

Studies on the Hydrolysis of Metal Ions. 62. The Plutonyl Ion in Sodium Perchlorate Medium

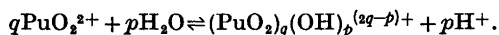
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The hydrolysis equilibria of plutonyl ion in 3 M (Na)ClO₄ have been studied at 25 °C using a glass electrode. The concentration range for PuO₂²⁺ (*B*) was 10–150 mM and the average number of ligands, OH⁻, bound per PuO₂²⁺ (*Z*) was 0–1.3. Fresh Pu(VI) solutions were always used, in which the concentration of other plutonium ions was less than one per cent.

About 20 species (*p,q*) = (PuO₂)_q(OH)_p^{(2q-p)+} were tried in the LETAGROP "species selector".

For *Z* < 0.3, where the attainment of chemical equilibria could be proved by back titrations, all the data could be explained by (2,2), with the "best" equilibrium constant log *β_{2,2} = -8.24 ± 0.01, where *β_{p,q} is the equilibrium constant for



For higher *Z* the data are uncertain as equilibrium could not be proved. The best fit is given by (2,2) and (7,4) with the equilibrium constant *β_{2,2} = -8.23 ± 0.04 and (*β_{7,4} = -29.13 ± 0.04).

A short survey is also given of some properties of plutonium ions in aqueous solutions, as they might have affected this investigation.

It is well-known, that the plutonyl ion hydrolyzes in water solution, but there is still much uncertainty about what species that are formed upon hydrolysis. For this reason it was considered of great interest to try to get further information on this basic problem in plutonium chemistry.

Until recently very little has been published in the literature on this subject, as shown in Table 1. O'Connor¹ made an early investiga-

tion in 1944, and he found PuO₂OH⁺, here called (1,1). Kraus and Dam² made potentiometric titrations in 1949. They worked at rather low concentrations (0.718–1.32 mM PuO₂²⁺) and found the mononuclear complexes PuO₂OH⁺ and PuO₂(OH)₂. Krevinskaya *et al.*³ dissolved a known amount of a plutonium salt in a certain amount of nitric acid and measured pH with a glass electrode. They found five different complexes, some of which also contained nitrate. Their results must be considered unreliable as the accuracy obtained in this way is rather low. Moskvina *et al.*⁴ made solubility investigations. Their experimental procedures are not recorded in detail. They dissolved a solid plutonium phase at different pH and measured [H⁺] potentiometrically. The solid phase was prepared by adding ammonia to a Pu(VI) solution and was considered to be ammonium diplutonate. However Cleveland⁵ later found that a precipitate prepared in the same way mainly contained plutonium(VI) hydroxide. Recently, in 1972, Cassol *et al.*⁶ reported potentiometric measurements of [H⁺] at 25 °C in 1 M (Na)ClO₄ containing plutonium in the concentration range 0.1–30 mM. They found PuO₂OH⁺ in agreement with Kraus *et al.* and (PuO₂)₂(OH)₂²⁺ in agreement with our earlier paper⁷ and a new species (PuO₂)₃(OH)₆⁺, which they considered a little uncertain. Their data seem to be the most reliable yet published and are complementary to our investigation, in which higher *B* values have mainly been studied.

Table 1. Hydrolysis of plutonyl ion. Complexes found in the literature and in our investigation. They are given as $-\log^*_{p,q}$, for the (p,q) values shown at the top of each column.

(1,1)	(2,1)	(2,2)	(3,2)	(5,2)	(5,3)	(7,4)	Ionic medium	B range mM	°C	Year	Ref.
5.30	—	—	—	—	—	—				1944	1
5.71	11.42	—	—	—	—	—	1 M NaClO ₄	0.718–1.32		1949	2
3.33	7.38	—	—	—	—	—	0.186 mM HNO ₃	0.001–0.01		1959	3
3.39	8.64	—	17.77	31.50	—	—		0.122–58.5		1962	4
—	—	8.21	—	—	—	—	3 M (Na)ClO ₄	15–130	25	1971	7
5.97	—	8.51	—	—	22.16	—	1 M (Na)ClO ₄	0.1–30	25	1972	6
—	—	8.24	—	—	—	(29.13)	3 M (Na)ClO ₄	10–150	25	1974	^a

^a Present paper.

EXPERIMENTAL

All work where plutonium was involved in these experiments, was performed in glove boxes. The preparation of plutonium solutions was made in a special box in order to avoid acidic fumes during analysis and hydrolysis. The analytical determination of plutonium in solution took place in another box and was performed by a special staff. The titrations were performed in a third glove box.

All inactive reagents were prepared and stored outside the glove boxes, where necessary in rooms kept at 25.0 ± 1.5 °C.

Reagents and solutions

Sodium perchlorate stock solution was prepared by neutralization of concentrated HClO₄, Merck *p.a.*, with Na₂CO₃, Merck *p.a.* waterfree. To avoid some impurities, *e.g.* Fe, the solution was made slightly alkaline and allowed to stand for a week. It was filtered through a G4 Jena glass filter and recrystallized once and standardized by evaporation at about 120 °C. The reproducibility was within 0.1 %. This method of analysis had previously been checked against an ion exchange method used on another stock solution prepared in the same way. The agreement was better than 0.2 %.

Perchloric acid solutions were made by dilution of HClO₄, Merck *p.a.*, and standardized against recrystallized KHCO₃ with a reproducibility of 0.2 %. They were also checked against the NaOH stock solution, which gave the same result to within 0.2 %.

Sodium hydroxide was prepared as a 50 % solution from solid NaOH, EKA *p.a.* Na₂CO₃ was removed by filtering through a G4 Jena glass filter. The solution was diluted with boiled distilled water under an N₂ atmosphere and standardized against hydrazine sulfate with a reproducibility of 0.2 %.

Silver(II) oxide was prepared according to Hammer *et al.*⁸ from K₂S₂O₈, N-free, Merck *p.a.*

It was decanted three times from very dilute NaOH solutions, and washed several times with water during filtration.

Sodium chloride used was NaCl, Merck suprapur.

The *distilled water* used was always boiled to expel CO₂.

Plutonium solutions were prepared from plutonium metal. Two different castings were used. Their purity, which was examined by spectral analysis, was high (less than 0.02 % impurities).

Due to the autoreduction of Pu(VI) in solution it is important to use freshly prepared samples. A method was developed to prepare in one day a solution of PuO₂²⁺ with an accurately known concentration in 3 M (Na)ClO₄. A weighed piece of Pu metal was dissolved in a known aliquot of 5 M HClO₄. More dilute acid gave a black, insoluble precipitate, probably Pu(IV) oxide. The blue Pu(III) solution, formed during dissolution, was rapidly and completely oxidized to PuO₂²⁺ by a known amount of AgO(s). The silver(II) oxide was added in small portions under shaking, as some of it reacted with water with O₂ evolution. Thus AgO had to be added in excess; usually 50 % was used. The excess oxide was easily destroyed by heating to about 80 °C. At the same time the excess acid, added at the dissolution of Pu metal, was neutralized. Finally the proper amount of NaClO₄ was added. Excess Ag⁺ was precipitated as AgCl by NaCl(s) and filtered off.

The determination of plutonium was performed according to Andersson, Baurén and Helleday⁹ and in cooperation with these authors. The method used was potentiometric titration of Pu(VI) with Fe(II) after oxidation with AgO. This gave the total amount of plutonium. If we omitted the oxidation step, we got a slightly lower value of plutonium due to the autoreduction of Pu(VI). As the solutions, used in these experiments, were never more than one day old, it was assumed, following Rabideau,¹⁰ that practically only Pu(V) had been formed. If this assumption was

Table 2. Hydrolysis of plutonyl ion in 3 M (Na)ClO₄. The result of the plutonium analysis. [Pu_{tot}] and [PuO₂²⁺] are usually the mean of two determinations with the limits given.

Titration No.	[Pu _{tot}] mM	[PuO ₂ ²⁺] mM	[PuO ₂ ⁺] mM	$\frac{[\text{PuO}_2^+]}{[\text{Pu}_{\text{tot}}]} 10^2$
1	27.102 ± 0.004	26.32	0.78	1.4
2	40.69 ± 0.06	39.91 ± 0.02	0.78	2.0
3	56.66 ± 0.01	55.40 ± 0.00	1.26	2.2
4	79.20 ± 0.01	78.60 ± 0.01	0.60	0.78
5	129.94 ± 0.05	127.62 ± 0.05	2.32	1.8
6	223.94 ± 0.06	222.91 ± 0.04	0.82	0.36

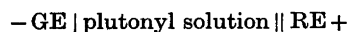
correct, we could get a good value for [PuO₂²⁺] (cf. discussion below). The results are shown in Table 2. There are also given the amount of Pu(V) and the decrease of Pu(VI) in per cent of total Pu, which are both determined from a small difference between two large numbers and must be considered uncertain. On the average the decrease in the concentration of PuO₂²⁺ was 1.4 % per day. Other authors have given figures of the same order, e.g. Rabideau,¹⁰ who found 1.5 % per day.

The agreement between the value calculated in advance for [Pu_{total}] and that found by analysis was usually better than 1 %.

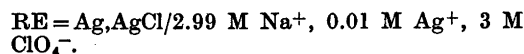
The isotopic composition of the plutonium used corresponded to the atomic weight 239.1.

Procedure

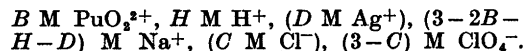
All experiments were carried out as potentiometric titrations with a glass electrode (GE) and a reference electrode (RE). The cell was:



where



The plutonyl solution in the titration vessel (S) had the general composition:



C and *D* are small amounts of Cl⁻ or Ag⁺, one of which may remain after the precipitation of AgCl during the preparation of the plutonyl solution. Naturally the ideal case would be, where *C* = *D* = 0, but this is impossible to achieve in practice without special precautions. Mostly there seemed to be a small excess of Ag⁺, but neither Ag⁺ nor Cl⁻ were considered of any harm because of the low concentrations of these species.

The solution in the buret (T) only contained NaOH (negative *H*) or HClO₄ and ionic medium. It had the general composition:



It was impractical in this case to keep the total amount of plutonium (*B*) constant by adding it from a buret, which is the usual method. The composition of a plutonyl solution changes so rapidly that the content of PuO₂²⁺ and H⁺ in solution T would be uncertain. The radiolytic reactions also produce H₂(g) and O₂(g) in small bubbles, which would give erratic values for the volume of solution added from the buret of at most a few per cent per day at the highest concentrations of plutonium studied.

The initial solution S was always acidic and NaOH was added from the buret. The first part of the titration was a neutralization of H⁺ for the determination of better values of *H* and *E*₀. Then the hydrolysis started and the titration was continued during all day. Next day a back titration with HClO₄ was performed ending with the same neutralization part as in the beginning.

Using Nernst's formula it is possible to calculate the concentration of free H⁺ (*h*) for each point on the titration curve:

$$E = E_0 + E_j + 59.16 \log h \quad (1)$$

Following Biedermann and Sillén¹¹ it was assumed that *E*_{*j*} = *j* *h*. The *j* value was determined in solutions not containing plutonium. Then *E*₀ could be determined from the first part of the forward titrations and the last part of the back titrations, where no hydrolysis was involved. First a Gran plot¹² was made to get a better value of the analytical excess of H⁺ (*H*), which in this part of the curve is equal to *h*. With knowledge of this and from a plot of (*E* - 59.16 log *h*) versus *h*, *E*₀ was obtained.

It was now possible to calculate *Z*, the average number of OH⁻ bound per Pu, which is defined as:

$$Z = (h - H) / B \quad (2)$$

From the material balance equations for Pu(VI) and protons we get

$$B = b + \sum q^* \beta_{p,q} h^{-p} b^q \quad (3)$$

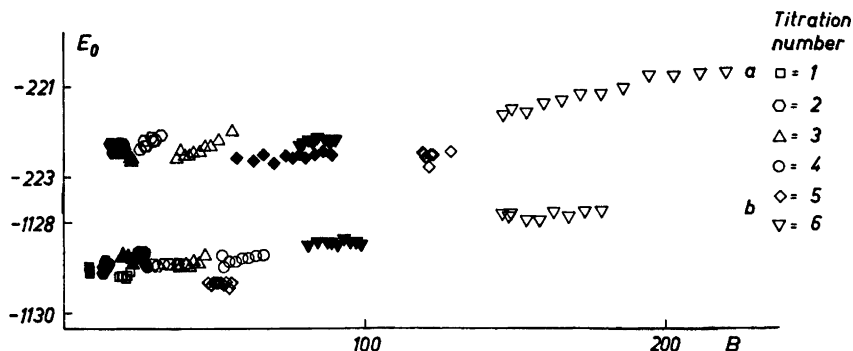
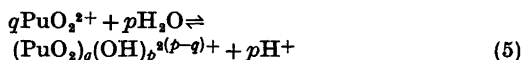


Fig. 1. Potentiometric titrations of plutonyl solutions. $E_0 = f(B)$ in the points before (open points) and after the hydrolysis (full points) in Titrations 1–6 for the two glass electrodes used. In Titrations a: Beckman 41 263 and in Titrations b: Jena Thalamid U 161.

$$BZ = \sum p^* \beta_{p,q} h^{-bq} \quad (4)$$

where $\beta_{p,q}$ is the equilibrium constant for the reaction



The H values obtained from the Gran plots did not agree for the forward and back titrations. An increase in H , probably due to radiolytic effects, was always found. A correction was added to all points under the assumption that the increase of H was direct proportional to time, though it might not be correct. The order of the change in H was about 0.001 mol per Pu and hour, which would give a correction in Z of at most 0.01 for a titration performed in one day.

E_0 seemed to vary with the plutonium content. In Fig. 1 ($E - E_j - 59.16 \log h$) is plotted versus B ($= [\text{Pu}_{\text{total}}]$). Another term of the type $E_B = kB$ or $E_B = kb$ should be necessary above $B = 150$ mM. For that reason titrations have only been performed for $B < 150$ mM.

Apparatus

When this work started very little plutonium was available. For that reason much attention was paid to the development of smaller titration assemblies as illustrated in an earlier paper.¹³ Gradually more and more plutonium became available and in the final apparatus we worked with an initial volume of 10 ml.

The titration vessel was the Ingold Titration Vessel 604.¹³

The reference electrode was finally of the Wilhelm type,¹⁴ but reduced in size and containing only 10 ml. It was also provided with some spherical joints to make it more flexible to minimize the risk of breakage in the glove box.

Many different glass electrodes were tried. Some makes, e.g. Ingold and Radiometer, were impossible to use in the glove box. They were too sensitive to static electricity built up by the gloves in the plexiglass box, or by people passing the apparatus, probably due to poor shielding. On the other hand the electrodes from Jena and Beckman were found to be very good. In the final experiments a Jena glass electrode, type Thalamid U 161, and Beckman glass electrodes, type 41 263 and 40 498, were used.

The burets used were Metrohm piston buret EA 902, volume 10 ml. The outlet was a rather long glass tube supplied with three spherical joints for flexibility, and a pointed tip, that fitted in the cap of the titration vessel.

The solution was stirred with a teflon covered rod by a magnetic stirrer.

All different parts were mounted on a stand to make it easy to handle. Two identical titration assemblies were placed in the glove box and used parallel to make the best use of the freshly prepared plutonium solutions. For example one apparatus could be used for the study of low and the other of high Z values.

The EMF was measured by two valve potentiometers pHM4 from Radiometer placed outside the box. They were calibrated against a Cambridge Vernier Potentiometer.

The whole glove box was thermostated as described earlier.¹³ The temperature around the vessel was 25.0 ± 0.1 °C. The temperature of the solution was also checked sometimes and was within the same limits.

DATA

The experimental data are collected in Table 3 and shown in Fig. 2 as $Z = f(-\log h)$. Each curve corresponds to one titration, the values of B decreasing when Z increases due to dilution.

Table 3. Hydrolysis of plutonyl ion in 3 M (Na)ClO₄. The experimental data ($-\log h$, Z , B mM) are given together with their value of $1000(Z_{\text{calc}} - Z_{\text{obs}})$ found in the LETAGROP calculations using the "best" set of equilibrium constants. Two titrations (a and b) were performed simultaneously using the same initial solutions but in different titration assemblies.

Titration 1a. 3.200, 0.002, 17.21, -1; 4.089, 0.032, 16.88, -4; 4.224, 0.051, 16.77, -1; 4.351, 0.080, 16.61, +4; 4.440, 0.110, 16.45, +7; 4.527, 0.151, 16.25, +9; 4.618, 0.212, 15.96, +7; 4.728, 0.316, 15.48, +4; 4.882, 0.523, 14.63, +20; 4.985, 0.689, 14.01, +53; 5.063, 0.836, 13.50, +64.

Titration 1b. 3.210, 0.002, 17.19, -1; 4.102, 0.033, 16.86, -3; 4.353, 0.083, 16.57, +1; 4.537, 0.152, 16.23, +14; 4.719, 0.318, 15.47, -9; 4.866, 0.529, 14.60, -17; 4.992, 0.738, 13.83, +14; 5.107, 0.946, 13.14, +38; 5.228, 1.156, 12.51, +45; 5.369, 1.365, 11.94, +30.

Titration 2a. 3.335, 0.003, 26.27, -2; 3.999, 0.029, 25.92, 0; 4.214, 0.067, 25.59, +3; 4.393, 0.125, 25.11, +13; 4.544, 0.224, 24.34, +7; 4.653, 0.344, 23.48, -14; 4.723, 0.442, 22.82, -26.

Titration 2b. 2.811, 0.001, 26.60, -1; 3.123, 0.002, 26.34, -1; 3.724, 0.010, 26.08, -1; 4.699, 0.446, 22.80, -65; 4.768, 0.544, 22.16, -65; 4.833, 0.643, 21.56, -54; 4.888, 0.743, 20.99, -51; 4.951, 0.843, 20.45, -24; 5.007, 0.943, 19.94, -12; 5.063, 1.042, 19.46, -4; 5.132, 1.163, 18.90, -3.

Table 3. Continued.

Titration 3a. 4.266, 0.110, 35.05, +3; 4.440, 0.189, 34.21, +17; 4.576, 0.313, 32.98, +7; 4.687, 0.458, 31.66, 0; 4.812, 0.664, 29.93, +6; 4.983, 0.975, 27.71, +29.

Titration 3b. 2.877, 0.002, 36.68, -2; 3.216, 0.003, 36.44, -2; 3.938, 0.031, 35.96, -1; 4.158, 0.071, 35.50, +4; 4.334, 0.131, 34.83, +13; 4.530, 0.253, 33.56, +24; 4.616, 0.357, 32.57, +8; 4.757, 0.564, 30.76, +7; 4.870, 0.772, 29.14, +11; 4.980, 0.980, 27.68, +18.

Titration 4. 2.794, 0.001, 51.33, -1; 3.659, 0.013, 50.66, -1; 3.871, 0.031, 50.33, 0; 4.156, 0.091, 49.38, +7; 4.344, 0.172, 48.16, +18; 4.476, 0.274, 46.71, +16; 4.601, 0.437, 44.58, -9; 4.704, 0.601, 42.63, -14; 4.784, 0.744, 41.06, -11; 4.888, 0.951, 38.98, -17; 5.019, 1.177, 36.95, -7; 5.135, 1.361, 35.44, -22.

Titration 5a. 3.247, 0.000, 117.1, +4; 3.715, 0.036, 115.0, -2; 3.911, 0.076, 113.0, 0; 4.084, 0.136, 110.0, +7; 4.229, 0.214, 106.5, +14; 4.341, 0.315, 102.2, +1.

Titration 5b. 4.337, 0.301, 103.0, +12; 4.435, 0.421, 98.21, -7; 4.501, 0.523, 94.59, -25; 4.560, 0.624, 91.22, -39; 4.621, 0.724, 88.08, -37; 4.674, 0.825, 85.15, -43; 4.782, 1.028, 79.84, -48; 4.897, 1.231, 75.15, -55.

Titration 6a. 4.368, 0.385, 127.4, +9; 4.435, 0.486, 123.8, -10; 4.554, 0.683, 117.3, -22.

Titration 6b. 2.865, 0.003, 143.8, -2; 3.648, 0.034, 141.9, -3; 3.856, 0.072, 140.1, +2; 4.035, 0.133, 137.5, +10; 4.151, 0.192, 135.0, +16; 4.287, 0.290, 131.1, +23; 4.378, 0.389, 127.3, +18; 4.501, 0.587, 120.4, -14.

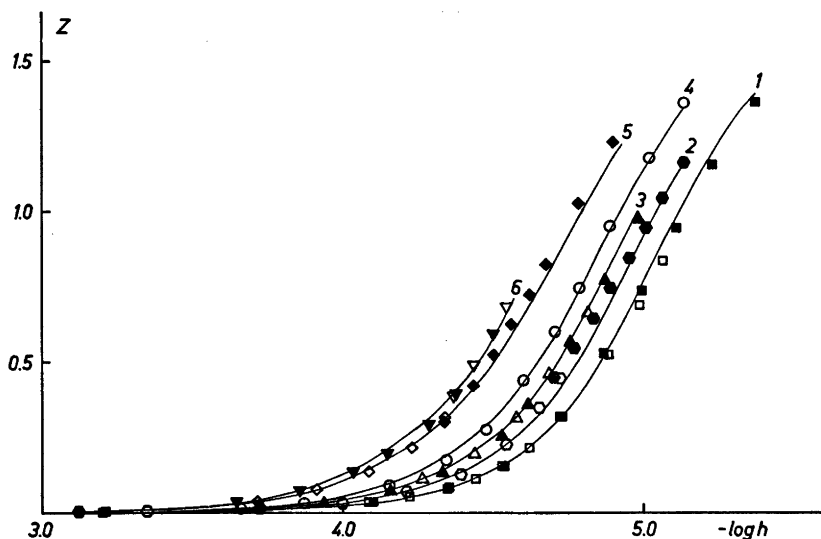


Fig. 2. Hydrolysis of plutonyl ion in 3 M (Na)ClO₄. Points are all experimental data $Z=f(-\log h)$ and curves are calculated with "best" values of $*\beta_{2,3}$ and $*\beta_{7,4}$. Open and full points of the same shape are from different titrations using identical solutions.

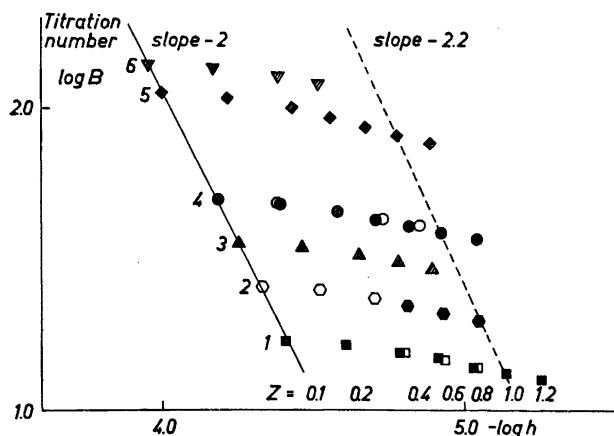


Fig. 3. Hydrolysis of plutonyl ion in 3 M (Na)ClO₄. Experimental data from Fig. 2 here transformed to $\log B = f(-\log h)_Z$. Points from the same titration have the same shape here as in Fig. 2 and shaded points mean coinciding full and open points. The full straight line is the "best" curve through the points with $Z = 0.1$. The broken curve is the "best" straight line through the points with $Z = 1.0$.

The concentration range for plutonium was 10–150 mM.

With the procedure used it was necessary to have exactly the same solutions when an experiment was to be repeated. As the starting material was a piece of plutonium metal this was hard to achieve quickly enough and was never done. For comparison the different Z -curves were transformed to $\log B = f(-\log h)_Z$ (Fig. 3). The points seemed to fall on the same straight line for different experiments. This can be taken as an indication that the experiments were reproducible.

TREATMENT OF DATA

All calculations were made on the assumption, that the law of mass action was valid, which means that in every point the solution must have been in equilibrium. In this respect the data could be divided into two parts. One part includes the points with low Z ($Z < 0.3$), where chemical equilibrium could be proved by agreement between forward and back titrations. The rest of the data must be treated with some caution as no stable potentials could be achieved during the back titrations. It has been assumed, however, that the forward titrations correspond to equilibrium.

The computer program LETAGROP¹⁵⁻¹⁹ was used for the analysis of data. Various sets of

complexes (p, q) and rough values of their stability constants $^*\beta_{p,q}$ were given to the computer, which then calculated the error squares sum $U = \sum (Z_{\text{calc}} - Z_{\text{obs}})^2$. In this program the set of equilibrium constants is searched for, which gives the lowest U -value.

To speed up the search for plausible complexes the so called "species selector" of the LETAGROP program¹⁹ was used. This means that beside the probable main complexes a pile of new species were given one by one. The new one was first varied alone to get a better value of $^*\beta_{p,q}$ and then together with the main complexes. The computer calculated $^*\beta_{p,q}$ and $\sigma(^*\beta_{p,q})$ and also $^*\beta/\sigma$, which is called "sigfak". If the value of "sigfak" was smaller than a given value, the complex was rejected.

Our first trial was with the complexes found in the literature. The next step was to try species found in the uranyl system, which has many properties in common with plutonyl and has been thoroughly investigated. Finally those (p, q) combinations were tried, where size and charge were reasonable. Species with a higher charge than +3 were not considered. The 20 different (p, q) values tried are shown in Fig. 4.

If only the more accurate data with $Z < 0.3$ were used in the calculations the complex (2,2) alone gave an acceptable fit to the data (cf. Fig. 5). The result was:

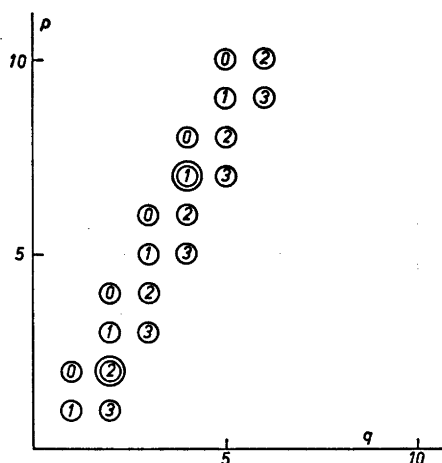


Fig. 4. Hydrolysis of plutonyl ion in 3 M (Na)ClO₄. (p, q) values tried in the LETAGROP calculations. The figures in the circles show the positive charge of the complex. The double circles show our two, most plausible complexes.

$$*\beta_{2,2} = (0.574 \pm 0.004)10^{-8} \text{ or } \log *\beta_{2,2} = -8.24 \pm 0.01 \text{ with } \sigma(Z) = \pm 0.0045.$$

Including all experimental points, (2,2) alone could not explain the data. It gave $U_{\min} = 0.330$ and $\sigma(Z) = 0.180$. Some higher complex had to be added as was pointed out in our earlier paper.⁷ Every complex in Fig. 4 was passed through the "species selector" at least twice, using "sigfak" = 1.0 and 1.5. With these rather low values of "sigfak" the following higher complexes were retained at least once during the calculations: (3,2), (5,3), (7,4), (9,5), (4,3), (6,4), (8,5), and (10,6). Together with the well

established (2,2) each of these species were given a new opportunity in an "ordinary" LETAGROP calculation (Rurik = 3) with the results given in Table 4. It should be mentioned that lower values than $U_{\min} = 0.040$ and $\sigma(Z) = 0.021$ were never achieved during any of the calculations, even if several complexes were combined.

It is obvious from Fig. 3, that the data, transformed to $\log B = f(-\log h)_z$, give rather good straight lines with a slope of approximately -2 . According to Sillén²⁰ this indicates the formation of "core and links" species with the general composition $B(A_2B)_n$. The five first in this serie are all to find among the retained complexes in Table 4, while the rest could be generally written $AB(A_2B)_n$.

If the data were used without any correction in H with time, the calculations seemed to give the same main species.

The computer program HALTAFALL²¹ was used to calculate how the amounts of the different species vary with pH and B . In Fig. 6 α -curves are given for $B = 0.15$ M and $B = 0.01$ M, which are about the maximum and minimum values used in this work, and $B = 0.001$ M, which is about the concentration investigated by Kraus *et al.*² $B = 0.001$ M and $B = 0.01$ M are also in the lower and upper part of the concentration range studied by Cassol *et al.*⁶ Four different stability constants were taken into consideration namely for (1,1) and (2,1) found by Kraus *et al.* and for (2,2) and (7,4) found in this investigation. α is the fraction of plutonium present in each species.

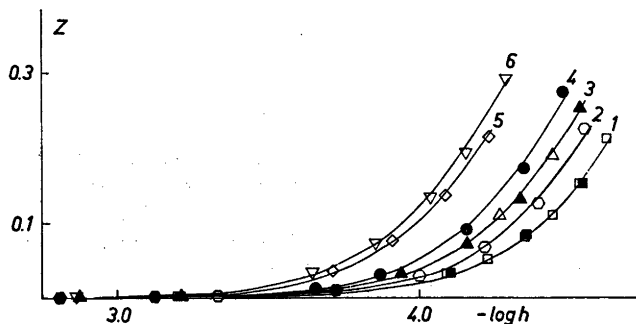


Fig. 5. Hydrolysis of plutonyl ion in 3 M (Na)ClO₄. Points are the same experimental data $Z = f(-\log h)$ as in Fig. 2 but limited to $Z < 0.3$. Curves are calculated with the "best" value of $*\beta_{2,2}$.

Table 4. Hydrolysis of plutonyl ion in 3 M (Na)ClO₄. The "best" constants obtained in the LETAGROP calculations (Rurik=3) assuming only two species: (2,2) and some of the higher species previously retained at least once by the "species selector" (Rurik=17) using all data.

$*\beta_{2,2} 10^8$		$U_{\min} \times 10^3$	$\sigma(Z) \times 10^3$
0.587 ± 0.017	$*\beta_{7,4} = (0.768 \pm 0.022)10^{-29}$	44.8	22.3
0.417 ± 0.021	$*\beta_{5,3} = (0.776 \pm 0.022)10^{-21}$	75.3	28.9
0.686 ± 0.022	$*\beta_{6,5} = (0.850 \pm 0.039)10^{-37}$	72.5	28.4
0.314 ± 0.038	$*\beta_{6,4} = (0.881 \pm 0.049)10^{-24}$	213	48.6
0.714 ± 0.408	$*\beta_{3,2} = (0.106 \pm 0.004)10^{-12}$	300	57.8
MIKO	$*\beta_{4,3} = (0.103 \pm 0.007)10^{-15}$	516	75.7
0.498 ± 0.026	$*\beta_{8,5} = (0.945 \pm 0.047)10^{-32}$	103	33.8
0.607 ± 0.023	$*\beta_{10,6} = (0.111 \pm 0.006)10^{-39}$	76.4	29.1
0.579 ± 0.072	$*\beta_{2,1} = (0.687 \pm 0.054)10^{-10}$	941	102

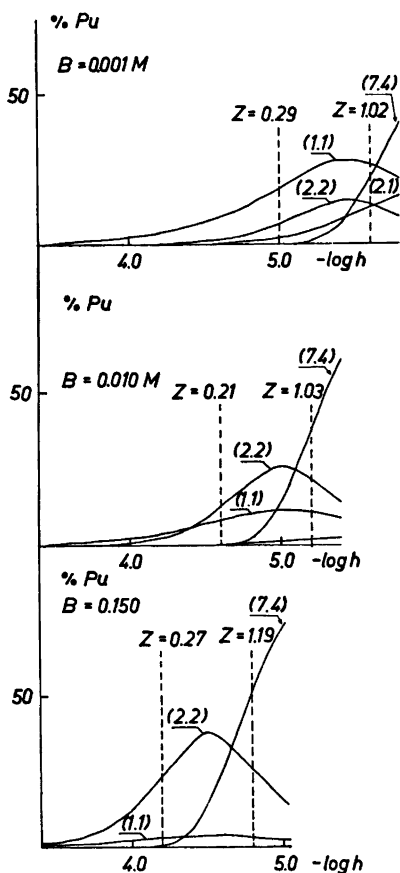
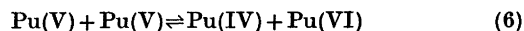


Fig. 6. Hydrolysis of plutonyl ion. α -curves or the fraction of total Pu present in the different complexes in per cent as a function of pH and B, calculated by HALTAFALL using the constants $*\beta_{1,1}$ and $*\beta_{2,1}$ found by Kraus *et al.*² and $*\beta_{2,2}$ and $*\beta_{7,4}$ found by us.

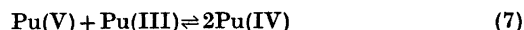
DISCUSSION

The complex chemical nature of plutonium and the effect of irradiation on aqueous solutions will be briefly discussed here, as they have affected the accuracy in this work.

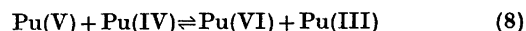
Disproportionation. At least four different plutonium ions can exist together in aqueous solutions: Pu³⁺, Pu⁴⁺, PuO₂⁺, and PuO₂²⁺. In fact the oxidation potentials are such that coexistence is favoured.²² PuO₂⁺ and Pu⁴⁺ can both spontaneously disproportionate and give a mixture of all four oxidation states. For Pu(V) Connick²³ found two possible paths:



or if also Pu(III) is present:

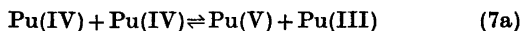


Both these reactions involve the rupture of a chemical bond, when PuO₂⁺ is reduced to Pu⁴⁺ and are rather slow reactions. Connick found reaction (6) to be the slowest. These rate-determining steps are followed by the rapid reversible equilibrium

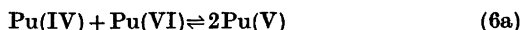


which only requires the transfer of one electron. It is a fast reaction and can mostly be considered in completion. Rabideau¹⁰ studied the kinetics of reaction (6), and Rabideau and Kline²⁴ the kinetics of reaction (8) and confirmed the mechanisms.

The mechanism for the disproportionation of Pu(IV) was suggested by Connick²³ to be the reverse of reaction (7) or (6):



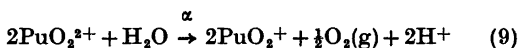
and if Pu(VI) is also present:



Again these must be the rate-determining steps, and he considered (7a) to be the fastest. They were also followed by the fast reaction (8). This description was confirmed through kinetic studies by Rabideau²⁵ in HClO₄ and by Rabideau and Cowan²⁶ in HCl.

Irradiation ²³⁹Pu, which was the main isotope in this work, is an α -emitter with a half-life of about 24 000 years and an energy of 5.15 MeV. The α -particles with their high energy are able to ionize molecules in their path. Water molecules are considered to be decomposed, possibly *via* activated molecules, into free radicals as H \cdot , \cdot OH, HO₂ \cdot , which then combine under formation of H₂, O₂ and H₂O₂ as described by Miner and Seed.²⁷ According to Rabideau *et al.*,²⁸ who studied the effect of radiolysis in perchlorate medium, the gas generated consisted of about 60 % O₂ and 40 % H₂. This does not correspond to the pure decomposition of water, which would give a much lower O₂ content.

The difference in *H* found in this work between the first and last Gran plot was also assumed to be a radiolytic effect. Considering that the formation of oxygen was greater than corresponded to the decomposition of water into hydrogen and oxygen, the over all reaction of the reduction of Pu(VI) and oxidation of water initiated by α -particles, might be:



This would give an increase in *H* of the same order as the decrease in Pu(VI) of 1.5 % per day. In our work a somewhat higher value, 2.4 %, was observed, which might be explained by addition from some, other radiolytic reaction. The change in *H* could also be due to some irreversible protolytic reaction or analytical error, which must be of the order 1–1.5 % to explain the whole increase. Since analytical errors in *H* mostly are about 0.2 %, the latter explanation seems rather unlikely.

The irradiation causes a continuous reduction of a Pu(VI) solution. As mentioned above, Rabideau¹⁰ found the decrease in the plutonyl concentration to be 1.5 % per day in perchlorate

medium, and similar values have been obtained by others. The mechanism of this reduction seems not to be completely understood, but H₂O₂ is considered to take part as a reductant of PuO₂²⁺. Rabideau found that no Pu(IV) could be detected after one day. His explanation was that in the beginning only Pu(V) was formed with the rate of 1.5 % per day. Then Pu(V) disproportionated according to the slow reaction (6) followed by the rapid reaction (8), when the concentration of Pu(IV) increased. If this is correct the amount of the undesirable Pu(IV) must have been very low in the fresh solutions used in our experiments.

Rabideau *et al.*²⁸ also found that the auto-reduction was independent of many parameters such as the initial value of the mean oxidation number, pH and temperature, and that the steady state, reached after a couple of weeks, was just above a mean oxidation number of 3 (3.02–3.05).

The ionic medium seems to play an interesting role in the radiolysis reactions. In chloride medium no reduction was observed. The molecules of the ionic medium could also be decomposed. In perchlorate medium Cl⁻ was found. This was also observed during this work as a precipitate of AgCl in old solutions containing Ag⁺.

The net result of disproportionation and radiolysis reactions in a Pu(VI) solution in NaClO₄ medium will in a few days be a solution containing an unknown amount of Pu(III), Pu(IV), Pu(V), Pu(VI), an unknown change in H⁺ concentration, decomposition products of the ionic medium as Cl⁻ beside NaClO₄. Of course all these reactions must have had influence on the accuracy of the data in the present investigation.

Hydrolysis of other Pu ions. Naturally it is of interest to know the hydrolytic behaviour of the other plutonium ions, as they might be present in small quantities in our solutions. Rather little seems to be known about Pu(III) and Pu(V). Kraus and Dam²⁹ made some experiments on Pu(III) and found its hydrolysis weak and to occur around pH=7. They also studied Pu(V),³⁰ whose hydrolysis seems to start around the same pH. It is thus obvious that the presence of these two ions does not disturb the investigation of the hydrolysis of Pu(VI).

On the other hand the hydrolysis of Pu(IV)

starts at very low pH. The first hydrolytic product PuOH^{3+} has been recognized by Rabideau³¹ in a potentiometric study as well as spectrophotometrically by Rabideau and Kline.³² On further alkalification the hydrolytic species grow and a rather stable colloid appears before the precipitation of hydroxide starts. This polymerization is an irreversible process, and the colloid may be extremely hard to dissolve. This colloid may easily appear, when a solution is diluted with water or whenever a local deficit of acid arises. It is obvious that Pu(IV) must be avoided and our efforts have been to keep its concentration as low as possible. In order to analyze for Pu(IV) some of the solutions were studied with a Cary 14 M recording spectrophotometer. No trace of Pu(IV) was ever seen after one day. However, the detection limit is rather high, about 1% without special precautions. Also the possible presence of small amounts of colloidal Pu(IV) would not give the typical Pu(IV) peaks but only result in a slight increase of the background.

Chemical equilibrium. During the titrations some observations were made about the reaction rates and the time necessary to reach chemical equilibrium. When NaOH was added to the Pu(VI) solutions, it took a considerable time to get stable potentials for the first points, between 20 min and a couple of hours. It was also found that when the value of Z had increased to about 0.2–0.3, the EMF seemed to be constant within 5 or 10 min. At the highest Z values studied the equilibration became slow again. The EMF was now instead increasing after each addition, and the titrations were interrupted here.

It was desirable to make back titrations with HClO_4 to check that the same curve was obtained and that chemical equilibrium had been reached, but it was very difficult to get stable potentials. The pH values achieved were too low and only slowly increased towards the values obtained in the forward titration, never actually reaching them. As Pu(VI) solutions are so quickly destroyed, it was impossible to wait for equilibrium to be reached. This has been a great dilemma during this work: on one side the desire to wait long enough to be sure of chemical equilibrium, on the other hand the wish

to work fast enough to be certain of the composition of the Pu solutions.

If the forward titration was interrupted at a Z value of 0.2–0.3 and the back titration was started from this point, stable potentials could be achieved, which fitted well on the forward curve. Here chemical equilibrium seems to have been attained and these data, for $Z < 0.3$, must be considered reliable.

The change in EMF during the night between the forward and the back titration was 0.3–2.0 mV measured at the highest value of Z . Probably the solutions were not too far from equilibrium, as the radiolysis must be taken into consideration, which causes a continuing change in the content of Pu(VI) and H.

CONCLUSIONS

The most important result of this investigation is the establishment of the dimer $(\text{PuO}_2)_2(\text{OH})_2^{2+}$, which alone can explain all the points for $Z < 0.3$, which we consider accurate and reliable. It is interesting to note that Cassol *et al.* probable unaware of our earlier results, also have found (2,2) to be one of the main species.

That at least one more higher complex must exist is quite clear. Its influence is greatest on the higher values of Z , where the data are less accurate and chemical equilibrium could not be proved. So unfortunately the composition of the higher complex must still be considered uncertain. From Table 4 it is obvious that (7,4) gave the best fit followed by (5,3) and (9,5). At the highest Pu concentrations (5,3) gave increasing deviations at the highest Z values (titrations 4 and 5), so it was excluded from the discussion. Assuming (2,2) and (7,4) we got the same "best" value of $\beta_{2,2}$ as was found in the region $Z < 0.3$. As this combination also gave the lowest U_{min} and $\sigma(Z)$ it is considered the most plausible. However, the explanation might as well be the existence of a serie of higher complexes, *e.g.* of the type $\text{AB}(\text{A}_2\text{B})_n$ or $\text{B}(\text{A}_2\text{B})_n$ mentioned earlier, but that could not be deduced from the present data.

It is interesting to make a comparison between the observations made during the titrations regarding reaction rates and equilibration and the amount of the different species in Fig. 6, calculated by HALTAFALL. As can be

seen in Fig. 6 (2,2) predominates, where $Z < 0.3$ in both 0.01 and 0.15 M Pu(VI) solutions. When $Z > 0.3$ (7,4) grows and predominates at the highest Z , where (2,2) disappears. The slow, reversible reactions for $Z < 0.3$ thus coincide with the formation of (2,2). For higher Z values faster equilibration was noticed, and thus connected with the building up of (7,4) and the disappearance of (2,2).

Using the data of Kraus *et al.*² the amount of (2,1) in the B region examined in our investigation would be extremely small according to Fig. 6 and this complex was never found by us. (1,1) would however be possible to find at the lower B concentrations. Special calculations were performed using only Titration 1, which has the lowest B value, but (1,1) could not be established in this investigation even at this low concentration. However, it must be kept in mind that Kraus *et al.* used a different ionic medium than we did.

For $B = 0.001$ M the picture is quite different. Here (1,1) dominates for $Z < 1$, where (2,1) and (7,4) grow. The amount of (2,2) is never large. This may explain, why Kraus *et al.* found (1,1) and (2,1) in their investigation at $B = 0.718 - 1.32$ mM. Using LETAGROP on their data the following result was obtained:

$$\log * \beta_{1,1} = -5.58 \pm 0.05, \log * \beta_{2,1} = -11.50 \pm 0.03 \text{ with } \sigma(Z) = 0.038.$$

Cassol *et al.*⁶ suggested (1,1) (2,2), and (5,3) in their investigation at $B = 0.1 - 30$ mM. Unfortunately they have only published the data from one single titration at $B = 2 - 3$ mM. We made some LETAGROP calculations on that figures and found (2,1) to give a good fit together with (2,2):

$$\log * \beta_{2,1} = -11.24 \pm 0.02, \log * \beta_{2,2} = -8.68 \pm 0.10 \text{ with } \sigma(Z) = 0.017.$$

Surprisingly (2,1) was never mentioned by Cassol *et al.* neither was (7,4). As long as their complete data are not available it is not possible to make any further conclusions about the existence of higher complexes.

Kraus *et al.* reported the same failure to get stable potentials during the back titrations as was found by us, while Cassol *et al.* mentioned nothing about that problem. The drift in pH during the back titrations went towards higher

pH, which means that OH^- was liberated, and the new species must have contained less OH^- . One explanation may be that for some reason the breaking up of the large molecules, when *e.g.* (7,4) disintegrates into (2,2) and PuO_3^{3+} and OH^- , is a slower reaction than the reverse. If this is the case the forward curve would still be useful for obtaining information about the hydrolysis. Another explanation may be that the drift in EMF was caused by some impurity, *e.g.* Pu(IV), which reacted slowly. If this was the case, all the data for $Z < 0.3$ would be unreliable and useless, and (2,2) the only certain result.

Thus our "best" set of species and their equilibrium constants together with their standard deviations are considered to be:

$$* \beta_{2,2} = (0.574 \pm 0.004)10^{-8}, * \beta_{7,4} = (0.768 \pm 0.022)10^{-29} \text{ or } \log * \beta_{2,2} = -8.23 \pm 0.01, \log * \beta_{7,4} = -29.11 \pm 0.04 \text{ with } \sigma(Z) = 0.022.$$

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