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THE AQUEOUS CHEMISTRY OF ZIRCONIUM

By

R. E. Connick and W. H. McVey

March 1, 1948

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THE AQUEOUS CHEMISTRY OF ZIRCONIUM

R. E. Connick and W. H. McVey

March 1, 1948

AbstractCLASSIFICATION CANCELLED BY AUTHORITY
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A system involving a two phase equilibrium was used to study the chemistry of zirconium in the +4 oxidation state in dilute acid solution. The equilibrium studied was one between the various zirconium species in an aqueous phase and the thenoyltrifluoroacetone chelate of zirconium in a benzene phase.

From this study it was shown that the zirconium species in 2.00 M perchloric acid is principally $ZrOH^{+3}$ which hydrolyzes further at lower acidities to form $Zr(OH)_2^{+2}$.

Equilibrium quotients were obtained for the equilibria existing between $ZrOH^{+3}$ and zirconium species complexed by one and two sulfate groups in 2.00 M $HClO_4$. It was established that in a 2.00 M solution, 0.015 M in bisulfate ion, there is an average of one sulfate group per zirconium and two sulfate groups per zirconium at a bisulfate concentration of 0.2 M.

The fluoride complexes of zirconium in 2.00 M $HClO_4$ were found to be by far the most stable of any of the complexes studied. Values for the equilibrium quotients for reactions involving complexing of zirconium by one, two and three fluoride ions were obtained. At a hydrofluoric acid concentration of 2×10^{-5} M, there is an average of one fluoride group per zirconium; at 3×10^{-4} M, an average of 2 fluoride ions per zirconium and at 10^{-2} M hydrofluoric acid an average of three fluorides attached to each zirconium.

The oxalate complex of zirconium is very stable even in 2 M $HClO_4$, whereas the next three members of the aliphatic, dibasic acids show little tendency toward complexing. Chloride and nitrate ions form only weak zirconium complexes of nearly equal stability.

Introduction

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Zirconium is one of the principal fission products formed in the fission of uranium, thorium and plutonium. Its chemistry is of importance in many of the problems associated with the development of atomic energy. Since little is known of the aqueous solution chemistry of zirconium, it was believed worthwhile to identify the zirconium species present in solution under a variety of conditions. This study involves the determination of the species present and the equilibria existing between these species in solutions containing various complexing agents and in solutions of varying acidities.

The existing information on the aqueous solution chemistry of zirconium is very slight. The book "Zirconium and its Compounds" by Francis P. Venable, American Chemical Society Monograph Series, New York, 1921, purports to cover the literature up to 1921, though the book deals only briefly with the aqueous chemistry of zirconium. The most recent survey of the literature may be found in Pascal, "Traite de Chimie Minerale", 1931-2. In addition there are many articles on zirconium in the literature; however, nearly all of them are concerned with the identification of solid phases rather than the species in solution.

When normal salts of Zr(IV) are dissolved in water, the solutions become acidic, indicating hydrolysis with the formation of $Zr(OH)_n^{+(4-n)}$, usually written as zirconyl ion ZrO^{++} , when $n = 2$. Conductivity measurements have been carried out on solutions, made quarter normal in zirconyl chloride¹,

¹R. Ruer, Z. Anorg. Chem., 43, 85 (1905)

as a function of time. There is a rapid initial increase in specific con-

ductivity which nearly levels off in one hour and then shows a slow but steady increase for a period of 168 hours longer. The increase in conductivity is caused by the hydrolysis of the zirconyl ion, which produces hydrogen ion. The fact that the hydrolysis proceeds at a measurable rate indicates that hydrolyzed species containing many zirconiums are being formed. It is not feasible to interpret the data in terms of specific species. Nor is it possible to tell whether ZrO^{++} is at all hydrolyzed as a monomer, i.e., with only one zirconium per ion.

By dissolving a zirconyl salt in water and measuring the hydrogen ion concentration, it should be possible to determine the degree of hydrolysis of ZrO^{++} . The data reported in the literature² for such measurements indicate

²A. W. Laubengayer and R. B. Eaton, J. Am. Chem. Soc., 62, 2704 (1940).

that the zirconyl ion is hydrolyzed to $ZrO(OH)^+$ in solutions ranging from 0.01 to 10^{-4} M $ZrOCl_2$ in 0.1 M KCl. The extent of colloid formation was not determined; if colloidal material was present the above interpretation would have to be modified.

Evidence that has been cited for the existence of ZrO^{++} , even in solutions of high acidity, is the formation of -yl type compounds precipitated out of solution on the addition of acid. For example, $ZrOCl_2 \cdot 8 H_2O$ is precipitated when concentrated hydrochloric acid is added to a Zr(IV) solution.

The published complex-ion chemistry of zirconium is very meagre. Evidence has been claimed for the existence of complex ions of the type $ZrO(SO_4)_2 = ^3$ and $ZrOCl_4 = ^4$. However the data could be interpreted equally

³R. Ruer. Z. anorg. allgem. chem. 42. 87 (1904); 43, 85, 282 (1905); 46, 449, 456 (1905).

⁴W. Pauli and M. Adolf, Kolloid - Z., 29, 173 (1921).

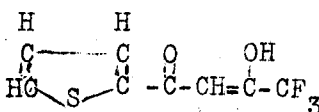
well by assuming other species.

Many qualitative results reported in the literature indicate the formation of zirconium complexes with negative ions such as oxalate, tartrate, carbonate, fluoride, sulfate, nitrate, etc., but in no case have quantitative results been obtained nor the species identified unambiguously.

Experimental Method

The method employed in the present study of hydrolysis and complexing of zirconium in the +4 state in aqueous solution is one involving the use of a two phase system, an aqueous phase and a benzene phase containing a chelating agent, thenoyltrifluoroacetone. (The term TTA will be used for thenoyltrifluoroacetone, when it is referred to in the text, and HK will be used to designate it in equations for chemical reactions.) The metal ion remains uncomplexed by this chelating agent in aqueous solutions at low chelate concentrations, but forms a chelate compound which is soluble in the organic phase and which is in equilibrium with whatever species exist in the aqueous phase. Thus, the zirconium species present in a solution containing a substance which forms a complex ion with zirconium can be determined by measuring the relative concentrations of zirconium in the benzene and aqueous phases as a function of the concentration of the complexing agent. The formation of a zirconium complex in the aqueous phase will be reflected in a decrease in the extraction of the zirconium into the benzene phase. The method of interpreting the experimental results of such measurements in terms of the zirconium species present will be described in detail later.

The chelating agent, thenoyltrifluoroacetone (TTA), is a weak acid having the following structure in the enol form, the acid hydrogen being the



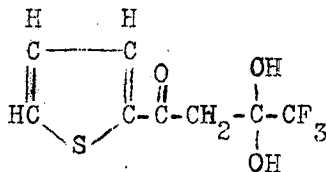
one attached to the oxygen. The acid ionization constant⁵ is 6.8×10^{-7} .

⁵E. Zebroski, BC-63, July 1, 1947.

The activity coefficient of TTA in benzene has been determined by King and Reas⁶; it does not differ significantly from unity until the concentration

⁶E. L. King and W. H. Reas, BC-69, July, 1947.

of TTA in the benzene phase is greater than 0.01 M. The distribution coefficient of TTA between benzene and dilute hydrochloric acid solution, at low TTA concentrations, is 40, i.e., $\frac{(\text{TTA})_b}{(\text{TTA})_{aq}} = 40$. The distribution coefficient increases with increasing concentration of TTA, probably due, at least in part, to dimerization in the benzene phase; but this increase is simply expressed as a change in the activity coefficient. When TTA is equilibrated between dilute acid and benzene, the main species in the aqueous phase is the hydrate,



while in the benzene phase, about 15% of the TTA occurs in the hydrate form and about 85% occurs in the enol form. The change in relative amounts of these two species as a function of TTA concentration, is, of course, also taken care of by the activity coefficient of TTA in benzene. The keto form apparently is not an important species in this system.

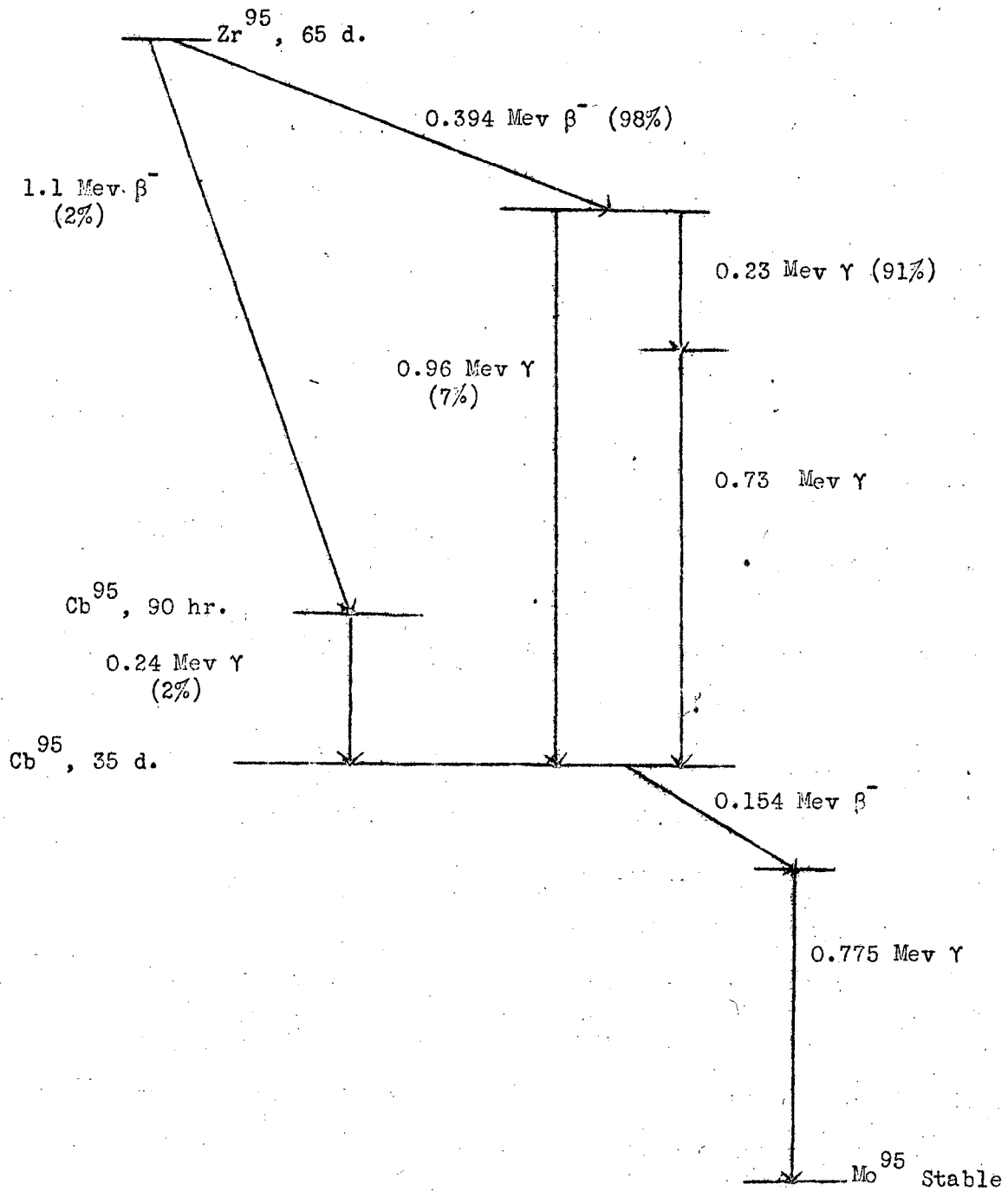
The neutral molecule, ZrK_4 , which is extracted into the benzene phase, is formed through coordination by the zirconium of the two oxygens on each of the four ionized TTA groups. Compounds of this type, formed by coordination of two or more atoms of the same ion or molecule are known as chelate compounds ($\chi \eta \lambda \eta$, a crab's claw).

Most of the experiments were carried out using trace concentrations of carrier-free radioactive zirconium. Some experiments were run with macro concentrations of inactive zirconium and, with a few, both radioactive zirconium and macro amounts of inactive zirconium were employed. The source of macro zirconium was City Chemical Corporation's $ZrOCl_2 \cdot 6H_2O$ which was recrystallized several times from concentrated hydrochloric acid to give relatively large needles of pure white $ZrOCl_2 \cdot 8H_2O$. This was dissolved to give a concentration of 0.1 M Zr(IV) in 1.00 M $HClO_4$, making the solution 0.2 M in chloride ion. The solution was clear, giving only a slight Tyndall beam, and remained so over a period of several months.

The radioactive zirconium decays according to the scheme on the following page. The carrier-free tracer was received from Oak Ridge in 5% oxalic acid. This solution was made about 10 M in nitric acid and a small amount of 0.1 N $KMnO_4$ was added. Manganese dioxide, which precipitated, carries columbium but not zirconium. This process was repeated several times, the $KMnO_4$ being reduced by water in the later precipitations. The purification served the dual purpose of eliminating both the oxalic acid and the columbium. The zirconium was further purified from columbium by diluting the nitric acid to about 1 M, extracting the zirconium into a benzene-TTA solution, and washing the benzene phase repeatedly with 2.0 M $HClO_4$. This treatment was used to eliminate nitric acid also, since it was desired to have the tracer in perchloric acid. Finally, the TTA was diluted ten-fold with benzene and the zirconium was re-extracted into a small volume of 2.00 M $HClO_4$.

A colorimetric method of analysis was used for measuring the concentration of macro zirconium. The method, developed by Liebhafsky and Winslow⁷,

⁷H. Liebhafsky and E. Winslow, J. Am. Chem. Soc., 60, 1776 (1938).

Decay Scheme of Zr^{95} 

is capable of determining quantitatively a few micrograms of zirconium.

Briefly, the method consists of adding an alcoholic solution of alizarin to a dilute aqueous acid solution of zirconium. Zirconium forms with alizarin a colored lake, colloidal in nature, which absorbs light at 5600 \AA much more strongly than pure alizarin. The solution is made basic with ammonium hydroxide, to speed the process of lake formation, after which it is re-acidified and diluted to a volume of 25 ml with alcohol. The solution is next placed in a 5 cm cell and the light absorption measured on a Beckman Spectrophotometer against an alcohol blank.

The reproducibility of the alizarin analysis was fairly good, of the order of 3%. However, the process of lake formation was much slower in the presence of TTA. The apparent concentration of zirconium increased slowly over a period of several hours. Several attempts were made to improve the analysis of zirconium in the benzene phase by destruction of the TTA through addition of Br_2 or Cl_2 and by hydrolysis of the TTA through warming the solution with sodium hydroxide. None of the methods tried was successful. The spectrophotometer reading used for calculating the zirconium concentration was the constant value obtained after the solution had stood for some time.

The analysis for zirconium in the experiments where it was present in trace concentrations was carried out by the usual radioactive counting methods. Aliquots from both phases, usually 0.100 ml in size, were mounted on 22 mm square glass cover slides and counted on either a Geiger counter or a vibrating reed electrometer equipped with a Brown recording potentiometer. The reproducibility of these analyses was generally of the order of 2 to 3%. The samples were counted through approximately 10 mg per cm^2 aluminum absorbers in an effort to cut down the activity due to columbium which grows into the sample from zirconium. This was not as successful as initially

expected, as will be explained later. The activity and the counting times used were such as to give a probable counting error of about 0.7% on those experiments where the extraction coefficients were of the order of unity.

Most of the experiments were carried out in perchloric acid solution. G. Frederick Smith, double vacuum distilled perchloric acid was used and diluted to approximately 2 M with conductivity water. The solution was standardized using the mercuric oxide-potassium iodide method and adjusted to 2.000 M perchloric acid. The hydrolysis experiments were carried out in mixtures of perchloric acid and lithium perchlorate. G. Frederick Smith $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ was crystallized once from water and a solution in conductivity water was made up from this solid. The solution was analyzed by evaporating 5 ml aliquots with sulfuric acid, igniting and weighing as anhydrous lithium sulfate. The solution was 1.958 M in lithium perchlorate. The various solids and solutions used in the complexing experiments were of at least cp-grade and were used without further purification.

The TTA, which was kindly supplied by Dr. James C. Reid, was vacuum distilled and therefore believed to be quite pure.

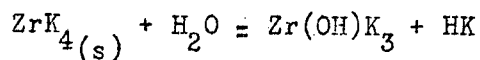
The experiments herewith described were carried out by mixing the two phases, aqueous and benzene, in 100 ml volumetric flasks, the volume of each phase being 25 ml. The shaking was done by a mechanical shaker so arranged that the flask containing the two phase system was immersed in a water thermostat at $25.00 \pm 0.05 \text{ C}^\circ$. The shaking was quite vigorous, the flasks going through 1520 up and down movements per minute with a stroke of 2.5 cm. It was found necessary to coat the ground glass stopper with paraffin since there was a preferential loss of the aqueous phase upon shaking. This was presumably due to the fact that benzene will not pass through a porous glass surface which has been wet by water.

All concentrations are expressed in moles of solute per liter of solution

at room temperature.

Dependence of the Extraction Coefficient on the TTA Concentration

One of the first pieces of information required is the formula of the chelate species present in the benzene phase. It is also necessary to know if the zirconium species in the aqueous phase is complexed to an appreciable extent by the chelating agent. The formula of the chelate species in the benzene solution may be determined by measuring the solubility of the solid zirconium chelate in benzene as a function of the TTA concentration. The composition of the solid chelate must also be known. Thus, assuming the solid chelate to be ZrK_4 , its solubility in benzene should remain constant as the TTA concentration is varied (except for small activity coefficient corrections), if the zirconium species dissolved in the benzene phase is ZrK_4 . If the dissolved species is $Zr(OH)K_3$, the solubility should vary inversely as the TTA concentration, at constant activity of water as shown by the equation:



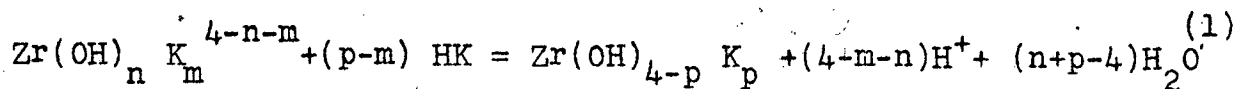
$$K = (Zr(OH)K_3)(HK).$$

Various other solubility relationships would be obtained if other species were present in the benzene phase or if the composition of the solid were other than that assumed above.

The number of chelate groups attached to the zirconium species in the aqueous phase could be determined in a similar fashion by studying the solubility of the chelate in an aqueous solution of constant acidity but varying TTA concentration.

Another method for determining the formula of the zirconium species in the benzene phase and the number of ketones in the zirconium species in the

aqueous phase depends on measuring the extraction coefficient of zirconium as a function of the TTA concentration at constant acidity. This is the method which was actually used. The reaction may be written:



and we may define the equilibrium constants:

$$K_{m,n,p} = \frac{[\text{Zr(OH)}_{4-p} \text{K}_p] [\text{H}^+]^{4-m-n} [\text{H}_2\text{O}]^{n+p-4}}{[\text{Zr(OH)}_n \text{K}_m^{4-n-m}] [\text{HK}]^{p-m}} \quad (2)$$

Brackets have been used to indicate activities of the enclosed species.

The designation of the phase in which each species exists has been omitted to simplify the writing of the equation. The species $\text{Zr(OH)}_n \text{K}_m^{4-n-m}$ and H^+ occur in the aqueous phase while the species $\text{Zr(OH)}_{4-p} \text{K}_p$ and HK are components of the benzene phase. The letter K has been used to indicate both an equilibrium constant and the ion of TTA, however there should be no confusion as in the latter case it will always appear within brackets.

An extraction coefficient expressed in terms of activities is defined as:

$$E_a = \frac{\sum_p [\text{Zr(OH)}_{4-p} \text{K}_p]}{\sum_n \sum_m [\text{Zr(OH)}_n \text{K}_m^{4-n-m}]} \quad (3)$$

From equation (2) the following relationship holds:

$$[\text{Zr(OH)}_n \text{K}_m^{4-n-m}] = \frac{[\text{ZrK}_4] [\text{H}^+]^{4-m-n} [\text{H}_2\text{O}]^n}{K_{m,n,4} \text{HK}^{4-m}} \quad (4)$$

From equations (2) and (4)

$$\frac{[\text{ZrK}_4] [\text{H}^+]^{4-m-n} [\text{H}_2\text{O}]^n}{K_{m,n,4} [\text{HK}]^{4-m}} = \frac{[\text{Zr(OH)}_{4-p} \text{K}_p] [\text{H}^+]^{4-m-n} [\text{H}_2\text{O}]^{n+p-4}}{K_{m,n,p} [\text{HK}]^{p-m}} \quad (5)$$

Solving for the activity of the general species in the benzene phase:

$$\left[\text{Zr}(\text{OH})_{4-p} K_p \right] = \frac{[\text{ZrK}_4] [\text{H}_2\text{O}]^{4-p} K_{m,n,p}}{[\text{HK}]^{4-p} K_{m,n,4}} \quad (6)$$

Since this equation holds for any set of values of m and n , we shall for simplicity choose m and n to be zero. Then

$$\left[\text{Zr}(\text{OH})_{4-p} K_p \right] = \frac{[\text{ZrK}_4] [\text{H}_2\text{O}]^{4-p} K_{0,0,p}}{[\text{HK}]^{4-p} K_{0,0,4}} \quad (7)$$

Substituting equations (7) and (4) into equation (3), one obtains:

$$E_a = \frac{\sum_p \frac{[\text{ZrK}_4] [\text{H}_2\text{O}]^{4-p} K_{0,0,p}}{[\text{HK}]^{4-p} K_{0,0,4}}}{\sum_m \sum_n \frac{[\text{ZrK}_4] [\text{H}^+]^{4-m-n} [\text{H}_2\text{O}]^n}{K_{m,n,4} [\text{HK}]^{4-m}}} \quad (8)$$

The factor $[\text{ZrK}_4]$ cancels completely between the numerator and denominator. Taking the partial derivative of the logarithm of E_a with respect to the activity of HK gives:

$$\frac{\partial \ln E_a}{\partial [\text{HK}]} = \frac{\sum_p \frac{(p-4) [\text{H}_2\text{O}]^{4-p} K_{0,0,p}}{[\text{HK}]^{5-p} K_{0,0,4}}}{\sum_p \frac{[\text{H}_2\text{O}]^{4-p} K_{0,0,p}}{[\text{HK}]^{4-p} K_{0,0,4}}} - \frac{\sum_m \sum_n \frac{(m-4) [\text{H}^+]^{4-m-n} [\text{H}_2\text{O}]^n}{K_{m,n,4} [\text{HK}]^{5-m}}}{\sum_m \sum_n \frac{[\text{H}^+]^{4-m-n} [\text{H}_2\text{O}]^n}{K_{m,n,4} [\text{HK}]^{4-m}}} \quad (9)$$

Multiplying both sides of the equation by $[\text{HK}]$ and substituting from equations (7) and (4), one obtains:

$$\frac{\partial \ln E_a}{\partial \ln [\text{HK}]} = \frac{\sum_p (p-4) \left[\text{Zr}(\text{OH})_{4-p} K_p \right]}{\sum_p \left[\text{Zr}(\text{OH})_{4-p} K_p \right]} - \frac{\sum_m \sum_n (m-4) \left[\text{Zr}(\text{OH})_n K_m^{4-m-n} \right]}{\sum_m \sum_n \left[\text{Zr}(\text{OH})_n K_m^{4-m-n} \right]} \quad (10)$$

Limits may be placed on the values of m and p on the basis of the size of

the zirconium ion. It is found both theoretically and experimentally that the maximum coordination number of Zr^{4+} for oxygens never exceeds eight. Assigning two coordination positions to each chelate group then limits the maximum possible number values of m and p to four. With this assumption equation (10) may be rewritten in the following form:

$$\frac{\partial \ln E_a}{\partial \ln(HK)} = -4f_0 - 3f_1 - 2f_2 - f_3 + 4f_0' + 3f_1' + 2f_2' + f_3', \quad (11)$$

where each f is the sum of the activities of all species containing the number of chelate groups indicated by the subscript, divided by the total activity of all zirconium species in that phase. The unprimed f 's refer to the benzene phase and the primed f 's to the aqueous phase. Thus each f is the fraction of the total activity contributed by species containing the indicated number of chelate groups. It should be pointed out that in performing the differentiation leading to equation (11), it was necessary that the activity of water and of hydrogen ion remain constant.

An equation having exactly the same form as equation (11) may be derived on the basis of concentrations rather than activities. In this case the equilibrium quotients and the extraction coefficient are expressed in terms of concentrations. Equations (10) and (11) then become:

$$\frac{\partial \ln E_p}{\partial \ln(HK)} = \frac{\sum_p (p-4) (Zr(OH)_{4-p} K_p)}{\sum_p (Zr(OH)_{4-p} K_p)} - \frac{\sum_m \sum_n (m-4) (Zr(OH)_{n,m}^{4-m-n})}{\sum_m \sum_n (Zr(OH)_{n,m}^{4-m-n})} \quad (12)$$

and

$$\frac{\partial \ln E_c}{\partial \ln(HK)} = -4f_0 - 3f_1 - 2f_2 - f_3 + 4f_0' + 3f_1' + 2f_2' + f_3'. \quad (13)$$

In these equations E_c is defined as the ratio of the sum of the concentrations of all the zirconium species in the benzene phase to the sum of the

concentrations of all the zirconium species in the aqueous phase, and parentheses are used to represent the concentration of the enclosed species. In equation (13) each f is that fraction of the total concentration which is derived from species containing the indicated number of chelate groups. Primes indicate the aqueous phase.

Equation (13) applies to the experimental conditions that the activity coefficients of all species in the aqueous and benzene phases remain constant and that the concentration of hydrogen ion be unchanged as the TTA concentration varies.

A third equation having the same form as the previous two may be derived using activities for the species in the benzene phase and concentrations for the species in the aqueous phase. This form of the equation will be most useful in interpreting the results of the experiments on the dependence of the extraction coefficient on TTA concentration, since the activity coefficients of the species entering into the reaction in the aqueous phase remain constant while those in the benzene phase do not as the TTA concentration is varied. The equations now take the form

$$\frac{\partial \ln E'}{\partial \ln [HK]} = \frac{\sum_p (p-4) [Zr(OH)_{4-p} K_p]}{\sum_p [Zr(OH)_{4-p} K_p]} - \frac{\sum_m \sum_n (m-4) (Zr(OH)_n K_m^{4-m-n})}{\sum_m \sum_n (Zr(OH)_n K_m^{4-m-n})} \quad (14)$$

and

$$\frac{\partial \ln E'}{\partial \ln [HK]} = -4f_0 - 3f_1 - 2f_2 - f_3 + 4f_0' + 3f_1' + 2f_2' + f_3' \quad (15)$$

In these equations, E' is defined as the ratio of the sum of the activities of the zirconium species in the benzene phase to the total concentration of all zirconium species in the aqueous phase. Brackets are used to represent activities and parentheses to represent concentrations, as before. In equation (15) each f represents the fraction contributed to the total activity

by species in the benzene phase having the number of chelate groups indicated by the subscript, and each f' represents the fraction contributed to the total concentration by species in the aqueous phase having the indicated number of chelate groups.

Equation (15) is valid for the experimental conditions where the activity coefficients of the species entering into the reaction in the aqueous phase do not change and where the hydrogen ion concentration remains constant as the activity of TTA varies. These experimental conditions correspond to the ones used in the determination of the dependence of the extraction coefficient on TTA activity, but unfortunately only E_c and not E' can be determined experimentally. Therefore it is necessary to make an assumption about the activity coefficients of the zirconium species in the benzene phase before a relation between E' and E_c may be established.

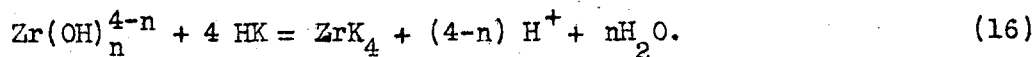
The activity coefficients of the individual zirconium chelate species in the benzene phase as a function of the TTA concentration are not known. However Reas⁸ has measured the solubility of the uranium chelate, UK_4 ,

⁸W. H. Reas, unpublished work.

in benzene as a function of the TTA concentration, which he expressed in terms of a gross activity coefficient. He found that the activity coefficient of UK_4 in benzene solution does not vary greatly from unity in the range of concentrations of TTA which was used in this work. Due to the lack of information concerning the individual zirconium chelate species in benzene, it will be assumed that the activity coefficients of all the species vary in the same way and further that the zirconium chelate species behave in the same manner as do the uranium chelate species in benzene solution with varying concentrations of TTA. Since the variation in the activity coefficient of the uranium chelate with TTA concentration is small, no appreciable

error should be introduced by this assumption. On this basis, the relation between E_c and E' is given by the equation $E' = E_c \gamma_{ZrK_4}$, where γ_{ZrK_4} is assumed to be equal to the activity coefficient of the uranium (IV) chelate in benzene. The quantity E_c , which is the ratio of the total concentration of zirconium species in the benzene to the total concentration of zirconium species in the aqueous phase, is an experimentally measurable quantity.

Equation (15) gives a relationship between the change of extraction coefficient, E' , with changing TTA activity and the zirconium chelate species present in both phases. From the slope of the line obtained by plotting the logarithm of the extraction coefficient E' versus the logarithm of the activity of the TTA, one should be able to identify the zirconium chelate species present in the benzene phase and in the aqueous phase. (Of course experiments in which only the TTA activity is varied provide no information about the number of hydroxide groups or other anions associated with the various zirconium species). However, for any slope less than four, a number of combinations of the various f 's would fit the data. The important thing is that should the slope be four, there is only one combination which will fit the data and that is for all of the f 's to be zero, and all of the f 's to be zero except f'_0 which must be unity, i.e., $p=4$ and $m=0$. Then the equation for the reaction must be written:



As the set of experiments described below actually shows the slope in question to be four, it may be concluded that the species in the benzene phase is ZrK_4 and that complexing of zirconium by TTA in the aqueous phase is not significant under the experimental conditions used.

Experiments on TTA Dependence of Extraction Coefficient

The following experiments, designed to test the dependence of the extraction coefficient on the TTA concentration, were run in 2.00 M HClO_4 at various TTA concentrations. The experimental conditions and results are presented in Table 1. In the first column are given the TTA concentrations in the benzene phase at equilibrium, calculated from the known initial concentration of the added TTA and a distribution ratio of 35 for TTA between the benzene phase and the aqueous phase. (The distribution coefficient of TTA between benzene and 0.1 M hydrochloric acid is 40^6 .) In column two are listed values of the activity coefficient of TTA^6 corresponding to the concentrations in column one. Reas⁸ found that the activity coefficient of uranium (IV) chelate in benzene at various TTA concentrations was, within experimental error, the same as for TTA itself, hence the values of column two also represent γ_{ZrK_4} in benzene. In column three are given the concentrations of zirconium in the benzene and aqueous phases as determined from the zirconium radioactivity. In columns four and five are listed the values of the activity of TTA and E' , calculated from the relationships $[\text{HK}] = (\text{HK}) \gamma_{\text{HK}}$ and $E' = E \gamma_{\text{ZrK}_4}$, respectively. The logarithms of the values of the activity of TTA and E' are given in columns six and seven and are plotted in Figure 1. In the experiments of Table 1 and all following experiments, both phases were analyzed as a function of time in order to be sure that equilibrium had been established.

Table 1

Dependence of Extraction Coefficient on TTA Activity
Trace Concentrations of Zirconium, 2.00 M HClO_4 , 25°C

$(\text{HK})_b$	$\gamma_{\text{HK}} = \gamma_{\text{ZrK}_4}$	E_c	$[\text{HK}]$	E'	$\text{Log} [\text{HK}]$	$\text{log } E'$
0.00506	0.999	0.046	0.005051	0.046	-2.2966	-1.337
0.00583	0.998	0.090	0.00582	0.0898	-2.2351	-1.047
0.00778	0.997	0.258	0.00776	0.257	-2.1101	-0.590
0.00972	0.996	0.65	0.00968	0.647	-2.0141	-0.189
0.01361	0.992	2.19	0.01350	2.17	-1.8697	0.337
0.01673	0.988	4.45	0.01653	4.40	-1.7817	0.644
0.01945	0.986	6.8	0.01918	6.70	-1.7172	0.826
0.02918	0.977	14.3	0.02851	14.0	-1.5450	1.146
0.02839	0.977	45.0*	0.02774	44.0	-1.5569	1.644*

*Value obtained when new aqueous phase was used with same benzene phase of previous experiment, in order to eliminate columbium. Discussion in text.

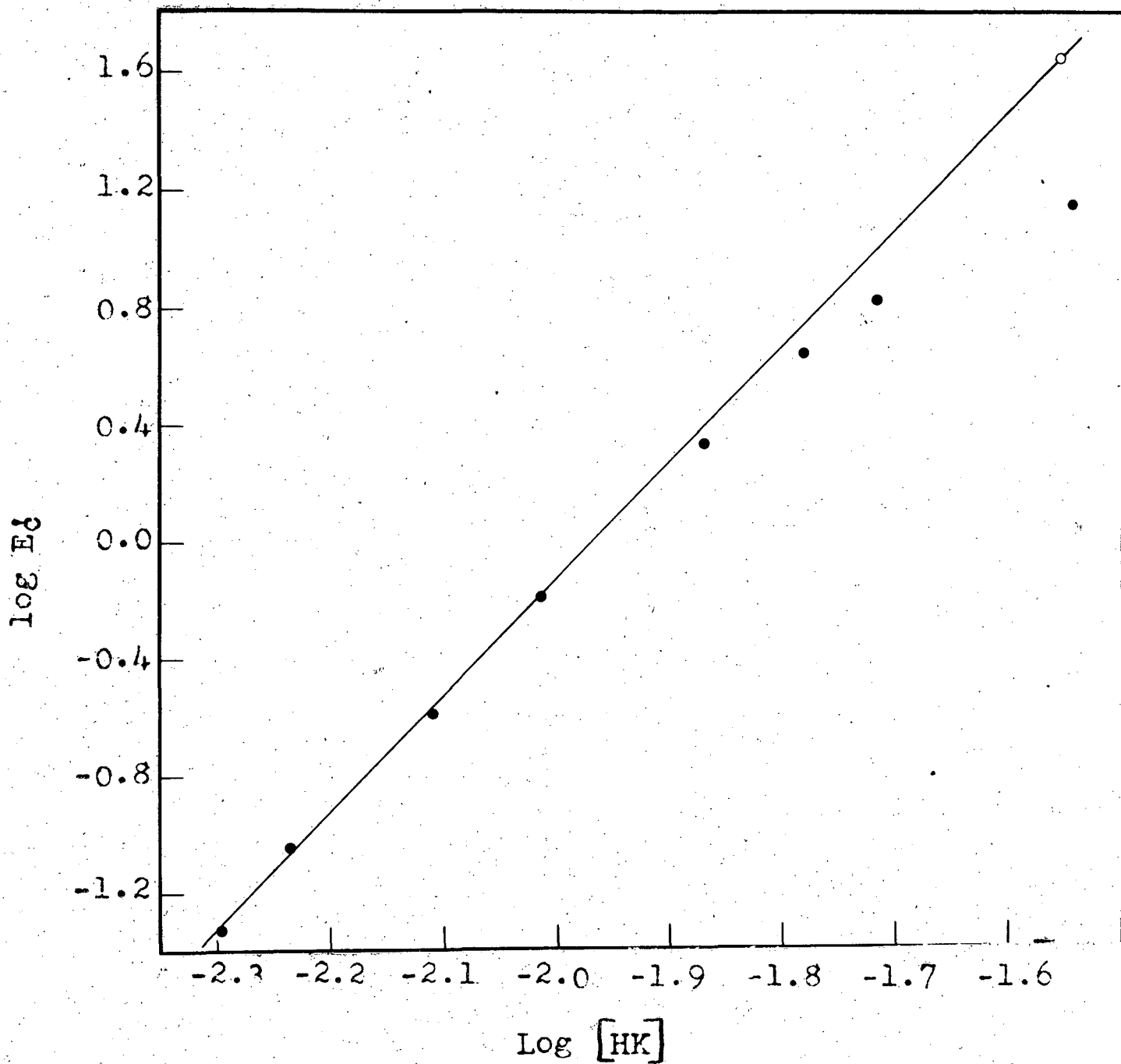


Figure 1.

Dependence of Extraction Coefficient
on TTA Activity.

The straight line in Figure 1 has been drawn with a slope of four. It can be seen that the experimental points indicated by solid circles fit the slope of four within experimental error up to a TTA activity of 10^{-2} M but from here on, the points fall off to a smaller slope. This decrease in slope can be explained in either of two ways. First, one could assume that the TTA is beginning to complex the zirconium in the aqueous phase at the higher TTA activities, thus making the dependence of the extraction coefficient upon the TTA activity less than fourth power. However, the change in slope is so abrupt that, in order to fit the data with a theoretical curve based on chelate complexing in the aqueous phase, it is necessary to assume that the complex being formed in the aqueous phase at high TTA concentrations is the one completely chelated with four TTA groups, the intermediate chelate species being relatively unimportant. It seems unlikely that the chelate species with 1, 2, and 3 groups should not exist with appreciable ranges of stability, as this explanation would require.

A second explanation is that there is a small amount of some non-extractable species present in the aqueous phase which is counted by the Geiger counter, along with the zirconium, in the analysis for the aqueous phase. This substance would not make an appreciable contribution to the analysis of the aqueous phase samples at low extraction coefficients but would become very important at high extraction levels, causing the observed extraction coefficients to be too low. To test this hypothesis, an extraction experiment was run at 0.03 M TTA until equilibrium was reached. The aqueous phase was then removed and replaced with a new 25 ml portion of 2.00 M HClO_4 with the intention that the non-extractable species would have been removed with the first aqueous phase. The system was again equilibrated and the extraction coefficient measured. The apparent extraction coefficient did increase to the value expected for no complexing by TTA in the aqueous

phase, as can be seen from the point marked with an open circle on the plot. Actually, it was possible to calculate that there could have been sufficient columbium present to account for the observed results, the columbium activity having grown into the zirconium tracer solution since the time it had been purified. Sufficient columbium activity would have been recorded by the Geiger counter even though an aluminum absorber was placed between the sample and the Geiger counter tube. Since columbium may be mainly radio-colloidal in these solutions, effects due to its presence would be expected to be irreproducible. The amount of columbium present in any extraction experiment would depend not only on the age of the zirconium stock solution but also on how samples were removed from this stock. Therefore, there is no certain way in which the extraction coefficient can be corrected for effects due to the presence of columbium since the correction would differ from experiment to experiment. The correction due to the presence of columbium in the experiments at low activities of TTA should have been negligible. It is presumed that all points at high TTA activities which deviate from the fourth power slope in Figure 1 would be raised to the line of slope four if the experiments were repeated in the absence of columbium, as was the case with the experiment at 0.03 M TTA.

From the above results, it appears that the complexing of zirconium by TTA, in the aqueous phase, does not occur, or is very slight up to TTA concentrations, in the benzene phase, of 0.03 M (which corresponds to a TTA concentration in the aqueous phase of 8.6×10^{-4} M). The zirconium species in the aqueous phase, then, are uncomplexed by TTA, and the only important species in the benzene phase is ZrK_4 .

Comparison of Extraction Coefficients of Trace and
Macro Amounts of Zirconium

Experiments were performed with macro amounts of zirconium to check the results obtained with trace concentrations. The extraction coefficients should be the same provided there is no colloid or radio-colloid formation and that there are no zirconium species, actually dissolved, which contain more than one zirconium.

In experiments run with macro amounts of Zr(IV), the Zr(IV) concentration was sufficiently high to use up an appreciable amount of TTA on being extracted into the benzene phase. The concentration of free TTA in the benzene phase was then lower than it was before extraction of the zirconium. Comparison of the extraction coefficient obtained using macro concentrations of Zr(IV) with the extraction coefficient obtained using trace concentrations showed the two to have nearly the same value even though the concentration of free TTA in the macro experiment was appreciably lower. The colorimetric analysis in the case of the experiments with macro zirconium was checked by adding radioactive zirconium and carrying out a radioactive analysis. The extraction coefficient of the macro experiment was corrected to the same TTA concentration as used in the trace-concentration experiment, by means of the fourth power dependence of the extraction coefficient on the TTA concentration. It was then found to have a considerably higher value than the extraction coefficient of the trace experiment. It was thought that this might be due to the presence of an impurity which was complexing the zirconium in the aqueous phase and thus lowering the extraction coefficient in the experiments where trace concentrations of Zr(IV) were used. It was further necessary to assume that the concentration of the impurity was of the same order of magnitude or smaller than the concentration of Zr(IV) used in the

macro-concentration experiment so that an appreciable amount of the impurity could have been used up by the zirconium, thus raising the extraction coefficient.

To test this hypothesis, a set of three experiments was run in which 5.1×10^{-4} M Zr(IV) was used in one, about one-tenth this concentration was used in another, and no macro zirconium was added to the third. Radioactive zirconium was added to all three. The results of the experiments are given in Table 2.

Table 2.

Extraction Coefficients at Various Concentrations
of Zirconium(IV).

2.00 M HClO₄, 25°C, 0.0100 M total, initial TTA

(Zr(IV))	E	E _{corr.}
trace	0.580	0.580
4.7×10^{-5} M	0.70	0.74
5.1×10^{-4} M	0.559	0.911

In the first column is listed the total concentration of zirconium present in both phases; in the second, the observed extraction coefficient; and in the third, the extraction coefficient corrected to the value it would have if the free TTA concentration were the same as in the trace experiment. If it is assumed that the total amount of impurity is the same in all three experiments, certain deductions may be made. Since the extraction coefficients of the two macro experiments are higher than that of the trace experiment, an appreciable fraction of the impurity must have been used up in these two experiments. Yet, not all of it could have been tied up in the middle experiment, as otherwise there would have been no change in the extraction coefficient in going to the last experiment. Therefore the concen-

tration of the impurity must be of the order of 10^{-4} to 10^{-5} M. Further it may be concluded that the extraction coefficient in the last experiment is near the value that would be obtained in the absence of the impurity and that about 40 percent of the Zr(IV) in the aqueous phase is complexed by the impurity in the trace experiment.

A second type of experiment was carried out in which, after the system was equilibrated, the two phases were separated and the benzene phase re-equilibrated with a new aqueous phase and the aqueous phase re-equilibrated with a new benzene-TTA phase, both phases having the same composition used originally. If the impurity had originally been present in one phase and had transferred to the other phase during the first equilibration, then, in the second two experiments, one should have given a higher extraction coefficient and the other a lower extraction coefficient than was obtained in the initial equilibration. However, if the impurity is introduced in one of the phases and remains in that phase, the extraction coefficients of the second two experiments should be equal and equal to that of the first experiment. The results of this set of experiments are presented in Table 3.

Table 3

Extraction Coefficients after Separation of Phases
and Re-equilibration with New Phases

2.00 M HClO_4 , 25°C, 0.0100 M total, initial TTA

Experiment	System	E
1	original	0.580
2	new aqueous, old benzene	0.584
3	new benzene, old aqueous	0.523

Since about 2% of the TTA originally in the benzene phase is extracted into the aqueous phase, the extraction coefficients had to be corrected to

take into account the lower TTA concentration in experiment 2. The values of E given in table 3 have been so corrected.

The results of these experiments cannot be adequately explained. The experiment using the new aqueous phase has about the same extraction coefficient as in the original experiment, whereas the experiment using the new benzene phase and the old aqueous phase has an extraction coefficient somewhat smaller. It would appear, however, that most of the impurity must stay in the phase in which it is introduced, throughout the experiments.

A number of substances were used in separate extraction experiments in an effort to establish the identity of the impurity. Of all the substances tried, only sulfate gave the correct complexing power at the concentration believed to be required. However, at this concentration of sulfate, it is quite easy to detect its presence using barium ion. A test of the solutions used in the extraction experiments showed sulfate to be absent.

The complexing power of each of the following substances was tested to see if it could be the impurity: H_2SO_4 , H_3PO_4 , $\text{H}_2\text{C}_2\text{O}_4$, H_3BO_3 , HF, CF_3COOH , H_2SiO_3 , H_2SO_3 , and H_2CO_3 . None except H_2SO_4 had the complexing properties exhibited by the impurity. The data for these experiments are given later.

Several other experiments were run in an attempt to locate the source of the impurity. Benzene from several different sources was used; little or no effect on the extraction coefficient was observed. Two different preparations of TTA were tried, and again no significant difference in the extraction coefficient was found. One extraction was carried out in a quartz vessel with no change in the experimental results being observed.

The radioactivity of the tracer used must be largely that of zirconium since experiments carried out using trace amounts of radioactive zirconium added to macro amounts of inactive zirconium gave the same extraction coefficient, whether it was calculated from the radioactive zirconium analysis

or the macro zirconium analysis.

One possible explanation of the observed results is that there was radio-colloid formation in the trace experiments, i.e., the zirconium was adhering to dust particles in the solution. At high concentrations of zirconium this effect would disappear as there would not be sufficient dust to hold an appreciable part of the zirconium. However, this explanation seems unlikely, as the addition of 0.01 M silicic acid to one of the extraction solutions did not change the extraction coefficient significantly.

If the zirconium were tending to form a true colloid in the aqueous phase with macro concentrations of zirconium, the effect would be just the reverse of that observed; i.e., the extraction coefficient should decrease with increasing concentrations of zirconium. A similar effect would be observed if ionic species containing more than one zirconium were being formed in the aqueous phase.

At the present time neither the identity of the impurity nor the source of the impurity is known. It is believed that the explanation of the results of the experiments of Table 2 does require the presence of an impurity in the system.

The presence of the impurity will, of course, introduce an uncertainty into the interpretation of the data of the trace experiments. The identification of the various zirconium species present in the aqueous phase is believed to be correct, but the calculated stabilities of these species may be somewhat in error. It should be noted that the fourth power TTA dependence of the extraction coefficient would not be affected provided the amount of impurity was the same in all of the TTA dependence experiments.

Hydrolysis Experiments

A set of experiments was run in order to establish the species of zirconium existing in perchloric acid solutions. Perchlorate ion is known to have little or no complexing tendencies, so the zirconium species we are dealing with should be only those complexed by hydroxide groups.

In these experiments the variation of the extraction coefficient was measured as a function of the hydrogen ion concentration.* From this information the number of hydroxide groups attached to the zirconium species in the aqueous phase may be calculated.

In performing the hydrolysis experiments it was necessary to vary the TTA concentration as the hydrogen ion concentration was varied, in order to obtain measurable extraction coefficients. It was assumed that at all of the concentrations of TTA used there was no complexing of the species in the aqueous phase by TTA and that the extraction coefficient varied as the fourth power of the TTA activity. In 2.00 M H^+ , the complexing of the

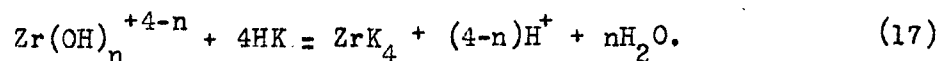
*Similar experiments have been carried out by Tompkins and Broido⁹ for

⁹P. C. Tompkins and A. Broido, MonN-311, June 24, 1947.

hydrochloric acid solutions. However, the experiments were not run at constant ionic strength and therefore cannot be easily interpreted. Further, the results appear to be in error since the extraction coefficient reported for 2 M HCl is a factor of 16 smaller than the extraction coefficient obtained in this work under the same experimental conditions. Presumably some complexing impurity was interfering with the extraction.

aqueous species by TTA has already been shown to be negligible, while it is known from the results of the present section that hydroxide ion does complex zirconium under the same conditions. In the hydrolysis experiments at acidities lower than 2.00 M, the concentration of TTA was always decreased more, relative to the 2.00 M H^+ experiments than was the concentration of hydrogen ion. It therefore seems likely that there would be even less chance in these experiments of having a zirconium complexed by TTA rather than by hydroxide ion.

The equation for the net reaction is



The experiments were carried out in mixtures of lithium perchlorate and perchloric acid at constant ionic strength in the aqueous phase in an attempt to maintain the activity coefficients of the species in the aqueous phase constant. It will be assumed that the activity coefficients of these species did remain constant. It is known that the activity coefficient of hydrochloric acid in lithium chloride solutions does not change from 10^{-3} M HCl to 3 M HCl at a total molality of 3 M^{10} . It is probably safe to

¹⁰ H. S. Harned and B. B. Owen, p. 457, Reinhold Publishing Corporation, New York, (1943).

assume the activity coefficients of perchloric acid and the aqueous zirconium species change very little in this set of experiments.

By determining the dependence of the extraction coefficient on hydrogen ion concentration at constant TTA activity, it should be possible to interpret the data in terms of the number of hydroxide groups in the zirconium species in the aqueous phase. An equilibrium quotient expressed in terms of concentrations may be written for reaction (17).

$$K_n = \frac{(ZrK_4) (H^+)^{4-n}}{(Zr(OH)_n^{4-n}) (HK)^4} \quad (18)$$

and an extraction coefficient in terms of concentrations may be defined

$$E_c = \frac{(ZrK_4)}{\sum_n (Zr(OH)_n^{4-n})} \quad (19)$$

Combining the two equations and carrying out the indicated operations, one obtains

$$\frac{\partial \ln E_c}{\partial \ln (H^+)} = \frac{\sum_n n (Zr(OH)_n^{4-n})}{\sum_n (Zr(OH)_n^{4-n})} - 4. \quad (20)$$

which may be expressed as

$$\frac{\partial \ln E_c}{\partial \ln (H^+)} = -4 + f_1 + 2f_2 + 3f_3 + \dots \quad (21)$$

Each f in equation (21) is equal to that fraction of the total zirconium in the aqueous phase which has the number of hydroxide groups per zirconium indicated by the subscript. In these equations, E_c is the extraction coefficient for a series of experiments in which the activity coefficients of all species remain constant and in which the concentration of TTA is held constant. Actually the TTA concentration was varied along with the hydrogen ion concentration, so it was necessary to correct the experimentally determined E_c to the value that it would have had if the TTA concentration and the activity coefficients of TTA and ZrK_4 had not changed. This corrected value of the extraction coefficient will be denoted as E_c^o and is given by the relationship:

$$E_c^o = \frac{E_c \gamma_{ZrK_4}}{(HK)^4 \gamma_{HK}^4} \quad (22)$$

Equation (20) applies to E_c^o and a plot of the logarithm E_c^o versus the loga-

rithm of the TTA concentration should give a slope corresponding to the number of hydroxide groups on the zirconium minus four.

Experimental Data on Hydrolysis

Most of the hydrogen ion dependence experiments were run using trace concentrations of zirconium, though in a few, macro concentrations were employed. The analysis of the benzene phase in the trace concentration experiments was performed by mounting directly on cover glasses 0.1 ml aliquots from this phase. However, when aliquots from the aqueous phase were mounted directly, there was considerable solid lithium perchlorate present on the cover glass after the solution had evaporated. This caused difficulty in the counting, since the β^- radiation is soft enough so there is appreciable absorption of it by this solid. In order to circumvent this difficulty, the zirconium in the aqueous phase samples was extracted into a benzene-TTA solution and aliquots of this solution were then mounted to give plates free of solid. This procedure also served to minimize the effects due to any columbium present, since the columbium would remain in the aqueous phase by virtue of its lower extraction coefficient. The analysis for zirconium in the experiments in which macro concentrations of zirconium were used was carried out using the alizarin method described previously; the presence of lithium perchlorate apparently causes no difficulty in this analysis.

The experimental conditions and results of the trace concentration experiments are recorded in Table 4. In column one are listed the perchloric acid concentrations used. In column two are given the TTA concentrations in the benzene phase, calculated from the concentrations of the initially added TTA and a distribution ratio of 35. In columns three and four are listed the corresponding activity coefficients and activities of TTA in the benzene phase. The zirconium concentrations in the aqueous and benzene

Table 4

Dependence of Extraction Coefficient on Hydrogen Ion Concentration.

Trace Concentrations of Zirconium, 25°C

(HClO ₄)	(HK) _b	$\gamma_{HK} = \gamma_{ZrK_4}$	[HK] _b	(c/m) _{aq}	(c/m) _b	total c/m	E _c	E _c ^o	log(HClO ₄)	log E _c ^o
2.00	0.00583	0.998	0.00582	5024	494	5518	0.0983	9.56x10 ⁷	0.3010	7.980
1.60	0.00778	0.997	0.00776	4042	2275	6317	0.563	1.55x10 ⁸	0.2041	8.191
1.20	0.00583	0.998	0.00582	3710	1472	5182	0.398	3.46x10 ⁸	0.0792	8.539
0.80	0.00583	0.998	0.00582	2523	3522	6045	1.40	1.22x10 ⁹	-0.0969	9.085
0.40	0.00583	0.998	0.00582	531	4859	5390	9.15	7.95x10 ⁹	-0.3979	9.900
0.24	0.00117	1.000	0.00117	4352	243	4625	0.0558	3.01x10 ¹⁰	-0.6198	10.478
0.080	0.00117	1.000	0.00117	1666	1288	2954	0.772	4.16x10 ¹¹	-1.0969	11.619
0.044	0.00117	1.000	0.00117	932	3963	4895	4.25	2.29x10 ¹²	-1.3565	12.360
0.012	0.00117	1.000	0.00117	70*	2950	3020	42.5	2.29x10 ¹³	-1.9208	13.360
0.080	0.00117	1.000	0.00117	3311	1688	4999	0.510	2.31x10 ¹¹	-1.0969	11.363
0.044	0.00117	1.000	0.00117	1784	3770	5554	1.93	1.04x10 ¹²	-1.3565	12.017
0.012	0.00117	1.000	0.00117	100**	5066	5166	51.0	2.75x10 ¹³	-1.9208	13.439
0.004	0.000389	1.000	0.000389	739	4159	4898	5.63	2.46x10 ¹⁴	-2.3979	14.391

*Based on 0.2 ml aliquot counting 139 c/m.

**Based on 0.5 ml aliquot counting 498 c/m.

Last four experiments carried out in flasks coated with "Dri-film".

phases and the total zirconium concentrations are given in columns five, six and seven in terms of counts per minute, per 0.1 milliliter of solution as determined on a Geiger counter through 13.2 mg/cm² of aluminum. In column eight are listed the extraction coefficients calculated from the data of columns five and six. In column nine are given the values that these extraction coefficients would have had if the TTA were present at unit activity and the activity coefficient of ZrK₄ in the benzene phase had been unity in all the experiments, i.e.,

$$E_c^o = E_c \frac{Y \cdot ZrK_4}{[HK]^4} \quad (22)$$

The logarithms of the values listed in columns one and nine are given in columns ten and eleven and these values are plotted in Figure 2.

The experimental conditions and results of the macro experiments are recorded in Table 5. The perchloric acid concentrations are listed in column one. In columns two and three are listed the zirconium concentrations in the benzene and aqueous phases in moles of zirconium per liter of solution, determined by the alizarin analysis method. The concentrations of free TTA which are listed in column four were calculated by subtracting the amount of TTA used in forming the zirconium chelate, ZrK₄, from the concentration of the initially added TTA and calculating the equilibrium concentration of TTA from this value of the free TTA concentration and a distribution ratio of 35. The remaining columns of this table have the same significance as the corresponding columns in Table 4. The values of the logarithms of E_c^o and the perchloric acid concentration are plotted in Figure 2.

A theoretical curve has been drawn through the experimental points using the following values for the equilibrium constants of the reactions:



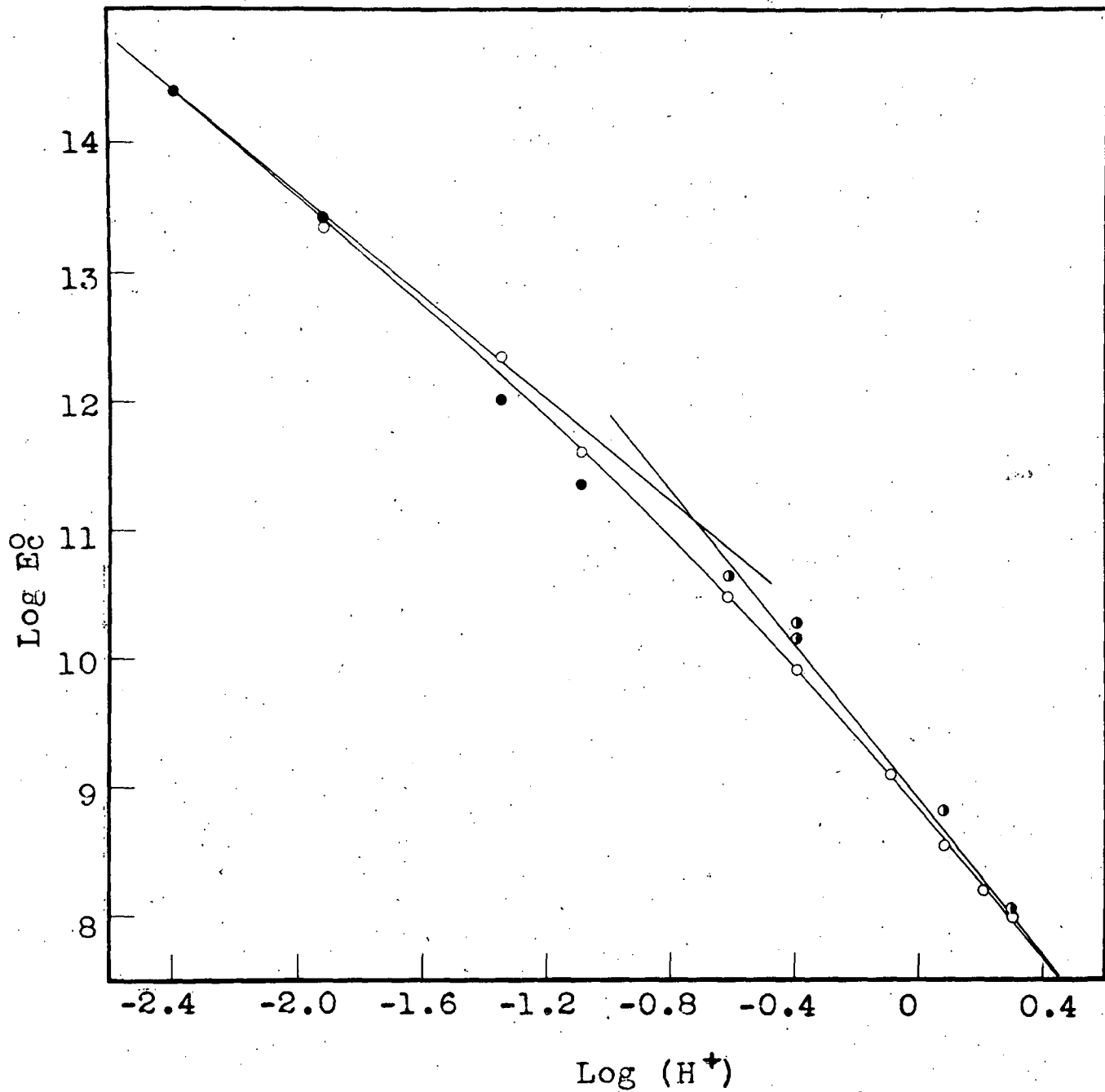


Figure 2

Dependence of Extraction Coefficient
on Hydrogen Ion Concentration.

- Trace Zr, Uncoated Vessel
- Trace Zr, "Dri-Film" Coated Vessel
- ◉ Macro Zr, Uncoated Vessel

Table 5.

Dependence of Extraction Coefficient on Hydrogen Ion Concentration

Macro Concentrations of Zirconium, 25° C.

(HClO_4)	$(\text{ZrK}_4)_b \times 10^4$	$(\text{Zr(IV)}) \times 10^4$	$(\text{HK})_b \times 10^3$	$\gamma_{\text{HK}} = \gamma_{\text{ZrK}_4}$	$(\text{HK})_b \times 10^3$	E_c	E_c°	$\log(\text{HClO}_4)$	$\log E_c^\circ$
1.975	4.63	3.90	10.36	0.995	10.31	1.19	1.05×10^8	0.2956	8.020
1.975	3.01	5.15	8.56	0.996	8.53	0.58	1.10×10^8	0.2956	8.041
1.183	5.60	2.74	7.55	0.997	7.53	2.05	6.34×10^8	0.0730	8.802
0.399	2.41	1.67	2.96	0.999	2.96	1.44	1.87×10^8	-0.3990	10.273
0.399	0.50	3.77	1.75	1.000	1.58	0.13	1.41×10^{10}	-0.3990	10.148
0.241	0.92	3.36	1.58	1.000	1.75	0.27	4.37×10^{10}	-0.6180	10.640

Both equilibrium constants are expressed in terms of concentrations. All other zirconium species were neglected for the purpose of calculating this theoretical curve.

Two limiting slopes have also been drawn in: one with a slope of -3 has been drawn in at an acidity of 2 M and one with a slope of -2 has been drawn in at the lowest acidity. Actually, the theoretical curve was calculated on the basis of these two limiting slopes. As can be seen from equation (21), a slope of -3 corresponds to a zirconium species $\text{Zr}(\text{OH})^{+3}$. Hence it appears as though the principle zirconium species in 2.00 M HClO_4 is the one with only one hydroxide group attached. As mentioned earlier, the zirconium species generally believed to exist, even at much higher acidities than this, is the one with two hydroxide groups attached, or zirconyl ion, ZrO^{++} . It is only at much lower acidities, of the order of 0.005 M in hydrogen ion, that the species of the type $\text{Zr}(\text{OH})_2^{++}$ or ZrO^{++} appears to become important.

As can be seen from the data of Table 4 there is considerable loss of zirconium from solution in the experiments run at acid concentrations of 0.08 M and lower. Most of this zirconium was recovered by washing out the flask with $1 \text{ M H}_2\text{SO}_4$, so it appeared that at these low acidities, zirconium was hydrolyzing onto the glass surface of the extraction vessels. In an effort to minimize the loss due to this effect, the experiments at the lower acidities were repeated using extraction vessels which had been coated with "Dri-film". "Dri-film", which is $\text{SiCl}_2(\text{CH}_3)_2$, hydrolyzes in the presence of the thin film of water which is always present on a glass surface which has been air dried without baking. The hydrocarbon surface which is formed is not wet by water, so there should be little tendency for the zirconium to hydrolyze onto this surface. The possibility of radio-colloid formation on solid impurities in the solution is still present, of course.

The treatment of the flask with "Dri-film" apparently was fairly success-

ful, since it can be seen from Table 4 that there was not nearly so great a loss of zirconium in the experiments at low acidity which were run in the coated flasks.

However, from Figure 2, it will be noted that the experimental points at the lower acidities do not fall on a smooth curve. This is perhaps an indication of radio-colloid formation. To test for the possible presence of a radio-colloid, a small portion of the aqueous phase of the experiment run at 0.012 M perchloric acid in a coated vessel was centrifuged in a clinical centrifuge for 3 1/2 hours using a coated centrifuge cone. There was a decrease in the zirconium concentration of the top layer of about 30%, so there evidently was some radio-colloid present. The presence of zirconium as a radio-colloid in the aqueous phase would have the effect of lowering the extraction coefficient. If the tendency toward colloid formation increased with decreasing acidity, it would make it appear as though the acid dependence were decreasing from third power to second power more rapidly than would be observed if only ionic zirconium were present. This would mean that the ionic species of zirconium with only one hydroxide group attached is important at even lower acidities than would be indicated by these experiments. The location of the experimental points of Figure 2 at acidities lower than 0.1 M are not to be regarded as having any great significance.

From Figure 2 it can be seen that most of the extraction coefficients obtained using macro amounts of zirconium are somewhat larger than those obtained in the trace concentration experiments under the same conditions. The major part of this discrepancy can be attributed to the lowering of the extraction coefficients in the trace experiments by the unidentified impurity, as discussed earlier. In addition, a similar effect would be observed if there is a tendency toward radio-colloid formation in the aqueous phase in the trace concentration experiments. In the experiments run with macro

concentrations of zirconium all of the surface available on solid impurities upon which radio-colloid formation could take place would be exhausted before there was a significant decrease in the ionic zirconium concentration. However, there is no evidence of hydrolysis onto the glass surface at these acidities, so that if radio-colloid formation is the correct explanation for the observed results, there must be a greater tendency for zirconium to hydrolyze onto the solid impurities which may be present than onto a glass surface.

Laubengayer and Eaton² have made pH measurements with a glass electrode on solutions prepared by dissolving zirconyl chloride in 0.1 M potassium chloride. Their results indicate that the hydrolyzed zirconium species present from 10^{-2} M to 10^{-4} M $ZrOCl_2$ is principally $Zr(OH)_3^+$ or a polymer of this species. This is confirmed roughly by the work of Adolf and Pauli¹¹ in which pH measurements were made using a hydrogen electrode.

¹¹M. Adolf and W. Pauli, *Kolloid-Z*, 29, 173 (1921).

The range of zirconyl chloride concentrations studied was from 0.125 M to 0.0022 M. Jander and Jahr¹² measured the diffusion coefficient of 0.1 M

¹² G. Jander and K. F. Jahr, *Kolloid-Beihefte*, 43, 295 (1935).

$ZrO(ClO_4)_2$ in 1 M $NaClO_4$ diffusing into 1 M $NaClO_4$, at acidities ranging from no added perchloric acid to 1.2 M perchloric acid. Over this range of acidity, they found the diffusion coefficient of zirconium(IV) to be only half as great as for solutions of uranyl nitrate. They concluded that there must be polymers formed, containing several zirconiums each. Adolf and Pauli¹¹ measured the freezing point lowering in solutions ranging from 0.125 M to 0.0078 M in zirconyl chloride. The best interpretation of their data is that

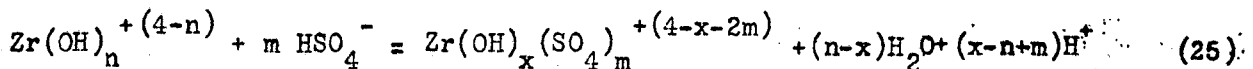
there is both hydrolysis and polymerization of the zirconyl chloride.

In none of the experiments described above were the conditions the same as in the present work. All the experiments mentioned above were carried out using either lower acid concentrations or higher zirconium concentrations, both of which would favor the formation of hydrolyzed polymers. From the results of experiments of the present work in which macro and trace concentrations of zirconium were used, one would conclude that there is no indication of formation of polymers of zirconium under the experimental conditions tested. Any tendency toward polymerization in the macro concentration experiments would have the effect of giving too low an extraction coefficient relative to the trace concentration experiments. Just the opposite effect was observed. It would be of interest to run experiments using the method of this work and the conditions of the above cited work in order to confirm or disprove the results reported.

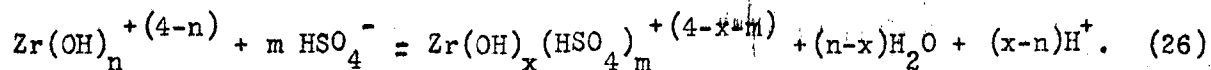
Sulfate Complexing

Experiments were run to determine the dependence of the extraction coefficient on the sulfuric acid concentration, and hence, the zirconium sulfate complex species present at various concentrations of sulfuric acid. The experiments were carried out at constant acidity and at constant ionic strength. The solutions were prepared by mixing appropriate volumes of 2.00 M HClO_4 and 1.95 M H_2SO_4 to give the desired sulfuric acid concentration. In 2 M H^+ the sulfuric acid is present almost entirely as HSO_4^- .

Two reactions are possible for the complexing reaction by bisulfate ion in the aqueous phase, i.e., the formation of sulfate complexes and the formation of bisulfate complexes:

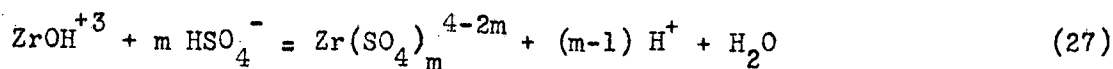


and:



By determining the dependence of the extraction coefficient on the bisulfate ion concentration, it should be possible to determine the number of sulfate or bisulfate groups in the zirconium complex at any bisulfate concentration used in the experiments.

From the experiments on the dependence of the extraction coefficient on hydrogen ion concentration, it was shown that the zirconium species in 2.00 M HClO_4 is principally $\text{Zr}(\text{OH})^{+3}$. These experiments on sulfate complexing were run at constant acidity so the number of hydroxide groups in the zirconium sulfate complex cannot be determined from these data. Even from experiments run at constant sulfuric acid concentration and varying acidity, it would not be possible to distinguish between the two species $\text{Zr}(\text{OH})\text{HSO}_4^{+2}$ and ZrSO_4^{+2} , for example. However, certain reasonable assumptions can be made concerning the sulfate complex species. Since the presence of one hydrogen ion on sulfuric acid tends to make the second hydrogen ion completely strong, one would conclude that the highly charged zirconium attached to a bisulfate ion would make the hydrogen ion strong and hence the group attached to zirconium would probably be sulfate ion rather than bisulfate ion. Further, it has been shown that there is little tendency for two hydroxide groups to be attached to zirconium in 2.00 M acid. Therefore it would appear to be unlikely that zirconium with one sulfate group attached would also have a hydroxide group attached at the same time. For the purpose of this discussion, it will be assumed that the reaction in which the first sulfate goes onto zirconium is a replacement of the one hydroxide group by sulfate ion with the formation of ZrSO_4^{++} and water. Equation (25) may then be written



As the experiments were carried out at constant acidity and constant ionic strength, it will be assumed that the activity coefficients of all the aqueous species were constant. An equilibrium quotient expressed in terms of concentrations can be written for reaction (27)

$$K_m = \frac{(\text{Zr}(\text{SO}_4)_m)^{4-2m} (\text{H}^+)^{m-1}}{(\text{ZrOH}^{+3}) (\text{HSO}_4^-)^m} \quad (28)$$

Also, an extraction coefficient may be written in terms of concentrations:

$$E_c = \frac{(\text{ZrK}_4)}{\sum_m (\text{Zr}(\text{SO}_4)_m)^{4-2m}} \quad (29)$$

By combining equations (28) and (29) and carrying out the indicated operations, one obtains:

$$\frac{\partial \ln E_c}{\partial \ln(\text{HSO}_4^-)} = \frac{\sum_m m (\text{Zr}(\text{SO}_4)_m)^{4-2m}}{\sum_m (\text{Zr}(\text{SO}_4)_m)^{4-2m}} \quad (30)$$

which may be expressed

$$\frac{\partial \ln E_c}{\partial \ln(\text{HSO}_4^-)} = -f_1 - 2f_2 - 3f_3 - \dots \quad (31)$$

Each f in equation (31) is equal to that fraction of the total zirconium in the aqueous phase which is complexed by the number of sulfate groups indicated by the subscript numbers. These expressions are true only for experimental conditions in which the activity coefficient of each species remains constant and the concentrations of hydrogen ion and TTA remain constant. In the experiments the hydrogen ion concentration did remain constant, but it was necessary to increase the TTA concentration at the higher bisulfate concentrations, which resulted in a change of the activity coefficient of ZrK_4 as well as a change in the activity of TTA. It was then necessary to convert the experimental extraction coefficient E_c to the value it

would have had if the activity coefficients of ZrK_4 and TTA had not changed. The extraction coefficients, E_c were corrected to unit activity of TTA and unit activity coefficient of ZrK_4 by the expression

$$E_c^{\circ} = \frac{E_c \gamma_{ZrK_4}}{(HK)^4 \gamma_{HK}} \quad (22)$$

which defines E_c° . Equation (31) should then be written

$$\frac{\partial \ln E_c^{\circ}}{\partial \ln(HSO_4^-)} = -f_1 - 2f_2 - 3f_3 - \dots \quad (32)$$

A plot of the logarithm E_c° versus the logarithm (HSO_4^-) then gives a line, the slope of which at any point corresponds to the average number of sulfate groups on the zirconium.

The experimental conditions and results are given in Table 6. In columns one and two are given the concentrations of bisulfate ion in the aqueous phase and the concentrations of TTA in the benzene phase. In column three are given the activity coefficients of TTA and in column four are given the activities of TTA calculated from these activity coefficients and the concentrations of column two, i.e., $(HK)_b = (HK)_b \gamma_{HK}$. The experimentally determined values of the extraction coefficient, E_c , are given in column five and the values of E_c° , calculated from the expression

$$E_c^{\circ} = E_c \frac{\gamma_{ZrK_4}}{[HK]^4} \quad (22)$$

are given in column six. The logarithm of the bisulfate concentrations and the logarithms of E_c° are given in columns seven and eight and are plotted in Figure 3. The line drawn through the points is a theoretical one, constructed using the following equilibrium quotients, expressed in terms of concentrations, for the reactions:

Table 6

Dependence of Extraction Coefficient on Bisulfate Concentration

Trace Concentration of Zirconium, Total Acidity 2.00 M, 25°C

(HSO_4^-)	$(\text{HK})_b$	$\gamma_{\text{HK}} = \gamma_{\text{ZrK}_4}$	$[\text{HK}]_b$	E_c	E_c^0	$\log(\text{HSO}_4^-)$	$\log E_c^0$
0.2726	0.0499	0.959	0.0478	0.692	1.40×10^5	-0.5645	5.146
0.2396	0.0499	0.959	0.0478	0.831	1.68×10^5	-0.6205	5.225
0.1013	0.0195	0.986	0.0192	0.113	8.22×10^5	-0.9945	5.915
0.02921	0.0195	0.986	0.0192	0.850	6.18×10^6	-1.5345	6.791
0.00974	0.0167	0.989	0.0166	1.50	1.98×10^7	-2.0116	7.297
0.00312	0.0167	0.989	0.0166	3.28	4.34×10^7	-2.5065	7.637
0.0000	0.0195	0.986	0.0192	10.4	7.55×10^7		7.878
0.0000	0.0167	0.989	0.0166	6.09	8.02×10^7		7.904
					Average of last two values	7.79×10^7	7.891

Extraction coefficients, E_c , based on total zirconium activity of 5200 counts per minute.

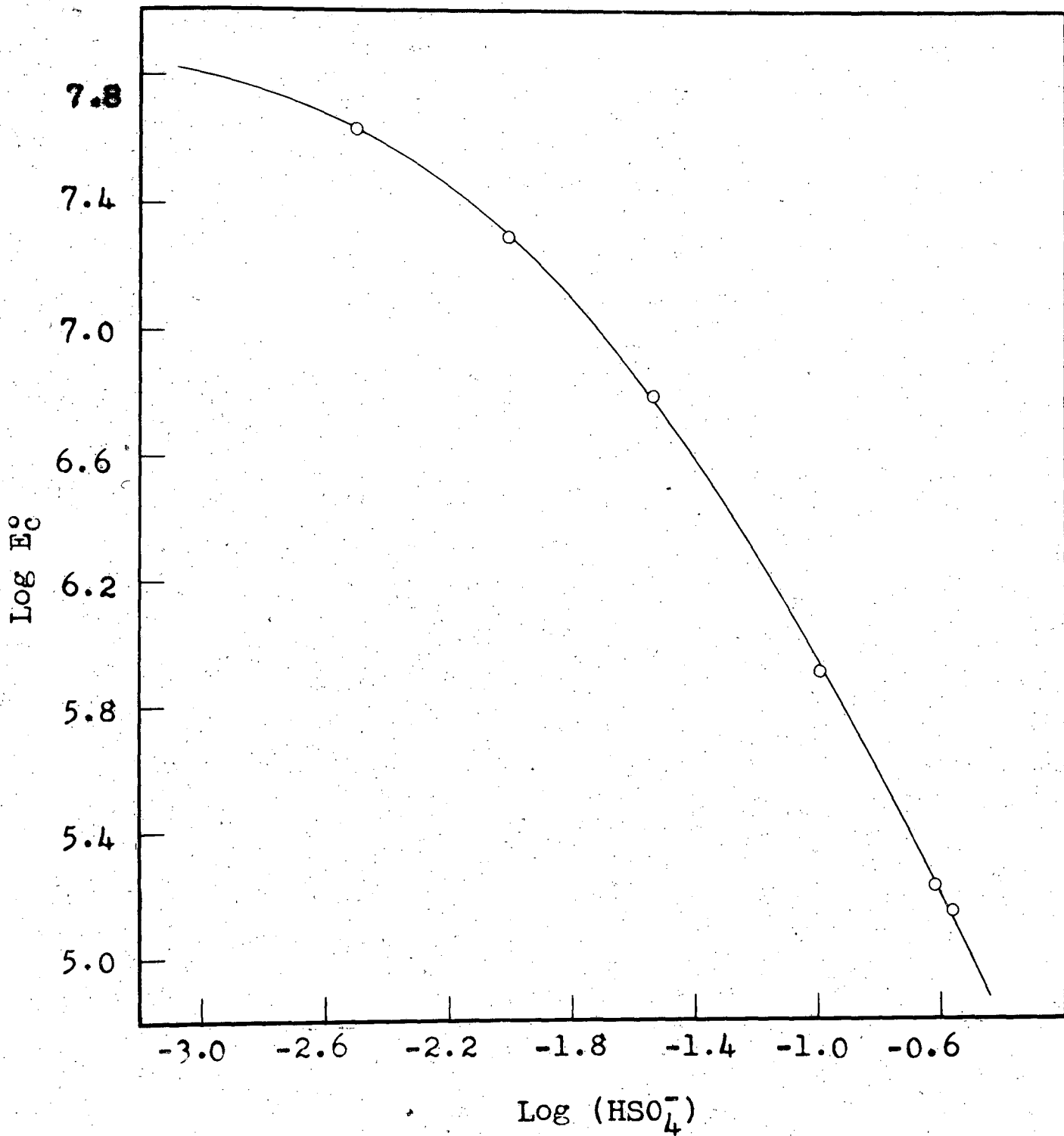
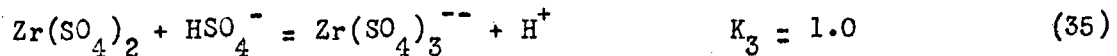


Figure 3

Dependence of Extraction Coefficient on
Bisulfate Ion Concentration.



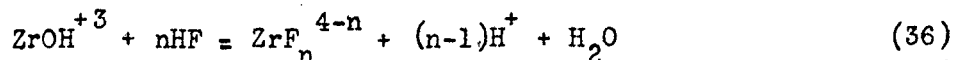
The values of these equilibrium quotients may be in error due to the presence of the unidentified impurity mentioned earlier. The values are probably not in error by more than a factor of 1.5. Further, if the first sulfate that goes onto the zirconium replaces the impurity, the values of the second two quotients should be correct. From the slope of the curve of Figure 3 and equation (32), the average number of sulfate groups per zirconium may be determined. There is an average of one sulfate group at 0.015 M HSO_4^- and an average of 2 sulfate groups at 0.27 M HSO_4^- . At neither of these points is just one species present but rather several species, of which the predominant one is that with one and two sulfates respectively. A mixture of species is always obtained because the successive complexing constants do not differ greatly in magnitude.

Fluoride Complexing

In order to establish the zirconium species present in acid solutions of hydrofluoric acid, a series of experiments was run at nearly constant acidity but with varying hydrofluoric acid concentration. The experiments were carried out by adding small aliquots of an aqueous sodium fluoride solution to 2.00 M perchloric acid. There was a small acidity correction made on the extraction coefficient because of the dilution of the perchloric acid solution and because of the formation of hydrofluoric acid from sodium fluoride.

In 2.00 M H^+ , hydrofluoric acid exists almost entirely as HF. It will be assumed, as in the case of the sulfate complexes, that the first fluoride

to go onto the zirconium replaces the one hydroxide group present on the zirconium in 2.00 M perchloric acid. The reactions for fluoride complex formation in the aqueous phase may be written



Equations of the same form as used for sulfate complexing may be derived for fluoride complexing:

$$\frac{\partial \log E_c^0}{\partial (\text{HF})} = \frac{\sum_n n (\text{ZrF}_n^{(4-n)})}{\sum_n (\text{ZrF}_n^{(4-n)})} \quad (37)$$

$$\frac{\partial \log E_c^0}{\partial (\text{HF})} = -f_1 - 2f_2 - 3f_3 - \dots \quad (38)$$

where the f_n 's are the fractions with 1, 2, 3---n fluorides attached to the zirconium. These equations apply to conditions where the activity coefficients of all species remain constant and the concentrations of hydrogen ion and TTA do not vary. Actually, in this case also, the extractions were not carried out at constant TTA concentration, but all the extraction coefficients were corrected to unit activity of TTA, i.e., E_c^0 was calculated. The activity corrections were, in some cases, quite large. Since the fluoride complex is so stable, high TTA concentrations had to be used— up to 0.4 M in the experiment run at the highest HF concentration.

The data are given in Table 7 and plotted in Figure 4. The table headings have the same significance as in Table 6, except that in column 5 is given the small correction for hydrogen ion due to dilution and the formation of HF on the addition of sodium fluoride. The correction was calculated in accordance with the equilibria of equation (36).

The solid curve of Figure 4 was plotted using the following values of the equilibrium quotients of the indicated equilibria:



Table 7

Dependence of Extraction Coefficient on Hydrofluoric Acid Concentration

Trace Concentration of Zirconium, Total Acidity 2.0 M, 25°C.

(HF)	(HK) _b	$\gamma_{HK} - \gamma_{ZrK_4}$	$[HK]_b$	H ⁺ * correction	E _c	E _c ^o	log(HF)	log E _c ^o
7.92x10 ⁻³	0.3907	0.836	0.3266	0.986	1.30	9.47x10 ¹	-2.1013	1.976
3.98x10 ⁻³	0.1951	0.887	0.1731	0.992	0.659	6.47x10 ²	-2.4001	2.811
1.99x10 ⁻³	0.1462	0.905	0.1323	0.990	1.40	4.09x10 ³	-2.7011	3.611
9.94x10 ⁻⁴	0.0389	0.966	0.0385	0.987	0.033	1.58x10 ⁴	-3.0026	4.200
4.98x10 ⁻⁴	0.0487	0.958	0.0466	0.991	0.367	7.41x10 ⁴	-3.3023	4.870
1.99x10 ⁻⁴	0.0389	0.966	0.0385	0.994	0.791	3.81x10 ⁵	-3.7011	5.581
9.94x10 ⁻⁵	0.0292	0.977	0.0285	0.982	0.850	1.23x10 ⁶	-4.0026	6.090
2.99x10 ⁻⁵	0.0195	0.986	0.0192	0.990	0.857	6.18x10 ⁶	-4.5343	6.791
9.94x10 ⁻⁶	0.0167	0.989	0.0166	0.982	1.32	1.71x10 ⁷	-5.0026	7.233

Extractions coefficients, E_c, based on total zirconium activity of 5000 counts per minute.

*Factor by which E_c is to be multiplied to give the value it would have at 2.00 M H⁺.

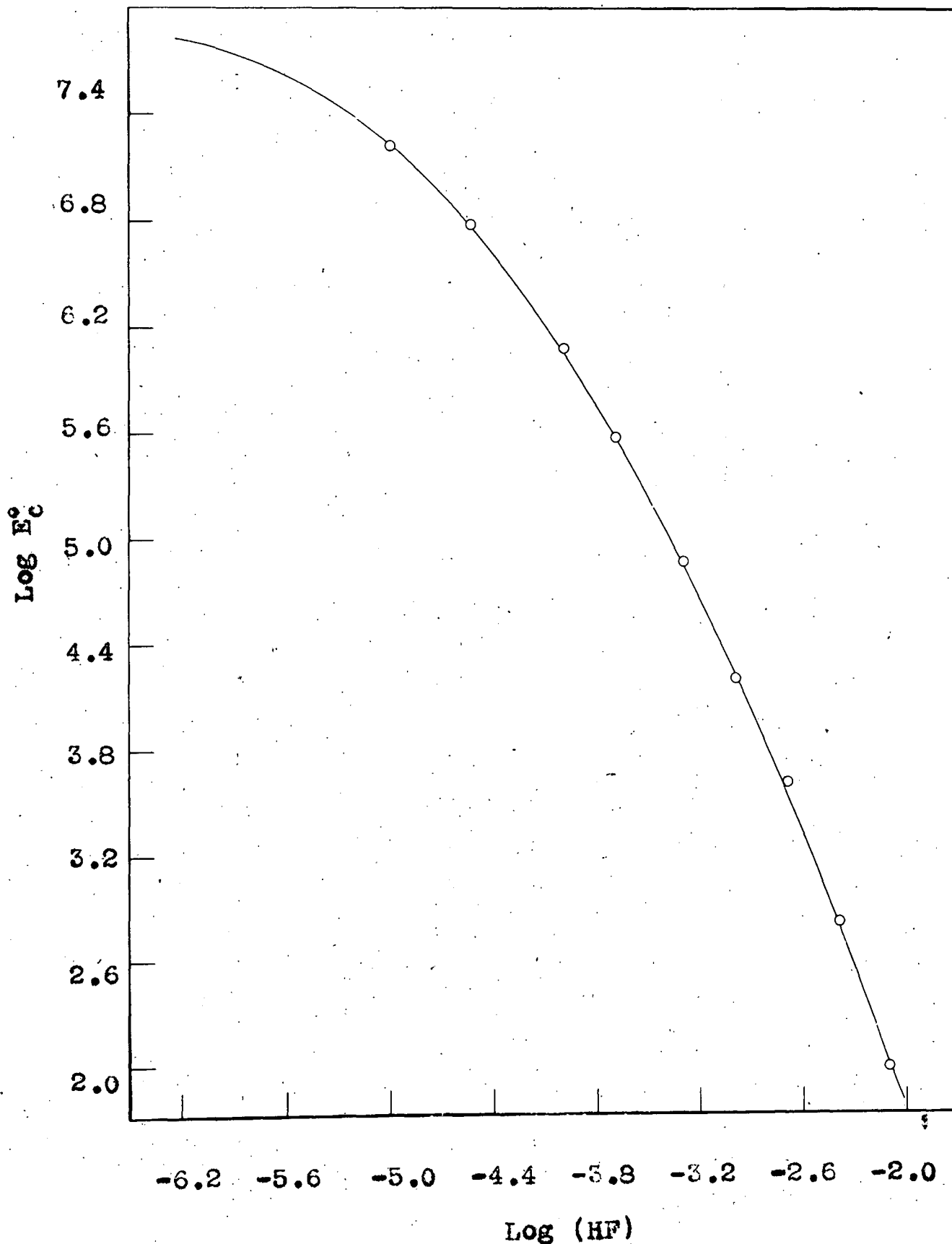


Figure 4.

Dependence of Extraction Coefficient
on Hydrofluoric Acid Concentration.



The equation for the calculated curve is

$$E = \frac{K(\text{HK})^4}{\sum_{n=0}^3 K_n (\text{H}^+)^{4-n} (\text{HF})^n} \quad (42)$$

where K was assumed to be 7.73×10^7 .

To show the order of magnitude of the strength of the fluoride complexes, one calculates from the data of Table 7 that in 10^{-5} M hydrofluoric acid, 78% of the zirconium is complexed by fluoride and that at 8×10^{-3} M hydrofluoric acid, all but 0.00012% of the zirconium is complexed. From the slope of the curve of Figure 4 and equation (38), the average number of fluoride groups in the zirconium complex may be determined. At 2×10^{-5} M HF there is an average of one fluoride per zirconium, at 3×10^{-4} M HF there is an average of two fluorides per zirconium and at 10^{-2} M HF there is an average of 3 fluorides per zirconium. The same considerations apply here as in the case of the sulfate complexes as to the presence of other fluoride complexes in addition to the one mentioned at each of the HF concentrations cited, i.e., the successive complexing constants differ so little that all solutions contain appreciable amounts of several species.

At the high concentrations of TTA used there would certainly be complexing of zirconium by TTA in the aqueous phase if there were no HF present, and there is the possibility that the zirconium is complexed by both fluoride ion and TTA. However in view of the extreme stability of the fluoride complex, it seems unreasonable that there could be much competition by TTA for the zirconium in the presence of HF. In order to determine whether or not this is so, it would be necessary to determine the TTA dependence in the presence of HF. In these experiments a fourth power TTA dependence was

used in correcting the extraction coefficients to unit activity of TTA.

The aqueous phase analysis was carried out by removing 5 ml of the aqueous phase and extracting with 5 ml of a TTA solution having a TTA concentration sufficiently higher than that used in the experiment to extract all but about 1% or less of the zirconium. This was done primarily to minimize the counting error due to columbium. With no HF present, the TTA concentrations used in some of these analyses are high enough to extract all the columbium. It is then necessary to assume that the fluoride complexing power of HF, for columbium, is at least as strong as that for zirconium and that the TTA dependence for columbium is the same or smaller, both of which assumptions seem reasonable. It was thought that HF would attack the glass walls of the container and be converted to fluosilicate ion or some hydrolyzed form of this ion. Therefore all of the above experiments were run in vessels coated with "Dri-film" to prevent the HF from coming in contact with the glass. In no case was there any evidence of attack of the glass and the extraction came to equilibrium and remained steady thereafter. Also several preliminary experiments were run in non-coated glass vessels, but even here there were no signs of attack as the extraction coefficients were about the same as with the coated vessels. Perhaps the HF does not attack silica at this rather high acidity (2.0 M) and the relatively low concentrations of HF used in the experiments.

Miscellaneous Experiments on Complexing.

A number of experiments were run using various substances in order to determine the order of magnitude of their ability to complex aqueous zirconium ion. Further, it was hoped that this study would give an indication of the identity of the impurity which was discussed earlier. Generally the extraction coefficient was determined at only one concentration of the substance whose

complexing power was being tested, so no conclusions can be drawn concerning the species present. Unless otherwise noted, all the experiments were carried out in 2.00 M HClO_4 . The results of these experiments are summarized in Table 8. The complexing agents used are given in column one and the concentrations are given in column two. The results are given in column three and are in terms of the percent of the total zirconium in the aqueous phase remaining uncomplexed.

The data for bisulfate ion and hydrofluoric acid are taken from Tables 6 and 7. The fluoride complex is by far the most stable studied. In the series of aliphatic dibasic acids from oxalic to glutaric, only oxalic shows any complexing tendency. The apparent value of 6% of the zirconium complexed by glutaric acid is probably not significant. Oxalic acid has a much greater complexing power relative to the other members of the series than can be accounted for simply by comparison of the acid dissociation constants. Also, geometry considerations cannot be too important since the carboxyl groups of all the acids are able to assume very nearly the same relative configurations. Therefore, the explanation for the great difference in complexing ability observed must lie in more complicated effects.

The two unsaturated dibasic acids, fumaric and maleic, seem to have some complexing tendencies, with perhaps the cis configuration showing a slightly greater complexing power. The result of the experiment with phosphoric acid probably has little significance since there was a continual decrease with time in the zirconium concentration. The value of the extraction coefficient used to calculate the percent zirconium uncomplexed given in this table, was one determined early in the experiment.

There was no indication of any complexing by either 0.1 M boric acid or 1 M acetic acid. Trifluoroacetic acid complexed approximately half of the zirconium when present at a concentration of 0.1 M. It should be

Table 8

Complexing Ability of Various Substances for Zirconium.

Trace Concentrations of Zirconium, 2.00M HClO₄, 25° C.

Substance	Concentration	Percent Zirconium Uncomplexed
Bisulfate ion, HSO ₄ ⁻	0.0031 M	56%
Bisulfate ion, HSO ₄ ⁻	0.272 M	0.18%
Hydrofluoric acid, HF	10 ⁻⁵ M	22%
Hydrofluoric acid, HF	0.008 M	0.00012%
Oxalic acid, H ₂ C ₂ O ₄	0.001 M	0.36%
Malonic acid, HOOC-CH ₂ -COOH	0.01 M	100%
Succinic acid, HOOC-(CH ₂) ₂ -COOH	0.005 M	100%
Glutaric acid, HOOC-(CH ₂) ₃ -COOH	0.1 M	94%
Fumaric acid, HC - COOH // HOOC - CH	0.05 M	88%
Maleic acid, HC - COOH HC - COOH	0.05 M	74%
Ortho phosphoric acid, H ₃ PO ₄	0.012 M	68%
Ortho boric acid, H ₃ BO ₃	0.1 M	100%
Meta silicic acid, H ₂ SiO ₃	0.01 M	87%
Acetic Acid, CH ₃ COOH	1.0 M	100%
Trifluoroacetic acid, CF ₃ COOH	0.11 M	51%
Carbonic acid, H ₂ CO ₃	1 atm. CO ₂	90%

Table 8 (Continued)

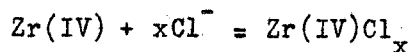
Substance	Concentration	Percent Zirconium Uncomplexed
Hydrogen peroxide, H_2O_2	0.015 M	63%
Chloride ion, Cl^-	2.0 M ^a	19%
Chloride ion, Cl^-	1.2 M ^a	29%
Nitrate ion, NO_3^-	2.0 M ^a	20%
Nitrate ion, NO_3^-	1.2 M ^a	30%

^aIn the experiments with Cl^- and NO_3^- the aqueous solution contained HClO_4 and HCl or HNO_3 in such proportions as to give 2.00 M H^+ .

pointed out that the presence of a very small amount of hydrofluoric acid in the trifluoroacetic acid would account for the observed results. The silicic acid solution used was very cloudy, so the result probably does not indicate complexing but rather the formation of species which are radio-colloidal in nature. Probably little significance should be attached to the apparent value of 10% of the zirconium being tied up in the aqueous phase when carbon dioxide gas is present in the extraction flask at a pressure of one atmosphere.

It has been observed that plutonium at macro concentrations forms a complex with hydrogen peroxide involving two plutoniums in the complex ion. It is interesting that zirconium present at trace concentrations apparently forms a complex with hydrogen peroxide, which must certainly contain only one zirconium in the complex ion. It would be worth while to study the zirconium peroxide complexes at higher concentrations of zirconium, to see if peroxy complexes containing two zirconiums are formed.

From the data of Table 8 it is possible to calculate the number of chloride and nitrate groups on the zirconium chloride and nitrate complexes. Since the number of hydroxide groups associated with these complexes is unknown, an equation of the following type will be written for the chloride complex formation reaction



from which an equilibrium quotient may be written in terms of the concentrations of these species

$$K = \frac{(\text{Zr(IV)Cl}_x)}{(\text{Zr(IV)})(\text{Cl}^-)^x}$$

The calculations of the percent zirconium uncomplexed, the results of which are given in Table 8, were made assuming that the change in extraction coefficient upon the addition of chloride or nitrate was due entirely to com-

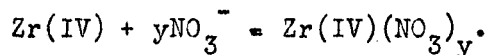
plexing of the zirconium and not to changes in the activity coefficients of any of the species present. The assumption that the activity coefficients of all the species remain constant will be made here since the data of Table 8 will be used in the following calculations.

Equating the equilibrium expressions for two different chloride concentrations, one obtains

$$\frac{(\text{Cl}^-)_1^x}{(\text{Cl}^-)_2^x} = \frac{(\text{Zr(IV)Cl}_x)_1 (\text{Zr(IV)})_2}{(\text{Zr(IV)Cl}_x)_2 (\text{Zr(IV)})_1}$$

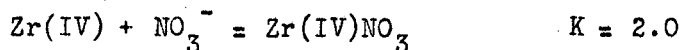
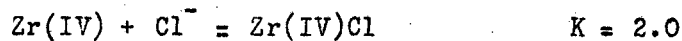
where the subscripts 1 and 2 are used to indicate the two different experiments. Substituting the data from Table 8 into this equation, one calculates $x = 1.08$ for the chloride complex.

The reaction for nitrate complexing may be written in a similar fashion



By employing a treatment analogous to that used for the chloride complex, one calculates $y = 1.06$. There appears to be approximately one chloride and one nitrate present in the respective complexes in this range of nitrate or chloride concentration.

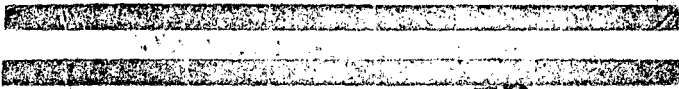
Assuming there is one chloride or one nitrate per zirconium on the complex, values for the equilibrium quotients of the following reactions may be calculated



These values apply to solutions 2.00 M in hydrogen ion.

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