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THE EXTRACTION OF HAFNIUM FROM NITRIC ACID SOLUTIONS WITH THENOYL TRIFLUOROACETONE

J. P. McBRIDE

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THE EXTRACTION OF HAFNIUM FROM NITRIC ACID SOLUTIONS WITH THENOYL TRIFLUOROACETONE

J. P. McBride

Abstract

Data are presented which indicate that the extraction of Hf from 0.5 to 3.5 M HNO_3 with TTA has a 3rd power dependence on hydrogen ion and a fourth power dependence on TTA corresponding to the equation

$$Hf(OH)_A^{+3} + 4HT_B \rightleftharpoons HfT_{4B} + 3H_A^+ + H_2O$$

The small deviations from fourth power dependence on TTA are explained by the formation of an aqueous soluble Hf-TTA complex by the reaction

$$Hf(OH)_A^{+3} + HT_B \rightleftharpoons HfT_A^{+3} + H_2O$$

with an equilibrium constant, k_t, equal to 15.5.

An apparent or effective value for the molar hydrogen ion activity coefficient, $f_c'(H^+)$, has been calculated for use in calculations involving the extraction of Hf from HNO_3 with TTA which may be of use in calculations involving the extraction of other metallic species from HNO_3 with TTA.

A semi-empirical expression has been derived for the calculation of the distribution ratio of Hf between benzene phases 0.005 to 0.1 M in TTA and aqueous phases 0.5 to 3.5 M in HNO_3.

THE EXTRACTION OF HAFNIUM FROM NITRIC ACID SOLUTIONS WITH THENOYL TRIFLUOROACETONE

J. P. McBride

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Introduction

The extraction of Hf and Zr into benzene from an aqueous solution of a non-complexing acid using thenoyl trifluoroacetone (henceforth referred to as TTA) is commonly represented by the equation

$$M(OH)^{+n}_{4-n}{}_A + n\,HT_B \rightleftharpoons MT_{n_B} + nH^+_A + (4-n)H_2O$$

where HT refers to the TTA and the subscripts to the phases in which the various species appear (i.e., A-aqueous; B-benzene). Corresponding to the above equation the following equilibrium constant is formulated

$$K_e = \frac{[MT_n]}{[M(OH)^n_{4-n}]} \frac{[H^+]^n}{[HT]^m}$$

where $[H^+]$ and $[HT]$ are the hydrogen ion and TTA activities and where $[M(OH)^n_{4-n}]$ represents the activity of the aqueous metallic species (assuming a single species), n the charge, and m the number of T anions associated with each M species in the benzene phase. When the activity coefficients of MT_n and $M(OH)^n_{4-n}$ remain constant the expression becomes

$$K = \frac{D.R._{(B/A)}\ [H^+]^n}{[HT]^m}$$

whence

$$D.R._{(B/A)} = \frac{K\,[HT]^m}{[H^+]^n}$$

where $D.R._{(B/A)}$ refers to the distribution ratio of the metal, organic over aqueous. If more than one species in each phase were present to a significant concentration the above equations would of course, have to be modified.

Previous investigators have shown that in the extraction of macro amounts of Hf and Zr (ca. 10^{-3} M) from 2 M $HClO_4$ the distribution ratios of the metals have a fourth power dependence on the TTA activity(1). Others have shown that

(1) K. H. Huffman, L. J. Beaufait, Report UCRL-194, "The Separation of Zirconium and Hafnium by Extraction with Thenoyl Trifluoroacetone", October 7, 1948.

in the extraction of Zr tracer from dilute $HClO_4$ the inverse dependence on H^+ is not fourth power but varies from 3rd to 2nd power as the acid concentration is lowered from 2 to 0.1 M, and formulated an equation for the extraction of Zr from 2 M $HClO_4$ as follows:

$$Zr(OH)^{+3}_A + 4HT_B \rightleftharpoons ZrT_{4B} + 3H^+_A + H_2O \quad (2)$$

(2) R.E.Connick and W. H. McVey, UCRL-101, "The Aqueous Chemistry of Zirconium", March 1, 1948.

Recent information on the TTA extraction of Hf tracer from dilute nitric acid (0.3 to 1 M) indicated that the $D.R._{(B/A)}$ of Hf in this system had a 2nd power dependence on the TTA concentration in the benzene phase and a 3rd power inverse dependence on H^+.(3) It was to check this recent work that the following

(3) J. F. Flagg and B. E. Daaring, KAPL Monthly Report, September 27, 1948.

experiments were performed and this report may be considered a progress report on the general problem of determining the effect of various acid systems on the extraction of Zr and Hf with TTA.

Experimental

The TTA solutions were prepared with thiophene-free benzene using a better than 99.5% pure TTA obtained from Melvin Calvin of the University of California.

A stock solution of Hf tracer in 10 M HNO_3 was prepared from irradiated Hf (99.8% pure HfO_2) which was first dissolved in HNO_3-HF solution. The resulting solution was allowed to evaporate to dryness, fumed repeatedly with $HClO_4$, and then, after diluting, the Hf was extracted into a TTA-benzene solution. The organic phase was washed several times with dilute HNO_3 and the Hf finally stripped into 10 M HNO_3.

The experiments on acid dependence were performed by diluting the stock tracer solution to the desired acidities and then equilibrating the resulting solutions with equal volumes of a 0.02 M TTA-benzene solution. In the first series $NaNO_3$ was added to the acid solution to give a constant ionic strength of 3.95 while the second series was run at varying ionic strengths without adding $NaNO_3$.

The Hf tracer stock solution in 10 M HNO_3 showed some deterioration on standing, in that extractions performed three weeks after the preparation of the solution showed distributions much lower than could be expected from the earlier data. Hence, the runs performed to determine the TTA dependency (constant acidity, varying TTA concentration) were made by first equilibrating the TTA solutions of the required molarities with the diluted tracer solution and then re-equilibrating the benzene phases containing the Hf-TTA with fresh acid. The distribution values from the second equilibration were in accord with the data obtained with the freshly prepared stock solution and were taken to be the correct ones. The slow formation of a non-extractable

species in the 10 M HNO_3 solution could be due to the complexing of Hf by products of a reaction of HNO_3 with organic residues in the solution but it could also be indicative of a slow formation of Hf hydrolysis products in this solution. Some of the extraction data given below would indicate that the rate of formation of the non-extractable species increases at lower acidities.

All equilibrations were made at room temperature and for approximately 2-1/2 hours. Acid analyses were made after re-equilibration by direct titration.

Hf distribution ratios were determined by mounting samples of each phase on glass plates in the usual manner and counting without inserting an absorber between plate and G-M tube. The ratio of the activity in the benzene phase to that in the aqueous is, of course, equal to the distribution ratio.

The Determination of Extraction Dependency on Hydrogen Ion Activity

As indicated in the introduction, under the conditions where the activity coefficient of the metallic species in the organic and aqueous phases are constant the extraction of Hf from nitric acid may be represented by

$$D.R._{(B/A)} = \frac{K\,[HT]^{m}}{[H^{+}]^{n}}$$

It follows that

$$\log D.R._{(B/A)} = \log K + m \log [HT] - n \log [H^{+}]$$

Hence, if one performs a series of extractions at constant TTA concentration but at various acidities, a plot of $\log D.R._{(B/A)}$ vs. $\log [H^{+}]$ should yield a straight line whose slope, n, should be equal to the average charge on the aqueous hafnium species.

Table I gives the results obtained in a series of runs performed by diluting the stock tracer solution with water and $NaNO_3$ solution to give the desired acidities and a constant ionic strength of 3.95 and equilibrating the resulting solutions with equal volumes of 0.02 M TTA in benzene. It is expected that under these conditions the hydrogen ion activity will be nearly proportional to the HNO_3 concentration. Figure 1 illustrates the data with a plot of log $D.R._{(B/A)}$ vs. log HNO_3. A straight line drawn with a slope of 3.1 fits the data very well. It is to be expected that at this ionic strength in which one goes from a solution in which $NaNO_3$ predominates to a pure HNO_3 solution that the hydrogen ion activity coefficient while remaining approximately constant, should, if it changes at all, exhibit a slight increase. Such an argument is based on the fact that in solutions of comparable strength the $\gamma_{\pm}$'s for HNO_3 and $NaNO_3$ are 1.1 and 0.382, respectively.(4)

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(4) Landolt-Bornstein-Roth, Erg. Bd. 2, pp. 1119-1125.

For an analogous case it is to be noted that the $\gamma_{\pm}$'s for HCl in a 3 M NaCl-0.01 M HCl solution and in a 3 M HCl solution are 1.07 and 1.3, respectively.(5)

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(5) H.S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", Reinhold Publishing Co., 1943, pp. 575, 577.

Therefore, the slope of 3.1 probably represents an upper limit for the acid dependency and indicates the average charge on the hafnium species to be ≤ 3.1.

Figure 1 Dependence of Hf-TTA Extraction from HNO_3 on Acid Concentration at constant ionic strength

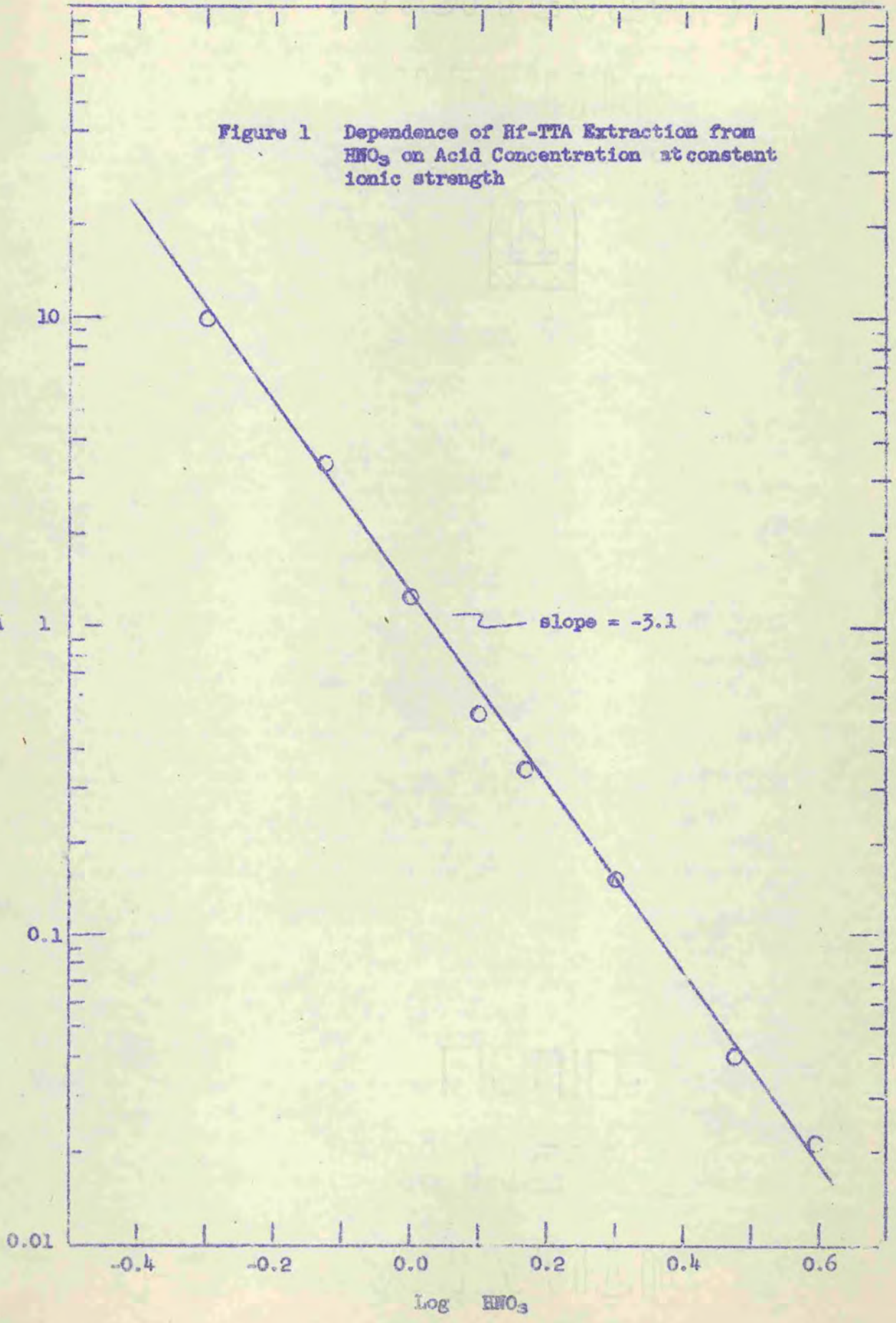


Table I

Dependence of TTA-Hf Extraction on HNO_3 Molarity at Constant Ionic Strength

Conditions: initial concentration of TTA 0.02 M; μ = 3.95 ($NaNO_3$ + HNO_3); equivolume extraction.

Concentration HNO_3	Log HNO_3	D.R. B/A
3.97	0.599	0.021
3.01	0.478	0.038
2.01	0.304	0.147
1.50	0.175	0.333
1.28	0.107	0.508
1.02	0.0072	1.21
0.758	-0.120	3.27
0.514	-0.289	9.68

Table II lists the data obtained in another set of experiments performed as above by diluting the tracer stock solution, but without adding $NaNO_3$, and equilibrating the resulting solutions with equal volumes of 0.02 M TTA in benzene. Column 1 gives the molar concentrations of HNO_3 while Column 2 lists the approximate hydrogen ion molar activity coefficients defined by

$$f_{c\,(H^+)} = \frac{m\,\gamma_{(H^+)}}{M} = \frac{[H^+]}{M}$$

where M and m are the molarity and corresponding molality and $\gamma_{(H^+)}$ is a molal activity coefficient taken as being equal to the geometric mean of the $\gamma_{\pm}$ for HNO_3 given in Landolt-Bornstein[4] and an activity coefficient for hydrogen ion calculated by the use of the McInnes assumption, $\gamma_{M(H^+)}$ (cf. section on the estimation of the hydrogen ion activity coefficient).

Columns 3, 4 and 5 list the hydrogen ion activities, $[H^+] = \underline{M} f_c (H^+)$, the corresponding logs, and the activities of TTA in the benzene phases, $[HT]$, the latter being determined by the use of the activity coefficients calculated by King and Reas[6], correcting the TTA concentrations for solubility in the

(6) E. L. King and W. H. Reas, (University of California Radiation Laboratory) BC-69, July 1947, page 11.

aqueous phase by estimating the distribution of TTA from data obtained for 0.5 M TTA as a function of ionic strength ($NaClO_4$-$HClO_4$).[7] Column 6 gives

(7) H. W. Alter, KAPL, Redox - Monthly Report, December 28, 1948, page 6.
Note: Perhaps a better choice of distribution data would have been that of Connick and Reas for the distribution of TTA between a 0.013 M TTA solution in benzene and $HClO_4$ solutions of various molarities (cf. UCRL-226, pp. 46-47). They noted but little variation in distribution ratio when the acid concentration was varied from 0.016 to 400 M. The difference in TTA concentrations estimated using this data would be negligible at lower acidities and be lower by about 1.5% at the higher acidities. This would make a 6% difference in the K's calculated for the higher acidities.

the distribution ratios, benzene over aqueous, for the hafnium while column 8 lists equilibrium constants calculated assuming a 3rd power $[H^+]$ dependence and a 4th power $[HT]$ dependence:

$$K = D.R._{(B/A)} \frac{[H^+]^3}{[HT]^4}$$

Figure 2 shows a plot of log $D.R._{(B/A)}$ vs. log $[H^+]$. A straight line drawn with a slope of 3.0 represents the data very well for acidities up to 1.5 molar discounting the low distribution ratio obtained at the lower acidity where the system would be particularly sensitive to hydrolytic effects. Moreover, included in the figure are two points taken from the data of the next section, at comparable TTA concentrations, obtained by equilibrating benzene

phases containing Hf-TTA with freshly prepared acid solutions. These points confirm the slope of the line representing the acid dependency but are slightly higher than the distribution ratios obtained here, indicative that even in these runs made one week after the preparation of the stock HNO_3-Hf solution a small amount of the non-extractable species mentioned in the previous section may have already formed.

The values in parentheses in Table II for $f_{c(H^+)}$, $[H^+]$, $\log [H^+]$, and K are obtained from Figure 2 by extrapolating the straight line obtained for the lower acidities, and reading the value of $\log [H^+]$ where the line intersects the horizontals corresponding to the observed distribution ratios. One thus obtains an apparent or effective value for $f_{c(H^+)}$ henceforth distinguished by a prime ($f'_{c(H^+)}$) for use in extraction calculations at higher acidities. It is assumed that the apparently large deviations indicated here for the distribution ratios at the higher acidities are due in part to errors in the estimation of hydrogen ion activity at these acid concentrations and also to indeterminate changes in the activity coefficients with concentration for other aqueous species concerned in the extraction (the latter causing a change in the value of K). An extrapolation such as that made above is felt to be justified by the fact that, (1) the acid dependence at constant ionic strength over the same range is linear and is less than 3.1 and (2) by such an extrapolation one obtains a value for $f_{c(H^+)}$ which corrects for all activity coefficient changes in the more concentrated acid solutions in terms of the acid activity coefficient and permits an empirical expression for the

distribution at higher acidities to be formulated (cf. later sections of the report and particularly Table VI and Figure 6).

In view of the above it is concluded that the average charge on the aqueous hafnium species between 0.5 and 3.5 molar HNO_3 is close to 3.

Table II

Dependence of TTA-Hf Extraction from HNO_3 on Hydrogen Ion Activity

Conditions: initial concentration TTA, 0.02 M ($f_{c(HT)} = 0.985$); equivolume extractions.

Concentration HNO_3 M/L	$f_{c(H^+)}$	$[H^+]$	log $[H^+]$	$[HT]$	D.R.$_{(B/A)}$	K x 10^{-7}
	(1.43)	(4.89)	(0.689)			(2.32)
3.420	2.74	9.38	0.9722	0.0195	0.0288	16.45
2.921	(1.40)	(4.09)	(0.612)			(2.34)
	2.08	6.09	0.7846	0.0195	0.0493	7.70
1.999	(1.22)	(2.43)	(0.386)			(2.36)
	1.37	2.74	0.4378	0.0194	0.232	3.37
1.469	1.11	1.63	0.2122	0.0193	0.786	2.40
1.252	1.04	1.30	0.1139	0.0193	1.39	2.20
1.012	0.978	0.988	-0.0052	0.0193	3.46	2.41
0.771	0.907	0.699	-0.1555	0.0193	10.4	2.56
0.515	0.837	0.431	-0.3655	0.0193	25.1	1.45

The Determination of Extraction Dependency on TTA Activity

If only one species is extracted into the benzene phase and there is no appreciable complexing of Hf by TTA in the aqueous phase it is apparent by arguments similar to those above that at constant acidity

$$\log \text{D.R.}_{(B/A)} = K' + m \log [HT]$$

where m equals the number of T^- anions associated with each Hf in the benzene phase.

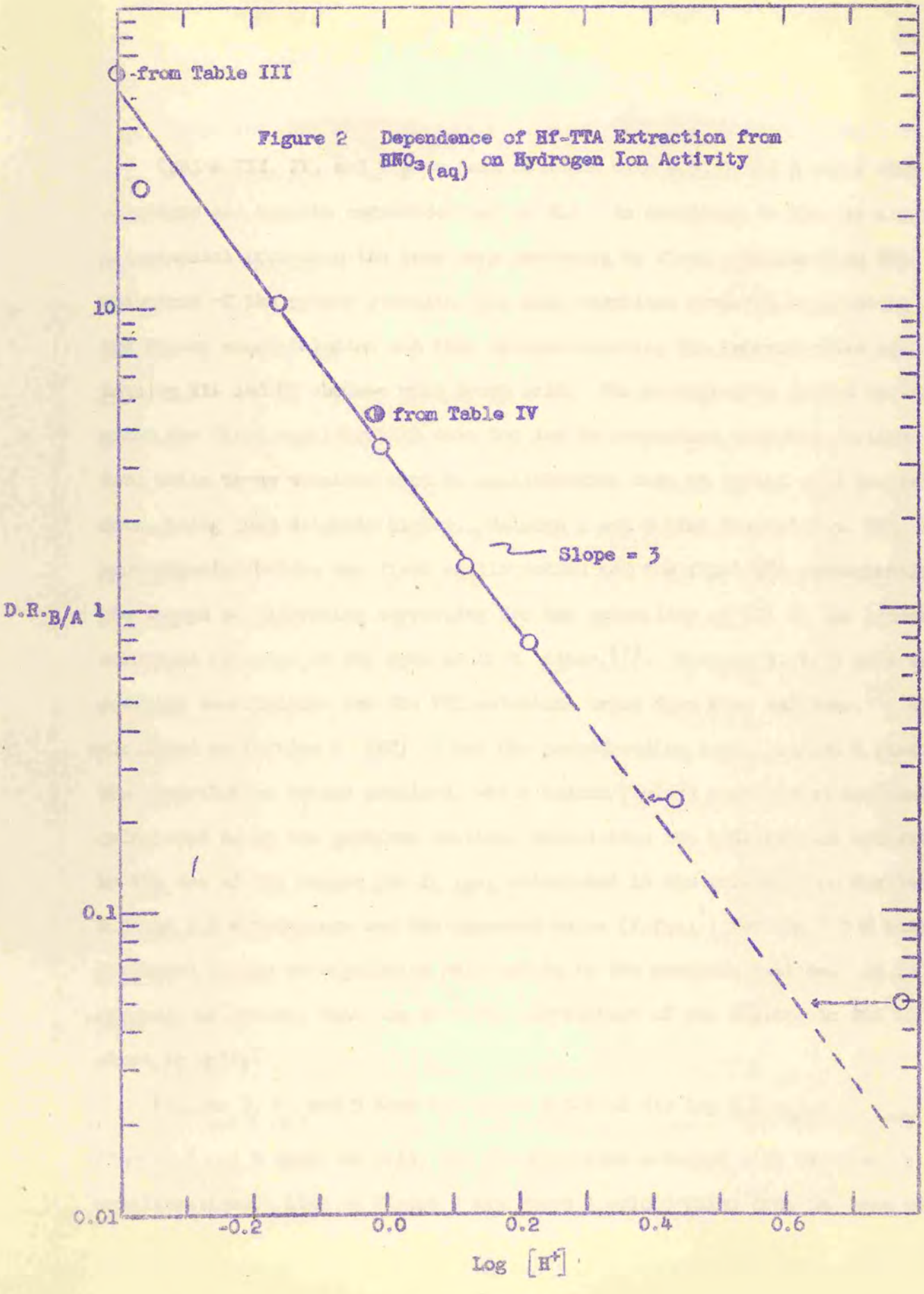


Figure 2 Dependence of Hf-TTA Extraction from $HNO_{3(aq)}$ on Hydrogen Ion Activity

Tables III, IV, and V give data obtained with 0.5, 1 and 3 molar HNO_3 solutions and various concentrations of TTA. As mentioned in the section in experimental procedure the runs were performed by first equilibrating TTA solutions of the proper strength with acid solutions prepared by diluting the tracer stock solution and then re-equilibrating the benzene phase containing TTA and Hf chelate with fresh acid. The distribution ratios obtained after the first equilibration were too low by comparison with the earlier data while those obtained upon re-equilibration were in accord with previous data, being just slightly higher. Columns 1 and 2 list the original TTA concentrations before the first equilibration and the final TTA concentrations after the second equilibration correcting for the solubility of TTA in the aqueous solutions by means of the data of H. W. Alter.(7). Columns 3, 4, 5 give the activity coefficients for the TTA solutions taken from King and Reas,(7) the calculated activities ($[HT]$) and the corresponding logs. Column 6 lists the distribution ratios obtained, while column 7 gives equilibrium constants calculated as in the previous section, calculating the hydrogen ion activities by the use of the values for $f_c\,(H^+)$ calculated in the next section for the 0.5 and 1.0 M solutions and the apparent value ($f_c(H^+)'$) for the 3.0 M solution, estimated by the extrapolation referred to in the previous section. It is assumed, as before, that the activity coefficient of the chelate in the benzene phase is unity.

Figures 3, 4, and 5 show the plots obtained for log D.R.(B/A) vs. log $[HT]$. Figures 4 and 5 show, as well, the distributions obtained with the primary equilibrations. Also in Figure 4 are shown 4 points taken from the data of

Table III

Dependence of TTA-Hf Extraction from 0.480 M HNO_3 on HT Activity

Conditions: $[H^+]$ = 0.397; equivolume extractions

Original Conc. HT	Final Conc. HT	f_o(HT)	[HT]	log [HT]	D.R.$_{(B/A)}$	K x 10^{-7}
0.005	0.00464	1.00	0.00464	-2.334	0.280	3.62
0.0100	0.00928	0.995	0.00923	-2.035	4.95	4.27
00.0151	0.0140	0.990	0.0138	-1.860	18.5	3.20
0.0200	0.0186	0.985	0.0183	-1.738	61.5	3.29
0.0250	0.0232	0.982	0.0228	-1.642	95.1	2.10
0.0300	0.0278	0.978	0.0272	-1.565	178.5	1.94

Table IV

Dependence of TTA-Hf Extractions from 0.997 M HNO_3 on HT Activity

Conditions: $[H^+]$ = 0.970; equivolume extractions.

Original HT.Conc.	Final HT Conc.	f_o(HT)	[HT]	log [HT]	D.R.$_{(B/A)}$	K x 10^{-7}
0.010	0.0096	0.995	0.00954	-2.021	0.270	2.91
0.015	0.0144	0.990	0.01425	-1.846	1.59	3.43
0.020	0.0192	0.985	0.0189	-1.724	4.47	3.10
0.040	0.0384	0.967	0.0371	-1.431	46.7	2.19
0.050	0.0480	0.959	0.0460	-1.337	118	2.33
0.060	0.0575	0.951	0.0547	-1.262	236	2.33

Table V

Dependence of TTA-Hf Extraction from 2.98 M HNO_3 on Hf Activity

Conditions: $[H^+]$ = 4.2 ; equivolume extractions

Original Hf Conc.	Final * Hf Conc.	$f_{c(Hf)}$	$[Hf]$	log $[Hf]$	D.R.$_{(B/A)}$	K x 10^{-7}
0.020	0.0186	0.987	0.0184	-1.735	0.047	3.04
0.0399	0.0368	0.970	0.0357	-1.447	0.530	2.42
0.0610	0.05694	0.954	0.0543	-1.265	2.60	2.21
0.0797	0.07438	0.942	0.0701	-1.154	6.71	2.06
0.100	0.09335	0.931	0.0869	-1.061	14.5	1.89

* Concentrations after second equilibration referred to in text. After first equilibration aqueous phase was diluted by a factor of three to make Hf distribution more favorable and then benzene phase was reequilibrated with fresh acid to obtain above results.

Huffman and Beaufait for the extraction of Hf from 2 M $HClO_4$ in which the Hf concentrations were determined by the use of tracer. All the data show essentially the same linear dependence with a slope of 3.7-3.8. The low extraction values observed at the two highest TTA concentrations for the runs at 0.5 M HNO_3 are believed due to hydrolysis or polymerization phenomena in the aqueous phase to which at this point the system would be particularly sensitive. This is further indicated by the fact that these two points could be adequately represented by a straight line drawn parallel to the other line.

The last section of this report will point out that the deviation of the slopes from 4 could be due to the formation of an aqueous soluble Hf-TTA

Figure 3 Dependence of Hf-TTA Extraction from 0.480 in HNO_3 on HT Activity

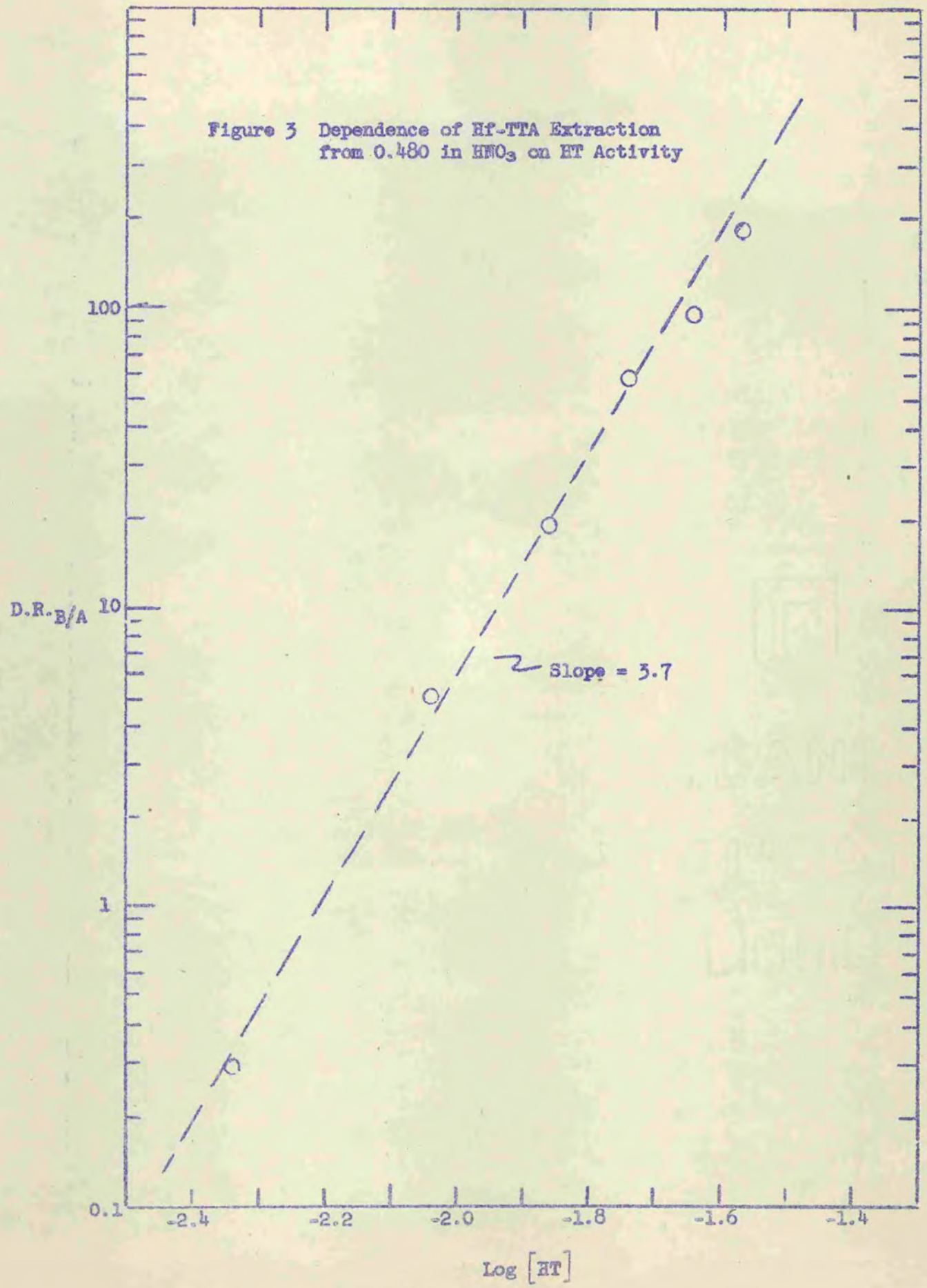


Figure 4 Dependance of Hf-TTA Extraction from 0.997 M HNO_3 on HT Activity

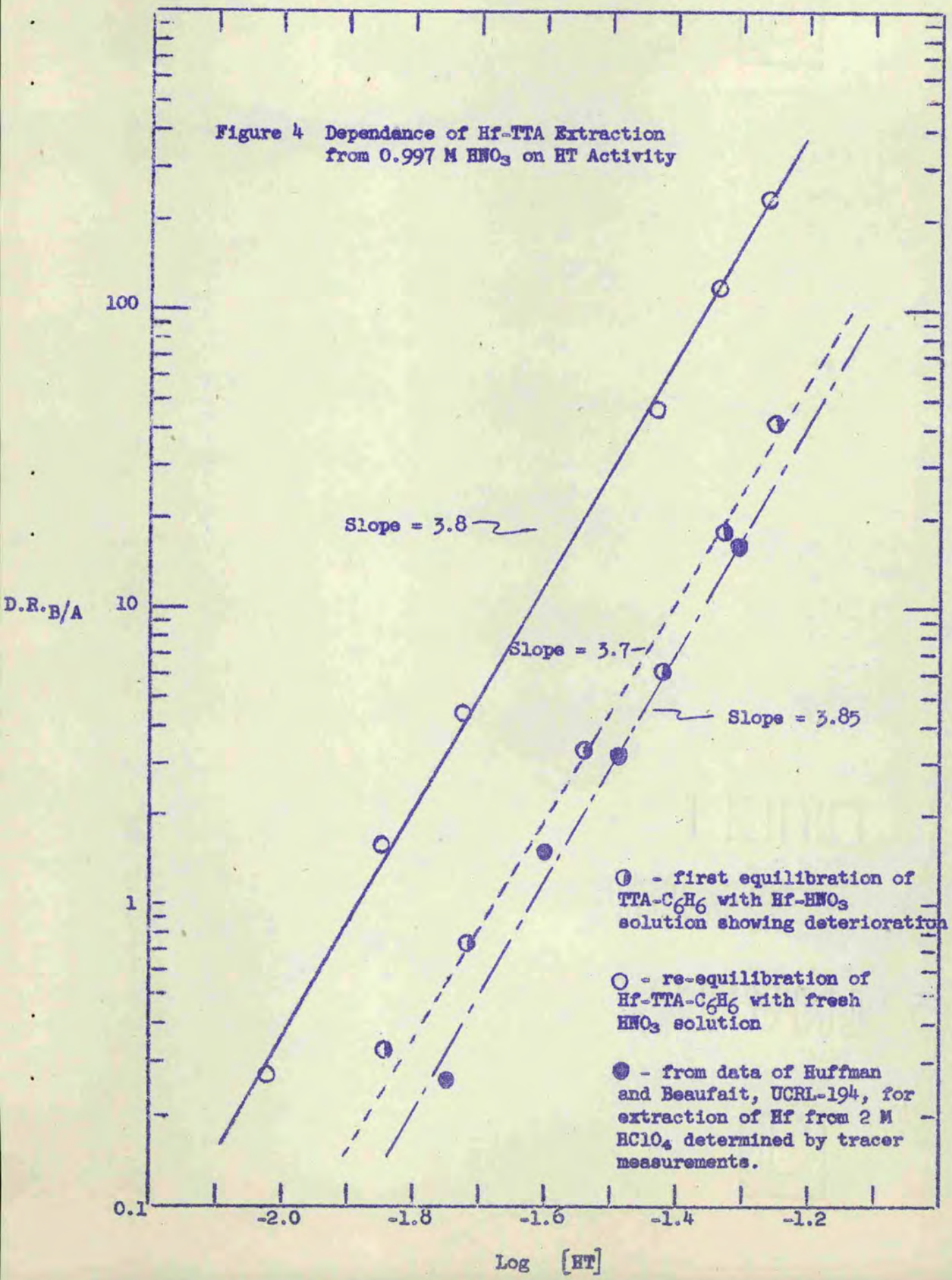
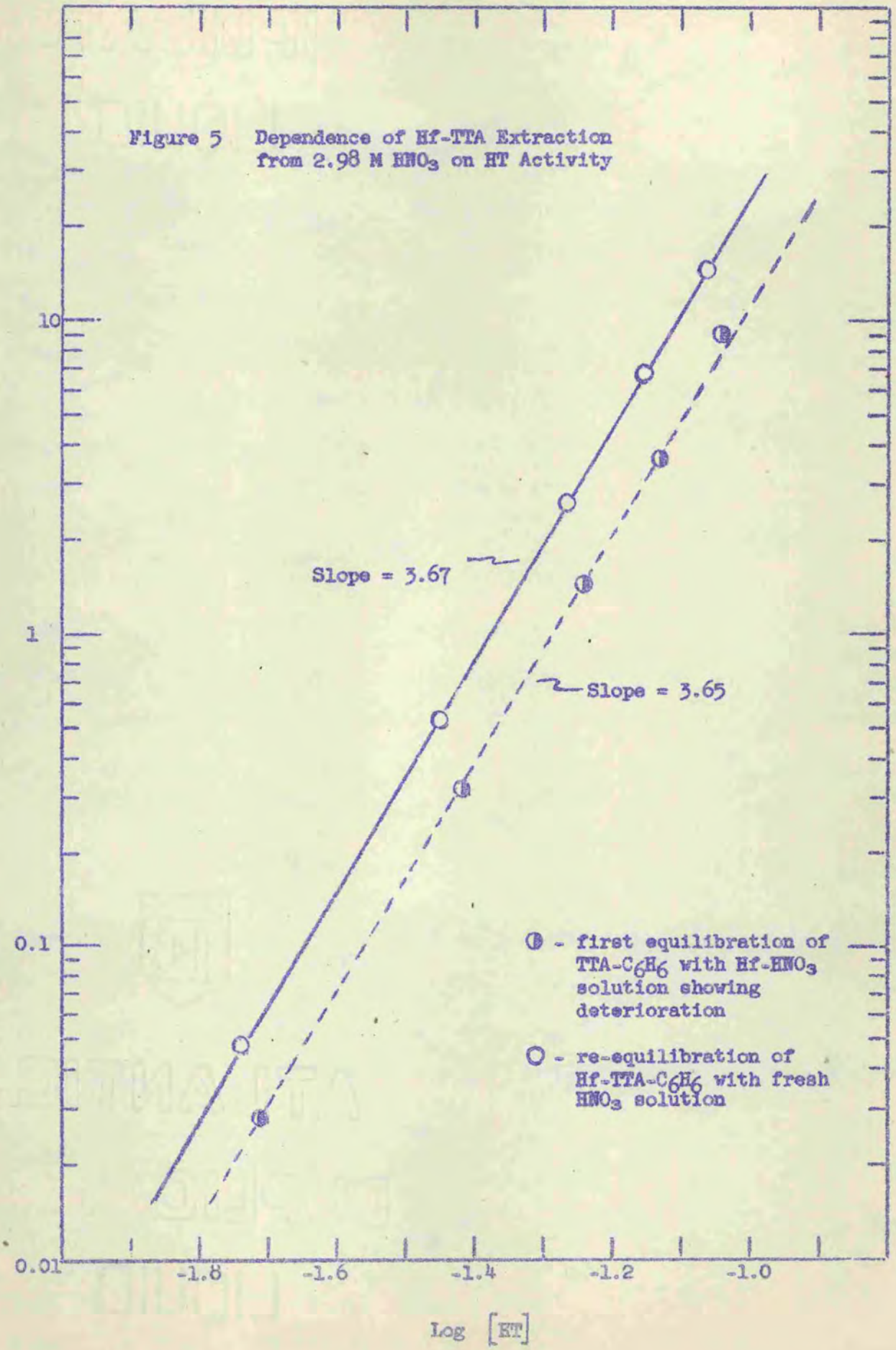


Figure 5 Dependence of Hf-TTA Extraction from 2.98 M HNO_3 on HT Activity



complex formed by the reaction

$$Hf(OH)^{+3} + HT \rightleftharpoons HfT^{+3} + H_2O$$

It will also be indicated that the two low values obtained above for 0.5 M HNO_3 at the higher TTA concentrations are probably not due to an additional TTA complex, which, of necessity, would be acid dependent.

Estimation of the Hydrogen Ion Activities

In order to determine the value of the equilibrium constant for the reaction expressing the Hf extraction and to compare distribution values obtained at different acidities it was necessary to make an estimation of the activity coefficients for hydrogen ion in the various acid solutions. Two methods have been in rather common use: one is to assume that the cation and anion in the HNO_3 solutions have equal activities and therefore that the activity coefficient of the hydrogen ion is equal to the mean activity coefficient for HNO_3:

$$\gamma(H^+) = \gamma_{\pm}(HNO_3)$$

The other is to follow the McInnes hypothesis(8) and assume that the activity

(8) D. A. McInnes, "The Activities of the Ions of Strong Electrolyes", Jour. Am. Chem. Soc. 41, 1086-92(1919).

of an univalent ion is the same in all univalent salt solutions of the same ionic strength and calculate the γ_{H^+} for a particular HNO_3 solution from the $\gamma_{\pm}$ for the same solution by the expression

$$\frac{(\gamma_{\pm}(HNO_3))^2}{\gamma(NO_3^-)} = \gamma(H^+)$$

The value for $\gamma(NO_3^-)$ is estimated by assuming as McInnes did, that, since K^+ and Cl^- have nearly equal weights and mobilities,

$$\gamma_{\pm\ KCl} = \gamma_{K^+} = \gamma_{Cl^-}$$

and calculating the ionic activity coefficient for NO_3^- from the mean activity coefficients for NH_4Cl and NH_4NO_3 in solutions of the same ionic strength by the method illustrated below and in table VI

$$\frac{(\gamma_{\pm\ NH_4Cl})^2}{\gamma_{Cl}} = \gamma_{NH_4^+} \quad ; \quad \frac{(\gamma_{\pm NH_4NO_3})^2}{\gamma_{NH_4^+}} = \gamma_{NO_3^-}$$

Examination of the mean activity coefficients for several univalent NO_3^- salts, and the ionic activity coefficients for NO_3^- calculated as above leads one to conclude that the γ_{H^+} values taken as equal to $\gamma_{\pm\ HNO_3}$ would be too low and that those calculated by the McInnes assumption would be too high. Hence it was felt that lacking better information, the γ_{H^+} would be best represented by the geometric mean of the two values:

$$\gamma_{H^+} = \sqrt{\gamma_{\pm(HNO_3)}\ \gamma_{M(H^+)}}$$

Given γ_{H^+}, fc_{H^+} can be calculated for the same solution by

$$fc_{H^+} = n\,\gamma_{H^+}/M$$

as mentioned previously. It is expected that activity coefficients calculated in this manner may be quite accurate up to moderately high ionic strength values (i.e., $\mu = 1$ or 2).

The values in the last column of Table VI are plotted against HNO_3 molarity in Fig. 6. The values in parentheses in the table are the apparent molar activity coefficients calculated by the straight line extrapolation of Fig. 2. The shape of the curve becomes concave downward rather than

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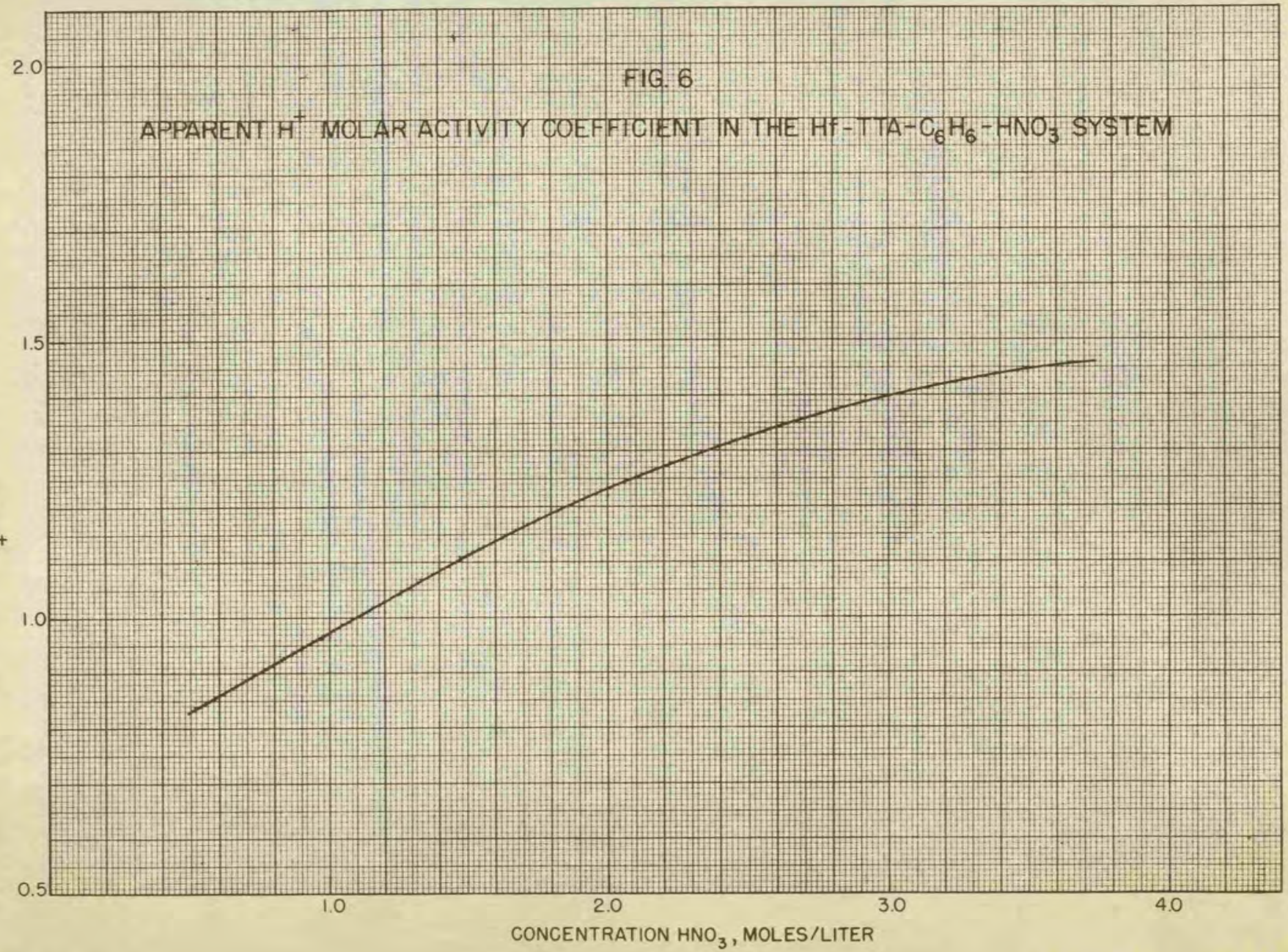
FIG. 6

APPARENT H^+ MOLAR ACTIVITY COEFFICIENT IN THE Hf-TTA-C_6H_6-HNO_3 SYSTEM



upward as expected at higher acidities. This is probably due to the fact that the activity coefficient determined by the extrapolation is not a true activity coefficient but corrects for the changes in the activity coefficients of other aqueous species as well.

Table VI

Estimation of the Hydrogen Ion Activity Coefficients

Molarity	$\gamma_{\pm HCl}\gamma_{Cl^-}$	$\gamma_{\pm NH_4Cl}$	$\gamma_{NH_4^+}$	$\gamma_{\pm NH_4NO_3}$	$\gamma_{NO_3^-}$	$\gamma_{\pm HNO_3}$	$\gamma_{(M)H^+}$	$\sqrt{\gamma_{\pm HNO_3}\gamma_{(M)H^+}}$	f_{cH^+}	f'_{cH^+}
0.5	0.660	0.644	0.628	0.587	0.549	0.713	0.926	0.814	0.827	0.827
1.0	0.612	0.603	0.594	0.506	0.431	0.721	1.206	0.933	0.962	0.962
2.0	0.576	0.571	0.566	0.426	0.321	0.790	1.944	1.240	1.316	(1.206)
3.0	0.576	0.574	0.572	0.371	0.241	0.909	3.429	1.765	1.927	(1.365)
4.0	0.581	0.590	0.599	0.335	0.187	1.10	6.47	2.67	2.871	(1.46)

Evidence for an Aqueous-Soluble Hf-TTA Complex

If one assumes that the deviation from a quadruple slope in the TTA dependency plots is due to the formation of an aqueous soluble complex represented by the reaction

$$Hf(OH)_A^{+3} + HT_B \rightleftharpoons HfT_A^{+3} + H_2O$$

then the $D.R._{(B/A)}$ for Hf may be represented by

$$D.R._{(B/A)} = \frac{(HfT_4)}{(Hf(OH)^{+3}) + (HfT^{+3})}$$

whence

$$D.R._{(B/A)} = \frac{(HfT_4)}{(Hf(OH)^{+3})}\left(\frac{1}{1 + k_T[HT]}\right)$$

in which k_T is the equilibrium constant for the previous equation, $[HT]$ is

the activity of TTA in the benzene phase, and the parentheses indicate concentrations in moles per liter. Given the value of the equilibrium constant K for the extraction of Hf, where aqueous complexing of Hf by TTA is negligible, $(HfT_4)/(Hf(OH)^{+3})$ may be calculated for any TTA or acid concentration by the expression

$$\frac{(HfT_4)}{(Hf(OH)^{+3})} = \frac{K\ [HT]^4}{[H^+]^3}$$

Having a value for $(HfT_4)/(Hf(OH)^{+3})$ for any particular equilibration k_t may be calculated by the following:

$$k_t = \frac{[(HfT_4)/(Hf(OH)^{+3})/D.R.] - 1}{HT}$$

In the calculations illustrated in Table VII_a, the value assumed for $K(4.0 \times 10^7)$ is the average value of K calculated from the distribution ratios observed for 0.5 M HNO_3 and the two lowest TTA concentrations. Columns 1 to 4 list the values of $[H^+]$, $[HT]$, log $[HT]$ and $D.R._{(B/A)}$. Column 5 gives the calculated values of $(HfT_4)/(Hf(OH)^{+3})$ while column 6 shows the values of k_t calculated from the above expression. Taking the mean value of 15.5 for k_t and substituting in the equation for the distribution ratio one obtains:

$$D.R._{(B/A)} = \frac{(HfT_4)}{(Hf(OH)^{+3})}\left(\frac{1}{1 + 15.5\ [HT]}\right)$$

Substituting the value of $(HfT_4)/(Hf(OH)^{+3})$, thus obtained, into the expression for the equilibrium constant gives the following

$$K = \frac{D.R._{(B/A)}\ (1 + 15.5\ [HT])\ [H^+]^3}{[HT]^4}$$

whence, taking the logs of both sides

$$\log K = \log \left\{ D.R._{(B/A)} \left(1 + 15.5 \left[HT\right]\right) \left[H^+\right]^3 \right\} - 4 \log \left[HT\right]$$
$$= \log \psi - 4 \log \left[HT\right]$$

where ψ equals the quantity enclosed in brackets. The value of ψ may be calculated for any equilibration using the value of $f_{c(H^+)}$ given in Table VI to obtain $\left[H^+\right]$. Column 7 of Table VII_a lists values of ψ calculated for the distribution runs listed in Tables III, IV, and V. In column 8 are the values of K calculated using the above expression. Fig. 7 shows a plot of log ψ vs log $\left[HT\right]$. The straight line through the data is drawn with a slope of 4.00.

It has been assumed throughout this report that the activity coefficient of the chelate in the benzene phase is unity. There is evidence in the case of the U(IV) chelate, that the activity coefficient of the chelate is the same as that for TTA for the same TTA concentrations as here employed.(9)

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(9) R. E. Connick and W. H. Reas, "The Activity Coefficient of Plutonium (IV) Salts in Acidic Solutions". UCRL-226, November, 1948, pp 48-55.

It may be reasonable to assume that this is also true in the case of Hf(IV). Table VII_b shows the calculation of the D.R. and k_t assuming $f_{c(HfT_4)} = f_{c\ (HT)}$, listing them as D.R.' and k_t'. A value of ψ' analgous to ψ is calculated from the mean value of k_t' (16.9). The last column gives the corresponding values of ψ, showing ψ' and ψ to be almost identical. Hence, a fourth power dependence on TTA activity is again indicated on this assumption for the chelate activity coefficient.

Table VII$_a$

Data Illustrating Aqueous Soluble Hf-TTA Complex

$[H^+]$	$[HT]$	log $[HT]$	D.R.$_{(B/A)}$	$\frac{HfT_4}{Hf(OH)^{+3}}$	k_t	ψ	K x 10^{-7}
0.397	0.00464	-2.334	0.280	-	-	0.0047	4.1
0.397	0.00923	-2.035	4.95	-	-	0.0888	4.9
0.397	0.0138	-1.860	18.53	24.14	21.94	0.353	3.9
0.397	0.0183	-1.738	61.50	75.07	12.04	1.24	4.4
0.397	0.0228	-1.642	95.09	180.9	39.58	2.02	3.0
0.397	0.0272	-1.565	178.5	366.3	38.68	3.98	2.9
0.970	0.00924	-2.021	0.270	0.370	40.08	0.071	3.9
0.970	0.01425	-1.846	1.590	1.845	11.26	0.442	4.3
0.970	0.0189	-1.724	4.466	5.713	14.77	1.32	4.2
0.970	0.0371	-1.431	46.69	84.82	22.01	16.8	3.6
0.970	0.0460	-1.337	117.7	200.5	15.28	46.1	4.1
0.970	0.0547	-1.262	235.6	400.9	12.83	99.4	4.4
(4.20)	0.0184	-1.735	0.047	0.0619	17.23	1.12	3.9
(4.20)	0.0357	-1.447	0.530	0.0877	18.32	15.3	3.8
(4.20)	0.0543	-1.265	2.598	4.69	14.87	88.6	4.1
(4.20)	0.0701	-1.154	6.710	13.0	13.50	261.	4.3
(4.20)	0.0869	-1.061	14.52	30.5	12.66	631	4.4

Table VII$_b$

Calculation of D.R.', k_T' and Ψ'

$[H^+]$	[HT]	D.R.	f_c (HT)	D.R.'	$\frac{HfT_4}{Hf(OH)^{+3}}$	k_T'	Ψ'	Ψ
0.397	0.00464	0.280	1.000	0.280	–	–	0.0047	0.0047
0.397	0.00923	4.95	0.993	4.93	–	–	0.0894	0.0888
0.397	0.0138	18.53	0.990	18.34	24.14	22.91	0.359	0.353
0.397	0.0183	61.50	0.985	60.58	75.07	13.07	1.24	1.24
0.397	0.0228	95.09	0.982	93.38	180.9	41.1	2.03	2.02
0.397	0.0272	178.5	0.978	174.6	366.3	40.4	4.00	3.98
0.970	0.00924	0.270	0.995	0.269	0.370	40.6	0.071	0.071
0.970	0.01425	1.590	0.990	1.574	1.845	12.08	0.445	0.442
0.970	0.0189	4.466	0.985	4.399	5.713	15.80	1.32	1.32
0.970	0.0371	46.69	0.967	45.15	84.82	23.68	16.8	16.8
0.970	0.0460	117.7	0.959	112.9	200.5	16.87	45.8	46.1
0.970	0.0547	235.6	0.951	224.1	400.9	14.43	98.4	99.4
(4.20)	0.0184	0.047	0.987	0.0464	0.619	18.16	1.13	1.12
(4.20)	0.0357	0.530	0.970	0.514	0.877	19.76	15.3	15.3
(4.20)	0.0543	2.598	0.954	0.478	4.695	16.48	88.1	88.6
(4.20)	0.0701	6.710	0.942	6.32	13.04	15.16	257	261
(4.20)	0.0869	17.52	0.931	13.52	30.49	14.44	618	631

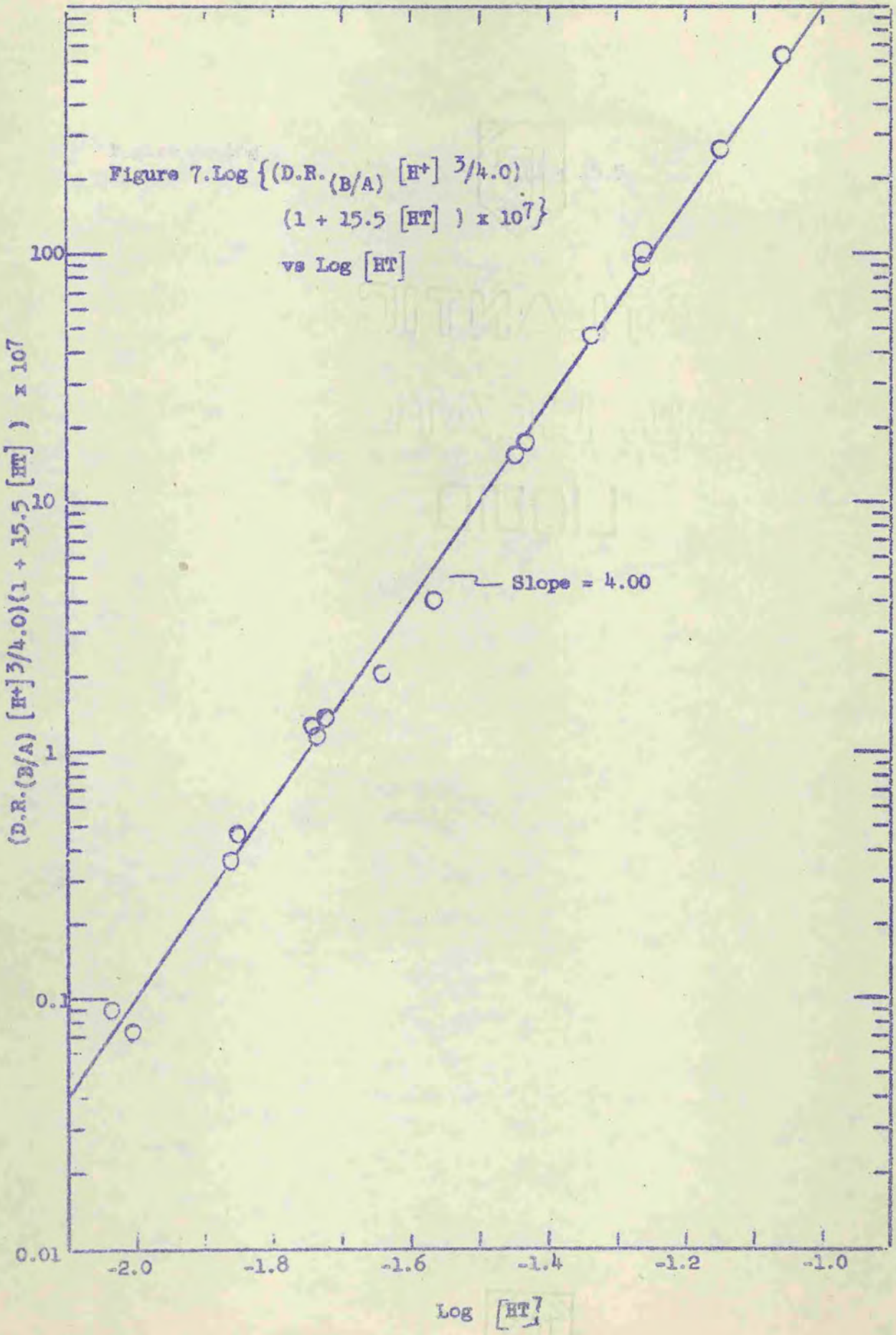
Figure 7. Log {(D.R.(B/A) [H+] 3/4.0) (1 + 15.5 [HT]) x 10^7} vs Log [HT]
Slope = 4.00
(D.R.(B/A) [H+]3/4.0)(1 + 15.5 [HT]) x 10^7
100
10
1
0.1
0.01
-2.0
-1.8
-1.6
-1.4
-1.2
-1.0
Log [HT]

It may be that additional aqueous Hf-TTA complexes of the form $Hf(OH)T^{+2}$ or HfT_2^{+2} (which are acid dependent), are formed by reactions of the type

$$Hf(OH)^{+3} + HT \rightleftharpoons Hf(OH)T^{+2} + H^+$$

which would explain the unusually low distribution values observed at high TTA concentration and low acid and noted in Table III and Fig. 3. However, this seems unlikely since one would assume that if this is the case here, a similar effect should be observed at the highest TTA concentration for the 1.0 M HNO_3 equilibrations (Table IV, Fig. 4) where the $[HT] / [H^+]$ ratio is 0.056 as compared with 0.057 in the case of the lower acid solution. Also since the acid dependence for TTA extraction is close to three for 0.02 M TTA solutions it is to be expected that complexes of the form $Hf(OH)T^{+2}$ or HfT_2^{+2}, which would tend to lower the acid dependency to 2, are not prominent.

The following expression for the distribution ratio may be used for calculating the distribution ratios for Hf tracer between nitric acid solutions, 0.5 to 3.5 molar, and benzene solutions, 0.005 to 0.1 M in TTA (where H^+ is calculated by the use of the $f_c'(H^+)$ taken from Fig. 6).

$$D.R._{(B/A)} = \frac{4.0\,[HT]^4}{[H^+]^3}\left(\frac{1}{1 + 15.5\,[HT]}\right) \times 10^7$$

Nitrate Complexing

Since the apparent hydrogen ion activity coefficient ($f_c'(H^+)$) referred to in this report attempts to correct for all changes in the solution due to the increase in HNO_3 concentration in terms of an acidity correction factor the effect of nitrate complexing is completely obscured and but little can be said about it. However, it should be pointed out that the K value of 4.0×10^7 calculated for the 0.5 molar acid runs at low TTA concentration compares favorably with the 3.3×10^7 calculated by the same equation using the data of Huffman and Beaufait[1] for the extraction of Hf from 2 M $HClO_4$ (where no complexing by the anionic species is to be expected), assuming the molar H^+ activity coefficient is 0.827 in 0.48 M HNO_3 and unity in 2 M $HClO_4$. Some of the preceding experiments will be duplicated in $HClO_4$ in the near future to determine the order of magnitude of nitrate complexing.