this fact it is best not to use standard substances at all, but to apply the method used here.

Acknowledgment.—The authors wish to express their sincere appreciation to Professor A. Legsdin, Department of Metallurgical Engineering and Mineral Dressing of the Missouri School of Mines and Metallurgy, for his coöperation in carrying out spectrographic analyses of the diamond samples.

Grateful acknowledgments for supplying the diamond samples are made to Dr. R. W. Young of the Diamond Research Laboratory, Johannesburg, South Africa.

ROLLA, MISSOURI RECEIVED APRIL 2, 1951

[CONTRIBUTION FROM THE KNOLLS ATOMIC POWER LABORATORY, GENERAL ELECTRIC COMPANY]

Thorium Complexes with Chloride, Fluoride, Nitrate, Phosphate and Sulfate[1]

BY E. L. ZEBROSKI, H. W. ALTER AND F. K. HEUMANN

The dependence of the thorium extraction equilibrium on the fourth power of TTA activity and the minus fourth power of hydrogen ion activity was demonstrated, confirming that Th(IV) is a simple (hydrated) tetrapositive ion in perchlorate solutions of acidity greater than about 0.08 *M*. The association constants for the first several complexes of thorium ion with fluoride, chloride, nitrate, sulfate and phosphate ions, respectively, have been determined in acid media by the TTA distribution method. Evidence was obtained that complexes like $Th(H_2PO_4)^{+++}$, $Th(H_2PO_4)_2^{++}$ and $Th(SO_4)_2$ are measurably weak acids in 1 to 2 molar acid solutions.

Thorium Ion Complex Equilibria

Of the tetravalent ions thorium ion is of particular interest in complexing studies because of its large ionic radius relatively simple electronic configuration, and the absence, in acid solutions, of the complicating effects of hydrolysis and polymerization. Its complexing properties have been rarely studied until recently, however, because many of the usual methods of measurement of complex ion equilibria are inapplicable to most thorium complexes, particularly when the complexing ion or molecule is present in excess.

The method used here has been applied by Connick and Reas[2] and Connick and McVey to the investigation of the complexing and hydrolytic behavior of zirconium.

Experimental

Experimental.—The distribution measurements were performed using a solution of thenoyltrifluoracetone,[3] which for convenience is called TTA, in benzene as extractant for thorium. The aqueous phases contained thorium ion at a concentration of 3 to 5 × 10^{-4} *M*, from 0.0875 to 2.00 *M* perchloric acid, and added salts as indicated. The solutions were maintained at constant ionic strength, μ, with sodium or lithium perchlorate.

The two liquid phases were contacted at 25.0 ± 0.1° by shaking in glass stoppered vessels or by mechanical stirring in small long-necked flasks fitted with close fitting teflon or fluorothene bearing sleeves to prevent evaporation. Preliminary experiments showed that the extraction equilibrium with respect to thorium was probably diffusion limited with a half-time of the order of 0.1 minute, but since equilibrium with respect to TTA distribution is slow the phases were agitated for a period of 30 minutes or longer. Aliquot parts were withdrawn from both phases by micropipet. Results are given as a distribution coefficient R = (thorium in organic phase)/(thorium in aqueous phase) based on the average of duplicate or quadruplicate analyses of both phases. The thorium activity from either phase was then transferred to 8 *N* HNO_3 by appropriate semi-micro-extractions and re-extractions with 1 *M* TTA in benzene and 8 *N* HNO_3, respectively. The resulting nitric acid solution was evaporated on one-inch platinum discs and the alpha activity counted with a methane proportional counter. In the individual extractions the total concentration of Th(IV) in aqueous phases (before extraction) averaged about 3 × 10^{-4} *M*.

Materials.—Vacuum distilled TTA was obtained from Prof. M. Calvin of the University of California Radiation Laboratory; it was used without further purification. Stock solutions were made up in thiophene-free benzene and stored in glass vessels covered with aluminum foil to exclude light.

Sodium and lithium perchlorates obtained from the G. Frederick Smith Company were recrystallized before use. The major impurity from a complexing standpoint was sulfate. Since this was not completely removed by recrystallization, barium sulfate was precipitated from the reagents during purification, except in the study of nitrate and sulfate complexing. About 10^{-3} *M* $Ba(ClO_4)_2$ was present in other extraction experiments.

Sodium nitrate, sodium chloride and sodium sulfate were recrystallized reagent grade salts. The perchloric acid was the triple distilled G. F. Smith product.

The tracer was Th^{230} (ionium) which emits 4.68 mev. alpha particles with a half-life of 80,000 years. It was obtained from the Argonne National Laboratory in dilute nitric acid solution. It contained about six times as much by weight of Th^{232}.

Treatment of Distribution Data.—For purposes of calculation the data are treated as though the activity coefficients of all species in solution remain strictly constant at constant ionic strength. The association constants are expressed as concentration equilibrium constants and are strictly valid only for solutions of the compositions of a given experiment.

The reactions of thorium in acid solution with an anion whose electrical charge is $-x$ may be written

$$Th^{+4} + nX^{-x} = ThX_n^{+4-nx} \quad (1)$$

the general equilibrium constant is

$$K_n = (ThX_n^{+4-nx})/(Th^{+4})(X^{-x})^n \quad (2)$$

From material balance

$$(Th_t) = (Th^{+4})\left(1 + \sum_n K_n(X^{-x})^n\right) \quad (3)$$

where (Th_t) is the total metal ion concentration in an aqueous phase and n covers the range of the number of ligands considered.

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[1] Presented at the 119th Meeting of the American Chemical Society, April 11, 1951, Cleveland, Ohio. The method employed here and examples of its application to nitrate, sulfate and phosphate complexes was described in a paper by E. L. Zebroski and F. K. Heumann and presented at an A. E. C. Information Meeting, Chicago, Ill., October 19, 1948. This work was carried out under the auspices of the Atomic Energy Commission.

[2] R. E. Connick and W. Reas, AECD-2491; R. E. Connick and W. McVey, THIS JOURNAL, **71**, 3181 (1949).

[3] J. C. Reid and M. Calvin, *ibid.*, **72**, 2948 (1950).

The extraction equilibrium is

$$\text{Th}^{+4} + 4\text{HT}_b = \text{ThT}_{4b} + 4\text{H}_a^+ \qquad (4)$$

at constant $(\text{H}^+)_a$ and $(\text{HT})_b$, where the subscripts refer to solutes in aqueous and benzene phases, respectively. Then let

$$R_0 = (\text{ThT}_4)_b/(\text{Th}^{+4})_a \qquad (5)$$

where R_0 is the distribution coefficient of metal in the absence of aqueous complexer and $(\text{ThT}_4)_b$ is metal concentration in the organic phase. Let R be the extraction coefficient in the presence of varying concentrations of complexer and constant acid and TTA activities. Then from equation (5)

$$R = (\text{ThT}_4)_b/(\text{Th}_t) = R_0(\text{Th}^{+4})/(\text{Th}_t) \qquad (6)$$

where (Th_t) is the total thorium concentration, complexed plus uncomplexed, in the aqueous phase. Then from equation (3)

$$\left(\frac{R_0}{R} - 1\right) = \sum_n K_n(\text{X}^{-x})^n \qquad (7)$$

It is assumed that the extractable species in the benzene phase remains the same for all concentrations of X. The parameters K_n may be evaluated from the measurement of R as a function of X. If the ligand is a weak acid with a net electrical charge of $-x$, reaction (1) is written

$$\text{Th}^{+4} + n\text{H}_m\text{X}^{m-x} = \text{ThX}_n\text{H}_{nm-q}^{+4-q+n(m-x)} + q\text{H}^+ \qquad (8)$$

and (7) becomes

$$\frac{R_0}{R} - 1 = \sum_n\sum_q K_{nq}(\text{H}_m\text{X}^{m-x})^n/(\text{H}^+)^q \qquad (9)$$

where K_{nq} is the equilibrium constant for equation (8).

A correction should be made in the material balance for the metal ion combined in the first aqueous chelate complex by the reaction[4]

$$\text{Th}_a^{+4} + \text{HT}_a = \text{ThT}_a^{+3} + \text{H}_a^+ \qquad (10)$$

Equation (7) then becomes

$$d\left(\frac{R_0}{R} - 1\right) = \sum_n K_n(\text{X}^{-x})^n \qquad (11)$$

where $d = 1 + K_c(\text{HT})_a/(\text{H}^+)_a$ and K_c is the measured equilibrium constant for reaction (10), and $(\text{HT})_a$ is calculated from the concentration of TTA in the organic phase and the distribution coefficient of TTA for the given ionic strength.

In the case of relatively weak association and "tracer" metal ion concentrations, a negligible fraction of the X is bound and (X^{-x}) is simply the added concentration of X^{-x}. This is the case for nitrate and chloride solutions. For HSO_4^-, a correction was made for dissociation to sulfate ion. For strong association where an appreciable fraction of X is bound in complexes (as is the case with HF), correction must be made for the binding of an appreciable fraction of added X by metal ion.

The data in the next section are in qualitative agreement with previous work[5] which indicated negligible hydrolysis of thorium ion at pH 1.1 or less. Accordingly, no corrections for hydrolysis were necessary.

Acid Dependence of the Distribution Equilibrium.—It can be shown that a plot of log R *versus* log $a_\text{H}{}^+$ at constant (TTA) should yield a straight line of slope -4 in the special case where Th(IV) is uncomplexed and unhydrolyzed[2] and where a_{H^+} is the perchloric acid activity. This is a consequence of the assumed extraction equilibrium (4). If Th(IV) is hydrolyzed to any extent, the slope will be greater than -4, provided that the species in the benzene phase remains the same.

The acid dependence of R at acidities greater than 0.0986 M is shown in Fig. 1. The change in the activity coefficient of perchloric acid in sodium perchlorate at constant ionic strength was assumed to be negligible for the region covered. The data of Robinson and Baker[6] converted to the molar scale, were used to determine the activity of perchloric acid at varying ionic strengths. The error in slope due to neglecting the change in the extent of formation of the aqueous thorium–TTA complex with acidity is negligible for the experiments at constant ionic strength of 4.00 giving a value of -3.87 for the slope. For the experiments at lower and varying ionic strength, the change in the value of the d factor is about 20%, which would increase the numerical value of the slope of the log R *versus* log a_{H^+} plot by about 4%. The change in $(\text{TTA})_b$ due to changing ionic strength is calculated to be 0.33%, which would also increase the numerical value of the slope by 0.3%, giving a net corrected value of -4.17 for the slope at varying ionic strength.

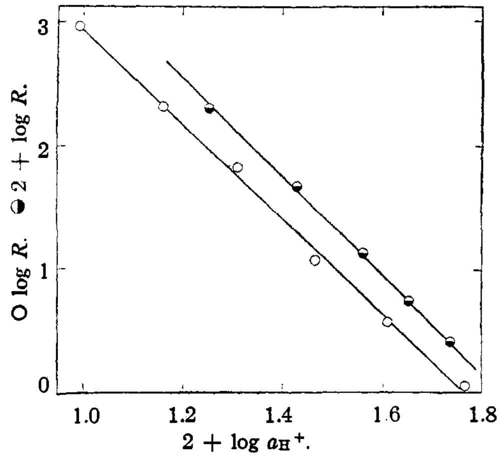

Fig. 1.—Acid dependence at high acidities: ○, μ = 4.00 M in NaClO_4 and HClO_4; $(\text{TTA})_b$ = 0.100 M; line drawn with slope -3.78. ●, data at varying ionic strength equal to (HClO_4) and corrected for the changing activity of HClO_4; $(\text{TTA})_b$ = 0.40 M; line drawn with slope -4.00.

Both sets of data are considered to be in satisfactory agreement with the expected fourth power hydrogen ion activity dependence in view of the unknown effect of varying ionic strength on the activity coefficient of thorium perchlorate, and the unknown, though probably small, effect of solution composition at constant ionic strength on the activity coefficients of both perchloric acid and thorium perchlorate.

The distribution coefficient at low acidities was measured as a function of pH as the solution was titrated with acid. The pH was measured with a glass electrode with a 2 M sodium nitrate salt bridge and saturated calomel electrode, using a vibrating reed electrometer for potential measurements. The relative potential measurements were reproducible to about 0.05 millivolt. In the plot of log R *versus* $-$ log (H^+) shown in Fig. 2 the fourth power acid dependence fails at about 0.08 M hydrogen ion for this Th(IV) concentration ($\sim 10^{-4}$ M). Attempts to fit the data at lower acidities to simple hydrolytic equilibria were unsuccessful.

The acidity scale was standardized by known concentrations of perchloric acid in lithium perchlorate.

TTA Dependence of the Distribution Equilibrium.—Distribution data were obtained for tracer thorium between an aqueous phase and varying TTA concentrations in benzene. The small changes in acidity as the concentration of TTA varied were determined by means of the glass electrode and vibrating reed electrometer arrangement previously mentioned. Concentrations of TTA in benzene were converted to activities, a_{HT}, using the data of King and Reas.[7] The activity of tracer ThT_4 in benzene is assumed to be

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(4) E. L. Zebroski, Plutonium Project Report BC-63, July 1, 1947.

(5) J. Kasper, Dissertation, Johns Hopkins University, 1941; J. C. Hindman, Argonne National Laboratory Report ANL-4143, April 15, 1948; K. A. Kraus and R. W. Holmberg, AECD-2919, August 29, 1950.

(6) R. A. Robinson and O. J. Baker, *C.A.*, **41**, 5000 (1947).

(7) E. L. King and W. H. Reas, THIS JOURNAL, **73**, 1804 (1951).

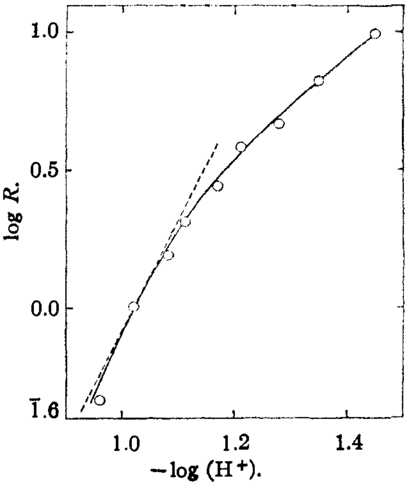

Fig. 2.—Acid dependence at low acidities: $\mu = 3.0$ M in $LiClO_4$; dotted line drawn with slope 4.00.

equal to that for TTA itself.[8] The corrected value of the logarithm of R is then given by

$$\log R_{cor.} = \log R + 4\Delta \log(H^+) + \log \gamma_{HT} = n \log a_{HT} + \text{constant} \quad (12)$$

Figure 3 shows a plot of log $R_{cor.}$ against log a_{HT}.

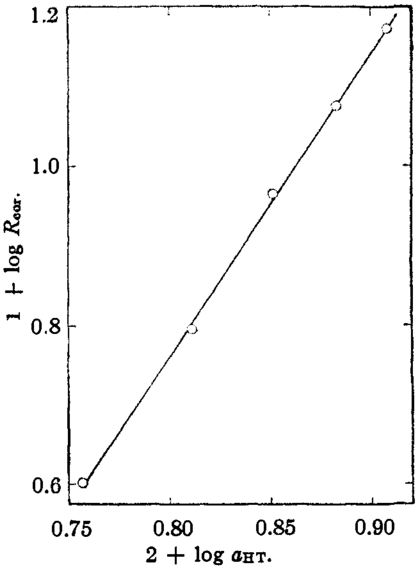

Fig. 3.—TTA dependence at $\mu = 3.00$ M in $LiClO_4$ and $HClO_4$; $(HClO_4) = 0.120$ M; line drawn with a slope 3.83.

The observed fourth power dependence on TTA activity and the minus fourth power dependence on hydrogen ion activity are taken to establish the assumed distribution equilibrium expression

$$K_R = \frac{(ThT_4)_b(H^+)_a^4}{(Th^{+4})_a(HT)_b^4} \quad (13)$$

Chloride Complexes.—Distribution data for chloride solutions up to almost 2 molar chloride are fitted with only two constants. The data at higher chloride concentrations require two additional complexes. Although the precision of the radiochemical analysis used is such that the third and fourth constants are uncertain by a factor of two, the qualitative requirement of four species to describe the behavior of these solutions is unaffected.

Neglecting the d factor of about 1.04, the solid curve in Fig. 4 is calculated from the equation

$$\left(\frac{R_0}{R} - 1\right)/(Cl^-) = 1.30 + 0.12(Cl^-) + 0.087(Cl^-)^2 + 0.014(Cl^-)^3 \quad (14)$$

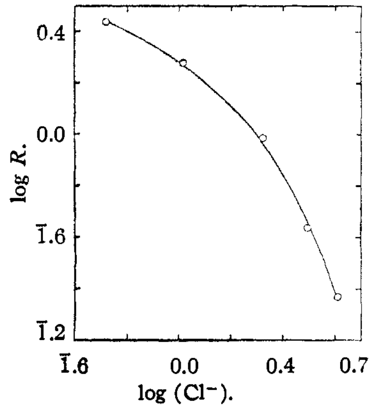

Fig. 4.—Chloride dependence at $\mu = 4.00$ M in $NaClO_4$, NaCl and $HClO_4$; $(HClO_4) = 0.100$ M; $(TTA)_b = 0.100$ M.

where the coefficients are the respective equilibrium constants for the reactions

$$Th^{+4} + nCl^- = ThCl_n^{+4-n} \quad (15)$$

Day and Stoughton found a constant for the first complex of 1.76 at an ionic strength of 0.5 by similar distribution measurements.[8]

Fluoride Complexes.—Fluoride complexing constants were measured to provide a comparison between the TTA distribution method and the potentiometric method employed by Dodgen and Rollefson.[9] The two reactions considered are

$$Th^{+4} + HF = ThF^{+3} + H^+ \quad (16)$$

$$Th^{+4} + 2HF = ThF_2^{+2} + 2H^+ \quad (17)$$

with equilibrium constants K_1 and K_2, respectively.

Under their conditions we obtain $K_1 = 5.0 \times 10^4$ and $K_2 = 2.9 \times 10^7$. Dodgen and Rollefson give $K_1 = 4.5 \times 10^4$ and $K_2 = 2.92 \times 10^7$.

Nitrate Complexes.—Only two complexes were observed up to the highest nitrate concentration used, 4.93 M. The constants for the reactions

$$Th^{+4} + NO_3^- = Th(NO_3)^{+3} \quad (18)$$

$$Th^{+4} + 2NO_3^- = Th(NO_3)_2^{+2} \quad (19)$$

were found to be 2.83 and 1.91, respectively, from Fig. 5.

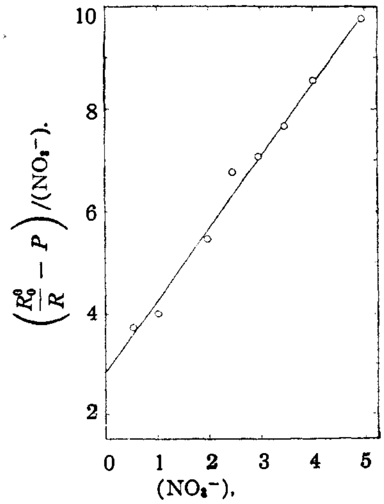

Fig. 5.—Nitrate dependence at $\mu = 5.97$ M in $NaClO_4$, $NaNO_3$ and $HClO_4$; $(HClO_4) = 0.0875$ M; $(TTA)_b = 0.08$ M; initial aqueous thorium concentration 3.02×10^{-6} M; (SO_4^-) varied from 8.7×10^{-6} M to 4.9×10^{-5} M; as (NO_3^-) varied from 0.0 M to 4.93 M.

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[8] R. A. Day and R. W. Stoughton, THIS JOURNAL, 72, 5662 (1950).

[9] H. W. Dodgen and G. K. Rollefson, *ibid.*, 71, 2600 (1949).

In making this calculation, it is necessary to correct for the small amount of sulfate present as an impurity in the reagents. The expression which includes a sulfate correction is

$$\left(\frac{R_0^0}{R} - P\right)/(\mathrm{NO_3^-}) = K_1 + K_2(\mathrm{NO_3^-})$$

where $R_0^0 = (\mathrm{ThT_4})_b/(\mathrm{Th^{+4}})_a$ at zero nitrate and sulfate, $R = (\mathrm{ThT_4})_b$/(total aqueous thorium) and $P = d + K_S \frac{(\mathrm{HSO_4^-})}{(\mathrm{H^+})}$. K_S is the same as the K_1 defined in the sulfate complexing section. Day and Stoughton found only the first complex at an ionic strength of 0.5 with a formation constant of 4.73.[8]

Sulfate Complexes.—The distribution data shown in Fig. 6 can be represented by equilibrium constants for the reactions

$$\mathrm{Th^{+4} + HSO_4^- = ThSO_4^{++} + H^+} \quad (20)$$

$$\mathrm{Th^{+4} + 2HSO_4^- = Th(SO_4)_2 + 2H^+} \quad (21)$$

In order to correct for the dissociation of bisulfate it is necessary to have a value of the acid constant at the ionic strength of 2.0 *M*. This was estimated for this calculation by measuring the *p*H of eight solutions 0.040 *M* in $\mathrm{Na_2SO_4}$, 1.85 *M* $\mathrm{NaClO_4}$, and containing from 0.005 to 0.091 *M* perchloric acid. A concentration constant of 0.084 ± 0.02 was obtained for the dissociation of bisulfate ion in this medium. A value of about 0.08 can be estimated from activity data.[10]

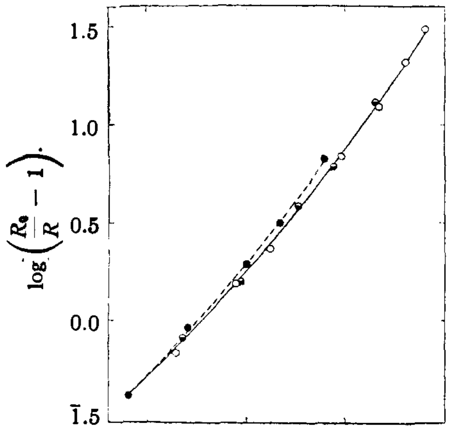

Fig. 6.—Bisulfate dependence at $\mu = 2.00$ *M* in $\mathrm{NaClO_4}$, $\mathrm{HClO_4}$ and $\mathrm{NaHSO_4}$; ○, $(\mathrm{HClO_4}) = 0.500$ *M*; $(\mathrm{TTA})_b = 0.25$ *M*; ◒, $(\mathrm{HClO_4}) = 1.00$ *M*, $(\mathrm{TTA})_b = 0.50$ *M*; ●, $(\mathrm{HClO_4}) = 1.99$ *M*, $(\mathrm{TTA})_b = 1.00$ *M*.

The data require the assumption of inverse first power hydrogen ion dependence for the first complex as in equation (20), and inverse second power dependence for the second complex as in equation (21).

The data for 0.50 and 1.00 molar acid fall on the same line within the error of measurement. The equilibrium constants for equations (20) and (21) corresponding to the smooth line are $K_1 = 159$ and $K_2 = 2850$. These were evaluated by plotting the quantity $(R_0/R - 1)d(\mathrm{H^+})/(\mathrm{HSO_4^-})$ against $(\mathrm{HSO_4^-})/(\mathrm{H^+})$. A straight line results whose intercept is K_1 and whose slope is K_2 (*cf.* equations (9) and (11)). The points for 1.99 *M* acid fall appreciably above this curve at higher sulfate concentrations.

Assuming that the activities are strictly constant the departure can be described by the additional equilibrium

$$\mathrm{Th^{+4} + 2HSO_4^- = Th(SO_4HSO_4)^+ + H^+} \quad (22)$$

for which a very approximate equilibrium constant of K_3 = 800 is estimated.

Phosphate Complexes.—The values of the parameters K_1' and K_2' in Table I correspond to the equation

$$\left(\frac{R_0}{R} - 1\right)(\mathrm{H^+})/(\mathrm{H_3PO_4}) = K_1' + K_2'(\mathrm{H_3PO_4})/(\mathrm{H^+}) \quad (23)$$

TABLE I

EXTRACTION PARAMETERS FOR DISTRIBUTION FROM PHOSPHATE SOLUTIONS

$(\mathrm{HClO_4})_a$	$(\mathrm{TTA})_b$	K_1'	K_2'
0.250	0.125	180	9900
.500	.250	232	17,900
1.00	.500	187	24,000
2.00	1.00	312	36,200

Plots of the left-hand member of this equation against $(\mathrm{H_3PO_4})/(\mathrm{H^+})$ in Fig. 7 give straight lines within experimental uncertainty for all the data except at 0.25 molar acid, where large departures occur at the higher phosphoric acid concentrations. The results on the solutions at lower acidities were difficult to reproduce and precipitates containing a large part of the thorium developed on standing for a day or more.

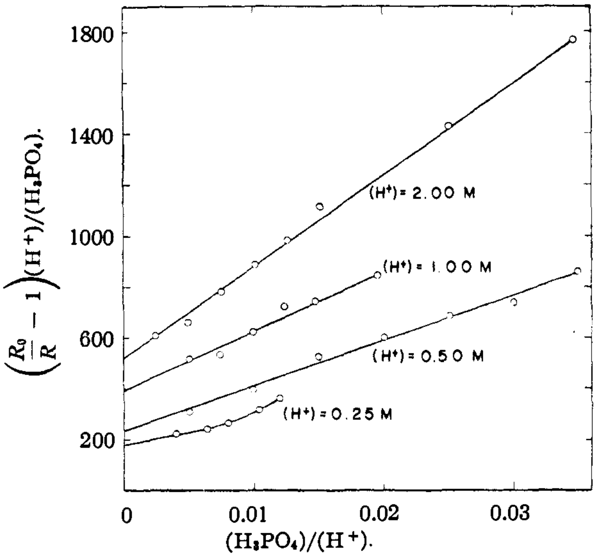

Fig. 7.—Phosphate dependence at varying acid concentrations; $\mu = 2.00$ *M* in $\mathrm{NaClO_4}$ and $\mathrm{HClO_4}$; for clarity, 200 has been added to the ordinate of the upper two curves.

The trend of K_1' and K_2' with changing acidity suggests that the number of hydrogen ions associated with the mono- and diphosphate thorium complexes varies with acidity. The variation in K_1' and K_2' can be expressed by the equations

$$K_1' = K_{10}(\mathrm{H^+}) + K_{11} \quad (24)$$

$$K_2' = K_{21}(\mathrm{H^+}) + K_{22} \quad (25)$$

where the subscripts are used in the same sense as in the general equation (9).

The set of reactions corresponding to the constants in equations (24) and (25) are

$$\mathrm{Th^{+4} + H_3PO_4 = Th(H_3PO_4)^{+4}} \quad K_{10} = 78 \quad (26)$$

$$\mathrm{Th^{+4} + H_3PO_4 = Th(H_2PO_4)^{+3} + H^+} \quad K_{11} = 150 \quad (27)$$

$$\mathrm{Th^{+4} + 2H_3PO_4 = Th(H_2PO_4H_3PO_4)^{+3} + H^+} \quad K_{21} = 14{,}000 \quad (28)$$

$$\mathrm{Th^{+4} + 2H_3PO_4 = Th(H_2PO_4)_2^{++} + 2H^+} \quad K_{22} = 8{,}000 \quad (29)$$

The data are adequately represented by the above equilibria but are not sufficiently precise to eliminate the possible existence of species like $\mathrm{Th(HPO_4)^{++}}$ and $\mathrm{Th(H_3PO_4)_2^{++++}}$. Under comparable conditions King[11] found similar indica-

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[10] Yost and Russel, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 341.

[11] E. L. King, National Nuclear Energy Series, "The Transuranium Elements," McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 660.

tions in the solubility dependence of Pu(IV) phosphate. The monophosphate plutonium complex has a ratio of hydrogen/phosphate of nearly 3, while for all complexes containing up to five phosphate residues, ratios greater than 2 were obtained.

Distribution of TTA.—Table II gives the distribution of TTA between an aqueous phase 0.09 molar in $HClO_4$ of the indicated ionic strength in $NaClO_4$ and 0.50 *M* TTA in benzene. Concentrations of TTA in the aqueous phase were determined by measurement of light absorption at 267 and 292 mμ. A value of 6.3 was used for K_e in equation (11) at an ionic strength of 2.0. A value of 7.6 was estimated for an ionic strength of 6.0.

TABLE II

DISTRIBUTION OF TTA (BENZENE/WATER)

μ	0.59	1.09	2.09	4.09	6.09
R	49	57	76	167	443

TABLE III

SUMMARY OF CONSTANTS

	Ionic strength *M* μ	Equilibrium constants *K*
$Th^{+4} + NO_3^- = Th(NO_3)^{+++}$	5.97	2.83
$Th^{+4} + 2NO_3^- = Th(NO_3)_2^{++}$	5.97	1.41
$Th^{+4} + HF = ThF^{+++} + H^+$	0.5	5.0×10^4
$Th^{+4} + 2HF = ThF_2^{++} + 2H^+$	0.5	2.9×10^7
$Th^{+4} + Cl^- = ThCl^{+3}$	4.0	1.30
$Th^{+4} + 2Cl^- = ThCl_2^{++}$	4.0	0.125
$Th^{+4} + 3Cl^- = ThCl_3^+$	4.0	~0.037
$Th^{+4} + 4Cl^- = ThCl_4$	4.0	~0.014
$Th^{+4} + HSO_4^- = ThSO_4^{++} + H^+$	2.0	159
$Th^{+4} + 2HSO_4^- = Th(SO_4)_2 + 2H^+$	2.0	2850
$Th^{+4} + 2HSO_4^- = Th(HSO_4SO_4)^+ + H^+$	2.0	~800
$Th^{+4} + H_3PO_4 = Th(H_3PO_4)^{+4}$	2.0	78
$Th^{+4} + H_3PO_4 = Th(H_2PO_4)^{+3} + H^+$	2.0	150
$Th^{+4} + 2H_3PO_4 = Th(H_2PO_4H_3PO_4)^{+3} + H^+$	2.0	14000
$Th^{+4} + 2H_3PO_4 = Th(H_2PO_4)_2^{++} + 2H^+$	2.0	8000

Discussion

The change in composition of the organic layer at constant $(TTA)_b$ with changing concentration of complexers in the aqueous phase is very slight and it is reasonable to assume that the activity coefficients for TTA and ThT_4 remain very nearly constant. The activity coefficients of the aqueous species may, however, undergo substantial variation if the composition of the solution is extensively changed at constant ionic strength. The activity coefficient for thorium enters into the complexing and extraction equilibria in opposite directions with respect to its effect on the distribution coefficient. Changes in the activity coefficients of a complexing anion and of the corresponding complex may also tend to compensate. A change in the activity coefficient of hydrogen ion, however, which enters into the distribution expression to the fourth power, probably accounts for a significant part of the observed change in distribution with changing complexer concentration. For the chloride and nitrate complex data, in which another salt is substituted for a large part of the initial perchlorate medium, the constants, particularly those beyond the first one, may be seriously affected. Development of satisfactory methods for estimating activities in mixed electrotypes is necessary to permit a more generally significant treatment of the data for higher complex equilibria in the case of such weak association.

SCHENECTADY, N. Y.

RECEIVED MAY 21, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WESTERN AUSTRALIA]

Transference Numbers in Aqueous Solutions of Zinc Sulfate

BY E. P. PURSER AND R. H. STOKES

Transference numbers of zinc sulfate in aqueous solution at 25° have been measured over the concentration range 0.005 to 2.0 molal by the electromotive force method. The results show normal behavior in concentrated solution with no indication of the formation of negatively charged zinc complex ions. At high dilution the slope of the curve $t_+ = f(\sqrt{m})$ approaches the Onsager limiting slope from above.

Data for transference numbers of aqueous solutions of zinc sulfate at 25° were reported by Wolten and King,[1] their results being derived from e.m.f. studies of concentration cells with zinc sulfate electrolyte and two-phase zinc amalgam electrodes, after the method of Stokes and Levien.[2] The measurements extended over the concentration range 0.005 to 2.270 molal.

The results of these workers for concentrated solutions gave negative values for the transference numbers of the cation, indicating the formation of negatively charged complex zinc ions at high concentration. This conclusion is contrary to the findings of Davies[3] in his work on the conductivity of zinc sulfate solutions. His results are consistent only with the formation of ion pairs (Zn^{++}-SO_4^{--}) which should cause no change in the transference numbers.

The present work is a redetermination of the transference numbers of zinc sulfate at 25° by the same method.

Experimental

Stock solutions of zinc sulfate, 2.0 and 0.1 *M*, were prepared from B.D.H. "Analar" zinc sulfate and double-distilled water. The crystalline salt was checked for purity and the solutions standardized by zinc and sulfate determinations. The solutions for use in the cells were made up as required by weight dilution of the stock solutions with double-distilled water.

Mercury for the amalgam electrodes was first treated by anodic oxidation after the method of Reilly and Rae,[4] then

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[1] Wolten and King, THIS JOURNAL, **71**, 576 (1949).

[2] Stokes and Levien, *ibid.*, **68**, 333 (1946).

[3] Davies, *Trans. Faraday Soc.*, **23**, 351 (1927); Davies, *ibid.*, **29**, 834 (1933).

[4] Reilly and Rae, "Physico-Chemical Methods," 2nd ed., revised, Methuen and Co., Ltd., London, 1933, p. 725.