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THE SEPARATION OF ZIRCONIUM AND HAFNIUM BY EXTRACTION WITH THENOYLTRIFLUOROACETONE

E. H. Huffman and L. J. Beaufait

Berkeley, California

UCRL-194

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The Separation of Zirconium and Hafnium by Extraction with Thenoyltrifluoroacetone

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October 7, 1948

ABSTRACT

Distribution ratios for zirconium and hafnium have been found for extraction from 2 M perchloric acid with thenoyltrifluoroacetone of varying concentration and the equilibrium constants for the extractions determined.

Two extractions with 0.025 M thenoyltrifluoroacetone of a solution containing 59% as much zirconium as hafnium yielded 27% of the original hafnium with a content of less than 2% zirconium.

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

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AUTHORITY
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[1] This paper is based on work done under the auspices of the Atomic Energy Commission.

The synthesis of thenoyltrifluoroacetone has recently been reported by Reid and Calvin[2] and a study of the extraction of its zirconium chelate into benzene reported by Connick and McVey[3]. The work reported in this paper on the separation of zirconium and hafnium by means of this β-diketone was undertaken at the suggestion of M. Calvin and G. T. Seaborg. A study has been made of some differences in the extractions of zirconium and hafnium by benzene solutions of thenoyltrifluoroacetone (referred to as HT in equations and tables) from aqueous 2 M perchloric acid and the results applied to a successful separation of these elements.

It is believed that the zirconium is principally in the form of Zr^{+4} in 2 M perchloric acid.[4] The complexing of zirconium by the diketone is negligible in the aqueous phase and the only important

[2] J. C. Reid and M. Calvin, MDDC-1405 (BC-75), August 13, 1947.

[3] R. E. Connick and W. H. McVey, The Aqueous Chemistry of Zirconium, UCRL-101, March 1, 1948.

[4] W. H. Reas, Thesis, University of California, 1948.

species in the benzene phase is ZrT_4.[3] The reaction then is expressed by the equation

$$Zr^{+4} + 4\ HT = ZrT_4 + 4\ H^+$$

and, assuming constant acid concentration, the equilibrium constant by

$$\log K = \log \frac{[ZrT_4]}{[Zr^{+4}]} - 4\log [HT] = \log R - 4\log [HT]$$

where R is the extraction coefficient.

Values for R and K have previously been determined[3] for zirconium using trace amounts of radioactive Zr^{95}.

The determination of values for R and K for both zirconium and hafnium, using macro quantities and concentrations for which the zirconium ion has been shown to be a monomer in 2.0 M perchloric acid[4], has been carried out in this work in the thenoyltrifluoroacetone concentration range of 4×10^{-3} to 3×10^{-2} for zirconium and 10^{-2} to 7×10^{-2} for hafnium.

Experimental

Materials. - Thenoyltrifluoroacetone of 99.5% purity was obtained from M. W. Davis and H. R. Lehman of this laboratory. Weighed amounts were dissolved in reagent thiophene-free benzene to give solutions of the desired concentrations.

Zirconium solutions were prepared in a manner similar to that of Connick and McVey[3]. Recrystallized $ZrOCl_2 \cdot 8H_2O$ was dissolved in 2.0 M perchloric acid to prepare a stock solution of approximately 0.09 M zirconium.

Tracer zirconium solutions were prepared from carrier-free Zr^{95} in 5% oxalic acid which was received from the Isotopes Branch, United States Atomic Energy Commission. This solution was made about 10 M in nitric acid and carrier zirconium added from the above stock solution. The solution was purified by the following treatment[3]. A small amount of 0.1 N potassium permanganate was added to precipitate manganese dioxide which carries the radioactive columbium but not zirconium. This precipitation was carried out three times to remove both oxalic acid and columbium. The zirconium solution was then diluted to about 1 M nitric acid and extracted with 0.02 M thenoyltrifluoroacetone in benzene, and the benzene phase washed twice with 2 M perchloric acid. The benzene solution was removed to a platinum dish and fumed with sulfuric acid with the addition of small amounts of 30% hydrogen peroxide to destroy organic matter. It was then diluted and zirconium hydroxide precipitated with ammonium hydroxide. The precipitate was dissolved in hydrochloric acid and the zirconium hydroxide precipitated twice more to remove sulfate. Concentrated hydrochloric acid was then used to dissolve the hydroxide and this solution diluted to 6-7 M hydrochloric acid to precipitate $ZrOCl_2 \cdot 8H_2O$. A weighed amount of this salt was then dissolved in 2 M perchloric acid to give a stock solution approximately 0.003 M in zirconium.

Hafnium solutions were prepared from hafnium dioxide which contained 0.4% zirconium. A weighed amount was warmed with concentrated nitric acid and a small amount of 48% hydrofluoric acid in a platinum dish until a clear solution was obtained which was then

evaporated to near dryness. About 0.5 ml of concentrated sulfuric acid was added and fumed for 5-10 minutes. The preparation of $HfOCl_2 \cdot 8H_2O$ then followed the method given above for tracer $ZrOCl_2 \cdot 8H_2O$, beginning with dilution of the sulfuric acid solution. Tracer Hf^{181} solutions were prepared in the same way, using hafnium dioxide obtained from the Isotopes Branch, United States Atomic Energy Commission.

Analysis. - Colorimetric analyses were made with a Beckman spectrophotometer by G. Iddings who adapted the following method from that of Liebhafsky and Winslow[5] to correct for the effects of

[5] H. Liebhafsky and E. Winslow, J. Am. Chem. Soc. 60, 1776 (1938).

the organic substances and perchloric acid present. One-half ml. of saturated alizarin is added to a 25 ml. volumetric flask and then, in order, 10 ml. 95% ethanol, 4 ml. 2 M perchloric acid including that to be added from the sample, 1.0 ml. 0.02 M thenoyltrifluoroacetone in benzene including that to be added from the sample, benzene or aqueous phase sample containing 25-90 μg. Zr or 25-125 μg. Hf, and 1 ml. 2 M hydrochloric acid. After mixing add ammonium hydroxide carefully until the red color just appears and allow to stand for 5 minutes. Add 1 N hydrochloric acid until the red color disappears and then 0.10 ml. 7 M hydrochloric acid. Make to 25 ml. volume with 95% ethanol and allow to stand for 4 hours before taking the spectrophotometer reading. Standard curves prepared by this procedure show that the zirconium and hafnium are colorimetrically equivalent, on a mole basis, in contrast to previous results[5].

Radioactive analyses of zirconium were made using micropipets to obtain samples containing 500-1500 counts per minute. The samples were evaporated on platinum discs under an infra-red lamp and counted in a Geiger counter, first with an aluminum absorber of 30 mg/cm^2. and then with one of 150 mg/cm^2.. The difference in the two counts gives that of the zirconium alone without the count of the active columbium which had grown in. The ratio of count to weight was obtained by evaporating a larger sample of the stock solution, igniting to zirconium dioxide and weighing. Hafnium radioactive analyses were made in a similar manner but counted without absorbers.

Experimental. - For the determination of extraction coefficients micro-pipets were used to obtain approximate weights of zirconium or hafnium from the stock solutions and the volume made to 5 ml. with 2 M perchloric acid. Five ml. of a benzene solution of thenoyltrifluoroacetone was then added and the mixture shaken for 80 minutes, although equilibrium was found to be reached within 40 minutes for these amounts. Aliquots of the benzene and aqueous phases were then taken for analysis.

Results

Table I gives the results found for zirconium on the distribution ratios and equilibrium constant. Columns one, two and three give, respectively, the molar concentrations of diketone added, the micrograms per ml. of zirconium in the benzene phase and the micrograms per ml. in the aqueous phase at equilibrium. The free diketone concentration, not allowing for solubility in the aqueous phase, is obtained by multiplying the molar concentration of zirconium found

in the benzene phase by four and subtracting the product from the molar concentration of diketone added. This answer is then multiplied by 0.974 to correct for solubility in 2 M perchloric acid[4] and to obtain the diketone concentration in the benzene phase. In column four are given the activity coefficients for these corrected diketone concentrations[6]. These also represent the activity

[6] E. L. King and W. H. Reas, U. C. R. L. BC-69, July 1947.

coefficients of the chelate[3]. Column five gives the diketone activities found by multiplying the corrected concentrations by the corresponding activity coefficients. The distribution ratios in column six are obtained by multiplying the ratios of values from columns two and three by the activity coefficients of column four. Table II gives similar results for hafnium.

The dependence of the extraction coefficients on the diketone activities for zirconium and hafnium are given in the figure. The straight lines are drawn with a slope of four and corresponding to the average values found for the equilibrium constants.

A good separation of hafnium was carried out on a solution in 2 M perchloric acid containing 22.9 mg.hafnium and 13.6 mg. zirconium in 150 ml. Two extractions were made with 150 ml. portions of 0.025 M thenoyltrifluoroacetone and 6.31 mg. hafnium recovered in the aqueous phase. The zirconium present in the aqueous phase was then too small to be determined by a combination of colorimetric and tracer Hf^{181} analysis. Spectrographic analysis, made by J. Conway and M. Moore of this laboratory, showed the presence of

less than 2% zirconium based on the hafnium present. Calculations from the curves show that about 1% zirconium should be present.

Summary

Distribution ratios for zirconium and hafnium have been found for extraction from 2 M perchloric acid with thenoyltrifluoroacetone of varying concentration and the equilibrium constants for the extractions determined.

Two extractions with 0.025 M thenoyltrifluoroacetone of a solution containing 59% as much zirconium as hafnium yielded 27% of the original hafnium with a content of less than 2% zirconium.

Table I

Zirconium

$(HT)_B$ added	$(\mu g\ Zr/ml)_B$	$(\mu g\ Zr/ml)_H$	Act. Coef. of HT and of ZrT_4	Activity of HT in benzene $[HT]$	Dist. Ratio R	log $[HT]$	log R	X
0.004900	6.50	181	0.999	0.00450	0.0358	-2.3468	-1.4449	6.76×10^{7}
.007950	21.5	144	.998	.00682	0.149	-2.1662	-0.8268	6.89
.00980	37.0	80.0	.997	.00798	0.481	-2.0996	-0.3363	11.54
.00980	43 *	136 *	.997	.00768	0.316	-2.1146	-0.5003	9.08
.01470	81.0	50.7	.995	.01081	1.42	-1.9662	0.1523	10.40
.01470	86.8	76.3	.995	.01056	1.14	-1.9763	0.0569	9.16
.01960	101	19.3	.991	.01465	5.18	-1.8342	0.7143	11.25
.01960	115	39.5	.992	.01407	2.89	-1.8517	0.4612	7.58
.01960	35.7	5.00	.986	.01735	7.05	-1.7607	0.8482	7.78
.01960	10	41.0	.991	.01452	2.53	-1.8380	0.4031	5.69
.01960	176	123	.994	.01142	1.44	-1.9423	0.1584	8.46
.01960	224	235	.996	.00949	0.949	-2.0227	-0.0227	11.70
.01960	135 *	44 *	.992	.01331	3.04	-1.8791	0.4829	9.98
.02485	162	31.2	.988	.01706	7.56	-1.7675	0.8790	8.87
.02040	126	9.33	.983	.02238	23.2	-1.6501	1.3653	9.25
.03430	173	3.42	.979	.02550	49.7	-1.5935	1.6965	11.73
.05920	120	0.940	.974	.03220	126	-1.4921	2.0969	11.62

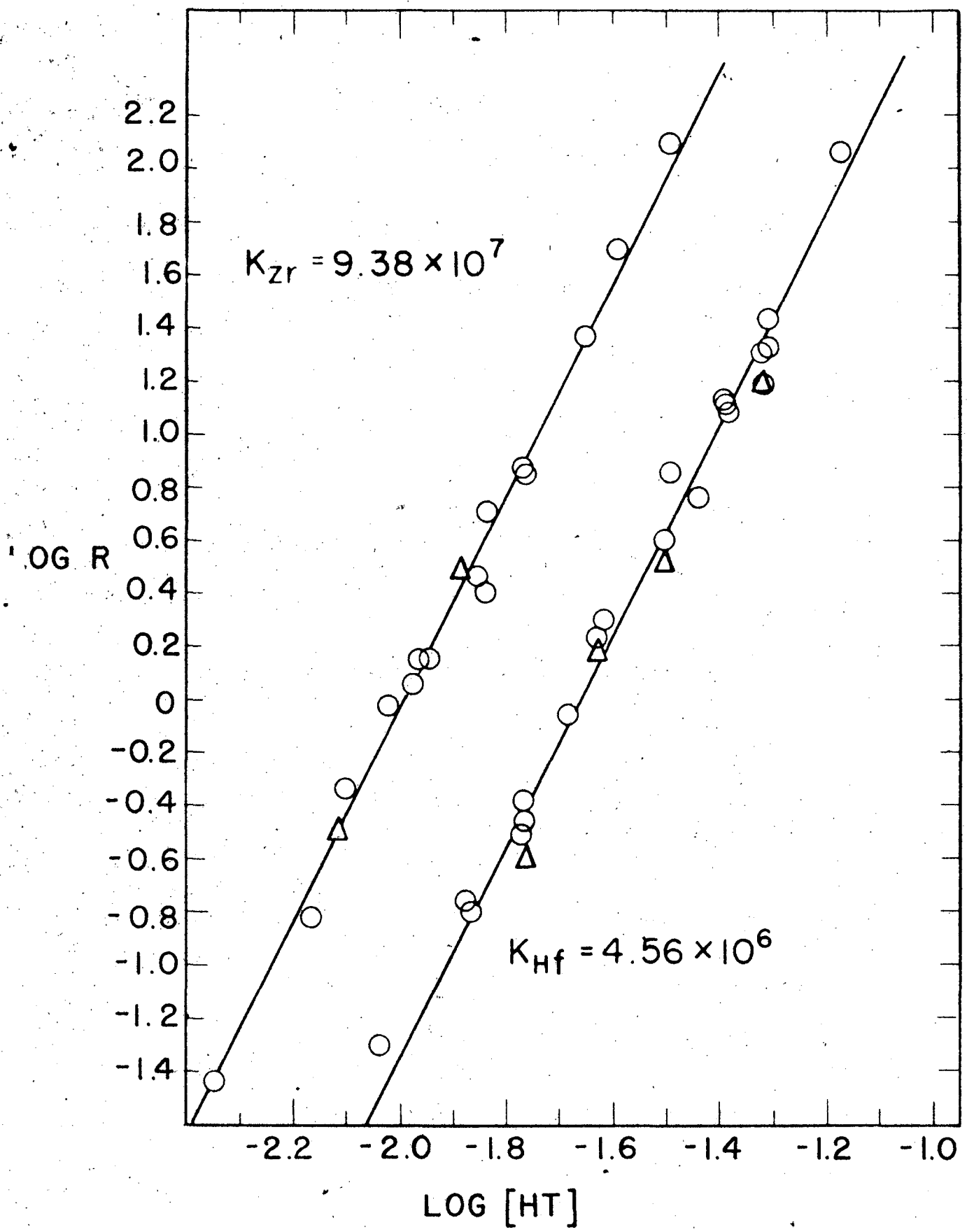
* Analysis by tracer Zr[95]

Table II

Hafnium

$(HT)_B$ added	$(\mu g\ Hf/ml)_B$	$(\mu g\ Hf/ml)_W$	Act. Coef. of HT and of HfT_4	Activity of HT in benzene [HT]	Dist. Ratio R	log [HT]	log R	K
0.00980	15.0	296	0.997	0.00916	0.0506	-2.0381	-1.2967	7.17×10^{5}
.01470	41.0	234	.993	.01333	0.174	-1.8752	-0.7570	5.54
.01491	45.0	280	.993	.01345	0.160	-1.8713	-0.7959	4.89
.01960	73.8	212	.988	.01727	0.344	-1.7627	-0.4634	3.87
.01960	83.0	202	.988	.01707	0.406	-1.7678	-0.3915	4.78
.01960	89.0	282	.988	.01694	0.312	-1.7710	-0.5088	3.79
.01960	70 *	270 *	.988	.01735	0.258	-1.7607	-0.5884	2.91
.02450	132	148	.985	.02087	0.879	-1.6847	-0.0560	4.82
.02940	184	90.5	.981	.02415	1.99	-1.6171	0.2989	5.85
.02940	221	128	.982	.02338	1.70	-1.6312	0.2304	5.89
.02940	205 *	135 *	.982	.02373	1.49	-1.6247	0.1732	4.70
.03920	238	31.8	.973	.03210	7.29	-1.4935	0.8627	6.87
.03920	272	66.7	.974	.03141	3.97	-1.5029	0.5988	4.08
.03920	261 *	79 *	.974	.03164	3.22	-1.4998	0.5079	3.21
.04473	277	46.5	.969	.03637	5.78	-1.4393	0.7619	3.30
.04900	238	19.0	.966	.04115	11.9	-1.3856	1.0756	4.15
.04900	266	19.0	.966	.04049	13.5	-1.3927	1.1303	5.02
.04900	260	19.0	.966	.04063	13.2	-1.3912	1.1206	4.85
.05880	320	20.0	.958	.04818	15.3	-1.3171	1.1847	2.84
.05880	272	9.67	.958	.04918	26.9	-1.3082	1.4298	4.60
.05880	292	13.3	.958	.04876	21.1	-1.3119	1.3243	3.73
.05880	324	15.0	.958	.04809	20.7	-1.3180	1.3160	3.87
.05880	321 *	19 *	.958	.04816	16.1	-1.3173	1.2068	2.99
.07840	263	3.16	.945	.06674	115	-1.1756	2.0607	5.80

* Analysis by tracer Hf^{181}


$K_{Zr} = 9.38 \times 10^7$
$K_{Hf} = 4.56 \times 10^6$
LOG R
LOG [HT]
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-2.2
-2.0
-1.8
-1.6
-1.4
-1.2
-1.0