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Disproportionation Equilibria and Rates in Perchloric and Hydrochloric Acid Solutions of Plutonium: Influence of α-Particles

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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 α-particles. It was necessary to assume reaction paths for the α-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°. An apparent fifth-power dependence was obtained for hydrochloric acid solutions, not at constant ionic strength. The disproportionaton 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 the 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° are -1.043 ± 0.003 and -1.022 ± 0.002 volt, respectively. The corresponding values for one molar hydrochloric acid are -1.053 ± 0.003 and -1.025 ± 0.002 volt. 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.

Introduction.—Attention[1,2] has been called to a discrepancy between the observed properties of plutonium(VI) with chloride ion and that calculated from e.m.f. and disproportionation equilibrium measurements. Spectral observations show plutonyl ion, PuO_2^{++}, to be appreciably complexed in one molar hydrochloric acid.[3] The e.m.f. and equilibrium results indicate the unlikely 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

$$3Pu^{+4} + 2H_2O = 2Pu^{+3} + PuO_2^{++} + 4H^+ \quad (1)$$

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.[3] 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[4] and hydrochloric[5] acids have been made by Kasha and Sheline. They studied the reaction as a function of acidity at 25° 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[6] that there are only two plausible mechanisms for the oxidation–reduction reactions between plutonium ions in acidic solutions. According to available experimental data[6] the one by which such reactions actually occur is

$$\mathrm{Pu(IV)} + \mathrm{Pu(IV)} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{Pu(V)} + \mathrm{Pu(III)} \quad (2)$$

$$\mathrm{Pu(IV)} + \mathrm{Pu(V)} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \mathrm{Pu(III)} + \mathrm{Pu(VI)} \quad (3)$$

Reaction (3) is a rapid equilibrium[7] while reaction (2) is rate determining. The equilibrium quotient for the disproportionation reaction, with the hydrogen ion dependence omitted, and for reaction (3) are defined as

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

$$K_b = (\mathrm{III})(\mathrm{VI})/(\mathrm{IV})(\mathrm{V}) \quad (5)$$

where parentheses 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[8] of the oxidation–reduction chemistry of plutonium shows that the Pu^{+3}–Pu^{+4} couple and the PuO_2^+–PuO_2^{++} couple are highly reversible in such reactions. On the contrary the Pu^{+4}–PuO_2^+ couple is very irreversible. This behavior is explained by the fact that only an electron transfer occurs in reactions of the

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[1] R. E. Connick and W. H. McVey, THIS JOURNAL, **73**, 1798 (1951).

[2] R. E. Connick and W. H. McVey, *ibid.*, **74**, 1341 (1952).

[3] 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, N. Y., 1949, p. 559. Hereafter this book will be designated as I.

[4] M. Kasha, *ibid.*, p. 295.

[5] M. Kasha and G. E. Sheline, *ibid.*, p. 180.

[6] R. E. Connick, *ibid.*, p. 268; THIS JOURNAL, **71**, 1528 (1949).

[7] R. E. Connick, M. Kasha, W. H. McVey and G. E. Sheline, I, p. 227.

[8] R. E. Connick, U. S. Atomic Energy Commission report CC-3869, July 6, 1948.

former two couples, but bonds must be formed or broken along with the electron transfer in the case of the Pu^{+4}–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^+.[9] We may then write

$$\mathrm{Pu(VI)} + \mathrm{P}_\alpha \xrightarrow{k_{\alpha 1}} \mathrm{Pu(V)} \qquad (6)$$

$$\mathrm{Pu(IV)} + \mathrm{P}_\alpha \xrightarrow{k_{\alpha 2}} \mathrm{Pu(III)} \qquad (7)$$

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)

$$\mathrm{d(VI)}/\mathrm{d}t = R_3 - R_4 - R_{\alpha 1} \qquad (8)$$

$$\mathrm{d(V)}/\mathrm{d}t = + R_1 - R_2 - R_3 + R_4 + R_{\alpha 1} \qquad (9)$$

$$\mathrm{d(IV)}/\mathrm{d}t = - 2R_1 + 2R_2 - R_3 + R_4 - R_{\alpha 2} \qquad (10)$$

$$\mathrm{d(III)}/\mathrm{d}t = R_1 - R_2 + R_3 - R_4 + R_{\alpha 2} \qquad (11)$$

Because the concentration of Pu(V), and therefore d(V)/dt, was small in most of the experiments, equation (9) was combined with each of the others to give

$$\frac{\mathrm{d(VI)}}{\mathrm{d}t} + \frac{\mathrm{d(V)}}{\mathrm{d}t} = R_1 - R_2 \qquad (12)$$

$$-\frac{\mathrm{d(IV)}}{\mathrm{d}t} + \frac{\mathrm{d(V)}}{\mathrm{d}t} = 3R_1 - 3R_2 + R_{\alpha 1} + R_{\alpha 2} \qquad (13)$$

$$\frac{\mathrm{d(III)}}{\mathrm{d}t} + \frac{\mathrm{d(V)}}{\mathrm{d}t} = 2R_1 - 2R_2 + R_{\alpha 1} + R_{\alpha 2} \qquad (14)$$

Experimentally[4,5] 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 $R_{\alpha 1}$ and $R_{\alpha 2}$ is a constant which will be denoted as R_α. 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)

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

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

$$R_1 - R_2 = k_1(\mathrm{IV})^2 - \frac{k_2}{K_\mathrm{b}} \frac{(\mathrm{III})^2(\mathrm{VI})}{(\mathrm{IV})}$$

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

$$K_\mathrm{a} = k_3 k_1/k_4 k_2 = K_\mathrm{b} k_1/k_2$$

Therefore

$$R_1 - R_2 = k_1(\mathrm{IV})^2 - \frac{k_1}{K_\mathrm{a}} \frac{(\mathrm{III})^2(\mathrm{VI})}{(\mathrm{IV})}$$

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

$$\frac{1}{(\mathrm{IV})^2}\left\{\frac{\mathrm{d(VI)}}{\mathrm{d}t} + \frac{\mathrm{d(V)}}{\mathrm{d}t}\right\} = k_1 - \frac{k_1}{K_\mathrm{a}} \frac{(\mathrm{III})^2(\mathrm{VI})}{(\mathrm{IV})^3} \qquad (15)$$

$$\frac{1}{3(\mathrm{IV})^2}\left\{-\frac{\mathrm{d(IV)}}{\mathrm{d}t} + \frac{\mathrm{d(V)}}{\mathrm{d}t} - R_\alpha\right\} = k_1 - \frac{k_1}{K_\mathrm{a}} \frac{(\mathrm{III})^2(\mathrm{VI})}{(\mathrm{IV})^3} \qquad (16)$$

$$\frac{1}{2(\mathrm{IV})^2}\left\{\frac{\mathrm{d(III)}}{\mathrm{d}t} + \frac{\mathrm{d(V)}}{\mathrm{d}t} - R_\alpha\right\} = k_1 - \frac{k_1}{K_\mathrm{a}} \frac{(\mathrm{III})^2(\mathrm{VI})}{(\mathrm{IV})^3} \qquad (17)$$

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_α, was calculated by the equation[5]

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

A plot of the left sides of equations (15), (16) and (17) as ordinate *versus* $(\mathrm{III})^2(\mathrm{VI})/(\mathrm{IV})^3$ 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 reproportionation. It is clear from the scatter of the points that no great accuracy can be claimed for the data.

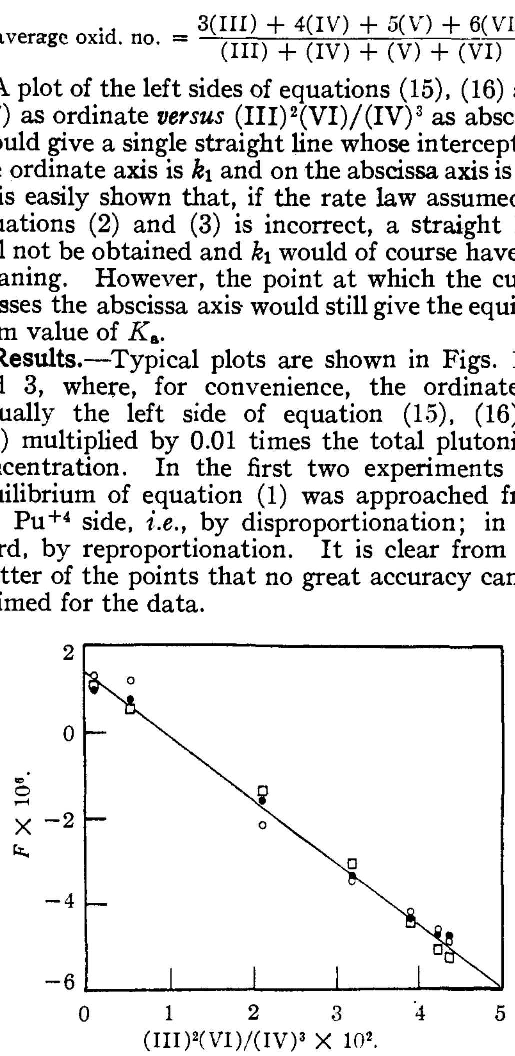

Fig. 1.—Equilibrium and rate of disproportionation of plutonium(IV) in 0.994 *M* perchloric acid at 25°. "*F*" is the value of the left side of equation 15, 16 or 17, multiplied by 0.01 times the total plutonium concentration. The symbols ●, ○ and □ refer to Pu(III), Pu(IV) and Pu(VI), respectively.

Perchloric Acid.—These results are presented in Table I. Kasha[4] measured only the disproportionation reaction except for the 0.516 *M* acid experi-

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[9] 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. 8, p. 97ff.).

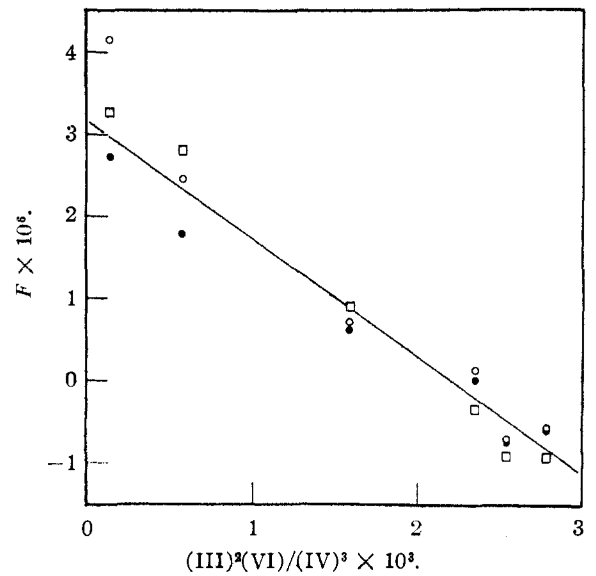


Fig. 2.—Equilibrium and rate of disproportionation of plutonium(IV) in 0.950 M hydrochloric acid at 25°. "F" is the value of the left side of equation 15, 16 or 17, multiplied by 0.01 times the total plutonium concentration. The symbols ●, ○ and □ refer to Pu(III), Pu(IV) and Pu(VI), respectively.

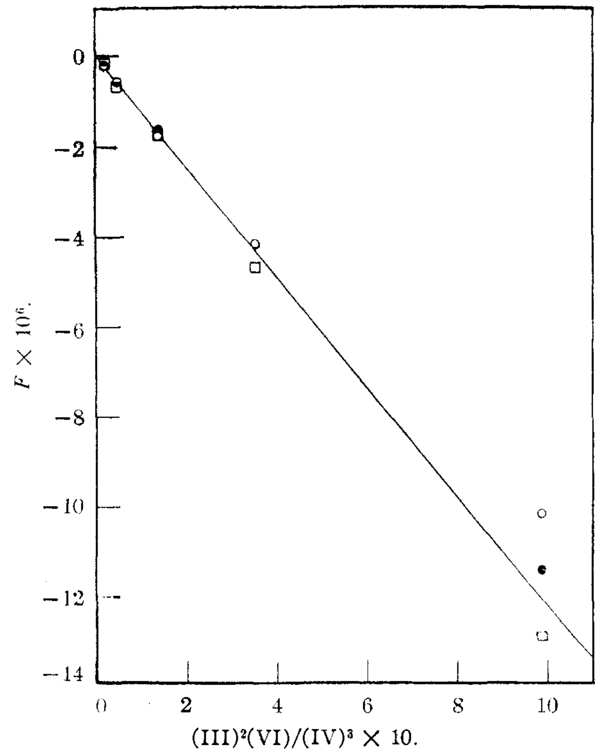


Fig. 3.—Equilibrium and rate of reproportionation of plutonium(IV) in 0.950 M hydrochloric acid at 25°. "F" is the value of the left side of equation 15, 16 or 17, multiplied by 0.01 times the total plutonium concentration. The symbols ●, ○ and □ refer to Pu(III), Pu(IV) and Pu(VI), respectively.

ment 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 (4). The experiment at 0.052 M perchloric acid was omitted because of uncertainties in the data and because of the unknown correction for hydrolysis of Pu^{+4}.[10,11] The latter cannot be estimated reliably because the molar extinction coefficients of the hydrolyzed species are unknown.

TABLE I

VALUES OF K_a AND k_1 FOR PERCHLORIC ACID SOLUTIONS AT 25 ± 0.5°

$HClO_4$, 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 ± 0.002	0.09 ± 0.03
.516	1.50	1.00[a]	.13 ± .03	.9 ± .3
.481	1.73	0.49	.23 ± .03	.75 ± .12
.1019	1.30	1.00[a]	40 ± 10	150 ± 80

[a] Sodium perchlorate added.

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 I the concentration of Pu(V) and the d(V)/dt term were negligible. 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 *versus* time. The correction was large only near the start of the experiment.

The uncertainties in K_a and k_1 indicated by ± in Table I (and the other tables) are based on the maximum spread in the plots of equations (15), (16) and (17). To this error must be added any systematic errors in the analyses.

In Fig. 4 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). The data uncorrected for the α-particle induced reaction gave a third power dependence.[4] For reaction (1) at $\mu = 1$ and 25° the equilibrium quotient becomes

$$K'_a = \frac{(Pu^{+3})^2(PuO_2^{++})(H^+)^4}{(Pu^{+4})^3} = 0.009 \pm 0.002\ M^4$$

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 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,[6] it failed to give a straight line.

In the logarithmic plot of k_1 *versus* the acid con-

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

(11) S. W. Rabideau and J. F. Lemons, THIS JOURNAL, **73**, 2895 (1951).

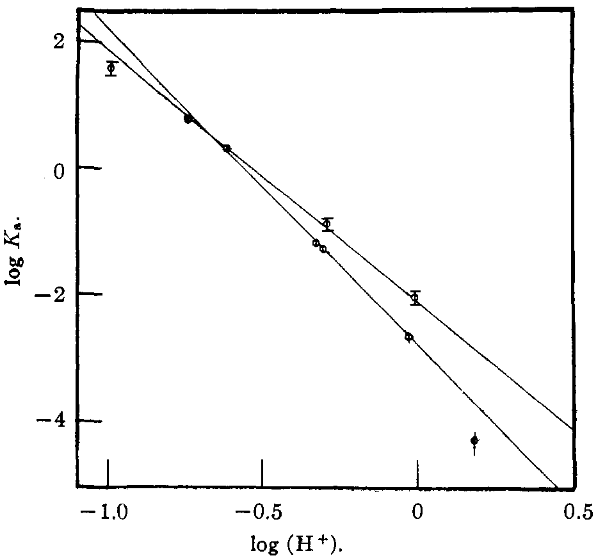


Fig. 4.—Equilibrium quotient values for disproportionation of plutonium(IV) at 25° as a function of acidity: Φ, $HClO_4$; φ, HCl.

centration in Fig. 5, 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

$$-\frac{d(Pu^{+4})}{dt} = \frac{3k_1'(Pu^{+4})^2}{(H^+)^3} - \frac{3k_1'}{K_a'}\frac{(Pu^{+3})^2(PuO_2^{++})(H^+)}{(Pu^{+4})}$$

where $k_1' = 0.13$ mole^2 liter^{-2} hr.$^{-1}$ at $\mu = 1$ and 25°.

Hydrochloric Acid.—The data (unsmoothed) from reference (6) were used. Except for 0.183 *M* acid, equilibrium was approached by both disproportionation and reproportionation of Pu(IV). Reproportionation was observed after heating to 70° to shift reaction (1) to the right.

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 acid concentrations is not known with certainty, but in most cases the correction was small. In the disproportionation experiments the plutonium(V) was negligible except for 0.183 *M* acid where K_b was assumed to be 8.5, the value for 0.5 *M* hydrochloric acid.[7] In the reproportionation 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 II and they have been plotted logarithmically against the acidity in Fig. 4 (symbol φ). The straight line is drawn with a slope of −5.00. 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 (1). It is interesting to note that the perchloric and hydrochloric acid curves (Fig. 4) 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.

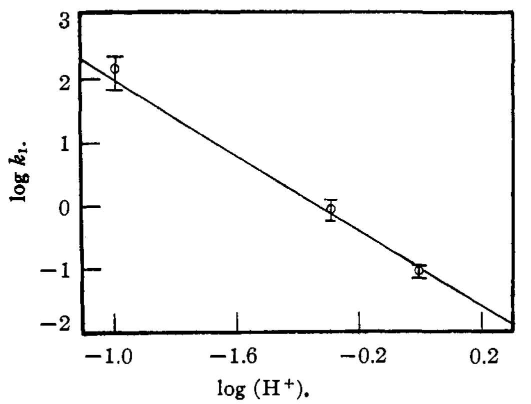


Fig. 5.—Values of k_1 for the disproportionation of plutonium (IV) in perchloric acid solutions at 25°.

Table II

Values of K_a in Hydrochloric Acid at 25°

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]
~ .5	1.93	0.053 ± .005
.474	4.25	0.065 ± .005
.244	1.38	2.1 ± .2
.183	4.38	6.5 ± .5

[a] The ionic strength varied according to the acidity and plutonium concentration. [b] This value appears to be unchanged from that obtained by Kasha and Sheline[5] because of an error in their calculations. Their value should have been 2.5×10^{-3}.

Accurate values of K_a could not be found from the reproportionation 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* acid experiment. Here K_a appeared to be threefold higher in the reproportionation experiment. It is difficult to reconcile this discrepancy. The disproportionation value has been chosen as being more reliable.

Table III contains the hydrochloric acid rate data. Values of k_1 calculated from disproportionation and reproportionation are in rough agreement. The more accurate values obtained from disproportionation, when plotted logarithmically *versus* acidity, show a −3.5 power acid dependence, which 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 reproportionation reaction. This quantity was determined more accurately in the reproportionation experiments than either k_1 or K_a and is therefore presented in Table III. The slope obtained from reproportionation 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

TABLE III

VALUES OF k_1 FOR DISPROPORTIONATION AND REPROPORTIONATION IN HYDROCHLORIC ACID AT 25°

HCl, moles/l.	Total Pu, moles/l.	k_1(disprop.), moles^{-1} liters hr.$^{-1}$	k_1(reprop.), moles^{-1} liters hr.$^{-1}$	k_1/K_a, moles^{-1} liters hr.$^{-1}$
1.545	1.50×10^{-3}	0.025 ± 0.015	[a]	$(3.6 \pm 0.4) \times 10^2$
0.950	1.60	0.19 ± .06	0.50 ± 0.25	74 ± 4
~ .5	1.93	1.6 ± .2	1.1 ± .4	24 ± 3
.474	4.25	3.3 ± .5	2.1 ± .5	33 ± 2
.244	1.38	11 ± 2	11 ± 5	5.4 ± 1.1
.183	4.38	64 ± 7	[b]	[b]

[a] Equilibrium not approached closely enough to give independent values of k_1 and K_a. [b] Reproportionation not measured.

while for the 0.244 M acid the slopes appeared to be equal. We are unable to offer a plausible explanation for these discrepancies.

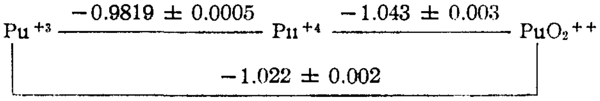
A fairly severe test of the assumed rate law could be obtained from the reproportionation experiments. The data gave straight lines within the experimental accuracy in every case; *e.g.*, see Fig. 3. Definite deviations from straight lines were found when the data were plotted according to the second 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 $(\mathrm{III})^2(\mathrm{VI})/(\mathrm{IV})^3$. There seemed to be no correlation with acidity and we are unable to account for the effect. The second mechanism would have increased the deviation.

A value for k_1 of $(1.7 \pm 0.7) \times 10^3$ liters moles^{-1} hr.$^{-1}$ was calculated for the 0.950 M acid experiment at 70°. The heat and entropy of activation were estimated to be approximately 40 kcal. and +60 e.u., respectively. A large positive $\Delta S^{\ddagger}$ 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.[11,1] 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.

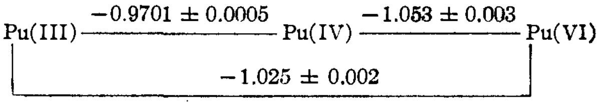
For one molar perchloric acid and one molar hydrochloric acid at 25.0°,[12] the following formal potential schemes are obtained

One molar perchloric acid, 25.0°



$$\underbrace{\mathrm{Pu}^{+3} \overset{-0.9819 \pm 0.0005}{\overline{\hspace{6em}}} \mathrm{Pu}^{+4} \overset{-1.043 \pm 0.003}{\overline{\hspace{6em}}} \mathrm{PuO_2}^{++}}_{-1.022 \pm 0.002}$$

One molar hydrochloric acid, 25.0°



$$\underbrace{\mathrm{Pu(III)} \overset{-0.9701 \pm 0.0005}{\overline{\hspace{6em}}} \mathrm{Pu(IV)} \overset{-1.053 \pm 0.003}{\overline{\hspace{6em}}} \mathrm{Pu(VI)}}_{-1.025 \pm 0.002}$$

The uncertainties in the Pu(III)–Pu(IV) potentials are those quoted by Rabideau and Lemons; for the other potentials they correspond to that for the 3–4 couples combined with the uncertainties given in Tables I and II for the 0.994 M $HClO_4$ and 0.950 M HCl solutions, respectively.

The thermodynamic functions for the reaction (eq. 8 of ref. 1)

$$\mathrm{Pu}^{+3} + 2\mathrm{H_2O} = \mathrm{PuO_2}^{++} + 3/2\mathrm{H_2} + \mathrm{H}^+$$

for one molar perchloric acid, 25°, one atmosphere pressure of hydrogen and equal but small concentrations of Pu^{+3} and $\mathrm{PuO_2}^{++}$, become: $\Delta F = 70.7$ kcal., $\Delta H = 77.8$ kcal. and $\Delta S = 24$ e.u.

The previously reported entropies of Pu^{+3}, Pu^{+4} and $\mathrm{PuO_2}^{++}$ (ref. 1, Table VI), when corrected for the new equilibrium data and the new value of −43 e.u. for Gd^{+3},[13] become −41, −87 and −31 e.u., respectively. The value of $S_{\mathrm{PuO_2}^{++}}$ appears to be much too negative relative to uranyl ion and the recently reported value of −13 for neptunyl ion.[14] The ΔH value for oxidation of Pu^{+3} to $\mathrm{PuO_2}^{++}$ is the most likely source of error.

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[3] 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.[15,16] However this fact does not necessarily indicate lack of 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[17]

$$(\mathrm{LaCl}^{++})/(\mathrm{La}^{+3})(\mathrm{Cl}^-) = 0.7$$

If plutonium(III) were complexed to the same extent by chloride ion, the Pu(III)–Pu(VI) e.m.f. values would then give roughly 20% complexing of Pu(VI) by chloride ion in one molar hydrochloric acid.

[12] The e.m.f. data of Rabideau and Lemons for the Pu(III)–Pu(IV) couple were corrected to 25.0° by adding +0.2 millivolt.

[13] W. M. Latimer, "Oxidation Potentials," Second Edition, Prentice-Hall, Inc., New York, N. Y., 1952.

[14] D. Cohen and J. C. Hindman, Argonne National Laboratory report, ANL-4783, June, 1951.

[15] J. C. Hindman, I, p. 370.

[16] J. C. Hindman and D. P. Ames, I, p. 348.

[17] R. E. Connick and K. L. Mattern, to be published.

There is some additional support for the idea of a weak chloride complex of Pu(III). From partition measurements, Reas[18] found 66% of Pu(IV) to be complexed by chloride in 1 *M* hydrochloric acid at 25°. From the Pu(III)–Pu(IV) e.m.f. measurements the percentage 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.

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[18] W. H. Reas, unpublished work, this Laboratory.

NOTES

Absorption Spectra of Some α- and β-Diketones[1,2]

BY R. PERCY BARNES AND GLADYS ESTELLE PINKNEY

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Several α- and β-diketones have been studied spectroscopically. In carbon tetrachloride solutions the enols of the α-diketones are unchelated while the enols of the β-diketones have a chelated structure.

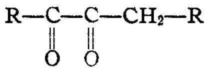
Many investigators have studied β-diketones from the standpoint of structure. Hilbert and co-workers[3] studied acetylacetone, benzoylacetone, and dibenzoylmethane and found no characteristic OH absorption for these β-diketones which fulfill the geometric requirements for chelated six-membered rings. Compounds were studied also which if chelated would give rise to five- or seven-membered rings. They showed characteristic OH absorption.

On the other hand, Morton and co-workers[4] concluded that dibenzoylmethane exists as the unchelated enol. Henecka[5] supports the chelated structure of the enol. In his review he points out that the enol is less soluble in polar media, contrary to what one would expect. The basis for the reverse behavior is that the chelate is formed, thereby tying-up the OH in the ring.

We decided to study a number of β-diketones in the 3 and 6 μ regions of the spectra. However, we considered it best to study a number of α-diketones first which if chelated would result in five-membered rings. That this would be unlikely[3] was supported also by Kohler and Barnes[6] who found in studying phenylbenzylglyoxal that upon distillation of the α-diketone, the distillate was rich in the keto form which is evidence against chelation.

The following α-diketones were studied in 0.01 molar solutions with carbon tetrachloride as the solvent. The curves were run from two to seven microns.

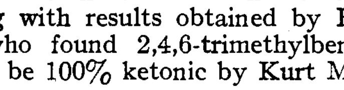
TABLE I

GENERAL FORMULA 

$R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}CH_2{-}R^1$

I, R and R^1 = phenyl
II, R = mesityl; R^1 = phenyl
III, R = nitromesityl; R^1 = phenyl
IV, R = dinitromesityl; R^1 = phenyl
V, R = mesityl; R^1 = *m*-nitrophenyl
VI, R = mesityl; R^1 = *p*-methoxyphenyl
VII, R = phenyl; R^1 = mesityl

In compounds I through VI we found absorption bands at 2.95 μ and 6 μ which are the regions of OH and carbonyl absorption, respectively, and also bands at 3.5 μ and 6.25 μ indicating CH and phenyl absorption, respectively. These results indicate that diketones I through VI exist as unchelated enols.



The fact that they do not form five-membered ring chelates is in keeping with Hilbert's[3] and Kohler's[6] findings.

Diketone VII was found to have no band at 2.95 μ. A new band appeared at 5.85 μ and the bands at 3.5, 6.25 and 6 μ remained. This indicates that diketone VII exists in the ketonic form, in keeping with results obtained by Barnes and Brown[7] who found 2,4,6-trimethylbenzylphenylglyoxal to be 100% ketonic by Kurt Meyer titration.

The disappearance of the OH band alone would not indicate chelation since the carbonyl bands would disappear also, because they as well as the OH would be tied-up in the ring.

We then turned our attention to the following β-diketones which were measured in 0.04 molar carbon tetrachloride solutions in the 2–7 μ region.

Diketones VIII through XIII did not exhibit absorption at 2.95, 6 and 5.85 μ, indicating that they are neither unchelated enols nor diketones.

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[2] The authors wish to acknowledge the invaluable aid of Mr. Jonas Carroll of the Food and Drug Administration, Federal Security Agency, and the use of their Perkin-Elmer 21 infrared spectrometer.

[3] G. E. Hilbert, O. R. Wulf, S. B. Hendricks and M. Liddel, THIS JOURNAL, 58, 548 (1936).

[4] R. A. Morton, A. Hassan and T. C. Calloway, *J. Chem. Soc.*, 900 (1934).

[5] H. Henecka, "Chemie der Beta-Dicarbonyl-Verbindungen," Springer Verlag, Berlin-Gottingen-Heidelberg, 1950.

[6] E. P. Kohler and R. P. Barnes, THIS JOURNAL, 56, 211 (1934).

[7] R. Percy Barnes and Robert J. Brown, *ibid.*, 65, 412 (1943).