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Computer Analysis of Potentiometric and Thenoyltrifluoroacetone (TTA) Solvent Extraction Studies on the Fluoride Complexes of Hafnium

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Measurements on fluoride-containing hafnium solutions in 3 M perchlorate media at 25° by precision potentiometry and by solvent extraction distribution using TTA have been subjected to high-speed digital computer analysis and the results interpreted in terms of the nature and stabilities of complex hafnium fluoride species present. Potentiometric hydrogen ion measurements with a quinhydrone half-cell gave the formation function for the mononuclear series of hafnium fluoride complexes from an average ligand number of about 2 to a maximum value of 6. At radioactive trace concentrations of hafnium, TTA extracted only Hf^{+4} and useful information was obtained on the formation of the first four fluoride complexes. The TTA and potentiometric data were combined in a weighted least squares machine program to calculate simultaneously the stepwise formation constants of the first six mononuclear fluoride complexes of hafnium. The values obtained were $\log k_1 = 4.89 +0.05, -0.06$; $\log k_2 = 3.67 +0.15, -0.23$; $\log k_3 = 2.97 +0.20, -0.39$; $\log k_4 = 2.77 +0.18, -0.32$; $\log k_5 = 1.55 +0.27, -0.82$; and $\log k_6 = 2.54 +0.27, -0.81$; where $k_n = (HfF_n)(H^+)/(HfF_{n-1})(HF)$. The equilibrium constant for the extraction of Hf^{+4} from 3 M perchloric acid with TTA was $\log K_{eq} = 6.63 \pm 0.03$. The distribution coefficient of HF between 0.5 M TTA and 3 M perchloric acid was $K_d = (HF)_0/(HF)_{aq} = 0.000347 \pm 0.000015$.

Potentiometric Studies

In principle the direct potentiometric measurement of hydrogen ion concentration as a function of hydrofluoric acid and metal concentrations could be used to calculate the formation function and thus the stability constants of the hafnium fluoride system.[1-4] By the direct Calvin–Bjerrum titration procedure, using the method and relations given in ref. 4, it was found that the formation curve was a function of hydrogen ion concentration up to 0.8 M perchloric acid concentration at an ionic strength of one.[5] Above 0.8 M perchloric acid the titration data were not sufficiently accurate, so for studies at 1, 2, and 3 M perchloric acid at 3 M perchlorate ion a simplified point by point potential difference method was devised. It was determined by this method that appreciable hydrolysis of Hf(IV) also occurred in 1.0 M perchloric acid.[5] In this paper only the results obtained in 2 and 3 M perchloric acid will be described.

Theory.—For the calculation of free ligand concentrations from the stoichiometric hydrofluoric acid concentration and the measured hydrogen ion concentration, the hydrofluoric acid constants reported by Caglioti[3] in 3 M perchlorate medium were used.

$$HF = H^+ + F^- \qquad K_a = 5.37 \times 10^{-4} \tag{1}$$

$$HF_2^- = HF + F^- \qquad K_{a_2} = 8.1 \times 10^{-2} \tag{2}$$

If the stoichiometric concentrations of ligand, C_A, and metal, C_M, are known and allowed to vary independently, the average ligand number, $\bar{n}$, for systems of strong complexes may be calculated from Bjerrum's relation[6]

$$\bar{n} = \frac{C_A - (A)}{C_M} \tag{3}$$

where in the fluoride system

$$(A) = (F^-) + (HF) + 2(HF_2^-) \tag{4}$$

If the concentrations of weak acids other than hydrofluoric are negligible and if hydrolysis of the metal species does not contribute appreciably to the acidity, the stoichiometric acid concentration, C_H, is given by

$$C_H = (H^+) + (HF) + (HF_2^-) \tag{5}$$

When weighed amounts of K_2HfF_6 are added to a known volume of solution of known C_H and total HF, eq. 3 may be written

$$\bar{n} = \frac{6C_M + (A)_i - (A)_f}{C_M} \tag{6}$$

which from eq. 1, 2, 4, and 5 becomes

$$\bar{n} = \frac{1}{C_M}\left(6C_M + (H^+)_f - (F^-)_f\left[1 + \frac{C_H - (H^+)_f}{K_{a_2}}\right] - (H^+)_i + (F^-)_i\left[1 + \frac{C_H - (H^+)_i}{K_{a_2}}\right]\right) \tag{7}$$

where the subscripts i and f refer to the initial and final values of the concentrations. In practice it was found that at high acidities the free (F^-) and (HF_2^-) concentrations were so low compared to (HF) that the terms containing (F^-) in eq. 7 were negligible and the equation reduced to

$$\bar{n} = \frac{6C_M + (H^+)_f - (H^+)_i}{C_M} \tag{8}$$

Over the short period of time between reading an initial potential corresponding to some value of $(H^+)_i$, dissolving a weighed amount of K_2HfF_6 in the cell solution, and reading the final potential corresponding to $(H^+)_f$,

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(1) S. Ahrland, R. Larsson, and K. Rosengren, *Acta Chem. Scand.*, **10**, 705 (1956).

(2) S. Ahrland and B. Noren, *ibid.*, **12**, 1595 (1958).

(3) V. Caglioti, L. Ciavatta, and A. Liberti, *J. Inorg. Nucl. Chem.*, **15**, 115 (1960).

(4) L. P. Varga and H. Freund, *J. Phys. Chem.*, **66**, 21 (1962).

(5) (a) D. N. Hume and L. P. Varga, Progress Report, Laboratory for Nuclear Science, M.I.T., Cambridge, Mass., May 6, 1961; (b) L. P. Varga and D. N. Hume, Paper presented at the Eighth Tetrasectional Oklahoma Meeting, American Chemical Society, Stillwater, Oklahoma, March 3, 1962.

(6) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

potential drifts due to liquid junction effects and other causes were minimal and potential differences were interpreted in terms of the species formed.

Distribution Studies

Solvent extraction data have been used extensively[7] in studies on complex ions and several reviews and discussions are available.[8] TTA has been a particularly useful extracting agent in quantitative complex ion studies on a variety of metal species[9,10] in addition to its well known usefulness in separation chemistry.

Of crucial importance in most complex ion studies by this method is the identification of the species extracted by the organic phase. In the absence of direct comparative studies such as by spectrophotometry, reasonable assumptions are made or detailed studies of all the parameters are attempted.[8-11] The application of high speed computers in the interpretation of partition and other types of data as reported by Rydberg, Sullivan, Moore, and associates[12] made it possible in the present studies using TTA to determine the dependence of the experimental distribution ratio on the organic extractant concentration, the ligand number of the extractable species, and the maximum ligand number of the system as an integral part of the calculations of the system. The constants calculated within each experiment were taken to have physical meaning if it could be demonstrated that they represented the minimum number of statistically significant parameters required to represent the experimental data.[12]

In the extraction systems considered here it usually is assumed that only uncharged species migrate across phase boundaries (however, see ref. 11). The partition equilibrium in the hafnium fluoride–TTA system, indeed, is best represented as an ion-exchange process

$$\mathrm{HfF}_j{}^{4-j}(\mathrm{aq}) + p\mathrm{HTTA}(\mathrm{org}) = \mathrm{HfF}_j(\mathrm{TTA})_p(\mathrm{org}) + p\mathrm{H}^+(\mathrm{aq}) \qquad (9)$$

TTA appears to chelate only the free hydrated species of metal ions, and when the chelation involves species of coördination number eight, j and p may be expected to be 0 and 4, respectively.

The observed distribution ratio, ϕ, the ratio of the specific activities of hafnium in the organic and aqueous phases, then is related to the aqueous phase formation constants by

$$\frac{B^p \sum_{j=0}^{J} \beta_j K_j (\mathrm{HF})^j}{\phi} = \sum_{n=0}^{N} \frac{\beta_n}{(\mathrm{H}^+)^n} (\mathrm{HF})^n \qquad (10)$$

where B is TTA but may be generalized to include many extractants. The summation term on the left includes only those values of j which correspond to extractable species and, therefore, need not necessarily represent a continuous series. The constant K equals the equilibrium constant for extraction according to eq. 9 divided by $(\mathrm{H}^+)^4$, $K = K_{\mathrm{eq}}(\mathrm{H}^+)^4$. The β's are the over-all formation constants of the hafnium–fluoride system in 3 M perchlorate ion at 25° for the reactions

$$\mathrm{Hf}^{+4} + n\mathrm{HF} = \mathrm{HfF}_n{}^{4-n} + n\mathrm{H}^+ \qquad (11)$$

In this study no prior assumptions were made as to which species were extracted; these decisions were made by analyses described below of the least squares regression calculations performed by high-speed computers.

The extent by which the aqueous phase was depleted of hydrofluoric acid by direct transfer to the organic phase containing TTA was determined by distribution studies using 118-min. F^{18}.

Experimental

Procedure.—Stock solutions of reagent grade perchloric and hydrofluoric acids were standardized with sodium hydroxide. Sodium perchlorate was prepared by neutralizing perchloric acid with sodium carbonate. The solution was boiled, the pH adjusted to 7 using a glass–calomel cell, and the effluent from aliquots of the solution which had been passed through a column containing Dowex 50 cation exchange resin was titrated with standard base. Pipets, volumetric flasks, and other containers used with fluoride-containing solutions all were constructed of fluoride- and acid-resistant plastics.

Potassium hexafluorohafnate, $\mathrm{K_2HfF_6}$, was prepared from reactor-grade hafnium metal manufactured by the Wah Chang Corporation. The major non-gaseous impurities were Zr 3%, Ta < 200 p.p.m., Nb < 100 p.p.m., and Fe 150–200 p.p.m. A weighed sample of metal was dissolved with a small excess of concentrated hydrofluoric acid using a polypropylene beaker in a hot water bath, the solution was diluted twofold, and then neutralized hot with the stoichiometric amount of potassium carbonate. The potassium carbonate for this neutralization was dissolved in a volume of water such that most of the hafnium salt was in solution at 100° at the end of the neutralization (about 0.8 M).[13] The hot solution was filtered rapidly through coarse paper, the filtrate was cooled and filtered, and the colorless $\mathrm{K_2HfF_6}$ then was air-dried and stored in a desiccator.

The hydrogen ion measurements were made by saturating the solutions with quinhydrone and using a gold indicator electrode with a saturated sodium chloride calomel electrode. A very slow but continuously flowing liquid junction was maintained by a constant head of saturated sodium chloride flowing through a cotton fiber wick sealed into the end of a polyethylene tube used as the bridge arm. A Leeds and Northrup Type K-3 potentiometer was used with an Eppley low temperature coefficient form of the standard Weston cell. A Rubicon mirror galvanometer with a sensitivity of 0.0007 μa./mm. gave a deflection of 0.2 to 0.3 mm. for a potential change of 0.1 mv. at a total cell potential of 0.4 volt. The calomel electrode and the

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TABLE I

POTENTIAL DATA AND CALCULATION OF THE FORMATION FUNCTION FOR HAFNIUM FLUORIDE, $(ClO_4^-) = 3.0\ M$, $t = 25°$
Cell: $Hg/Hg_2Cl_2(s)$, NaCl(s), H^+, (3.0 M ClO_4^-, Hf(IV), HF) quinhydrone(s)/Au

C_H, M	C_M, mM	$(HF)_{add}$, M	E_{cell_i}, v.	E_{cell_f}, v.	$(H^+)_i$, M	$(H^+)_f$, M	$\bar{n}$[a]	(F^-),[b] M
3.0	0.5	0	0.49251	0.49249	3.0000	2.9980	1.9[c]	3.68×10^{-7}
3.0	1.0	0	.49234	.49231	3.0000	2.9966	2.6	6.10×10^{-7}
3.0	1.0	0	.49243	.49240	3.0000	2.9967	2.7	5.94×10^{-7}
2.0	1.0	0	.48248	.48245	2.0000	1.9971	3.1	7.86×10^{-7}
2.0	1.0	0.0153	.48220	.48218	2.0582	2.0565	4.3	4.45×10^{-6}
3.0	1.0	.0200	.49224	.49223	2.9902	2.9888	4.6	3.85×10^{-6}
3.0	0.5	.0200	.49221	.49220	3.0000	2.9995	5.0	3.67×10^{-6}
2.0	1.0	.0251	.48227	.48226	2.0556	2.0547	5.1	6.81×10^{-6}
3.0	1.0	.0964	0.49210		2.9717	2.9717	6	1.74×10^{-5}
2.0	1.0	.157	.48090		1.9561	1.9561	6	4.32×10^{-5}
2.0	1.0	.314	.47943		1.8536	1.8536	6	9.11×10^{-5}
2.0	1.0	.628	.47567		1.6232	1.6232	6	2.08×10^{-4}

[a] See eq. 8. [b] See ref. 4. [c] This point fell below the combined TTA–potentiometric curve and was omitted from the final calculation.

working cell were partially immersed in a water bath at 25 ± 0.02°.

In the calculation of hydrogen ion concentrations from potential data, corrections were applied for the basicity constant of p-benzoquinone[14] and for the liquid junction potentials. From cell potential measurements in solutions of known perchloric acid concentration in the absence of hydrofluoric acid and hafnium, error potentials as a function of hydrogen ion concentration were taken as the difference between the stoichiometric hydrogen ion concentration and that calculated from the Nernst equation as described previously.[4] This error potential thus corrected for activity coefficient changes and errors in the standard potentials, as well as the liquid junction potential. These corrections which yielded a more nearly absolute value of the hydrogen ion concentration were not important for the calculation of $\bar{n}$ by eq. 8 or for the calculation of (HF) but were important for the calculation of free fluoride ion concentrations.

Hafnium-181 was received from the Oak Ridge National Laboratory as 0.006 M hafnyl chloride solution in 1 M hydrochloric acid. A 0.12-ml. aliquot containing 1 mc. was twice fumed almost to dryness with 1-ml. portions of 70% perchloric acid, taken up in a little water, and then evaporated three times on a water bath with 2-ml. portions of concentrated hydrofluoric acid. The final concentration of hydrofluoric acid in the solution was negligible as measured by acidity tests on the escaping vapors and by an etch test on soft glass. Eastman Kodak White Label thenoyltrifluoroacetone was weighed directly to make solutions 0.050 and 0.50 M in Mallinckrodt reagent grade xylene.

Five-ml. portions of the various fluoride solutions in 3 M perchloric acid were pipeted into 50-ml. Lusteroid test tubes, 5 or 10 μl. of the Hf-181 solution and 5 ml. of the organic phase were added, and the mixtures were equilibrated in a water bath shaker at 25 ± 0.2° for a minimum of 4 hr. Studies on the effect of equilibration time showed no difference in the distribution ratios between 4 and 17 hr. equilibration. After equilibration the tubes were centrifuged and from 0.010 to 3.0-ml. samples were pipeted into plastic vials which contained a volume of solvent such that the final volumes of the counting samples were equal for both phases. Counting was done with a NaI(Tl) γ-scintillation detector and a recording single channel analyzer constructed at the Laboratory for Nuclear Science, M.I.T. The γ-spectra was calibrated with a Cs-137 source and the sample Hf-181 peaks were identified. γ-Energy counting in the range 0.3 to 0.5-Mev. was necessary because of the 1% Sc-46 impurity reported by Oak Ridge in their Hf-181 product. The counting rates were corrected for background and the normalized distribution ratios are given in Table II.

For the production of F^{18}, 0.846-g. samples of KF were bombarded for 10 min. with 15 Mev. deuterons at 30 μa. beam current in the M.I.T. cyclotron. The thick target yield for the reaction $F^{19}(d,t)F^{18}$ has been reported by Irvine[11] as 2.5 mc./μa.-hr. at this beam energy. The resultant green crystals were dissolved in about 25 ml. of water and passed through a strong acid cation exchange resin column (H^+ form) to rid the solution of radioactive sodium and potassium isotopes. The column was rinsed several times and the effluent containing the HF^{18} was made up to 100 ml. in a calibrated polyethylene graduate. Aliquots of this stock solution were used to make solutions containing 4×10^{-7}, 1×10^{-6}, 2×10^{-6}, 5×10^{-6}, and 1×10^{-5} M fluoride ion concentrations in 3 M perchloric acid. Five-ml. aliquots of the solutions were equilibrated 3 hr. with 5 ml. of 0.5 M TTA in xylene, the mixtures were centrifuged and sampled as before, and the 0.51-Mev. annihilation peak was counted. Corrections were made for background and for decay of the F^{18} during the counting period when this was greater than 30 min.

Results

Potential data and calculations of the formation function for several values of C_H and C_M are given in Table I. At the higher acid concentrations attempts to follow potential changes of only 0.01 mv. per unit change in $\bar{n}$ led to considerable scatter, as shown by the portion of the formation curve plotted from potentiometric data in Fig. 1. At the two acidities studied, it was found that the average ligand number leveled off at the value 6 at the higher fluoride ion concentrations. At Hf(IV) concentrations greater than 1 mM erratic values of $\bar{n}$ were found, suggesting polymerization, or low solubility, or both.[5] Calculation of the formation constants using the potentiometric data combined with the TTA extraction data is described in a subsequent section.

The dependence of the distribution ratio on the concentration of TTA in the organic phase was determined by iteration procedures using a form of eq. 10 in which log ϕ/B^p was plotted $vs.$ log (HF) at various values of p. When p was assigned the value 4 for the TTA extractions, log ϕ/B^p as a function of log (HF) gave a single smooth curve for both concentrations of organic extractant, as shown in Fig. 2. The fourth-power dependence of the TTA agrees with the conclusions of Connick and McVey[9] in their studies on zirconium.

The distribution for the extraction of HF^{18} from 3

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[14] G. Biedermann, *Acta Chem. Scand.*, **10**, 1340 (1956).

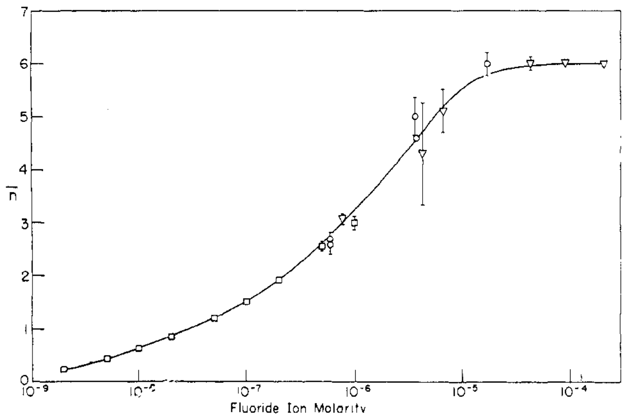

Fig. 1.—Formation function of the hafnium fluoride system, (ClO_4^- = 3.0 M, t = 25°). The curve was calculated from the over-all formation constants: ⊡, TTA extraction data; ⊙, potentiometric data at C_H = 3.0 M; ∇, potentiometric data at C_H = 2.0 M. The standard deviations of the points are based on the final estimate of weights.

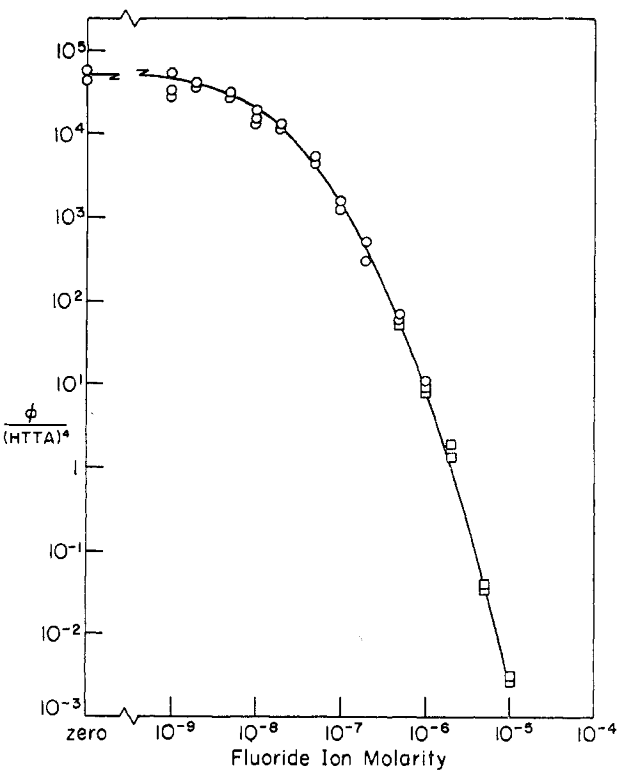

Fig. 2.—Normalized distribution ratio, $\phi/(\text{HTTA})_o{}^4$, of hafnium between 3.0 M $HClO_4$ and thenoyltrifluoroacetone in xylene as a function of fluoride ion concentration at 25°. The curve was calculated from the constants of Table III: ⊙, 0.05 M TTA in xylene; ⊡, 0.50 M TTA in xylene.

M perchloric acid into 0.5 M TTA in xylene was essentially constant over the fluoride ion concentration range 4.0×10^{-7} to 1.0×1.0^{-5} M. The average value of 7 measurements was

$$K_d = (\text{HF})_o/(\text{HF})_a = 0.000347 \pm 0.000015 \qquad (12)$$

where the error term is the standard deviation of the mean. The constancy of the distribution ratio indicated that a single species, probably HF, was involved in a true Nernst distribution as implied in eq. 12. The low distribution of hydrofluoric acid indicated further that no significant error was made in assuming that the pre-equilibration concentration of hydrofluoric acid was equal to the final concentration.

Constants Calculated from the TTA Data.—In the hafnium fluoride–TTA system, eq. 10 may be put in the form

$$\frac{(\text{HTTA})^4}{\phi} = \frac{1}{K} = \frac{1}{K_0} \sum_{n=0}^{N} \frac{\beta_n}{(\text{H}^+)^n} (\text{HF})^n \qquad (13)$$

where K is the normalized distribution ratio. Since $\beta_0 = 1$, this may be rearranged to

$$Y = \left[\frac{K_0}{K} - 1\right] /(\text{HF}) = \frac{\beta_1}{(\text{H}^+)} + \frac{\beta_2(\text{HF})}{(\text{H}^+)^2} + \frac{\beta_3(\text{HF})^2}{(\text{H}^+)^3} + \frac{\beta_4(\text{HF})^3}{(\text{H}^+)^4} \qquad (14)$$

where K_0 is the normalized distribution ratio measured at (HF) = 0. The value of 4 for N, the maximum number encountered in the ligand concentration range studied, was chosen initially from the maximum negative slope of the distribution curve at the highest fluoride concentrations studied (see Fig. 2). In eq. 13, N is also the degree of the polynomial but in eq. 14 the degree has been reduced to 3 and only four constants are calculated. An attempt to force a calculation of $\beta_5/(\text{H}^+)^5$ with the same data gave statistically meaningless values according to the criteria suggested by Sullivan and associates.[12b,c] Calculated values for formation constants which came out negative or which were within one standard deviation of zero were taken to mean that the corresponding complex species did not exist in appreciable concentration in the ligand concentration range investigated. The program used with Argonne National Laboratories "George" computer automatically recalculated the constants, omitting entirely the parameters which initially were negative. As shown in Table II, a set of 13 data points, Y_i, $(\text{HF})_i$, were calculated from the distribution data as input data to the computer. The weights, $W_i = 1/\sigma_y{}^2$, were determined from the theory of propagation of errors, *viz.*

$$\sigma_y{}^2 = \left(\frac{\partial Y}{\partial K}\right)^2 \sigma_K{}^2 + \left(\frac{\partial Y}{\partial K_0}\right)^2 \sigma_{K_0}{}^2 \qquad (15)$$

or

$$\sigma_y{}^2 = \frac{0.02K_0{}^2}{K^2(\text{HF})^2} \text{ (see eq. 19b, ref. 12c)} \qquad (16)$$

where it is assumed that all of the error in Y resides in 10% error in K and K_0 so that $\sigma_K = 0.1K$ and $\sigma_{K_0} = 0.1K_0$.

The least squares calculation using the "George" computer determined a set of $\beta_n/(\text{H}^+)^n$ for the model (eq. 16) which minimized

$$S = \sum_{i=1}^{I} W_i \left(\sum_{n=1}^{N} \frac{\beta_n}{(\text{H}^+)^n} (\text{HF})_i{}^{n-1} - Y_i \right)^2 \qquad (17)$$

The calculated parameters and their standard deviations are given in Table III.

The over-all goodness of the fit is obtained from the value $S_{\min}/(I - N - 1) = 0.95$. When the correct

TABLE II

DISTRIBUTION DATA FOR THE HAFNIUM FLUORIDE–TTA SYSTEM AND INPUT FOR THE LEAST SQUARES CALCULATION OF THE FORMATION CONSTANTS

(HF), M	(F^-), M	$(HTTA)_o$, M	No. of points	$\frac{\phi}{(HTTA)_o^4} = K$	Y^a	W_y
0	0	0.05	2	$5.219 \times 10^4 = K_0$	...	...
5.587×10^{-6}	1×10^{-9}	.05	3	3.794×10^4	6.723×10^4	1.649×10^{-9}
1.117×10^{-5}	2×10^{-9}	.05	2	4.013×10^4	2.690×10^4	7.377×10^{-9}
2.794×10^{-5}	5×10^{-9}	.05	2	3.009×10^4	2.629×10^4	2.595×10^{-8}
5.587×10^{-5}	1×10^{-8}	.05	3	1.687×10^4	3.747×10^4	3.261×10^{-8}
1.117×10^{-4}	2×10^{-8}	.05	2	1.348×10^4	2.571×10^4	8.325×10^{-8}
2.794×10^{-4}	5×10^{-8}	.05	2	4.985×10^3	3.389×10^4	7.122×10^{-9}
5.587×10^{-4}	1×10^{-7}	.05	2	1.723×10^3	5.243×10^4	3.437×10^{-8}
1.117×10^{-3}	2×10^{-7}	.05	2	3.887×10^2	1.193×10^5	6.923×10^{-11}
2.794×10^{-3}	5×10^{-7}	.05	2	67.93	2.746×10^5	1.322×10^{-11}
		.50	1			
5.587×10^{-3}	1×10^{-6}	.05	1	9.540	9.789×10^5	1.043×10^{-11}
		.50	2			
1.117×10^{-2}	2×10^{-6}	.50	2	1.055	4.429×10^6	5.099×10^{-12}
2.794×10^{-2}	5×10^{-6}	.50	2	3.979×10^{-2}	4.694×10^7	4.537×10^{-14}
5.587×10^{-2}	1×10^{-5}	.50	2	2.998×10^{-3}	3.116×10^8	1.030×10^{-17}

[a] See eq. 14.

functional form of eq. 10 is used with properly weighted data, this quantity, which has the χ-squared distribution with $k - 1$ degrees of freedom,[12b,c] may be expected to lie within 1.0 ± 0.5 at the 70% probability level. The value of 0.95 for $\chi^2/k - 1$ corresponds to an average error of 5.4% in each measured K; thus the original estimate of 10% error was too high. The curve drawn in Fig. 2 was calculated from the average values of the formation constants and gives a further measure of the fit to the experimental data. In the 3 M perchloric acid solutions used, K_{eq} for the reaction of eq. 9 may be calculated from the measured distribution ratio at zero fluoride concentration, $K_{eq} = K_0(H^+)^4 = (4.23 \pm 0.23) \times 10^6$, using the average error of 5.4%. Thus $\log K_{eq} = 6.63 \pm 0.03$.

Constants Calculated from the Combined Potentiometric and TTA Data.—The high degree of correlation between the parameters calculated from the extraction data made it advisable to perform a new calculation on the complete data set when the model was changed to include six hafnium fluoride species in simultaneous equilibrium. The required data set was obtained by calculating the formation function from the TTA results and combining this with $\bar{n}$, fluoride concentration data points (Table I) obtained from the potentiometric measurements.

TABLE III

OVER-ALL FORMATION CONSTANTS AND THEIR STANDARD DEVIATIONS CALCULATED FROM THE TTA EXTRACTION DATA, $HClO_4$ = 3.0 M, t = 25°

n	$\beta_n/(H^+)^n$
1	$(2.622 \pm 0.307) \times 10^4$
2	$(3.491 \pm 1.347) \times 10^7$
3	$(1.526 \pm 0.692) \times 10^{10}$
4	$(1.546 \pm 0.387) \times 10^{12}$

In Fig. 1 is shown a smooth series of points at low fluoride ion concentrations calculated from the average values of the over-all formation constants from the TTA data. The experimental potentiometric data points crossed the calculated TTA data points, which may be interpreted as indicating that the potentiometric method was not sensitive in the low fluoride concentration region and the TTA extraction method was not sensitive to changes in the concentrations of higher species in the higher fluoride concentration region. Eliminating the points that fell below the combined curve on the above basis, the remaining points shown in Fig. 1 yielded a reasonably smooth set which was used to calculate the formation constants for the first six simple mononuclear fluoride complexes of hafnium. The functional form of the equation used[6]

$$\bar{n} = \frac{\sum_{n=0}^{6} n \frac{\beta_n}{(H^+)^n} (HF)^n}{\sum_{n=0}^{6} \frac{\beta_n}{(H^+)} (HF)^n} \tag{18}$$

was solved for the $\beta_n/(H^+)^n$ by an iterative machine calculation using weighted data.[15] Weight assignments of ±5% to the HF concentrations from the TTA data, ±10% to (HF) from the potentiometric results at C_H = 3.0 M, and ±20% to (HF) from the potentiometric results at C_H = 2.0 M combined with initial estimates of the six constants allowed an initial calculation of the weight of $\bar{n}_i$, W_i, using error propagation calculations with eq. 18. Machine calculation of an improved set of constants than allowed calculation of an improved weight set, etc., until on the fourth cycle a set of constants, $\beta_n/(H^+)^n$, and a weight set were found which minimized

$$S = \sum_{i=1}^{20} W_i(\bar{n}_i' - \bar{n}_i)^2 \tag{19}$$

where $\bar{n}'$ is the machine calculated $\bar{n}$. The value of $S_{min}/k - 1$ found was 1.09, indicating that the weight set and the mathematical model were consistent with the data. However, in this machine program an in-

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(15) G. Pulley, IBM-650 non-linear regression routine, Oklahoma State University Computer Center, Stillwater, Okla.

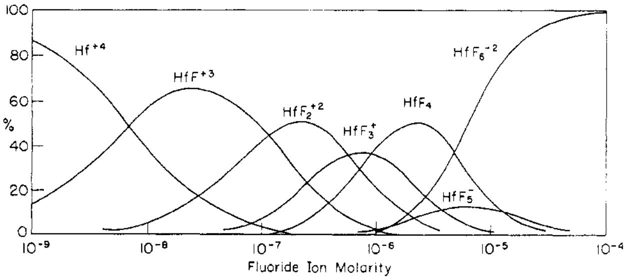

Fig. 3.—Relative abundances of the hafnium fluoride complexes in 3.0 M ClO_4^- at 25° as a function of fluoride ion concentration, calculated from combined TTA–potentiometric data.

verse matrix was not formed, so the standard deviations of the individual formation constants were not obtained as in the "George" program. The error values associated with the constants given below were estimated by calculating a set of alternate constants using the standard deviation limits of the experimental $\bar{n}$ values[4] as input to the computer. These errors, or the average errors of the constants calculated from the TTA data, whichever were larger, are the values associated with the individual constants given here: $\beta_1/(H^+) = (2.575 \pm 0.302) \times 10^4$, $\beta_2/(H^+)^2 = (3.997 \pm 0.540) \times 10^7$, $\beta_3/(H^+)^3 = (1.238 \pm 0.560) \times 10^{10}$, $\beta_4/(H^+)^4 = (2.411 \pm 0.604) \times 10^{12}$, $\beta_5/(H^+)^5 = (2.86 \pm 2.32) \times 10^{13}$, $\beta_6/(H^+)^4 = (3.31 \pm 0.83) \times 10^{15}$.

These average values of the constants were used to calculate both the formation curve drawn in Fig. 1 and the relative distribution of the hafnium species shown in Fig. 3. Inspection of the relative abundance of HfF_5^- from Fig. 3 and the estimated error of $\beta_5/(H^+)^5$ above indicates some question as to the existence of the species HfF_5^- based on these data alone. Confirmatory evidence for this species would require extremely good equilibrium data of the type described here.

Stepwise Formation Constants.—From the relations

$$Hf^{+4} + HF = HfF^{+3} + H^+,\ k_1 = \beta_1$$

$$HfF^{+3} + HF = \underset{\substack{|\\ \text{etc.}}}{HfF_2^{+2}} + H^+,\ k_2 = \frac{\beta_2}{\beta_1} \qquad (20)$$

the stepwise formation constants for the simple hafnium fluoride complexes were calculated from the TTA and the combined TTA–potentiometric results. The values given in Table IV allow comparison between the two calculations and help explain some anomalies in the results. The constants and their errors expressed on the log scale are given in the abstract. One interesting feature of the system is that k_4 is less than $^1/_4$ of k_3 as calculated from the TTA data. From the combined TTA–potentiometric data, however, the high degree of correlation between constants resulted in the value of k_4 being only about $^1/_2$ of the value of k_3. Close inspection of Fig. 3, nevertheless, shows that the maximum relative concentration of HfF_4 is considerably greater than the maximum for the species HfF_3^+ in spite of the larger formation constant of the latter. The reason for this is the high relative concentrations of HfF_2^{++} and HfF_4 at the maximum in the HfF_3^+ abundance. On the other hand, the low abundance of HfF_5^- and other species in the neighborhood of the HfF_4 maximum requires a high abundance of the neutral species.

Table IV

The Stepwise Formation Constants of the Hafnium Fluoride System Calculated from the TTA and Combined TTA–Potentiometric Data, $HClO_4 = 3.0\ M$, $t = 25°$

$k_n = (HfF_n)(H^+)/(HfF_{n-1})(HF)$

	TTA	TTA–potentiometric
k_1	$(7.87 \pm 0.92) \times 10^4$	$(7.73 \pm 0.91) \times 10^4$
k_2	$(3.99 \pm 1.61) \times 10^3$	$(4.66 \pm 1.88) \times 10^3$
k_3	$(1.31 \pm 0.78) \times 10^3$	$(9.29 \pm 5.52) \times 10^2$
k_4	$(3.04 \pm 1.58) \times 10^2$	$(5.84 \pm 3.02) \times 10^2$
k_5	...	$(3.57 \pm 3.03) \times 10^1$
k_6	...	$(3.48 \pm 2.94) \times 10^2$

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