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Solutions of Plutonium: Influence of Alpha Particles

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Solutions of Plutonium: Influence of Alpha Particles

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ABSTRACT

The data of Kasha and Sheline on rates and equilibria of the disproportionation reaction of plutonium (IV) to give plutonium (III) and plutonium (VI) have been corrected for the reduction caused by the plutonium alpha particles. It was necessary to assume reaction paths for the alpha particle induced reduction and one electron reductions of Pu(VI) and Pu (IV) were chosen as most plausible. The disproportionation mechanism was found to be consistent with that previously deduced from the disproportionation of plutonium (V). The equilibrium for the disproportionation of plutonium (IV) exhibited approximately the expected fourth power dependence on hydrogen ion concentration in perchloric acid at unit ionic strength and 25°C. An apparent fifth power dependence was obtained for hydrochloric acid solutions, not at constant ionic strength. The disproportionation rate showed an inverse third power acid dependence in perchloric acid at constant ionic strength and an apparent -3.5 power dependence in hydrochloric acid solutions, without added salt. Approximate values of 40 kcal. and + 60 e.u. were calculated for heat and entropy of activation of the disproportionation reaction in one molar hydrochloric acid. The formal potentials of the Pu(III)-Pu(VI) and Pu(IV)-Pu(VI) couples in one molar perchloric acid at 25°C are -1.043 ± 0.003 and -1.022 ± 0.002 volts, respectively. The corresponding values for one molar hydrochloric acid

are -1.053 ± 0.003 and -1.025 ± 0.002 volts. The discrepancy concerning chloride complexing of PuO_2^{++} is nearly eliminated by the new values for the disproportionation equilibrium quotient. It is pointed out that the assumption of a small amount of complexing of Pu^{+3} by chloride ion would give complete agreement and evidence is advanced in support of this hypothesis.

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Introduction.—Attention^(2,3) has been called to a discrepancy between the

(2) R. E. Connick and W. H. McVey, J. Am. Chem. Soc. 73, 1798 (1951).

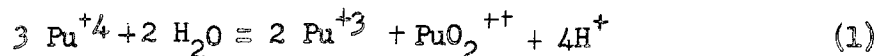
(3) R. E. Connick and W. H. McVey, J. Am. Chem. Soc. (to be published).

observed complexing properties of plutonium (VI) with chloride ion and that calculated from EMF and disproportionation equilibrium measurements. Spectral observations show plutonyl ion, PuO₂⁺⁺, to be appreciably complexed in one molar hydrochloric acid⁽⁴⁾. The EMF and equilibrium results indicate the unlikely

(4) R. E. Connick, M. Kasha, W. H. McVey and G. E. Sheline, "The Transuranium Elements", National Nuclear Energy Series, Division IV, Vol. 14B, McGraw-Hill Book Co., Inc., New York, 1949, p 559. Hereafter this book will be designated as I.

result that plutonyl ion is more strongly complexed by perchlorate than by chloride ion.

The source of the discrepancy has been traced to an error in the equilibrium quotient for the reaction:



The average oxidation number of plutonium in a solution containing these species slowly decreases with time. The α -particles, from the disintegration of plutonium, in their passage through the solution produce species which bring about the reduction⁽⁴⁾. When the rate of reduction by the α -particle radiation becomes of the same order of magnitude as the rate of attainment of the disproportionation equilibrium of

equation (1), then true equilibrium will not be established. The results of the calculations of this paper show that this correction is much more important than was previously suspected and that the apparent equilibrium quotients were seriously in error.

Extensive measurements of the rate of reaction and the equilibrium quotient for reaction (1) in perchloric⁽⁵⁾ and hydrochloric⁽⁶⁾ acids

(5) M. Kasha, *ibid*, p 295.

(6) M. Kasha and G. E. Sheline, *ibid*, p 180.

have been made by Kasha and Sheline. They studied the reaction as a function of acidity at 25°C and obtained limited data on the effect of ionic strength and temperature. In some cases "equilibrium" was approached from both sides. These data serve as the basis for the calculations presented here.

Method.--For each experiment the rate and equilibrium quotient were obtained by a graphical method. In order to apply the method, rate laws for both the disproportionation reaction and the reduction reaction, arising from the α -particles, must be assumed. The correctness of the former is tested by the linearity of the resulting plot.

It has been shown⁽⁷⁾ that there are only two plausible mechanisms

(7) R. E. Connick, *ibid*, p 268; *J. Am. Chem. Soc.* 71, 1528 (1949).

for the oxidation-reduction reactions between plutonium ions in acidic

solutions. According to available experimental data⁽⁷⁾ the one by which such reactions actually occur is the following:



Reaction (3) is a rapid equilibrium⁽⁸⁾ while reaction (2) is rate deter-

⁽⁸⁾R. E. Connick, M. Kasha, W. H. McVey and G. E. Sheline, I, p 227.

mining. The equilibrium quotient for the disproportionation reaction, with the hydrogen ion dependence omitted, and for reaction (3) are defined as:

$$K_a = \frac{(\text{III})^2 (\text{VI})}{(\text{IV})^3} \quad (4)$$

$$K_b = \frac{(\text{III}) (\text{VI})}{(\text{IV}) (\text{V})} \quad (5)$$

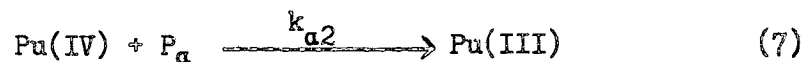
where parenthesis indicate the molar concentration, i.e. moles per liter of solution, of the enclosed plutonium species.

Nothing is known experimentally about the mechanism of the reduction induced by α -particles. It is not possible to analyze the data without knowledge of this mechanism. Fortunately, one can make a plausible choice. A survey⁽⁹⁾ of the oxidation-reduction chemistry of plutonium

⁽⁹⁾R. E. Connick, U. S. Atomic Energy Commission report CC-3869,
July 6, 1948.

shows that the $\text{Pu}^{+3}-\text{Pu}^{+4}$ couple and the $\text{PuO}_2^+-\text{PuO}_2^{++}$ couple are highly reversible in such reactions. On the contrary the $\text{Pu}^{+4}-\text{PuO}_2^+$ couple is very irreversible. This behavior is explained by the fact that only an electron transfer occurs in reactions of the former two couples, but bonds must be formed or broken along with the electron transfer in the case of the $\text{Pu}^{+4}-\text{PuO}_2^+$ couple. It therefore seems safe to conclude that the net effect of the chemical species produced in the solution by α -particle radiation will be to reduce Pu^{+4} to Pu^{+3} and PuO_2^{++} to PuO_2^+ (10). We may then write:

(10) It is interesting to note that hydrogen peroxide, which is probably one of the species produced by the α -particles, is known to reduce Pu(VI) to Pu(V) and Pu(IV) to Pu(III) at a considerably greater rate than it reduces Pu(V) (R. E. Connick and W. H. McVey, ref. 9, p 97ff).



where P_α indicates species produced by the α -particles. The symbols $R_{\alpha 1}$ and $R_{\alpha 2}$ will be used for the rates of reduction of plutonium in the respective reactions.

From equations (2), (3), (6) and (7), the following rate laws are obtained where R_1 , R_2 , R_3 and R_4 represent the rates of the two forward and reverse steps of equations (2) and (3):

$$\frac{d(\text{VI})}{dt} = R_3 - R_4 - R_{a1} \quad (8)$$

$$\frac{d(\text{V})}{dt} = + R_1 - R_2 - R_3 + R_4 + R_{a1} \quad (9)$$

$$\frac{d(\text{IV})}{dt} = - 2R_1 + 2R_2 - R_3 + R_4 - R_{a2} \quad (10)$$

$$\frac{d(\text{III})}{dt} = R_1 - R_2 + R_3 - R_4 + R_{a2} \quad (11)$$

Because the concentration of Pu(V), and therefore $\frac{d(\text{V})}{dt}$, was small in most of the experiments equation (9) was combined with each of the others to give:

$$\frac{d(\text{VI})}{dt} + \frac{d(\text{V})}{dt} = R_1 - R_2 \quad (12)$$

$$- \frac{d(\text{IV})}{dt} + \frac{d(\text{V})}{dt} = 3R_1 - 3R_2 + R_{a1} + R_{a2} \quad (13)$$

$$\frac{d(\text{III})}{dt} + \frac{d(\text{V})}{dt} = 2R_1 - 2R_2 + R_{a1} + R_{a2} \quad (14)$$

Experimentally^(5,6) it is found that, for a given set of conditions, the α -particles produce a constant rate of decrease of the average oxidation number of the plutonium. Therefore, in a single experiment the sum of R_{a1} and R_{a2} is a constant which will be denoted as R_a . It is equal to the rate of decrease of the average oxidation number multiplied by the total plutonium concentration.

The rates R_1 and R_2 can be expressed in terms of the corresponding rate laws according to the mechanism of reaction (2):

$$R_1 - R_2 = k_1(\text{IV})^2 - k_2(\text{III})(\text{V})$$

Substituting for the concentration of Pu(V) from equation (5), which represents the rapid equilibrium of reaction (3), gives:

$$R_1 - R_2 = k_1(\text{IV})^2 - \frac{k_2}{K_b} \frac{(\text{III})^2(\text{VI})}{(\text{IV})}$$

From the equality of the forward and back reactions at equilibrium it can be shown that:

$$K_a = \frac{k_3 k_1}{k_4 k_2} = \frac{K_b k_1}{k_2}$$

Therefore

$$R_1 - R_2 = k_1(\text{IV})^2 - \frac{k_1}{K_a} \frac{(\text{III})^2(\text{VI})}{(\text{IV})}$$

Equations (12), (13) and (14) can then be written as:

$$\frac{1}{(\text{IV})^2} \left\{ \frac{d(\text{VI})}{dt} + \frac{d(\text{V})}{dt} \right\} = k_1 - \frac{k_1}{K_a} \frac{(\text{III})^2(\text{VI})}{(\text{IV})^3} \quad (15)$$

$$\frac{1}{3(\text{IV})^2} \left\{ \frac{d(\text{IV})}{dt} + \frac{d(\text{V})}{dt} - R_a \right\} = k_1 - \frac{k_1}{K_a} \frac{(\text{III})^2(\text{VI})}{(\text{IV})^3} \quad (16)$$

$$\frac{1}{2(\text{IV})^2} \left\{ \frac{d(\text{III})}{dt} + \frac{d(\text{V})}{dt} - R_a \right\} = k_1 - \frac{k_1}{K_a} \frac{(\text{III})^2(\text{VI})}{(\text{IV})^3} \quad (17)$$

All of the quantities in the above expressions, except k_1 and K_a , can be obtained readily from the data of Kasha and Sheline. The rates were determined from slopes of plots of the concentrations of the various species versus time. The average oxidation number, which was used to evaluate R_a , was calculated by the equation: (6)

$$\text{average oxid. no.} = \frac{3(\text{III}) + 4(\text{IV}) + 5(\text{V}) + 6(\text{VI})}{(\text{III}) + (\text{IV}) + (\text{V}) + (\text{VI})}.$$

A plot of the left sides of equations (15), (16) and (17) as ordinate versus $\frac{(\text{III})^2(\text{VI})}{(\text{IV})^3}$ as abscissa should give a single straight line whose intercept on the ordinate axis is k_1 and on the abscissa axis is K_a . It is easily shown that, if the rate law assumed in equations (2) and (3) is incorrect, a straight line will not be obtained and k_1 would of course have no meaning. However, the point at which the curve crosses the abscissa axis would still give the equilibrium value of K_a .

Results.--Typical plots are shown in Figs. 1, 2, and 3, where, for convenience, the ordinate is actually the left side of equation (15), (16) or (17) multiplied by 0.01 times the total plutonium concentration. In the first two experiments the equilibrium of equation (1) was approached from the Pu^{+4} side, i.e. by disproportionation; in the third, by reproporationation. It is clear from the scatter of the points that no great accuracy can be claimed for the data. The principal source of error is in the original concentration data. This introduced uncertainties into the drawing of the concentration curves versus time, with the result that the rates obtained from the slopes of these curves were uncertain.

A plot of the average oxidation number versus time is given in Fig. 1 for the experiment shown in Figs. 2 and 3. In some cases the data did not fall so closely on a straight line, especially for the experiments in hydrochloric acid. Frequently large systematic deviations occurred near the start of the experiment.

Perchloric Acid.--These results are presented in Table 1. Kasha (5) measured only the disproportionation reaction except for the 0.516 M acid experiment where equilibrium was approached through reproportionation of Pu(IV). The original, unsmoothed concentration data (unpublished) were used instead of the smoothed values given in reference (5). The latter give a false idea of the accuracy. The experiment at 0.052 M perchloric acid was omitted because of uncertainties in the data, especially in R_a , and because of the unknown correction for hydrolysis of Pu^{+4} (11,12). The latter cannot be estimated reliably because the

(11) K. A. Kraus, I, p 241.

(12) S. W. Rabideau and J. F. Lemons, J. Am. Chem. Soc. 73, 2895 (1951).

molar extinction coefficients of the hydrolyzed species at the wave lengths used in the spectrophotometric analyses are unknown.

In the experiment at 0.1019 M perchloric acid the change in concentration of Pu(III) was small compared to that of Pu(IV), Pu(V) and Pu(VI). Therefore equation (11) was combined with equations (8), (9) and (10) to yield three equations similar to (15), (16) and (17) except that each contained the rate of change of Pu(III) concentration.

In the first, second and fourth experiments of Table 1 the concentration of Pu(V) was too small to measure and the $d(V)/dt$ term was omitted. In the third experiment Kasha reported no Pu(V) concentrations but significant amounts should have been present. Its concentration was calculated using a value of 10 for K_b and slopes were read from the plot of these values versus time. The correction was large only near the

Table 1

Values of K_a and k_1 for Perchloric Acid Solutions at $25 \pm 0.5^\circ\text{C}$.

HClO_4 , moles/l	total Pu, moles/l	μ	K_a	k_1 , moles ⁻¹ liters hr ⁻¹
1.992	1.72×10^{-3}	2.00	$\sim 10^{-3}$	$\sim 10^{-1}$
0.994	1.55	1.00	$0.009 \pm .002$	0.09 ± 0.03
0.516	1.50	1.00^a	$0.13 \pm .03$	0.9 ± 0.3
0.481	1.73	0.49	$0.23 \pm .03$	0.75 ± 0.12
0.1019	1.30	1.00^a	40 ± 10	150 ± 80

^aSodium perchlorate added.

start of the experiment.

The uncertainties in K_a and k_1 indicated by \pm in Table 1 are based on the plots of equations (15), (16) and (17). They represent approximately the maximum spread in values obtained on these plots. To this error must be added any systematic errors in the analyses, which unfortunately are very difficult to estimate.

In Fig. 5 the logarithm of K_a is plotted versus the logarithm of the perchloric acid concentration for the experiments at unit ionic strength (symbol Φ). The straight line, which fits the points within the estimated uncertainty (denoted by the vertical lines), is drawn with a slope of -4.00 . This is the power dependence on hydrogen ion expected from equation (1). It might be noted that the data uncorrected for the α -particle induced reduction gave a third power dependence⁽⁵⁾. For reaction (1) at $\mu = 1$ and 25° the equilibrium quotient becomes:

$$K_a^1 = \frac{(\text{Pu}^{+3})^2(\text{PuO}_2^{++})(\text{H}^+)^4}{(\text{Pu}^{+4})^3} = 0.009 \pm 0.002 \underline{\underline{M}}^4$$

The correctness of the assumed rate law was difficult to check by the linearity of the plots, because of the scattering of the points. Within the accuracy of the data straight lines were observed in all cases. The $0.516 \underline{\underline{M}}$ perchloric acid experiment was the only one in which a severe test could be made. When plotted according to the one other rate law which seems plausible on theoretical grounds⁽⁷⁾, it failed to give a straight line.

The logarithm of k_1 is plotted versus the logarithm of the perchloric acid concentration in Fig. 6. The data at $\mu = 1$ are fitted

well by an inverse third power hydrogen ion dependence. The complete rate law for reaction (1), when the concentration of Pu(V) is negligible, becomes:

$$-\frac{d(\text{Pu}^{+4})}{dt} = \frac{3k_1' (\text{Pu}^{+4})^2}{(\text{H}^+)^3} - \frac{3k_1'}{K_a'} \frac{(\text{Pu}^{+3})^2 (\text{PuO}_2^{++}) (\text{H}^+)}{(\text{Pu}^{+4})}$$

where $k_1' = 0.13 \text{ moles}^2 \text{ liters}^{-2} \text{ hr}^{-1}$ at $\mu = 1$ and 25°C .

Hydrochloric Acid.--The data (unsmoothed) published in reference (6) were used. The experiments at 0.1081 and 0.0615 M hydrochloric acid were not calculated because of the very small concentration changes in the former and the large uncertainty arising from Pu(IV) hydrolysis (see previous section). In each experiment, except that at 0.183 M perchloric acid, data were available for approach to equilibrium by both disproportionation and reproporationation of Pu(IV). Each solution was prepared for the reproporationation reaction by heating to 70° to shift reaction (1) to the right and then cooling rapidly to 25° .

The spectrophotometric analysis for plutonium (V) becomes inaccurate at low concentrations. In those cases where plutonium (V) was significant, the concentration was calculated by inserting the plutonium (III), (IV) and (VI) concentrations in the expression for K_b (see Eq. 5). The value of K_b at different hydrochloric concentrations is not known with certainty, but in most cases the correction was small. In all of the disproportionation experiments the plutonium (V) was negligible except

for 0.183 M acid where K_b was assumed to be 8.5. This is the value measured for 0.5 M hydrochloric acid⁽⁸⁾. In the reproporationation experiments K_b was assumed to be 10 for 1.545 and 0.950 M HCl and 8.5 for 0.5 M and 0.474 M HCl. In the 0.244 M acid experiment the analytically determined values were used.

Values of the equilibrium quotient obtained from disproportionation are given in Table 2 and their logarithm has been plotted against the logarithm of the hydrochloric acid concentration in Fig. 5 (symbol ϕ). The straight line is drawn with a slope of -5.00. It must be remembered that this apparent fifth power dependence on the hydrochloric acid concentration arises from the composite effect of hydrogen ion, chloride complexing and ionic strength on the equilibrium of reaction (2). It is not possible at the present time to separate these effects. It is interesting to note that the perchloric and hydrochloric acid curves (Fig. 5) approach each other at low acid concentration, where chloride complexing should be smallest. Perfect agreement cannot be expected because of differences in the ionic strengths.

Accurate values of K_a could not be found from the reproporationation data because the experiments were not carried sufficiently close to equilibrium. Where values could be read from the curves, they were in excellent agreement with those measured in disproportionation except for the 0.950 M hydrochloric acid experiment. Here K_a appeared to be three fold higher in the reproporationation experiment. It is difficult to reconcile this discrepancy. The disproportionation value has been chosen as being more reliable.

Table 2
 Values of K_a in Hydrochloric Acid at 25°C

HCl, ^a moles/liter	total Pu, moles/liter	K_a
1.545	1.50×10^{-3}	$(5 \pm 2) \times 10^{-5}$
0.950	1.60	$(2.1 \pm 0.4) \times 10^{-3}$ ^b
~ 0.5	1.93	$0.053 \pm .005$
0.474	4.25	0.065 ± 0.005
0.244	1.38	2.1 ± 0.2
0.183	4.38	6.5 ± 0.5

^aThe ionic strength varied according to the acidity and plutonium concentration.

^bThis value appears to be unchanged from that obtained by Kasha and Sheline⁽⁶⁾ because of an error in their calculations. Their value should have been 2.5×10^{-3} .

Table 3 contains the hydrochloric acid rate data. Values of k_1 calculated from disproportionation and reproporationation are in rough agreement. The more accurate values obtained from disproportionation are plotted logarithmically in Fig. 7. The straight line, which is drawn with a slope of -3.50 , once again represents a combination of effects.

In the graphical method used for finding k_1 and K_a the slope of the line is equal to k_1/K_a , which is the rate constant for the reproporationation reaction. This quantity was determined more accurately in the reproporationation experiments than either k_1 or K_a and is therefore tabulated in Table 3. The slope obtained from reproporationation usually did not agree well with the less accurately measured slope from disproportionation. For the 1.545, 0.950, and ~ 0.5 M acid experiments it was approximately 1.3 fold greater for disproportionation. For the 0.474 M acid it was 1.6 fold greater while for the 0.244 M acid the slopes appeared to be equal. We are unable to offer a plausible explanation for these discrepancies.

A fairly severe test of the assumed rate law could be obtained from the reproporationation experiments. The data gave straight lines within the experimental accuracy in every case; e.g. see Fig. 3. Definite deviations from straight lines were found when the data were plotted according to the second plausible mechanism discussed in the previous section. The disproportionation data did not always give straight lines within the apparent accuracy of the original data. The deviations were in the direction of increasing slope with decreasing values of $\frac{(III)^2(VI)}{(IV)^3}$. There seemed to be no correlation with acidity

Table 3

Values of k_1 for Disproportionation and Reproportionation in Hydrochloric Acid at 25°C

HCl, moles/l	total Pu moles/l	k_1 (disprop.), moles ⁻¹ liters hr ⁻¹	k_1 (reprop.), moles ⁻¹ liters hr ⁻¹	$\frac{k_1}{K_a}$, moles ⁻¹ liters hr ⁻¹
1.545	1.50×10^{-3}	$0.025 \pm .015$	a	$(3.6 \pm 0.4) \times 10^2$
0.950	1.60	0.19 ± 0.06	0.50 ± 0.25	74 ± 4
~0.5	1.93	1.6 ± 0.2	1.1 ± 0.4	24 ± 3
0.474	4.25	3.3 ± 0.5	2.1 ± 0.5	33 ± 2
0.244	1.38	11 ± 2	11 ± 5	5.4 ± 1.1
0.183	4.38	64 ± 7	b	b

^aEquilibrium not approached closely enough to give independent values of k_1 and K_a .

^bReproportionation not measured.

and we are unable to account for the effect. The second mechanism would have increased the deviation. Accurate rate constants could not be calculated for the 70° experiments⁽⁶⁾ because equilibrium was obtained so rapidly. Only the data for the 0.950 M acid experiment were treated. A value of k_1 was obtained by comparing the concentration versus time data with those for the 0.183 M acid experiment at 25°. These two experiments compare closely in initial and final percentage concentrations of plutonium species. Therefore the ratio of the times at which equal percentage reaction had taken place in the two experiments should be inversely proportional to the ratio of the rate constants expressed in percentages. The value found for k_1 was $(1.7 \pm 0.7) \times 10^3$ liters moles⁻¹ hr⁻¹. From this value and the value at 25° the heat of activation was calculated to be approximately 40 kcal. The entropy of activation then is roughly +60 entropy units. A large positive value would be expected from the ionic charge effects.

Thermodynamic functions.--Oxidation potentials for the Pu(III)-Pu(VI) and Pu(IV)-Pu(VI) couples can be calculated by combining K_a with the directly measured Pu(III)-Pu(IV) potentials.⁽¹²⁾⁽²⁾ Because activity coefficient values are unknown only formal potentials can be calculated. The formal potential of a reaction under a given set of conditions is defined as the directly measured cell potential corrected to unit concentration of the substances entering into the reaction. The formal potential for an oxidation-reduction couple is the formal potential of the reaction of the couple with the $H_2=H^+$ couple.

For one molar perchloric acid and one molar hydrochloric acid at

The previously reported entropy (ref. 2, Table VI) of PuO_2^{++} , when corrected for the new equilibrium data, becomes -21 e.u., compared to -17 e.u. for UO_2^{++} .

Chloride Complexing of Pu(VI).---The anomaly of the chloride complexing of plutonium (VI) is nearly but not completely resolved. The Pu(III)-Pu(VI) potential in 1 M perchloric acid is 3 millivolts more positive than in 1 M hydrochloric acid, but, within the experimental accuracy, the two could be equal. This would correspond to no complexing of Pu(VI) by chloride ion, if it is assumed that Pu(III) is not complexed by chloride. Yet the spectrophotometric measurements⁽⁴⁾ show that there is appreciable complexing of plutonium (VI) in 1 M hydrochloric acid.

We believe that the remaining discrepancy may be due to the assumption of no complexing of plutonium (III) by chloride ion. The spectrum of Pu(III) is nearly the same in 1 M hydrochloric acid as in 1 M perchloric acid^(14,15). However this fact does not necessarily indicate

(14) J. C. Hindman, I, p 370.

(15) J. C. Hindman and D. P. Ames, I, 348.

no complexing, because the spectrum of the complex ion may not differ greatly from that of Pu^{+3} itself. The value of the equilibrium quotient for complexing of lanthanum ion by chloride at unit ionic strength is⁽¹⁶⁾

(16) R. E. Connick and K. L. Mattern, to be published.

$$\frac{(\text{LaCl}^{++})}{(\text{La}^{+3})(\text{Cl}^{-})} = 0.7$$

Plutonium (III) would be expected to behave similarly to lanthanum. If it were complexed to the same extent by chloride ion, the Pu(III)-Pu(VI) EMF values would then give roughly 20 percent complexing of Pu(VI) by chloride ion in one molar hydrochloric acid.

There is some additional support for the idea of a weak chloride complex of Pu(III). From partition measurements, Reas⁽¹⁷⁾ found 66%

(17) W. H. Reas, unpublished work, this Laboratory.

of Pu(IV) to be complexed by chloride in 1 M hydrochloric acid at 25°C. From the Pu(III)-Pu(IV) EMF measurements the percent Pu(IV) complexed is only ca. 40%, if it is assumed that Pu(III) is itself not complexed. If, however, the same degree of complexing is assumed for Pu(III) as for lanthanum, the complexing of Pu(IV) becomes approximately 60%, which is in good agreement with Reas' value.

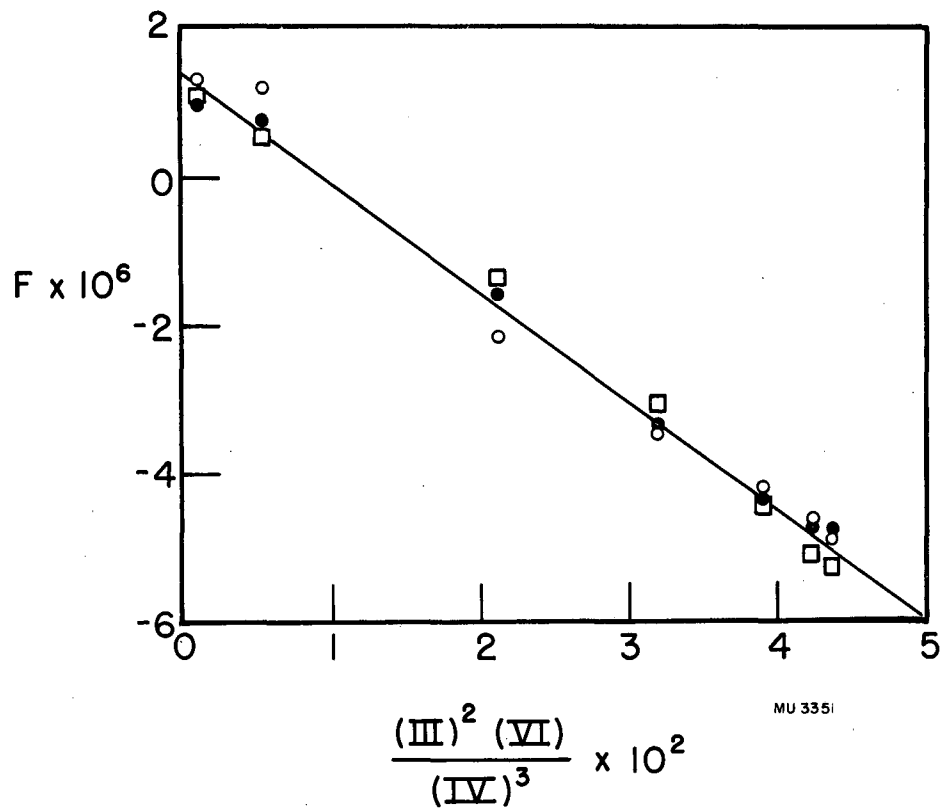
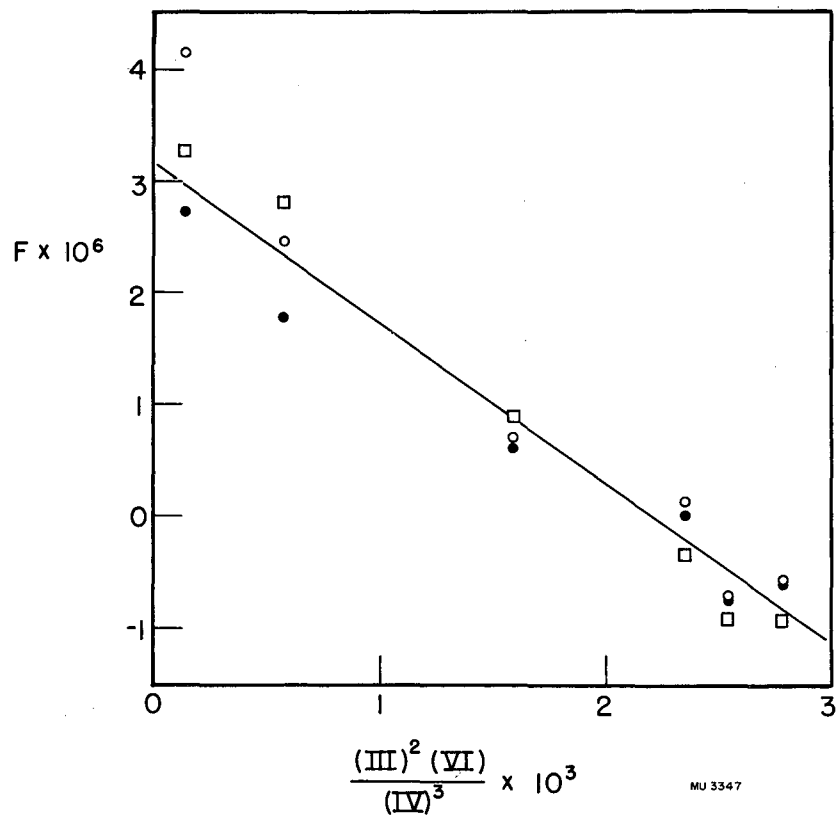
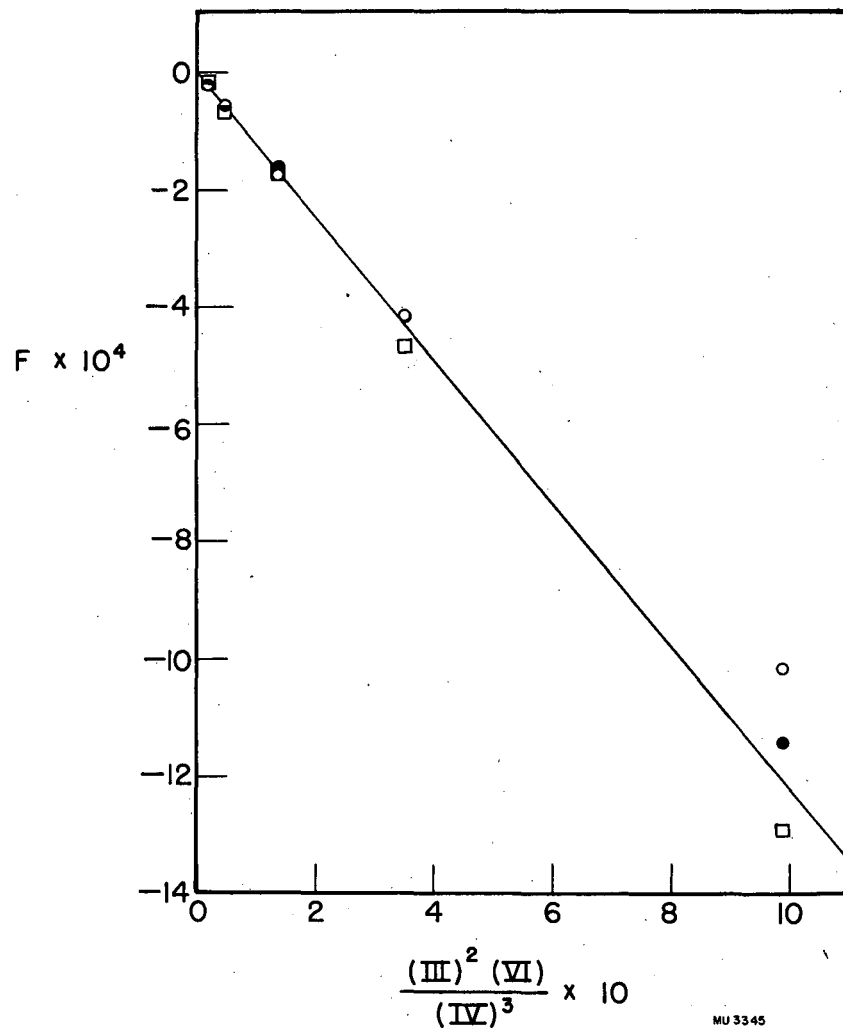


Fig. 1
 Equilibrium and rate of disproportionation of plutonium (IV) in 0.994 M perchloric acid at 25°C. "F" is the value of the left side of equation 15, 16, or 17, multiplied by 0.01 times the total plutonium concentration. The symbols ●, ○ and □ refer to Pu (III), Pu (IV) and Pu (VI), respectively



MU 3347

Fig. 2
 Equilibrium and rate of disproportionation of plutonium (IV) in 0.950 M hydrochloric acid at 25°C. "F" is the value of the left side equation 15, 16 or 17, multiplied by 0.01 times the total plutonium concentration. The symbols ●, ○ and □ refer to Pu (III), Pu (IV) and Pu (VI), respectively.



MU 3345

Fig. 3
 Equilibrium and rate of repropor-
 tionation of plutonium (IV) in 0.950 M
 hydrochloric acid at 25°. "F" is
 the value of the left side of equation
 15, 16 or 17, multiplied by 0.01 times
 the total plutonium concentration.
 The symbols ●, ○ and □ refer to
 Pu (III), Pu (IV) and Pu (VI), re-
 spectively.

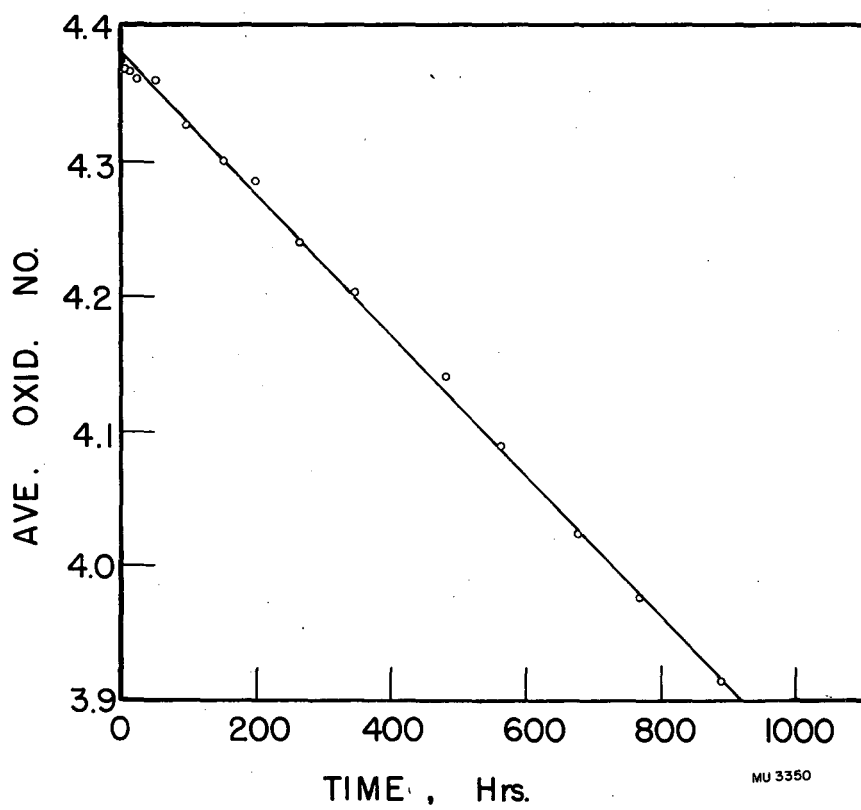


Fig. 4
Average oxidation number of plutonium
as a function of time in 0.994 M per-
chloric acid at 25°.

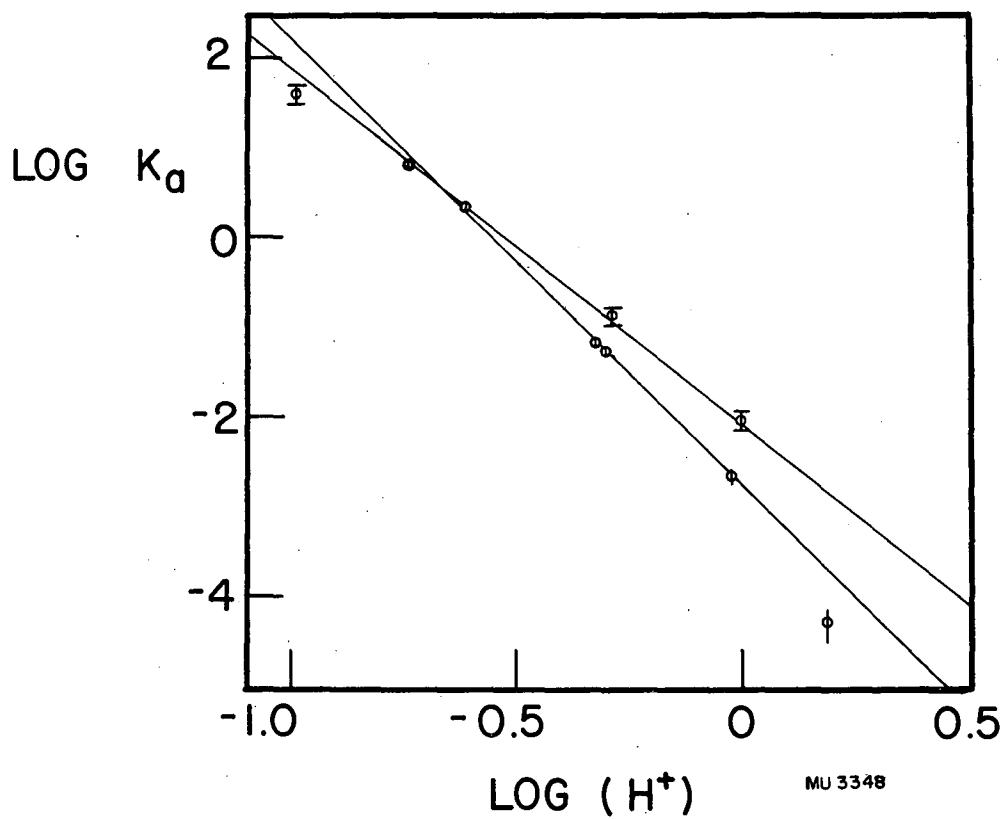


Fig. 5
 Equilibrium quotient values for dis-
 proportionation of plutonium (IV) at
 25° as a function of acidity: Φ , HClO_4 ,
 \bullet , HCl .

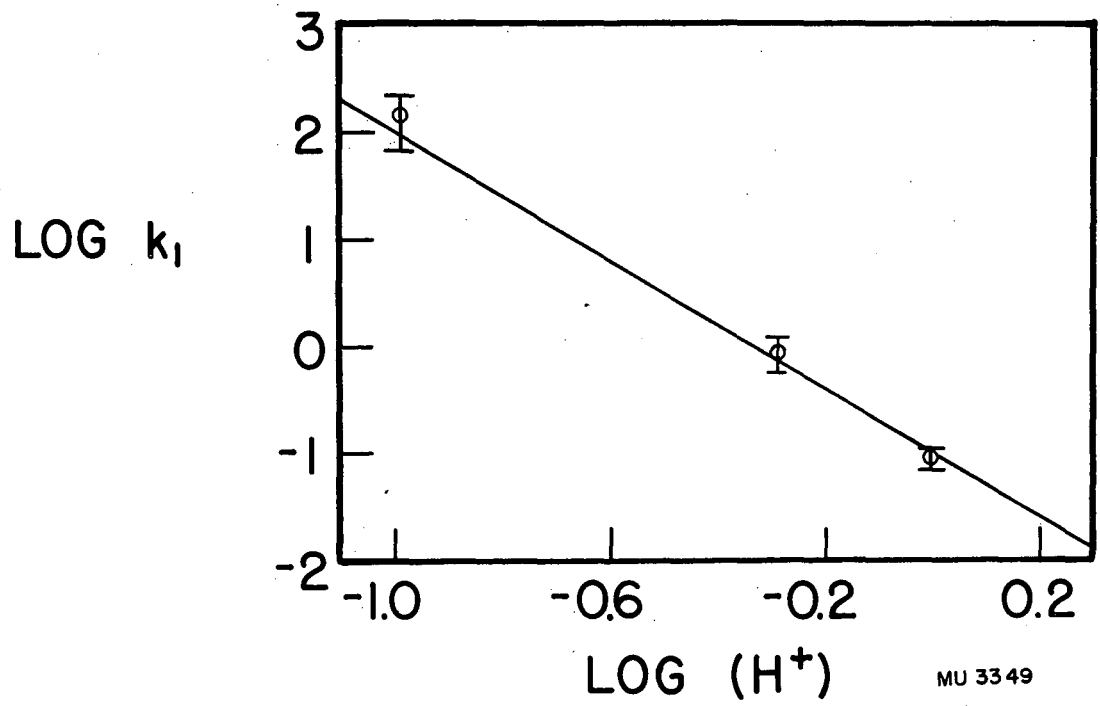


Fig. 6
Values of k , for the disproportionation
of plutonium (IV) in perchloric acid
solutions at 25°.

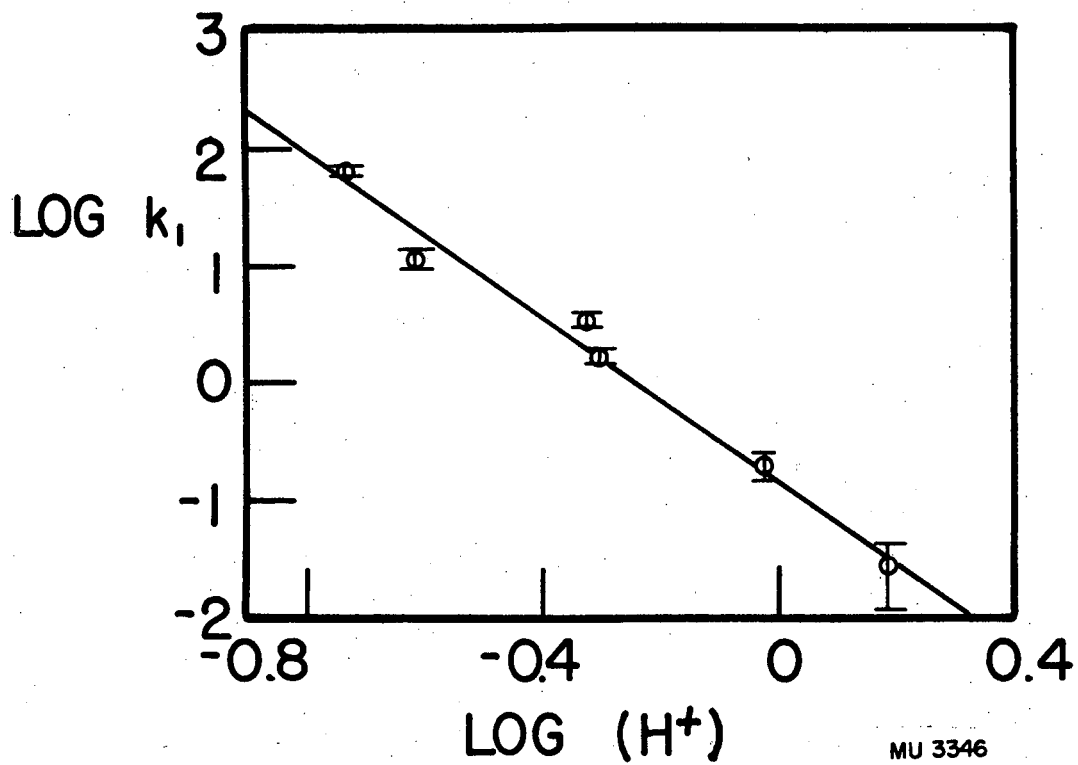


Fig. 7
Values of k_1 for the disproportionation
of plutonium (IV) in hydrochloric acid
solutions at 25°.