per mole. The values have uncertainties of about ±1000 calories per mole. Beyond the fact that they are of the same order of magnitude as those reported for other electron transfer exchange reactions, little can be said about the values because of the complex nature of the solutions. The actual reactants in some, and possibly all, of the reaction paths suggested by our data are hydrolyzed or complexed species present in unknown concentrations. Hence, the apparent activation energies include unknown contributions from the heats of the reactions in which they are formed. It is correspondingly impossible to estimate meaningful values of the entropies of activation. It is of some interest to note, however, that if nitrate complexes of both cerous and ceric species are assumed to be essentially saturated in 6 *f* nitric acid, the data would lead to an entropy of activation[21] of about −40 cal./deg.-mole. Such a large negative value is consistent with expectation[21] for a reaction between two ions of large, and like, charge.

The apparent activation energy of the first order term of the rate in the perchlorate system is much larger than the excitation of the state through which, it is suggested, the exchange may occur. This is not particularly surprising since the observed temperature coefficient may simply be a measure of the heat of formation of the species in which activation by collision occurs.

It has been variously suggested[22] that the rates of oxidation–reduction reactions are predominantly governed by electrostatic interactions between the reactants, the number of electrons donated or received, or by the free energy change of the reaction. The results reported here and those obtained by other workers on electron transfer exchange reactions show that no one of these hypotheses is an adequate guide in predicting the rate of an oxidation reduction reaction. Other factors include the nature of any complexes which may be formed, the number of degrees of freedom of the intermediate complex, and, possibly, the electronic state of the reactants. This subject has been discussed more fully elsewhere.[5]

[21] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 417.

[22] J. Weiss, *J. Chem. Soc.*, 309 (1944); B. Krishna, *J. Chem. Phys.*, **17**, 846 (1949); P. A. Shaffer, THIS JOURNAL, **55**, 2169 (1933); L. Michaelis, *Trans. Electrochem. Soc.*, **71**, 107 (1937); A. E. Remick, THIS JOURNAL, **69**, 94 (1947).

UPTON, LONG ISLAND, N. Y. RECEIVED AUGUST 4, 1950

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

The Potential of the Pu(III)–Pu(IV) Couple and the Equilibrium Constants for Some Complex Ions of Pu(IV)[1]

BY SHERMAN W. RABIDEAU AND JOE F. LEMONS

The formal potentials of the Pu(III)–Pu(IV) couple *vs.* the H_2–H^+ couple in perchloric acid and in hydrochloric acid were measured at 25.2 ± 0.1° through potentiometric titrations of Pu(III) in cells with negligible liquid junction potentials. Values of −0.9821 ± 0.0005 volt and −0.9703 ± 0.0005 volt were obtained for this couple in molar perchloric and in molar hydrochloric acid, respectively. A value of 3.1×10^{-2} was obtained for the hydrolysis constant of Pu(IV) at 25.1 ± 0.03° from a study of the variation of the Pu(III)–Pu(IV) formal potential with acidity at unit ionic strength. The formulas and the dissociation constants of a Pu(IV) sulfate and a Pu(IV) nitrate complex have been obtained from the shift of the cell potential to more positive values with the addition of the complexing agent. A value of $2.17 \pm 0.05 \times 10^{-4}$ was found for the dissociation constant of $PuSO_4^{++}$ and 0.287 ± 0.004 for the dissociation constant of $PuNO_3^{+++}$ at 25.2 ± 0.1°.

Introduction

The formal potential of the Pu(III)–Pu(IV) couple has been reported by Howland, Hindman and Kraus[2] to be −0.953 ± 0.01 volt in 1 *M* perchloric acid and −0.966 ± 0.002 volt in 1 *M* hydrochloric acid. However, Connick and McVey[3] obtained a value of −0.982 ± 0.001 volt in molar perchloric acid for the formal potential of the reaction: $Pu^{+++} + H^+ \rightleftarrows Pu^{++++} + {}^1/_2\, H_2$. The more negative potential in 1 *M* perchloric acid as compared to that in 1 *M* hydrochloric acid is in agreement with the accepted relative complexing tendencies of the perchlorate and chloride ions; however, Connick and McVey[3] encountered unexplained difficulties in the analysis of the mixed Pu(III)–Pu(IV) solutions which limited somewhat the reliability of their determination.

Kraus and Nelson[4] by a spectrophotometric method obtained a value of 0.025 for the first hydrolysis constant of Pu(IV) in acidic perchlorate solutions at an ionic strength of 0.5. The association constant for the reaction $Pu^{++++} + NO_3^- \rightleftarrows PuNO_3^{+++}$ was determined by Hindman.[5] He obtained a value of 2.9 ± 0.6 by spectrophotometric means. It is of interest to determine these constants by independent methods.

No precise value has been reported for the dissociation constant of a Pu(IV) sulfate complex.

In this investigation the formal potentials of the Pu(III)–Pu(IV) couple in 1 *M* perchloric acid and in 1 *M* hydrochloric acid have been determined by means of potentiometric titrations of Pu(III) solutions. The hydrolysis constant of Pu(IV) has been evaluated from a study of the formal potential of the Pu(III)–Pu(IV) couple as a function of acidity at unit ionic strength. The dissociation constants of a plutonium sulfate complex ion with the formula

---

[1] Work done under the auspices of the AEC and presented in part before the Physical-Inorganic Division of the American Chemical Society, Chicago, Illinois, September 3–8, 1950.

[2] J. J. Howland, J. C. Hindman and K. A. Kraus, Natl. Nuclear Energy Ser., Div. IV, 14B, Transuranium Elements, Pt. I, 133 (1949).

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

[4] K. A. Kraus and F. Nelson, *ibid.*, **72**, 3901 (1950).

[5] J. C. Hindman, Natl. Nuclear Energy Ser., Div IV, 14B.Transuranium Elements, Pt. I, 388 (1949).

$PuSO_4^{++}$ and a plutonium nitrate complex with the formula $PuNO_3^{+++}$ have been evaluated from a study of the shift of the potential to more positive values as a Pu(III)–Pu(IV) mixture of known composition was titrated either with sodium sulfate or with nitric acid.

Apparatus

The cell assembly varied in detail depending on the particular cell arrangement and composition selected for the various potential measurements. The composition of the individual cells will be shown later. In general, the assembly consisted of one or more bright platinum electrodes dipping into a closed titration vessel containing the solution of unknown half-cell potential. This solution was connected by a suitable bridge to a hydrogen half-cell containing one or more platinized platinum electrodes.

The titration vessel, together with the reference half-cell, was placed in a small water-bath maintained at a constant temperature of 25°. The temperature of this bath was controlled by water circulated through a copper coil from a larger, auxiliary, thermostated bath of conventional design. Stirring of the bath-water surrounding the cell assembly as well as the solution being titrated was accomplished with a single magnetic stirrer driving two Pyrex glass-enclosed magnets placed one above the other in their respective containers.

A stream of nitrogen, which was purified by passing the gas over copper turnings at 450°, was used to remove dissolved oxygen and to provide an inert atmosphere over the solution being investigated. The nitrogen was saturated with water vapor to minimize evaporation losses. Flexible copper tubing was used to carry the nitrogen to the titration vessel.

The potential measurements were made with a Rubicon precision potentiometer employing a conventional electrical circuit which included an Eppley standard cell, a six volt lead-acid storage battery, and a Leeds and Northrup lamp and scale with a sensitivity of 15 microvolts per mm. The leads used to connect the cell with the potentiometer were shielded, and a multiple selector switch was employed to permit rapid shifting between sets of electrodes.

Reagents

The plutonium(III) perchlorate stock solutions were prepared by dissolving an accurately weighed sample of oxide-free plutonium metal in a weighed quantity of Mallinckrodt analytical reagent grade 71% perchloric acid. The plutonium(III) chloride stock solutions were prepared by dissolving the metal in C.P. reagent grade concentrated hydrochloric acid. These stock solutions were diluted to a final acid concentration of 1 *M* after solution of the metal was complete. Stock solutions were used within twenty-four hours of the time of preparation to avoid uncertainties caused by the slow air oxidation of Pu(III).

The perchloric and hydrochloric acids were standardized against mercuric oxide using phenolphthalein as an indicator. The approximately 0.04 *N* ceric perchlorate solution, prepared by dilution of a 0.5 *M* reagent grade ceric perchlorate solution obtained from the G. Frederick Smith Chemical Company, was standardized against a Bureau of Standards sample of sodium oxalate with the ferrous-phenanthroline complex serving as the indicator. This reaction is sufficiently rapid to permit titration at room temperature or slightly above without the aid of a catalytic agent. The perchloric acid content of the ceric perchlorate solution was determined by the procedure of Sherrill, King and Spooner.[6] Sodium perchlorate was prepared by mixing equivalent quantities of C.P. grades of perchloric acid and sodium carbonate. The salt was twice recrystallized from water and then converted to the anhydrous salt.

Experimental Procedure

In measuring the Pu(III)–Pu(IV) formal potentials in molar perchloric acid and in molar hydrochloric acid, a weight aliquot of the plutonium(III) perchlorate or chloride stock solution was taken for each titration. The initial Pu(III) concentration in each case was approximately 0.001 *M*. Mixtures of Pu(III) and Pu(IV) of known concentrations were prepared by adding dropwise a weighed quantity of the oxidant to the stirred solution of Pu(III). The cell potentials were determined over a rather wide range of Pu(IV)/Pu(III) ratios. The stability of the observed potentials was excellent, and the values were read to the nearest 0.02 millivolt.

The hydrolysis constant for Pu(IV) was obtained from a study of the formal potential of the Pu(III)–Pu(IV) couple as a function of the hydrogen ion concentration. Weighed quantities of sodium perchlorate, water, and a standardized perchloric acid solution were added to a solution of Pu(III) in such proportions as to maintain an ionic strength of unity in the solutions for the hydrolysis study. The hydrogen electrode was used as the reference half-cell. The liquid junction potential in this series of titrations was made negligible by using a solution in the salt bridge which had the same composition as that in the hydrogen electrode compartment. The solution in the titration compartment differed from that bathing the hydrogen electrode only insofar as the 0.001 *M* plutonium solution was not included in the latter half-cell. The temperature was held constant within ±0.03° and was read with a Beckmann thermometer which had been calibrated against a platinum resistance thermometer certified by the Bureau of Standards. The hydrogen ion concentration of the solution in the hydrogen electrode compartment was determined by titration with standard carbonate-free sodium hydroxide. Duplicate determinations of the formal potential were obtained at each hydrogen ion concentration. Within a given determination, several values of the formal potential of this couple were obtained by varying the Pu(IV)/Pu(III) ratio with the addition of a weighed quantity of standard 0.05 *N* potassium dichromate solution.

In the studies on the complexing of the Pu(IV) ion by the sulfate and nitrate ions, the ratio of the Pu(IV)/Pu(III) concentrations was adjusted by titrating a Pu(III) solution with a standard potassium dichromate solution. The respective complexing ions were added from a capillary weight buret in the form of a sodium sulfate or a nitric acid solution. The latter reagents were C.P. grade and were subjected to no additional purification.

Experimental Results and Calculations

Potential of the Pu(III)–Pu(IV) Couple in 1 *M* Perchloric Acid.—The formal potential of the Pu(III)–Pu(IV) couple in 1 *M* perchloric acid was obtained at various Pu(IV)/Pu(III) ratios from measurements of the potential of the cell

$$\text{Pt; } Pu(ClO_4)_3,\ Pu(ClO_4)_4,\ HClO_4\ (1\ M);\ HClO_4\ (1\ M);\ H_2,\ \text{Pt} \quad (I)$$

The formal potentials given in Table I and designated as $E^{0\prime}$ values were calculated from the Nernst expression, and have been corrected to a pressure of one atmosphere of hydrogen, to *unit concentration* of hydrogen ion, and to equal and small concentrations of Pu(III) and Pu(IV) at 25.2 ± 0.1°.

The mean value of $E^{0\prime}$, −0.9821 volt with an aver-

TABLE I

THE FORMAL POTENTIAL OF THE Pu(III)–Pu(IV) COUPLE IN 1 *M* $HClO_4$

Pu(IV)/Pu(III)	$E^{0\prime}$, volt
0.2758	−0.98239
.4116	.98226
.4800	.98218
.6048	.98222
.7249	.98212
.8658	.98203
.9852	.98190
1.122	.98198
1.391	.98197
1.607	.98194
Mean	−0.98210

---

(6) M. S. Sherrill, C. B. King and R. C. Spooner, THIS JOURNAL, 65, 171 (1943).

age deviation from the mean of 0.0001 volt, is in good agreement with the value obtained by Connick and McVey[3] for this couple. Since the temperature was known only to ±0.1°, it is believed that the best value of this couple is −0.9821 ± 0.0005 volt. A potential of −0.9767 ± 0.0005 volt is obtained if a correction is made for the *activity* of the hydrogen ion in the perchloric acid solution.

Potential of the Pu(III)–Pu(IV) Couple in 1 *M* Hydrochloric Acid.—The formal potential of the Pu(III)–Pu(IV) couple in 1 *M* hydrochloric acid was found from measurements of the potential of the cell

Pt; $PuCl_3$, $PuCl_4$, HCl (1 *M*); HCl (1 *M*); H_2, Pt (II)

The formal potentials denoted as $E^{0\prime}$ values in Table II have been corrected to *unit hydrogen ion concentration*, to one atmosphere of hydrogen, and to small and equal concentrations of Pu(III) and Pu(IV) at 25.2 ± 0.1°.

TABLE II

THE FORMAL POTENTIAL OF THE Pu(III)-Pu(IV) COUPLE IN 1 *M* HCl

Pu(IV)/Pu(III)	$E^{0\prime}$, volt
0.3085	−0.97013
.4210	.97025
.5368	.97035
.6468	.97035
.7806	.97039
.8921	.97039
Mean	−0.97032

A mean value of −0.9703 volt with an average deviation from the mean of 0.0001 volt was obtained for the formal potential of the Pu(III)–Pu(IV) couple in 1 *M* hydrochloric acid. Since the temperature was not controlled to better than ±0.1°, the best value is believed to be −0.9703 ± 0.0005 volt. If the formal potential value for this couple in 1 *M* hydrochloric acid as found by Howland, Hindman and Kraus[2] is changed to conform to the convention used in this work for representing the formal potentials, a value of −0.971 ± 0.002 volt is obtained.[6a] Thus it is seen that our value is in good agreement with the result obtained by these investigators. A potential of −0.9649 ± 0.0005 volt is obtained from our measurements for the Pu(III)–Pu(IV) couple if a correction is made for the *activity* of the hydrogen ion in the hydrochloric acid solution.

If it is assumed that the difference in the formal potentials, corrected to unit activity of the hydrogen ion, for the Pu(III)–Pu(IV) couple in 1 *M* perchloric acid and 1 *M* hydrochloric acid results from the formation of a Pu(IV) complex with the formula $PuCl^{+++}$, a value of 1.72 is calculated for the dissociation constant at 25°.

The Hydrolysis Constant of Pu(IV).—The apparent formal potential of the Pu(III)–Pu(IV) couple may be expected to exhibit a hydrogen ion concentration dependence as a result of the formation of any hydrolyzed species. It has been shown by Kraus and Dam[7] that the hydrolysis of Pu(III) is sufficiently small to be neglected in acid concentrations of 0.1 *M* and above; consequently, the hydrolysis of Pu(IV) will result in a more positive value for the observed formal potential. The presence of polymeric Pu(IV) would similarly make the potential of this couple more positive. Examination of mixtures of Pu(III) and Pu(IV) in 0.03, 0.05 and 0.1 *M* perchloric acid with the Cary spectrophotometer showed a radical difference in the appearance of the absorption spectrum at an acidity of 0.03 *M* as compared with the spectra at higher acidities. The Pu(IV) concentration in each solution was about 4×10^{-4} *M*. The initial absorption spectrum measurements were made within one minute after mixing the solutions. It was immediately evident that the 470 mμ Pu^{++++} peak which had been observed in the 0.05 and 0.1 *M* solutions had been masked by a strong absorption presumably caused by the presence of polymeric Pu(IV) in the 0.03 *M* perchloric acid solution.

The hydrolysis constant of Pu(IV) was evaluated from measurements of the potential of the cell

Pt; $Pu(ClO_4)_3$, $Pu(ClO_4)_4$, $HClO_4$ (*X*)*M*, $NaClO_4$ (1 − *X*) *M*; $HClO_4$ (*X*)*M*, $NaClO_4$ (1 − *X*) *M*; H_2, Pt (III)

Since the total plutonium concentration was about 10^{-3} *M*, the liquid junction potential of cell (III) can be neglected. The perchloric acid concentration was varied between 0.10 and 0.20 *M*. In order to evaluate the potential of the hydrogen half-cell, it is necessary to know the activity of the perchloric acid in the acid–salt solution. Bates and Urmston[8] have measured the mean activity coefficient of hydrochloric acid in sodium perchlorate solutions at unit ionic strength. Since Schuhmann[9] and Popoff, *et al.*,[10] have shown that the activities of the hydrogen ion from perchloric and hydrochloric acids are equal in the region from 0.02 to 1 molar, it seems justified to apply the results of Bates and Urmston[8] to the mixture of sodium perchlorate and perchloric acid at unit ionic strength.

Betts and Leigh[11] have shown that hydrolysis of U(IV) can be represented by the equation

$$U^{++++} + H_2O \rightleftarrows UOH^{+++} + H^+$$

If it is assumed that the hydrolysis of the Pu(IV) ion can be represented by an analogous reaction, the hydrolysis constant is given by the equation

$$K = [PuOH^{+++}][H^+]/[Pu^{++++}]$$

The potential, E_c, of cell (III) is related to the hydrolysis constant, *K*, by the expression

---

(6a) NOTE ADDED IN PROOF.—An error appears to have been made by Connick and McVey[3] in the calculation of the formal potential for the Pu(III)-Pu(IV) couple *vs.* the H_2-H^+ couple from Hindman's[2] measurement in molar hydrochloric acid of the Pu(III)-Pu(IV) couple *vs.* the Ag-AgCl couple. The potential should read −0.971 volt instead of −0.959 volt for the Pu(III)-Pu(IV) potential. The relationship between the two methods of representation is E_f (*vs.* H_2-H^+) = E_f (*vs.* Ag-AgCl) + $RT/F \ln \gamma^2_{\pm HCl}$. The quantity of complexed Pu(IV) in molar hydrochloric acid is then about 37% instead of 59% as calculated by these authors.

(7) K. A. Kraus and J. R. Dam, Natl. Nuclear Energy Series, Div. IV, 14B, Transuranium Elements, Pt. I, **388** (1949).

(8) S. R. Bates and J. W. Urmston, THIS JOURNAL, **55**, 4068 (1933).

(9) R. Schuhmann, *ibid.*, **46**, 58 (1924).

(10) S. Popoff, J. A. Riddick, V. I. Worth and L. D. Ough, *ibid.*, **53**, 1195 (1931).

(11) R. H. Betts and R. M. Leigh, *Can. J. Research*, **B28**, 514 (1950).

$$E_c = E^{0\prime} - 0.05915 \log \frac{\Sigma \mathrm{Pu(IV)}}{[\mathrm{Pu}^{+++}]} - 0.05915 \log p_{\mathrm{H}_2}{}^{1/2}/a_{\mathrm{H}^+} - 0.05915 \log \frac{[\mathrm{H}^+]}{[\mathrm{H}^+] + K}$$

A plot of $E_c + 0.05915 \log \Sigma\mathrm{Pu(IV)}/[\mathrm{Pu}^{+++}] + 0.05915 \log p_{\mathrm{H}_2}^{1/2}/a_{\mathrm{H}^+}$ vs. $\log [\mathrm{H}^+]/([\mathrm{H}^+] + K)$ with an appropriately chosen value for the hydrolysis constant should yield a straight line with a slope of -0.05915. In Table III are given the data which were used to evaluate the hydrolysis constant.

TABLE III

THE HYDROLYSIS CONSTANT OF Pu(IV) IN PERCHLORATE SOLUTIONS OF UNIT IONIC STRENGTH

$[\mathrm{H}^+]$, M/l.	$E_c + 0.05915 \log \frac{\Sigma\mathrm{Pu(IV)}}{[\mathrm{Pu}^{+++}]} + E_{\mathrm{H}_2}$, v.	$\log \frac{[\mathrm{H}^+]}{[\mathrm{H}^+] + K}$
0.0967	−0.96897	−0.1437
.0990	.96930	.1381
.1220	.97109	.1082
.1505	.97262	.0824
.1489	.97259	.0830
.1750	.97386	.0614
.1741	.97394	.0600
.1990	.97401	.0589
.1999	.97408	.0577
.9566[a]	.97669	.0139

[a] This is the $E^{0\prime}$ value, corrected for the activity of the hydrogen ion, as obtained from measurements with cell I; since no sodium perchlorate was added the potential was not observed at precisely unit ionic strength.

Each of the potentials given in column 2 of Table III represents the mean value of about ten independent observations over a rather wide range of Pu(IV) to Pu(III) ratios. The average deviation from the mean for these potentials is approximately 0.05 mv.

The theoretical slope of -0.05915 is obtained for the above plot as shown in Fig. 1 if a value of 3.1×10^{-2} is taken as the hydrolysis constant for Pu(IV) in perchlorate solutions of unit ionic strength at 25.1 ± 0.03°.[12] This result is in fairly good agreement with the spectrophotometrically obtained constant of 2.5×10^{-2} reported by Kraus and Nelson[5] at an ionic strength of 0.5 in perchlorate media.

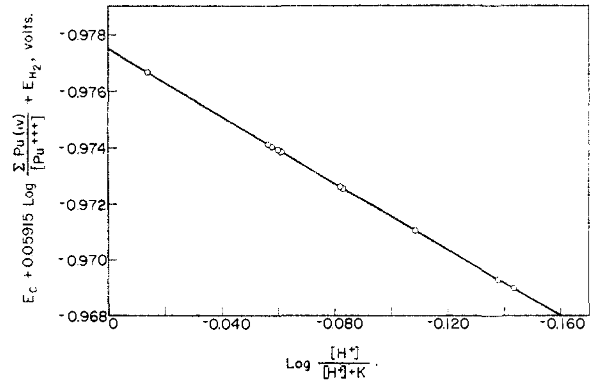

Fig. 1.

The Dissociation Constant of $\mathrm{PuSO_4}^{++}$.—The complexing of Pu(IV) by sulfate ion has been studied by observing the potential of cell (I) as a function of sulfate ion concentration. The dissociation of a generalized form of the complex is given by the expression

$$\mathrm{Pu}_x(\mathrm{SO_4})_y{}^{4x-2y} \rightleftarrows x\mathrm{Pu}^{++++} + y\mathrm{SO_4}^{=}$$

The dissociation constant is defined as

$$K = [\mathrm{Pu}^{++++}]^x[\mathrm{SO_4}^{=}]^y/[\mathrm{Pu}_x(\mathrm{SO_4})_y{}^{4x-2y}]$$

Connick, Kasha, McVey and Sheline[13] have shown from spectrophotometric measurements that Pu(III) is not complexed by dilute sulfate solutions. Thus, the potential decrease with the addition of sodium sulfate was attributed solely to the formation of a plutonium(IV) sulfate complex. When no sulfate has been added to the mixture of Pu(III) and (IV), the initial concentration of Pu(IV) ion, $[\mathrm{Pu}^{++++}]_0$, equals ΣPu(IV), the total concentration of plutonium in the tetravalent state, and the potential of cell (I) is designated by E_1. After the addition of sulfate ion a new potential, E_2, is observed, and the remaining concentration of uncomplexed Pu(IV) is given by the expression

$$[\mathrm{Pu}^{++++}]_f = (\Sigma\mathrm{Pu(IV)} \times 10^{(E_1 - E_2)/0.0592})$$

The concentration of the complex is given by

$$[\mathrm{Pu}_x(\mathrm{SO_4})_y{}^{4x-2y}] = (\Sigma\mathrm{Pu(IV)}/x) \times (1 - 10^{(E_1 - E_2)/0.0592})$$

The sulfate ion concentration was calculated by taking a value of 0.24 for the dissociation constant of the bisulfate ion at unit ionic strength.[14] The quantity of sulfate ion consumed in the formation of the complex for different y values was taken into consideration. An appropriate choice of x and y in the formula of the plutonium sulfate complex should give consistent values for the dissociation constant. As shown in Table IV, at low sulfate concentrations the formula of the complex is $\mathrm{PuSO_4}^{++}$ as evidenced by the constancy of K. A mean value of $2.17 \pm 0.05 \times 10^{-4}$ has been obtained for the dissociation of the $\mathrm{PuSO_4}^{++}$ complex in 1 M perchloric acid at 25 ± 0.1°. Inconsistent values of the dissociation constant were obtained if the formula of the complex were assumed to be either $\mathrm{Pu_2(SO_4)_3}^{++}$ or $\mathrm{Pu(SO_4)_2}$. It is also apparent from Table IV that with increasing sulfate ion concentration beyond a value of about 5×10^{-4} M, another complex is being formed. This experiment was repeated at an acidity of 0.76 M perchloric acid and again values closely approximating

---

(12) As a result of an earlier study of the variation of the formal potential with acidity in which the saturated calomel electrode was used as a reference half-cell, a value of 6.8×10^{-2} was reported[1] for the hydrolysis constant of Pu(IV). This has subsequently been found to be in error. It is felt that the use of the saturated calomel electrode gave rise to unsatisfactory results because of the uncertain liquid junction potentials which were neglected.

(13) R. E. Connick, M. Kasha, W. H. McVey and G. E. Sheline, Natl. Nuclear Energy Ser., Div. IV, 14B, Transuranium Elements, Pt. I, 575 (1949).

(14) This value was derived from solubility data for calcium sulfate as compiled by A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds, Vol. I," D. Van Nostrand Company, Inc., New York, N. Y., 1940. Designating the solubility of calcium sulfate in moles/liter in a strong acid, HA, having no common ion by S_a, and the solubility at the same ionic strength in a neutral salt by S_s, the relation between the dissociation constant of the bisulfate ion and the solubilities can easily be derived.

$$\frac{[\mathrm{H}^+][\mathrm{SO_4}^{=}]}{[\mathrm{HSO_4}^-]} = \frac{[S_a(\mathrm{A}^-) - S_a^2 + S_s^2]S_s^2}{S_a[S_a^2 - S_s^2]}$$

It was assumed in this derivation that the activity coefficients of the calcium and the sulfate ions are functions only of the ionic strength. The solubility data of calcium sulfate in the HCl–NaCl, $\mathrm{HNO_3}$–$\mathrm{NaNO_3}$ and the $\mathrm{HNO_3}$–$\mathrm{KNO_3}$ acid–salt pairs were used in the evaluation of this constant.

2.17×10^{-4} were obtained for the dissociation constant.

TABLE IV

EVALUATION OF THE DISSOCIATION CONSTANT OF PLUTONIUM SULFATE

Σ Pu(IV) $\times 10^{-4}$	$E_1 - E_2$, mv.	$[Pu^{+4}]_f$ $\times 10^{-4}$ M	$[Na_2SO_4]$ $\times 10^{-3}$ M	$[SO_4^=]$, M	$K \times 10^4$
9.37	5.22	7.66	0.419	4.76×10^{-5}	2.12
9.25	12.48	5.72	1.044	1.33×10^{-4}	2.14
9.22	14.30	5.31	1.246	1.64	2.23
9.18	16.22	4.91	1.460	1.99	2.28
9.14	18.34	4.50	1.657	2.29	2.22
9.08	21.50	3.96	1.986	2.83	2.19
9.02	24.40	3.51	2.292	3.35	2.13
9.00	27.88	3.06	2.758	4.16	2.14
8.98	31.28	2.96	3.233	5.00	2.10
8.95	38.20	2.05	4.208	6.76	(2.01)
8.85	51.96	1.19	6.856	11.7	(1.82)

The Dissociation Constant of $PuNO_3^{+++}$.—The dissociation of the nitrate complex may be expressed in general terms as

$$Pu(NO_3)_x^{4-x} \rightleftarrows Pu^{++++} + xNO_3^-$$

The dissociation constant expression is

$$K = \frac{[Pu^{++++}][NO_3^-]^x}{[Pu(NO_3)_x^{4-x}]}$$

Connick, *et al.*,[13] found the perturbations of the plutonium(III) spectrum by $0.5M$ nitric acid to be very slight. Hence, the assumption seems justified that the shift of the potential of cell (I) to more positive values with the addition of nitric acid can be attributed to the complexing of Pu(IV).

Rearranging the expression for the dissociation constant, the concentration of uncomplexed plutonium may be written as

$$[Pu^{++++}]_f = \Sigma Pu(IV) \times \frac{K}{K + [NO_3^-]}$$

From the Nernst equation it is possible to derive the relation between ΔE, the potential shift for a given nitrate concentration, and K, the dissociation constant of the complex. This expression is

$$\Delta E = C - 0.0592 \log \frac{K}{K + [NO_3^-]}$$

where C is a constant.

A plot of ΔE *vs.* $- \log K/(K + [NO_3^-])$, see Fig. 2, gives a straight line with a slope of 0.0592, thus indicating that one nitrate ion is involved in the formation of the complex. This is in agreement with the statement of Hindman[5] that the formula of the complex may be expressed as $PuNO_3^{+++}$ in nitric acid solutions below 4.6 M. A mean value of 0.287 ± 0.004 was obtained for the dissociation constant of the nitrate complex of plutonium(IV) (Table V). It was obtained in a manner similar to that outlined in the treatment of the plutonium sulfate complex.

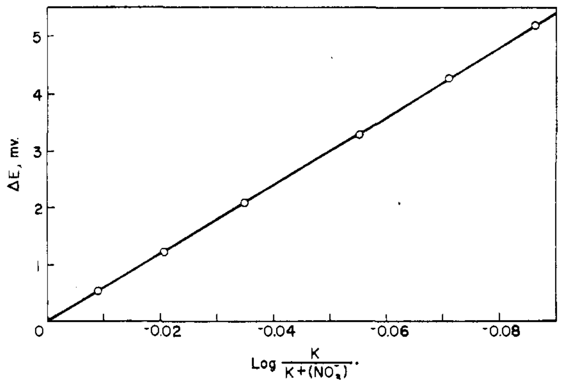

Fig. 2.

TABLE V

THE DISSOCIATION CONSTANT OF PLUTONIUM(IV) NITRATE AT 25.2 ± 0.1°

Σ Pu(IV) $\times 10^{-3}$ M	$[Pu^{+4}]_f$ $\times 10^{-3}$ M	$[NO_3^-]$, M	K
7.79	7.43	0.0142	0.292
7.71	7.11	.0244	.292
7.58	6.67	.0390	.286
7.48	6.36	.0509	.289
7.38	6.03	.0626	.278
		Mean	0.287 ± 0.004

The association constant then is the reciprocal of 0.287, or 3.48 ± 0.06, which is in fair agreement with Hindman's[5] spectrophotometrically determined value of 2.9 ± 0.6.

Acknowledgment.—The authors wish to acknowledge their indebtedness to Professor G. K. Rollefson, consultant to the L. A. S. L., for valuable suggestions and useful contributions to this investigation.

LOS ALAMOS, N. MEX. RECEIVED JANUARY 2, 1951