

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

The Hydrolysis of Plutonium(IV)¹

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The hydrolysis quotient, $(\text{PuOH}^{+++})(\text{H}^+)/(\text{Pu}^{+4})$, has been evaluated in lithium perchlorate-perchloric acid solutions at a constant total molarity of two from measurements of the Pu(III)-Pu(IV) formal potential as a function of acidity. The temperature dependence of this hydrolysis quotient was obtained from formal potential measurements at 14.88, 25.00 and 34.35°; the value of ΔH for the reaction $\text{Pu}^{+4} + \text{H}_2\text{O} \rightleftharpoons \text{PuOH}^{+++} + \text{H}^+$ was computed to be 7.3 ± 0.5 kcal./mole. At 25° the value of ΔF is 1.73 ± 0.01 kcal./mole; hence, $\Delta S = 19 \pm 2$ e.u. The value of ΔH for the reaction $\text{Pu}^{+3} + \text{H}^+ \rightleftharpoons \text{Pu}^{+4} + \frac{1}{2}\text{H}_2$, in 2 M perchloric acid at 25° was found to be 13.3 ± 0.5 kcal./mole which is very nearly equal to the value obtained previously for this reaction in molar perchloric acid. Virtually identical Pu(III)-Pu(IV) formal potentials were obtained in those cases in which sodium perchlorate was used to replace lithium perchlorate as the added salt to maintain an ionic strength of two in the solutions. Thus, it would appear that the concentration of the perchlorate ion plays a more significant role than the sodium or lithium ion in determining the value of the activity coefficient ratio $\gamma^{\text{Pu}^{+4}}\text{Pu}(\text{ClO}_4)_4 / \gamma^{\text{Pu}^{+3}}\text{Pu}(\text{ClO}_4)_3$; $\gamma^{\text{Pu}^{+4}} \pm \text{Pu}(\text{ClO}_4)_4$; $\gamma^{\text{Pu}^{+3}} \pm \text{HClO}_4$.

Introduction

In the study of the isotopic exchange between Pu(III) and Pu(IV) Keenan² observed that his results indicated that the hydrolyzed species of Pu(IV), PuOH^{+++} appeared to be involved in the reaction mechanism. The present work was directed toward the evaluation of this hydrolysis quotient in the media in which the exchange experiments were performed, *i.e.*, lithium perchlorate-perchloric acid mixtures, and the determination of some of the thermodynamic quantities applicable to the hydrolysis reaction, $\text{Pu}^{+4} + \text{H}_2\text{O} \rightleftharpoons \text{PuOH}^{+++} + \text{H}^+$. The hydrolysis of Pu^{+4} has been studied previously³⁻⁵ by spectrophotometric and potentiometric methods at ionic strengths ranging from 0.5 to 1.1. However, none of these previous studies included measurements of the temperature coefficient of the hydrolysis quotient. Hindman⁶ has considered the evaluation of the degree of hydrolysis of some trivalent and tetravalent ions, including plutonium, from a theoretical point of view in which an attempt is made to calculate the electrostatic free energy involved in the hydrolytic reaction. However, this treatment appears to be semi-quantitative in scope.

Experimental

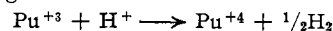
The experimental apparatus has been described previously.⁷ The Pu^{+3} solutions were prepared by dissolving weighed quantities of oxide-free metal in Mallinckrodt Analytical Reagent grade 70% perchloric acid, then diluting with water redistilled from alkaline permanganate. The lithium perchlorate was prepared by neutralizing C.P. lithium carbonate with perchloric acid followed by recrystallization of the salt from water as the trihydrate. This salt was analyzed for perchlorate content by precipitation with tetraphenylarsonium chloride, and for water content by heating to about 160° to form the anhydrous salt. Electrolytic grade hydrogen was purified by passing the gas through a uranium furnace heated to 600°. The gas was saturated with the cell solution in a bubbler maintained at the temperature of the cell; then the gas was passed into the

hydrogen electrode compartment. Dual hydrogen and bright platinum electrodes were used and intercompared to assure proper electrode behavior. The plutonium solutions of known $(\text{Pu}(\text{IV})) / (\text{Pu}(\text{III}))$ ratio were prepared by adding weighed aliquots of a standard potassium dichromate solution to the Pu^{+3} solutions. The same acid-salt concentration was used in both the dichromate and Pu^{+3} solutions to maintain the ionic strength at two during the potentiometric titration. The temperature of the plutonium solutions was maintained at $\pm 0.01^\circ$ during the course of an experiment and was obtained from measurements of the resistance of a type 20D Western Electric thermistor which was calibrated against a platinum resistance thermometer certified by the National Bureau of Standards. A voltage of 1.0000 was impressed upon the thermistor by using a voltage divider and Mallory type 302157 mercury batteries to maintain the resistance-temperature calibration over a period of several months.

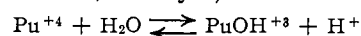
To correct the hydrogen electrode for the partial pressure of hydrogen gas, the vapor pressure of the lithium perchlorate-perchloric acid solutions was required. Since it appeared that the vapor pressure data required had not been published previously, the vapor pressures of the acid-salt solution were measured between 5 and 25° by using a high vacuum line and a mercury manometer. The air was removed from the solutions during repeated freezing-melting cycles. Pearce and Nelson⁸ found that in the 2 M perchloric acid concentration region the experimentally observed vapor pressures differed only slightly from the theoretical fractional lowering of the vapor pressure of the solvent. The deviations from the ideal theoretical vapor pressure lowerings have been found to be small for the lithium perchlorate-perchloric acid solutions also.

Results and Discussion

The cell Pt; Pu^{+3} , Pu^{+4} , $\text{HClO}_4(c_1)$, $\text{LiClO}_4(c_2)$; $\text{LiClO}_4(c_2)$, $\text{HClO}_4(c_1)$; H_2 , Pt was used in the measurement of the formal potential of the Pu^{+3} - Pu^{+4} couple as a function of acidity and temperature at constant total molarity. Since the total plutonium concentrations were about 8×10^{-3} , the liquid junction potential has been assumed to be negligibly small. The cell reaction that occurs upon the passage of a faraday of electricity from left to right through the cell is



The ion Pu^{+4} undergoes a hydrolytic reaction which occurs to a considerable extent in solutions of low acidity (*ca.* 35% hydrolyzed in 0.1 M perchloric acid at 25°, *vide infra*)



The concentration quotient, K , for this hydrolysis reaction is

$$K = (\text{PuOH}^{+3})(\text{H}^+)/(\text{Pu}^{+4})$$

(8) J. N. Pearce and A. F. Nelson, *ibid.*, **55**, 3075 (1933).

(1) This work was done under the auspices of the Atomic Energy Commission.

(2) T. K. Keenan, *THIS JOURNAL*, **78**, 2339 (1956).

(3) J. C. Hindman, "The Transuranium Elements," Nat. Nuclear Energy Ser. Div. IV, Vol. 14-B, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 370.

(4) K. A. Kraus and F. Nelson, *THIS JOURNAL*, **72**, 3901 (1950).(5) S. W. Rabideau and J. F. Lemons, *ibid.*, **73**, 2895 (1951).

(6) J. C. Hindman, "The Actinide Elements," Natl. Nuclear Energy Ser., Div. IV, Vol. 14-A, McGraw-Hill Book Co., Inc., New York, N. Y., 1954, p. 301.

(7) S. W. Rabideau, *THIS JOURNAL*, **75**, 798 (1953).

The formal potential of the $\text{Pu}^{+3}\text{-Pu}^{+4}$ couple is given by the expression

$$E^{\circ'} = E_{\text{cell}} + RT/F \ln \frac{\Sigma \text{Pu(IV)}/\text{Pu(III)} + RT/F \ln p_{\text{H}_2}^{1/2}/(\text{H}^+)}{RT/F \ln \frac{\gamma^{\pm}_{\text{Pu}(\text{ClO}_4)} / \gamma^{\pm}_{\text{Pu}(\text{ClO}_4)} \gamma^{\pm}_{\text{HClO}_4}}{\gamma^{\pm}_{\text{Pu}(\text{ClO}_4)} \gamma^{\pm}_{\text{HClO}_4}}}$$

This formal potential is related to the concentration quotient, K , by the formula

$$E^{\circ'} = E^{\circ} - RT/F \ln \left[\frac{(\text{H}^+)}{(\text{H}^+) + K} \right] - RT/F \ln \frac{\gamma^{\pm}_{\text{Pu}(\text{ClO}_4)} / \gamma^{\pm}_{\text{Pu}(\text{ClO}_4)} \gamma^{\pm}_{\text{HClO}_4}}{\gamma^{\pm}_{\text{Pu}(\text{ClO}_4)} \gamma^{\pm}_{\text{HClO}_4}}$$

If it is assumed that the activity coefficient ratio $\gamma^{\pm}_{\text{Pu}(\text{ClO}_4)} / \gamma^{\pm}_{\text{Pu}(\text{ClO}_4)} \gamma^{\pm}_{\text{HClO}_4}$ is constant in perchloric acid-lithium perchlorate solutions of constant ionic strength, the value of the concentration quotient, K , can be evaluated from a plot of the formal potential of the $\text{Pu}^{+3}\text{-Pu}^{+4}$ couple versus $\log [(\text{H}^+)/(\text{H}^+) + K]$. This plot should result in a straight line relation with a slope of $-2.303RT/F$ if the assumption with reference to the constancy of the activity coefficient ratio is valid. It appears that this assumption is justified since reasonably good straight lines do result from plots of the formal potentials versus $\log [(\text{H}^+)/(\text{H}^+) + K]$.

In Table I are given the formal potentials of the $\text{Pu}^{+3}\text{-Pu}^{+4}$ couple in lithium perchlorate-perchloric acid solutions as a function of temperature and of acidity at a total constant molarity of two.

The uncertainty of the formal potentials is about ± 0.0002 volt. The values of the hydrolysis quotients were obtained as shown in Fig. 1 by adjusting the value of K in the plot of $E^{\circ'}$ vs. $\log [(\text{H}^+)/(\text{H}^+) + K]$ until the theoretical slope of $-2.303RT/F$ was obtained. The values of K are considered to have an uncertainty of ± 0.001 .

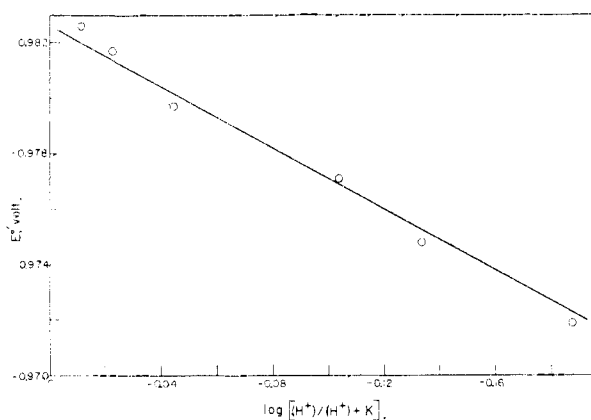


Fig. 1.—Evaluation of hydrolysis quotient of plutonium(IV) from potentiometric measurements in lithium perchlorate-perchloric acid solutions at 25° and at an ionic strength of two.

From the temperature coefficient of the hydrolysis quotient a value of $+7.3 \pm 0.5$ kcal./mole was obtained for ΔH . Since at 25° the value of ΔF equals 1.73 ± 0.01 kcal./mole, the increase in entropy accompanying the hydrolysis of Pu^{+4} is $+19 \pm 2$ e.u. The data given in Table II were used in the evaluation of the heat of the hydrolysis reaction. It is of interest to compare the thermodynamic quantities for the hydrolysis of Pu^{+4}

TABLE I
TEMPERATURE AND ACIDITY DEPENDENCE OF Pu(III)-Pu(IV) FORMAL POTENTIALS IN LITHIUM PERCHLORATE-PERCHLORIC ACID SOLUTION AT AN IONIC STRENGTH OF TWO

$T, ^\circ\text{K.}$	(H^+) , moles/l.	$E^{\circ'}$, volt	$\frac{[(\text{H}^+)]}{(\text{H}^+) + K}$	$\log \frac{[(\text{H}^+)]}{(\text{H}^+) + K}$	K
288.05	2.000	-0.9681	0.98087	-0.00839	
	1.000	.9657	.96246	.01662	
	0.500	.9651	.92764	.03262	0.039
	.200	.9620	.83682	.07737	
	.150	.9611	.79365	.10037	
	.100	.9587	.71942	.14302	
298.16	2.000	-0.9826	0.97371	-0.01157	
	1.000	.9817	.94877	.02284	
	0.500	.9797	.90253	.04454	0.054
	.200	.9771	.78740	.10380	
	.150	.9748	.73529	.13354	
	.100	.9719	.64935	.18752	
307.51	2.000	-0.9944	0.95785	-0.01871	
	1.000	.9891	.91912	.03663	
	0.500	.9879	.85034	.07041	0.088
	.200	.9818	.69444	.15837	
	.150	.9795	.63025	.20048	
	.100	.9733	.53191	.27416	

with those reported^{9,10} for U^{+4} . With spectrophotometric methods these authors obtained values which were in essential agreement. Values of $\Delta H = 11.0$ kcal./mole and $\Delta S = 33$ e.u. were obtained for the reaction $\text{U}^{+4} + \text{H}_2\text{O} \rightleftharpoons \text{UOH}^{+3} + \text{H}^+$. These values refer to the hydrolysis reaction at zero ionic strength whereas in the hydrolysis of Pu^{+4} the ionic strength of two was used.

TABLE II

DETERMINATION OF ΔH FOR HYDROLYSIS OF Pu(IV)			
$T, ^\circ\text{K.}$	$1/T \times 10^3$	K	$\log K$
288.05	3.472	0.039	-1.409
298.16	3.354	.054	-1.263
307.51	3.252	.088	-1.056

The value of ΔH for the reaction $\text{Pu}^{+3} + \text{H}^+ \rightleftharpoons \text{Pu}^{+4} + \frac{1}{2}\text{H}_2$ also was determined since values of the formal potential of the $\text{Pu}^{+3}\text{-Pu}^{+4}$ couple in 2 M perchloric acid as a function of temperature were measured. From a plot of $E^{\circ'}/T$ vs. $1/T$ a value of 13.3 ± 0.5 kcal./mole was computed for ΔH for this reaction at 25°. This value is very nearly equal to the value reported¹¹ for this reaction in molar perchloric acid.

A point of interest was examined in connection with changes in activity coefficient ratios in mixed electrolytes at constant ionic strength as sodium perchlorate is substituted for lithium perchlorate. In Table III are given the formal potentials of the $\text{Pu}^{+3}\text{-Pu}^{+4}$ couple as a function of acidity in the presence of either sodium or lithium perchlorate.

Thus, as evident from a comparison of the formal potentials of the $\text{Pu}^{+3}\text{-Pu}^{+4}$ couple in sodium or lithium perchlorate-perchloric acid solutions, the alteration of the hydrolysis quotient with the change in added salt is very small. It would seem that the activity coefficient ratio $\gamma^{\pm}_{\text{Pu}(\text{ClO}_4)} / \gamma^{\pm}_{\text{Pu}(\text{ClO}_4)} \gamma^{\pm}_{\text{HClO}_4}$ is not very sensitive to the substitution of lithium ions for hydrogen ions, or to

(9) K. A. Kraus and F. Nelson, *THIS JOURNAL*, **77**, 3721 (1955).

(10) R. H. Betts, *Can. J. Chem.*, **33**, 1775 (1955).

(11) S. W. Rabideau and H. D. Cowan, *ibid.*, **77**, 6145 (1955).

TABLE III
EFFECT OF TYPE OF ADDED SALT UPON Pu^{+3} - Pu^{+4} FORMAL POTENTIALS AT CONSTANT IONIC STRENGTH AND 25°

(H^+), moles/l.	(NaClO_4), moles/l.	(LiClO_4), moles/l.	E^0 , volts
2.000	0.000	0.000	-0.9826
0.500	.000	1.500	-.9797
.500	1.500	0.000	-.9791
.200	0.000	1.800	-.9771
.200	1.800	0.000	-.9768
.100	0.000	1.900	-.9719
.100	1.900	0.000	-.9728

the substitution of sodium ions for lithium ions in these solutions of constant ionic strength.

It might have been predicted from the treatment of Robinson and Stokes¹² that the above activity coefficient ratio would be significantly altered in the solution of mixed electrolytes since the osmotic coefficients and the hydration numbers of sodium perchlorate and lithium perchlorate are appreciably different. However, it appears that this difference is not observed experimentally in view of the small changes noted in the formal potentials of the Pu^{+3} - Pu^{+4} couple.

(12) R. A. Robinson and R. H. Stokes, "Electrolytic Solutions," Butterworths Publications, Ltd., London, 1955, p. 443.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Composition and Formation of Cobalt Complexes with 1-Nitroso-2-naphthol

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Controversial statements are found in the literature on the composition and the mode of formation of the complex which precipitates upon addition of a solution of 1-nitroso-2-naphthol (HR) to a cobalt(II) solution in an acetate buffer. The precipitate is soluble in benzene and acetonitrile (AN). From its polarographic properties in AN, from amperometric titrations in water and AN, and from gravimetric studies it was concluded that the complex has the formula $\text{Co(III)}\text{R}_3\cdot\text{H}_2\text{R}'$, $\text{H}_2\text{R}'$ being the semiquinone obtained by a one-electron reduction of HR. $\text{H}_2\text{R}'$ is unstable in a vacuum at 110°. $\text{H}_2\text{R}'$ is soluble in 40% acetic acid; the precipitate obtained from this medium has the composition $\text{Co(III)}\text{R}_3$. It is proposed that $\text{Co(II)}\text{R}_2$ is the first reaction product which, in acid medium, decomposes rapidly according to the equation: $2\text{Co(II)}\text{R}_2 \rightarrow \text{Co(III)}\text{R}_3 + \text{H}_2\text{R}' + \text{Co(II)}$. A precipitate of $\text{Co(II)}\text{R}_2$ is obtained from neutral and slightly alkaline aqueous medium. When dissolved in AN which contains acid, the reaction products of the disproportionation are found in the solution. The polarographic properties of some other metal-HR complexes have been determined.

Ilinsky and v. Knorre¹ reported in 1885 that upon addition of excess cobalt(II) to a neutral aqueous solution of the sodium salt of 1-nitroso-2-naphthol (designated in this paper as HR) a brown-red precipitate is formed. By addition of acid to the mixture and heating, the precipitate is transformed to a purple-red compound. The purple complex is also obtained when the precipitation is carried out in acid medium. The percentage of cobalt in the complexes was determined and the formulas CoR_2 and CoR_3 for the brown-red and purple-red complexes were suggested.

During this century HR has been recommended by a number of investigators for the determination of cobalt. The precipitate has been reported to be of variable composition, and for this reason is ignited to and weighed as Co_3O_4 or the oxide is reduced with hydrogen to the metal.^{2,3}

Mayer and Feigl⁴ suggest that divalent cobalt is partly oxidized by the reagent to the trivalent state and claim that the precipitate formed by addition of HR to an acid solution of divalent cobalt is not a pure compound but contains both divalent and trivalent cobalt. In order to obtain all cobalt in the trivalent form they first convert cobalt(II) into cobaltic hydroxide by addition of hydrogen peroxide and sodium hydroxide. The hydroxide is dissolved by heating in a fairly concentrated solution of acetic acid to yield a complex trivalent cobalt acetate. After dilution the cobalt(III) is

precipitated with the reagent and the precipitate weighed as $\text{CoR}_3\cdot 2\text{H}_2\text{O}$. It is not realized by these authors that on heating of a cobalt(III) solution in aqueous acetic acid reduction to cobalt(II) occurs.

Kolthoff and Langer⁵ titrated divalent cobalt in acetate buffer amperometrically with HR. The ratio of cobalt to HR in the purple-red precipitate was found to be 1:4 and they suggested the formula $\text{CoR}_2\cdot 2\text{HR}$.

In a discussion of these results Feigl⁶ suggested that HR reacts with cobalt(II) salts to form an inner complex containing trivalent cobalt. He suggests that the precipitate is composed of the trivalent cobalt complex with one molecule of coordinated reagent. No experimental evidence however was presented and no simple reaction mechanism would account for this suggestion.

From the above review it is evident that the composition of the red cobalt complex and its mode of formation are not yet clear. In the present paper experiments are described which establish the composition of the red precipitate and the reactions leading to its formation.

It was observed that some of the metal complexes with HR, which are precipitated from aqueous medium, are soluble in benzene and acetonitrile (designated in this paper as AN). In AN as solvent or in mixtures of AN with benzene well-de-

(1) M. Ilinski and G. von Knorre, *Ber.*, **18**, 699 (1885).

(2) P. Slawik, *Chem. Z.*, **38**, 514 (1914); *C. A.*, **8**, 2541 (1914).

(3) H. Willard and D. Hall, *THIS JOURNAL*, **44**, 2219 (1922).

(4) C. Mayer and F. Feigl, *Z. Anal. Chem.*, **90**, 15 (1932).

(5) I. M. Kolthoff and A. Langer, *THIS JOURNAL*, **62**, 3172 (1940).

(6) F. Feigl, "Chemistry of Specific, Selective and Sensitive Reactions," Academic Press, New York, N. Y., 1949, pp. 252-262; *Anal. Chem.*, **21**, 1298 (1949).