III demonstrates. In this table we compare diffusion coefficients at equal molalities rather than at equal molarities, since the resemblance between the activity coefficients is most marked when the molal scale is used for the comparison.

In view of the close similarity in effective ionic sizes for these two electrolytes, it is highly probable that the Onsager–Fuoss electrophoretic effects on the diffusion mobilities are nearly equal. Thus, even if the mathematical theory which Onsager and Fuoss presented for the magnitude of these effects is inapplicable at high concentrations, a comparison of diffusion data at equal concentrations for the two salts should eliminate most of the uncertainty due to the electrophoretic terms. Hence, by comparing values of $D' = D/(1 + m\ \mathrm{d}\ln \gamma/\mathrm{d}m)$ for the two salts, we might expect to estimate the difference in the hydration factors of equation (1). We have, using this equation, and provided that $0.018nm$ is small compared to unity

$$D'_{\mathrm{NH_4Cl}}/D'_{\mathrm{KCl}} \cong \frac{\eta_{\mathrm{KCl}}}{\eta_{\mathrm{NH_4Cl}}}\,[1 + 0.036m(D^*/D_0 - n_{\mathrm{NH_4Cl}})]/[1 + 0.036m(D^*/D_0 - n_{\mathrm{KCl}})]$$

$$\cong \frac{\eta_{\mathrm{KCl}}}{\eta_{\mathrm{NH_4Cl}}}\,[1 + 0.036m(n_{\mathrm{KCl}} - n_{\mathrm{NH_4Cl}})] \qquad (2)$$

When these calculations are carried out, we find that if the quantity $(n_{\mathrm{KCl}} - n_{\mathrm{NH_4Cl}})$ is given the value 0.3, the values of $D'_{\mathrm{NH_4Cl}}/D'_{\mathrm{KCl}}$ can be reproduced within 1% up to 4 molal, though the function $D'_{\mathrm{NH_4Cl}}/D'_{\mathrm{KCl}}$ *vs.* m shows some curvature which cannot be reproduced by the linear equation (2). A much better straight line is obtained by omitting the viscosity factors; the quantity $(n_{\mathrm{KCl}} - n_{\mathrm{NH_4Cl}})$ then requires the value 0.53, but the equation thus modified gives a considerably better fit. However, it is difficult to decide between these two courses, for the viscosities of both potassium chloride and ammonium chloride change little with concentration, and the viscosity factors are therefore small.

The difference of 0.3 to 0.5 in the hydration parameters obtained by this treatment is entirely consistent with that obtained by applying the one-parameter form of the hydration-corrected Debye–Hückel equation developed by Stokes and Robinson. There, the values $n_{\mathrm{KCl}} = 1.9$[14] and $n_{\mathrm{NH_4Cl}} = 1.6$[13] fit the experimental activity coefficients up to $4m$ and $7m$, respectively.

NEDLANDS, WESTERN AUSTRALIA

[14] R. H. Stokes and R. A. Robinson, THIS JOURNAL, **70**, 1870 (1948).

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

Extraction of Zirconium and Hafnium with Various β-Diketones[1]

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Distribution coefficients for the partition of zirconium and hafnium between perchloric acid solution and a β-diketone-containing benzene phase were determined for 2-thenoyltrifluoroacetone (HTTA), 2-furoyltrifluoroacetone (HFTA), 2-pyrryltrifluoroacetone (HPTA) and trifluoroacetylacetone (HCTA). The ratios of $D_{\mathrm{Zr}}/D_{\mathrm{Hf}}$ at constant hydrogen ion and constant diketone activity were: HTTA, 23; HFTA, 24; HCTA, 13; HPTA, 12.

Certain β-diketones[2,3] have been used for the fractional separation of zirconium and hafnium. It seemed desirable to make a comparison of the β-diketones which could be used for this purpose and to compare the efficiency of the processes under similar conditions.

The diketones selected were acetylacetone (HCCA), trifluoroacetylacetone (HCTA), 2-furoylacetone (HFCA), 2-furoyltrifluoroacetone (HFTA), 2-thenoylacetone (HTCA), 2-thenoyltrifluoroacetone (HTTA) and 2-pyrroyltrifluoroacetone (HPTA).

The experimental conditions selected were those established in the work of Connick and Reas.[4] The aqueous solutions were 2 M $\mathrm{HClO_4}$ (except in the HCTA runs) and had equilibrium metal ion concentrations of 3×10^{-3} M or less. Under these conditions it was assumed that the metal ion species was mainly $\mathrm{M^{+4}}$ and the polymer concentration was negligible. The equilibrium studied was, then

$$\mathrm{M^{+4} + 4HK \rightleftharpoons MK_4 + 4H^+} \qquad (1)$$

and at constant hydrogen ion concentrations the equilibrium constant was expressed by the equation

$$\log K' = \log D - 4 \log [\mathrm{HK}] \qquad (2)$$

where D was the metal distribution coefficient $[\mathrm{MK_4}]/[\mathrm{M^{+4}}]$, and [HK] the diketone activity.

Under the conditions selected only HTTA, HFTA and HPTA gave a reasonable degree of metal extraction. For the HCTA studies, the hydrogen ion concentration was reduced to 0.5 M $\mathrm{H^+}$ although it was realized that as a consequence the nature of the metal ion species was different than in the preceding cases, and the K' values could then not be compared directly. The ratio $K'_{\mathrm{Zr}}/K'_{\mathrm{Hf}}$ could be compared with the others, however. The HCCA did not give metal extraction at hydrogen ion concentrations as low as 0.4 M and diketone concentrations as high as 0.1 M, while the HTCA did give a slight metal extraction at 0.1 M diketone concentration.

Experimental

Materials.—The β-diketones were all synthesized. The crude trifluoroacetylacetone[5] was dried over phosphorus

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[1] Based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy and carried out under Task Order 4 of Contract N7onr-28504 between the office of Naval Research and the University of Wisconsin.

[2] E. H. Huffman and L. J. Beaufait, THIS JOURNAL, **71**, 3179 (1949).

[3] B. G. Schultz and E. M. Larsen, *ibid.*, **72**, 3610 (1950).

[4] R. E. Connick and W. H. Reas, *ibid.*, **73**, 1171 (1951).

[5] A. Henne, M. Newman, L. L. Quill and R. Staniforth, *ibid.*, **69**, 1819 (1947).

pentoxide, separated and then fractionally distilled, with the fraction coming over at 105–107° kept.

The 2-thenoyltrifluoroacetone[6] and 2-furoyltrifluoroacetone[6] and 2-pyrroyltrifluoracetone[7] were purified by vacuum distillation.

A stock solution of mixed zirconium and hafnium perchlorates in about a 50:50 mole ratio was prepared from the required quantities of ignited zirconium oxide (0.04% hafnium) and ignited hafnium oxide (0.8% zirconium), and converted to the perchlorate. This conversion was accomplished by dissolving the oxide mixture contained in a platinum dish with hydrofluoric acid followed by repeated evaporations with sulfuric acid to eliminate the last traces of fluoride. The resulting solution was transferred to a large volume of water, the hydroxide precipitated with freshly prepared aqueous ammonia, washed by decantation until free of sulfate, centrifuged, the wash liquor removed, and then dissolved in perchloric acid and diluted to the desired concentration. To this solution was added the desired quantity of hafnium perchlorate solution containing tracer Hf^{181}.

Analyses.—The hafnium distribution was followed by using hafnium^{181},[8] having a 0.63 Mev. beta, 0.52 Mev. gamma and a 46 day half-life. To determine the amount of hafnium in each phase, aliquots were removed from each layer using micropipets. The size of the aliquots was adjusted, so that each sample would contain over 500 counts per minute. The samples were mounted on 1-in. watch glasses, evaporated to dryness in the air at room temperature in the case of the benzene phase, and under an infrared lamp in the case of the aqueous phase. The samples were counted using a thin windowed Geiger tube.

To determine the zirconium distribution, the total metal in the aqueous phase was determined by development of the alizarin lake in perchloric acid solution[9,10] and then corrected for the hafnium found by the radioactivity assay. Zirconium and hafnium were considered to behave in identical fashion for lake formation.

Distribution Coefficients of the Diketones.—The distribution coefficients, (HK_b/HK_{aq}), were determined by equilibrating equal volumes of a standard diketone-(0.075 *M*) containing benzene phase and a 2 *M* perchloric acid phase, separating, and analyzing for the diketone in the aqueous phase by means of its ultraviolet absorption spectra. This procedure was checked for HCTA and HFTA by preparing the copper chelate of the diketone in both of the separated phases, extracting the copper compound with ether and then weighing the recovered product directly. The data pertinent to the ultraviolet absorption measurements of the diketone in the 2 *M* perchloric acid phases are given in Table I.

TABLE I

Diketone	λ_{max}, mμ	ϵ_{max}	Concn. range of diketone, mole/l.	Distribution coefficient
HTTA	293	7625	$15–3.0 \times 10^{-5}$	37.0
HFTA	281	14,600	$64–6.0 \times 10^{-6}$	7.42 (7.4)[a]
HPTA	297	15,350	$59–6.0 \times 10^{-5}$	2.92
HCTA	283	95	$45–6.0 \times 10^{-3}$	1.50 (1.50)[a]

[a] By recovery of copper chelate from both equilibrated phases.

The λ_{max} and the molar extinction coefficient, ϵ_{max}, used in these measurements are given in columns 1 and 2 of Table I. In column 3 are given the concentration ranges over which a satisfactory absorption spectra measurement may be made. In column 4 the distribution coefficient, defined as the ratio of the concentration of the chelating agent in the benzene phase to its concentration in the aqueous phase, are given. These agree with the previously determined values of 1.5 for HCTA[4] in hydrochloric acid solution and a value of 40 for HTTA in perchloric acid.[11]

Procedure.—The extraction experiments were carried out by mixing equal volumes of a perchloric acid phase containing initially all of the zirconium and hafnium, including the tracer hafnium, with a benzene phase containing initially only the β-diketone. The samples were mixed on a rotating device for 24 to 48 hours in a constant temperature bath at 25 ± 0.05°. Since the data obtained for HTTA under our conditions were almost identical with the data of Huffman and Beaufait who reported that equilibrium had been reached in 40 minutes, it was concluded that the method of preparation of the solution and the time of mixing were satisfactory. After equilibration the two phases were separated and then sampled. The metal distribution coefficients were determined at a variety of diketone concentrations.

Results

In general the diketones could be placed in two categories, those containing the CF_3 group which gave a measurable extraction of the metals into the benzene phase, and those without the CF_3 group which did not give a measurable extraction under the experimental conditions used. The diketones with the CF_3 group were relatively strong acids when compared to the diketones which did not contain this group.

The data used for the calculation of the equilibrium constants (eq. 2) are given in Table II. These were calculated in the same fashion as previously reported.[12] The activity coefficients of all the diketones and chelates were assumed to be equivalent and to be equal to those determined for HTTA by King and Reas.[11] This assumption represents a first best guess and may be somewhat in error. However, since the diketone concentrations in the benzene phase never exceeded 0.068 mole/l., for which the activity coefficient is 0.97, and since the structural characteristics of the diketones are very similar, the difference in activity coefficients for these diketones in the benzene phase probably would be small.

The data of Table II are plotted in Fig. 1. If the equilibrium studied is truly represented by equation 2, then the points should lie on a straight line of slope 4. For each set of data a line was drawn with slope 4 to show, in fact, how closely these data do meet the requirement. For HPTA however at concentrations above 0.02 mole/liter the metal distribution coefficients are too low, with the deviation increasing with increasing diketone concentration. This must indicate that another reaction such as

$$xHK_{aq} + M^{+4} \rightleftarrows MK_{x(aq)}^{4-x} + xH^+$$

is entering into the equilibrium expression. The complexing in the aqueous phase in this case is probably related to the low distribution coefficient for the diketone and thus higher aqueous diketone concentrations than occur for HTTA and HFTA under the same benzene phase diketone concentrations. It is surprising then that the same effect is not observed in the case of HCTA for it, too, has a low distribution coefficient. However, in this case the trend, if any, is to higher metal distribution coefficients rather than lower ones at the highest diketone concentrations. Of course these two cases are not strictly comparable because of the difference in the hydrogen ion concentration of the aqueous phase.

It should be mentioned that since the zirconium values rely upon the hafnium values and are found by difference, the data at very low extraction or very high extraction may be subject to a relatively

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

[7] E. M. Larsen and G. Terry, *ibid.*, **73**, 500 (1951).

[8] Isotopes Branch, United States Atomic Energy Commission, Oak Ridge, Tennessee.

[9] J. F. Flagg, H. A. Liebhafsky and E. H. Winslow, THIS JOURNAL, **71**, 3630 (1949).

[10] R. Guenther and R. H. Gale, KAPC-305, 1950.

[11] E. L. King and W. Reas, THIS JOURNAL, **73**, 1804 (1951).

[12] R. E. Connick and W. McVey, *ibid.*, **71**, 3182 (1949).

TABLE II

Diketone	(M^{+4}) g. ions/l. × 10^3 Zr	Hf	$[MK_4]$ γ(moles/l.) × 10^3 Zr	Hf	[HK] γ(moles/l.) × 10^2	D $[MK_4]/(M^{+4})$ Zr	Hf	$K' \times 10^{-7}$ Zr	$K' \times 10^{-6}$ Hf
HTTA	0.858	1.69	0.945	0.089	1.05	1.10	0.0524	9.0	4.3
	.484	1.74	1.31	.213	1.34	2.71	.122	8.4	3.8
	.224	1.53	1.57	.425	1.63	7.00	.278	9.9	3.9
	.055	1.23	1.73	.721	1.93	31.4	.586	23	4.2
HFTA	1.23	1.92	0.571	.034	1.10	0.464	0.0176	3.2	1.20
	0.877	1.87	0.925	.076	1.39	1.05	.0408	2.8	1.09
	.613	1.79	1.18	.161	1.70	1.93	.0899	2.3	1.08
	.352	1.66	1.44	.288	1.99	4.09	.173	2.6	1.10
	.020	1.31	1.75	.626	2.61	8.75	.478	1.9	1.03
	...	0.88	1.81	1.07	3.29	....	1.18	...	1.00
HPTA	1.49	1.93	0.315	0.0169	1.01	0.211	0.00876	2.0	0.84
	1.40	1.91	.410	.0446	1.34	.293	.0234	0.98	.73
	1.02	1.85	.779	.0970	1.58	.764	.0524	1.22	.84
	1.08	1.86	.725	.0940	1.60	.671	.0505	1.0	.77
	0.835	1.79	.960	.158	1.87	1.15	.0883	0.94	.72
	.645	1.71	1.15	.241	2.15	1.78	.141	.83	.66
	.476	1.59	1.31	.378	2.42	2.75	.238	.80	.69
	.361	1.46	1.40	.458	2.73	3.88	.314	.70	.57
	.285	1.34	1.49	.600	3.01	5.22	.448	.64	.55
HCTA	.548	1.23	0.646	.119	2.23	1.18	.0967	.48	.39
	.377	1.18	.813	.167	2.47	2.16	.142	.59	.38
	.300	1.10	.896	.247	2.72	2.99	.225	.55	.41
	.131	0.909	1.05	.433	3.16	8.02	.476	.80	.48
	.098	0.742	1.07	.593	3.53	10.9	.799	.70	.52

large error. This probably explains why some of the points at either end of the lines fall a considerable distance away.

The data for HTTA compares favorably with that of Huffman and Beaufait,[2] in which case the values for zirconium and hafnium were determined on individual rather than mixed solutions. The data on HCTA previously reported[3] were from hydrochloric acid solutions and at higher metal ion concentrations than used here, so as expected, the K' values reported here are much higher, although interestingly enough the K'_{Zr}/K'_{Hf} values are about the same for both sets of data.

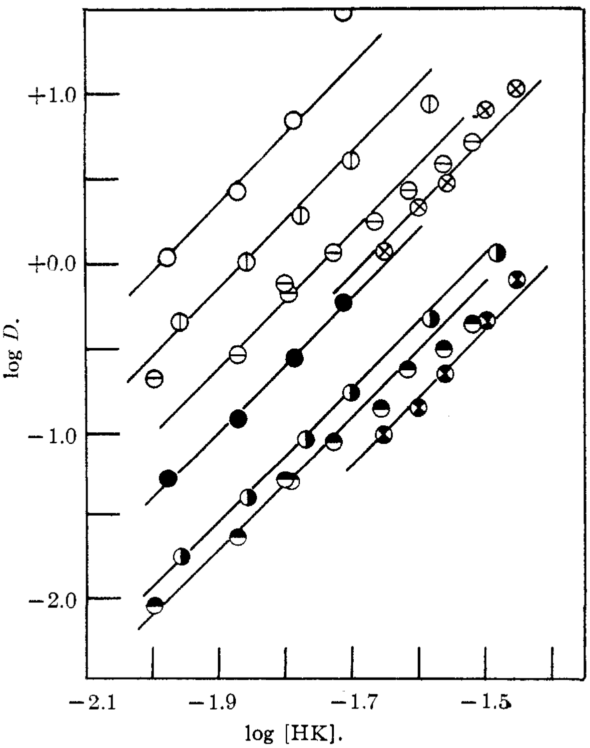

Fig. 1.—Diketone dependence of metal distribution coefficient at constant hydrogen concentration: O, HTTA; ⦶, HFTA; ⊖. HPTA; ⊗, HCTA; unshaded circles, zirconium; shaded circles, hafnium.

The K' values reported in Table III were calculated from the curves in Fig. 1. The magnitude of the zirconium and hafnium equilibrium constants decreases in the order HTTA > HFTA > HPTA. The ratio of the equilibrium constants, which is a measure of separation efficiency, puts HTTA and HFTA in one group, and HCTA and HPTA in another. From this one would conclude that HFTA and HTTA were just about as efficient in the separation of zirconium and hafnium, but because of the magnitude of the diketone distribution coefficient HTTA would be favored over HFTA. Equilibrium conditions have not been confirmed by starting with all the metal as the chelate in the benzene phase. However, the metal distribution coefficients at constant diketone and constant hydrogen ion activity, K', still hold for the conditions specified. They can be properly called equilibrium constants only if true equilibrium has been achieved.

TABLE III

Diketone	$K'_{Zr} \times 10^{-7}$	$K'_{Hf} \times 10^{-6}$	K'_{Zr}/K'_{Hf}
HTTA	9.1	4.0	23 (21)[a]
HFTA	2.8	1.15	24
HPTA	0.98	0.81	12
HCTA[b]	0.55	0.41	13

[a] Huffman and Beaufait. [b] Aqueous phase 0.5 M $HClO_4$, others 2 M $HClO_4$.

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