Cryoscopic Molecular Weight Determinations.—The diarylformamidines were prepared from ethyl orthoformate and the aromatic amines. They were recrystallized from dry benzene–petroleum ether mixtures or benzene alone: N,N′-diphenylformamidine, m. p. 139.0–140.1°; N,N′-di-*o*-chlorophenylformamidine, m. p. 142.2–143.4°; N,N′-di-*p*-chlorophenylformamidine, m. p. 182.7–183.6°. The benzene used was dried by azeotropic distillation and stored in a flask protected by a calcium chloride tube. The naphthalene was recrystallized from petroleum ether before use; f. p. 79.7°.

The apparatus used was essentially that of Beckmann.[8] The freezing-mixture was stirred mechanically at almost constant speed by a windshield-wiper motor. Supercooling was noted and was not excessive. When benzene was used, a slow stream of dry air was introduced through a small tube near the top of the freezing-mixture tube and passed out through the stirrer bearing, preventing the entrance of moisture. In some of the first experiments, benzene was used which had been distilled several weeks previously and had not been protected adequately from moisture; the molecular weight values were higher than those obtained in really dry benzene. This behavior was checked by using as a solvent in one experiment benzene saturated with water; the following molecular weight values were obtained at the concentrations (g. solute/100 g. solvent) indicated: 286 (0.91), 308 (1.69), 317 (2.67).[9] This may account partly for the high values of Lewis, *et al.*[2]

All the molecular weight values recorded in Tables I and II were calculated from the average of several freezing point depressions which checked closely.

Summary

Cryoscopic molecular weight determinations have been carried out with three diarylformamidines in benzene and naphthalene solutions at various concentrations. N,N′-Diphenylformamidine and N,N′-di-*p*-chlorophenylformamidine are associated in both solvents, more extensively at the lower temperature of freezing benzene, while N,N′-di-*o*-chlorophenylformamidine is not appreciably associated in either solvent. The neutralization equivalent of N,N′-diphenylformamidine hydrochloride was found to indicate the expected formula weight.

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[8] See Findlay, "Practical Physical Chemistry," Longmans, Green and Co., New York, N. Y., 1925, p. 113, and Reilly and Rae, "Physico-Chemical Methods," D. Van Nostrand Co., Inc., New York, N. Y., 3rd ed., 1939, p. 621.

[9] Wright [*J. Chem. Soc.*, 683 (1949)] found that the presence of water in benzene increased the association of carboxylic and sulfinic acids.

AUSTIN, TEXAS RECEIVED DECEMBER 27, 1949

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

The Fractional Separation of Zirconium and Hafnium by Extraction with Trifluoroacetylacetone[1]

BY BOYD G. SCHULTZ[2] AND EDWIN M. LARSEN

Zirconium and hafnium were successfully separated by extracting a hydrochloric acid solution of the ions with a benzene solution of trifluoroacetylacetone. The zirconium was preferentially extracted into the benzene phase as the chelate compound, tetrakis-(1,1,1-trifluoro-2,4-pentanediono)-zirconium in a manner similar to that observed in the extraction of a zirconium, hafnium perchlorate solution, with thenoyltrifluoroacetone.[3]

A study of the variables involved in the extraction process showed that the diketone concentration, acid concentration, total metal ion concentration, and ion species were all factors to be considered.

Experimental

Materials.—Mixed zirconium, hafnium sulfate solutions were obtained from fractions available in this Laboratory. Stock solutions were prepared for extraction by precipitating the hydrated oxides with a slight excess of aqueous ammonia and washing the precipitate three times with distilled water by decantation. The precipitate was separated from its supernatant liquid by centrifugation, redissolved in hydrochloric acid and reprecipitated with aqueous ammonia. This process was repeated three times to ensure the absence of all anions other than chloride. The hydrated oxide was then dissolved in a measured amount of standard hydrochloric acid and diluted to the desired volume with water. A total oxide analysis was run on the resulting solution and, from this and the other known data, the normality of the resulting solution was calculated.

Tracer hafnium^{181},[4] used in following the hafnium in the extraction process, was received as the oxide and converted to a solution of the oxychloride by dissolving the oxide in 48% hydrofluoric acid, fuming with concentrated sulfuric, and precipitating the hydrated oxide with aqueous ammonia. After the sulfate had been eliminated by successive precipitations, the hydrated oxide was dissolved in hydrochloric acid.

Trifluoroacetylacetone was prepared by a Claisen condensation between ethyltrifluoroacetate and acetone.[5] Weighed amounts of trifluoroacetylacetone, at least 99.5% pure as determined by titrating with standard sodium hydroxide solution, were dissolved in thiophene-free benzene to give solutions of the desired concentrations.

Analyses.—The Zr, Hf composition of the stock solutions was determined by selenite analysis[6] or spectrographic analysis.[7]

Oxide analyses were run to determine the total oxide content of the aqueous solutions used. These analyses were made by precipitating an aliquot of the aqueous

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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 in part under Task Order 4 of Contract N7 onr-28504 between the Office of Naval Research and the University of Wisconsin.

[2] Westinghouse Electric Corporation, Atomic Power Division, Bettisfield, Pittsburgh, Pa.

[3] Huffman and Beaufait, THIS JOURNAL, **71**, 3179 (1949).

[4] Isotopes Branch, United States Atomic Energy Commission, Oak Ridge, Tenn.

[5] Henne, Newman, Quill and Staniforth, THIS JOURNAL, **69**, 1819 (1947).

[6] Schumb and Pittman, *Ind. Eng. Chem., Anal. Ed.*, **14**, 512 (1942).

[7] C. Feldman, Oak Ridge National Laboratory, Oak Ridge, Tenn.

phase with a slight excess of aqueous ammonia, filtering the precipitated hydrated oxide on No. 40 Whatman "ashless" filter paper, and igniting the paper containing the sample to the oxide in a tared crucible over a Meker burner.

Chelate compound analyses were run on the benzene solutions in order to determine the total oxide content of the benzene solutions. These analyses were made by transferring an aliquot of the benzene phase to a tared crucible and carefully evaporating the benzene either in a very slow, filtered air stream or simply by standing in the air at room temperature. After evaporating to dryness, the samples were evacuated in a desiccator until they came to constant weight. The weight of oxide upon ignition of the chelate was found to correspond to the calculated weight within experimental error.

In order to determine the amounts of hafnium in each phase, tracer hafnium^{181} solution was added to the stock solution which had a known hafnium–zirconium ratio. Aliquots from each phase were taken using micropipets to obtain samples containing 500–1500 counts per minute, where it was possible. The samples were mounted on steel discs,[8] especially constructed for beta counting, evaporated to dryness by allowing them to stand in the air at room temperature and counted with a Geiger counter. In case of the acid samples, the steel discs were protected with a coating of Glyptal. Since the initial hafnium concentration of the stock solution (5 mole % Hf) was known, the percentage distributions of the radioisotope in the two phases permitted the calculation of the moles of hafnium oxide in each phase.

Distribution Coefficient of Trifluoroacetylacetone.—The distribution coefficient of trifluoroacetylacetone between benzene and series of dilute hydrochloric acid solutions was determined by delivering 50 ml. of a 0.075 *M* benzene solution of trifluoroacetylacetone into a vessel containing 50 ml. of standardized hydrochloric acid solution and equilibrating the two phases by rotating. The phases were then carefully separated, the copper derivative of the trifluoroacetylacetone formed in each phase, extracted with diethyl ether, recovered by evaporation of the ether, and weighed. From the weight of the derivative in each phase, the weight of the trifluoroacetylacetone in each was calculated and the distribution coefficient was determined. The distribution coefficient was independent of the acid concentration, but temperature dependent, being 1.5 at 24°, and 1.8 at 30.06 ± 0.05°.

Procedure.—In the study of the extraction process, equal volumes of the benzene solution of the trifluoroacetylacetone and of the zirconium, hafnium aqueous solution were placed in suitable glass-stoppered vessels, the stoppers greased with a minimum of stopcock grease, and the vessels placed in the mixing device. The runs made at constant temperature were rotated in a constant temperature bath at 30.06 ± 0.05°. After equilibrium had been attained, the samples were removed, allowed to stand for fifteen minutes and each phase sampled to determine the hafnium distribution. The amount of the chelate compound in the benzene phase was determined as previously described and the amount of zirconium in the aqueous phase was obtained from the difference between the zirconium in the benzene phase and the amount in the original sample.

Results

Factors Affecting the Extraction Coefficients: Diketone Concentration.—A series of extraction studies were made in which the dependence of the extraction coefficient on the diketone concentration was studied. The aqueous solutions were made up in 0.2 *N* HCl at two different metal ion concentrations, 0.0165 and 0.0245 g. ions/l. for series B and A, respectively. This represents a ten-fold increase in metal ion concentration over the highest concentrations used by other investigators.[3,9] To determine the dependence of the extraction coefficient on the diketone concentration, it was assumed that extraction with trifluoroacetylacetone behaved in a manner analogous to that for thenoyltrifluoroacetone,[9] for which it was concluded that the species extracted into the benzene phase was ZrK_4, and that complexing of zirconium by the diketone in the aqueous phase was not significant.

It was further assumed that the variation in the ionic strength of the aqueous phase was not significant, and therefore the activity coefficients of the metal ions remained constant. For the benzene phase the activities of the MK_4 and HK were calculated on the assumption that the data used by Connick and McVey for thenoyltrifluoroacetone and its derivatives held here, since there were no data available on the variation of the activity coefficients of trifluoroacetylacetone and the zirconium and hafnium derivatives. The extraction coefficient *R* was thus the ratio of the metal chelate activity divided by the concentration of the metal ion in the aqueous phase at equilibrium.

Since these extractions were made in chloride rather than perchlorate solutions, it was also necessary to assume that the chloride ion complexing was negligible in order to express the equilibrium reaction by the equation

$$M(OH)_n^{4-n} + 4HK \rightleftharpoons MK_4 + nH_2O + 4 - nH^+$$

and the equilibrium constant as

$$\log K_1 = \log R - 4 \log [HK]$$

at constant hydrogen ion and for monomeric metal ion species.

Table I gives the necessary data for the calculation of the extraction coefficients and the diketone activities. The free diketone concentration at equilibrium, not corrected for the distribution into the water layer, was obtained by multiplying the total molar concentration of zirconium and hafnium in the benzene phase by four, and subtracting the product from the initial molar diketone concentration. This value was then corrected for the solubility of the diketone in water. The logarithms of the values of the activities of trifluoroacetylacetone and of the extraction coefficients are plotted in Fig. 1. The lines are drawn with a slope of four. The data show a good fourth power dependence for the extraction coefficient upon the diketone concentration. The average *K* value for Run A was 6.69×10^5 and 0.65×10^5 for zirconium and hafnium, and for Run B, 1.74×10^6 and 0.17×10^6 for zirconium and hafnium, respectively. One might conclude that the variation in *K* values was a temperature effect, since the two runs cited were made at 30 and 24°; instead the variation in the metal ion concentration proved to be the more important factor.

Metal Ion Concentration and Ion Species.—A stock solution with a total metal ion concen-

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[8] D. P. Ames, University of Wisconsin, Madison 6, Wis.

[9] Connick and McVey, THIS JOURNAL, **71**, 3182 (1949).

TABLE I

EFFECT OF DIKETONE CONCENTRATION

Initial HK (mole/l.)	Act. coef. of HK and ZrK_4	Act. of HK	log HK	G. ions/l. × 10^5 Benzene		Aqueous		Ext. coef. *R*		log *R*		*K* × 10^{-5}	
				Zr	Hf	Zr	Hf	Zr	Hf	Zr	Hf	Zr	Hf
A. Temperature 30.06 ± 0.05°. Total metal ion concentration 0.0245 g. ions/l.													
0.025	0.993	0.0131	−1.8827	110	0.5	2310	125	0.0479	0.004	−1.3242	−2.3979	16.0	1.4
.050	.982	.0232	−1.6345	325	2	2090	123	.153	.016	−0.8153	−1.7959	5.28	.55
.075	.977	.0281	−1.5513	745	5	1665	120	.438	.041	−0.3585	−1.3872	7.03	.66
.075	.977	.0284	−1.5467	735	5	1680	120	.429	.041	−0.3675	−1.3872	6.60	.63
.100	.972	.0331	−1.4802	1160	10	1260	110	.898	.089	−0.0467	−1.0506	7.48	.74
.100	.972	.0334	−1.4763	1145	10	1270	115	.897	.085	−0.0560	−1.0706	7.07	.68
B. Room temperature, about 24°. Total metal ion concentration 0.0165 g. ions/l.													
0.025	0.993	0.0131	−1.8827	74	0.5	1503	78	0.049	0.006	−1.3098	−2.1938	16.6	2.2
.050	.985	.0204	−1.6904	387	2	1190	76	.319	.026	−0.4955	−1.5834	18.5	1.5
.075	.979	.0262	−1.5817	752	5	826	73	.891	.067	−0.0501	−1.1733	18.9	1.4
.100	.972	.0334	−1.4763	1053	13	524	65	1.952	.194	+0.2905	−0.7118	15.7	1.6

tration of 0.051 g. ion/l. was successively diluted in three stages to give solutions of 0.0380, 0.0254 and 0.013 g. ion/l. The distribution data for these solutions at almost constant diketone concentration are shown in Table II. If the metal ion species were monomeric, the extraction coefficient would have been independent of the concentration. Instead both the *R* and *K* values decreased with increasing metal ion concentration. This is consistent with the idea that the monomeric zirconium and hafnium ions exist in equilibrium with a polymeric species even at moderate metal ion concentrations.[10] If it is assumed that only the monomeric species react with the diketone, then the equilibrium must shift to increase the concentration of the extractable species upon dilution. This would be represented by

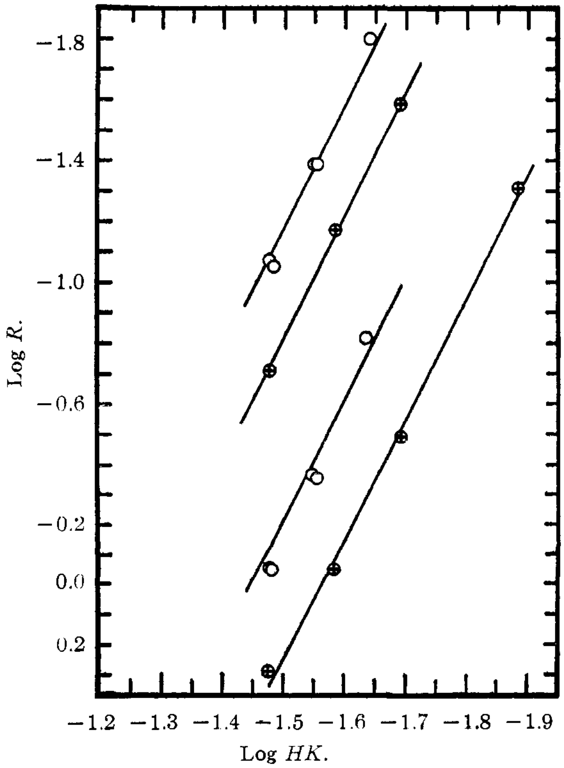

Fig. 1.—Dependance of the extraction coefficient on the diketone concentration: series A ○, series B ⊕.

$$M_n(OH)_{nx}^{n(4-x)} \rightleftharpoons nM(OH)_x^{4-x}$$

The general equation expressing the extraction would be given by

$$M_n(OH)_{nx}^{n(4-x)} + 4nHK \rightleftharpoons nMK_4 + n(4 - n)H^+ + nmH_2O$$

When the extraction coefficient is defined as

$$R = (MK_4)/n(M_n(OH)_{nx}^{n(4-x)})$$

then, K_2[11] at constant hydrogen ion is

$$K_2 = \frac{n^nR^n(M_n(OH)_{nx}^{n(4-x)})^{n-1}}{(HK)^{4n}}$$

Qualitatively this expression fits the data in Table II, as the *R* values are inversely proportional to the metal ion concentration.

The different *K* values for series A and B are due then to differences in the metal ion species at different metal ion concentrations since *K* values for the third and fourth dilutions given in Table II agree favorably with the *K* values for series A and B in Table I. It appears then that the fourth power dependence of the extraction coefficient on the diketone concentration, at least in series A, is in contradiction to the original requirement of monomeric species. Fourth power dependence would result if the equilibrium concentration of the metal ions was constant, or if one species predominated in the system. Since the equilibrium metal ion concentrations were not equal in these runs, one must conclude that one metal ion species was predominant.

Interpretation of these data was further complicated by the evidence for a non-extractable

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[10] Since acceptance of this paper, A. E. C. Document 2491 has come to our attention, in which R. E. Connick and W. H. Reas present detailed studies on the polymerization of zirconium ions in aqueous solution.

[11] Proposed by E. L. King.

TABLE II

EFFECT OF METAL ION CONCENTRATION

Temperature, 30.06°; hydrochloric acid concentration 0.2 *N;* initial diketone concentration 0.075 *M.*

Act. coeff. of HK and ZrK_4	Act. of HK	G. ions/l. × 10^5				Ext. coef. *R*		*K* × 10^{-5}	
		Benzene		Aqueous					
		Zr	Hf	Zr	Hf	Zr	Hf	Zr	Hf
0.972	0.0310	625	3	4185	245	0.145	0.012	1.57	0.13
.972	.0314	610	3	4200	245	.141	.012	1.45	.12
.972	.0298	670	5	2945	180	.221	.027	2.80	.34
.972	.0298	670	5	2945	180	.221	.027	2.80	.34
.977	.0282	735	5	1680	120	.427	.041	6.75	.64
.977	.0281	745	5	1665	120	.437	.041	7.01	.65
.978	.0278	760	7	450	55	1.651	.1244	27.6	2.08
.978	.0278	760	7	450	55	1.651	.1244	27.6	2.08

TABLE III

SECOND EXTRACTION SERIES B_1 (TEMP. ABOUT 24°)

Initial HK (mole/l.)	Act. coef. of HK and ZrK_4	Act. of HK	G. ions/l. × 10^5				Extraction coef.		*K* × 10^{-5}	
			Benzene		Aqueous					
			Zr	Hf	Zr	Hf	Zr	Hf	Zr	Hf
0.025	0.994	0.0117	134	1	1370	77	0.0972	0.0129	52.1	6.9
.050	.983	.0220	311	9	883	68	.346	.130	14.9	5.6
.075	.969	.0350	334	16	497	57	.651	.275	4.3	1.8
.100	.953	.0524	173	16	354	49	.466	.312	0.62	0.41

TABLE IV

EFFECT OF HYDROCHLORIC ACID CONCENTRATION

Temperature, 30.06°; initial HK concentration = 0.075.

Act. coef. of HK and ZrK_4	Act. of HK	HCl concn., *N*	G. ions/l. × 10^5				Extraction coef. *R*		*K*	
			Benzene		Aqueous					
			Zr	Hf	Zr	Hf	Zr	Hf	Zr	Hf
0.982	0.0230	0.07	945	15	1485	110	0.625	0.134	2.23×10^6	4.79×10^5
.980	.0251	.13	865	10	1565	110	.541	.089	1.36×10^6	2.24×10^5
.978	.0267	.20	765	5	1665	115	.449	.043	8.84×10^5	8.37×10^4
.971	.0314	.70	361	1	2070	120	.109	.008	1.74×10^5	8.32×10^3
.963	.0412	1.10	227	0.3	2200	120	.099	.0025	3.44×10^4	8.68×10^2
.9625	.0419	1.52	175	+	2265	125	.074	....	2.41×10^4	....

metal ion. A series of second extractions made on the aqueous phases of Series B (Table II) resulted in diminishing *K* and *R* values at high extraction values. It was found, however, that consistent extraction coefficients were obtained if zirconium and hafnium in the extracted aqueous phase were precipitated by aqueous ammonia, then redissolved in acid to give a new aqueous phase, and then re-extracted. This was the procedure used in the separation studies.

Effect of the Hydrochloric Acid Concentration.—The data in Table IV show the effect of the hydrochloric acid concentration on the extraction coefficient and equilibrium constant. Since the ionic strength of the aqueous phase was not held constant, and no corrections were made for chloride complexing, these data are not to be interpreted quantitatively. Qualitatively the data follow the expected trend. It appears that even in 0.2 *N* hydrochloric acid solution, chloride complexing is significant for the *K* value has already fallen off from the high value obtained at lower chloride concentrations. The data also show that the chloride complexing is greater for the hafnium than the zirconium, since the K_{Hf} values diminish more rapidly than the K_{Zr} values with increasing chloride concentration.

Separation Studies

On the basis of the previous experiments the following conditions for separation studies were selected. All of the extractions were run in 0.2 *N* hydrochloric acid, in which the hydrogen ion concentration was high enough to prevent hydrolysis of the metal ions to insoluble products, yet low enough to permit extraction of an appreciable amount of material; and the chloride concentration was such that the K_{Zr} and K_{Hf} values differed by a factor of about ten. The metal ion concentration was kept low, and a fresh aqueous phase was prepared after each extraction.

The aqueous solution was equilibrated with an equal volume of benzene solution of 0.025 to 0.075 *M* trifluoroacetylacetone. In the purification of hafnium it was desirable to remove the major constituent, zirconium, as rapidly as possible in the least number of fractionations. This was accomplished by using higher diketone concentrations in the benzene phase. In the purification of zirconium, it was desirable to remove zirconium with the least amount of hafnium accompanying it, so lower diketone concentrations were used.

Since the zirconium concentrated in the benzene phase as the zirconium chelate compound, it was necessary to return to an aqueous solution in prep-

TABLE V

PURIFICATION OF ZIRCONIUM

Volume of phases, ml.		Aqueous phase, g. ions/l. × 10^5		Mole %	Fraction	Init. diketone concn., *M*	Benzene phase mole/l. × 10^5		Mole %
		Hf	Zr	Hf			Hf	Zr	Hf
A	100	28.0	2060	1.34	1	0.050	1.4	470	0.30
	100	1.4	470	0.30	2	.025	0.095	100	.10[a]
B	50	25.60	1616	1.56	1	.0375	.28	176.8	.16
	50	0.28	1768	0.16	2	.0375	.10	112.0	.09[a]

[a] Checked spectrographically by G. A. Terry. No hafnium lines found.

aration for the next extraction. This was accomplished by shaking the benzene phase three times with an equal volume of 4.8 *N* hydrochloric acid and then precipitating the zirconium as the hydrated oxide with aqueous ammonia. The precipitate was washed with distilled water by decantation and then dissolved in the amount of hydrochloric acid necessary to give a solution of 0.20 *N* in HCl. The extraction was then continued.

Starting with zirconium–hafnium mixtures containing about 1.5 mole % hafnium, two extractions (Table V) reduced the hafnium concentration of the mixture to below spectroscopic limits (0.05 mole % Hf) as determined by the method of Feldman[12] although radiometric assay indicated 0.1–0.09 mole % hafnium. The yield was 5–7% of the original zirconium.

From a mixture containing 4.8 mole % hafnium, 99.98% hafnium was obtained in seven fractionations (Table VI) with a 19% yield, taking into account the material lost by analysis. In run B, the hafnium content of a zirconium, hafnium mixture containing 7.5 mole % of hafnium was increased to 99.94% in six fractionations, with a 37.6% yield of hafnium.

TABLE VI

PURIFICATION OF HAFNIUM

Volume of phases, ml.		Aqueous phase, g. ions/l. × 10^5		Mole %	Fraction[a]	Benzene phase mole/l. × 10^5		Mole %
		Hf	Zr	Hf		Hf	Zr	Hf
A.	300	123	2428	4.8	1	117	1567	6.9
	200	155	2085	6.9	2	144	1200	10.7
	150	180	1503	10.7	3	173	745	18.9
	100	221	963	18.7	4	202	482	29.5
	50	...	..	..	5[b]	...	..	..
	50	...	..	..	6[b]	...	..	..
	50	196	120	62.0	7	100	+	+
B.	200	143	1767	7.5	1	130	936	12.2
	100	244	1675	12.7	2	221	838	20.9
	50	396	1468	21.2	3	358	690	34.2
	50	340	638	34.8	4	264	194	57.7
	50	248	182	57.7	5	180	16	91.8
	50	176	16	91.7	6	158	+	99.94[c]

[a] Initial diketone concentration 0.075 *M* in all cases, except for fractions 4, 5 and 6 of Run A which were 0.056, 0.056 and 0.0375 *M*, respectively. [b] No analyses were run owing to the small amount of material. [c] Spectrographic analyses by C. Feldman, Oak Ridge National Laboratories, Oak Ridge, Tennessee.

Acknowledgment.—The authors wish to thank Mr. Cyrus Feldman of the Oak Ridge National Laboratory and Mr. Glenn Terry of this Laboratory for the spectrographic analysis. We also are indebted to Dr. E. L. King for his helpful suggestions. We acknowledge that the research on the chemistry of zirconium and hafnium has been supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

Summary

In the extraction of a hydrochloric acid solution of zirconium and hafnium with a benzene solution of trifluoroacetylacetone, the extraction coefficients appeared to follow a fourth power dependence on the diketone activity, at constant hydrochloric acid concentration and constant initial metal ion concentration.

Equilibrium constants calculated on the basis of monomeric ion species showed a decrease with increasing metal ion concentration. This observation was shown to be consistent with the idea that the zirconium and hafnium ions exist in equilibrium with non-extractable polymeric species even at moderate concentrations.

The change in *K* values with increasing chloride ion concentration indicated that the hafnium–chloride complex was stronger than the corresponding zirconium ion pair.

Zirconium was successfully separated from hafnium by extracting 0.2 *N* hydrochloric acid solutions of zirconium and hafnium with a benzene solution of trifluoroacetylacetone. In two extractions, the mole % of hafnium in a zirconium–hafnium mixture was reduced from 1.56 to less than 0.1–0.05 with a 6.9% yield of the original zirconium, and, in six extractions, the mole % of hafnium in a zirconium–hafnium mixture was increased from 7.5 to 99.98 mole % with a 37.6% yield of the original hafnium.

MADISON, WIS. RECEIVED JANUARY 12, 1950

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[12] Cyrus Feldman, *Anal. Chem.*, **21**, 1211 (1949).