can be added to their discussion except to say that a completely satisfying theory of the behavior of such solutions is not yet possible, and to emphasize again the fact that interactions between the unlike molecules are involved, in addition to the type of association of the alcohol postulated by Redlich and Kister.[10]

Summary

For the system ethanol–methylcyclohexane, densities and refractive indices have been measured at 25°. Total and partial vapor pressures have been determined at 35 and 55°. Thermodynamic consistency of the data was found to be satisfactory.

Vapor compositions are represented by the empirical equation previously developed by the authors, to within 0.005 mole fraction. They can be represented by an equation developed by Redlich and Kister, with somewhat less accuracy, and with rather anomalous values of the equilibrium constant involved.

The excess free energy, entropy and enthalpy have been calculated from the data, and exhibit a similar behavior to that of other alcohol–hydrocarbon systems.

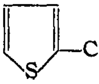
PEORIA 5, ILLINOIS RECEIVED MARCH 24, 1949

[CONTRIBUTION FROM THE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA]

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

BY E. H. HUFFMAN AND L. J. BEAUFAIT

The synthesis of thenoyltrifluoroacetone,



$-CO-CH_2-CO-CF_3$, has recently been reported by Reid and Calvin[2] and a study of the extraction of its zirconium chelate into benzene has been 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 separations of these elements.

Zirconium is generally regarded as being in the form of ZrO^{++} in acid solutions. The complexing of zirconium by the diketone is negligible in the aqueous phase and the only important species in the benzene phase is ZrT_4.[3] The reaction then is expressed by the equation

$$ZrO^{+2} + 4HT = ZrT_4 + H_2O + 2H^+$$

and, assuming constant acid concentration, the equilibrium constant by

$$\log K = \log [ZrT_4]/[ZrO^{+2}] - 4 \log [HT] = \log R - 4 \log [HT]$$

where *R* is the extraction coefficient. If the zirconium is in the form of the simple Zr^{+4} ion in 2 *M* perchloric acid, as recently reported,[4] the expression for the equilibrium constant is not changed, providing that the zirconium ion is monomeric. Values for *R* and *K* have previously been determined[3] for zirconium using trace amounts of radioactive Zr^{95}.

The close similarity of zirconium and hafnium in chemical behavior makes it logical to assume that the above equations apply to both elements. The determination of values for *R* and *K* for both zirconium and hafnium, using macro quantities and concentrations for which the zirconium ions 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

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

[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.

TABLE I

ZIRCONIUM

$(HT)_B$ added	$(\mu g\ Zr/ml.)_B$	$(\mu g\ Zr/ml.)_W$	Act. coef. of HT and of ZrT_4	Activity of HT in benzene [HT]	Dist. ratio *R*	*K*
0.004900	6.50	181	0.999	0.00450	0.0359	8.8×10^7
.007950	21.5	144	.998	.00682	0.149	6.9
.00980	37.0	80.0	.997	.00795	0.461	11.5
.00980	43^a	136^a	.997	.00768	0.316	9.1
.01470	81.0	56.7	.995	.01081	1.42	10.4
.01470	86.8	75.3	.995	.01056	1.14	9.2
.01960	101	19.3	.991	.01465	5.18	11.3
.01960	115	39.5	.992	.01407	2.89	7.4
.01960	35.7	5.00	.988	.01735	7.05	7.8
.01960	104	41.0	.991	.01452	2.53	5.7
.01960	178	123	.994	.01142	1.44	8.5
.01960	224	235	.996	.00949	0.949	11.7
.01960	135^a	44^a	.992	.01321	3.04	10.0
.02485	162	21.2	.988	.01708	7.55	8.9
.02940	126	5.33	.983	.02238	23.2	9.3
.03430	173	3.42	.979	.02550	49.7	11.7
.03920	120	0.940	.974	.03220	125	11.6

[a] Analysis by tracer Zr^{95}.

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. This material was prepared from a commercial product, containing 5% zirconium, during preliminary extractions with 0.02 *M* thenoyltrifluoroacetone to explore the possibilities of the separation method. The zirconium content before and after purification was based on spectrographic analyses, as reported below. A weighed amount of the dioxide 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 five to ten 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 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. of 95% ethanol, 4 ml. of 2 *M* perchloric acid including that to be added from the sample, 1.0 ml. of 0.02 *M* thenoyltrifluoroacetone in benzene including that to be added from the sample, benzene or aqueous phase sample containing 25–90 μg of Zr or 25–125 μg of Hf, and 1 ml. of 2 *M* hydrochloric acid. After mixing, ammonium hydroxide is added carefully until the red color just appears and the mixture allowed to stand for five minutes. One normal hydrochloric acid is added until the red color disappears and then 0.10 ml. of 7 *M* hydrochloric acid is added in excess. The volume is made to 25 ml. with 95% ethanol and the mixture allowed to stand for four hours before the spectrophotometer reading is taken. 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] The difference is probably due to the variation in the method of forming the lakes.

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 infrared lamp and counted in a Geiger counter, first with an aluminum absorber of 30 mg./sq. cm. and then with one of 150 mg./sq. cm. The differences in the two counts give 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.

For the determination of extraction coefficients micropipets 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 eighty minutes, although equilibrium was found to be reached within forty 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 cor-

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(5) H. Liebhafsky and E. Winslow, THIS JOURNAL, **60**, 1776 (1938).

rected diketone concentrations.[6] These also represent the activity 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.

TABLE II

HAFNIUM

$(HT)_B$ added	(µg Hf/ml)$_B$	(µg Hf/ml)$_W$	Act. coef. of HT and of HfT_4	Activity of HT in benzene [HT]	Dist. ratio R	K
0.00980	15.0	296	0.997	0.00916	0.0505	7.2×10^6
.01470	41.0	234	.993	.01333	0.174	5.5
.01491	45.0	280	.993	.01345	0.160	4.9
.01960	73.8	212	.988	.01727	0.344	3.9
.01960	83.0	202	.988	.01707	0.406	4.8
.01960	89.0	282	.988	.01694	0.312	3.8
.01960	70[a]	270[a]	.988	.01735	0.258	2.9
.02450	132	148	.985	.02067	0.879	4.8
.02940	184	90.5	.981	.02415	1.99	5.9
.02940	221	128	.982	.02338	1.70	5.7
.02940	205[a]	135[a]	.982	.02373	1.49	4.7
.03920	238	31.8	.973	.03210	7.29	6.9
.03920	272	66.7	.974	.03141	3.97	4.1
.03920	261[a]	79[a]	.974	.03164	3.22	3.2
.04473	277	46.5	.969	.03637	5.78	3.3
.04900	233	19.0	.965	.04115	11.9	4.2
.04900	266	19.0	.966	.04049	13.5	5.0
.04900	260	19.0	.966	.04063	13.2	4.9
.05880	320	20.0	.958	.04818	15.3	2.8
.05880	272	9.67	.958	.04918	26.9	4.6
.05880	292	13.3	.958	.04876	21.1	3.7
.05880	324	15.0	.958	.04809	20.7	3.9
.05880	321[a]	19	.958	.04816	16.1	3.0
.07840	263	2.16	.945	.06674	115	5.8

[a] Analysis by tracer Hf^{181}.

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. of hafnium and 13.6 mg. of zirconium in 150 ml. Two extractions were made with 150-ml. portions of 0.025 *M* thenoyltrifluoroacetone and 6.31 mg. of hafnium was recovered in the aqueous phase, as determined by tracer count. 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 on the perchloric acid solution, showed the presence of less than 1.2% zirconium based on the hafnium present. Calculations from the curves show that about 1% zirconium should be present.

In another separation, carried out before the data for the curves were obtained, 78.6 mg. of hafnium and 3.93 mg. of zirconium, from a commercial hafnium dioxide, were dissolved in 300 ml. of 2 *M* perchloric acid. This solution was then extracted with three 300-ml. portions of 0.02 *M* thenoyltrifluoroacetone. Precipitation and ignition of the oxide from the aqueous solution gave a recovery of 39.4 mg. of hafnium. Spectrographic analysis of a hydrofluoric acid solution of this product showed a 0.4% zirconium content, which is the value calculated from the curves. This is the material which was used in preparing hafnium solutions to obtain the data for the curve. Spectrographic analyses were made by J. Conway and M. Moore of this Laboratory who report that such analyses are more sensitive when carried out on hydrofluoric acid solutions than when on perchloric acid solutions.

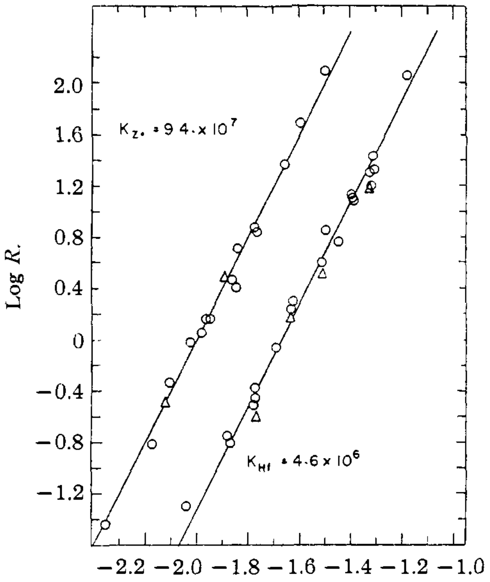

Fig. 1.—Dependence of distribution ratios on thenoyltrifluoroacetone activities: upper curve, zirconium; lower curve, hafnium; ○, colorimetric analysis; △, radioactive tracer analysis.

The similarity of zirconium and hafnium makes it unlikely that better separations would be attained at other acidities and temperatures, but it is possible that higher concentrations could be worked with at higher acidities where the monomeric state is retained.

Summary

Distribution ratios for zirconium and hafnium have been found for extraction from 2 *M* perchloric acid with benzene solutions of thenoyltrifluoroacetone of varying concentration. The equilibrium constants for the zirconium and hafnium extractions were found to be 9.4×10^7 and 4.6×10^6, respectively, at this acidity.

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 1.2% zir-

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(6) E. L. King and W. H. Reas, UCRL BC-69, July, 1947

conium. Three extractions with 0.02 *M* thenoyltrifluoroacetone of a solution containing 5.0% zirconium, based on the hafnium content, gave a recovery of 50% of the hafnium with zirconium content of 0.4%.

RECEIVED NOVEMBER 22, 1948

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

The Aqueous Chemistry of Zirconium[1]

BY ROBERT E. CONNICK AND WILLIAM H. MCVEY[2]

Although the chemistry of zirconium has been the subject of numerous investigations since its discovery in 1789, practically nothing is known about the species existing in aqueous solutions of its salts. Typical is the fact that not even the formula of the uncomplexed zirconium(IV) ion, present in perchloric acid solutions, has been identified. The formulas of several complex ions in aqueous solutions such as $ZrO(SO_4)_2^{=}$[3] and $ZrOCl_4^{=}$[4] have been reported but the data could be interpreted equally well by assuming other species. From a search of the literature we have been forced to the conclusion that the formula of not a single aqueous zirconium(IV) species has been unambiguously identified up to the present time.

The existing information on the chemistry of zirconium was collected in 1921 by Venable[5] and more recently by Pascal.[6] Nearly all of this work, as well as that published since 1931, deals with the identification of solid phases rather than the study of ions in solution.

The purpose of the present research was to determine the formulas of the zirconium species existing in acidic aqueous solutions and to study the complexing of zirconium(IV) by a number of the more common anions

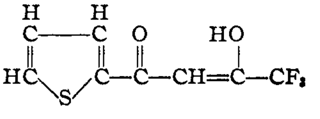
Experimental Method

The usual procedures for the determination of the formulas of species in solution, such as cell measurements, freezing point lowering, spectrophotometric analysis, *p*H determinations, solubility studies, etc., are not readily applicable in the case of zirconium because of the great tendency for hydrolysis to take place except in quite acidic solutions.

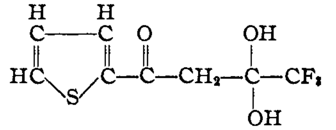
The experimental method employed involves the measurement of an equilibrium in which zirconium(IV) is distributed between the aqueous phase being investigated and an organic phase containing a chelating agent. The zirconium is inappreciably complexed by the chelating agent when in the aqueous phase, yet forms a chelate which is soluble in the organic phase and which is in equilibrium with whatever species exist in the aqueous phase. Any complexing of species in the aqueous phase is quantitatively reflected in a decrease of the extraction of the zirconium into the organic phase.

The method used in the present study is clearly a powerful one and it should find application in the study of many similar systems.

Calvin[7] has investigated the complexing properties of several chelating agents and the particular chelating agent used in this work, thenoyltrifluoroacetone was one prepared by Calvin and Reid.[8] This compound, hereafter referred to as TTA, is a weak acid having the following structure in the enol form



When TTA is equilibrated between dilute acid and benzene, the principal species in the aqueous phase is the hydrate[9]



while in the benzene phase, about 15% occurs in the hydrate form and 85% in the enol form. The keto form apparently is not an important species in this system. In aqueous solution TTA is a weak acid with an ionization constant[10] of 6.7×10^{-7}.

The distribution coefficient of TTA between benzene and a dilute acidic, aqueous phase favors the benzene phase, *i. e.*, at low TTA concentrations

$$(\mathrm{TTA})_b/(\mathrm{TTA})_{aq} = 40$$

The activity coefficient of TTA in benzene has been measured by King and Reas[9] who found it to decrease significantly below unity at TTA concentrations above 0.01 *M* in the benzene phase.

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[1] This research was carried out in the Radiation Laboratory and the Chemistry Department of the University of California under the auspices of the United States Atomic Energy Commission.

[2] Present address, General Electric Co., Hanford Engineer Works, Richland, Wash.

[3] R. Ruer, *Z. anorg. allgem. Chem.*, **42**, 87 (1904); **46**, 449 (1905).

[4] W. Pauli and M. Adolf, *Kolloid-Z.*, **29**, 173 (1921).

[5] Francis P. Venable, "Zirconium and Its Compounds," American Chemical Society Monograph Series, New York, N. Y., 1921.

[6] P. Pascal, "Traité de Chimie Minerale," Masson and Company, Paris, 1931-1932.

[7] M. Calvin, Manhattan Project Report, CN-2486, Dec. 1, 1944.

[8] J. C. Reid and M. Calvin, MDDC-1405, Aug. 13, 1947.

[9] E. L. King and W. H. Reas, "Atomic Energy Commission Report," BC-69, July, 1947.

[10] E. Zebroski, Atomic Energy Commission Report, BC-63, July 1, 1947.