zr salt
Pu(III)	Phenylarsonic acid	2	No ppt. Pu not carried down on Zr salt
Pu(IV)	*n*-Propylarsonic acid	2	Pale greenish-buff ppt. Pu carried down on Zr salt
Pu(III)	*n*-Propylarsonic acid	2	No ppt. Pu not carried down on Zr salt
Pu(IV)	*m*-Nitrobenzoic acid	1·5	Pale greenish-buff ppt. Pu carried down on Zr salt
Pu(III)	*m*-Nitrobenzoic acid	1·5	No ppt. Pu not carried down on Zr salt
Pu(IV)	Sebacic acid	1—2	Pu carried down on Zr salt
Pu(III)	Sebacic acid	1—2	Pu poorly carried down on Zr salt
Pu(IV)	5-*p*-Acetamidophenylazo-8-hydroxy-quinoline	4	Complex extractable in amyl acetate. Insol. in water
Pu(IV)	8-Hydroxyquinoline	—8	Purple-brown ppt. extractable in amyl acetate

Ion.	Reagent.	pH range.	Reaction.
Pu(VI)	8-Hydroxyquinoline	4—8	Orange-brown ppt. extractable in amyl acetate
Pu(IV)	1'-Sulphonaphthalene-4'-azo-5 : 8-dihydroxyquinoline	3	Purple ppt.
Pu(IV)	Anthranilic acid	3	Complex extractable in amyl acetate
Pu(IV)	Cinnamic acid	2·5—4·5	Complex extractable in amyl alcohol
Pu(IV)	Cresotinic acid	2·5—4·5	Complex extractable in amyl acetate
Pu(IV)	2 : 4-Dihydroxybenzoic acid	3	Complex extractable in methyl *iso*butyl ketone
Pu(IV)	2 : 4-Dinitrosalicylic acid	3	Complex extractable in amyl acetate
Pu(IV)	Salicylic acid	2—3	Complex extractable in amyl acetate. Pu carried down on Th, La and Zr salts
Pu(IV)	Benzoic acid	2	Green-yellow ppt.
Pu(IV)	Citric acid	1—11	Soluble complex
Pu(IV)	Dihydroxytartaric acid	1	Pu carried down on Th salt
Pu(III)	Dihydroxytartaric acid	1	Pu poorly carried on Th salt
Pu(IV)	3 : 5-Dinitrobenzoic acid	3	Complex extractable in amyl acetate
Pu(IV)	Phthalic acid	2	Pu carried down on Zr salt
Pu(III)	Phthalic acid	2	Pu not carried down on Zr salt
Pu(IV)	Tartaric acid	1—11	Soluble complex
Pu(VI)	Tartaric acid	1—11	Soluble complex
Pu(IV)	Thiobarbituric acid	2	Pu carried down on Th, Zr, and La salts
Pu(III)	Thiobarbituric acid	3	Pu poorly carried down on Th, Zr, and La salts
Pu(IV)	" Cupferron "	0·5—2	Complex extractable in chloroform
Pu(IV)	Ethylenediamine	—	Brown ppt., insol. in water and organic liquids
Pu(IV)	α-Nitroso-β-naphthol	2	Complex extractable in methyl *iso*butyl ketone
Pu(IV)	Sodium benzenesulphinate	2	Buff ppt. not extractable in amyl acetate
Pu(VI)	Sodium benzenesulphinate	2	Complex extractable in amyl acetate
Pu(VI)	Sodium diethyldithiocarbamate	3	Purple-brown complex extractable in amyl acetate or amyl alcohol

(N) *Extraction of* Pu(IV) *salicylate into amyl acetate.*

Salicylate concn. in aq. layer, moles/l.	pH of aq. layer.	Extrn. coeff. of Pu.	Salicylate concn. in aq. layer, moles/l.	pH of aq. layer.	Extrn. coeff. of Pu.
0·0058	4·0	0·23	0·053	5·2	0·15
0·0116	4·0	0·16	0·214	5·2	0·22
0·0232	4·0	0·64	0·428	5·2	3·7
0·0464	4·0	7·9	0·642	5·2	4·8
0·0696	4·0	3·4	0·856	5·2	2·1
0·0928	4·0	4·7	1·07	5·2	12·8
0·116	4·0	8·12			