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Title
I. THE ACTIVITY COEFFICIENT OF PLUTONIUM (IV) SALTS IN ACIDIC AQUEOUS SOLUTIONS.
II. THE HYDROSLYTIC BEHAVIOR OF ZIRCONIUM IN PERCHLORIC ACID SOLUTIONS

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I. The Activity Coefficient of Plutonium(IV) Salts in Acidic Aqueous Solutions.

II. The Hydrolytic Behavior of Zirconium in Perchloric Acid Solutions

by

William Harry Reas
B.S. (University of California) 1943

DISSERTATION

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1948.

Approved:

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Summary

Part I. The Activity Coefficient of Plutonium(IV) Salts in Acidic Aqueous Solutions.

The activity coefficient of Pu(ClO₄)₄ was measured in perchloric acid solutions. The procedure used was to measure the extraction of the neutral plutonium(IV)-TTA chelate into benzene-TTA solutions at different perchloric acid concentrations. Equations are presented which show the relation of the extraction coefficients, obtained in the above manner, to the activity coefficient of plutonium(IV) perchlorate.

The activity coefficient of Pu(ClO₄)₄ is similar to that of a strong acid, e.g., perchloric acid, in that its value increases rapidly when the perchloric acid concentration becomes greater than 2M.

The distribution coefficient of TTA between benzene and aqueous perchloric acid solutions was found first to decrease slightly and then to increase two fold as the perchloric acid was varied from 0.01 to 6M.

The activity coefficient of the uranium-TTA chelate in benzene was calculated from the results of solubility measurements. The values of the activity coefficient of U(IV) are within experimental error, identical with the values of the activity coefficient of TTA itself.
Summary

Part II. The hydrolytic Behavior of Zirconium in Perchloric Acid Solutions.

The polymerization of zirconium perchlorate was determined in aqueous perchloric acid solution. The procedure consisted of partially extracting the zirconium from an acidic aqueous phase into a benzene-TTA phase as the neutral zirconium-TTA chelate.

Several equations are presented which are used in the interpretation of the data.

It is found that zirconium polymers begin to form at relatively low zirconium concentrations, i.e., ca. $10^{-4}$ M zirconium in 1 M perchloric acid and ca. $10^{-3}$ M zirconium in 2 M perchloric acid.

The hydrogen ion dependence of the extraction coefficient of the monomer was found to be nearly four. This indicates that the principle monomeric species in solutions of 1 to 2 M perchloric acid is $Zr^{+4}$.

Figures representing the experimental data, which can be interpreted in terms of the average number of zirconium atoms per polymer at various zirconium perchlorate concentrations, are shown.

It is possible to deduce from the data that a zirconium dimer is formed. Since polymers containing large numbers of zirconium atoms are also shown to exist, it is probable that all the intermediate polymers are formed.
It is concluded that the composition of the higher polymers approach that of the neutral hydroxide, i.e., $\text{(Zr(OH)}_4)_x$. 
Part I. The Activity Coefficient of Plutonium (IV).

Introduction

Any rigorous treatment of thermodynamic quantities requires a knowledge of the activity coefficients (or the equivalent) of the species involved. In the study of equilibria, potentials, etc., involving plutonium in aqueous solution it is of great importance to have a measure of these quantities. The following dissertation outlines a method for making such measurements and gives the initial results obtained with plutonium (IV). The procedure has many attractive features and should find extensive use in determining activity coefficients of many substances other than plutonium.

Before discussing the present method of measuring activity coefficients it seems worthwhile to digress for a moment to review the possible procedures that might be used.

Activity coefficients may be measured over a wide variety of conditions, but to be useful they must correspond to conditions which are of interest in other work. In plutonium chemistry this usually means solutions of moderate acidity and relatively low plutonium concentration. For example, it is desirable to know the activity coefficient of $10^{-3}\text{ M }\text{Pu(ClO}_4\text{)}_4$ in $1.00 \text{ M HClO}_4$. This type of activity coefficient, where the salt being measured is at low concentration in a moderately concentrated acid solution,
differs from the type commonly measured and also limits the possible experimental methods.

**Solubility.** One of the most simple and direct methods of measurement of activity coefficients is by the study of the solubility of a relatively insoluble salt as a function of the composition of the medium. This method, which has been extensively used in the past, yields directly the activity coefficient of the insoluble salt in the most simple case. If the net reaction corresponds to

\[ AB(\text{solid}) = A^+ + B^- , \]

we obtain from the solubility the relative activity coefficients of the salt \( AB \) dissolved in the solution. Thus the solubility product \( K \) may be defined as

\[ K = (A^+)(B^-) \gamma_A \gamma_B = (A^+)(B^-) \gamma^2_{AB} \]

where parentheses indicate concentrations and \( \gamma \) the activity coefficient of the indicated species\(^{(1)} \). Relative activity coefficients are obtained by comparing two solubility determinations for different solutions.

In case the anion is the ion of a weak acid the reaction becomes

\[ H^+ + AB(\text{solid}) = A^+ + HB \]

If the solubility measurements are being made in the presence of a strong acid such as perchloric acid and the activity coefficients of perchloric acid and of HB are known for the solution in question, one may calculate the activity coefficient of the salt $\text{AClO}_4$ from the solubility as is evident from the expression for the solubility product:

$$K = \frac{(A^+)(HB)\gamma_{A^+}\gamma_{HB}}{(H^+)\gamma_{H^+}} = \frac{(A^+)(HB)\gamma_{\text{AClO}_4}^2\gamma_{HB}}{(H^+)\gamma_{\text{HClO}_4}^2}$$

This provides a possible means of obtaining activity coefficients of salts such as perchlorates even though they may be very soluble. However, if the cation is at all complexed by the anion of the weak acid, the measurements will not yield correct results unless this is corrected for and in the case of highly charged ions where there is a strong tendency toward complex ion formation this is a very serious limitation.

It seems probable that relatively insoluble compounds of Pu(III) and Pu(VI) could be found that would fulfill the above criterion, i.e., not be complexed by the anion of the insoluble compound under the conditions of the experiments. On the other hand it does not seem likely that such a compound could be found for Pu(IV) or at least one that would be at all practical for such measurements. For example plutonium (IV) phenylarsenate which has a low solubility was tried but it was found that the plutonium in solution was complexed by phenylarsenate ion even at very low phenylarsenic acid concentrations.
**EMF Measurements** - A second useful method of determining activity coefficients is by cell measurements. In the case of plutonium such measurements could be readily applied to the Pu(III)-Pu(IV) couple and the Pu(V)-Pu(VI) couple. If both Pu(III) and Pu(IV) are in solution, one obtains the relative activity coefficients of the salts of these two ions and the anion present in solution. By having the activity of one plutonium species maintained at a known value by saturating the solution with an insoluble salt of that species it is possible in principle to obtain the activity coefficient of some salt of the other plutonium species. No such measurements have been carried out but the activity coefficients of Pu(III) salts might be measured using phenylarsonic acid to maintain the activity of the insoluble plutonium(IV) phenylarsonate at a known value. In dilute mineral acid solutions, such as 1 M HClO₄, plutonium(III) is probably not complexed by phenylarsonate ion, although this point would have to be checked. The net reaction, using a hydrogen electrode for the other half cell, would be:

$$\text{Pu}^{3+} + 2\text{H}_2\text{AsO}_3\text{C}_6\text{H}_5 = \text{Pu(AsO}_3\text{C}_6\text{H}_5)\text{₂ (solid)} + 1/2 \text{H}_2 + 3\text{H}^+.$$ 

To obtain activity coefficients of a plutonium(III) salt it would be necessary to know the activity coefficients of phenylarsonic acid and the mineral acid. If the solution were kept saturated with phenylarsonic acid, which is only moderately soluble, only the activity coefficient of the mineral acid need be known.
Resin Exchange Method - G. F. Boyd and coworkers (2)


have introduced an ingenious method for measuring the activity coefficients of salts which makes use of cation (or anion) exchange resins. In a cation exchange resin there are positions which can be occupied by positive ions. The competition of two different positive ions such as Na⁺ and PuO₂²⁺ for these positions may be used to measure relative activity coefficients of the salts of the two ions. The results are interpreted in terms of an equilibrium between the ions in aqueous solution and the ions in a solid solution in the resin, the activity coefficients being assumed to be unity in the solid phase. The method seems applicable to PuO₂²⁺ but so far cannot be used readily for Pu⁴⁺ and Pu⁺³ as it is found that the behavior of +3 and +4 ions is not reversible at least in the resins now employed (3).


There are many other methods for measuring activity coefficients, however the methods cited above together with the method proposed below appear to offer the most promise in determining the activity coefficients of plutonium in its various oxidation states.

Distribution Method - The method which appears to us to offer the most promise for determining the activity coef-
ficients of Pu⁴⁺ directly and those of Pu³⁺, PuO₂⁺ and PuO₂⁺⁺ indirectly is that of distribution measurements between an organic and an aqueous phase. This is the method which has been tried in the following work.

The method is an old one and one which at first sight does not appear too promising. The chief difficulty lies in finding some reagent which will make plutonium(IV) partially extractable into a non-aqueous phase yet not complex it in the aqueous phase. An initial search was made for such a reagent in 1943 but none was found that offered any promise. Not long afterwards a promising possibility was uncovered when Calvin (4) demonstrated the ability of trifluoracetylacetone to chelate Pu⁴⁺ and render it extractable into benzene and other organic phases. However on testing this reagent it was found that it partially complexed Pu⁴⁺ in the aqueous phase when used at concentrations sufficiently high to give partial extraction of the Pu(IV) into benzene.

Soon several derivatives of trifluoracetylacetone were prepared by Calvin and Reid (5) and one of these was shown by Crandall and Thomas (6) to have the requisite properties for

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(4) M. Calvin, CN-2486, p. 2, December 1, 1944.

(5) J. C. Reid and M. Calvin, AECO-1405, August 1947.


---

the determination of activity coefficients of Pu⁴⁺, i.e., it
did not complex Pu\(^{+4}\) in an aqueous solution under conditions where it would give partial extraction of Pu\(^{+4}\) into the organic phase.

The distribution method is particularly suited to the study of radioactive substances in that trace amounts of material may be used just as readily as macro amounts. This follows from the fact that the distribution ratio is independent of the concentration of Pu\(^{+4}\) as long as there is no polymerization in either phase.
Theory of Application of Distribution Method

In the practical application of the distribution method to the measurement of activity coefficients it is necessary to make several simplifying assumptions and these must be justified.

The equation for the equilibrium distribution of plutonium(IV) between an aqueous phase and a benzene phase may be written:

\[ \text{Pu}^{+4}(aq) + 4\text{H}^+(b) = \text{PuK}_4(b) + 4\text{H}^+(aq). \]

The symbols (aq) and (b) designate the aqueous and benzene phases respectively, while \( \text{H}^+ \) is used to designate the ketone. The above equation may or may not represent the actual net reaction taking place. If the Pu(IV) is partially complexed by the ketone in the aqueous phase, the above equation is not correct. However, as has been previously mentioned, an extracting agent should be chosen such that plutonium complexing in the aqueous phase is negligible, and we shall assume for further purposes of discussion that a ketone has been selected which does not complex the Pu(IV) appreciably in the aqueous phase.

If the Pu(IV) is complexed in the aqueous phase by other negative ions, again our equation does not represent the net reaction. However, thermodynamically it is possible to go ahead and use the equation and include any effects of this sort in the variation of the activity coefficient of the Pu(IV) salt. (Of course this is not a necessary procedure and in many cases of strong complexing, one would
want to treat it separately). Then we may write the equilibrium constant:

$$K = \frac{(PuK_4)_b (H^+)^4_{aq} \gamma_{PuK_4} \gamma_{H^+}^4}{(Pu^{+4})_{aq} (HK)^4_b \gamma_{Pu^{+4}} \gamma_{HK}^4}$$

(1)

Parenthesis indicate concentrations and \( \gamma \) indicates the activity coefficient of the designated species. If the concentration of HK in the benzene layer is maintained at a low value, Henry's Law should apply to this solution and the activity of HK and PuK\(_4\) in the benzene should be proportional to their respective concentrations. The activity coefficients of these species should equal unity if the usual standard state is used. Making use of this fact and multiplying the numerator and denominator of the equation by \( \gamma_A \) - where \( A^- \) is an anion present in the aqueous phase we obtain

$$K = \frac{(PuK_4)(H^+)^4_{aq} \gamma_{H^+}^4 \gamma_A^4}{(Pu^{+4})(HK)^4 \gamma_{Pu^{+4}} \gamma_A^4}$$

(2)

or:

$$K = \frac{(PuK_4)(H^+)^4_{aq} \gamma_{H^+}^4 \gamma_{HA}^8}{(Pu^{+4})(HK)^4 \gamma_{Pu^{+4}}^4 \gamma_{HA}^5}$$

(3)

If the activity coefficient of the acid, \( HA \), is known for the particular solution being investigated, only the value of \( K \) and \( \gamma_{PuK_4} \) are not directly measurable. From measurements at two or more sets of conditions one may immediately calculate relative values of \( \gamma_{PuK_4} \) for those conditions.
In practice it is convenient to use very low concentrations of plutonium and ketone in the aqueous phase in order that their presence should not affect the activity of the acid HA. Since the ketones used in this work are much more soluble in benzene than in water their concentration in the aqueous phase could always be kept small. Then, for the common acids, data on activity coefficients in the literature for pure HA solutions may be used if there are no other substances present to an appreciable extent in the aqueous phase. In a few cases data are available on the activity coefficients of mixtures of different acids and mixtures of acids with salts, such as HCl and NaCl, which are applicable to activity coefficient determinations of plutonium in such systems.

Standard State - Activity coefficients are measured relative to a standard state and in order to obtain a value for an activity coefficient this standard state must be defined. The choice of a standard state is arbitrary but, in general, in aqueous solutions it is chosen to be such that the activity coefficient approaches unity as the concentrations of all substances present in solution approach infinite dilution. In the case of Pu\(^{+4}\) such a standard state is unsuitable because it is not possible to have solutions of Pu\(^{+4}\) which are near infinite dilution with respect to hydrogen ion. This arises from the fact that Pu\(^{+4}\) undergoes hydrolysis at a relatively high acidity. Since it does not appear feasible to extrapolate activity curves of Pu(IV) salts to zero ionic
strength, it seems wiser to redefine the standard state so that it can be reached experimentally. This argument of course applies to +4 ions in general. Therefore the standard state for plutonium(IV) will be chosen such that the ratio of the activity of Pu(ClO$_4$)$_4$ to its concentration, in a solution of unit concentration of perchloric acid, approaches unity as the plutonium concentration approaches zero. Thus the activity coefficient of Pu(ClO$_4$)$_4$ is unity in a solution of perchloric acid of unit concentration and at very low plutonium(IV) concentration. Perchloric acid has been chosen because it is believed that complexing of Pu(IV) by ClO$_4^-$ is less than with any other common anion.

Once the activity coefficient of Pu(ClO$_4$)$_4$ has been fixed by the above definition of the standard state, the activity coefficients of all other plutonium(IV) salts are determinable in any solution. Thus, if the activity coefficient of Pu(ClO$_4$)$_4$ has been determined for a particular solution, one can calculate the activity coefficient of PuCl$_4$ by the following equation:

$$\gamma_{\text{PuCl}_4} = \frac{\gamma_{\text{Pu(ClO}_4)_4}^{8/5} \gamma_{\text{HClO}_4}^{3/5}}{\gamma_{\text{HCl}}}$$

(4)

where all activity coefficients refer to the particular solution being investigated. Thus it is necessary to know the activity coefficients of both HCl and HClO$_4$ in the particular
solution which will in general contain a mixture of electrolytes. In only a few cases are such data available.

The fixing of the standard state of Pu(ClO$_4$)$_4$ automatically fixes the activity coefficients of all other plutonium(IV) salts and thus constitutes the standard state for all Pu(IV) salts. In many cases it will not be easy to obtain activity coefficients in terms of this standard state because of the lack of data necessary to convert from perchloric acid solutions to other solutions. In such cases it will probably be convenient to define a new standard state similar to the one in perchloric acid. For example if activity coefficients of Pu(IV) were measured in nitric acid solutions a standard state could be chosen at unit concentration of nitric acid and at vanishingly small plutonium(IV) concentration. Since only relative values of activity coefficients are of interest in thermodynamics, such a procedure will not cause trouble as long as only data based on the same standard state are used together. However, it should always be born in mind that the single standard state in perchloric acid in theory suffices to fix the activity coefficients of all plutonium salts.

**Complexing and Hydrolysis - Distribution measurements** are well adapted to the measurement of complexing of ions. The most convenient procedure as applied to plutonium would be to have Pu$^{+4}$ dissolved in perchloric acid which is believed not to complex Pu$^{+4}$, and to determine the effect on the distribution coefficient of adding various amounts of some reagent which complexes plutonium. From the data it is possible by
elementary methods to calculate the average number of groups attached to a Pu$^{+4}$ in each complex. In carrying out the experiments care must be taken not to change the medium sufficiently to alter the activity coefficients of the various species. Thus one would keep the ionic strength constant, etc. The above method, using fluorinated diketones, promises to be a very powerful tool in the study of the complexing of ions.

Hydrolysis is of course a special case of complexing, so would be treated as above. The distribution method should be readily applicable in this case to most +4 ions, but is difficult to apply in the case of plutonium because of oxidation and reduction interferences. This point is discussed at length in the experimental results of this paper.

**Activity Coefficients of Pu(III), Pu(V) and Pu(VI)**

The distribution procedure outlined above furnishes the activity coefficient of only the +4 state of plutonium. The simplest method of obtaining that of the +3 state appears to be by cell measurements of the Pu$^{+3}$ - Pu$^{+4}$ couple. This couple is readily reversible. For measurements in perchloric acid cells of the following type can be used:

$$\text{Au: Pu}^{+3}, \text{ Pu}^{+4}, \text{HClO}_4; \text{HClO}_4, \text{H}_2; \text{Pt}$$

By keeping the plutonium concentration low the liquid junction potential becomes negligible. The equation for the potential is:

$$E = E^0 - \frac{RT}{2F} \ln \left( \frac{(\text{Pu}^{+3})(\text{H}^+)^4 \gamma^{4+}\text{Pu}^{+3}(\text{ClO}_4)^2 \gamma^{2+} \text{HClO}_4}{(\text{Pu}^{+4}) \gamma^5 \text{Pu}^{+4}(\text{ClO}_4)_4 \gamma^{5+} \text{H}_2} \right)$$

(5)
Knowing $\gamma_{\text{HClO}_4}$ and $\gamma_{\text{Pu(ClO}_4)_4}$ (from the distribution measurements), all the other quantities are measurable except $\gamma_{\text{Pu(ClO}_4)_3}$ which can then be calculated from the data.

Activity coefficients of the +5 and +6 state are then determinable by equilibrium measurements involving plutonium in its various oxidation states. For example the +5 activity coefficient of Pu(VI) in perchloric acid may be obtained from the equilibrium

$$2\text{H}_2\text{O} + 3\text{Pu}^{+4} = 2\text{Pu}^{+3} + \text{PuO}_2^{++} + 4\text{H}^+$$

$$K = \frac{(\text{Pu}^{+3})^2(\text{PuO}_2^{++})(\text{H}^+)^4}{(\text{Pu}^{+4})^5} \frac{\gamma_{\text{Pu(ClO}_4)_3} \gamma_{\text{PuO}_2\text{(ClO}_4)_2} \gamma_{\text{HClO}_4}}{\gamma_{\text{Pu(ClO}_4)_4}}$$

The activity coefficient of Pu(V) may be determined from the equilibrium involving all four oxidation states:

$$\text{Pu}^{+4} + \text{PuO}_2^+ = \text{PuO}_2^{++} + \text{Pu}^{+3}.$$
Measurement of Activity Coefficient of Pu(ClO₄)₄ in Perchloric Acid Solutions.

The first activity coefficient measurements of Pu(IV), using the distribution method, have been made with perchloric acid solutions at 25°C. The ketone which was used is thenoyltrifluoroacetone which will be abbreviated to TTA*. The formula is:

\[
\begin{align*}
{\text{CH}_3}_2\text{C} - \text{CH} = \text{C} - \text{C} &= \text{H}^{\text{H}} \quad \text{or} \quad \text{CH}_3 - \text{C} = \text{CH} - \text{C} - \text{H}^{\text{H}} \\
\end{align*}
\]

TTA is a pale yellow solid at room temperature which melts at 42°C. It is slightly soluble in water (0.039 M at 25°C), but much more so in benzene (ca. 5 moles per liter), which is the organic phase used in the measurements. Other organic solvents undoubtedly be used in place of benzene as the chlorides are readily extracted by many organic liquids. The ketone is distributed heavily in favor of the benzene phase, the distribution ratio being at 25°C for dilute hydrochloric acid and low ketone concentration⁷:


\[
\frac{(\text{TTA})(\text{org})}{(\text{TTA})(\text{aq})} = 40.0
\]

(7)

In the aqueous phase TTA exists as a hydrate⁷.

I am indebted to Dr. J. C. Reid for the preparation of the TTA.
The TTA forms chelate compounds with metal ions by coordinating two oxygens to the metal ion in the following manner:

![Chemical structure](image)

Presumably there is resonance of the carbon-oxygen double bond between the two carbonyl groups, with simultaneous shifting of the carbon-carbon double bond. The plutonium chelate species which is extracted into benzene consists of a Pu$^{4+}$ with four TTA ions coordinated to it to form a neutral molecule.

The extent of extraction of the Pu(IV) chelate into benzene from perchloric acid solutions was measured in the following manner. A perchloric acid solution containing ca. $10^{-6} \text{ M Pu(IV)}$ was stirred mechanically with an equal volume of benzene containing TTA. The distribution of plutonium(IV) was measured by aliquoting both phases, mounting these aliquots on platinum plates, and counting them in an alpha counter. These measurements were continued until equilibrium was established between the two phases.

Establishment of Non-complexing of Pu(IV) by TTA in Aqueous Phase - In order to show that the Pu(IV) in the aqueous phase was uncomplexed by TTA, experiments were performed at the same perchloric acid concentration but at different TTA concentrations. In such a series of experiments the ionic strength remained constant and consequently the activity
coefficients of ions remained nearly constant so it was possible to measure the dependence of the extraction on the ketone concentration. Thus, if the reaction

$$\text{PuK}_n^{+4-n}(aq) + (4-n)\text{HK}(b) = \text{PuK}_4(b) + (4-n)\text{H}^+(aq) \quad n = 0,1,2,3,4.$$  

represents what occurs in the two phase system, we may write

$$E = \frac{(\text{PuK}_4)(b)}{\sum_{n=0}^{4} \frac{(\text{PuK}_n^{+4-n})}{(\text{H}^+)(b)}}$$  

The extraction coefficient, $E$, as defined above, is the concentration of Pu(IV) in the benzene phase divided by the total Pu(IV) concentration in the aqueous phase. The value of $E$ is measured experimentally in the extraction experiments. As a matter of convenience the following equations were used in interpreting the results of these diketone dependence experiments. The equilibrium constants for the above reactions are

$$K_n = \frac{(\text{PuK}_4)(b)(\text{H}^+)^{+4-n}}{(\text{PuK}_n^{+4-n})(\text{HK})(b)} \quad n = 0,1,2,3,4.$$  

The parentheses here represent concentrations which may be used in place of activities since the activity coefficients remain nearly constant when only the TTA concentration is varied in a series of experiments. (In the experiments at highest TTA concentrations it was necessary to make a correction for the change of the activity coefficient of TTA in the benzene phase). Therefore
\[(\text{PuK}^4_{n}) = \frac{(\text{PuK}_{4})_{(b)} (\text{H}^+)^{4-n}}{K_n (\text{HK})^{6-n}} \tag{10}\]

Substituting the above equations into the equation for the extraction coefficient, equation 8, and performing the indicated operations one finds

\[\frac{d \log \frac{E}{d}}{d \log (\text{HK})} \bigg|_{\text{H}^+, \text{ClO}_4^{-}} = 4 - \frac{\sum n(\text{PuK}_{n}^{+4-n})}{\sum (\text{PuK}_{n}^{+4-n})} \tag{11}\]

or

\[\frac{d \log \frac{E}{d}}{d \log (\text{HK})} \bigg|_{\text{H}^+, \text{ClO}_4^{-}} = 4 - f_1 - 2f_2 - 3f_3 - 4f_4 \tag{12}\]

where \(f_1, f_2, \ldots\) are the fractions of the Pu(IV) ions existing in solution as \(\text{PuK}^3\), \(\text{PuK}^2_2\), \(\text{PuK}^3\), and \(\text{PuK}^4\). Therefore, if the logarithm of the extraction coefficient is plotted against the logarithm of the diketone concentration, the slope of the curve will represent the diketone dependence and therefore the average number of diketone ions attached to each Pu(IV) ion in the aqueous phase. If there is no appreciable complexing of Pu(IV) by WPA in the aqueous phase the slope should be +4.

While it was assumed in the above equations that there was no complexing of Pu(IV) in the aqueous phase by \(\text{ClO}_4^-\) or \(\text{OH}^-\), the same type of equation for the dependence of the extraction coefficient would have been obtained if these effects
were not neglected. Thus we may generalize the extraction reaction to:

\[ \text{PuK}_n(\text{OH})_m(\text{ClO}_4)_p + 4 - m - n \cdot p + (4 - n)\text{HK} = \text{PuK}_4^+ p\text{ClO}_4^- + m\text{H}_2\text{O} + (4 - m - n)\text{H}^+ \]

\[ E = \frac{\text{(PuK}_4^+)}{\sum_\text{m} \sum_\text{n} \sum_\text{p} \text{(PuK}_n(\text{OH})_m(\text{ClO}_4)_p)} \]  

(The charge on the plutonium ion in aqueous solution has been omitted from the last equation to simplify the writing). The following equilibrium constants may be defined:

\[ K_{m,n,p} = \frac{\text{(PuK}_4^+)(\text{ClO}_4^-)^p(\text{H}_2\text{O})^m(\text{H}^+)^{4-m-n}}{\text{(PuK}_n(\text{OH})_m(\text{ClO}_4)_p)^{4-n}} \]  

Activity coefficients have been omitted as the equation is to be applied to solutions of the identical composition except for the ketone concentration. By the same methods used in the above derivation one obtains

\[ \frac{d \log E}{d \log (\text{HK})}_{\text{H}^+, \text{ClO}_4^-} = 4 - \frac{\sum_\text{m} \sum_\text{n} \sum_\text{p} n(\text{PuK}_n(\text{OH})_m(\text{ClO}_4)_p)}{\sum_\text{m} \sum_\text{n} \sum_\text{p} (\text{PuK}_n(\text{OH})_m(\text{ClO}_4)_p)} \]  

\[ = 4 - \sum_\text{p} \sum_\text{m} \sum_\text{n} n f_{m,n,p} \]

where \( f_{m,n,p} \) is the fraction of the Pu(IV) in the aqueous phase which is complexed by \( n \) diketone ions, \( m \) hydroxide ions and \( p \) perchlorate ions. Again, if there is no complexing by diketone in the aqueous phase, the plot of the logarithm of the extraction coefficient versus the logarithm of the diketone concentration at constant perchloric acid con-
centration should be a straight line with a slope of +4.

The extraction of Pu(IV) chelate into benzene as a function of the TTA concentration was measured in various perchloric acid solutions. The perchloric acid concentration was varied from 0.186M to 6.21M. In all cases it was found that in a given perchloric acid concentration the diketone dependence was fourth power within experimental error. The results of these experiments will be found in Figure 1.

Inspection of Figure 1 reveals that even though the experimental points are well represented by lines of slope four the data could also be fitted by lines of slope somewhat less than four, e.g., 3.9. Since these measurements were made, Zebroski (7a) has determined the value of the complexing constant

\[ K_c = \frac{(\text{Pu}^{+3})(\text{H}^+)}{(\text{Pu}^{+4})(\text{HK})_{\text{aq}}} \]

for the reaction

\[ \text{Pu}^{+4} + \text{HK} = \text{Pu}^{+3} + \text{H}^+ \]

He found a value of ca. 75 for 1M hydrochloric acid.

McVey (7b) has estimated from cell and distribution
The Extraction of the Pu(IV)-chelate in Various Perchloric Acid Solutions. These acidities, from left to right, are: 0.1863, 0.373, 0.473, 0.745, 0.946, 1.491, 1.363, 2.235, 4.345, and 6.215.
measurements the fraction of plutonium(IV) which exists in the form of a chloride complex in 1 M hydrochloric acid. If the assumption is made that the perchlorate ion does not complex plutonium(IV), it is then possible to estimate the equilibrium for the formation of PuK$^+$ from Pu$^{+4}$ in perchloric acid solution by correcting Zobroski's value for the fraction of plutonium which is present as PuCl$^{+3}$. The result of this calculation indicates that approximately seven percent of the plutonium in solution exists as the PuK$^+$ species in 1 M perchloric acid under conditions where the extraction coefficient is unity. The activity coefficients of Pu(ClO$_4$)$_4$ were calculated in such a fashion that the correction due to complexing nearly cancels out. The values of the extraction coefficient used in these calculations were obtained from Figure 1 by reading the TTA concentration necessary to give an extraction coefficient of unity, and then calculating the extraction coefficient at unit concentration of TTA using a fourth power dependence. If all coefficient changes are assumed to be small over the range of acidity covered in the experiments, the fraction plutonium(IV) complexed by TTA in the aqueous phase would remain constant at an extraction coefficient of unity and the correction for complexing would vanish since only relative values of the extraction coefficient enter into the determination of the activity coefficient of Pu(ClO$_4$)$_4$. If activity coefficient changes are allowed for,
it is predicted that the fraction complexed remains nearly
contant from 0.2 to 1M perchloric acid and decreases, if
anything, above 1M perchloric acid. Therefore the correction
for complexing is believed to be small under all conditions,
especially since the extraction coefficient enters to only
the one-fifth power in the determination of the mean activity
coefficient of Pu(ClO$_4$)$_4$. 

\[ \frac{\gamma_{Pu^{+4}}^{3/4}}{\gamma_{PuK^{+3}}} \]

This quantity should remain nearly constant from 0.2 to 1.0M
perchloric acid, since activity coefficients are generally
constant in this region (as shown by the activity coefficients
of Pu(ClO$_4$)$_4$ and HClO$_4$). Above 1M perchloric acid this ratio
should be intermediate between:

\[ \frac{\gamma_{Pu^{+4}}^{3/4}}{\gamma_{H^+}^3} \quad \text{and} \quad \frac{3/4}{\gamma_{Pu^{+4}}^{3/4}} \]

This first quantity is known to decrease as the perchloric
acid concentration increases (see later) while the second
quantity is of course constant. Therefore $\gamma_{Pu^{+4}}^{3/4} / \gamma_{PuK^{+3}}$ 
would be expected to decrease slowly and the correction for
complexing would decrease at acidities above 1M.
In the experiments at high TTA concentrations it was necessary to apply a correction to the measured extraction coefficients because of variations in the activity coefficients of TTA and the plutonium chelate in the benzene phase. In deriving equations 12 and 15 it was assumed that the activity coefficients of TTA and PuK$_4$ remained constant in a series of experiments at constant acidity. Actually, above 0.02 M TTA in benzene, the activity coefficient of TTA decreases below unity (?). In such experiments the measured extraction coefficient was corrected to the value it would have had if the $\gamma_{\text{HK}}$ had been unity, assuming a fourth power ketone dependence.

The variation of the activity coefficient of PuK$_4$ in benzene with increasing TTA concentration is unknown. However, as discussed in a later section, the variation of the activity coefficient of UK$_4$ with TTA concentration in benzene has been determined. It is believed that the activity coefficient of PuK$_4$ would vary in a similar manner and this assumption has been applied to the data of Figure 1.

*The concentrations for all species in this paper are either expressed in moles per liter of solution (designated by M) or in moles per kilogram of water (designated by m).*
The plotted extraction coefficients are those that would have been measured if the activity coefficient of PuK₄ had been unity. Both this correction and the one for the TTA activity were small except at the highest TTA concentrations.

In equation 14 the general case of complexing by ClO₄⁻ and hydroxide was assumed. It would in principle be possible to determine the degree of complexing of Pu(IV) by those ions by measuring the extraction coefficient as only the ClO₄⁻ or only the OH⁻ concentration was varied. Since the activity coefficients of the various ions are unknown it would be necessary to work under conditions where they remained nearly constant, i.e., at constant ionic strength. Thus, to determine the complexing by ClO₄⁻, measurements could be made of the extraction coefficient in mixtures of HClO₄ and HClO₄ at constant ClO₄⁻ concentration. It is planned to make such measurements in the near future. Complexing by ClO₄⁻ presents a more difficult problem. No anion is known which would be expected to have significantly less tendency to complex Pu⁴⁺ than ClO₄⁻. Thus in trying to maintain constant ionic strength while varying the ClO₄⁻ concentration it is necessary to add an anion which probably has a greater tendency than ClO₄⁻ to complex plutonium(IV).

Activity Coefficients of Pu(ClO₄)₄ in Perchloric Acid Solutions - In the absence of information on the complexing of Pu(IV) by ClO₄⁻ and OH⁻ it is convenient to adopt the
common expedient of lumping all such effects in the activity coefficient. The net reaction for extraction is thus written as:

$$\text{Pu}^{+4}(aq) + 4\text{H}^+(b) = \text{PuK}_4(b) + 4\text{H}^+(aq)$$

Here the symbol $\text{Pu}^{+4}$ represents the total plutonium(IV) in the aqueous phase even though part of it may be complexed by $\text{ClO}_4^-$ or be hydrolyzed.

The equilibrium constant for this reaction is:

$$K = \frac{(\text{PuK}_4)(\text{H}^+)^4}{(\text{Pu}^{+4})(\text{HK})^4} = \frac{E (\text{H}^+)^4 \gamma_{\text{Pu(ClO}_4)}^4}{(\text{HK})^4 \gamma_{\text{HK}}^4 \gamma_{\text{Pu(ClO}_4)}^4}$$

and the lowering of the activity of $\text{Pu}^{+4}$ due to any perchlorate complexing or hydrolysis will appear in $\gamma_{\text{Pu(ClO}_4)}$. This is the basis upon which the activity coefficients of $\text{Pu(IV)}$ perchlorate have been calculated.

In this paper, the activity coefficient of $\text{Pu(ClO}_4)_4$ at unit concentration $\text{HClO}_4$ was taken as unity in accordance with the chosen standard state. Thus we may write for 1 M $\text{HClO}_4$:

$$\gamma_{\text{Pu(ClO}_4)_4} = 1 = \frac{8}{E \gamma_{\text{Pu(ClO}_4)_4} \gamma_{\text{PuK}_4}}$$

This equation serves to define the thermodynamic equilibrium constant $K$. Then in any perchloric acid solution the activity coefficient of $\text{Pu(ClO}_4)_4$ is given by the expression:

$$\gamma_{\text{Pu(ClO}_4)_4} = \left[ \frac{E (\text{H}^+)^4 \gamma_{\text{Pu(ClO}_4)}^4}{K (\text{HK})^4 \gamma_{\text{HK}}^4} \right]^{1/5}$$
In equation 18 the concentrations of hydrogen ion and TTA(HK) are known, and the value of K is determined experimentally. Therefore to calculate activity coefficients of Pu(ClO₄)₄ it is necessary to know the value of K and the activity coefficients of HK, HClO₄ and PuK₄. The activity coefficient of TTA has been measured and activity coefficient data for perchloric acid were taken from a paper by R. A. Robinson and O. J. Baker (8). The activity coefficient of PuKr₄ has not been measured however, as previously mentioned, the activity coefficient of UK₄ in the presence of TTA and benzene has been determined. The assumption is made that the activity coefficient of PuK₄ is identical with that of UK₄.

The value of K, the equilibrium constant for the extraction reaction, is calculated by equation 17. It has been found that K is equal to $6.32 \times 10^6$ when all concentrations are measured in moles per liter of solution and all activity coefficients are based on the corresponding standard states.

The values of the activity coefficient of Pu(ClO₄)₄ are presented in Table 1. The first column gives the concentration of perchloric acid expressed in moles per liter of solution and the second column lists the same quantity expressed in moles per 1000 grams of water. In the third column are tabulated values which the extraction coefficient (8) R. A. Robinson and O. J. Baker, Tran. Proc. Roy. Soc., New Zealand, 76, 250, (1946).
Table 1
Activity Coefficients of Pu(ClO₄)₄ in Perchloric Acid at 25.0° C

<table>
<thead>
<tr>
<th>(HClO₄) moles/l</th>
<th>(HClO₄) moles/1000 g H₂O</th>
<th>E₀ M</th>
<th>γ⁺ M HClO₄</th>
<th>γ⁺ M HClO₄ Pu(ClO₄)₄</th>
<th>γ⁺ M Pu(ClO₄)₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1863</td>
<td>0.1324</td>
<td>1.46 x 10¹³</td>
<td>0.7856</td>
<td>0.7793</td>
<td>0.818</td>
</tr>
<tr>
<td>0.373</td>
<td>0.389</td>
<td>1.23 x 10⁹</td>
<td>0.7786</td>
<td>0.7661</td>
<td>0.856</td>
</tr>
<tr>
<td>0.473</td>
<td>0.485</td>
<td>4.66 x 10⁸</td>
<td>0.7845</td>
<td>0.7686</td>
<td>0.863</td>
</tr>
<tr>
<td>0.745</td>
<td>0.773</td>
<td>7.59 x 10⁷</td>
<td>0.8139</td>
<td>0.7913</td>
<td>0.926</td>
</tr>
<tr>
<td>0.946</td>
<td>0.991</td>
<td>2.56 x 10⁷</td>
<td>0.8570</td>
<td>0.8211</td>
<td>0.969</td>
</tr>
<tr>
<td>1.491</td>
<td>1.601</td>
<td>3.77 x 10⁶</td>
<td>1.004</td>
<td>0.9469</td>
<td>1.244</td>
</tr>
<tr>
<td>2.233</td>
<td>2.037</td>
<td>1.56 x 10⁶</td>
<td>1.162</td>
<td>1.066</td>
<td>1.548</td>
</tr>
<tr>
<td>2.236</td>
<td>2.482</td>
<td>6.43 x 10⁵</td>
<td>1.360</td>
<td>1.223</td>
<td>1.930</td>
</tr>
<tr>
<td>4.345</td>
<td>5.386</td>
<td>5.92 x 10⁴</td>
<td>4.482</td>
<td>3.664</td>
<td>13.75</td>
</tr>
<tr>
<td>6.21</td>
<td>8.52</td>
<td>5.40 x 10²</td>
<td>20.09</td>
<td>15.14</td>
<td>83.9</td>
</tr>
</tbody>
</table>
would have had if the activity of TTA and PuK_4 had been unity. These values were calculated from the data of Figure 1 assuming a fourth power dependence of the extraction coefficient on ketone concentration. All concentrations and activity coefficients used in calculating $E^0$ were based on concentrations expressed in moles per liter of solution.

Columns four and five list the activity coefficients of perchloric acid for the moles per liter basis and the moles per 1000 grams of water basis. The two quantities are related by the expression:

$$\gamma_{\pm M} \text{HClO}_4 = \frac{\gamma_{\pm M} \text{HClO}_4 M}{d_{25}} (\text{HClO}_4)_M$$

(19)

where $M$ and $m$ designate the respective concentration systems and $d_{25}$ is the density of water at 25°C relative to the density at 4°C.

In columns six and seven are given the mean activity coefficients of Pu(ClO_4)_4 on a moles per liter basis and a moles per 1000 grams water basis. The values of $\gamma_{\pm M}$ were calculated using equation 18 after substituting $E^0$:

$$\gamma_{\pm M} = \frac{E^0 (H^+)_4 \gamma_{\pm \text{HClO}_4}}{K}$$

(20)

The value of $K$ was obtained by graphical interpolation of the $E^0$ values at 1 M HClO_4 and substitution into equation 20 with $\gamma_{\pm M} = 1$.

The values of $\gamma_{\pm M}$ were calculated in a similar manner. Values of $E^0$ converted to a moles per 1000 grams of water basis with respect to the concentration of Pu^{+4} in the aqueous phase
were calculated from the expression:

$$E^0_{\text{ur}} = E^0_{\text{m}} \times \frac{(\text{Pu}^{+4})_M}{(\text{Pu}^{+4})_m} \quad (21)$$

The relation between the concentration of $\text{Pu}^{+4}$ on a moles per liter basis and a moles per 1000 grams of water basis is:

$$\frac{(\text{Pu}^{+4})_M}{(\text{Pu}^{+4})_m} = \frac{10^3 \, d \, (\text{HClO}_4)_m}{10^5 + (\text{HClO}_4)_m \, W} \quad (22)$$

where $d$ is the density of the solution at 25°C relative to water at 4°C and $W$ is the molecular weight of perchloric acid. The ratio of concentrations of plutonium in the two systems is, of course, the same as the ratio of concentrations of perchloric acid in the two systems.

The values of $E^0_{\text{m}}$ were plotted and the value at 1 m $\text{HClO}_4$ interpolated. This was substituted into equation 20 with all values expressed in the moles per 1000 grams of water system and the value of $K_m$ calculated, letting $\gamma_{\text{H}}$ 1 m $\text{HClO}_4$ equal unity. Values of $\gamma_{\text{m}}$ were then calculated for other perchloric acid concentrations using this value of $K_m$ which was found to be $5.24 \times 10^5$.

The values of $\gamma_{\text{H}}$ and $\gamma_{\text{m}}$ of $\text{Pu(ClO}_4)_4$ are plotted in Figure 2.

It is interesting to calculate the limiting slope of the activity coefficient curve obtained for $\text{Pu(ClO}_4)_4$ from the Debye - Hückel law. According to this law the activity coefficient of a salt at 25°C as the ionic strength approaches zero is

$$\log \gamma_{\pm} = -0.505 \, Z \cdot Z \quad (23)$$
Figure 2.

Activity Coefficients of Pu(ClO₄)₄ in Perchloric Acid.
Therefore as the ionic strength, \( \mu \), becomes vanishingly small the slope of the activity coefficient curve (log \( Y_\pm \) vs. \( \sqrt{\mu} \)) becomes -0.505 \( Z_- Z_- \). For a salt of the type \( \text{Pu}(\text{ClO}_4)_4 \), the limiting slope would be -2.02. However this behavior is not to be expected with \( \text{Pu}^{(IV)} \) salts since the +4 ion hydrolyzes in solutions of low acidity. For example, at low acidities the predominant ion in solution might change to \( \text{Pu}(\text{OH})^+3 \) or \( \text{Pu}(\text{OH})^+2 \) and therefore the limiting slope as predicted by the Debye - Hückel equation would no longer be valid. Since data are lacking regarding the species in solution, it is not possible to predict the shape of the curve at low acidities. An attempt to measure the hydrolysis constants will be made at a later date using the extraction procedure as outlined in this paper.

If activity coefficients are calculated for plutonium(IV) assuming that the net reaction for the extraction is

\[
\text{Pu}(\text{OH})^+3 + 4\text{H}^+ = \text{Pu}^4 + 3\text{H}^+ + \text{H}_2\text{O}
\]

an entire new set of values is obtained. The shape of the plot of log \( Y_\pm \) vs. \( \sqrt{\mu} \) is about the same as in Figure 2 except for a clockwise rotation of the curve about the standard state, i.e., 1 M HClO\(_4\).

It can be seen from Figure 2 that the activity coefficient curve obtained for plutonium is similar to that of a strong acid such as perchloric acid, since at high ionic strengths the value of log \( Y_\pm \text{Pu}(\text{ClO}_4)_4 \) increases tremendously. The large increase of the activity coefficient at high acidities is probably due to the change in the nature of the solvent. Because of the interaction of the ions with water molecules, the.
activity of water must be greatly reduced as the concentration of perchloric acid is increased, which in turn must reduce considerably the hydrating action of water on perchlorate and plutonium (IV) ions. The reduction in hydration of these ions would of course increase the activity of the plutonium perchlorate.

**Distribution Measurements at Low Acidity** - It can be seen from Table 1 or Figure 2 that there are no measurements of activity coefficients of Pu(IV) below 0.18 M HClO₄. The reason for this will be discussed below.

In the early part of this work it was found that there was an impurity in the perchloric acid TTA-benzene system. This impurity was capable of reducing Pu(IV) rapidly to Pu(III). If, for example, Pu(IV) tracer were added to a perchloric acid solution and then stirred mechanically with a solution of TTA in benzene, the extraction coefficient, E, as function of time was found to increase, reach a maximum, and then decrease. In about an hours time the extraction coefficient would fall to zero. An aliquot of the perchloric acid solution containing the plutonium tracer from such an experiment after the extraction coefficient had fallen to zero was taken and analyzed for Pu(IV) and Pu(VI) by the holding oxidant procedure.

(9) W. H. McVey, CN-1588, p.10, April 15, 1944.

It was found that all of the plutonium tracer was carried by the lanthanum fluoride precipitate which was interpreted to mean that the plutonium had been reduced to the +3 state.
The above experiment was carried out at 0.5 M perchloric acid, and at this same acid concentration it was found that if \(5 \times 10^{-4} M \ Na_2 Cr_2O_7\) were added to the perchloric acid solution, the extraction coefficient rose to a certain value and remained constant with time. Apparently the dichromate either destroyed the impurity or rapidly oxidized the Pu(III) formed by the impurity. Therefore it was possible to measure the distribution of Pu(IV) between perchloric acid and a TTA-benzene solution in the presence of a small amount of dichromate. In all the experiments reported earlier in this paper \(5 \times 10^{-4} M \ Na_2 Cr_2O_7\) was present in the perchloric acid phase to keep the plutonium tracer in the +4 oxidation state. However when the acid concentration was lower than 0.18 molal, it was found that the extraction coefficient decreased again as a function of time. A holding oxidant analysis on the tracer in the above perchloric acid solution showed that Pu(VI) was being formed. From earlier project work\(^{10}\) it was known that the rate of oxidation of Pu(IV) to Pu(VI) by dichromate has an inverse hydrogen ion dependence. Therefore the possibility existed that dichromate at perchloric acid concentrations of ca. 0.1 molal and below was responsible for the formation of Pu(VI) in the extraction solutions.

\(^{10}\) cf. R. E. Connick, CC-3869, July 6, 1943.

The rate of oxidation of Pu(IV) to Pu(VI) by dichromate was measured in the following manner. Plutonium(IV) tracer was added to 1.0 ml of a solution of 0.112 M HClO₄ and
$5 \times 10^{-4} \text{N Na}_2 \text{Cr}_2\text{O}_7$. Ten milliliter aliquots were removed at approximately 25 minute intervals. Each 10 ml aliquot was stirred mechanically with a solution made up of 1 ml of 0.1068 M TTA and 14 ml of benzene. The TTA concentration in this extraction is sufficient to extract about 99.5% of any plutonium existing in the +4 state in the perchloric acid solution. The non-extractable plutonium in the aqueous phase after the extraction was then assumed to be in the +6 state since it was shown from earlier experiments that Pu(VI) was being formed in these solutions and there would be no Pu(III) in the presence of the Na$_2$ Cr$_2$O$_7$. Two other such experiments were performed in an identical manner except that the perchloric acid and dichromate concentrations were 0.0466 M and $4.42 \times 10^{-5}$ N in the first and 0.100 M and 0.115 N in the second. The results of these experiments will be found in Tables 2, 3 and 4.

In figures 3 and 4 the logarithm of the percent Pu(IV) has been plotted as a function of time and the linearity of the lines shows that the reaction is first order with respect to the Pu(IV) concentration. The first order rate constants defined by the equation

$$- \frac{d(\text{Pu(IV)})}{dt} = k_1(\text{Pu(IV)})$$

are $7.0 \times 10^{-3}$, $3.9 \times 10^{-3}$ and 0.7 min$^{-1}$ for the experiments of Tables 2, 3 and 4 respectively.

The stoichiometric concentration of Cr$_2$O$_7^{2-}$ is so low in these experiments that the principal species is actually HCrO$_4^-$ as shown by the equilibrium:
Table 2
Rate of Oxidation of Pu(IV) to Pu(VI) by
8.33x10^{-5}M Na_{2}Cr_{2}O_{7} in 0.112 N HClO_{4} at
c.a.-23°C.

concentration of HCrO_{4}^{-}  1.06 x 10^{-4}M

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>% Pu(IV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>ca. 95.5 (extrapolated)</td>
</tr>
<tr>
<td>5</td>
<td>90</td>
</tr>
<tr>
<td>31</td>
<td>74.9</td>
</tr>
<tr>
<td>58</td>
<td>66.3</td>
</tr>
<tr>
<td>82</td>
<td>53.2</td>
</tr>
<tr>
<td>108</td>
<td>45.5</td>
</tr>
<tr>
<td>135</td>
<td>37.8</td>
</tr>
</tbody>
</table>

The original Pu(IV) stock contained ca. 4.5% Pu(VI).
This amount of Pu(VI) was calculated from the plot of log(%)Pu(IV)) vs. time extrapolated to zero time.
Table 3

Rate of Oxidation of Pu(IV) to Pu(VI) by 7.4x10^{-5} M Na₂Cr₂O₇ in 0.0466 M HClO₄ at ca. 23°C.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>% Pu(IV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>ca. 91.2 (extrapolated)</td>
</tr>
<tr>
<td>2</td>
<td>93.5</td>
</tr>
<tr>
<td>29</td>
<td>79.5</td>
</tr>
<tr>
<td>55</td>
<td>72.0</td>
</tr>
<tr>
<td>84</td>
<td>66.3</td>
</tr>
<tr>
<td>113</td>
<td>56.6</td>
</tr>
<tr>
<td>129</td>
<td>53.5</td>
</tr>
</tbody>
</table>

concentration of HCrO₄⁻: 1.20 x 10⁻⁵ M
Table 4
Rate of Oxidation of Pu(IV) to Pu(VI) by
1.92 \times 10^{-2} \text{M} \text{Na}_2 \text{Cr}_2\text{O}_7 \text{ in } 0.100 \text{ M} \text{HClO}_4 \text{ at } 25^\circ \text{C}.

- Concentration of HCrO$_4^-$: 1.46 \times 10^{-2} \text{M}
- Concentration of H$^+$: 0.093 \text{ M}

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>% Pu(IV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>93 (assumed)</td>
</tr>
<tr>
<td>ca. 2</td>
<td>22</td>
</tr>
</tbody>
</table>
Figure 3.

Rate of oxidation of Ru(IV) to Ru(VI) by
$8.53 \times 10^{-5}$ H$_2$Cr$_2$O$_7$ in 0.1N HCl, at
c. 25° Centigrade.
Rate of oxidation of Pu(IV) to Pu(VI) by
$7.4 \times 10^{-6}$ M Na$_2$Cr$_2$O$_7$ in 0.0466 M HClO$_4$ at
c. $25^\circ$ Centigrade.
\[
\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} = 2 \text{HCrO}_4^- \quad K_{25^\circ} = 2.3 \times 10^{-2} \quad (25)
\]

In addition there is some H$_2$CrO$_4$ present as indicated by the equation:

\[
\text{H}_2\text{CrO}_4 = \text{H}^+ + \text{HCrO}_4^- \quad K_{25^\circ} = \text{ca. 0.2} \quad (26)
\]

The approximate concentrations of HCrO$_4^-$ calculated for the three experiments from these equilibrium constants, without activity coefficient corrections, are given in Tables 2, 3 and 4.

The experiments of Tables 2 and 4 differ by a factor of approximately 140 in HCrO$_4^-$ concentration while the other conditions are roughly the same. The first order rate constants differ by approximately a factor of 100, indicating that the rate is first order with respect to the concentration of HCrO$_4^-$. The bichromate dependence may be included in the rate law by means of the following expression:

\[
-\frac{d(\text{Pu(IV)})}{dt} = k_2 (\text{Pu(IV)})(\text{HCrO}_4^-). \quad (27)
\]

Values of $k_2$ for the experiments of Tables 2, 3 and 4 are 66, 325 and 50 liters moles$^{-1}$ min$^{-1}$. The effect of hydrogen ion concentration on the rate may be represented by

\[
-\frac{d(\text{Pu(IV)})}{dt} = k_3(\text{Pu(IV)})(\text{HCrO}_4^-)(\text{H}^+)^n. \quad (28)
\]

Using the data of the experiments of Tables 2 and 3, which are the most accurate, $n$ is calculated to be -1.8. Therefore the rate of oxidation varies inversely as approximately the
second power of the hydrogen ion concentration in the acidity region studied.

By lowering the dichromate concentration in the extraction experiments at low acidity it should be possible to control the rate of oxidation of Pu(IV) to Pu(VI) by Cr$_2$O$_7^{2-}$ such that the extent of oxidation during the time of extraction would be negligible. Extraction experiments were then continued in an effort to obtain activity coefficients of Pu(ClO$_4$)$_4$ at 0.112 M HClO$_4$. It was found that, under conditions such that only one percent of the Pu(IV) should be oxidized in 15 minutes, the value of the extraction coefficient rose and then became constant as a function of time. However, when the ketone dependence was tested it was found not to be fourth power, but always less than fourth power. Further it was observed that the values of the extraction coefficients were not reproducible in duplicate experiments.

To make sure all of the plutonium in the stock solution was in the +4 oxidation state this solution was reworked and converted to the nitrate which was kept in concentrated nitric acid. A holding oxidant experiment was performed on this stock to determine the amount of Pu(VI) present and it was found to constitute about 0.2 percent of the total activity. Further, extraction experiments with this stock gave irreproducible results as with the previous tracer. It was found that only 93 percent of this tracer could be extracted at 0.112 M HClO$_4$ in the presence of sodium dichromate. It seems that something happens to part of the plutonium tracer at the beginning of each extraction or during the time
the Pu(IV) tracer is added to the perchloric acid and that this process ceases after a few minutes since the extraction coefficient is found to be fairly constant with time. Whatever happens to the tracer must be irreproducible since the value of the extraction coefficient, although constant in any one experiment, varies from experiment to experiment.

The following experiments were designed to measure the amount of the non-extractable plutonium after the extraction coefficient had been measured. The first part of the experiment was performed in the usual manner. That is, Pu(IV) tracer was added to a perchloric acid-dichromate solution which had been stirred briefly with a TTA-benzene solution. After the Pu(IV) was added, the two phase system was stirred mechanically and aliquots of both layers were taken about every ten minutes over a period of about an hour. In every case equilibrium was reached within 15 minutes and in some experiments the extraction coefficient was measured by taking aliquots of both layers at the end of 15 minutes. After the extraction coefficient was measured, additional TTA was added to the benzene such that all but a few tenths of a percent of the Pu(IV) existing in the aqueous phase would be extracted. Therefore the plutonium in the aqueous phase after the final extraction would be the amount of the non-extractable material, and using this datum, the true Pu(IV) distribution between the two phases could be calculated. This type of experiment was investigated, and it was found that the fourth power ketone dependence was not obeyed and results of identical experiments were still erratic. The above experiments were performed at Cr₂O₇⁻ con-
entrations such that 1% Pu(VI) would be formed in about 5 hours.

A modification of the above experiment was tried. The extraction coefficient was first measured at low acidity and low dichromate concentration. The acidity was then increased to 1 M with perchloric acid and the dichromate concentration made $5 \times 10^{-4} \text{N}$. Additional TTA was added to extract all of the Pu(IV). The results were again erratic and did not conform to a fourth power ketone dependence. The correction of the extraction coefficient for the amount of non-extractable plutonium was small and changed the observed extraction coefficient only slightly. Therefore the presence of this non-extractable plutonium is not fully responsible for the erratic behavior of the extractions at low acidity.

An experiment was performed using Pu(III) tracer. The Pu(III) tracer was added to a perchloric acid and sodium dichromate solution. The TTA concentration was adjusted such that virtually all the Pu(IV) formed by oxidation would be extracted. It was found, however, that only 90 to 92 percent of the plutonium was extracted. Since the dichromate concentration in this experiment was not high enough to permit the oxidation of more than 1 or 2 percent of the plutonium to Pu(VI) in about 5 hours, some rapid change other than oxidation of Pu(III) to Pu(IV) must have occurred when the tracer was added which rendered part of the plutonium non-extractable.

A further experiment was performed using a very low concentration of permanganate (ca. $5 \times 10^{-4} \text{N}$), however it was
found that less than one percent of the plutonium was extracted into the benzene-TTA phase. Since it was observed that the characteristic color of \(\text{MnO}_4^-\) in the solution was much less intense after 15 minutes of stirring, it is likely that the \(\text{MnO}_4^-\) was attacking the TTA.

Two further experiments with permanganate were attempted. In both experiments the perchloric acid, benzene, and TTA were treated briefly with a low concentration of permanganate followed by an excess of \(\text{Mn}^{++}\). In the first experiment the Pu(IV) tracer was added approximately 1/2 hour after the \(\text{Mn}^{++}\) and the extraction coefficient measured. It was found that the extraction coefficient was zero, and a holding oxidant experiment showed the plutonium in the aqueous phase to be in the +6 oxidation state. Since the \(\text{Pu}^{++}\)– \(\text{MnO}_4^-\) reaction was visibly slow under these conditions a second experiment was run which was identical with the one above except that the Pu(IV) was added 2 hours after the \(\text{Mn}^{++}\). Again it was found that the extraction coefficient was zero.

The effect of \(\text{MnO}_2\) on Pu(IV) was determined. A small amount of freshly prepared \(\text{MnO}_2\) which had been carefully washed was added to the benzene-TTA-0.11 M HClO\(_4\) system and stirred for a few minutes. The Pu(IV) tracer was then added and the extraction coefficient measured. Analyses of the solution showed that complete oxidation of the Pu(IV) to Pu(VI) occurred within five minutes.

Two other oxidizing agents were tried, i.e., \(\text{Hg}^{++}\) and \(\text{H}^{+3}\). In the case of \(\text{Hg}^{++}\) it was found that the Pu(IV) was reduced to Pu(III), presumably by some impurity. Appar-
ently the oxidation of Pu(III) by Tl\(^{+3}\) is slow under the conditions of this experiment. In the case of Hg\(^{++}\) either oxidation to Pu(VI) or reduction to Pu(III) occurred. An analysis to determine the oxidation state of the non-extractable plutonium was not performed.

This anomalous behavior of plutonium tracer in solutions of low acidity has so far not been circumvented. The cause of the behavior is not known but is believed to be due to oxidizing or reducing impurities in the solutions used.
The Distribution Coefficient of TTA Between Benzene-TTA and Various Aqueous Perchloric Acid Solutions.

In order to calculate the activity coefficient of plutonium(IV) it was necessary to correct the original TTA concentration in the benzene phase for the amount which transferred into the aqueous phase. The equilibrium amount of TTA which exists in the aqueous phase is not only a function of the TTA concentration in the benzene phase but also the acid concentration in the aqueous phase. The distribution ratio has been studied as a function of the concentration of TTA in the benzene phase. Five further experiments were performed to determine the effect of the perchloric acid concentration upon the distribution coefficient. Five 15 ml solutions of 0.01113 M TTA in benzene were shaken with equal volumes of 0.0157, 1.00, 2.00, 4.00, and 6.54 M perchloric acid. The distribution coefficient was determined by removing 2.00 ml aliquots from the aqueous phase, diluting them to 50.0 ml with 0.133 M HCl, and measuring the TTA concentration in this solution spectrophotometrically. The concentration of TTA in the benzene phase was corrected for the amount of TTA which was extracted into the aqueous phase. The results of these analysis are shown in Table 5. It can be seen from Table 5 that the distribution coefficient is 40.0 at 0.0157 M perchloric acid, 37.1 at 2.00 M perchloric acid, and increases sharply above 4.0 M perchloric acid to a value of 84.9 at 6.54 M perchloric acid. These data were plotted and distribution coefficients were determined by interpolation for the various acidities which were employed in the activity coefficient determination experiments for plutonium(IV).
Table 5

Distribution Coefficient of TTA between Benzene-TTA and Various Aqueous Perchloric Acid Solutions.

<table>
<thead>
<tr>
<th>M</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0157</td>
<td>40.0</td>
</tr>
<tr>
<td>1.00</td>
<td>37.4</td>
</tr>
<tr>
<td>2.00</td>
<td>37.1</td>
</tr>
<tr>
<td>4.00</td>
<td>45.7</td>
</tr>
<tr>
<td>6.54</td>
<td>84.9</td>
</tr>
</tbody>
</table>

D is defined by the following equation:

\[ D = \frac{[\text{TTA}]_{\text{benzene}}}{[\text{TTA}]_{\text{aqueous}}} \]

The TTA concentrations are expressed in moles per liter of solution.
The Solubility and Activity Coefficient of Uranous TTA Chelate in Benzene-TTA Solutions.

In determining the activity coefficients of plutonium(IV) salts it was necessary to know the variation of the activity coefficient of PuK₄ in the benzene phase as the TTA concentration varied. Instead of measuring the activity coefficient of PuK₄, the activity coefficient of UK₄ was determined, in order to avoid the hazards of working with relatively large amounts of plutonium. It is assumed that the behavior of the activity coefficient of PuK₄ is very similar to that of UK₄.

In order to measure the activity coefficient of the uranous TTA chelate the following net reaction was studied:

\[ \text{UK}_4 (S) = \text{UK}_4 \text{ (in } X \text{ M TTA-benzene solutions).} \]

The thermodynamic equilibrium constant for the above reaction may be written:

\[ K = (\text{UK}_4) \gamma_{\text{UK}_4} \quad (29) \]

Further, if the activity coefficient, \( \gamma \), is calculated using infinite dilution of the benzene with respect to TTA as the standard state, the activity coefficient at any TTA concentration may be calculated by the use of the following equation:

\[ \frac{(\text{UK}_4)_{0.0M \text{ TTA}}}{(\text{UK}_4)_{X \text{ M TTA}}} = \gamma_{\text{UK}_4} \quad (30) \]

The uranous-TTA chelate was prepared by adding the
stoichiometric amount of TTA in benzene to an acidic uranous sulfate solution. The two phase system was stirred in an open beaker for two days and at the end of that time the chelate appeared as a dense, dark brown crystalline precipitate. The chelate was washed with benzene and water and then air dried. The chelate was analyzed by two different procedures. One method consisted of igniting a known weight of the chelate to $\text{U}_3\text{O}_8$. The results of these analyses indicated that the solid chelate contained a 1-2 mole percent deficiency of uranium. The second procedure consisted of dissolving the chelate in benzene and separating the uranium from the TTA by sulfuric acid extractions, thus allowing one to analyze for both uranium and TTA. The results of these analyses showed a 3 mole percent deficiency of TTA. The reason for this discrepancy between the two procedures is not known, but it appears as though the solid chelate has about the correct composition.

Since TTA is generally employed in two phase extraction work, the solubility of $\text{UK}_4$ in benzene was measured in the presence of an aqueous phase containing 0.167M HCl.

The chelate solubility in benzene was measured by the use of the Beckman spectrophotometer. The spectrum of the uranous chelate was measured at various concentrations against blank cells containing different concentrations of TTA. The results of the spectral measurements and the validity of Beer's law over a somewhat limited range are presented in Table 6. It can be seen from Table 6 that over a six fold concentration range the molar extinction coefficients are
Table 6

Spectrum of UK₄ in Benzene and the Validity of Beer's Law.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>max. dev. value</th>
<th>taken</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>μ(°)</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td></td>
<td></td>
</tr>
<tr>
<td>560</td>
<td>258</td>
<td>256</td>
<td>261</td>
<td>260</td>
<td>256</td>
<td>1.5</td>
<td>256</td>
</tr>
<tr>
<td>580</td>
<td>127</td>
<td>125</td>
<td>130</td>
<td>129</td>
<td>128</td>
<td>3.9</td>
<td>128</td>
</tr>
<tr>
<td>600</td>
<td>67</td>
<td>65</td>
<td>69</td>
<td>68</td>
<td>68</td>
<td>7.3</td>
<td>68</td>
</tr>
<tr>
<td>625</td>
<td>85</td>
<td>83</td>
<td>87</td>
<td>87</td>
<td>87</td>
<td>4.6</td>
<td>87</td>
</tr>
<tr>
<td>650</td>
<td>109</td>
<td>107</td>
<td>112</td>
<td>111</td>
<td>110</td>
<td>4.5</td>
<td>110</td>
</tr>
<tr>
<td>675</td>
<td>83</td>
<td>80</td>
<td>84</td>
<td>84</td>
<td>82</td>
<td>4.9</td>
<td>82</td>
</tr>
<tr>
<td>700</td>
<td>42</td>
<td>40</td>
<td>43</td>
<td>44</td>
<td>43</td>
<td>9.3</td>
<td>43</td>
</tr>
</tbody>
</table>

1. \((UK_4) = 6.5 \times 10^{-4} M\) - blank pure benzene.
2. \((UK_4) = 1.53 \times 10^{-4} M\) - blank pure benzene.
3. \((UK_4) = 8.5 \times 10^{-4} M\) in 0.1 M TTA - blank pure benzene.
4. \((UK_4) = 8.5 \times 10^{-4} M\) in 0.1 M TTA - blank 0.1 M TTA in benzene.
5. \((UK_4) = 8.9 \times 10^{-4} M\) - blank pure benzene.

(a) Samples 1 through 4 were analyzed after several dilutions. Sample 5 was analyzed without dilution and is believed to be the most accurate.

(b) \(E\) is the molar extinction coefficient.

(c) The blank solution in experiment 4 contained 0.1 M TTA to show that the light absorption of TTA was negligible in this region of the spectrum.

(d) Wave length in millimicrons.
constant within the accuracy of the measurements.

The solubilities of UK₄ observed in various TTA-benzene solutions are presented in Table 7 and a graphical representation is shown in Figure 5. It can be seen from Table 7 or Figure 5 that the solubility of UK₄ increases about 1.3 fold as the concentration of TTA varies from 0.00 to 1.05 M. Smoothed values of the solubility were taken from Figure 5 and the activity coefficients were calculated from these data. The results of these calculations appear in Table 8 and are shown graphically in Figure 6. It can be seen from Figure 6 that the activity coefficient of UK₄ in benzene-TTA solutions is unity below 10⁻² M TTA. A rather rapid decrease in the value of γ is observed at higher TTA concentrations.

An interesting comparison can be made between the activity coefficients of TTA⁷ and those of UK₄. It is found


that within experimental error the two are identical.

There is no obvious reason why the activity coefficients should be the same although a trend in the same direction might be expected since the exteriors of the chelate molecule and the TTA molecule which are exposed to the benzene are similar.
Table 7

Data on Solubility of UK₄ in Benzene - TTA Solutions.

<table>
<thead>
<tr>
<th>mol</th>
<th>log I₀/I</th>
<th>E(a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>700</td>
<td>0.148</td>
<td>0.157</td>
</tr>
<tr>
<td>675</td>
<td>0.296</td>
<td>0.312</td>
</tr>
<tr>
<td>650</td>
<td>0.392</td>
<td>0.412</td>
</tr>
<tr>
<td>625</td>
<td>0.506</td>
<td>0.521</td>
</tr>
<tr>
<td>600</td>
<td>0.237</td>
<td>0.251</td>
</tr>
<tr>
<td>580</td>
<td>0.450</td>
<td>0.476</td>
</tr>
<tr>
<td>560</td>
<td>0.910</td>
<td>0.963</td>
</tr>
</tbody>
</table>

TTA-moles/l
0.000 0.101 0.0505 0.21 0.502 1.0510.05x 10⁻² 10⁻³

Volume
0.1673
HCl
60 ml 60 ml 20 ml 20 ml 20 ml 20 ml 20 ml 20 ml

Volume
benzene
phase 100ml 35 ml 35 ml 35 ml 35 ml 35 ml 35 ml 35 ml

Solubility UK₄ mol/liter

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00538</td>
</tr>
<tr>
<td>2</td>
<td>0.00630</td>
</tr>
<tr>
<td>3</td>
<td>0.00601</td>
</tr>
<tr>
<td>4</td>
<td>0.00645</td>
</tr>
</tbody>
</table>

(a) cell length = 5.0 cm
- dilution factor in analysis = 8.133
SOLUBILITY OF UK, IN BENZENE - TTA SOLUTIONS

Figure 5.
Figure 6. Activity coefficient of $\text{UK}_4$ in benzene - TTA solutions.
<table>
<thead>
<tr>
<th>expt.</th>
<th>(TTA) mol/l</th>
<th>(UK₄) mol/l</th>
<th>(UK₄) mol/l smoothed values</th>
<th>log(TTA)</th>
<th>γ₄UK₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>0.00558</td>
<td>0.00558</td>
<td>-∞</td>
<td>1.00</td>
</tr>
<tr>
<td>7</td>
<td>1.05x10⁻³</td>
<td>0.00587</td>
<td>0.00588</td>
<td>-2.979</td>
<td>1.00</td>
</tr>
<tr>
<td>8</td>
<td>1.05x10⁻²</td>
<td>0.00594</td>
<td>0.00598</td>
<td>-1.979</td>
<td>1.00</td>
</tr>
<tr>
<td>3</td>
<td>0.0505</td>
<td>0.00601</td>
<td>0.00602</td>
<td>-1.297</td>
<td>0.978</td>
</tr>
<tr>
<td>2</td>
<td>0.1010</td>
<td>0.00620</td>
<td>0.00620</td>
<td>-0.996</td>
<td>0.949</td>
</tr>
<tr>
<td>4</td>
<td>0.210</td>
<td>0.00645</td>
<td>0.00650</td>
<td>-0.678</td>
<td>0.905</td>
</tr>
<tr>
<td>5</td>
<td>0.502</td>
<td>0.00718</td>
<td>0.00709</td>
<td>-0.299</td>
<td>0.829</td>
</tr>
<tr>
<td>6</td>
<td>1.05</td>
<td>0.00776</td>
<td>0.00731</td>
<td>+0.0212</td>
<td>0.755</td>
</tr>
</tbody>
</table>
Part 1.  

BIBLIOGRAPHY

(4) M. Calvin, CN-2486, p. 2, December 1, 1944.
(5) J. C. Reid and M. Calvin, MDDC-1405, August 1947.
(9) W. H. McVey, CN-1588, p. 10, April 15, 1944.
(10) R. E. Conaidick, CC-3869, July 6, 1948.
Part II. The Hydrolytic Behavior of Zirconium in Perchloric Acid Solution.

Introduction

The only stable oxidation state of zirconium in aqueous solution is the +4. Due to its high charge and small ionic radius \( r = 0.80\text{Å} \), zirconium in aqueous solution has a strong tendency to either hydrolyze or to form complexes with the negative ions which are present.

Aqueous solutions of zirconium salts are generally acidic. This is evidence, therefore, that the zirconium has reacted with water to form a hydrolyzed species. Most all zirconium salts which can be prepared from aqueous solution are zirconyl compounds, i.e., they contain the group \( \text{ZrO}^{++} \). For example, the zirconium halides prepared from aqueous solution at room temperature are \( \text{ZrF}_4 \cdot 3\text{H}_2\text{O} \) \((1)\) or \( \text{ZrOF}_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{H}_2\text{O} \) \((2)\).

\( \text{ZrOCl}_2 \cdot 3\text{H}_2\text{O} \), \( \text{ZrOBr}_2 \cdot 3\text{H}_2\text{O} \) and \( \text{ZrOI}_2 \cdot 3\text{H}_2\text{O} \). There seem to be some controversy whether the zirconium fluoride is \( \text{ZrOF}_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{H}_2\text{O} \) or \( \text{ZrF}_4 \cdot 3\text{H}_2\text{O} \).

Recently, McVey \((3)\) has studied the aqueous chemistry of

\( \text{(3) McVey, W. M., Thesis, University of California, 1947.} \)
zirconium using radioactive zirconium tracer and a two phase extraction procedure. Not only did he study the formation and stabilities of various aqueous zirconium complexes but also the hydrolysis of zirconium as a function of the acidity. The two phase extraction procedure used by McVey consisted in extracting the zirconium from an acidic aqueous phase into a benzene phase as a β-diketone chelate. The chelating agent used was thenoyltrifluoracetone (TTA). Since the distribution of zirconium between the two phases is a function of the activity of the zirconium in the aqueous phase, the formation of any complex is reflected in a change of the distribution of zirconium between the two phases. McVey concluded from his hydrolysis experiments at tracer concentrations of zirconium that the principle species in 2 M perchloric acid was Zr(OH)+3. In 0.01 M perchloric acid the principle species was Zr(OH)2+.

There is abundant evidence in the literature that at high zirconium concentrations the zirconium hydrolyzes to form high molecular weight polymeric species. For example, Jander and Jahr (4) measured the diffusion coefficient of zirconium in solutions at constant zirconium concentration with various perchloric acid and nitric acid concentrations. From their data, for example, they concluded that species such as 

\[
\left[\text{Zr} \cdot \text{O_2} \cdot \text{Zr} \cdot \text{ClO_4}\right]^+ 
\]

existed in the zirconium perchlorate solutions. Many other experimentalists(5)(6) have presented evidence,

obtained by a variety of methods, which was also interpreted in terms of high molecular weight zirconium species in solution. In no case is it possible to determine precisely the species in solution from the data published in the literature.

The purpose of this work was to determine, if possible, the polymeric zirconium species which are formed at high zirconium concentrations in solutions of moderate acidity. The experiments were designed so as to keep constant all variables but one in a given series of experiments in order to simplify the interpretation. In most of the work presented in the literature this was not done, and the simultaneous change of several variables made the interpretation of the data almost impossible.
Derivation of Equations

McVey (3) in his study of the aqueous chemistry of zirconium
determined the stabilities of various zirconium complexes by a
two phase extraction procedure. This procedure consisted in
extracting zirconium from an acidic aqueous solution into a
benzene-TTA phase as the neutral zirconium chelate. The ex-
tractability of zirconium is a function of the activity of
the zirconium in the aqueous phase. When complexing ions
such as $SO_4^-$, $F^-$, $C_2O_4^{2-}$, etc. are added to the system, the
activity of the zirconium is decreased and this decrease is
reflected in the extraction coefficient. The extent to which
the extraction coefficient is diminished is thus a measure of
the stability of the zirconium complex being formed in the
aqueous phase. The hydrolysis of zirconium can be considered
as a special case of complex ion formation.

In the present work the experimental data were obtained
by employing the two phase extraction procedure in much the
same fashion as used by McVey. Before presenting the experimen-
tal data, the equations used in the interpretation of the data
will be derived.

Presuming that zirconium polymers are formed in the per-
chloric acid solutions employed in the experimental work, the
extraction coefficient may be defined as follows:
The assumption will be made in the derivation that only the zirconium monomer is extracted into the benzene phase as the neutral TTA chelate. A further assumption is made (and later substantiated experimentally) that equilibrium is established between the monomer and the polymeric forms, which may be represented by the equation

\[ nZr = Zr_n \]  \hspace{1cm} (2)

where the equilibrium expression in terms of concentrations (moles per liter of solution) is:

\[ K_n = \frac{(Zr_n)}{(Zr)^n} \]  \hspace{1cm} (3)

The \( K_n \)'s are, of course, functions of the hydrogen ion concentration. Solving for \( (Zr_n) \) and summing, equation 3 becomes:

\[ \sum_{n=1}^{\infty} (Zr_n) = \sum_{n=1}^{\infty} K_n (Zr)^n \]  \hspace{1cm} (4)

and

\[ \sum_{n=1}^{\infty} n(Zr_n) = \sum_{n=1}^{\infty} nK_n (Zr)^n \]  \hspace{1cm} (5)

To simplify the equations the following terminology will be used:

- \( (Zr) \) = concentration in moles per liter of solution of the monomer. According to McVey's results the principal species at low zirconium concentration in 2M HClO$_4$ is ZrOH$^+$. The symbols \( (Zr_2) \), \( (Zr_3) \) and \( (Zr_n) \) represent the concentration of the dimer, trimer and \( n \)'th polymer respectively. The actual formulas and charges of the polymeric forms are unknown.

Some evidence will be presented in the next section which indicates that only \( ZrK_4 \) is present in the benzene phase.
By substituting equation 5 in equation 1 the following relationship is obtained:

\[ E = \frac{(ZrK_4)_b}{\sum_{n=1}^{\infty} nK_n(Zr)^n} \]  

(6)

Since the assumption has been made that the monomer is extracted into the benzene as the neutral chelate, and since it is known that equilibrium is established readily between the chelate and the monomer\(^2\), the concentration of the zirconium chelate in the benzene phase is related to the concentration of the monomer in the aqueous phase by an equilibrium constant. The concentration of monomer is therefore proportional to the chelate concentration as expressed by the following equation:

\[ k(Zr)_{aq} = (ZrK_4)_b \]  

(7)

The proportionality factor, \( k \), in equation 7 is a function of the TTA concentration in the benzene phase and the acidity of the aqueous phase. It will be presumed in equation 8 and further equations that these variables are held constant. Substituting equation 7 into 6, one obtains:

\[ E = \frac{k(Zr)}{\sum_{n=1}^{\infty} nK_n(Zr)^n} \]  

(8)

where \((H^+)^{\infty}\) and \((TTA)_b\) are constant. If the logarithm of the extraction coefficient is taken in equation 8 and differentiated with respect to the concentration of the monomer in the aqueous phase, the following equation is obtained:

\[ \frac{d \log E}{d(Zr)} = \frac{1}{(Zr)} - \frac{\sum_{n=1}^{\infty} n^2K_n(Zr)^{n-1}}{\sum_{n=1}^{\infty} nK_n(Zr)^n} \]  

(9)
Upon changing variables by use of equation 5, equation 9 becomes:

\[
\frac{d \log E}{d \log \sum n(Zr)} = \frac{1}{(Zr)} - \left[ \frac{\sum\limits_{n=1}^{\infty} n^2 K_n(Zr)^{n-1}}{\sum\limits_{n=1}^{\infty} n K_n(Zr)^n} \right]^{-1}\left[ \sum\limits_{n=1}^{\infty} n K_n(Zr)^n \right]^{-1}
\]

Upon simplifying:

\[
\frac{d \log E}{d \log \sum n(Zr)} = -1 + \frac{\sum\limits_{n=1}^{\infty} n K_n(Zr)^n}{\sum\limits_{n=1}^{\infty} n^2 K_n(Zr)^n}
\]

or

\[
\frac{d \log E}{d \log \sum n(Zr)} = -1 + \frac{\sum\limits_{n=1}^{\infty} n(Zr)^n}{\sum\limits_{n=1}^{\infty} n^2(Zr)^n}
\]

or

\[
\frac{d \log E}{d \log \sum n(Zr)} = -1 + \frac{1}{\sum\limits_{n=1}^{\infty} n f_n}
\]

where \(f_n\) is the fraction of the total zirconium which exists as a particular polymer containing \(n\) zirconium atoms. The function \(f_n\) is defined by the following equation:

\[
f_n = \frac{n(Zr_n)}{\sum\limits_{n=1}^{\infty} n(Zr_n)}
\]

The expression \(\sum\limits_{n=1}^{\infty} n f_n\) represents the average number of zirconium atoms per polymer. Therefore in the general case, when the solution contains a mixture of polymers, equation 13 gives a relationship between the slope and the average number of zirconium atoms...
per polymer:

$$\sum_{n=1}^{\infty} n f_n = \frac{1}{\text{slope} + 1} \quad (15)$$

If the logarithm of the extraction coefficient is plotted versus the logarithm of the total zirconium concentration in the aqueous phase, the slope of the curve at any point will determine the sum of the right hand terms of equation 13. If it is assumed that only one polymer of zirconium is formed then the slope of the curve (log $E$ vs. log $\sum_{n=1}^{\infty} n(Zr\ n)$) will approach a constant value at high concentrations of zirconium. The characteristic slopes for several particular polymers will be found in Table 1. It can be seen from Table 1 that as the monomer is converted to an infinite polymer the slope of the line changes from zero to minus one.
Table 1

The Relation of the Slope of the Curve, \( \log E \) versus \( \log \sum_{n=1}^{\infty} n(Zr_n) \), to the Number of Zirconium Atoms in the Zirconium Polymer.

<table>
<thead>
<tr>
<th>Number Zr atoms in polymer</th>
<th>slope of curve ( \log E ) vs. ( \log (\sum_{n=1}^{\infty} n(Zr_n)) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>-1/2</td>
</tr>
<tr>
<td>3</td>
<td>-2/3</td>
</tr>
<tr>
<td>4</td>
<td>-3/4</td>
</tr>
<tr>
<td>10</td>
<td>-9/10</td>
</tr>
<tr>
<td>( \infty )</td>
<td>-1</td>
</tr>
</tbody>
</table>
Experimental Procedure

In the derivation of equations it was stated that a two phase extraction procedure was used to determine the polymerization of zirconium in perchloric acid solution. More precisely, the zirconium was extracted from 2 M perchloric acid in one series of experiments and 1 M perchloric acid in a second series, as the neutral zirconium-TTA chelate.

The zirconium perchlorate was prepared in the following manner. Zirconyl chloride, which had been purified by recrystallizing from hydrochloric acid, was converted to the perchlorate by fuming with perchloric acid. The hot zirconium perchlorate solution was rapidly transferred to a dry box and allowed to cool. The zirconium perchlorate precipitate which formed was very crystalline. The composition was not determined. The zirconium perchlorate crystals were centrifuged away from the concentrated perchloric acid and then dissolved in 2 M HClO₄. An aliquot of this solution was treated with an excess of sodium fluoride, and then titrated for hydrogen ion with sodium hydroxide. The concentration of perchloric acid in the stock zirconium perchlorate solution (assuming the zirconium to be Zr(ClO₄)₄) was calculated to be 2.06 M. The zirconium concentration was determined by taking an aliquot of the stock solution, converting the zirconium to zirconium hydroxide, and then igniting this to zirconium dioxide. The zirconium concentration was calculated to be 0.229 M.

In the two series of experiments, the zirconium concentration in the aqueous phase was varied from about $10^{-5}$ to 0.2 M.
The acidity in each series of experiments was maintained as constant as possible because nothing is known about the acid dependence of the equilibria between the various polymers. In the derivation of the equations used in the interpretation of the data, (see preceding section), constant acidity as well as constant ionic strength were necessary prerequisites. Since the zirconium concentration is small compared to perchloric acid concentration, the acidity and ionic strength remain nearly constant, except at the highest zirconium concentrations.

Because zirconium is extracted into the benzene phase as the chelate, the concentration of TTA decreases. It is therefore necessary to have means of calculating or measuring the free ketone concentration. If the original TTA concentration in the benzene phase, before shaking, is known, and if the extraction coefficient is known, it is possible to calculate the TTA concentration in the benzene phase at equilibrium by the following equation provided one assumption is made. This equation is:

\[ (TTA)^0_b = (TTA)^0_b - \frac{1}{D + 1} \left[ (TTA)^0_b - 4(ZrK^4)_b \right] \]  

(16)

The symbol \((TTA)^0_b\) represents the TTA concentration in the benzene phase before shaking. \(D\) is the distribution coefficient for TTA between the benzene phase and the aqueous phase. The necessary assumption that was made in the derivation of equation 16 was that the entire amount of TTA in the aqueous phase must exist in the free state, i.e., only an inappreciable quantity can be present as an aqueous zirconium-TTA complex. It was found, however, by spectrophotometric measurements of the aqueous
phase of the experiments at high zirconium concentrations that a small fraction of the zirconium was being complexed by TTA. Although the fraction of zirconium complexed was quite small, the concentration of TTA in the benzene phase was appreciably altered because of the high zirconium concentration. It was therefore necessary to measure the TTA concentration in the benzene phase experimentally.

The analytical procedure that was adopted consisted in measuring the TTA concentration in the benzene phase spectrophotometrically. It was necessary to correct the observed spectrum for the absorption of light by the zirconium chelate present in the benzene phase. The concentration of ZrK₄ was calculated by the equation:

\[(ZrK₄)₀ = \frac{E}{E+1} (Zr)_b \]  (17)

where \((Zr)_b\) represents the original zirconium concentration in moles per liter in the aqueous phase before the extraction.

(This equation is only applicable when the volumes of the two phases are equal, as is also true for equation 16.)

The zirconium chelate spectrum has been measured by Zebroski (7). Zebroski's measurements were repeated, and it was found that the values of the molar extinction coefficient varied with time. A possible reason for this change may be the presence of a small amount of water in the benzene solution.
thus allowing the zirconium chelate to slowly hydrolyze. It was noted that the molar extinction coefficient of the zirconium chelate remained constant at 3300Å. At this particular wavelength the molar extinction coefficient of the zirconium chelate is almost exactly four times greater than that of pure TTA. Thus as the chelate hydrolyzes TTA is liberated and as a result of the relative value of their extinction coefficients at this wavelength, the concentration of ZrK₄ appears to remain constant.

It is possible therefore to use results of the spectrophotometric analysis at 3300Å in conjunction with the extraction coefficient data to calculate the free TTA concentration in the benzene phase. Thus, when the optical density of a sample containing both ketone and chelate is measured, the reading at 3300Å is correct even though the chelate may be hydrolyzing. This value can then be corrected for the optical density contributed by the chelate, using the molar extinction coefficient and the concentration of the chelate calculated from the extraction coefficient. The free TTA concentration is then calculated from the residual optical density by means of the known molar extinction coefficient of TTA.

In theory, it is possible with the aid of Beer's Law to calculate the concentration of both the TTA and the zirconium chelate providing the molar extinction coefficients are known for both species at two different wavelengths. Even though it was known that the zirconium chelate extinction coefficients were slowly changing over a period of time, this calculation
was performed. The results of the calculation were not precise, however they did give approximately the correct concentrations of HX and X2. The calculations therefore indicate that the zirconium species in the benzene phase is X2.

The 2 N perchloric acid experiments were all performed in the same manner. Equal volumes of 0.0115 N HCl in benzene and aqueous 2 N perchloric acid solutions at various zirconium perchlorate concentrations were placed in 50 ml volumetric flasks. In addition radioactive zirconium tracer was added to the benzene phase in the form of a benzene solution of the X2 chelate.

The radioactive zirconium tracer which was obtained from Oak Ridge always contained an appreciable fraction of colubrini. The mixture of activities was purified by a method developed by LeVay (3). There was a significant difference, however, in the final step of the purification procedure. LeVay's tracer stock was stored in an aqueous perchloric acid solution, thus as the zirconium decayed the colubrini activity grew. It was therefore necessary to rework this aqueous stock solution occasionally to remove the colubrini.

The zirconium tracer used in the experiments described here was prepared in the same manner except the final aqueous solution was extracted with a 15% benzene solution. The zirconium tracer readily extracted into the aqueous phase leaving the colubrini in the benzene phase. As colubrini was formed by the radioactive decay of zirconium chelate, it was removed from the aqueous phase by re-equilibrating the two phase system. With this procedure it was never necessary to rework the zirconium stock solution.
The interior surface of each flask used in the extraction experiments was coated with dri-film. Dri-film is a chemical reagent, \((\text{C}_{12} \text{H}_{24} \text{SiCl}_{2})\), which hydrolyzes readily. When the vapors of this chemical are introduced into a flask, the compound reacts rapidly with the water which is normally adsorbed on the surface. The hydrolysis product adheres firmly to the surface and its organic nature prevents water from wetting the glass surface. It was found necessary in tracer experiments to use coated flasks because an impurity was being leached off the uncoated flask's surface by the 2 M perchloric acid. It had been found previously that most of this unidentified impurity could be removed by treating the flask with a careful cleaning procedure. These flasks, after the cleaning procedure, were treated with dri-film to prevent any residual impurity from being leached off the glass surface.

The flasks containing the two phase solutions were placed in a thermostat at 25°C and shaken by a mechanical shaker. The length of time each flask was shaken, before the first aliquots were taken for analysis, was always greater than six hours. After analysis, the flasks were shaken again for a minimum of six hours before the second analysis was performed. It can be seen from Table 2 that there is no evidence that equilibrium was not attained at the end of the first shaking period.

The extraction coefficient of zirconium was determined by aliquoting both phases with dri-filmed micro pipettes, mounting the aliquots on glass plates, and counting them in a Geiger counter. This procedure had been developed previously by McVey \(^3\).

The series of experiments at 1 M perchloric acid was
performed in exactly the same manner. It should be noted, however, that the ionic strength of the aqueous solution was adjusted to 0.0 by adding lithium perchlorate to each solution to make the concentration 1 M LiClO₄. The lithium perchlorate had been previously purified by recrystallization. The ionic strength of the 2 M and 1 M perchloric acid series was made the same to eliminate, as far as possible, differences in the activity coefficients of all species at these two sets of conditions. The data from the two acidities may then be used to calculate the acidity dependence of the polymerization process.
Experimental Results and Discussion

Tables 2 and 3 have been compiled to present the experimentally measured quantities in the 2 M and 1 M perchloric acid series. The second column gives the original zirconium concentration in the aqueous phase before the extraction with the TTA-benzene phase. The concentration of zirconium is expressed in moles per liter of solution. The figures in the third column are the extraction coefficients that are obtained by the radioactive tracer analysis. The definition of the extraction coefficient is given by equation 1 in a previous section. The fourth column is the total (TTA + ZrK₂) optical density of the benzene phase at 3300 Å. The fifth column gives the free TTA concentration that is calculated from the data in the previous columns as already described.

The extraction coefficients were all corrected to unit TTA activity. This was done since it is desirable to compare the change in extraction coefficients with the variation of zirconium concentration at constant TTA activity. These corrected extraction coefficients are shown in column six. The correction was made assuming a fourth power benzene dependence. Column seven shows the value of the zirconium concentration in the aqueous phase after the two phases are shaken and equilibrium is attained.

Columns eight and nine give the minimum and maximum hydrogen ion concentration in the aqueous phase. It can be seen that in the experiments of the highest zirconium concentrations that there is a large uncertainty as to the actual concentration of hydrogen ion. The laboratory analysis of the hydrogen ion concentration in the presence of excess TTA
Table 2

The Hydrolysis and Polymerization of Zirconium in 2 N Perchloric Acid at 25.0°C

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Zr., Initial</th>
<th>E</th>
<th>D 3500 2</th>
<th>(HK)</th>
<th>E°</th>
<th>Zr.Aq.</th>
<th>(H⁺)</th>
<th>(H⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Moles/l.</td>
<td></td>
<td>Moles/l. x 10^3</td>
<td></td>
<td></td>
<td>Moles/l.</td>
<td>Min.</td>
<td>Max.</td>
</tr>
<tr>
<td>1</td>
<td>7.63 x 10^-5</td>
<td>0.126</td>
<td>0.344</td>
<td>5.97</td>
<td>1.00 x 10^8</td>
<td>6.78 x 10^-5</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>2</td>
<td>7.61 x 10^-4</td>
<td>0.123</td>
<td>0.346</td>
<td>6.90</td>
<td>0.95 x 10^8</td>
<td>6.80 x 10^-5</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>3</td>
<td>2.27 x 10^-3</td>
<td>0.101</td>
<td>0.337</td>
<td>5.60</td>
<td>1.02 x 10^8</td>
<td>6.91 x 10^-5</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>4</td>
<td>7.63 x 10^-3</td>
<td>0.073</td>
<td>0.343</td>
<td>5.38</td>
<td>8.7 x 10^7</td>
<td>2.11 x 10^-3</td>
<td>2.00</td>
<td>2.01</td>
</tr>
<tr>
<td>5</td>
<td>3.05 x 10^-2</td>
<td>0.156</td>
<td>0.641</td>
<td>7.19</td>
<td>5.66 x 10^7</td>
<td>6.64 x 10^-3</td>
<td>2.01</td>
<td>2.03</td>
</tr>
<tr>
<td>6</td>
<td>7.63 x 10^-2</td>
<td>0.156</td>
<td>0.648</td>
<td>7.02</td>
<td>6.46 x 10^7</td>
<td>6.61 x 10^-3</td>
<td>2.05</td>
<td>2.07</td>
</tr>
<tr>
<td>7</td>
<td>0.229</td>
<td>5.03 x 10^-2</td>
<td>0.637</td>
<td>7.34</td>
<td>1.76 x 10^6</td>
<td>0.228</td>
<td>2.06</td>
<td>2.98</td>
</tr>
<tr>
<td></td>
<td>5.11 x 10^-3</td>
<td>0.608</td>
<td>7.33</td>
<td>1.78 x 10^6</td>
<td>0.228</td>
<td>2.06</td>
<td>2.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.01 x 10^-3</td>
<td>0.609</td>
<td>7.45</td>
<td>1.64 x 10^6</td>
<td>0.228</td>
<td>2.06</td>
<td>2.98</td>
<td></td>
</tr>
</tbody>
</table>

a. The optical density was measured in a 5 cm. cell after a 10^3 fold dilution.

The following molar extinction coefficients were used:

\[
E_{ZrK} = 46,000 \\
E_{HK} = 11,460
\]
### Table 3

The Hydrolysis and Polymerization of Zirconium in 1 M HClO₄ and 1 M LiClO₄ at 25.0°C

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.312 x 10⁻⁵</td>
<td>0.323</td>
<td>b</td>
<td>4.35</td>
<td>9.1 x 10⁻⁸</td>
<td>9.92 x 10⁻⁶</td>
<td>1.001</td>
<td>1.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.93 x 10⁻⁵</td>
<td>0.350</td>
<td>0.490</td>
<td>4.35</td>
<td>9.7 x 10⁻⁵</td>
<td>9.75 x 10⁻⁵</td>
<td>1.002</td>
<td>1.002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.313 x 10⁻⁴</td>
<td>0.401</td>
<td>0.491</td>
<td>4.33</td>
<td>1.12 x 10⁻⁴</td>
<td>2.33 x 10⁻⁴</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3.94 x 10⁻⁴</td>
<td>0.379</td>
<td>0.491</td>
<td>4.21</td>
<td>1.31 x 10⁻⁴</td>
<td>9.37 x 10⁻⁵</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.313 x 10⁻³</td>
<td>0.278</td>
<td>0.408</td>
<td>4.15</td>
<td>1.10 x 10⁻⁴</td>
<td>2.97 x 10⁻⁴</td>
<td>1.000</td>
<td>1.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>3.94 x 10⁻³</td>
<td>0.166</td>
<td>0.495</td>
<td>4.15</td>
<td>1.10 x 10⁻⁴</td>
<td>2.97 x 10⁻⁴</td>
<td>1.000</td>
<td>1.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1.313 x 10⁻²</td>
<td>0.152</td>
<td>0.498</td>
<td>3.94</td>
<td>6.87 x 10⁻³</td>
<td>1.126 x 10⁻³</td>
<td>1.001</td>
<td>1.003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>3.94 x 10⁻²</td>
<td>0.061</td>
<td>0.487</td>
<td>3.88</td>
<td>2.69 x 10⁻³</td>
<td>3.71 x 10⁻³</td>
<td>1.001</td>
<td>1.016</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. The optical density was measured in a 5 cm. cell after a 500-fold dilution.

b. There was no measurement of the optical density taken in the first analysis; it was assumed to be the same as in the second analysis.
ion gives only the value the solution would have if the zirconium were unhydrolyzed. Since the degree of hydrolysis varies from experiment to experiment and since the hydrolysis products are unknown, it is impossible to calculate precisely the true hydrogen ion concentration. However, it is possible to place limits on the concentration by assuming no hydrolysis in one case and complete hydrolysis to \( \text{[Zr(OH)\textsubscript{4}]x} \) in the other.

The logarithm of the extraction coefficient at unit TTA activity has been plotted against the logarithm of the equilibrium concentration of zirconium in the aqueous phase. The curves obtained for both series are presented in Figure 1.

In a previous section, two equations which are useful in interpreting the data were derived. Equation 13 was written:

\[
\frac{d \log E}{d \log \sum_{n} n(Zr)_{n}} = -1 + \frac{1}{\sum_{n} n f_{n}} \tag{13}
\]

where \( f_{n} \) represents the fraction of the total zirconium which contains \( n \) zirconium atoms. This equation expresses the shape of the theoretical curve upon which the experimental points of Figure 1 should lie. The slope of the curve at any point should have a value between 0 and -1. It can be seen from Figure 1 that the lines which are drawn through the experimental points have very nearly the correct shape. The following equation has perhaps an even more interesting application. This equation is:

\[
\sum_{n=1}^{\infty} n f_{n} = \frac{1}{\text{slope} + 1} \tag{13}
\]

The term \( \sum_{n=1}^{\infty} n f_{n} \) represents the average number of zirconium
Figure 1.

The Extraction Coefficient of Zirconium Between Benzene Containing TTA at Unit Activity and Perchloric Acid.
atoms per polymer. Keeping equations 13 and 15 in mind, a qualitative interpretation of the data can be deduced from Figure 1. It can be seen that the monomer is the principle species in 2 M perchloric acid when the zirconium concentration is less than $10^{-3} M$. In 1 M perchloric acid the monomer is the principle species when the zirconium concentration is less than $10^{-4} M$. It is to be noted in Figure 1 that the line in the 1 M perchloric acid series does not go through the experimental points at the lowest zirconium concentration. In theory, the experimental points should all lie on a line of zero slope in this region. It is believed that the decrease in the coefficient at this low zirconium concentration is due to the presence of an impurity which partially complexes the zirconium, thus lowering the extraction coefficient. The same difficulty with such an impurity was noted by McVey (3) in his tracer experiments.

In the 2 M perchloric acid experiments the value of the extraction coefficient at the lowest zirconium concentration is also believed to be low. The discrepancy in this extraction coefficient is not nearly as pronounced as in the 1 M perchloric acid series. There appear to be several possible reasons for the decrease in the complexing effect of the impurity at the higher acidity: (1) the amount of impurity is less in the 2 M HClO$_4$ solutions, (2) the complexing power of the impurity is diminished at the higher acidity, (3) the concentration of zirconium is greater in the 2 M perchloric acid series, thus a smaller fraction of the zirconium is complexed by the impurity.

It can be seen from Figure 1 that the lines in the 2 M of the lowest zirconium concentrations are not flat.

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experimental points. This was done in an attempt to correct roughly for the effect of the impurity.

It is interesting to calculate the hydrogen ion dependence of the extraction coefficient of the monomer from the two series of experiments. Using the values of the extraction coefficient read from the curves, the hydrogen ion dependence was found to be 3.8. This value is quite different from that obtained from McVoy's tracer experiments, i.e., slightly less than 3.0. McVoy also performed some extraction experiments using approximately $4 \times 10^{-4}$ molar zirconium. The results of his macro zirconium experiments, in agreement with the present work, indicated that the hydrogen ion dependence was a good deal higher than that obtained from the tracer experiments. Therefore it seems probable that the hydrogen ion dependence is approximately 4 rather than 3. This indicates that the zirconium in one to two molar perchloric solutions exists mainly as the $+4$ ion. The presence of the complexing impurity in the tracer experiments is presumed to be the cause of the large discrepancy between the tracer and macro experiments.

It can be seen from Figure 1 that at the higher zirconium concentrations the value of the extraction coefficients is decreasing. Recalling equation 15 which was derived in a previous section:

$$\sum_{n=1}^{\infty} \frac{n \nu_n}{\nu} = \frac{1}{\text{slope} + 1}$$
it is apparent that polymers are being formed at the higher zirconium concentrations since the term $\bar{z} n_f n$ represents the average number of zirconium atoms in the various polymers. It should be noted that in the application of equation 15 the slope of the curve must be calculated. The values of $\bar{z} n_f n$ obtained by such a calculation will then depend to some extent upon how one draws the curve through the experimental points. In Figure 7 it is seen that the curve for the 2M perchloric acid series was not drawn through the experimental points obtained at the highest zirconium concentration. In the section on the derivation of equations, it was shown that the theoretical slope of the curve ($\log E^0$ versus $\log \bar{z} n_f n$) should have a value between -1 and 0. Since the absolute value of the slope of the curve drawn through the experimental points at the highest zirconium concentration would, by necessity, be greater than unity, no attempt was made to draw the curve through these points. It is doubtful that these points should even be included on the plot because of the large uncertainty in the hydrogen ion concentration which is probably nearer 31 than 21.

The average number of zirconium atoms per polymer was calculated from the slope of the curve of Figure 1 by means of equation 15. Column five of Table 4 lists this quantity. It can be seen from this table that polymers containing large numbers of zirconium atoms are formed at the higher zirconium concentrations. The zirconium monomer is the principle species at the lowest zirconium concentrations.

It is possible to write an additional relation which
zirconium concentration, the lowest value of $N$ could have
would be three, corresponding to the trimer.

It can also be seen from Table 4 that the dimer is
not the only polymer present as the value of $N$ increases as
the zirconium concentration is increased. Since large polymers
are formed at high zirconium concentrations and since the
dimer exists, there is every reason to believe that all
intermediate polymers also exist. The higher values of $N$,
I.e., from three up, are only order of magnitude values. The
calculation of these higher values is extremely sensitive
to the slope of the curve as the slope approaches minus one.
The formation of polymers above the trimer appears, from
the data, to be more rapid with increasing zirconium con-
centration at 2M perchloric acid. However, because of the
uncertainty in drawing the curves, there is in reality no
significant difference.

By comparing the two curves in Figure 1 at the higher
zirconium concentration it can be seen that the two curves
are approaching each other. This means that the value of the
hydrogen ion dependence of the extraction coefficient is
approaching zero. This means that the successive polymers
are becoming more and more in nature like the neutral
hydroxide, I.e., $\left[\text{Zr(OH)}_{4}\right]_x$. It is impossible because of
the inaccuracy of the data to calculate the exact number of
zirconium atoms in the higher polymers or their respective
charges.
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