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Zirconium Thenoyltrifluoroacetate: Solubility and Extraction

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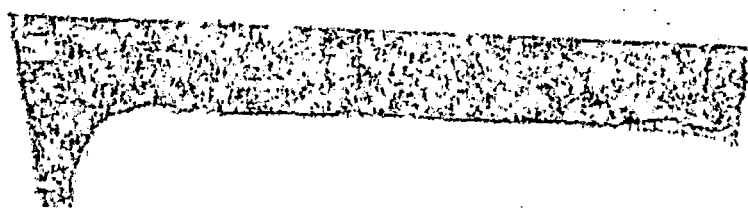
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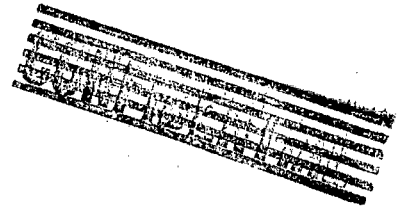


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ZIRCONIUM THENOYLTRIFLUOROACETONATE: 8.50

SOLUBILITY AND EXTRACTION 5.50

E. H. Huffman and G. M. Iddings 5.50 +

June 17, 1949

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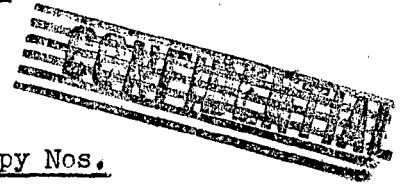
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Zirconium Thenoyltrifluoroacetate: 6.25
Solubility and Extraction 4.00 +

E. H. Huffman and G. M. Iddings
Radiation Laboratory, University of California 7.75
Berkeley, California 3.50

ABSTRACT 2.00

Solubilities of zirconium thenoyltrifluoroacetate have been determined in anhydrous benzene at 20°, 30° and 40° C., in 0.01, 0.02, 0.04 and 0.08 molar thenoyltrifluoroacetone in benzene at 20° C., in benzene saturated with water at 20° C., and in 0.02 molar thenoyltrifluoroacetone in benzene in contact with 2 molar perchloric acid at 20° C.

June 16, 1949.

Zirconium Thenoyltrifluoroacetate:
Solubility and Extraction

E. H. Huffman and G. M. Iddings
Radiation Laboratory, University of California
Berkeley, California

June 16, 1949 2.25

The data herein were obtained following a decision made at the Oak Ridge conference in December, 1948 on the chelation-extraction separation of zirconium and hafnium. Solubilities of zirconium thenoyltrifluoroacetate, hereafter referred to as ZrT_4 , have been determined in anhydrous benzene at 20° , 30° and 40° C., in 0.01, 0.02, 0.04 and 0.08 molar thenoyltrifluoroacetone (TTA) in benzene at 20° C., in benzene saturated with water at 20° C, and in 0.02 M TTA in benzene in contact with 2 M perchloric acid at 20° C.

No data have been obtained in this laboratory on extractions from acids other than perchloric, as it was decided at the conference that other laboratories would investigate this phase of the work. No data have yet been obtained here on solubilities and extractions from other organic solvents and with other beta-diketones, though it is planned to obtain such information.

Experimental 2.25

The solubilities of the zirconium chelate were run on material prepared in the following manner. A solution of one molar TTA in benzene was allowed to evaporate in contact with the theoretical amount of 0.1 M zirconyl chloride in 5 M perchloric acid. The product obtained was filtered and washed with water to remove excess salt and acid. Benzene was then used to wash out any excess TTA

and air was drawn through the filter to evaporate the benzene. The product was finally dried at room temperature over anhydrous magnesium perchlorate. Analysis of this complex was carried out by moistening with concentrated sulfuric acid and igniting to zirconium dioxide. Found: 0.0262 g. ZrO_2 for 0.2097 g. sample; calculated for ZrT_4 : 0.0265 g. ZrO_2 . Direct ignition of the dry product leads to loss of zirconium, probably as the fluoride.

Anhydrous benzene was prepared by drying over Drierite (anhydrous calcium sulfate), followed by distillation. The solubilities were determined by rotating a quantity of the chelate with about 7 ml. of the solvent in a constant temperature bath for 5-20 hours and drawing off a 5 ml. sample through a cotton filter for analysis. More solvent was then added to the remaining portion of ZrT_4 and the process repeated until consistent values were obtained, as shown by analysis.

Analyses were made by evaporating the 5 ml. portions in vacuo, weighing to obtain total solute, moistening with sulfuric acid, igniting and weighing again to obtain ZrO_2 . The results are given in Tables I-IV and are all expressed as milligrams per 5 ml. solution.

Table I ^{1.25}

Solubility of ZrT_4 in Anhydrous Benzene ^{6.75}
at Different Temperatures. _{4.50}

<u>Sample No.</u>	<u>Temperature °C.</u>	<u>mg. ZrT_4 per 5 ml.</u>	<u>mg ZrO_2 per 5 ml.</u>
1	19.99° ± 0.02°	85.9	10.7
2	"	86.4	10.5
3	"	86.3	10.8
4	29.96° ± 0.02°	127.1	15.9
5	"	126.3	15.7
6	"	127.5	15.8
7	"	124.2	15.8
8	"	124.7	15.3
9	"	128.7	16.2
10	"	127.8	16.0
11	"	127.6	15.8
12	40.00° ± 0.03°	191.9	- -
13	"	189.9	- -
14	"	190.0	23.6
15	"	189.9	23.4

TABLE II 1.50

Solubility of ZrT_4 in solutions of TTA ^{6.50 -}
 in Anhydrous Benzene at $20.00 \pm 0.02^\circ C$. ^{7.00 -}

<u>Sample No.</u>	<u>TTA Conc.</u>	<u>mg. Solute per 5 ml.</u>	<u>mg. ZrO_2 per 5 ml.</u>
1	0.0	85.9	10.7
2	"	86.4	10.5
3	"	86.3	10.8
4	0.010 M	92.4	10.4
5	"	91.6	10.5
6	"	89.8	10.5
7	"	86.6	11.0
8	"	88.2	10.8
9	0.020 M	101.2	11.0
10	"	103.3	10.3
11	"	101.1	10.3
12	"	101.3	11.0
13	"	102.4	11.0
14	0.040 M	125.9	10.6
15	"	121.8	10.6
16	"	122.3	10.6
17	"	122.2	10.9
18	0.080 M	172.9	10.8
19	"	165.2	10.8
20	"	164.9	11.0
21	"	166.7	11.0

} From
Table I

Table III ^{1.50}

Solubility of ZrT_4 in Benzene and TTA ^{6.50}
 Saturated with Water at $20.00^\circ \pm 0.02^\circ$ C. ^{7.00}

<u>Sample No.</u>	<u>TTA Conc.</u>	<u>mg. Solute per 5 ml.</u>	<u>mg. ZrO_2 per 5 ml.</u>
1	0.0	90.2	11.1
2	"	90.1	11.1
3	"	90.0	11.2
4	"	90.1	11.4
5	¹⁶ 0.060 M	149.0	11.3
6	"	150.8	11.1
7	"	146.9	11.0
8	"	146.5	10.9
9	"	148.6	10.8
10	"	144.6	10.8
11	"	149.3	10.6

Table IV ^{1.50}

Solubility of ZrT_4 in 0.020 M TTA ^{5.75}
 in Benzene in Contact with 2 M $HClO_4$ at $20.00^\circ \pm 0.02^\circ$ C. ^{9.75}

<u>Sample No.</u>	<u>mg. Solute per 5 ml.</u>	<u>mg. ZrO_2 per 5 ml.</u>
1	105.9	10.8
2	103.8	10.6

Discussion 1.75

The results given in Table I show that there is an increase in solubility of ZrT_4 in benzene of approximately 50% for each $10^\circ C$. rise in temperature. No distribution ratios for the extraction of zirconium from acid solutions at other than room temperature have been determined, and so it is not known whether or not the separation of zirconium and hafnium formerly reported⁽¹⁾ can be improved

1 Huffman, E. H., and Beaufait, L. J., AECD-2387(UCRL-194), The Separation of Zirconium and Hafnium with Thenoyltrifluoroacetone, Oct. 7, 1948.

at other temperatures. Any advantage to a higher temperature would also depend upon the effect the change would have on the concentration range over which the zirconium would remain monomeric in the acid concentration chosen.

The results given in Table II show that the amount of zirconium dissolved as ZrT_4 in the benzene phase is independent of the concentration of TTA and is the same as that for benzene alone. This is somewhat surprising in view of the distribution ratio dependence on the TTA concentration for the extraction of zirconium from 2 M perchloric acid⁽¹⁾.

Some preliminary extractions from a 0.086 M zirconium solution in 5 M perchloric acid have been made. Zirconium is monomeric, a condition necessary for extraction, under these conditions⁽²⁾ and

2 Connick, R. E., and McVey, W. H., private communication.

distribution ratios into benzene solutions of TTA as high as 161 have been obtained. This means that the zirconium concentration in

the benzene phase is essentially 0.086 M at this ratio, a value approximately five times as high as that shown in Tables I and II (about 0.018 M). This indicates that the zirconium species in the benzene phase is not the simple ZrT_4 when it is extracted from perchloric acid solutions. It was thought that this species might be a hydrate, so the solubilities were then run in water-saturated organic solvent. The results shown in Tables III and IV indicate that if the extracted form is a hydrate it is not readily reformed when it has once been prepared as the anhydrous chelate. This possibility is in agreement with the fact that TTA itself forms a hydrate which is soluble in benzene but which does not readily form the hydrate again after dehydration⁽³⁾.

³ Calvin, M., private communication.

Future work is planned on chelation-extraction of zirconium and hafnium using other trifluoro beta-diketones and other organic solvents.

This work was performed under the auspices of the United States Atomic Energy Commission.

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