# The Hydrolysis of Zr^{4+} and Hf^{4+}

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The hydrolysis of Zr^{4+} and Hf^{4+} has been investigated by means of potentiometric and solvent extraction measurements. In the potentiometric investigations, a fluoride membrane electrode has been used for the determination of the stability constants, $*K_n$ for the complex equilibria

$$MF_{n-1} + HF \rightleftharpoons MF_n + H^+$$
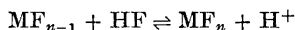
where $M = Zr^{4+}$ or Hf^{4+}. From the variation of the conditional constant, $*K_1^{calc}$, with the acidity of the solutions, the equilibrium constant, $*\gamma_1$, has been calculated for the reaction

$$M + H_2O \rightleftharpoons MOH + H^+$$
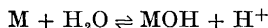
In the solvent extraction measurements, the distribution of the metal ions between xylene solutions of thenoyltrifluoroacetone and aqueous solutions containing various concentrations of perchloric acid has been studied.

All the measurements have been performed in a medium having a constant concentration of 4 M of perchlorate ions. The composition of the medium has been changed from 4 M $HClO_4$ to 0.5 M $HClO_4 + 3.5$ M $NaClO_4$. Th^{4+}, which is not hydrolysed in the hydrogen ion concentration range studied, has been used as a model ion for the determination of the activity changes caused by this variation of the medium. In the solvent extraction and in the potentiometric investigations, the temperature was 20°C and 25°C, respectively.

The limits of error given for the values of the constants calculated in the present paper correspond to 99 % confidence limits if not otherwise stated.

Four valent metal ions are known to be extensively hydrolysed in aqueous solution. Even in the most acid solutions some of them exist exclusively as yl-ions, *e.g.* TiO^{2+}, VO^{2+}. No simple hydrated ions with a charge of $+4$ are formed. For Zr(IV) and Hf(IV), it has long been discussed whether or not these too form yl-ions in solid salts and in aqueous solutions. Recently performed measurements of the infra-red spectra of hydrated and deuterated nitrates and chlorides of zirconium(IV)[1] show, however, no evidence of the existence of the zirconyl group (Zr=O) in these compounds. In aqueous solutions, zirconium(IV) and hafnium(IV) are both known to be involved in

complicated hydrolysis equilibria. The large amount of experimental results of the solution chemistry of these metal ions has been reviewed by Solovkin and Tsvetkova,[2] Caletka,[3] Hala [4] and recently by Larsen.[5] They concluded [2] that in aqueous solution there is no justification for the zirconyl theory. However, without doubt, both metal ions form, besides mononuclear species, also polynuclear hydrolysis products. Presumably, trimeric and tetrameric species of the type $M_3(OH)_4^{8+}$ and $M_4(OH)_8^{8+}$ are formed.[6-9] Even in rather acid solutions (2 M) the polynuclear species exist at low total metal ion concentrations (10^{-4} M).

For the mononuclear hydrolysis of Zr^{4+}, disparate values of the stability constants for the formation of the various hydroxo complexes have been reported in the literature.[10-12] Only one set of values of the corresponding stability constants for Hf^{4+} has been given.[13] Solvent extraction utilizing different organic acids as competing ligands is the only experimental method that has been used in Refs. 10 − 13. The values of the constants obtained in Ref. 10 for the hydrolysis of Zr^{4+} were calculated from the measurements of Connick and McVey.[14] With the exception of Ref. 14, the highest hydrogen ion concentration used was about 1 M. At this acidity only low concentrations of M^{4+} exist (17 % Zr^{4+}, 29 % Hf^{4+}). Hence, the calculated value of the first hydrolysis constant might be fairly uncertain. It therefore seems desirable to extend the study of the hydrolysis of Zr^{4+} and Hf^{4+} to more acid solutions and to try another method of investigation than the mentioned solvent extraction.

Since polynuclear hydrolysis products are formed, the experimental method chosen must give accurate results even at low total metal ion concentrations. Preferably a potentiometric method should be used, as such measurements are known to give results of high precision. However, due to the low metal ion concentrations (usually 10^{-4} M), direct measurements of the hydrogen ions set free in the hydrolysis reactions are not possible in strongly acid solutions. Obviously, the investigation has to be performed by means of some indirect method. Recently, a fluoride membrane (FME-)electrode was used by the present author to study the fluoride complexes of Th^{4+} and U^{4+}; cf. Ref. 15. This electrode was proved to be of great value for investigations of fluoride complex systems. From accurate determinations of the conditional equilibrium constant of

$$M^{4+} + HF \rightleftharpoons MF^{3+} + H^+$$
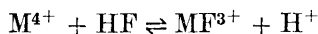
at different hydrogen ion concentrations, it is possible to obtain the hydrolysis constants of the metal ion in question, vide infra p. 1372. Hence, the fluoride complexes of Zr^{4+} and Hf^{4+} were investigated, using a fluoride membrane electrode, in 4.000 M $HClO_4$, 1.000 M $HClO_4 + 3.000$ M $NaClO_4$, and 0.500 M $HClO_4 + 3.500$ M $NaClO_4$. The composition of these ionic media varies considerably. Thus, it is likely that the values of the stability constants cannot be directly compared and that a correction for the change of the medium has to be applied. Th^{4+}, which is not hydrolysed [16,17] in the solutions investigated, was used as a model ion for a quantitative determination of this medium effect.

Some years ago, solvent extraction measurements were performed by the present author to elucidate the hydrolysis of Zr^{4+} and Hf^{4+}. The metal ions

were distributed between an acid aqueous phase and a xylene phase containing thenoyltrifluoroacetone as a competing ligand. The study was part of an investigation of the complexes formed by four valent cations with ligands of various donating properties. Values of the stability constants were collected at a temperature of 20°C. Thus, the solvent extraction experiments referred to were carried out at this temperature. The results, not yet published, are included in this paper for a comparison with the results of the potentiometric measurements performed at 25°C.

EXPERIMENTAL

Stock solutions were prepared and analysed in the same way as described in Refs. 15 and 18 – 20. These references should be consulted for experimental details of the procedure of the solvent extraction and potentiometric measurements.

To avoid errors in the emf measurements due to diffusion potentials between the reference half-cell and the FME half-cell, the composition of their solutions as well as that of the salt bridge was always the same except for the fairly small contents of metal ion and hydrofluoric acid in the FME half-cell.

SYMBOLS

$$*\gamma_m = [M(OH)_m][H^+]^m/[M].$$
$$*\beta_n = [MF_n][H^+]^n/[M][HF]^n.$$
$$\beta_{nH} = *\beta_n/[H^+]^n.$$
$$\beta_{nH}^{calc} = \beta_{nH}/1 + \sum_{m=1}^{M} *\gamma_m[H^+]^{-m}.$$
$$*K_n = [MF_n][H^+]/[MF_{n-1}][HF]; \quad *K_1 = *\beta_1.$$
$$*K_n^{calc} = \beta_{nH}^{calc}[H^+]/\beta_{(n-1)H}^{calc}; \quad *K_1^{calc} = \beta_{1H}^{calc}[H^+].$$

HA = thenoyltrifluoroacetone.
$[\;]$ = equilibrium concentration in the aqueous phase.
$[\;]_{org}$ = equilibrium concentration in the xylene phase.
C_{HA}' = initial total concentration of HA in the xylene phase.
K_a = $[H^+][A^-]/[HA].$
K_{dHA} = $[HA]_{org}/[HA].$
K_{dMA_4} = $[MA_4]_{org}/[MA_4].$
β_n = $[MA_n]/[M][A^-]^n.$

CALCULATIONS AND RESULTS OF THE EMF MEASUREMENTS

According to Farrer and Rossotti,[21] F^-, HF and HF_2^- exist in hydrofluoric acid solutions. However, from the results reported one obtains for the hydrogen ion concentrations used in the present investigation that $[F^-] < 10^{-3}$ $[HF]$ and $[HF_2^-] < 5 \times 10^{-5}$ $[HF]$. Thus, the concentrations of F^- and HF_2^- are negligible and can be excluded in the following derivations. If only mononuclear fluoride and hydroxo complexes are taken into consideration and mixed complexes containing these ligands are neglected, the total concentrations of hydrofluoric acid and metal ion can be written:

$$C_{HF} = [HF] + [M] \sum_{n=1}^{N} n\beta_{nH}[HF]^n \tag{1}$$

$$C_M = [M]\left(1 + \sum_{m=1}^{M} {}^*\gamma_m[H^+]^{-m} + \sum_{n=1}^{N} \beta_{nH}[HF]^n\right) \tag{2}$$

Since the hydrogen ion concentration is kept constant in each titration series, $\bar{n} = (C_{HF} - [HF])/C_M$ is a function of [HF] only given by:

$$\bar{n} = \frac{\sum\limits_{n=1}^{N} n\,\beta_{nH}{}^{calc}[HF]^n}{1 + \sum\limits_{n=1}^{N} \beta_{nH}{}^{calc}[HF]^n} \tag{3}$$

The free ligand concentration, [HF], is obtained from the measured emf's, E_F, using:

$$E_F = E_C - RTF^{-1}\ln[HF] \tag{4}$$

A numerical method for calculation of stability constants described by Sandell in Ref. 22, p. 2611, is easily verified to be applicable here and is used for the calculations of $\beta_{nH}{}^{calc}$. From corresponding values of $\beta_{nH}{}^{calc}$ and [H$^+$], the constants $^*K_n{}^{calc}$ are obtained. Of these constants, all except $^*K_1{}^{calc}$ are independent of the hydrogen ion concentration whether the investigated metal ions are hydrolysed or not. For $^*K_1{}^{calc}$, the following expression is valid:

$$\frac{1}{{}^*K_1{}^{calc}} = \frac{1}{{}^*K_1}\left(1 + \sum_{m=1}^{M} {}^*\gamma_m[H^+]^{-m}\right) \tag{5}$$

Evidently it is only for such metal ions which are not hydrolysed that $^*K_1{}^{calc}$ is a true constant. In the present investigation the stability constants have been determined in solutions with three different hydrogen ion concentrations. From the variation of $^*K_1{}^{calc}$ with [H$^+$], after a correction for medium changes has been introduced for the calculations in $^*K_1{}^{calc}$, the hydrolysis constants, $^*\gamma_m$, were obtained graphically according to eqn. (5).

The thorium system. The experimentally obtained results are given in Table 1. Different total concentrations of Th^{4+} within the range 0.18 mM $\leq C_{Th} \leq$ 4.48 mM were used. No variation of $\bar{n}$ with C_{Th} could be observed, confirming that only mononuclear complexes are formed. The maximum value of C_{HF} was about 10 mM, which is negligible compared to the total ionic strength of 4 M. The variation of the composition of the medium may therefore be neglected within the titration series having the same constant value of C_H. Using the numerical method of Sandell,[22] the following values for the constants were calculated:

[H$^+$]/M	$\beta_{1H}{}^{calc} \times 10^{-4}$/M^{-1}	$\beta_{2H}{}^{calc} \times 10^{-6}$/M^{-2}	$\beta_{3H}{}^{calc} \times 10^{-8}$/M^{-3}
4.000	1.043 ± 0.005	1.67 ± 0.06	0.4 ± 0.1
1.000	3.54 ± 0.02	17.6 ± 0.7	6 ± 5
0.500	6.53 ± 0.02	62 ± 1	32 ± 9

where the given errors are standard deviations. The constants determined for $C_H = 4.000$ M agree quite well with those earlier reported in Ref. 15, valid

Table 1. Corresponding values of C_{HF} mM and E_F mV obtained in the various titration series for thorium.

4.000 M HClO₄

$C_{Th} = 0.4482$ mM, $E_C = -24.6$ mV: 0.1430, 241.6; 0.2759, 219.8; 0.2759, 219.1; 0.5189, 193.6; 0.7316, 179.0; 0.9840, 167.0.

$C_{Th} = 1.810$ mM, $E_C = -23.7$ mV: 0.3557, 252.3; 0.4548, 244.4; 0.5429, 238.5; 0.6810, 230.9; 0.6948, 229.7; 0.8187, 223.4; 0.9560, 216.9; 1.022, 214.7; 2.011, 176.1; 3.276, 147.2; 4.483, 132.4; 5.634, 123.3; 7.817, 111.4.

$C_{Th} = 1.810$ mM, $E_C = -24.1$ mV: 1.391, 197.6; 1.999, 175.6; 2.591, 159.5; 3.554, 143.1; 3.739, 140.3; 4.837, 129.2; 5.889, 121.4; 8.603, 108.5.

$C_{Th} = 4.482$ mM, $E_C = -24.5$ mV: 0.4786, 268.9; 0.6932, 257.9; 1.056, 244.7; 1.345, 236.5; 1.582, 230.6; 1.844, 224.6; 3.885, 184.1; 2.573, 209.4; 3.872, 184.4; 5.109, 162.4; 6.287, 146.8; 7.410, 135.9; 9.538, 122.2.

1.000 M HClO₄ and 3.000 M NaClO₄

$C_{Th} = 0.8980$ mM, $E_C = -68.4$ mV: 0.1378, 245.4; 0.2687, 224.1; 0.3931, 209.8; 0.5116, 197.9; 0.6244, 187.1; 0.7321, 177.3; 0.8349, 168.3; 0.9333, 160.2; 1.027, 153.0; 1.117, 146.9; 1.204, 141.7.

$C_{Th} = 0.8980$ mM, $E_C = -70.4$ mV: 0.0992, 255.7; 0.1378, 245.1; 0.1947, 235.8; 0.2868, 222.2.

$C_{Th} = 0.8980$ mM, $E_C = -69.1$ mV: 0.0992, 255.1; 0.1378, 244.8; 0.1947, 235.0; 0.2868, 222.1; 0.3757, 212.0; 0.4615, 203.3; 0.5443, 195.3; 0.6243, 187.9; 0.7000, 180.9; 0.7748, 174,1; 0.8471, 167.9.

$C_{Th} = 0.8980$ mM, $E_C = -81.5$ mV: 0.9416, 147.0; 1.370, 120.9; 1.385, 120.3; 1.519, 114.5; 1.820, 104.7; 2.082, 98.3; 2.286, 94.0; 2.631, 88.0; 2.742, 86.3; 2.770, 85.8; 2.955, 83.2; 3.041, 82.2; 3.167, 80.5; 3.336, 78.6.

$C_{Th} = 1.796$ mM, $E_C = -68.2$ mV: 0.2353, 249.1; 0.4372, 229.8; 0.4660, 228.3; 0.6176, 217.7; 0.7797, 208.3; 1.058, 193.8; 1.290, 182.1; 1.486, 172.0; 1.654, 163.4.

$C_{Th} = 1.796$ mM, $E_C = -69.1$ mV: 0.7901, 208.6; 0.9305, 201.3; 1.091, 192.1; 1.324, 181.3; 1.705, 161.8; 2.073, 144.5; 2.428, 131.4.

$C_{Th} = 1.796$ mM, $E_C = -67.5$ mV: 0.3347, 239.9; 0.6156, 219.2; 0.8546, 206.0; 1.060, 195.3; 1.489, 173.6; 1.903, 152.6; 2.301, 136.2.

0.500 M HClO₄ and 3.500 M NaClO₄

$C_{Th} = 0.1796$ mM, $E_C = -84.7$ mV: 0.00923, 276.0; 0.01800, 258.7; 0.02632, 248.1, 0.03423, 240.4; 0.04177, 234.4; 0.05580, 225.1; 0.06861, 218.1; 0.09583, 205.1; 0.1219, 194.4; 0.1709, 177.1; 0.2161, 164.1; 0.2579, 154.8; 0.2968, 147.7; 0.3330, 142.3; 0.4103; 133.4; 0.5387, 122.8.

$C_{Th} = 0.3592$ mM, $E_C = -84.8$ mV: 0.03548, 258.0; 0.06914, 239.0; 0.1011, 226.8; 0.1315, 217.5; 0.1605, 209.8; 0.1881, 202.9; 0.2145, 196.7; 0.2637, 185.6; 0.3088, 176.0; 0.3503, 167.7; 0.3886, 160.5; 0.4240, 154.8; 0.4824, 146.3; 0.6115, 132.6; 0.8535, 116.4; 1.094, 106.2.

$C_{Th} = 0.5388$ mM, $E_C = -84.7$ mV: 0.05810, 255.3; 0.1114, 236.0; 0.1605, 223.8; 0.2058, 214.8; 0.2478, 207.0; 0.2868, 200.3; 0.3231, 194.3; 0.3571, 188.9; 0.3888, 183.9; 0.4465, 174.8; 0.4976, 167.0; 0.5433, 160.3; 0.6150, 150.8; 0.6750, 144.0; 1.338, 105.6; 1.667, 96.2.

$C_{Th} = 0.8980$ mM, $E_C = -84.1$ mV: 0.06986, 264.9; 0.1989, 234.2; 0.2588, 225.2; 0.3158, 218.1; 0.3702, 211.9; 0.4221, 206.2; 0.4718, 201.1; 0.5192, 196.3; 0.5647, 191.7; 0.6498, 183.2; 0.7283, 175.2; 0.8008, 167.9; 0.9200, 155.9; 1.025, 146.9; 1.118, 139.4.

$C_{Th} = 0.8980$ mM, $E_C = -84.4$ mV: 0.1021, 254.2; 0.1667, 239.8; 0.2282, 229.7; 0.2867, 221.8; 0.3954, 209.1; 0.4946, 198.9; 0.5854, 189.6; 0.6689, 181.1; 0.8050, 167.1; 0.9236, 155.2; 1.028, 145.9; 1.120, 138.8; 1.580, 115.0; 2.036, 100.9.

$C_{Th} = 0.8980$ mM, $E_C = -98.7$ mV: 0.7085, 163.4; 0.9241, 141.6; 1.118, 124.8; 1.293, 113.4; 1.452, 105.3; 1.555, 100.9; 1.597, 99.3; 1.730, 94.7; 1.852, 90.8; 1.964, 87.7; 2.069, 85.0; 2.165, 82.7; 2.223, 81.4; 2.255, 80.7; 2.339, 79.0; 2.477, 76.3.

in the same medium but at a temperature of 20.00°C. From corresponding values of $\beta_{nH}{}^{calc}$ and $[H^+]$ one obtains:

$[H^+]/M$	$*K_1{}^{calc} \times 10^{-4}$	$*K_2{}^{calc} \times 10^{-2}$
4.000	4.17 ± 0.05	6.4 ± 0.6
1.000	3.54 ± 0.06	5.0 ± 0.5
0.500	3.27 ± 0.03	4.7 ± 0.2

where $*K_3{}^{calc}$ is omitted because of the large errors in the determined values of $\beta_{3H}{}^{calc}$. This will not influence the conclusions drawn regarding the hydrolysis of Zr^{4+} and Hf^{4+}.

For the reason given on p. 1372, it is expected that $*K_1{}^{calc}$ and $*K_2{}^{calc}$ will have the same value for the three hydrogen ion concentrations used. Obviously there is a significant difference between the results obtained in the media used. The most probable explanation of this fact is that the values of the activity coefficients of the species involved in the different equilibria are not the same in the various media. Hence, the following correction factors have to be applied to relate the results of the zirconium and hafnium measurements to 4 M $HClO_4$ as a reference medium.

Medium	f_1	f_2
1 M $HClO_4$ + 3 M $NaClO_4$	1.18 ± 0.02	1.3 ± 0.2
0.5 M $HClO_4$ + 3.5 M $NaClO_4$	1.28 ± 0.02	1.4 ± 0.1

f_1 and f_2 are calculated by dividing the value of $*K_n{}^{calc}$ valid in 4 M $HClO_4$ with the value of the same constant obtained in the medium in question. Recently, the stability constants for the fluoride complexes of U^{4+} have been determined in 0.6 M $HClO_4$ and 3.4 M $NaClO_4$ at a temperature of 25°C by Grenthe and Varfeldt.[23] Using the values for these constants obtained in 4 M $HClO_4$ and 20°C [15] (no values at 25°C are available) f_1 and f_2 are calculated to be 1.5 and 1.8, respectively. Considering that the complex formation reactions probably are exothermic, the agreement with the results obtained in the present paper for Th^{4+} in almost the same medium is fairly good, thus supporting the method used for the medium corrections to Zr^{4+} and Hf^{4+}.

The zirconium system. To investigate whether polynuclear species were formed or not, titration series having different values of C_{Zr} were performed. For all the hydrogen ion concentrations used, $\bar{n}$ was found to be a function of both $[HF]$ and C_{Zr}, showing polynuclear species to exist in the solutions. However, when $[HF]$ or $[H^+]$ increased, $\bar{n}$ became more and more independent of C_{Zr}. For low enough values of C_{Zr}, $\bar{n}$ could be obtained as a function of the free ligand concentration only. Therefore, efforts were made to keep C_{Zr} within a concentration range where $\bar{n}$ was unaffected by the metal ion concentrations used. This was not the case at the lowest values of $[HF]$ where $\bar{n}$ varied with C_{Zr}. In such solutions, $\bar{n}$ was obtained by extrapolations to $C_{Zr} = 0$. Since the computer program cannot use data series having $C_M = 0$, corresponding values of E_F and C_{HF} valid for the extrapolated data were calculated from arbitrarily chosen values of C_{Zr} (within the metal concentration range used) and E_C. In the calculations of the stability constants, few extrapolated values were used. The values of the stability constants obtained were only slightly influenced by these.

Table 2. Corresponding values of $C_{HF} \times 10^5$ M and E_F mV obtained in the various titration series for zirconium.

4.000 M HClO₄

$C_{Zr} = 0.5000$ mM, $E_C = -25.0$ mV (extrapolated): 4.900, 347.8; 9.200, 330.3; 12.98, 319.5; 16.10, 312.2; 18.75, 306.4; 21.00, 301.7; 22.75, 297.8.

$C_{Zr} = 0.2420$ mM, $E_C = -23.8$ mV: 15.39, 283.1; 21.22, 262.8; 22.92, 257.0; 24.60, 251.3; 27.91, 241.2; 33.24, 227.8; 38.37, 217.7; 43.30, 209.8; 48.05, 203.4.

$C_{Zr} = 0.2420$ mM, $E_C = -24.6$ mV: 11.90, 295.1; 14.52, 285.7; 16.97, 277.1; 22.08, 259.3; 27.00, 243.5; 31.75, 230.7; 36.34, 220.9; 40.78, 213.1; 45.06, 206.9; 49.21, 201.7.

$C_{Zr} = 0.5035$ mM, $E_C = -24.9$ mV: 27.09, 290.5; 32.46, 281.0; 37.61, 271.9; 42.57, 262.9; 47.34, 254.3; 51.94, 246.1; 56.38, 238.6.

$C_{Zr} = 1.009$ mM, $E_C = -24.5$ mV: 51.55, 292.3; 72.86, 273.3; 91.67, 255.8; 177.3; 193.1; 243.3, 167.7.

$C_{Zr} = 2.523$ mM, $E_C = -25.7$ mV: 152.3, 281.8; 192.9, 267.0; 230.1, 252.6; 264.3, 239.1; 295.8, 227.2; 324.8, 217.4; 351.8, 209.0.

$C_{Zr} = 5.045$ mM, $E_C = -25.1$ mV: 297.5, 283.0; 344.3, 274.9; 408.3, 263.0; 461.6, 256.6; 575.1, 230.3; 684.9, 211.3.

1.000 M HClO₄ and 3.000 M NaClO₄

$C_{Zr} = 0.1000$ mM, $E_C = -66.0$ mV (extrapolated): 2.850, 302.1; 3.206, 298.1; 3.520, 294.7; 3.834, 291.7; 4.120, 289.0; 4.345, 286.5; 4.620, 284.3.

$C_{Zr} = 0.1009$ mM, $E_C = -67.5$ mV: 5.187, 276.9; 6.088, 269.5; 6.747, 263.9; 7.179, 260.6; 8.233, 251.8; 8.233, 252.1; 9.252, 243.9; 10.24, 236.2; 11.19, 229.1; 12.11, 222.9; 13.01, 217.5.

$C_{Zr} = 0.1017$ mM, $E_C = -66.2$ mV: 5.562, 276.8; 6.049, 273.0; 7.108, 264.5; 8.119, 256.4; 9.084, 248.6; 10.01, 241.4; 10.89, 234.6; 11.74, 228.6; 12.55, 223.2; 14.77, 210.6; 16.90, 200.9; 18.95, 193.2.

$C_{Zr} = 0.1017$ mM, $E_C = -66.0$ mV: 5.020, 280.3; 6.130, 271.0; 7.180, 262.5; 8.190, 254.3; 10.07, 239.4; 11.79, 226.8; 13.38, 216.7; 14.84, 208.8.

$C_{Zr} = 0.2518$ mM, $E_C = -66.0$ mV: 13.22, 276.2; 15.81, 267.7; 18.28, 259.4; 20.64, 251.3; 24.59, 237.7; 26.68, 230.3; 31.01, 216.6; 35.16, 204.9.

$C_{Zr} = 0.2518$ mM, $E_C = -65.9$ mV: 12.07, 280.3; 17.66, 261.7; 22.97, 243. 4; 25.35, 235.1; 27.63, 227.2; 29.80, 220.3; 34.37, 207.3; 38.74, 196.7; 42.93, 187.8.

$C_{Zr} = 0.5035$ mM, $E_C = -66.9$ mV: 37.45, 255.1; 41.85, 247.8; 46.06, 240.8; 53.93, 226.9; 61.18, 214.9; 67.87, 204.8; 74.06, 196.2.

$C_{Zr} = 1.009$ mM, $E_C = -67.5$ mV: 92.81, 237.3.

$C_{Zr} = 2.523$ mM, $E_C = -66.6$ mV: 256.8, 226.2.

0.500 M HClO₄ and 3.500 M NaClO₄

$C_{Zr} = 0.02500$ mM, $E_C = -85.0$ mV (extrapolated): 1.155, 279.1; 1.296, 274.1.

$C_{Zr} = 0.02523$ mM, $E_C = -84.4$ mV: 1.482, 268.7; 1.980, 253.9; 2.434, 241.5; 2.851, 231.3; 3.234, 223.4; 3.588, 217.2; 4.168, 208.7; 5.514, 193.7; 6.769, 184.0.

$C_{Zr} = 0.05045$ mM, $E_C = -84.5$ mV: 2.891, 267.8; 3.764, 254.3; 4.599, 241.4; 5.400, 229.7; 6.167, 219.8; 6.905, 211.3; 7.613, 204.7; 8.294, 199.0; 9.577, 189.7.

$C_{Zr} = 0.05045$ mM, $E_C = -83.0$ mV: 3.077, 265.0; 3.956, 251.6; 4.797, 238.7; 5.603, 227.0; 6.375, 217.2; 7.117, 209.2; 8.510, 196.9.

$C_{Zr} = 0.1017$ mM, $E_C = -84.7$ mV: 5.607, 266.0; 7.195, 254.3; 8.655, 243.7; 11.03, 225.4; 12.20, 217.1; 14.12, 204.7; 18.75, 182.4.

$C_{Zr} = 0.1017$ mM, $E_C = -84.3$ mV: 4.576, 274.1; 6.282, 261.1; 7.842, 250.0; 9.276, 239.3; 10.46, 230.3; 11.56, 222.1; 12.13, 218.1; 13.56, 208.7; 17.18, 189.5.

$C_{Zr} = 0.2518$ mM, $E_C = -84.3$ mV: 25.10, 228.0; 26.72, 223.1; 28.27, 218.5.

$C_{Zr} = 0.2518$ mM, $E_C = -84.1$ mV: 22.31, 237.1; 31.20, 210.2; 39.74, 187.1.

The results obtained in the various titration series are collected in Table 2. For all the given values (except those pointed out as extrapolated), having the same [HF], the variation of $\bar{n}$ with C_{Zr} was within a random experimental error of $\pm 2 \%$. The following values were obtained for the constants $\beta_{nH}{}^{calc}$:

$[H^+]/M$	$\beta_{1H}{}^{calc} \times 10^{-5}/M^{-1}$	$\beta_{2H}{}^{calc} \times 10^{-9}/M^{-2}$	$\beta_{3H}{}^{calc} \times 10^{-11}/M^{-3}$
4.000	2.20 ± 0.02	1.15 ± 0.02	2.6 ± 0.6
1.000	6.24 ± 0.06	11.8 ± 0.2	140 ± 50
0.500	9.46 ± 0.16	33 ± 1	600 ± 260

The errors quoted are standard deviations. The values valid in 4 M $HClO_4$ are in accordance with those given in Refs. 19, 20, and 24. The values of $*K_n{}^{calc}$ ($1 \leq n \leq 2$) calculated using the medium correction factors obtained in the thorium measurements are as follows:

$[H^+]/M$	$*K_1{}^{calc} \times 10^{-5}$	$*K_2{}^{calc} \times 10^{-4}$
4.000	8.8 ± 0.2	2.1 ± 0.1
1.000	7.4 ± 0.2	2.5 ± 0.4
0.500	6.1 ± 0.3	2.5 ± 0.3

Evidently there is still a significant decrease (the limits of error correspond to a confidence limit of 99 %) of $*K_1{}^{calc}$ as the hydrogen ion concentration decreases. It may therefore be concluded that Zr^{4+} is hydrolysed even in these fairly acid solutions.

Fig. 1 shows $(*K_1{}^{calc})^{-1}$ as a function of $[H^+]^{-1}$. A straight line can be drawn through the points indicating that predominantly the first hydroxo complex is formed. Using eqn. (5), the value of the stability constant, $*\gamma_1$, is calculated to be 0.28, with graphically estimated maximum limits of error of ± 0.05, As predicted, $*K_2{}^{calc}$ is independent of the hydrogen ion concentration. Furthermore, almost the same value is found as previously determined from results obtained using other methods of investigation.[19,20] As an average value of $*K_1$ for the equilibrium $Zr^{4+} + HF \rightleftharpoons ZrF^{3+} + H^+$ one obtains 9.4×10^5 (valid in a reference medium of 4 M $HClO_4$) using $*\gamma_1 = 0.28$. The three different media give values within a fairly small interval ($\pm 0.05 \times 10^5$).

The hafnium system. For hafnium as well, $\bar{n}$ was found to depend both on [HF] and C_{Hf}. However, the variation of $\bar{n}$ values corresponding to the same free ligand concentration with C_{Hf} was smaller than the C_M variation in the zirconium system. As for zirconium, titration series having quite low metal ion concentrations were performed in order to prevent formation of polynuclear complexes. The results given in Table 3 are from measurements made in solutions which meet this condition. Only a few values had to be obtained from extrapolations to $C_M = 0$. From the numerical calculation method the following stability constants were determined:

$[H^+]/M$	$\beta_{1H}{}^{calc} \times 10^{-5}/M^{-1}$	$\beta_{2H}{}^{calc} \times 10^{-8}/M^{-2}$	$\beta_{3H}{}^{calc} \times 10^{-11}/M^{-3}$
4.000	0.778 ± 0.003	2.06 ± 0.04	0.4 ± 0.2
1.000	2.43 ± 0.06	19.0 ± 0.9	19 ± 6
0.500	4.30 ± 0.05	61 ± 2	170 ± 30

Table 3. Corresponding values of $C_{HF} \times 10^4$ M and E_F mV obtained in the various titration series for hafnium.

4.000 M HClO₄

$C_{Hf} = 0.6152$ mM, $E_C = -24.4$ mV: 0.6489, 320.0; 0.9386, 310.2; 1.208, 302.4; 1.696, 292.5; 1.696, 291.6; 2.577, 276.5; 3.405, 264.5; 5.108, 242.3; 6.756, 222.6; 7.415, 215.7; 8.955, 202.1; 10.45, 191.8.

$C_{Hf} = 1.538$ mM, $E_C = -25.1$ mV: 1.649, 319.0; 2.228, 310.5; 2.407, 308.5; 2.783, 303.9; 3.732, 294,7; 4.455, 289.6; 4.616, 287.6; 5.443, 281.7; 7.242, 270.2; 8.978, 260.3; 10.65, 251.0; 12.27, 242.1; 13.84, 233.5; 15.35, 225.3; 16.82, 217.7; 18.24, 210.8.

$C_{Hf} = 1.538$ mM, $E_C = -23.8$ mV: 1.223, 327.7; 2.146, 312.0; 2.922, 304.2; 5.977, 278.4; 8.837, 261.2; 9.564, 257.2; 11.11, 248,6; 12.93, 238.7; 13.28, 236.8; 15.37, 225.4.

$C_{Hf} = 3.076$ mM, $E_C = -24.8$ mV: 3.668, 316.0; 4.643, 309.0; 6.232, 300.2; 8.766, 289.8; 10.03, 284.2; 13.58, 272.5; 16.90, 262.7; 20.02, 253.8; 22.95, 245.5; 25.72, 237.7; 28.33, 230.3; 30.79, 223.3; 33.13, 216.9; 35.34, 211.0; 37.45, 205.8; 40.99, 197.5.

1.000 M HClO₄ and 3.000 M NaClO₄

$C_{Hf} = 0.5000$ mM, $E_C = -66.0$ mV (extrapolated): 0.5750, 306.8; 1.065, 289.0; 1.493; 278.5; 1.850, 271.2; 2.113, 265.4; 2.355, 263.7; 2.572, 256.8; 2.760, 253.3; 2.970, 250.3; 3.100, 247.6.

$C_{Hf} = 0.4614$ mM, $E_C = -67.6$ mV: 2.787, 240.9; 3.193, 233.7; 3.882, 221.3; 4.519, 209.9.

$C_{Hf} = 0.4614$ mM, $E_C = -67.3$ mV: 2.866, 239.6; 3.269, 233.0; 3.654, 226.2; 4.023, 219.4; 4.650, 208.2; 5.231, 198.4; 5.773, 190.1; 6.278, 183.0; 6.750, 177.1; 7.192, 172.0; 7.607, 167.6.

$C_{Hf} = 0.4614$ mM, $E_C = -66.4$ mV: 2.802, 246.1; 3.284, 237.3; 3.744, 229.0; 4.184, 221.1; 4.604, 213.6; 5.007, 206.8; 5.762, 195.0; 6.457, 185.6; 7.101, 177.8.

$C_{Hf} = 0.4614$ mM, $E_C = -66.6$ mV: 3.036, 241.8; 3.507, 233.3; 3.957, 225.1; 4.388, 217.5; 4.800, 210.4; 5.571, 198.2; 6.281, 188.3; 6.938, 180.2; 7.546, 173.4.

$C_{Hf} = 0.9228$ mM, $E_C = -67.3$ mV: 5.782, 242.2; 6.287, 237.9; 6.758, 233.7; 8.216, 220.4; 9.586, 208.1; 10.87, 197.1; 12.09, 187.8; 13.23, 179.7.

$C_{Hf} = 0.9228$ mM, $E_C = -66.9$ mV: 5.566, 243.9; 7.240, 229.1; 8.834, 209.5; 10.35, 200.8; 11.80, 188.8; 13.19, 178.8; 14.51, 170.2; 15.78, 162.8.

$C_{Hf} = 2.307$ mM, $E_C = -67.5$ mV: 20.35, 218.9; 22.38, 212.0; 24.26, 205.4; 26.01, 199.3; 27.64, 193.7; 31.56, 181.0; 35.36, 170.0.

$C_{Hf} = 4.614$ mM, $E_C = -66.9$ mV: 46.72, 205.9; 51.41, 198.5; 55.91, 191.2; 60.22, 184.2; 64.35, 177.8; 72.12, 166.2.

0.500 M HClO₄ and 3.500 M NaClO₄

$C_{Hf} = 0.03000$ mM, $E_C = -85.0$ mV (extrapolated): 0.05960, 287.8; 0.08243, 277.3; 0.1033, 270.0; 0.1224, 264.2; 0.1392, 259.5; 0.1535, 255.6; 0.1652, 252.2.

$C_{Hf} = 0.03076$ mM, $E_C = -84.7$ mV: 0.1978, 247.2; 0.2433, 237.3; 0.3167, 223.6; 0.3802, 213.8; 0.4355, 206.6.

$C_{Hf} = 0.03076$ mM, $E_C = -84.8$ mV: 0.2032, 244.0; 0.2224, 239.8; 0.2697, 230.1; 0.3490, 216.3; 0.4253, 205.9; 0.5563, 192.6; 0.7294, 180.5; 1.027, 166.8.

$C_{Hf} = 0.06200$ mM, $E_C = -82.8$ mV: 0.3439, 250.7; 0.3989, 243.7; 0.4476, 237.8; 0.4910, 232.6; 0.5591, 224.9; 0.6159, 218.9; 0.6640, 214.1; 0.8105, 201.3; 0.9456, 191.8.

$C_{Hf} = 0.06200$ mM, $E_C = -83.8$ mV: 0.3589, 247.6; 0.4515, 236.2; 0.5265, 227.4; 0.5886, 220.7; 0.7566, 204.8; 0.9101, 193.4; 1.051, 185.1; 1.279, 174.5.

$C_{Hf} = 0.1538$ mM, $E_C = -82.4$ mV: 0.8407, 249.2; 1.011, 240.4; 1.162, 232.8; 1.394, 221.2; 1.584, 212.0; 1.743, 204.8; 1.877, 199.1; 1.993, 194.5; 2.050, 192.4.

$C_{Hf} = 0.4614$ mM, $E_C = -84.0$ mV: 3.887, 220.8; 4.464, 211.7; 4.975, 203.2; 5.772, 190.3; 6.788, 176.2; 7.709, 165.0.

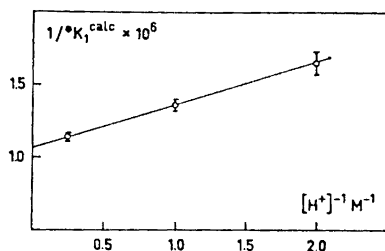$C_{Hf} = 1.538$ mM, $E_C = -84.6$ mV: 16.19, 199.7; 23.42, 169.0.

Fig. 1. The variation of $1/*K_1{}^{calc}$ with $1/[H^+]$ for zirconium(IV). The straight line has been calculated from the values $*K_1 = 9.43 \times 10^5$ and $*\gamma_1 = 0.28$ M.
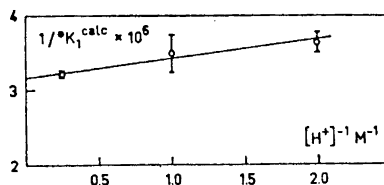

Fig. 2. The variation of $1/*K_1{}^{calc}$ with $1/[H^+]$ for hafnium(IV). The straight line has been calculated from the values $*K_1 = 3.15 \times 10^5$ and $*\gamma_1 = 0.08$ M.

The errors given for the constants are standard deviations. In Refs. 18 and 25, the fluoride complexes of hafnium were investigated by means of quite different methods. The measurements were performed (particularly in the solvent extraction experiments) with very low hafnium ion concentrations (10^{-6} M). The values of the stability constants agree very well with those obtained in the present investigation. Hence it may be concluded that no systematic errors emerge from formation of polynuclear species in the present measurements.

By application of the correction factors f_1 and f_2 on the values of the stability constants obtained, the following values of $*K_1{}^{calc}$ and $*K_2{}^{calc}$ are calculated:

$[H^+]/M$	$*K_1{}^{calc} \times 10^{-5}$	$*K_2{}^{calc} \times 10^{-4}$
4.000	3.11 ± 0.03	1.06 ± 0.06
1.000	2.9 ± 0.2	1.0 ± 0.2
0.500	2.8 ± 0.1	1.0 ± 0.1

The values of $*K_1{}^{calc}$ indicate that Hf^{4+} is only slightly hydrolysed in the solutions investigated. As for Zr^{4+}, the results indicate that only the first hydroxo complex is formed, *cf.* Fig. 2. $*\gamma_1 = 0.08 \pm 0.03$ is graphically obtained from Fig. 2 giving a value of the stability constant, $*K_1$, equal to 3.2×10^5. The concordant values of $*K_2{}^{calc}$ justify the applied medium corrections.

CALCULATIONS AND RESULTS OF THE SOLVENT EXTRACTION MEASUREMENTS

The calculation of the hydrolysis constants is based upon the assumption that MA_4 is the only metal containing species in the xylene phase. If, moreover, the formation of mixed complexes in the aqueous phase between M, A, and OH is neglected, the following expressions are valid for the total concentrations of the metal ion in the two different phases:

$$C_{MO} = [MA_4]_{org} \tag{6}$$

$$C_M = [M]\left(1 + \sum_{m=1}^{M} *\gamma_m[H^+]^{-m} + \sum_{n=1}^{N} \beta_n[A]^n\right) \tag{7}$$

In Ref. 18 it is shown that under the present conditions,

$$[HA]_{org} = k\, C_{HA}' \qquad (8)$$

where k is a constant (≈ 1). Thus it follows that the distribution ratio, q, can be expressed as:

$$q = \frac{K_{dMA_4}\, \beta_4\, (k\, K_a/K_{dHA})^4\, (C_{HA}')^4}{[H^+]^4 \left\{1 + \sum_{m=1}^{M} {}^*\gamma_m [H^+]^{-m} + \sum_{n=1}^{N} \beta_n (k\, K_a\, C_{HA}'/K_{dHA}[H^+])^n\right\}} \qquad (9)$$

Previously it was found for Zr(IV) [20] and Hf(IV) [18] that at a constant hydrogen ion concentration of 4.00 M:

$$q = \text{const. } (C_{HA}')^4 \qquad (10)$$

The same result is also found for Th(IV) in the present investigation; *cf.* Fig. 3. (In these calculations, f_{HA}, the activity factor of HA in the xylene phase, is used to correct for the activity variation of HA and MA₄ in the xylene phase; *cf.* Ref. 18.) It may therefore be concluded that the last term in the denominator of eqn. (9) is negligible, *i.e.* within the experimental errors no formation of complexes between M and A in the aqueous phase could be detected at a hydrogen ion concentration of 4.00 M. If this is true in the entire hydrogen ion concentration range investigated (1.50 M $\leq$ [H⁺] $\leq$ 4.00 M), eqn. (9) could be transformed to

$$Q([H^+]) \equiv \frac{1}{q\,[H^+]^4} = \frac{1}{K} + \sum_{m=1}^{M} \frac{{}^*\gamma_m}{K} [H^+]^{-m} \qquad (11)$$

where K is constant as long as C_{HA}' is the same in all the measurements. From corresponding values of q and [H⁺] the hydrolysis constants are obtained by plotting $Q([H^+])$ as a function of [H⁺]⁻¹, using graphical extrapolation methods.

Table 4. Corresponding values of [H⁺] and q obtained in the distribution measurements made for thorium. $Q([H^+])$ corrected to a 4 M HClO₄ reference medium using eqn. (12) on p. 1380, is given in the fourth column.

$\dfrac{[H^+]}{M}$	q	$\dfrac{Q([H^+]) \times 10^2}{M^{-4}}$	$\dfrac{Q([H^+])\, F([H^+]) \times 10^2}{M^{-4}}$
1.540	4.962	3.583	2.69
1.794	2.779	3.474	2.69
2.107	1.522	3.334	2.68
2.310	1.066	3.295	2.72
2.490	0.8117	3.205	2.70
2.724	0.5870	3.094	2.67
2.958	0.4175	3.129	2.78
3.264	0.2996	2.941	2.70
3.570	0.2162	2.848	2.70
4.000	0.1439	2.698	2.67

The thorium system. Table 4 shows the results obtained for the thorium system. The measurements were performed at a constant concentration of $C_{HA}' = 1.485$ M. The hydrogen ion concentration varied from 1.540 M to 4.000 M. Within this acidity range the hydrolysis of Th^{4+} could be completely neglected.[16],[17] Thus, one should expect $Q([H^+])$ to be independent of $[H^+]$. As Table 4 shows, this is not true. Probably, the activity coefficients of the
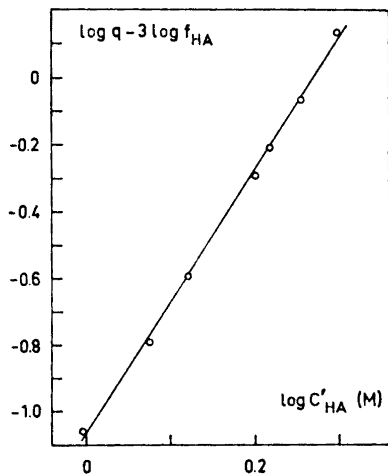

Fig. 3. $\log q - 3 \log f_{HA}$ as a function of log C_{HA}' for thorium. $C_{Th} = 4 \times 10^{-5}$ M. Aqueous phase 4.00 M $HClO_4$. The straight line drawn has a slope of 3.95.
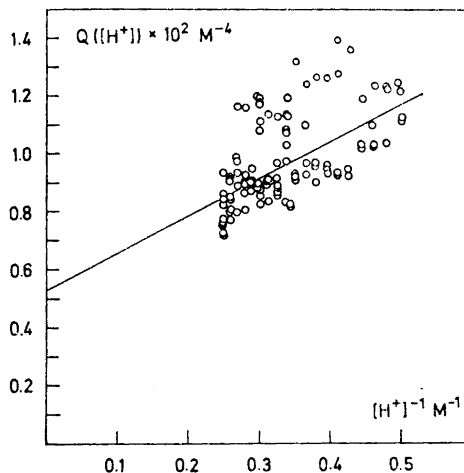
Fig. 4. $Q([H^+])$ as a function of $[H^+]^{-1}$ for zirconium. $C_{HA}' = 18.2$ mM; $C_{Zf} = 5 \times 10^{-6}$ M. The line was calculated using the constants $K^{-1} = 5.24 \times 10^{-3}$ M^{-4} and $*\gamma_1 K^{-1} = 1.27 \times 10^{-2}$ M^{-3}.

species involved in the different equilibria are influenced by the medium change taking place in going from pure 4 M $HClO_4$ to a solution of 1.5 M $HClO_4$ and 2.5 M $NaClO_4$. If all the activity coefficients in question are collected in a common function, $F([H^+])$, an exact thermodynamic derivation gives $Q([H^+])$ $F([H^+])$ to be a constant. Thus, by chosing 4 M $HClO_4$ as reference medium, $F([H^+])$ can be calculated from $Q(4)/Q([H^+])$. From the results given in Table 4, $F([H^+])$ was found to increase linearly with $[H^+]$ according to the following relationship:

$$F([H^+]) = 0.60 + 0.097 \, [H^+] \tag{12}$$

The zirconium and hafnium systems. The chemical properties of Zr^{4+} and Hf^{4+} are in many respects similar to Th^{4+}. Therefore, it seems reasonable to assume that the distribution of Zr^{4+} and Hf^{4+} is influenced by the medium changes to the same extent as Th^{4+}. Accordingly, the distribution ratios obtained for Zr^{4+} and Hf^{4+} are corrected to a 4 M $HClO_4$ reference medium by the use of $F([H^+])$ calculated from eqn. (12). The values of $Q([H^+])$ so obtained are given in Figs. 4 and 5 for Zr^{4+} and Hf^{4+}, respectively.

Fig. 5. $Q([H^+])$ as a function of $[H^+]^{-1}$ for hafnium. $C_{HA}' = 39.6$ mM; $C_{Hf} = 3 \times 10^{-5}$ M. The line was calculated using the constants $K^{-1} = 7.25 \times 10^{-3}$ M^{-4} and $*\gamma_1 K^{-1} = 4.97 \times 10^{-3}$ M^{-3}.
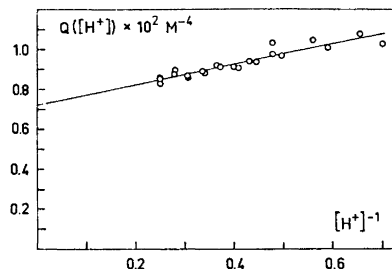
To avoid errors due to incomplete separation of the two phases, such values of C_{HA}' were chosen as to give distribution ratios within the range $0.1 < q < 10$. For hafnium as well as for thorium the q values could be determined with random errors of about 3 %. This is of a magnitude which is usually found in distribution experiments. However, the distribution ratios for zirconium were obtained with unexpectedly large random errors. Different preparations of zirconium stock solutions and of sodium perchlorate were used to find out the reason for this. Unfortunately, the cause of this poor reproducibility could not be traced. It may be due to some unknown impurity present in the chemicals used or introduced during the measurements. Another possibility is the formation of polynuclear hydroxo compounds in the preparation of the zirconium stock solutions. Polynuclear species of this type are notorious for their slow reactions. Hence, no definite conclusions may be drawn from the results obtained in the zirconium measurements.

According to eqn. (11), $Q([H^+])$ as a function of $[H^+]^{-1}$ will give a straight line if a metal ion forms only the first hydroxo complex. Within the experimental random errors, $Q([H^+])$ for both zirconium and hafnium can be described having such a linear relationship to $[H^+]^{-1}$. The best lines fitting the data are drawn in Figs. 4 and 5. These lines were calculated using the principle of least squares. From these results, the following stability constants were obtained for the formation of the first hydroxo complexes:

$$Zr^{4+} \quad *\gamma_1 = 2 \quad \pm 1 \quad (M)$$
$$Hf^{4+} \quad *\gamma_1 = 0.7 \pm 0.2 \ (M)$$

DISCUSSION

The values of the stability constants, computed from the results of the present investigation, for the formation of the first hydroxo complex of Zr⁴⁺

Table 5. Calculated values of $*\gamma_1/M$ obtained from the two different methods used.

Method	Temp. °C	Zr⁴⁺	Hf⁴⁺
Solvent extraction	20.00	2 ± 1	0.7 ± 0.2
FME-electrode	25.00	0.28 ± 0.05	0.08 ± 0.03

and Hf^{4+} are given in Table 5. At both temperatures zirconium(IV) is more strongly hydrolysed than hafnium(IV). This fact is in accordance with the theoretical prediction made from the values of the ionic radius of the two ions and also with the experimental results earlier found. The results of the two methods can be compared since the difference in the temperatures is fairly small. There is such a large difference between the values of the hydrolysis constant for both metal ions that a systematic error must be present in one of the investigations.

The calculations of the hydrolysis constant from the solvent extraction measurements are based upon the assumption that complexes between the metal ion and the anion of thenoyltrifluoroacetone are absent in the aqueous phase (a fact proved by the fourth power dependence of the distribution ratio on the concentration of thenoyltrifluoroacetone). These measurements were performed at only one acidity (4 M $HClO_4$). In the aqueous phase the concentration of the anion of thenoyltrifluoroacetone increases when the hydrogen ion concentration decreases. Thus, an appreciable complex formation might occur at lower acidities. To make sure that this is not the case, measurements of the dependence of the distribution ratio on the concentration of thenoyltrifluoroacetone have to be performed also at the lowest hydrogen ion concentrations used. It is evident from eqn. (9) that only maximum values of the hydrolysis constants are obtained from the solvent extraction measurements.

The calculations of the various equilibrium constants from the fluoride membrane measurements require fewer assumptions than from the solvent extraction measurements. Furthermore, the emf results are obtained with a high degree of accuracy. Hence, the values of the first hydrolysis constant for Zr^{4+} and Hf^{4+} obtained from the present potentiometric measurements are considered as the most reliable, as can be seen in Table 6 where values of

Table 6. $*K_1 \times 10^{-5}$ of the zirconium(IV) and hafnium(IV) fluoride systems computed from the potentiometric results of this work and from values of the hydrolysis constants previously published.

	Temp °C	Medium, I/M and inert salt	$[H^+]$/M 4.000	1.000	0.500
Zr^{4+}					
This work	25	$4(Na,H)ClO_4$	9.4	9.4	9.4
Refs. 10/14	25	$2(Li,H)ClO_4$	10	13	17
Ref. 11	25	$1(Na,H)ClO_4$	15	44	134
Hf^{4+}					
This work	25	$4(Na,H)ClO_4$	3.2	3.1	3.2
Ref. 13	25	$1(Na,H)ClO_4$	4	10	29

$*K_1$ are calculated using previously determined hydrolysis constants. The comparison is complicated by the fact that the different investigations were not performed in the same medium. However, when the values given in Refs.

11 and 13 are used, the variation of $*K_1$ with the hydrogen ion concentration is so pronounced that these values of the hydrolysis constants must be too high. Recently, Nazarenko and Mandzhgaladze,[26] using a spectrophotometric method, obtained results of the hydrolysis of zirconium(IV) in conformity with those of Ref, 11. However, the results of Ref. 26 are no independent confirmation of the results of Ref. 11. Their calculations assume that $Zr(OH)_2(HL)_2{}^{2-}$ ($H_3L = $ 3,4-dihydroxyazobenzene-4'-sulphonic acid) or $Zr(OH)_2(H_3K)_2$ ($H_4K = $ 9-o-hydroxyphenyl-2,3,7-trihydroxy-6-fluorone) are the light absorbing species in the solutions investigated. To prove this, Nazarenko and Mandzhgaladze [27] have to rely on the hydrolysis constants determined in Ref. 11. Consequently, concordant results should be obtained provided that the reproducibility of the spectrophotometric measurements is good enough.

An objection to the results of the present potentiometric measurements might be that mixed complexes are neglected in the calculations. Since the acid dissociation constant is very much larger for hydrofluoric acid than for water, it is much easier to split off a proton from HF than from H_2O. Thus, despite the larger concentration of H_2O than of HF, the concentrations of mixed complexes are probably much smaller than those of the pure fluoride complexes.

Finally, it may be concluded from the results of the present potentiometric measurements that within the acidity range $0.5 \leq [H^+] \leq 4$ M both zirconium(IV) and hafnium(IV) form only one hydroxo complex, presumably MOH^{3+}. At these hydrogen ion concentrations the predominant species are Zr^{4+} and Hf^{4+}, respectively. The hydrolysis of these ions is not at all so extensive as previously believed. If corrections are made for the hydrolysis, the value of the stability constant, $*K_1$, for the formation of the first fluoride complex is calculated to be 9.4×10^5 for zirconium(IV) and 3.2×10^5 for hafnium(IV). Hydroxide and fluoride ions are considered to be bonded to zirconium(IV) and hafnium(IV) mainly by electrostatic forces. Thus one should expect the ratio between $*K_1(Zr)$ and $*K_1(Hf)$ to be the same as that between $*\gamma_1(Zr)$ and $*\gamma_1(Hf)$. Almost the same ratios (≈ 3) are obtained using the values of the present investigation, while $*\gamma_1(Zr)/*\gamma_1(Hf)$ from Refs. 11 and 13 is found to be 1.6, which supports the conclusions drawn in the present work. These are further supported by the fact that the predicted independence of $*K_2$ (after the plausible correction for the medium changes) with the hydrogen ion concentration is confirmed both for Zr(IV) and Hf(IV).

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