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Summary

1. The isolation of chemically pure plutonium and the preparation of the first pure compounds of this element are described.

2. Methods are described for the preparation and purification of plutonium compounds on a one to thirty microgram scale.

3. The specific alpha activity of Pu^{239} was determined by weighing microgram samples of plutonium oxide, and the value $7.1 \pm 0.1 \times 10^4$ alpha counts per minute per microgram (in a 2π geometry counter) found.

4. The half life of the isotope Pu^{239} has been computed from specific activity and counting yield measurements to be 24,300 ± 370 years.

5. It is shown that the +4 state is a stable oxidation state of plutonium.

6. Approximate solubilities of plutonium iodate, ammonium plutonium fluoride, plutonium "hydroxide" and plutonium peroxide have been determined. The colors of these compounds and of plutonium oxide have been noted.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

Mechanism of the Disproportionation of Plutonium(V)[1]

BY ROBERT E. CONNICK

The +5 oxidation state of plutonium is unstable in moderately acidic solutions with respect to the reaction

$$2Pu(V) = Pu(IV) + Pu(VI) \qquad (1)$$

This reaction proceeds sufficiently slowly in 0.5 *M* hydrochloric acid that it is possible to produce plutonium(V) in solution and then measure its rate of disproportionation. From a study of the rate law several interesting conclusions can be drawn as to the mechanism of disproportionation.

In a previous paper[1a] an experiment was described in which plutonium(VI) in solution in 0.5 *M* hydrochloric acid was approximately 50% reduced to the +5 oxidation state by electrolytic reduction at a platinum electrode. The solution was then transferred to a quartz cell and its absorption spectrum measured as a function of time at room temperature by means of a Beckman Spectrophotometer. By analysis of the absorption curve it was possible to determine the amounts of plutonium(III), plutonium(IV), plutonium(V) and plutonium(VI) present in the solution at all times. The present paper deals with the information obtained from this experiment relating to the kinetics of the disproportionation of plutonium(V).

A plot of the data is given in Fig. 1 and the data are given in Table I, both of which have been taken from reference (1). The first interesting point to be observed is that plutonium(VI) and plutonium(III) are produced in the initial stages of the disproportionation of plutonium(V), rather than plutonium(VI) and plutonium(IV), although the latter combination is thermodynamically more stable than the former.

TABLE I

RELATIVE CONCENTRATIONS OF VARIOUS OXIDATION STATES IN THE DISPROPORTIONATION OF PLUTONIUM(V)

Time in hours	Plutonium oxidation states; per cent. of total plutonium				
	Pu(VI)	Pu(V)	Pu(IV)	Pu(III)	Total
1.0	48.1	45.3	<1	2.4	95.8
3.0	55.2	39.0	~1	4.7	99.9
5.0	62.3	29.6	2.0	7.2	101.1
7.0	68.5	20.8	3.7	9.3	102.3
9.0	72.5	14.2	5.8	9.8	102.3
11.0	74.5	10.0	8.0	9.5	102.0
13.0	75.6	7.8	9.6	8.5	101.5
15.0	76.4	6.3	11.4	7.7	101.8
17.0	76.8	5.2	12.9	7.1	102.0
19.0	77.0	4.5	14.0	6.6	102.1
24.0	76.5	3.6	16.5	5.1	101.7
29.0	76.0	3.0	18.8	4.0	102.8
39.0	75.1	1.5	21.7	3.0	101.3

This phenomenon has been explained[1] as being due to the rapid reduction of plutonium(IV) by plutonium(V) according to the equation

$$Pu(IV) + Pu(V) = Pu(III) + Pu(VI) \qquad (2)$$

From the experimental data of reference (1) it is clear that the equilibrium of equation (2) was rapidly established and was maintained at all times during the experiment. The ease of establishment of the equilibrium is readily understood when the equation is written using the actual ionic species, since the reaction consists of the transfer of only an electron

$$Pu^{+4} + PuO_2^+ = PuO_2^{++} + Pu^{+3} \qquad (3)$$

An average value of 8.5 was obtained for the equilibrium quotient of reaction (2) in 0.5 *M* hydro-

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(1) This research was carried out under the auspices of the Manhattan District at the Chemistry Department of the University of California during the summer of 1944.

(1a) "The +5 Oxidation State of Plutonium," R. E. Connick, M. Kasha, W. H. McVey and G. E. Sheline, MDDC-749, July 6, 1944.

chloric acid at room temperature when expressed as[2]

$$K = \frac{(\text{Pu(III)})(\text{Pu(VI)})}{(\text{Pu(IV)})(\text{Pu(V)})} = 8.5 \qquad (4)$$

This equilibrium, together with the one for the reaction

$$3\text{Pu(IV)} = 2\text{Pu(III)} + \text{Pu(VI)} \qquad (5)$$

permits the calculation of the equilibrium quotients of all equilibria involving plutonium in the +3, +4, +5 and +6 oxidation states. Kasha and Sheline[3] have found the following value for the equilibrium quotient of reaction (5) in 0.5 *M* hydrochloric acid at 25.0°

$$K_1 = \frac{(\text{Pu(III)})^2(\text{Pu(VI)})}{(\text{Pu(IV)})^3} = 0.050 \qquad (6)$$

In the disproportionation of plutonium(V) part of the plutonium is oxidized and part is reduced. The part which is oxidized changes from PuO_2^+ to PuO_2^{++}, which merely involves the removal of an electron. The part which is reduced must go to either the +3 or the +4 state, and, since neither of the ions corresponding to these states is oxygenated, the ion of the +5 state, PuO_2^+, must become deoxygenated in the course of the reaction. This process, which involves the breaking of bonds, is believed to be mainly responsible for the slowness of disproportionation of plutonium(V).

There are only two bimolecular reactions between plutonium species which bring about the reduction of plutonium(V) to the +4 or +3 state, *i. e.*

$$\text{Pu(V)} + \text{Pu(V)} = \text{Pu(IV)} + \text{Pu(VI)} \qquad (7)$$

$$\text{Pu(V)} + \text{Pu(III)} = 2\text{Pu(IV)} \qquad (8)$$

Both of these reactions involve the deoxygenation of a single plutonium(V) to give a Pu^{+4}. Any other reactions converting a plutonium(V) to a lower oxidation state involve three or more plutonium ions and therefore become much less probable reactions than these two bimolecular reactions, at least at the rather low (*ca.* 4 × 10^{-3} *M*) concentrations of plutonium studied. In addition, any termolecular reaction, or one of higher order, would also in each case necessitate the removal of the two oxygens from the plutonium(V) and would have the same inherent slowness in this respect as the bimolecular reactions, besides the slowness introduced by the low probability of obtaining three or more plutonium ions sufficiently close together at one time to react. Thus it seems almost certain that the plutonium(V) will be converted to a lower oxidation state through either or both of reactions (7) and (8).

In addition to the rate determining step of the reaction, either equation (7) or equation (8), the equilibrium represented by equation (2) is always established in the solution. The continual readjustment of this equilibrium as the reaction proceeds through equation (7) or (8) provides for the formation of species other than those given by equation (7) or (8) alone. Thus reaction by equation (7) converts plutonium(V) to plutonium(IV) and plutonium(VI). Through the equilibrium of equation (2) some of the plutonium(IV) will then react with plutonium(V) to give plutonium(VI) and plutonium(III).

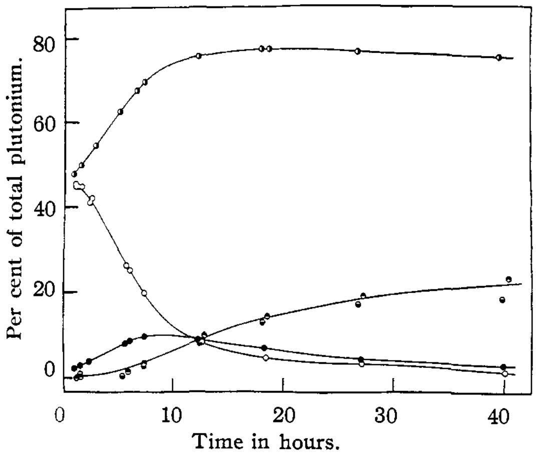

Fig. 1.—Disproportionation of plutonium(V): per cent. Pu(III), ●; Pu(IV), ◓ and ◒; Pu(V), ○; and Pu(VI), ◑, as a function of time. Total plutonium concentration is 4.27 × 10^{-3} *M*. The two sets of values for the percentage Pu(IV) were obtained at two different wave lengths.

From a study of the rate data of Fig. 1 it should be possible to distinguish between the mechanism of equation (7) and that of equation (8). Qualitatively the mechanism of reaction (8) would predict a rate proportional to the concentrations of plutonium(III) and plutonium(V). Since plutonium(III) is initially present at a very low concentration but is formed during the disproportionation of plutonium(V), the rate should exhibit an autocatalytic behavior. The decrease in the plutonium(V) concentration tends to offset this effect, but the percentage change in the plutonium(III) concentration near the start of the reaction is much greater than the percentage change of the plutonium(V) concentration, so the reaction should initially appear autocatalytic. Since in the experiment there was some plutonium(III) already present in the solution at the conclusion of the electrolytic reduction, this effect should not be highly pronounced. It is seen in Fig. 1 that the rate of disproportionation of plutonium(V) as measured by the slope of the plutonium(V) curve does actually increase during very early stages of the reaction. However, the effect is small and surely is not in itself sufficient evidence to prove that the reaction follows equation (8) rather than equation (7).

A definite proof of which mechanism is correct is obtained from an examination of the rate of reaction at several different times. First it is nec-

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[2] Parentheses are used throughout this paper to indicate concentrations of the enclosed species in moles per liter of solution.

[3] M. Kasha and G. E. Sheline, MDDC-392, January 17, 1945.

essary to set up the rate laws for the two different mechanisms.

Mechanism of Equation (7).—Reaction (7) is assumed to be the rate determining step. Reaction (2) is assumed to be a rapid reversible equilibrium with K equal to 8.5. The plutonium(V) disappears both by reaction (7) and through the equilibrium of reaction (2). The kinetics of the reaction are complicated by the fact that the equilibrium of equation (2) is continually shifting. At the start of the reaction nearly all of the plutonium(IV) that is produced by reaction (7) is converted to plutonium(III) by the equilibrium of reaction (2); near the end of the reaction, plutonium(IV) produced by reaction (7) remains as plutonium(IV), and there is actually a net decrease in the plutonium(III) concentration by the shifting of the equilibrium of reaction (2) to the left.

In order to develop the rate law it is convenient to use equation (2) in the form

$$\mathrm{Pu(IV)} + \mathrm{Pu(V)} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \mathrm{Pu(III)} + \mathrm{Pu(VI)} \quad (9)$$

Here k_3 and k_4 are the forward and reverse bimolecular rate constants. Their ratio must of course equal K, the value of the equilibrium quotient of the reaction.

Equation (7) is rewritten as

$$\mathrm{Pu(V)} + \mathrm{Pu(V)} \underset{k_2'}{\overset{k_1'}{\rightleftarrows}} \mathrm{Pu(VI)} + \mathrm{Pu(IV)} \quad (10)$$

with the back reaction included for the sake of generality.

The rate of disappearance of plutonium(V) according to equation (9) and (10) is then

$$2k_1'(\mathrm{V})^2 + k_3(\mathrm{IV})(\mathrm{V})$$

where, for simplicity, the Roman numeral of the oxidation state enclosed in parentheses indicates the concentration in moles per liter. The rate of appearance of plutonium(V) is

$$2k_2'(\mathrm{VI})(\mathrm{IV}) + k_4(\mathrm{III})(\mathrm{VI})$$

Therefore

$$\mathrm{d(V)}/\mathrm{d}t = 2[k_2'(\mathrm{VI})(\mathrm{IV}) - k_1'(\mathrm{V})^2] + k_4(\mathrm{III})(\mathrm{VI}) - k_3(\mathrm{IV})(\mathrm{V})$$

Similarly

$$\mathrm{d(IV)}/\mathrm{d}t = k_1'(\mathrm{V})^2 - k_2'(\mathrm{IV})(\mathrm{VI}) + k_4(\mathrm{III})(\mathrm{VI}) - k_3(\mathrm{V})(\mathrm{IV})$$

Combining the above two equations

$$\mathrm{d(V)}/\mathrm{d}t = 3[k_2'(\mathrm{VI})(\mathrm{IV}) - k_1'(\mathrm{V})^2] + (\mathrm{d(IV)}/\mathrm{d}t) \quad (11)$$

It is of interest to point out the significance of each term in equation (11) with respect to the experiment in question. The d(IV)/dt term on the right side is a measure of the extent to which the equilibrium of equation (2) enters into the reaction. If d(IV)/dt is very small, then practically no plutonium(IV) is present in the solution and reaction (2) is shifted far to the right. As it becomes of the same order of magnitude as the other terms on the right side of equation (11), the equilibrium of reaction (2) is such as to produce appreciable amounts of plutonium(IV) in solution. When the equilibrium of reaction (2) is shifted far to the left, no plutonium(III) is produced and the value of d(IV)/dt is just half the value of $-$d(V)/dt. The term in equation (11) involving k_1' is of course the measure of the rate of reaction (10) proceeding to the right and the term involving k_2' is a measure of the rate of the same reaction proceeding in the opposite direction.

Under the conditions of the experiment the solution initially had a composition such that reaction (10) was far from equilibrium. Under these circumstances the contribution of the back reaction measured by $k_2'(\mathrm{IV})(\mathrm{VI})$ was negligible compared to the magnitude of the forward reaction measured by $k_1'(\mathrm{V})^2$. Toward the end of the reaction this was no longer so; however, the concentration of plutonium(V) became so low near the end of the reaction that it was not possible to obtain an accurate measure of the rate and in the region where accurate measurements were made the contribution of the back reaction of equation (11) was negligible. Therefore, for the the purpose of this discussion equation (11) may be simplified to

$$\frac{\mathrm{d(V)}}{\mathrm{d}t} - \frac{\mathrm{d(IV)}}{\mathrm{d}t} = -3k_1'(\mathrm{V})^2 \quad (12)$$

One more fact should be pointed out with respect to Equation (12). In the derivation it was stated that it was convenient to generalize equation (2) to equation (10) using rate constants in the derivation rather than the equilibrium quotient, K. This generalization is reflected in the appearance in the final equation of two differentials rather than one, *i. e.*, d(IV)/dt as well as the desired differential, d(V)/dt. If the rate equation had been derived using K rather than the rate constants it would have contained only one differential, d(V)/dt, and would have involved the concentrations of Pu(III), Pu(IV) and Pu(VI) as well as that of Pu(V). (Both equations will be given in the next section where the rate law for the second possible mechanism is discussed.) No serious discrepancy can be introduced by the use of d(IV)/dt since it is only a small correction term over most of the range of the reaction considered. Further, the constancy of K over this range[1] insures that this equilibrium is established, in which case the two methods of calculation should give identical results within the accuracy of the measurements.

The experimental check of the mechanism of equation (7) was made by determining d(V)/dt and d(IV)/dt at various times by measuring the slopes of the Pu(V) and Pu(IV) curves in Fig. 1. These values are tabulated in Table II along with the time and the concentration of plutonium(V) and plutonium(III). According

TABLE II

RATE OF DISPROPORTIONATION OF PLUTONIUM(V)

0.50 *M* HCl, room temperature

Time in min.	$-$ d(V)/d*t* moles/l./min.	d(IV)/d*t* moles/l./min.	Pu(V), moles/l.	Pu(III), moles/l.	k_1', l./mole/min.	k_1, l./mole/min.
180	3.03×10^{-6}	0.36×10^{-6}	1.62×10^{-3}	0.201×10^{-3}	0.43	3.5
300	3.47	.57	1.26	.308	.85	3.5
420	2.67	.83	0.889	.397	1.48	3.3
540	1.87	.80	.606	.418	2.4	3.5
660	1.13	.71	.427	.406	3.4	3.5

to equation (12) the value of the rate constant k_1' is

$$k_1' = -\left[\frac{\mathrm{d(V)}}{\mathrm{d}t} - \frac{\mathrm{d(IV)}}{\mathrm{d}t}\right]\frac{1}{3\mathrm{(V)}^2}$$

The values of k_1' calculated for different times are tabulated in the sixth column. If the mechanism involving equation (7) is correct then the values of k_1' should be constant. It is seen that this is not the case and that this mechanism does not satisfactorily explain the experimental data.

Mechanism of Equation (8).—This mechanism may be represented by the two equations

$$\mathrm{Pu(V)} + \mathrm{Pu(III)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2\mathrm{Pu(IV)} \qquad (13)$$

$$\mathrm{Pu(IV)} + \mathrm{Pu(V)} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathrm{Pu(III)} + \mathrm{Pu(VI)} \qquad (9)$$

By the same procedure as used in the previous section the rate law is found to be

$$\mathrm{d(V)}/\mathrm{d}t = -3k_1\mathrm{(V)(III)} + 3k_2\mathrm{(IV)}^2 + \mathrm{d(IV)}/\mathrm{d}t \qquad (14)$$

Neglecting the back reaction of equation (13) and solving for k_1 we obtain

$$k_1 = -\left[\frac{\mathrm{d(V)}}{\mathrm{d}t} - \frac{\mathrm{d(IV)}}{\mathrm{d}t}\right]\frac{1}{3\mathrm{(V)(III)}} \qquad (15)$$

In Table II are given the quantities necessary for the calculation of k_1. From the values of column seven it is apparent that k_1 is constant well within the experimental accuracy of the data and that the mechanism of equation (8) thus satisfactorily explains the experimental results. Since there appear to be no other plausible mechanisms to account for the reaction it is concluded that reaction (8) along with reaction (2) does represent the mechanism of disproportionation of plutonium(V) under these conditions.

As was mentioned previously in connection with the other mechanism, the theoretical rate law involving equation (8) may also be calculated using the equilibrium constant of reaction (2). From equations (13) and (2) we readily obtain

$$\frac{\mathrm{d(V)}}{\mathrm{d}t} = -k_1\mathrm{(V)(III)} + k_2\mathrm{(IV)}^2 - \mathrm{d(VI)}/\mathrm{d}t \qquad (16)$$

It is assumed that equilibrium is established for equation (9)

$$K = \frac{k_3}{k_4} = \frac{\mathrm{(III)(VI)}}{\mathrm{(IV)(V)}} \qquad (17)$$

Two additional equations result from the constancy of the total plutonium concentration and the constancy of the average oxidation number of plutonium

$$\mathrm{(III)} + \mathrm{(IV)} + \mathrm{(V)} + \mathrm{(VI)} = a \qquad (18)$$

$$\mathrm{(IV)} + 2\mathrm{(V)} + 3\mathrm{(VI)} = b \qquad (19)$$

Differentiating equations (17), (18) and (19) and solving for d(VI)/d(V) one obtains

$$\frac{\mathrm{d(VI)}}{\mathrm{d(V)}} = \frac{K\mathrm{(IV)} - 2K\mathrm{(V)} - \mathrm{(VI)}}{\mathrm{(III)} + 2\mathrm{(VI)} + 3K\mathrm{(V)}}$$

Substituting in equation (16) we have

$$\frac{\mathrm{d(V)}}{\mathrm{d}t} = [k_2\mathrm{(IV)}^2 - k_1\mathrm{(V)(III)}]\frac{\mathrm{(III)} + 2\mathrm{(VI)} + 3K\mathrm{(V)}}{\mathrm{(III)} + K\mathrm{(IV)} + K\mathrm{(V)} + \mathrm{(VI)}}$$

If it is assumed that the back reaction of equation (13) is negligible compared to the forward reaction, the term involving k_2 may be omitted. Using equation (17) to eliminate *K*, we obtain

$$\frac{\mathrm{d(V)}}{\mathrm{d}t} = -k_1\mathrm{(V)(III)}\left[\frac{\frac{2}{\mathrm{(III)}} + \frac{1}{\mathrm{(VI)}} + \frac{3}{\mathrm{(IV)}}}{\frac{1}{\mathrm{(III)}} + \frac{1}{\mathrm{(IV)}} + \frac{1}{\mathrm{(V)}} + \frac{1}{\mathrm{(VI)}}}\right] \qquad (20)$$

Again, equations (17), (18) and (19) could be used to eliminate all variables except the concentration of plutonium(V), but since the analyses are available for all oxidation states this procedure is not worthwhile.

In Table III the constancy of k_1 is checked by means of equation (20). It is seen that the values of k_1 are again constant and equal to those of Table II within the accuracy of the measurements, in agreement with the conclusion that the mechanism of the disproportionation of Pu(V) is that represented by equations (8) and (2).

TABLE III

RATE OF DISPROPORTIONATION OF Pu(V) ACCORDING TO MECHANISM OF EQUATIONS (2) AND (8)

Rate equation containing only one derivative.

Time in min.	$\dfrac{\frac{1}{\mathrm{(III)}} + \frac{1}{\mathrm{(IV)}} + \frac{1}{\mathrm{(V)}} + \frac{1}{\mathrm{(VI)}}}{\frac{2}{\mathrm{(III)}} + \frac{1}{\mathrm{(VI)}} + \frac{3}{\mathrm{(IV)}}}$	k_1 l. moles^{-1} min.$^{-1}$
180	0.365	3.4
300	.385	3.4
420	.424	3.2
540	.488	3.6
660	.574	3.7

Discussion

The fact that the reaction between two plutonium(V) ions to give plutonium(IV) and plutonium(VI) is considerably slower than the reaction between a plutonium(III) and plutonium(V) merits some discussion. From the data of Table I an upper limit on the former rate of reaction may be set. Since there was no evidence at a time of 180 minutes of an appreciable contribution from this mechanism it may be safely concluded that k_1' is less than 0.10 liter moles^{-1} min.$^{-1}$. Thus the rate constant k_1 of equation (8) is at least 35 times greater than k_1' of equation (7). The two reactions differ only in that with reaction (7) an electron is removed from PuO_2^+ to give PuO_2^{++} whereas in reaction (8) an electron is removed from Pu^{+3} to give Pu^{+4}. In both cases the electron is given to a PuO_2^+ which then eventually changes to Pu^{+4}. Thermodynamically it is easier to furnish the electron to PuO_2^+ from another PuO_2^+ than from Pu^{+3}, although kinetically the opposite is true. The repulsive effect of the charge on the ions cannot explain this effect in that a Pu^{+3} and a PuO_2^+ would repel each other more strongly than would two PuO_2^+ ions. The greater rate of reaction of Pu^{+3} with PuO_2^+ may be principally due to a greater ease of removal of one or both of the oxygens of PuO_2^+ in the presence of Pu^{+3}, than the corresponding removal of these oxygens in the presence of another PuO_2^+ ion. The high charge of Pu^{+3} would be expected to exert a large attractive force on the oxygens of PuO_2^+, which in turn would make these plutonium–oxygen bonds easier to break.

Although the disproportionation of plutonium (V) proceeds by the mechanism of equations (8) and (2) under the conditions of this experiment, that cannot be true under all circumstances. At very low concentrations of plutonium(III) the mechanism must change to that represented by equations (7) and (2) since the rate by the mechanism of equations (8) and (2) is directly proportional to the plutonium(III) concentration. How low a concentration of plutonium (III) is necessary to bring about this change in the mechanism is not known. All that can be stated is that the value of k_1 is at least 35 times greater than that of k_1' at room temperature in 0.5*M* hydrochloric acid.

In all of the rate laws and mechanisms discussed in this paper no account has been taken of the effect of acidity on the rates of reaction since no experimental data are available to evaluate this effect. However, one may qualitatively predict the effect of acidity with reasonable certainty for the reaction of plutonium(III) with plutonium(V). Since in the reaction it is necessary to remove two oxide oxygens from the plutonium (V) it is almost certain that the rate would tend to increase with increasing acidity. Since the time the above work was completed, Gevantman[4] has reported some measurements on the rate of disproportionation of plutonium(V) in perchloric acid at low acidity which do in fact show a smaller rate at low acidity.

Mechanism of Disproportionation of Plutonium(IV).—The mechanism of the disproportion of plutonium(V) is closely related to that of the disproportionation of plutonium(IV) (eqn. (5)). In the first case the slow step involves the conversion of a plutonium(V) to a plutonium (IV), the slowness being principally due to the breaking of the plutonium–oxygen bonds of plutonium(V), while in the second case the slow step is just the reverse of this process. With the disproportionation of plutonium(IV) we are again limited to the two most reasonable mechanisms represented by the reverse reactions of equation (7) and equation (8), along with the rapid equilibrium of equation (2). The values of the equilibrium quotients for both of these reactions may be calculated from the data on the disproportionation of plutonium(IV) in 0.5*M* hydrochloric acid at 25°, equation (5), and the value of the equilibrium quotient of equation (4), equal to 8.5. The values obtained for 0.5*M* hydrochloric acid and *ca.* 25° are

$$K_2 = \frac{(\mathrm{Pu(IV)})(\mathrm{Pu(VI)})}{(\mathrm{Pu(V)})^2} = 1.44 \times 10^{-3} = k_1'/k_2'$$

$$K_3 = \frac{(\mathrm{Pu(IV)})^2}{(\mathrm{Pu(V)})(\mathrm{Pu(III)})} = 170 = k_1/k_2$$

From the value of k_1 and the upper limit for k_1' we may calculate the following quantities:

$$k_2 = 2.1 \times 10^{-2} \text{ liters moles}^{-1}\text{ min.}^{-1}$$

$$k_2' < 7 \times 10^{-5} \text{ liters moles}^{-1}\text{ min.}^{-1}$$

From the relative values of k_2 and k_2' it must be concluded that the reaction by the k_2 mechanism should be much faster than by the k_2' mechanism. It would therefore be expected that the disproportionation of plutonium(IV) in 0.5*M* hydrochloric acid at room temperature would be bimolecular with respect to plutonium(IV) and would proceed by the k_2 mechanism. Kasha and Sheline[3] have made measurements on the rate of disproportionation of plutonium(IV) which permit a check of the above ideas. The net reaction is that given by equation (5). The rate constant k_2 has already been defined such that as reaction (13) proceeds to the left

$$-\,d(\mathrm{Pu(IV)})/dt = 2k_2(\mathrm{Pu(IV)})^2$$

In the proposed mechanism for the disproportionation of plutonium(IV), the reaction

$$\mathrm{Pu(IV)} + \mathrm{Pu(IV)} \xrightarrow{k_2} \mathrm{Pu(III)} + \mathrm{Pu(V)}$$

is assumed to be the rate-determining step. Each time two plutonium(IV) ions react by this path a plutonium(V) ion is formed which very rapidly reacts with another plutonium(IV) ion according to equation (2). Thus the rate

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[4] L. H. Gevantman, Manhattan Project Report CLP-427, p. 6, June 19, 1945.

law for the disproportionation of plutonium(IV) in terms of k_2 becomes

$$-\,d(\mathrm{Pu(IV)})/dt = 3k_2(\mathrm{Pu(IV)})^2$$

From the data of Kasha and Sheline one calculates a value of $k_2 = 0.027$ liter mole^{-1} min.$^{-1}$ for a 1.93×10^{-3} M plutonium(IV) solution in *ca.* 0.5*M* hydrochloric acid at 25.0° and a value of $k_2 = 0.055$ liter mole^{-1} min.$^{-1}$ for a 4.25×10^{-3} M plutonium(IV) solution in 0.47*M* hydrochloric acid at 25.0°. These values are to be compared with the value for k_2 of 0.021 liter mole^{-1} min.$^{-1}$ obtained from the rate of disproportionation of plutonium(V). The agreement with the *ca.* 0.5*M* hydrochloric acid value is excellent considering the possible difference in temperature of the experiments, while there is a discrepancy of a factor of over 2 relative to the 0.47*M* hydrochloric acid value. No satisfactory explanation can be offered for this discrepancy. The difference in acidity in the two experiments is not large and the unknown temperature difference probably could not have been sufficiently great to produce this effect. According to the proposed mechanism the rate constants measured by Kasha and Sheline should have been equal except for the small acidity correction. The experiments should be checked before a final answer can be given as to the agreement of the mechanism, but the general correspondence as to order of magnitude of the values of k_2 obtained from the +5 and +4 disproportionation experiments is strong support for the proposed mechanisms.

Mechanism of Reduction of Plutonium(VI).—The mechanism and rate of disproportionation of plutonium(V) are of great importance in the reduction of plutonium(VI) to plutonium(IV) and plutonium(III) by various reducing agents. It has been found that in many reactions of this type the mechanism consists of the reduction of plutonium(VI) to plutonium(V), together with the disproportionation of plutonium(V). The combination of these two reactions results in the final reduction of the plutonium to the +4 or +3 state. The direct reduction of the plutonium (VI) to plutonium(V) by the reducing agent (and also the reduction of plutonium(IV) to plutonium(III)) is in general a much faster reaction than the direct reduction of plutonium (V) to plutonium(IV) or plutonium(III) by the reducing agent. Further, under many conditions the reduction of plutonium(V) by the reducing agent is slow compared to the disproportionation of plutonium(V) and consequently the reduction of plutonium(V) proceeds through the disproportionation mechanism. This is known to be the case for hydrogen peroxide, hydroxylamine, nitrous acid, silver and sulfur dioxide.[5] Many other reducing agents probably act in this manner, but have not been investigated sufficiently to determine this fact. It should be pointed out that in reduction reactions of this type the total concentration of plutonium plays an important role relative to the rate of reduction. Since the disproportionation of plutonium(V) is a bimolecular reaction with respect to plutonium, the rate of reduction below the +5 state will become very small at low plutonium concentrations. At sufficiently low concentrations of plutonium the mechanism must in every case switch over to that of direct reduction of plutonium(V) by the reducing agent. Low concentrations of the reducing agent should favor the disproportionation mechanism.

Similarly, oxidation of plutonium(IV) by various oxidizing agents may proceed through the plutonium(IV) disproportionation mechanism. No examples of this behavior have been definitely established although it has been suggested that oxidation of plutonium(IV) to plutonium(VI) in nitric acid occurs by this mechanism.[5]

Summary

The disproportionation of plutonium(V) into plutonium(VI) and plutonium(IV) or plutonium (III) is expected to proceed by either of two possible mechanisms. From a study of the rate of the disproportionation in 0.5*M* hydrochloric acid, it is shown that the actual mechanism consists of the slow reaction

$$\mathrm{Pu(V)} + \mathrm{Pu(III)} \longrightarrow 2\mathrm{Pu(IV)}$$

coupled with the rapid equilibrium

$$\mathrm{Pu(V)} + \mathrm{Pu(IV)} = \mathrm{Pu(III)} + \mathrm{Pu(VI)}$$

A possible explanation of the faster reaction through this mechanism compared to that of the other possible mechanism is given.

The mechanism of disproportionation of plutonium(V) is essentially the reverse of that for the disproportionation of plutonium(IV). The rate constant for this latter reaction is calculated and compared with experimental data.

The importance of the mechanism of disproportionation of plutonium(V) in the reduction of plutonium(VI) is discussed.

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[5] R. E. Connick, National Nuclear Energy Series, Plutonium Project Record, Vol. 14A, Chap. III, to be published.