conium. Three extractions with 0.02 M thenoyltrifluoroacetone of a solution containing 5.0% zirconium, based on the hafnium content, gave a recovery of 50% of the hafnium with zirconium content of 0.4%.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Aqueous Chemistry of Zirconium[1]

BY ROBERT E. CONNICK AND WILLIAM H. MCVEY[2]

Although the chemistry of zirconium has been the subject of numerous investigations since its discovery in 1789, practically nothing is known about the species existing in aqueous solutions of its salts. Typical is the fact that not even the formula of the uncomplexed zirconium(IV) ion, present in perchloric acid solutions, has been identified. The formulas of several complex ions in aqueous solutions such as $ZrO(SO_4)_2^{=}$ [3] and $ZrOCl_4^{=}$ [4] have been reported but the data could be interpreted equally well by assuming other species. From a search of the literature we have been forced to the conclusion that the formula of not a single aqueous zirconium(IV) species has been unambiguously identified up to the present time.

The existing information on the chemistry of zirconium was collected in 1921 by Venable[5] and more recently by Pascal.[6] Nearly all of this work, as well as that published since 1931, deals with the identification of solid phases rather than the study of ions in solution.

The purpose of the present research was to determine the formulas of the zirconium species existing in acidic aqueous solutions and to study the complexing of zirconium(IV) by a number of the more common anions

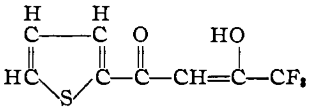
Experimental Method

The usual procedures for the determination of the formulas of species in solution, such as cell measurements, freezing point lowering, spectrophotometric analysis, *p*H determinations, solubility studies, etc., are not readily applicable in the case of zirconium because of the great tendency for hydrolysis to take place except in quite acidic solutions.

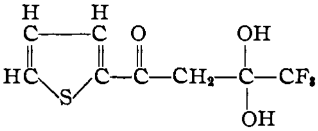
The experimental method employed involves the measurement of an equilibrium in which zirconium(IV) is distributed between the aqueous phase being investigated and an organic phase containing a chelating agent. The zirconium is inappreciably complexed by the chelating agent when in the aqueous phase, yet forms a chelate which is soluble in the organic phase and which is in equilibrium with whatever species exist in the aqueous phase. Any complexing of species in the aqueous phase is quantitatively reflected in a decrease of the extraction of the zirconium into the organic phase.

The method used in the present study is clearly a powerful one and it should find application in the study of many similar systems.

Calvin[7] has investigated the complexing properties of several chelating agents and the particular chelating agent used in this work, thenoyltrifluoroacetone was one prepared by Calvin and Reid.[8] This compound, hereafter referred to as TTA, is a weak acid having the following structure in the enol form



When TTA is equilibrated between dilute acid and benzene, the principal species in the aqueous phase is the hydrate[9]



while in the benzene phase, about 15% occurs in the hydrate form and 85% in the enol form. The keto form apparently is not an important species in this system. In aqueous solution TTA is a weak acid with an ionization constant[10] of 6.7 × 10^{-7}.

The distribution coefficient of TTA between benzene and a dilute acidic, aqueous phase favors the benzene phase, *i. e.*, at low TTA concentrations

$$(TTA)_b/(TTA)_{aq} = 40$$

The activity coefficient of TTA in benzene has been measured by King and Reas[9] who found it to decrease significantly below unity at TTA concentrations above 0.01 M in the benzene phase.

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[1] This research was carried out in the Radiation Laboratory and the Chemistry Department of the University of California under the auspices of the United States Atomic Energy Commission.

[2] Present address, General Electric Co., Hanford Engineer Works, Richland, Wash.

[3] R. Ruer, *Z. anorg. allgem. Chem.*, **42**, 87 (1904); **46**, 449 (1905).

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

[5] Francis P. Venable, "Zirconium and Its Compounds," American Chemical Society Monograph Series, New York, N. Y., 1921.

[6] P. Pascal, "Traité de Chimie Minerale," Masson and Company, Paris, 1931–1932.

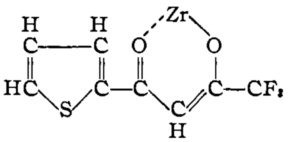
[7] M. Calvin, Manhattan Project Report, CN-2486, Dec. 1, 1944.

[8] J. C. Reid and M. Calvin, MDDC-1405, Aug. 13, 1947.

[9] E. L. King and W. H. Reas, "Atomic Energy Commission Report," BC-69, July, 1947.

[10] E. Zebroski, Atomic Energy Commission Report, BC-63, July 1, 1947.

The zirconium chelate species which is extracted into the benzene phase is a neutral molecule consisting of a zirconium ion bonded to four TTA ions. Presumably each TTA ion is attached by two oxygens in the following manner



with the two double bonds in the zirconium ring capable of resonating between the two carbon–oxygen and carbon–carbon bonds.

Materials and Analytical Procedures.—In most of the experiments carrier-free, radioactive Zr^{95} tracer was employed. In some experiments macro concentrations of inactive zirconium were used and in a few of the runs both radioactive and macro amounts of inactive zirconium were present. The inactive zirconium was obtained from City Chemical Corporation as $ZrOCl_2 \cdot 8H_2O$ and was recrystallized several times from concentrated hydrochloric acid in the form of large crystalline needles of $ZrOCl_2 \cdot 8H_2O$. This solid was dissolved in 1.00 *M* perchloric acid to give a 0.1 *M* solution of zirconium(IV) containing 0.2 *M* chloride ion. The solution was clear except for a slight Tyndall beam and remained so over a period of many months.

The Zr^{95} tracer, which was obtained from Oak Ridge, decays[11] with a 65 day half-life to Cb^{95} by emission of a beta particle and gamma rays. The columbium in turn decays with a 35 day half-life to stable Mo^{95} with the emission of a beta particle and a gamma ray. A small fraction of the columbium appears to be formed in an excited state, which drops to the ground state with a 90 hour half-life.

The zirconium tracer, containing radioactive columbium, was received in a 5% oxalic acid solution. The solution was made 10 *M* in nitric acid and a small amount of 0.1 *N* potassium permanganate added to precipitate manganese dioxide, which was removed by centrifugation. This process was repeated several times, the potassium permanganate being reduced by water in the later precipitations. The purification served the dual purpose of eliminating the oxalic acid and the radioactive columbium, which is carried by manganese dioxide. Further purification from columbium and removal of nitric acid were achieved by extracting the zirconium into a benzene–TTA solution and washing the benzene phase repeatedly with 2.0 *M* perchloric acid. Columbium is not as readily extracted into the organic phase as is zirconium. Finally the benzene phase was diluted ten-fold with benzene, to lower the TTA concentration, and the zirconium was re-extracted into a small volume of 2.00 *M* perchloric acid.

In the analysis for radioactive zirconium, aliquots from both phases, usually 0.100 ml. in size, were mounted on 22-mm. square glass cover slides and counted, either using a Geiger counter with a mica-window tube or an ionization chamber attached to a vibrating reed electrometer. The reproducibility of these analyses was generally of the order of 2 to 3%. The samples were counted through an approximately 10 mg. per sq. cm. aluminum absorber in an effort to minimize the activity from columbium, which grows into the samples from the decay of zirconium; the columbium beta particles are considerably less energetic than those of zirconium. The activity and counting times were such as to give a probable counting error of approximately 0.7% in those experiments where the extraction coefficient was about unity.

A colorimetric method, developed by Liebhafsky and Winslow[12] and capable of determining quantitatively a few micrograms of zirconium, was used for the analysis of macro amounts of zirconium. The reproducibility of the analysis was fairly good, *i. e.*, of the order of 3%; however, the process of lake formation was greatly slowed down in the presence of TTA. The apparent concentration of zirconium increased slowly over a period of several hours. Attempts to improve the analysis by destruction of the TTA with bromine, chlorine and sodium hydroxide were unsuccessful. The spectrophotometer reading used for calculating the zirconium concentration was the nearly constant value obtained after the solution had stood for several hours.

Perchloric acid solutions were prepared by diluting G. Frederick Smith double vacuum distilled perchloric acid with conductivity water. The solutions were standardized by the mercuric oxide–potassium iodide method. Lithium perchlorate, used in the hydrolysis experiments to maintain constant ionic strength, was purified by recrystallizing G. Frederick Smith $LiClO_4 \cdot 3H_2O$ from water. The solution was analyzed by evaporating aliquots with sulfuric acid, igniting and weighing as anhydrous lithium sulfate. Pure, vacuum distilled TTA was kindly furnished by Dr. James C. Reid. The benzene was thiophene-free. All other chemicals were of reagent or C. P. grade and were used without further purification.

The experiments were carried out by mixing 25-ml. portions of the two phases, aqueous and benzene, in 100-ml. volumetric flasks. A mechanical shaker was so arranged that the flask was immersed in a water thermostat at 25.00 ± 0.05°. The shaking was vigorous, the flasks going through 1520 up and down movements per minute with a stroke of 2.5 cm.

All concentrations are expressed in moles per liter of solution, designated by the symbol *M*.

Nature of Extraction Equilibrium

Formula of Zirconium Chelate and Evidence for Non-complexing of Zirconium by TTA in Aqueous Phase.—Before the zirconium chelate extraction equilibrium can be used in the study of zirconium species in aqueous solutions, it is necessary to determine the formula of the chelate compound extracted into benzene and to establish that there is no appreciable complexing of zirconium by TTA in the aqueous phase. These facts may be ascertained from a study of the extraction coefficient as a function of the TTA concentration at constant acidity.

One possible equation for the extraction of zirconium is

$$Zr^{+4}(aq) + 4HK(b) = ZrK_4(b) + 4H^+(aq) \quad (1)$$

where HK has been used to represent TTA. However, the zirconium in the aqueous phase may be hydrolyzed and complexed by TTA, and the chelate in the benzene phase may contain hydroxide as well as TTA groups. To include all possibilities we write the general equation for the reaction

$$Zr(OH)_nK_m{}^{+4-n-m} + (p - m)HK = Zr(OH)_{4-p}K_p + (4 - m - n)H^+ + (n + p - 4)H_2O \quad (2)$$

and we may define the equilibrium constants

$$K_{m,n,p} = \frac{[Zr(OH)_{4-p}K_p][H^+]^{4-m-n}[H_2O]^{n+p-4}}{[Zr(OH)_nK_m{}^{+4-n-m}][HK]^{p-m}} \quad (3)$$

Brackets have been used to represent activities of the enclosed species. (Parentheses will be used to indicate concentrations.) The designation of the phase in which each species exists has been omitted to simplify the writing of the equation. The spe-

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[11] G. T. Seaborg and I. Perlman, "Table of the Isotopes," Department of Chemistry and Radiation Laboratory, University of California, Report UCRL-179, August, 1948.

[12] H. Liebhafsky and E. Winslow, THIS JOURNAL, **60**, 1776 (1938).

cies $Zr(OH)_nK_m^{+4-n-m}$ and H^+ occur in the aqueous phase while the species $Zr(OH)_{4-p}K_p$ and HK are components of the benzene phase. All species in the benzene phase have been assumed to be neutral molecules because of the low dielectric constant of this solvent. 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 the sum of the activities of zirconium species in the benzene phase divided by the sum of the activities of zirconium species in the aqueous phase, *i. e.*

$$E_{\mathrm{a}} = \frac{\sum\limits_{p} [Zr(OH)_{4-p}K_p]}{\sum\limits_{n}\sum\limits_{m} [Zr(OH)_nK_m{}^{+4-n-m}]} \tag{4}$$

From equation (3) the relationship holds

$$[Zr(OH)_nK_m{}^{+4-n-m}] = \frac{[ZrK_4][H^+]^{4-m-n}[H_2O]^n}{K_{m,n,4}[HK]^{4-m}} \tag{5}$$

From equations (3) and (5)

$$\frac{[ZrK_4][H^+]^{4-m-n}[H_2O]^n}{K_{m,n.4}[HK]^{4-m}} = \frac{[Zr(OH)_{4-p}K_p][H^+]^{4-m-n}[H_2O]^{n+p-4}}{K_{m,n.p}[HK]^{p-m}} \tag{6}$$

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

$$[Zr(OH)_{4-p}K_p] = \frac{[ZrK_4][H_2O]^{4-p}K_{m,n,p}}{[HK]^{4-p}K_{m,n,4}} \tag{7}$$

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

$$[Zr(OH)_{4-p}K_p] = \frac{[ZrK_4][H_2O]^{4-p}K_{o,o,p}}{[HK]^{4-p}K_{o,o,4}} \tag{8}$$

Substituting equations (8) and (5) into equation (4), one obtains

$$E_{\mathrm{a}} = \frac{\sum\limits_{p} \frac{[ZrK_4][H_2O]^{4-p}K_{o,o,p}}{[HK]^{4-p}K_{o,o.4}}}{\sum\limits_{m}\sum\limits_{n} \frac{[ZrK_4][H^+]^{4-m-n}[H_2O]^n}{K_{m,n,4}[HK]^{4-m}}} \tag{9}$$

The factor $[ZrK_4]$ cancels completely between the numerator and denominator. Taking the partial derivative of the logarithm of E_{a} with respect to the logarithm of the activity of HK and substituting from equations (8) and (5) gives

$$\frac{\partial \ln E_{\mathrm{a}}}{\partial \ln [HK]} = \frac{\sum\limits_{p}(p-4)[Zr(OH)_{4-p}K_p]}{\sum\limits_{p}[Zr(OH)_{4-p}K_p]} - \frac{\sum\limits_{m}\sum\limits_{n}(m-4)[Zr(OH)_nK_m{}^{+4-m-n}]}{\sum\limits_{m}\sum\limits_{n}[Zr(OH)_nK_m{}^{+4-m-n}]} \tag{10}$$

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 coördination number of Zr^{+4} for oxygens does not exceed eight.[13] Assigning two coördination 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 form

$$\partial \ln E_{\mathrm{a}}/\partial \ln [HK] = -4f_0 - 3f_1 - 2f_2 - f_3 + 4f'_0 + 3f'_1 + 2f'_2 + f'_3 \tag{11}$$

where each f is the fraction of the total activity of that phase contributed by species containing the indicated number of chelate groups. The unprimed f's refer to the benzene phase and the primed f's to the aqueous phase. 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 remained constant.

An equation having exactly the same form as (11) may be derived on the basis of an extraction coefficient, E', defined as the ratio of the sum of the activities of the zirconium species in the benzene phase to the total concentration of zirconium in the aqueous phase. The f's represent fractions of the total zirconium activity in the benzene phase and the f''s fractions of the total zirconium concentration in the aqueous phase. An additional restriction is imposed on the differentiation, *i. e.*, that the activity coefficients of all species in the aqueous phase remain constant.

This equation corresponds to the experimental conditions used in the determination of the dependence of the extraction coefficient on TTA activity, but unfortunately only E_{c}, the extraction coefficient expressed in concentrations, and not E' can be determined experimentally.

The activity coefficients of the individual zirconium chelate species in the benzene phase as a function of the TTA concentration are not known. For simplicity it will be assumed that they all behave like γ_{ZrK_4}, the activity coefficient of ZrK_4, and that this in turn is equal to γ_{UK_4} measured by Reas.[14] No appreciable error should be introduced by these assumptions since γ_{UK_4} varies little over the range of TTA concentration used. On this basis $E' = E_{\mathrm{c}}\gamma_{ZrK_4}$.

From the slope of the line obtained by plotting the logarithm of the extraction coefficient E' *versus* the logarithm of the activity of TTA (see equation (11)), one should be able to determine the number of TTA groups present in the zirconium species in the benzene phase and in the aqueous phase. (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.) For any slope less than four, a number of combinations of the various f's and f''s would fit the data. The important point is that, should the slope be four, there is only one combination which will fit the

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[13] L. Pauling. "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

[14] W. H. Reas, unpublished work, this Laboratory.

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

$$Zr(OH)_n^{+4-n} + 4HK = ZrK_4 + (4 - n)H^+ + nH_2O \tag{12}$$

Experimental Results

The experiments designed to test the dependence of the extraction coefficient on the TTA concentration were carried out in 2.00 M perchloric acid. The conditions and results are presented in Table I.

TABLE I

DEPENDENCE OF EXTRACTION COEFFICIENT ON TTA ACTIVITY

Trace Concentrations of Zirconium, 2.00 M $HClO_4$, 25°

$(HK)_b$	$\gamma_{HK} = \gamma_{ZrK_4}$	E_c	[HK]	E'	log [HK]	log E'
.00506	0.999	0.046	0.00505	0.046	−2.2966	−1.337
.00583	.998	.090	.00582	.0898	−2.2351	−1.047
.00778	.997	.258	.00776	.257	−2.1101	−0.590
.00972	.996	.65	.00968	.647	−2.0141	− .189
.01361	.992	2.19	.01350	2.17	−1.8697	.337
.01673	.988	4.45	.01653	4.40	−1.7817	.644
.01945	.986	6.8	.01918	6.70	−1.7172	.826
.02918	.977	14.3	.02851	14.0	−1.5450	1.146
.02839	.977	45.0[a]	.02774	44.0	−1.5569	1.644[a]

[a] Value obtained when new aqueous phase was equilibrated with benzene phase of previous experiment, in order to eliminate columbium; see text.

In the first column is given the TTA concentration (moles per liter) in the benzene phase at equilibrium, calculated from the known concentration of TTA added and a distribution ratio of 35 for TTA between the benzene phase and the aqueous phase. (The distribution coefficient decreases from 40 in 0.1 M hydrochloric acid[9] to 35 in 2 M perchloric acid relative to benzene.) In column two is listed the value of the activity coefficient of TTA[9] corresponding to the concentration in column one. Reas[14] 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 is given the ratio of 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 $[HK] = (HK)\gamma_{HK}$ and $E' = E_c\gamma_{ZrK_4}$, respectively. The logarithms of the values of the activity of TTA and E', given in columns six and seven, are plotted in Fig. 1. In the experiments of Table I and all following experiments, both phases were analyzed as a function of time in order to make certain that equilibrium had been established.

The straight line in Fig. 1 has been drawn with a slope of four. It can be seen that the experimental points, indicated by solid circles fit this slope within experimental error up to a TTA activity of 10^{-2}, but, from there on, the points appear to fall off to a smaller slope. That this effect is not real, but arises from radioactive columbium impurity in the stock tracer, is shown by the point at highest TTA activity (designated by an open circle in Fig. 1) which falls on the line of slope four. In this experiment columbium was eliminated by reëquilibrating the benzene phase of the experiment at 0.02918 M TTA with a fresh aqueous phase. The columbium was removed along with the first aqueous phase as it is not extracted appreciably into benzene under these conditions. Presumably the other points which deviate would also be brought into line if the columbium were eliminated. No attempt was made to calculate a correction for these experiments because columbium is radio-colloidal in such solutions and probably does not behave reproducibly. The correction for columbium becomes small, *i. e.*, of the order of magnitude of the experimental accuracy in the experiments where the extraction coefficient is low.

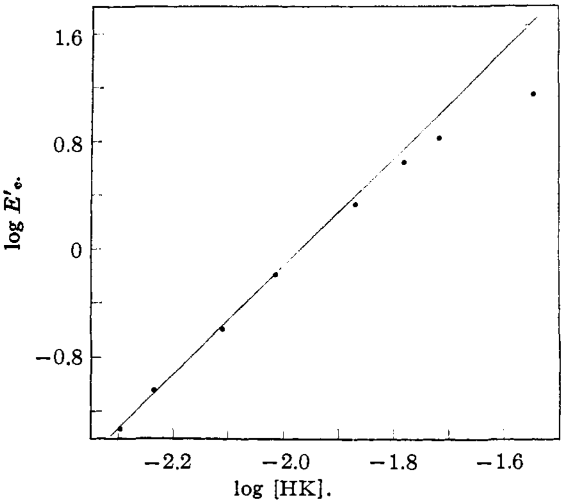

Fig. 1.—Dependence of extraction coefficient on TTA activity.

From the above results the extraction coefficient appears to follow a fourth power dependence on TTA activity within the accuracy of the measurements. Therefore the zirconium species in the aqueous phase are not appreciably complexed 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 performed with macro amounts of zirconium to check the trace results gave somewhat greater coefficients, as shown in Table II. The concentration of TTA in column 2 has been corrected for that used up in forming the chelate. The extraction coefficients, corrected to the same TTA concentration as in the first experiment, are given in the last column as E_{cor}.

The increase in the extraction coefficient at macro zirconium concentrations seems best explained by assuming the presence of a small

TABLE II

EXTRACTION COEFFICIENT AT VARIOUS CONCENTRATIONS OF ZIRCONIUM(IV)

2.00 M $HClO_4$, 25°, 0.0100 M total TTA

$(Zr(IV))_{(aq)}$ at equil.	$(HK)_b$	E_c	$E_{cor.}$
Trace	0.00972	0.58	0.58
4.7×10^{-5} M	.00964	.70	.74
5.1×10^{-4} M	.00861	.56	.91

amount of impurity which partially complexed the trace zirconium. At high zirconium concentrations the effect would become small if the total amount of impurity were small compared to the total zirconium. If it is assumed that the amount of impurity was the same in each experiment, certain deductions may be made. Since the extraction coefficient of the second experiment is greater than for the trace experiment, an appreciable part of the impurity must have been tied up in the second experiment. The relatively small change in extraction coefficient for a ten-fold increase in zirconium concentration in going from the second to the third experiment indicates that nearly all of the impurity must be complexed by zirconium in the third experiment. Therefore the concentration 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% of the zirconium(IV) in the aqueous phase is complexed by the impurity in the first experiment.

A strenuous effort was made to eliminate the impurity. Different sources of all reagents were tried. The magnitude of the effect varied somewhat but in no case was the effect eliminated. It was shown by a study of their complexing power that none of the substances listed in Table VI were responsible.

Impurities in the radioactive tracer were not interfering as experiments with and without tracer gave the same results and the radioactive analysis agreed with the colorimetric analysis.

Radio-colloid formation did not appear to be a likely explanation since addition of 0.01 M silicic acid did not decrease the extraction coefficient greatly (see Table VI). Polymer or true colloid formation would have caused a decrease in extraction coefficient with rising zirconium concentration.

At the present time neither the identity nor the source of the impurity is known. Its presence introduces an uncertainty into the interpretation of the data of the trace experiments. The identification of the various zirconium complexes 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 is not affected provided the amount of impurity remained the same in all of the TTA dependence experiments.

Hydrolysis

In order to determine the degree of hydrolysis of zirconium the extraction coefficient was measured as a function of the hydrogen ion concentration. Ignoring for the moment the perturbing effect of the unknown impurity, the equation for the net reaction may be written

$$Zr(OH)_n{}^{+4-n} + 4HK = ZrK_4 + (4 - n)H^+ + nH_2O \tag{13}$$

assuming that perchlorate ion, in conformity with its general chemical behavior, does not complex zirconium. Equilibrium quotients expressed in concentrations may be written for equation (13)

$$K_n = \frac{(ZrK_4)(H^+)^{4-n}}{(Zr(OH)_n{}^{+4-n})(HK)^4} \tag{14}$$

An extraction coefficient is defined in terms of concentrations

$$E_c = \frac{(ZrK_4)}{\sum\limits_n (Zr(OH)_n{}^{+4-n})} \tag{15}$$

Proceeding as before gives (for constant activity coefficient and TTA concentration)

$$\partial \ln E_c^0/\partial \ln (H^+) = -4 + f_1 + 2f_2 + 3f_3 + \ldots \tag{16}$$

Each f 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 the experiments, it was necessary to vary the TTA concentration as the acidity was varied in order to obtain measurable extraction coefficients. Therefore all measured values of E_c were corrected to a common basis, *i. e.*, the values the extraction coefficients would have had at unit activity of TTA and at $\gamma_{ZrK_4} = 1$. This quantity, E_c^0, is defined by the equation

$$E_c^0 = E_c\gamma_{ZrK_4}/(HK)^4\gamma_{HK}{}^4 \tag{17}$$

It was assumed that the activity coefficients of all species in the aqueous phase remained essentially constant since the ionic strength was maintained at 2.0 by adding lithium perchlorate as the perchloric acid concentration was decreased. Some justification is obtained from the fact that the activity coefficient of hydrochloric acid in lithium chloride solutions does not change measurably from 10^{-3} M hydrochloric acid to 3 M hydrochloric acid at a total molality of 3 M.[15]

In equation (13) it has been assumed that there is no complexing of zirconium in the aqueous phase by TTA over the whole acidity range studied. This has already been shown to be the case at 2.0 M hydrogen ion. From the hydrolysis data it appears that complexing by hydroxide ion does occur to some extent in the 2 M hydrogen ion region and therefore the hydroxide ion has a stronger tendency than the chelate ion to complex zirconium under these conditions. Since the

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[15] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, N. Y., 1943, p. 457.

ratio of chelate ion concentration to hydroxide ion concentration decreased in going to the experiments at lower acidity, it seems likely that no appreciable complexing by TTA occurred in any of the experiments.

In the trace experiments samples from the aqueous phase could not be evaporated directly for counting because of the self-absorption by lithium perchlorate. To circumvent this difficulty, the zirconium in samples from the aqueous phase was extracted completely into a benzene–TTA solution and aliquots of this phase were mounted to give plates free of solid. This procedure also served to eliminate any columbium impurity.

The experimental results are shown in Fig. 2 where log E_c^0 is plotted against log (H^+). According to equation (16) the average number of hydroxides per zirconium is the slope minus four. The two straight lines in Fig. 2 are drawn with slopes of -2 and -3 corresponding to $Zr(OH)_2^{++}$ and $ZrOH^{+3}$.

The three types of symbols in Fig. 2 represent experiments with trace amounts of zirconium in uncoated glass vessels, trace experiments in coated glass vessels and experiments with macro amounts of zirconium in uncoated glass vessels. In some of the experiments the glass was coated with "Dri-Film" to prevent the zirconium from sticking to the walls of the vessels at low acidity. "Dri-Film," which is $SiCl_2(CH_3)_2$, is hydrolyzed, by the thin film of water always present on a glass surface that has been air-dried, to give a hydrocarbon surface which is not wet by water. The coating was quite successful in preventing the sticking of zirconium to the glass but the possibility of radio-colloid formation on particles in solution was, of course, still present.

The extraction coefficients at low acidity did not fall on a smooth curve, which fact suggested the formation of a radio-colloid. This was confirmed by centrifuging experiments. Therefore the data of Fig. 2, for acidities below 0.1 *M*, should be regarded only as lower limits for the extraction coefficient.

The curve drawn through the points of the trace experiments was calculated assuming that the only important species were $ZrOH^{+3}$ and $Zr(OH)_2^{++}$. The significance of such a calculation is doubtful, however, because of the unknown effect of the impurity. If the impurity is the ion of a strong acid the break from slope -3 to -2 should have occurred at higher acidity than shown by the data. If the complexing impurity is the ion of a weak acid (which seems more likely since no ions of strong acids were found to complex zirconium strongly in 2 *M* perchloric acid), then the slope of the curve should be steeper everywhere, corresponding to less hydrolysis of the zirconium.

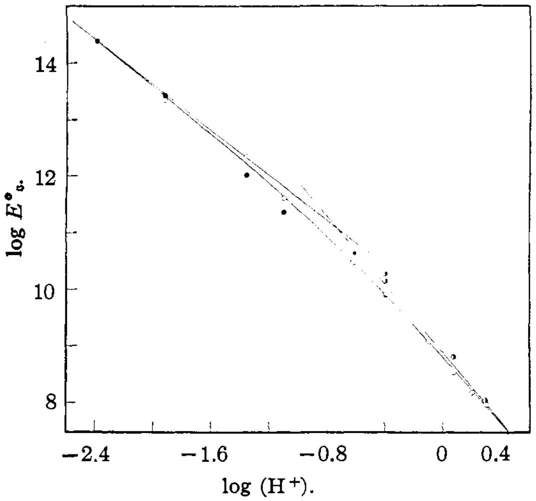

Fig. 2.—Dependence of extraction coefficient on hydrogen ion concentration: trace Zr(IV) in uncoated vessel, ○; trace Zr(IV) in "Dri-Film" coated vessel, ●; macro Zr(IV) in uncoated vessel, ◑.

The macro experiments, which were run with approximately 3×10^{-4} *M* zirconium(IV) in the aqueous phase, all show higher extraction coefficients than the trace experiments. Presumably this arises from the complexing action of the impurity in the trace experiments. The two points at highest acidity in the macro runs give a slope between three and four, indicating a mixture of Zr^{+4} and $ZrOH^{+3}$. The falling off of the points for the macro experiments at low acidity may be caused by polymer formation. The discrepancy in the two points at log $(H^+) = 0.4$ may arise from the same cause, since the concentration of zirconium in the aqueous phase of the higher point was only 0.4 times that in the other experiment.

From the results of the hydrolysis experiments it seems likely that at low zirconium concentrations the average zirconium species in 2 *M* perchloric acid has somewhere between zero and one hydroxide group attached, *i. e.*, lies between Zr^{+4} and $ZrOH^{+3}$.

Hydrolysis data reported in the literature give evidence of polymer formation at higher concentrations of zirconium and/or lower acidity.

Complexing

Sulfate Complexing.—The stability of the sulfate complexes of zirconium was determined by measuring the extraction coefficient as a function of sulfate concentration at constant acidity. The general equation may be written

$$Zr(OH)_n^{+4-n} + mHSO_4^- = Zr(OH)_x(SO_4)_m^{+4-x-2m} + (n-x)H_2O + (x-n+m)H^+ \quad (18)$$

The principle sulfate species in 2 *M* H^+ is HSO_4^-. Equilibrium quotients and an extraction coefficient are defined in terms of concentrations

$$K_{n,m,x} = \frac{(Zr(OH)_x(SO_4)_m^{+4-x-2m})(H^+)^{x-n+m}}{(Zr(OH)_n^{+4-n})(HSO_4^-)^m} \quad (19)$$

TABLE III

DEPENDENCE OF EXTRACTION COEFFICIENT ON BISULFATE CONCENTRATION. TRACE CONCENTRATIONS OF ZIRCONIUM. TOTAL ACIDITY 2.00 *M*, 25°

(HSO_4^-)	$(HK)_b$	$\gamma_{HK} = \gamma_{ZrK_4}$	$[HK]_b$	E_c	E_c^0	log (HSO_4^-)	log E_c^0
0.2726	0.0499	0.959	0.0478	0.692	1.40×10^5	−0.5645	5.146
.2396	.0499	.959	.0478	.831	1.68×10^5	− .6205	5.225
.1013	.0195	.986	.0192	.113	8.22×10^5	− .9945	5.915
.02921	.0195	.986	.0192	.850	6.18×10^6	−1.5345	6.791
.00974	.0167	.989	.0166	1.50	1.98×10^7	−2.0116	7.297
.003115	.0167	.989	.0166	3.28	4.34×10^7	−2.5065	7.637
.0000	.0195	.986	.0192	10.4	7.55×10^7	− ∞	7.878
.0000	.0167	.989	.0166	6.09	8.02×10^7	− ∞	7.904
				Av. of last two values	7.79×10^7	− ∞	7.891

$$E_c = \frac{(ZrK_4)}{\sum_m \sum_x (Zr(OH)_x(SO_4)_m{}^{+4-x-2m}) + \sum_n (Zr(OH)_n{}^{+4-n})} \qquad (20)$$

Proceeding as before one obtains

$$\partial \ln E_c^0/\partial \ln (HSO_4^-) = -f_1 - 2f_2 - 3f_3 \ldots \qquad (21)$$

Each f in equation (21) is equal to the fraction of the total zirconium in the aqueous phase which is complexed by the number of sulfate groups indicated by the subscript numbers. The equations apply to conditions of constant hydrogen ion and TTA concentrations and constant values of all activity coefficients. When log E_c^0 is plotted against log (HSO_4^-) the slope of the curve gives the average number of sulfate groups per zirconium.

To obtain measurable extraction coefficients it was necessary to vary the TTA concentration. Therefore the measured extraction coefficients, E_c, were corrected to the value they would have had at unit activity of TTA and unit activity coefficient of ZrK_4, according to equation (17).

The aqueous solutions were prepared by mixing the appropriate volumes of 2.00 *M* perchloric acid and 1.95 *M* sulfuric acid, which gave solutions of essentially constant ionic strength. It was assumed that, over the range of mixtures studied, all activity coefficients of species in the aqueous phase remained constant.

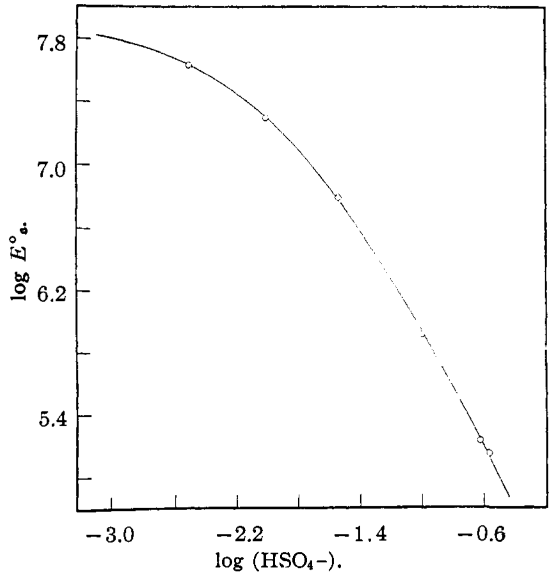

Fig. 3.—Dependence of extraction coefficient on bisulfate ion concentration.

The experimental data are presented in Table III and plotted in Fig. 3. From the slope of the curve it is found that there is an average of one sulfate per zirconium at 0.013 *M* HSO_4^- and an average of two sulfates at 0.3 *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 is obtained because the successive complexing constants do not differ greatly in magnitude.

It is not possible to determine from the data the number of hydroxide groups associated with each complex since the experiments were performed at constant acidity; however, some reasonable deductions may be made. The hydrolysis experiments indicated that zirconium in 2 *M* perchloric acid had between zero and one hydroxide groups attached, and therefore had little tendency to hold a second hydroxide when one was already present. It would be expected that, when a sulfate group is bonded to a zirconium ion, there would be little tendency for a hydroxide group to be attached in addition. Thus the sulfate complexes in 2 *M* hydrogen ion are not expected to contain hydroxide groups.

Further, it is believed that it is sulfate rather than bisulfate ion which is present in these complexes. The attachment of Zr^{+4} to a bisulfate ion should make the hydrogen ion readily ionizable, just as the attachment of one hydrogen ion in sulfuric acid makes the other hydrogen a strong acid.

The solid line drawn in Fig. 3 is a theoretical curve based on the equations

$$Zr^{+4} + HSO_4^- = ZrSO_4^{++} + H^+ \qquad K_1 = 4.6 \times 10^2$$

$$ZrSO_4^{++} + HSO_4^- = Zr(SO_4)_2 + H^+ \qquad K_2 = 53$$

$$Zr(SO_4)_2 + HSO_4^- = Zr(SO_4)_3^{=} + H^+ \qquad K_3 = 1$$

The equilibrium quotients were evaluated from the data by a modification of the method described

TABLE IV

DEPENDENCE OF EXTRACTION COEFFICIENT ON HYDROFLUORIC ACID CONCENTRATION

Trace Concentrations of Zirconium, 2.0 M $HClO_4$, 25°

(HF)	$(HF)_b$	$\gamma_{HK} = \gamma_{ZrK_4}$	$[HK]_b$	H^+ Correction[a]	E_0	E_0^0	log (HF)	log E_0
7.92×10^{-3}	0.3907	0.836	0.3266	0.986	1.30	9.47×10^1	−2.1013	1.976
3.98×10^{-3}	.1951	.887	.1731	.992	0.659	6.47×10^2	−2.4001	2.811
1.99×10^{-3}	.1462	.905	.1323	.990	1.40	4.09×10^3	−2.7011	3.611
9.94×10^{-4}	.0389	.966	.0385	.987	0.033	1.58×10^4	−3.0026	4.200
4.98×10^{-4}	.0487	.958	.0466	.991	.367	7.41×10^4	−3.3023	4.870
1.99×10^{-4}	.0389	.966	.0385	.994	.791	3.81×10^5	−3.7011	5.581
9.94×10^{-5}	.0292	.977	.0285	.982	.850	1.23×10^6	−4.0026	6.090
2.99×10^{-5}	.0195	.986	.0192	.990	.857	6.18×10^6	−4.5343	6.791
9.94×10^{-6}	.0167	.989	.0166	.982	1.32	1.71×10^7	−5.0026	7.233

[a] Factor by which E_0 is to be multiplied to give the value it would have at 2.00 M H^+.

by Leden.[16] The first is almost certainly too small because of the impurity. Comparison of the last two experiments of Table III with the last experiment of Table II indicates this error to be about 30%. In addition, it was assumed that all of the uncomplexed zirconium was Zr^{+4} which, if not true, again causes the first equilibrium quotient to be low. The values of K_2 and K_3 should not be affected by the presence of the impurity and should be correct provided the right species have been chosen. The precision in determining K_2 is estimated to be ±8% while K_3 could be evaluated only approximately at the bisulfate concentrations used, and may be in error by a factor of two.

Fluoride Complexing.—Experiments similar to the sulfate series were performed to establish the zirconium species present in acidic solutions containing hydrofluoric acid. The following equation may be derived

$$\partial \log E_0^0/\partial \log (HF) = -f_1 - 2f_2 - 3f_3 - \ldots \quad (22)$$

where each f represents the fraction of the zirconium which has the indicated number of fluoride ions attached.

The data are given in Table IV and plotted in Fig. 4. The solutions were prepared by adding small aliquots of a sodium fluoride solution to 2.00 M perchloric acid. A small acidity correction, for dilution of the perchloric acid and formation of HF, was applied (see column 5 of Table IV).

At the high concentrations of TTA used in some of the experiments there would probably be complexing of zirconium by TTA in the aqueous phase if there were no hydrofluoric acid 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 complexes, it seems unreasonable that there could be much competition by TTA for the zirconium in the presence of hydrofluoric acid, especially since the HF concentration was increased much more than the TTA concentration. To settle this point, it would be necessary to measure the TTA dependence in the presence of hydrofluoric acid. In the present experiments a fourth power TTA dependence was assumed in correcting the extraction coefficients to unit activity of TTA.

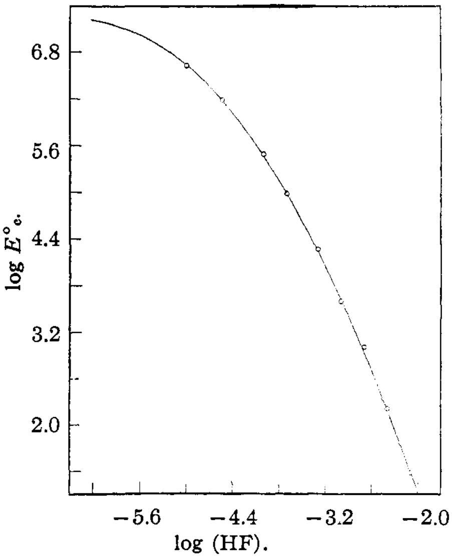

Fig. 4.—Dependence of extraction coefficient on hydrofluoric acid concentration.

The solid curve of Fig. 4 was plotted using the following values of the equilibrium quotients for the indicated equilibria

$Zr^{+4} + HF = ZrF^{+3} + H^+$ $K_1 = 6.3 \times 10^5$
$ZrF^{+3} + HF = ZrF_2^{+2} + H^+$ $K_2 = 2.10 \times 10^4$
$ZrF_2^{+2} + HF = ZrF_3^+ + H^+$ $K_3 = 6.7 \times 10^2$

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(16) I. Leden, *Z. physik. Chem.*, **188**, 160 (1941). The following modifications were made. The logarithm of the function on the left of Leden's equation (6) was plotted *versus* the logarithm of the HSO_4^- concentration. In the region where only the first and second complexes are important this curve has a universal shape, approaching a constant value at low HSO_4^- concentrations. This value is related to the first association constant and was determined by obtaining the best fit of the data to a theoretical plot. To get the second constant, the first constant was subtracted from the left side of (6) and this quantity divided by the HSO_4^- concentration. The logarithm of this quantity was plotted *versus* log (HSO_4^-) and now the same universal curve results, as long as complexes containing more than three sulfates are unimportant. The constant was determined as before. The process may be repeated to give higher constants.

The method of evaluating the equilibrium quotients was the same as in the preceding section; the estimated precision in evaluating K_1 and K_2 is ±10%, while that for K_3 is ±30%.

To illustrate the stability of the fluoride complexes, one calculates from the data of Table IV that in 10^{-5} M hydrofluoric acid, 78% of the zirconium is complexed by fluoride and that in 8×10^{-3} M hydrofluoric acid, all but 0.00012% of the zirconium is complexed. From the slope of the curve of Fig. 4 and equation (22) the average number of fluoride groups per zirconium ion is found to be one at 2×10^{-5} M hydrofluoric acid, two at 5×10^{-4} M hydrofluoric acid and three at 10^{-2} M hydrofluoric acid. The same considerations apply here as in the case of the sulfate complexes regarding the validity of the equations and the values of the equilibrium quotients. Again, the successive complexing constants differ so little that all solutions contain appreciable amounts of several species.

It was thought that hydrofluoric acid 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 hydrofluoric acid from coming in contact with the glass. In no case was there any evidence of attack of the glass and the extraction appeared to come to equilibrium and remained steady thereafter. Several preliminary experiments were run in non-coated glass vessels, but even here there was no sign of attack, as the extraction coefficients were about the same as with the coated vessels. Apparently the hydrofluoric acid does not attack silica at this rather high acidity (2.0 M) and relatively low concentration of hydrofluoric acid.

Chloride and Nitrate Complexing.—The extraction coefficient of trace zirconium was measured in mixtures of hydrochloric and perchloric acids at a total hydrogen ion concentration of 2.00 M. Similar experiments were carried out with mixtures of nitric acid and perchloric acid. The data are given in Table V. The per cent. uncomplexed was assumed to be equal to the extraction coefficient for the given solution divided by the extraction coefficient in 2.00 M perchloric acid. This presumes that there are no significant differences in activity coefficients in the various solutions studied.

TABLE V

CHLORIDE AND NITRATE COMPLEXING AT 25° AND 2.00 M H^+

$HClO_4$ moles/l.	HCl, moles/l.	HNO_3, moles/l.	Fraction Zr uncomplexed
0.80	1.20	..	0.29
.00	2.00	..	.19
.80	..	1.20	.30
.00	..	2.00	.20

Without specifying the nature of the uncomplexed and complexed zirconium species, the following equations may be written

$$\mathrm{Zr(IV)} + x\mathrm{Cl}^- = \mathrm{Zr(IV)Cl}_x \qquad (23)$$

$$K = (\mathrm{Zr(IV)Cl}_x)/(\mathrm{Zr(IV)})(\mathrm{Cl}^-)^x \qquad (24)$$

Equating the equilibrium quotients for two different chloride concentrations one obtains

$$\frac{(\mathrm{Cl}^-)_1}{(\mathrm{Cl}^-)_2^x} = \frac{(\mathrm{Zr(IV)Cl}_x)_1(\mathrm{Zr(IV)})_2}{(\mathrm{Zr(IV)Cl}_x)_2(\mathrm{Zr(IV)})_1} \qquad (25)$$

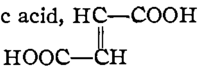
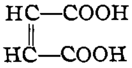
Substituting the data of Table V, x is found to be 1.08 for chloride ion and 1.06 for nitrate ion, in the corresponding expression. Therefore there is approximately one chloride ion and one nitrate ion present in the respective complexes in the range of conditions studied. Assuming x to be 1.00 the value of the equilibrium quotient for equation (24) is 2.0 for both the nitrate and chloride complexes. Elimination of the impurity would tend to raise these values about 30%.

Miscellaneous Complexes.—Single extraction experiments were run in the presence of a number of substances to ascertain the order of magnitude of their complexing action on zirconium at trace concentration. From one experiment, it is of course impossible to identify the species present. The results are presented in Table VI. Data for sulfuric and hydrofluoric acid are included for comparison. The fraction of zirconium uncomplexed was again assumed to be equal to the measured extraction coefficient divided by the extraction coefficient in 2.00 M perchloric acid.

TABLE VI

COMPLEXING ABILITY OF VARIOUS SUBSTANCES FOR ZIRCONIUM

Trace Concentrations of Zirconium, 2.00 M $HClO_4$, 25°

Substance	Concn. M	% Zr uncomplexed
Bisulfate, ion, HSO_4^-	0.0031	56
Hydrofluoric acid. HF	10^{-5}	22
Oxalic acid. $H_2C_2O_4$	0.001	0.36
Malonic acid, $HOOC-CH_2-COOH$	0.01	100
Succinic acid. $HOOC-(CH_2)_2-COOH$	0.005	100
Glutaric acid, $HOOC-(CH_2)_3-COOH$	0.1	94
Fumaric acid,  $\begin{matrix}HC-COOH\\ \|\\ HOOC-CH\end{matrix}$	0.05	88
Maleic acid.  $\begin{matrix}HC-COOH\\ \|\\ HC-COOH\end{matrix}$	0.05	74
Orthophosphoric acid, H_3PO_4	0.012	68
Orthoboric acid, H_3BO_3	0.1	100
Metasilicic acid, H_2SiO_3	0.01	87
Acetic acid, CH_3COOH	1.0	100
Trifluoroacetic acid. CF_3COOH	0.11	51
Carbonic acid, H_2CO_3	1 atm. CO_2	90
Hydrogen peroxide, H_2O_2	0.015	63

The fluoride complex is by far the most stable studied. In the series of aliphatic dibasic acids from oxalic to glutaric, only oxalic showed any strong complexing tendency. The apparent value of 6% of the zirconium complexed by glutaric acid may not be 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. Geometry considerations cannot be too important since the carboxyl groups of all the acids are able to assume very nearly the same relative configuration. The explanation for the great difference in complexing ability must lie in more complicated effects.

The two unsaturated dibasic acids, fumaric and maleic, seem to have some complexing tendencies, with 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 per cent. 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 0.11 *M*. It should be pointed out that the presence of a very small amount of hydrofluoric acid in the trifluoroacetic acid could account for the observed results. The experiment with the silicic acid solution, which was very cloudy, probably does not indicate complexing but rather the formation of a small amount of radio-colloid. It is believed that little significance should be attached to the apparent value of 10% complexing when carbon dioxide gas was present in the extraction flask at a pressure of one atmosphere.

It has been observed[17] that plutonium(IV) at macro concentrations forms complexes with hydrogen peroxide involving two plutonium atoms in the complex ion. Zirconium at trace concentrations apparently forms a complex with hydrogen peroxide, which must certainly contain only one zirconium atom in the complex ion. It would be interesting to study the zirconium peroxide complexes at higher concentrations of zirconium. to see if peroxy complexes containing two zirconium ions are formed.

A correlation of the stability of the various zirconium complexes will be presented in a later paper.

Summary

The nature of the zirconium(IV) species existing in aqueous solutions has been investigated by means of a two phase distribution equilibrium. The zirconium is partially extracted into benzene as the neutral chelate of thenoyltrifluoroacetone and the formulas of the zirconium species in the aqueous phase are deduced from the quantitative variation of the extraction coefficient as a function of the aqueous solution composition.

In 2 *M* perchloric acid at 25° and low zirconium concentrations, the average number of hydroxide ions attached to each zirconium ion lies between zero and one. The composition is not known precisely because of the interference in the experiments of an unidentified impurity.

The stabilities of several of the complexes formed with sulfate and fluoride ions were measured in 2 *M* perchloric acid solution. At bisulfate concentrations of 10^{-2} and 0.3 *M* there are on the average one and two sulfate groups in the complex, respectively. At hydrofluoric acid concentrations of 2×10^{-5}, 5×10^{-4} and 10^{-2} *M* the average number of fluorides per zirconium ion is one, two and three, respectively. In both cases the equilibrium constants for the formation of the successive complexes are so close together that any solution always contains appreciable amounts of several complexes.

Chloride and nitrate ions form only weak complexes of about the same stability in 2 *M* perchloric acid. Peroxide forms a moderately stable complex under the same conditions. The oxalate complex is very stable, while the next three members of the aliphatic, dibasic acid series show little tendency towards complex formation.

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[17] R. E. Connick and W. H. McVey, THIS JOURNAL, **71**, 1534 (1949).