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The Solubility of Zirconium Tetrafluoride
in Nitric Acid from 0 to 80° C.

A. G. Chapman and C. M. Slansky

April 30, 1958

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C. M. SlanskyA B S T R A C T

The solubility of zirconium tetrafluoride in concentrations of nitric acid from 1 to 16M and at temperatures from 0 to 80° C. has been determined. At least three solid species of zirconium fluoride as determined by X-ray diffraction and chemical analysis have been observed to be in equilibrium with nitric acid through these ranges of concentration and temperature: (1) Zirconium tetrafluoride monohydrate, $\text{ZrF}_4 \cdot \text{H}_2\text{O}$ or $\text{ZrOF}_2 \cdot 2\text{HF}$, is the stable solid phase in equilibrium with nitric acid greater than about 8 molar through the entire measured temperature range and in nitric acid concentrations above 4 molar at temperatures above 50 - 60° C; (2) Zirconium tetrafluoride trihydrate, $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$, at acid concentrations below about 6M and temperatures below about 50 - 60° C; and (3) A solid having unidentified X-ray diffraction pattern and chemical composition of approximately 3 moles of fluoride to 1 mole of zirconium in nitric acid of less than 4M and at temperatures above about 50 - 60° C.

The solubility of zirconium tetrafluoride in nitric acid expressed as grams ZrO_2 per liter ranges from about 0.5 grams per liter at 0° C. in 16M acid to approximately 215 grams per liter at 80° C. in 1M acid.

For presentation at the Northwestern Regional Meeting of the American Chemical Society to be held at Portland, Oregon, June, 1958.

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THE SOLUBILITY OF ZIRCONIUM TETRAFLUORIDE IN NITRIC ACID FROM 0 TO 80° C.

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I. INTRODUCTION

Zirconium is being widely used as a cladding or alloying material with uranium in the design of nuclear reactor fuel elements. In current practice, the recovery of unburned uranium-235 from the spent fuel is accomplished by dissolution of the fuel with hydrofluoric acid to give an aqueous system that is then processed by solvent extraction to separate the uranium from the bulk zirconium and fission products. Zirconium readily dissolves in hydrofluoric acid but uranium tetrafluoride has a very limited solubility; therefore, the use of hydrofluoric acid alone as a solvent is more or less limited to a narrow range of uranium-zirconium composition. Numerous efforts have been made to find dissolvents which would extend the solubility range and lead to the development of an improved process. Work by Gerke and McVey⁽¹⁾ and earlier scoping work in this laboratory⁽²⁾ showed possibilities for the use of a mixture of nitric acid and hydrofluoric acid as a more universal solvent for uranium-zirconium alloys. It was observed, however, in all of these preliminary studies that under certain conditions insoluble salts were formed during the dissolution. In order to gain a better understanding of the chemistry involved in these complex systems, a phase study of the zirconium-nitric acid-hydrofluoric acid system has been undertaken in this laboratory.

E. M. Vander Wall and E. M. Whitener⁽³⁾ have reported some of their findings on the kinetics of dissolution of zirconium in nitric hydrofluoric acid mixtures. In order to establish solubility limitations for their system, a program to determine the solubility of zirconium tetrafluoride in nitric acid was initiated. I. V. Tannanaev⁽⁴⁾ and his coworkers have determined the solid phase composition and isothermal solubility of zirconium fluoride in hydrogen fluoride concentrations ranging from 0 to 100 percent at 0.5° C., but no quantitative data for the solubility of zirconium tetrafluoride in nitric acid were found. Our measurements covered the concentration range of 1 to 16M nitric acid and temperatures from 0 to 80° C.

Work done by our X-ray diffraction laboratory on solids obtained in the course of this investigation has confirmed the X-ray diffraction data for $ZrF_4 \cdot H_2O$ and $ZrF_4 \cdot 3H_2O$ reported by R. W. M. D'Eye⁽⁵⁾ and his coworkers.

II. EXPERIMENTAL PROCEDURE

A. Materials

The monohydrated zirconium tetrafluoride used in this study was prepared by dissolving reactor grade zirconium metal in a mixture of analytical grade concentrated nitric acid and analytical grade 48 percent hydrofluoric acid. The reaction is carried out in a teflon vessel surrounded by a boiling water bath and equipped with a polyethylene reflux condenser. The zirconium coupons are placed in the vessel and preheated. The dissolving medium, consisting of 15.6M nitric acid and approximately 1M hydrofluoric acid, is preheated and slowly added through the reflux condenser. After the initial vigorous reaction subsides, additional 48 percent hydrofluoric acid is steadily metered through the condenser at a rate sufficient to maintain a vigorous reaction and in an amount approximately equal to four moles of fluoride for each mole of zirconium dissolved. The system is occasionally agitated by rotating the container. The amount of nitric acid is not critical but should be kept fairly concentrated. Excellent results were obtained when concentrated nitric acid was used in the ratio of about 4 milliliters of the acid for each gram of zirconium dissolved. If too little acid is used, the heavy precipitate of zirconium fluoride forms a thick paste near the end of the reaction. The rate of addition of the hydrofluoric acid affects the physical character of the precipitate; if it is added too rapidly the crystals of zirconium tetrafluoride form a dense adherent coating on the metal surface that practically stops the dissolution reaction; if the addition takes place too slowly the crystals are smaller and more difficult to separate from the mother liquor and wash solutions. If the free hydrofluoric acid in the system is maintained between 0.5 and 1M, the reaction is very rapid, there is no tendency for the solid to adhere to the metal surface, and easily workable, dense crystals of uniform size are formed. After the zirconium is completely dissolved, the system is digested about half an hour, filtered, the crystals washed free of nitric acid with acetone, and either air dried or oven dried at 96 to 100° C.

The trihydrated zirconium tetrafluoride can be prepared from the monohydrate in several ways: (1) by contacting the monohydrate with 1-4M nitric acid at room temperature for several hours, (2) by addition of acetone to a saturated solution of zirconium tetrafluoride in dilute nitric acid, and (3) by saturating dilute nitric acid with zirconium tetrafluoride at elevated temperature and allowing the solution to cool and stand for a day or two. Other methods of preparation have been described in the literature(1,2). Although experiments show that the same solubilities are obtained from the use of either the monohydrate or the trihydrate when sufficient time is allowed for equilibrium to be established, the monohydrate was used as the starting material in these studies.

B. Solubility Measurements

An excess of zirconium tetrafluoride monohydrate along with nitric acid of indicated concentration were charged into a polyethylene bottle and shaken in a thermostat controlled within $\pm 1^\circ \text{C}$. of the reported temperature. It was found that at lower temperatures equilibrium was attained very slowly, requiring about two weeks at the dilute acid concentrations at 0°C . Tannanaev⁽⁴⁾ observed that equilibrium in the zirconium-hydrofluoric acid system at 0.5°C . was established in about 3 hours. On the basis of experiments extended over 4 or 5 weeks, it is felt that the solubility data should be reliable within about 5 percent for equilibrium conditions. Failure to recognize the slow attainment of equilibrium of zirconium tetrafluoride in nitric acid will lead to ambiguous results in the solubility measurements.

After allowing the solid phase to settle, a measured volume of the clear supernate was withdrawn and evaporated to dryness in a platinum dish. The dried residue was ignited for several hours at 500 to 550°C . in a muffle furnace and finally ignited to constant weight at circa 1000°C . X-ray diffraction and chemical analysis showed the residue to be ZrO_2 . The analysis for zirconium by this procedure was verified by other methods. There was no evidence of any sublimation of zirconium tetrafluoride at 550°C .

III. RESULTS AND DISCUSSION

The solubility of zirconium tetrafluoride, computed as grams of ZrO_2 and grams of $\text{ZrF}_4 \cdot \text{H}_2\text{O}$ per liter, in nitric acid concentrations ranging from 1 to 16M and at temperatures from 0 to 80°C . is given in Table 1. The approximate densities of these solutions in grams per milliliter are given in Table 2. The densities were determined by weighing the pipetted volume of solution before evaporation. Figure 1 is a plot of these solubility values. In Figure 2 is plotted the solubility as a function of acid concentration at constant temperature. In nitric acid solutions less than 8M and at temperatures less than 55°C . monohydrated zirconium tetrafluoride dissolves initially in considerably greater amount, up to four times as much as is found in the equilibrium solution, to form supersaturated solutions from which trihydrated zirconium tetrafluoride crystallizes upon standing. When the trihydrate was used as the initial solid phase in these low acid solutions, equilibrium was achieved more rapidly and the final concentration of the saturated solution was essentially the same as that obtained by starting with the monohydrate.

A comparison of the relative solubilities of the mono and trihydrates in 12M nitric acid showed the opposite behavior. The trihydrate was initially more soluble to form a metastable solution of higher concentration than obtained from the monohydrate although after six or seven days at 40°C . both systems came to essentially the same concentration and the solid $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$ was converted to $\text{ZrF}_4 \cdot \text{H}_2\text{O}$. These results show that

Table 1
Solubility of Zirconium Tetrafluoride Monohydrate
in Nitric Acid, Grams Solute Per Liter

Molarity of HNO ₃	0° C ± 1		25° C ± 1		40° C ± 1		50° C ± 1		55° C ± 1		60° C ± 1		70° C ± 1		80° C ± 1	
	ZrO ₂	ZrF ₄ · H ₂ O	ZrO ₂	ZrF ₄ · H ₂ O	ZrO ₂	ZrF ₄ · H ₂ O	ZrO ₂	ZrF ₄ · H ₂ O	ZrO ₂	ZrF ₄ · H ₂ O	ZrO ₂	ZrF ₄ · H ₂ O	ZrO ₂	ZrF ₄ · H ₂ O	ZrO ₂	ZrF ₄ · H ₂ O
1	62	93	98	147	148	222	193	290	214	322	219	329	217	326	215	323
2	37	56	65	98	105	158	140	210	159	239	183	275	179	269	176	265
4	17	26	31	46	52	78	81	122	81	122	80	120	82	123	83	125
6	9.3	14	19	28	28	42	33	50	35	53			39	59	43	65
8	5.6	8.4	13	19	15	23	17	26	17	26	19	29	21	32	23	35
10	4.2	6.3	6.4	9.6	7.3	11	9	14	9.3	14	10.4	16	12.4	19	14	21
12	2.0	3.0	3.7	5.5	4.7	7.0	5.1	7.7	6.0	9	7	10.5	7.5	11.3	8.6	13
16	0.4	0.6	1.3	1.9	1.7	2.6	2.5	3.8	2.5	3.8	2.5	3.8	3.0	4.5	3.5	5.3

Table 2

Approximate Densities, D_4^t , of Saturated Solutions
of Zirconium Tetrafluoride in Nitric Acid

Temperature, °C HNO ₃ Concentration	0° ± 1	25° ± 1	40° ± 1	50° ± 1	55° ± 1	60° ± 1	70° ± 1	80° ± 1
<u>1M</u>	1.153	1.173	1.196	1.245	1.270	1.275	1.275	1.263
<u>2M</u>	1.163	1.174	1.177	1.218	1.236	1.262	1.254	1.247
<u>4M</u>	1.196	1.183	1.180	1.197	1.195	1.194	1.206	1.198
<u>6M</u>	1.227	1.208	1.208	1.208	1.198		1.199	1.201
<u>8M</u>	1.266	1.254	1.246	1.248		1.240	1.239	1.239
<u>10M</u>	1.314	1.301	1.285	1.288	1.264	1.284	1.279	1.265
<u>12M</u>	1.360	1.340	1.332	1.329		1.319	1.311	1.298
<u>16M</u>	1.425	1.406		1.379		1.375	1.370	

FIGURE 1

SOLUBILITY OF ZIRCONIUM TETRAFLUORIDE
IN NITRIC ACID

SOLUBILITY OF ZIRCONIUM TETRAFLUORIDE AS A FUNCTION
OF NITRIC ACID CONCENTRATION AT CONSTANT TEMPERATURES

the solid species which is unstable in the solutions tends to dissolve to higher metastable concentrations in the initial stage of the dissolution but subsequently transforms to the stable phase and produces a stable solution equilibrium. Factors such as presence of crystal nuclei and mechanical and thermal stress which normally affect metastable solutions seem to have an influence on the rate at which equilibrium is established.

The solubility of zirconium fluoride in nitric acid more concentrated than $8M$ shows a moderate, uniform increase as the temperature increases, but at lower concentrations there is a marked temperature dependence. At nitric acid concentrations below $4M$ and at temperatures above $50 - 60^{\circ} C$. the zirconium tetrafluoride undergoes an evident hydrolysis to form a less soluble compound or compounds as yet not fully identified by X-ray diffraction or chemical analysis. The hard dense crystals of zirconium tetrafluoride change to fluffy colloidal solids which resemble the solid species formed when zirconium tetrafluoride is equilibrated with water. The X-ray diffraction pattern is different from that for the tetrafluoride and chemical analysis shows about three moles of fluoride for each mole of zirconium. In $6M$ nitric acid solution, the solid phase in equilibrium with the solution at $80^{\circ} C$. is the monohydrate but at $25^{\circ} C$. the monohydrate is converted to the trihydrate. When the solution of $6M$ nitric acid saturated with zirconium fluoride at $80^{\circ} C$. is allowed to cool to room temperature and stand undisturbed for a day, clear crystals of the trihydrated zirconium tetrafluoride are formed and will continue to form for several days. A similar behavior is observed with the mother liquor removed from the $ZrF_4 \cdot H_2O$ preparation as described in the experimental part. Table 3 summarizes the experimental X-ray data used as the basis for this diagram. Figure 3 shows an approximate solid phase diagram for the solid zirconium fluorides in equilibrium with nitric acid solutions. More data, especially in the transition regions, are necessary to more closely define the phase boundaries.

IV. SUMMARY AND CONCLUSIONS

The solubility of zirconium tetrafluoride in nitric acid expressed as grams ZrO_2 per liter ranges from about 0.5 at $0^{\circ} C$. in $16M$ acid to 215 at $80^{\circ} C$. in $1M$ acid. Solubility equilibrium is attained at a slow rate at 0 to $50^{\circ} C$. The solid phase composition is identified by X-ray over the range of temperatures and acid concentrations. Hydrolysis of the tetrafluoride to a solid trifluoride is noted in the low acid, high temperature region.

V. ACKNOWLEDGEMENTS

The authors wish to acknowledge the assistance of W. A. Ryder in doing the X-ray diffraction analysis and the work done by the Analytical Development Group of the Chemical Processing Plant on fluoride and zirconium analysis.

Table 3

Solid Phases of Zirconium Tetrafluoride in
Equilibrium with Nitric Acid

<u>Solid Phase Added</u>	<u>Temperature ° C</u>	<u>Molar Concentration of Nitric Acid</u>	<u>Solid Phase at Equilibrium</u>
M	25	2	T
M	25	6	T
M	0	8	T
M	65	6	M
M	50	8	M
M	40	12	M
M	25	(H ₂ O) 0	X
M	50	1	X
M	55	2	X (inc)
T	40	12	M
T	25	6	T
M	50	4	M

T = ZrF₄ · 3H₂O

M = ZrF₄ · H₂O

X = Approximately ZrOF₂ · HF · H₂O

SOLID PHASE DIAGRAM
OF ZIRCONIUM FLUORIDES IN NITRIC ACID

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