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

by

R. E. Connick and W. H. Reas

November 1948

Special Review of Declassified Reports
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Summary

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

The activity coefficient of $Pu(ClO_4)_4$ 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 $Pu(ClO_4)_4$ 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 uranous-TTA chelate in benzene was calculated from the results of solubility measurements. The values of the activity coefficient of UK_4 are, within experimental error, identical with the values of the activity coefficient of TTA itself.

The Activity Coefficient of Plutonium(IV).

Introduction

Any rigorous treatment of thermodynamic quantitites 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 paper 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 worth-while 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}M $Pu(ClO_4)_4$ in 1.00M $HClO_4$. 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.

<u>Solubility</u> - 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

$$AB(solid) = A^+ + B^-,$$

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

$$K = (A^+)(B^-)\gamma_{A^+}\gamma_{B^-} = (A^+)(B^-)\gamma^2_{\pm AB}$$

where parenthesis indicate concentrations and γ the activity coefficient of the indicated species[1]. Relative activity coefficients

---

(1) For symbols and definitions see G. N. Lewis and M. Randall, "Thermodynamics", McGraw-Hill, New York, 1923.

---

are obtained by comparing two solubility determinations for different solutions.

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

$$H^+ + AB(solid) = A^+ + HB.$$

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 $ACl0_4$ from the solubility as is evident from the expression for the solubility product:

$$K = \frac{(A^+)(HB)\gamma_{A^+}\gamma_{HB}}{(H^+)\gamma_{H^+}} = \frac{(A^+)(HB)\gamma^2_{\pm ACl0_4}\gamma_{HB}}{(H^+)\gamma^2_{\pm HCl0_4}}$$

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) phenylarsonate which has a low solubility was tried but it was found that the plutonium in solution was complexed by phenylarsonate ion even at very low phenylarsonic 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 obtaines 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 1M $HClO_4$, 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:

$$Pu^{+3} + 2H_2AsO_3C_6H_5 = Pu(AsO_3C_6H_5)_2 \text{ (solid)} + 1/2\ H_2 + 3H^+.$$

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. E. Boyd and co-workers[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 PuO_2^{++} 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 PuO_2^{++} but so far cannot be used readily for Pu^{+4} 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].

(2) cf. J. Schubert, CN-1873, p. 15, January 1, 1945.

(3) J. Schubert, CN-1873, p. 35-47, January 1, 1945.

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 coefficients of Pu^{+4} directly and those of Pu^{+3}, PuO_2^{+} and PuO_2^{++} 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 trifluoracetyl-

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

acetone to chelate Pu^{+4} and render it extractable into benzene and other organic phases. However, on testing this reagent it was found that it partially complexed Pu^{+4} 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

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

Thomas[6] to have the requisite properties for the determination of

(6) H. W. Crandall and J. R. Thomas, CN-3733, p. 5, March 3, 1947.

activity coefficients of Pu^{+4}, 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:

$$Pu^{+4}(aq) + 4HK(b) = PuK_4(b) + 4H^+(aq).$$

The symbols (aq) and (b) designate the aqueous and benzene phase respectively, while HK 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 is neglgible, 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:

$$K = \frac{(PuK_4)_b \, (H^+)^4_{aq} \, \gamma_{PuK_4} \, \gamma^4_{H^+}}{(Pu^{+4})_{aq} (HK)^4_b \, \gamma_{Pu^{+4}} \, \gamma^4_{HK}} \qquad (1)$$

Parenthesis indicate concentrations and γ 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 γ_{A^-} where A^- is an anion present in the aqueous phase we obtain

$$K = \frac{(PuK_4)(H^+)^4\gamma^4_{H^+}\gamma^4_{A^-}}{(Pu^{+4})(HK)^4\gamma_{Pu^{+4}}\gamma^4_{A^-}} \qquad (2)$$

or:

$$K = \frac{(PuK_4)(H^+)^4\ \gamma^8_{\pm HA}}{(Pu^{+4})(HK)^4\ \gamma^5_{\pm PuA_4}} \qquad (3)$$

If the activity coefficient of the acid, HA, is known for the particular solution being investigated, only the value of K and $\gamma_{\pm PuA_4}$ are not directly measurable. From measurements at two or more sets of conditions, one may immediately calculate relative values of $\gamma_{\pm PuA_4}$ 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 States - 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:

$$\gamma_{\pm PuCl_4} = \gamma_{\pm Pu(ClO_4)_4} \frac{\gamma_{\pm HCl}^{8/5}}{\gamma_{\pm HClO_4}^{8/5}} \qquad (4)$$

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 it 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 measurement in perchloric acid cells of the following type can be used:

$$Au: Pu^{+3}, Pu^{+4}, HClO_4; HClO_4, H_2: Pt$$

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

$$E = E^\circ - \frac{RT}{nF} \ln \frac{(Pu^{+3})(H^+)\ \gamma_{\pm}^{4}{}_{Pu(ClO_4)_3}\ \gamma^{2}_{\pm HClO_4}}{(Pu^{+4})\ \gamma^{5}_{\pm Pu(ClO_4)_4}\ P_{H_2}^{1/2}} \qquad (5)$$

Knowing $\gamma_{\pm HClO_4}$ and $\gamma_{\pm Pu(ClO_4)_4}$ (from the distribution measurements), all the other quantities are measurable except $\gamma_{\pm Pu(ClO_4)_3}$ 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 +6 activity coefficient of Pu(VI) in perchloric acid may be obtained from the equilibrium

$$2\ H_2O + 3\ Pu^{+4} = 2\ Pu^{+3} + PuO_2^{++} + 4\ H^+$$

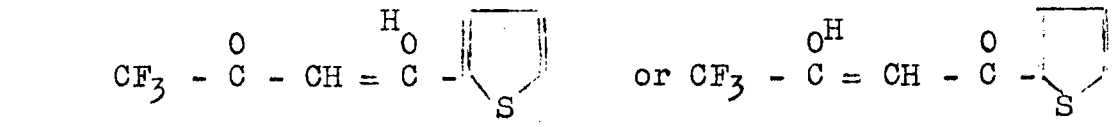
$$K = \frac{(Pu^{+3})^2(PuO_2^{++})(H^+)^4\ \gamma^{8}_{\pm Pu(ClO_4)_3}\ \gamma^{3}_{\pm PuO_2(ClO_4)_2}\ \gamma^{8}_{\pm HClO_4}}{(Pu^{+4})^3\ \gamma^{15}_{\pm Pu(ClO_4)_4}} \qquad (6)$$

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

$$Pu^{+4} + PuO_2^{+} = PuO_2^{++} + Pu^{+3}.$$

Measurement of Activity Coefficient of $Pu(ClO_4)_4$ 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 thenoyltrifluoracetone which will be abbreviated to TTA.* The formula is



TTA is a pale yellow solid at room temperature which melts at 42°C. It is slightly soluble in water (0.038 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 could undoubtedly be used in place of benzene as the chelates 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 concentration[7]:

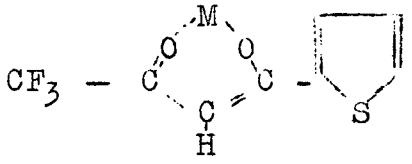
---

[7] E. L. King and W. H. Reas, BC-69, July, 1947.

$$\frac{(TTA)_{(b)}}{(TTA)_{(aq)}} = 40.0 \qquad (7)$$

In the aqueous phase TTA exists as a hydrate[7].

The TTA forms chelate compounds with metal ions by coordinating two oxygens to the metal ion in the following manner:



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*We are indebted to Dr. J. C. Reid for the preparation of the TTA used in this work.

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} 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

$$PuK_n^{+4-n}(aq) + (4-n)HK(b) = PuK_4(b) + (4-n)H^+(aq) \quad n = 0,1,2,3,4.$$

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

$$E = \frac{(PuK_4)_{(b)}}{\sum_{n=0}^{4} (PuK_n^{+4-n})_{(aq)}} \qquad (8)$$

The extraction coefficient, E, as defined above, is the concentration of Pu(IV) in the benzene phase divided by the total Pu(IV) concentra-

tion 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

$$K_n = \frac{(PuK_4)_{(b)}(H^+)^{+4-n}}{(PuK_n^{+4-n})(HK)_{(b)}^{+4-n}} \qquad n = 0,1,2,3,4. \qquad (9)$$

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

$$(PuK_n^{4-n}) = \frac{(PuK_4)_{(b)}(H^+)^{+4-n}}{K_n(HK)_{(b)}^{4-n}} . \qquad (10)$$

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

$$\frac{d \log E}{d \log (HK)_{H^+,\ ClO_4^-}} = 4 - \frac{\sum_0^4 n(PuK_n^{+4-n})}{\sum_0^4 (PuK_n^{+4-n})} \qquad (11)$$

or

$$\frac{d \log E}{d \log (HK)_{H^+,\ ClO_4^-}} = 4 - f_1 - 2f_2 - 3f_3 - 4f_4 \qquad (12)$$

where f_1, f_2, ... are the fractions of the Pu(IV) ions existing in solution as PuK^{+3}, PuK_2^{++}, PuK_3^{+} and 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 TTA 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 ClO_4^- or 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:

$$PuK_n(OH)_m(ClO_4)_p^{+4-m-n-p} + (4-n)HK = PuK_4 + pClO_4^- + mH_2O + (4-m-n)H^+$$

$$E = \frac{(PuK_4)}{\sum_m \sum_n \sum_p (PuK_n(OH)_m(ClO_4)_p)} \qquad (13)$$

(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:

$$K_{m,n,p} = \frac{(PuK_4)(ClO_4^-)^p(H_2O)^m(H^+)^{+4-m-n}}{(PuK_n(OH)_m(ClO_4)_p)(HK)^{+4-n}} \qquad (14)$$

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

$$\left.\frac{d \log E}{d \log (HK)}\right|_{H^+, ClO_4^-} = 4 - \frac{\sum_m \sum_n \sum_p n(PuK_n(OH)_m(ClO_4)_p)}{\sum_m \sum_n \sum_p (PuK_n(OH)_m(ClO_4)_p)} \qquad (15)$$

$$= 4 - \sum_p \sum_m \sum_n n\, f_{m,n,p}$$

where $f_{m,n,p}$ is the fraction of the Pu(IV) in the aqueous phase which is complexed by n diketonate 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 concentration 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

(7a) E. Zebroski, BC-63, July 1, 1947.

value of the complexing constant.

$$K_c = \frac{(PuK^{+3})(H^+)}{(Pu^{+4})(HK)_{aq}}$$

for the reaction

$$Pu^{+4} + HK = PuK^{+3} + H^+ .$$

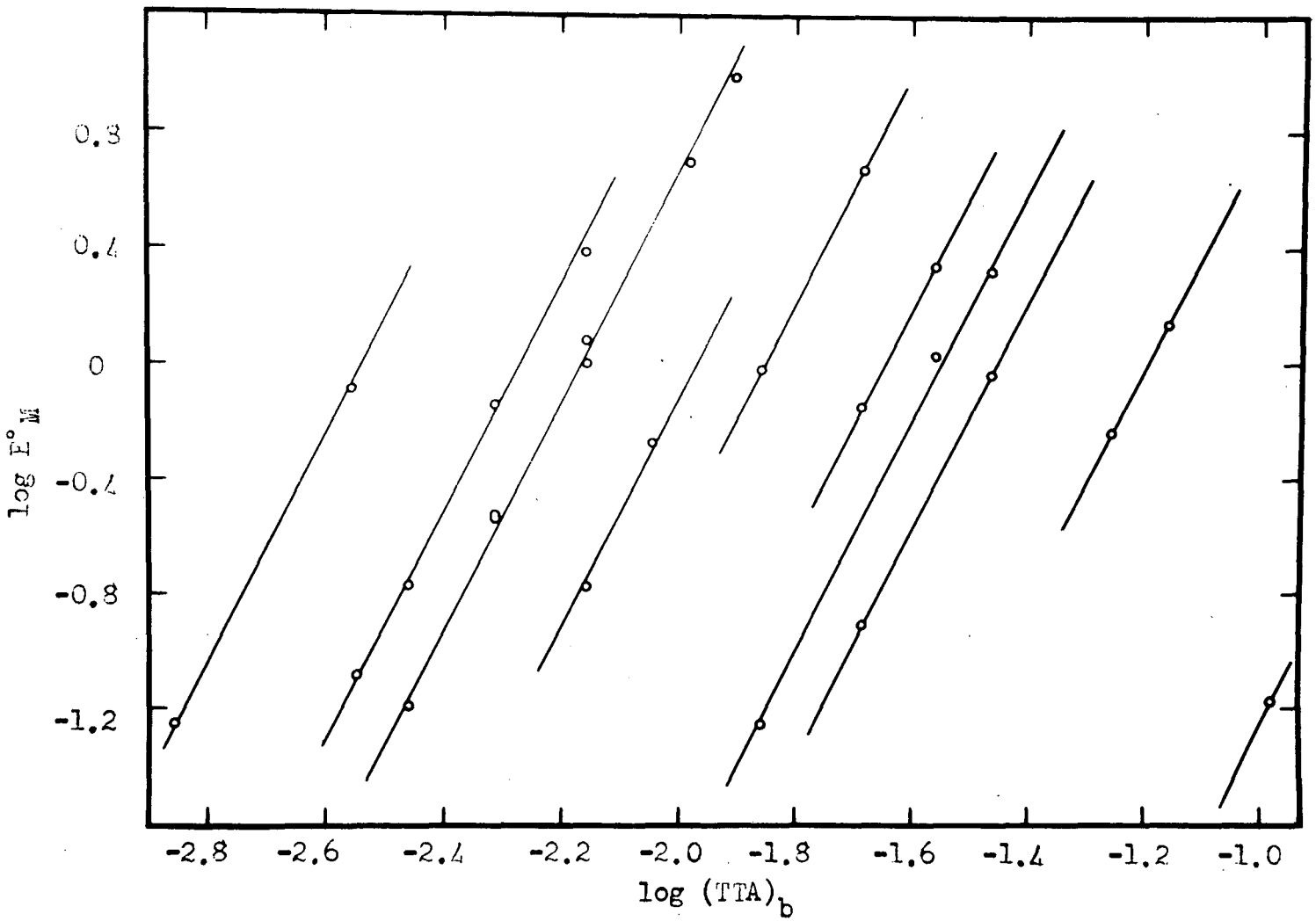
He found a value of ca. 75 for 1M hydrochloric acid.

McVey[7b] has estimated from cell and distribution measurements

(7b) W. H. McVey, Thesis, University of California, 1947

the fraction of plutonium(IV) which exists in the form of a chloride complex in 1M hydrochloric acid. If the assumption is made that the

Figure 1



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, 1,863, 2.235, 4.345, and 6.21 M.

perchlorate ion does not complex plutonium(IV), it is then possible to estimate the equilibrium for the formation of PuK^{+3} from Pu^{+4} in perchloric acid solution by correcting Zebroski'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^{+3} species in 1M 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 activity coefficient changes are assumed to be small over a 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 the activity coefficient changes are allowed for, it is predicted that the fraction complexed remains nearly constant from 0.2 to 1M perchloric acid and decreases, if anything, above 1M perchloric acid.* Therefore the correction for complexing is believed

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*It can be derived that the percentage correction to the extraction coefficient is to a very close approximation proportional to the expression:

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

(continued on next page)

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 $Pu(ClO_4)_4$.

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,

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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:

$$\frac{\gamma^{3/4}_{Pu^{+4}}}{\gamma^{3}_{H^{+}}} \qquad\qquad \frac{\gamma^{3/4}_{Pu^{+4}}}{\gamma^{3/4}_{Pu^{+4}}}$$

This first quantity is known to decrease as the perchloric acid concentration increases (see later) while the second quantity is, of course, constant. Therefore $\gamma^{3/4}_{Pu^{+4}}/\gamma_{PuK^{+3}}$ would be expected to decrease slowly and the correction for complexing would decrease at acidities above 1M.

above 0.02M* TTA in benzene, the activity coefficient of TTA decreases below unity[7]. In such experiments the measured extraction coefficient was corrected to the value it would have had if the γ_{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 plotted extraction coefficients are those that would have been measured if the activity coefficient of PuK_4 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 ClO_4^- and hydroxide was assumed. It would in principle be possible to determine the degree of complexing of Pu(IV) by these ions by measuring the extraction coefficient as only the ClO_4^- 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 OH^-, measurements could be made of the extraction coefficient in mixtures of $HClO_4$ and $LiClO_4$ at constant ClO_4^- concentration. It is planned to make such measurements in the near future. Complexing by ClO_4^- presents a more difficult problem.

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* The concentrations for all species in this paper are either expressed in moles per liter of solution (designated by M) or in moles per kilo-gram of water (designated by m).

No anion is known which would be expected to have significantly less tendency to complex Pu^{+4} than ClO_4^-. Thus in trying to maintain constant ionic strength while varying the ClO_4^- concentration it is necessary to add an anion which probably has a greater tendency than ClO_4^- to complex plutonium(IV).

Activity Coefficients of $Pu(ClO_4)_4$ in Perchloric Acid Solutions

In the absence of information on the complexing of Pu(IV) by ClO_4^- 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:

$$Pu^{+4}(aq) + HK(b) = PuK_4(b) + 4H^+(aq)$$

Here the symbol Pu^{+4} represents the total plutonium(IV) in the aqueous phase even though part of it may be complexed by ClO_4^- or be hydrolyzed.

The equilibrium constant for this reaction is:

$$K = \frac{(PuK_4)(H^+)^4\gamma^8_{\pm HClO_4}\gamma_{PuK_4}}{(Pu^{+4})(HK)^4\gamma^4_{HK}\,\gamma^5_{\pm Pu(ClO_4)_4}} = \frac{E(H^+)^4\gamma^8_{\pm HClO_4}\gamma_{PuK_4}}{(HK)^4\gamma^4_{HK}\gamma^5_{\pm Pu(ClO_4)_4}} \qquad (16)$$

and the lowering of the activity of Pu^{+4} due to any perchlorate complexing or hydrolysis will appear in $\gamma_{\pm Pu(ClO_4)_4}$. This is the basis upon which the activity coefficients of Pu(IV) perchlorate have been calculated.

In this paper the activity coefficient of $Pu(ClO_4)_4$ at unit concentration $HClO_4$ was taken as unity in accordance with the chosen standard state. Thus we may write for 1M $HClO_4$:

$$\gamma_{\pm Pu(ClO_4)_4} = 1 = \left[\frac{E\ \gamma^8_{\pm 1M\ HClO_4}\gamma_{PuK_4}}{K\ (HK)^4\ \gamma^4_{HK}}\right]^{1/5} \qquad (17)$$

This equation serves to define the thermodynamic equilibrium constant

K. Then in any perchloric acid solution the activity coefficient of $Pu(ClO_4)_4$ is given by the expression:

$$\gamma_{\pm Pu(ClO_4)_4} = \left[\frac{E(H^+)^4 \ \gamma^8_{\pm HClO_4} \ \gamma_{PuK_4}}{K \ (HK)^4 \ \gamma^4_{HK}} \right]^{1/5} . \qquad (18)$$

In equation 18 the concentrations of hydrogen ion and TTA(HK) are known, and the value of E is determined experimentally. Therefore to calculate activity coefficients of $Pu(ClO_4)_4$ it is necessary to know the value of K and the activity coefficients of HK, $HClO_4$ and PuK_4. 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 PuK_4 has not

(8) R. A. Robinson and O. J. Baker, Tran. Proc. Roy. Soc., New Zealand, 76, 250 (1946).

been measured however, as previously mentioned, the activity coefficient of UK_4 in the presence of TTA and benzene has been determined. The assumption is made that the activity coefficient of PuK_4 is identical with that of UK_4.

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 6.98×10^6 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 $Pu(ClO_4)_4$ 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

Table 1

Activity Coefficients of $Pu(ClO_4)_4$ in Perchloric Acid at 25.0°C

$(HClO_4)$ moles/l	$(HClO_4)$ moles/1000 g. H_2O	$E^\circ M$	$\gamma_{\pm M}$ $HClO_4$	$\gamma_{\pm m}$ $HClO_4$	$\gamma_{\pm M}$ $(Pu(ClO_4)_4$	$\gamma_{\pm m}$ $Pu(ClO_4)_4$
0.1863	0.1884	1.46×10^{10}	0.7856	0.7793	0.818	0.861
0.373	0.380	1.23×10^{9}	0.7786	0.7661	0.856	0.894
0.473	0.485	4.66×10^{8}	0.7845	0.7686	0.863	0.898
0.745	0.773	7.59×10^{7}	0.8189	0.7918	0.926	0.949
0.946	0.991	2.56×10^{7}	0.8570	0.8211	0.969	0.985
1.491	1.601	3.77×10^{6}	1.004	0.9469	1.244	1.233
1.863	2.037	1.56×10^{6}	1.162	1.066	1.548	1.508
2.236	2.488	6.43×10^{5}	1.360	1.223	1.930	1.840
4.345	5.386	5.92×10^{4}	4.482	3.664	13.75	12.00
6.21	8.52	5.40×10^{2}	20.89	15.14	83.9	64.2

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^o 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:

$$\gamma_{\pm m\ HClO_4} = \frac{\left[\gamma_{\pm M\ HClO_4}\right] (HClO_4)_M}{d_{25}\ (HClO_4)_m} \tag{19}$$

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 of water basis. The values of $\gamma_{\pm M}$ were calculated using equation 18 after substituting E°:

$$\gamma_{\pm M} = \frac{E^o\ (H^+)^4\ \gamma^8_{\pm\ HClO_4}}{K} \tag{20}$$

The value of K was obtained by graphical interpolation of the E^o values at 1M $HClO_4$ 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^o 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:

$$E^o{}_m = E^o{}_M x \frac{(Pu^{+4})M}{(Pu^{+4})_m} . \tag{21}$$

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

$$\frac{(Pu^{+4})_M}{(Pu^{+4})_m} = \frac{10^3 \; d \; (HClO_4)_m}{10^3 + (HClO_4)_m W} \tag{22}$$

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_m^o were plotted and the value at 1m $HClO_4$ 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 $\gamma_{\pm 1m\ HClO_4}$ equal unity. Values of $\gamma_{\pm m}$ were then calculated for other perchloric acid concentrations using this value of K_m which was found to be 5.24×10^6.

The values of $\gamma_{\pm M}$ and $\gamma_{\pm m}$ of $Pu(ClO_4)_4$ are plotted in Figure 2.

It is interesting to calculate the limiting slope of the activity coefficient curve obtained for $Pu(ClO_4)_4$ 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

$$\log \gamma_{\pm} = -0.505 \; Z_+ \; Z_- \sqrt{\mu}. \tag{23}$$

Therefore as the ionic strength, μ, becomes vanishingly small the slope of the activity coefficient curve ($\log \gamma_{\pm}$ vs. $\sqrt{\mu}$) becomes $-0.505 \; Z_+ \; Z_-$. For a salt of the type $Pu(ClO_4)_4$, the limiting slope would be -2.02. However this behavior is not to be expected with 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 $Pu(OH)^{+3}$ or $Pu(OH)_2^{+2}$ 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

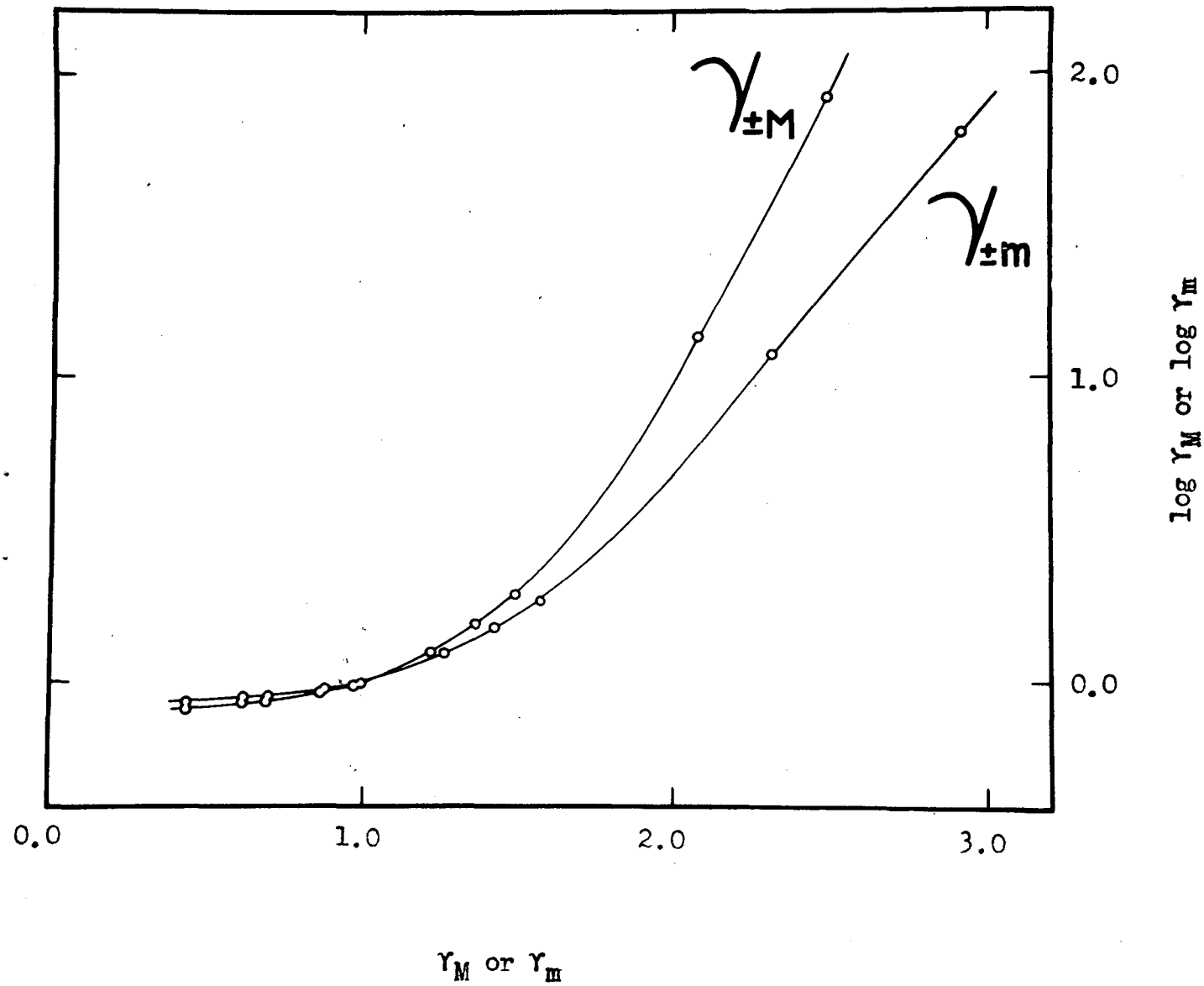


Figure 2.

Activity Coefficients of $Pu(ClO_4)_4$

in Perchloric Acid.

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

$$Pu(OH)^{+3} + 4HK = PuK_4 + 3H^+ + H_2O$$

an entire new set of values is obtained. The shape of the plot of log $\gamma_{\pm}$ 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. 1M $HClO_4$.

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 $\gamma_{\pm Pu(ClO_4)_4}$ 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 0.18M $HClO_4$. 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 co-

efficient, E, as a 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]. It was

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

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 0.5M perchloric acid, and at this same acid concentration it was found that if $5x10^{-4}$N $Na_2Cr_2O_7$ 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 $5x10^{-4}$N $Na_2Cr_2O_7$ 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

(10) cf. R. E. Connick, CC-3869, July 6, 1948.

Pu(VI) by dichromate has an inverse hydrogen ion dependence. Therefore the possiblility 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.

The rate of oxidation of Pu(IV) to Pu(VI) by dichromate was measured in the following manner. Plutonium(IV) tracer was added to 100 ml of a solution of 0.112M $HClO_4$ and $5x10^{-4}$N $Na_2Cr_2O_7$. 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 0.1068M 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_2O_7. Two other such experiments were performed in an identical manner except that the perchloric acid and dichromate concentrations were 0.0466M and $4.42x10^{-5}$N in the first and 0.100M and 0.115N 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

$$-\frac{d(Pu(IV))}{dt} = k_1(Pu(IV)) \qquad (24)$$

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

The stoichiometric concentration of $Cr_2O_7^{=}$ is so low in these ex-

Table 2

Rate of Oxidation of Pu(IV) to Pu(VI) by 8.33×10^{-5}M $Na_2Cr_2O_7$ in 0.112N $HClO_4$ at ca. 23°C.

concentration of $HCrO_4^-$ 1.06×10^{-4}M

Time (min)	% Pu(IV)
0	ca. 95.5 (extrapolated)
5	90
31	74.9
58	66.3
82	53.2
108	45.5
135	37.8

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 7.4×10^{-6}M $Na_2Cr_2O_7$ in 0.0466M $HClO_4$ at ca. 23°C.

concentration of $HCrO_4^-$ 1.20×10^{-5}M

Time (min)	% Pu(IV)
0	ca. 91.2 (extrapolated)
2	93.5
29	79.5
55	72.0
84	66.3
113	58.6
139	53.5

Table 4

Rate of Oxidation of Pu(IV) to Pu(VI) by 1.92×10^{-2}M $Na_2Cr_2O_7$ in 0.100M $HClO_4$ at 25°C

concentration of $HCrO_4^-$ 1.46×10^{-2}M

concentration of H^+ 0.093M

time (min)	% Pu(IV)
0	93 (assumed)
ca. 2	22

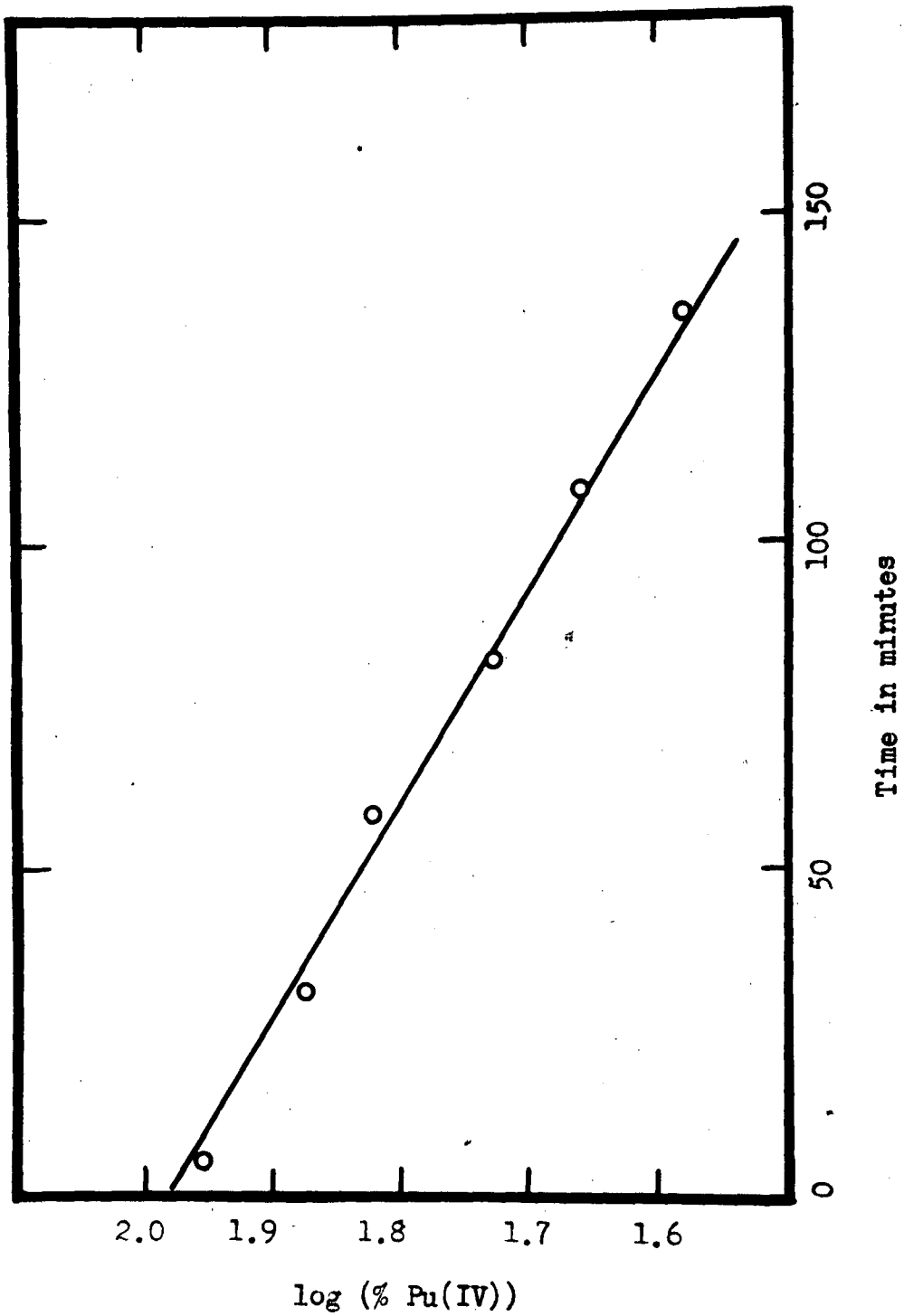


Figure 3.

Rate of Oxidation of Pu(IV) to Pu(VI) by 8.33×10^{-5}M $Na_2Cr_2O_7$ in 0.112 M $HClO_4$ at ca. 23° Centigrade.

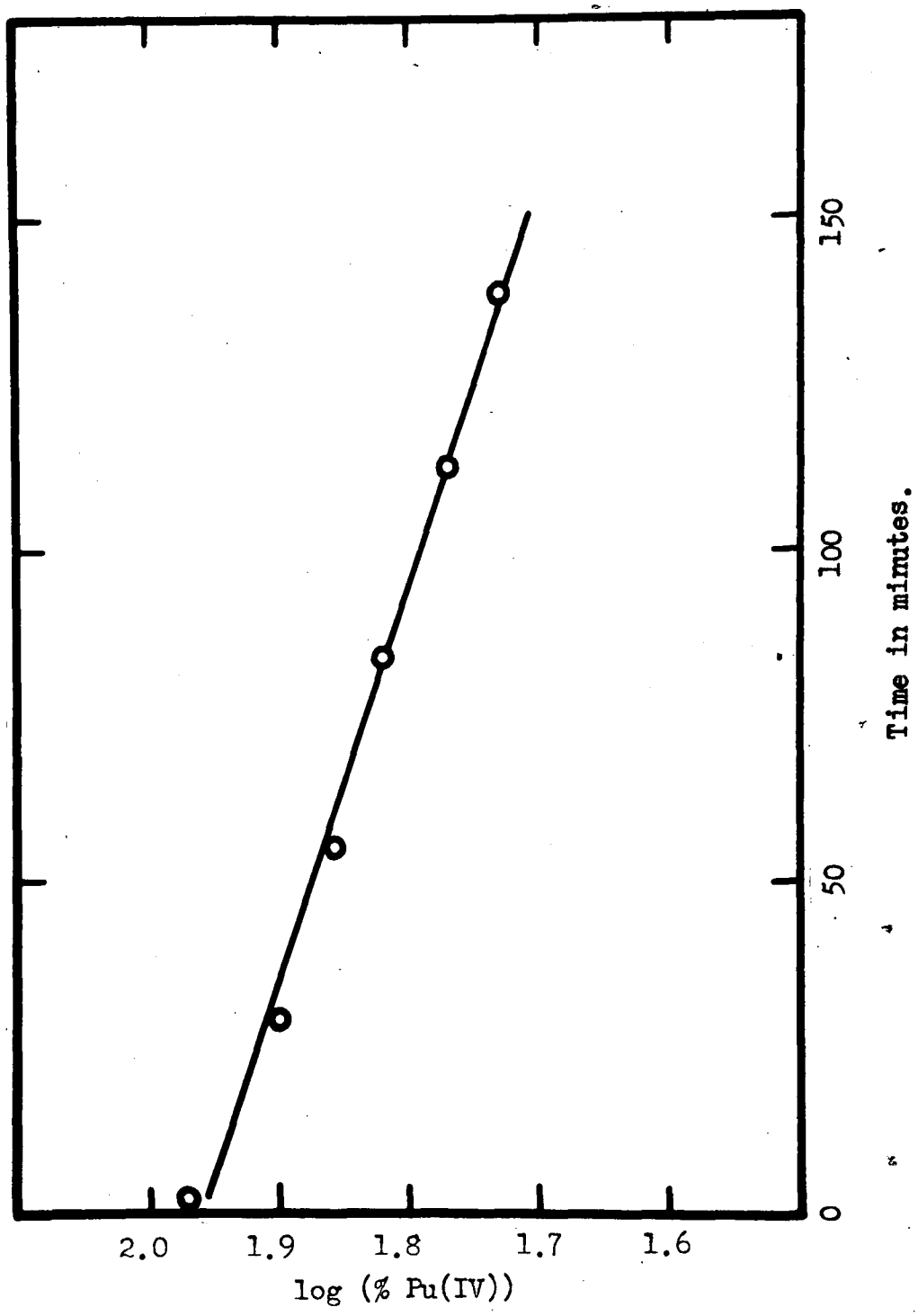


Figure 4.

Rate of Oxidation of Pu(IV) to Pu(VI) by 7.4×10^{-6}M $Na_2Cr_2O_7$ in 0.0466M $HClO_4$ at ca. 23° Centigrade.

periments that the principal species is actually $HCrO_4^-$ as shown by the equilibrium:

$$Cr_2O_7^{--} + H_2O = 2\ HCrO_4^- \quad K_{25^o} = 2.3 \times 10^{-2} \tag{25}$$

In addition there is some H_2CrO_4 present as indicated by the equation:

$$H_2CrO_4 = H^+ + HCrO_4^- \quad K_{25^o} = \text{ca. } 0.2 \tag{26}$$

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:

$$-\frac{d(Pu(IV))}{dt} = k_2\ (Pu(IV))(HCrO_4^-). \tag{27}$$

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

$$-\frac{d(Pu((IV))}{dt} = k_3(Pu(IV))(HCrO_4^-)(H^+)^n. \tag{28}$$

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 $Cr_2O_7^{--}$ such that the extent of oxidation during the time of extraction would be negligible. Extraction experi-

ments were then continued in an effort to obtain activity coefficients of $Pu(ClO_4)_4$ at 0.112M $HClO_4$. 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 0.112M $HClO_4$ 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 $Cr_2O_7^{--}$ concentrations such that one percent Pu(VI) would be formed in about five 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 $5x10^{-4}$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 five 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. $5x10^{-4}N$), 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 MnO_4^- in the solution was much less intense after 15 minutes of stirring, it is likely that the 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 Mn^{++}. In the first experiment the Pu(IV) tracer was added approximately 1/2 hour after the 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 Mn^{++}-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 two hours after the Mn^{++}. Again it was found that the extraction coefficient was zero.

The effect of MnO_2 on Pu(IV) was determined. A small amount of freshly prepared MnO_2 which had been carefully washed was added to the benzene-TTA-0.11M $HClO_4$ 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., Hg^{++} and Tl^{+3}. In the case of thallium it was found that the Pu(IV) was reduced to Pu(III), presumably by some impurity. Apparently 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[7]. Five further experiments were performed to determine the effect of the perchloric acid concentration upon the distribution coefficient. Five 15 ml solutions of 0.0113 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 analyses 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.

M	D
0.0157	40.0
1.00	37.4
2.00	37.1
4.00	45.7
6.54	84.9

D is defined by the following equation:

$$D = \frac{(TTA)_{benzene}}{(TTA)_{aqueous}}$$

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 PuK_4 in the benzene phase as the TTA concentration varied. Instead of measuring the activity coefficient of PuK_4, the activity coefficient of UK_4 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 PuK_4 is very similar to that of UK_4.

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

$UK_4(S) = UK_4$ (in X M TTA-benzene solutions).

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

$$K = (UK_4)\gamma_{UK_4} \tag{29}$$

Further, if the activity coefficient, γ, 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:

$$\frac{(UK_4)_{0.0M\ TTA}}{(UK_4)_{XM\ TTA}} = \gamma_{UK_4} \tag{30}$$

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 chelate to U_3O_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 UK_4 in benzene was measured in the presence of an aqueous phase containing 0.167 M 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 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 constant within the accuracy of the measurements.

The solubilities of UK_4 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 UK_4 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

Table 6

Spectrum of UK_4 in Benzene and the Validity of Beer's Law.

	Sample 1	2	3	4	5	max. dev.	value[a] taken
mμ[d]	E[b]	E	E	E	E	%	E
560	258	256	261	260	256	1.5	256
580	127	125	130	129	128	3.9	128
600	67	65	69	68	68	7.3	68
625	85	83	87	87	87	4.6	87
650	109	107	112	111	110	4.5	110
675	83	80	84	84	82	4.9	82
700	42	40	43	44	43	9.3	43

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[c].
5. $(UK_4) = 8.9 \times 10^{-4}M$ - blank pure benzene.

(a) Samples 1 through 4 analyzed after several dilutions. Sample 5 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) Wavelength in millimicrons.

Table 7

Data on Solubility of UK_4 in Benzene - TTA Solutions.

mμ	log I_o/I								$E^{(a)}$
	1	2	3	4	5	6	7	8	
700	0.148	0.157	0.154	0.165	0.186	0.201	0.149	0.146	43
675	0.296	0.312	0.302	0.326	0.359	0.388	0.297	0.294	82
650	0.392	0.412	0.401	0.431	0.471	0.511	0.396	0.392	110
625	0.306	0.321	0.311	0.334	0.369	0.398	0.309	0.306	87
600	0.237	0.251	0.243	0.264	0.293	0.316	0.241	0.238	68
580	0.450	0.476	0.459	0.496	0.550	0.599	0.456	0.450	128
560	0.910	0.963	0.926	1.011	1.10	1.19	0.923	0.919	256
TTA-moles/l	0.000	0.101	0.0505	0.21	0.502	1.05	1.05×10^{-2}	1.05×10^{-3}	
Volume 0.167M 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 UK_4 moles/liter	Sample		Sample	
	1	0.00588	5	0.00718
	2	0.00620	6	0.00776
	3	0.00601	7	0.00594
	4	0.00645	8	0.00587

(a) cell length = 5.0 cm

dilution factor in analysis = 8.333

Figure 5

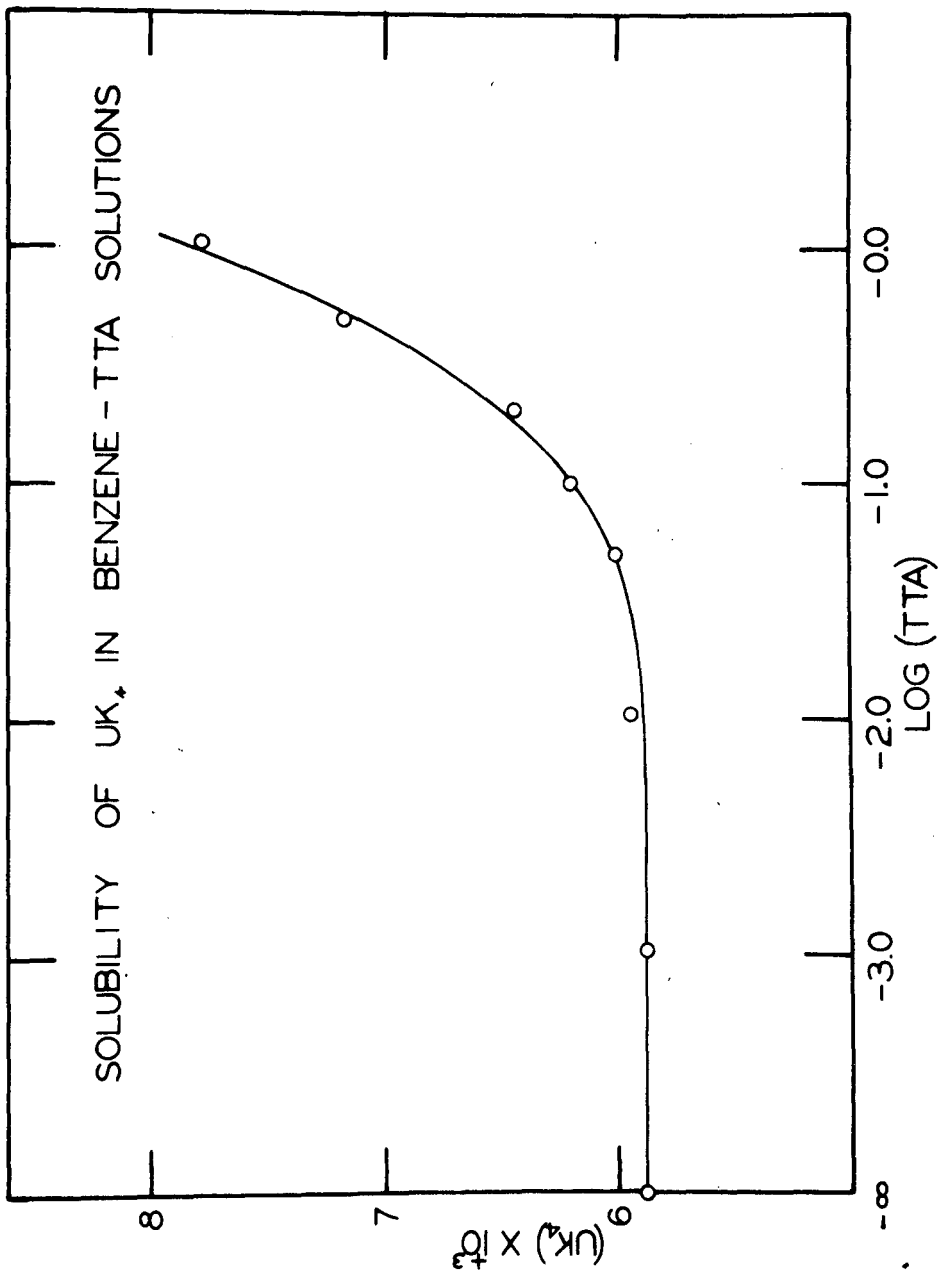

SOLUBILITY OF UK_4 IN BENZENE - TTA SOLUTIONS
8
7
6
$(UK_4) \times 10^3$
-8
-3.0
-2.0
-1.0
-0.0
LOG (TTA)

Table 8

Solubility and Activity Coefficient of UK_4 in Benzene as a Function of the TTA Concentration

expt.	(TTA) moles/l	(UK_4) moles/l	(UK_4) moles/l smoothed values	log(TTA)	γ_{UK_4}
1	0.000	0.00588	0.00588	$-\infty$	1.000
7	1.05×10^{-3}	0.00587	0.00588	-2.979	1.000
8	1.05×10^{-2}	0.00594	0.00588	-1.979	1.000
3	0.0505	0.00601	0.00602	-1.297	0.978
2	0.1010	0.00620	0.00620	-0.996	0.949
4	0.210	0.00645	0.00650	-0.678	0.905
5	0.502	0.00718	0.00709	-0.299	0.829
6	1.05	0.00776	0.00781	+0.0212	0.753

and are shown graphically in Figure 6. It can be seen from Figure 6 that the activity coefficient of UK_4 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.

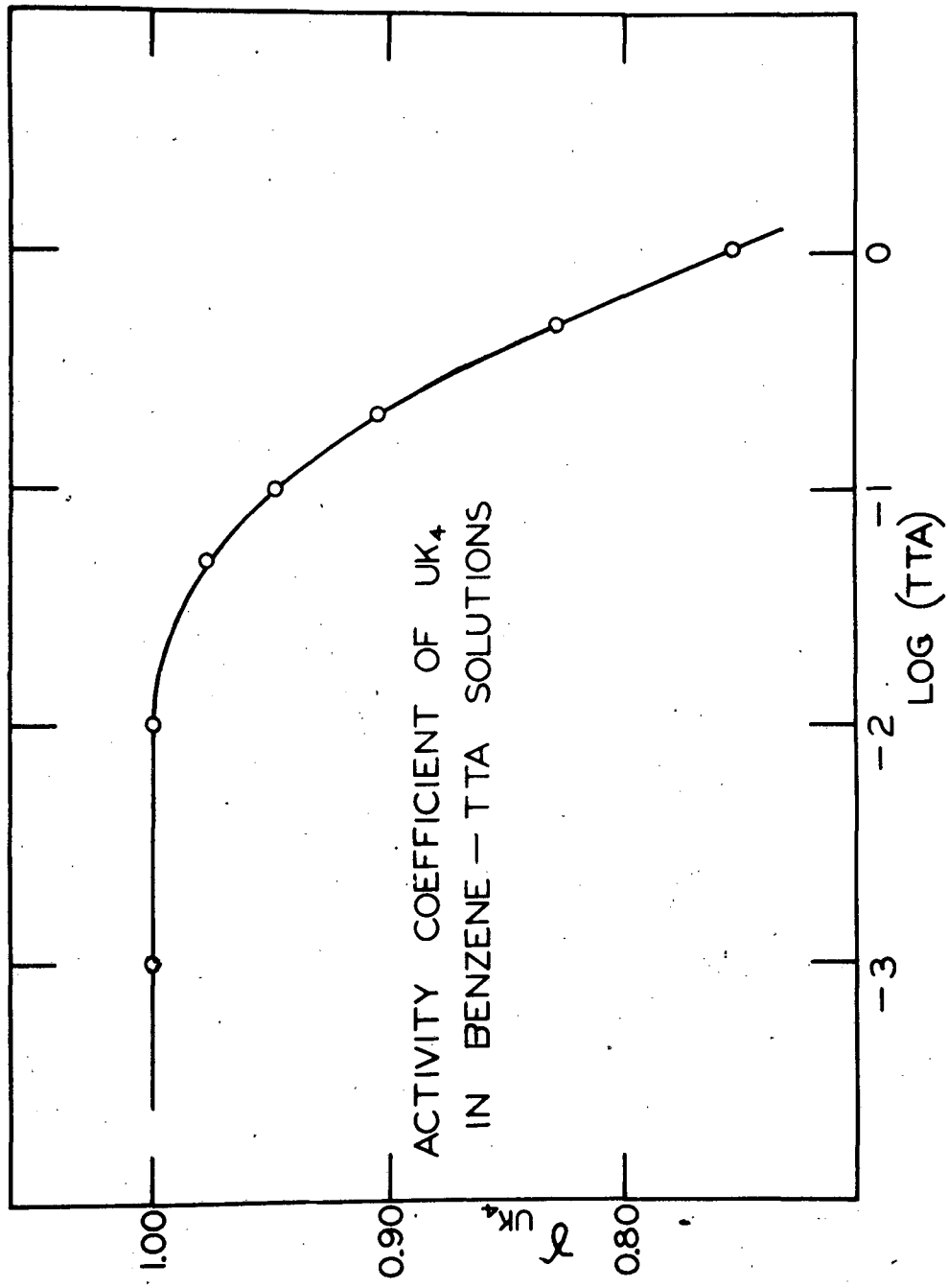
An interesting comparison can be made between the activity coefficients of TTA[7] and those of UK_4. It is found that within

(7) E. L. King and W. H. Reas, BC-69, July 7, 1947.

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.

Figure 6


ACTIVITY COEFFICIENT OF UK_4
IN BENZENE — TTA SOLUTIONS
1.00
0.90
0.80
γ_{UK_4}
-3
-2
-1
0
LOG (TTA)

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