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ZIRCONIUM FLUORIDE PHASE STUDIES

I. A Preliminary Investigation of Solid Phases

A. G. Chapman and R. A. Woodruff

June 10, 1959

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I. A Preliminary Investigation of Solid Phases

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A. G. Chapman
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Chemical Development Section
CPP Technical Branch

Date Written
January 15, 1959

PHILLIPS PETROLEUM COMPANY
Atomic Energy Division
Idaho Falls, Idaho
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A B S T R A C T

Solid phases in the zirconium-nitric acid-hydrofluoric acid system have been identified by chemical and X-ray diffraction methods. Five different compounds have been crystallized at various temperatures and fluoride concentrations from fluoride or fluoborate solutions. These include the mono- and trihydrates of zirconium tetrafluoride, plus three hydrolysis products which possess a fluoride-to-zirconium ratio of approximately three, yet produce different X-ray patterns. The trifluorides crystallize from solutions of low fluoride-to-zirconium ratio at temperatures of below 90°C, 65°-100°C, and above 95°C, respectively. Solubilities of these basic trifluorides have been measured at 25°C in 1M, 6M, and 16M nitric acid.

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I. SUMMARY

A basic study of solid phases in the system zirconium-hydrofluoric acid-nitric acid is required as an aid to the characterization of solids in dissolver solutions. Preliminary investigation shows that:

1. Monohydrated zirconium tetrafluoride is the principal solid phase that precipitates when zirconium is dissolved in a mixture of concentrated nitric acid and dilute hydrofluoric acid. In a mixture of dilute nitric acid and dilute hydrofluoric acid, the trihydrated zirconium tetrafluoride is the predominant species. In solutions of high fluoride-to-zirconium ratio, the monohydrate crystallizes when hot, while at lower temperatures the trihydrate precipitates.
2. On the basis of X-ray diffraction data three basic zirconium trifluorides precipitate from solutions of low fluoride-to-zirconium ratio. These appear respectively in the temperature ranges below 90°C, between 65° and 100°C, and above 95°C.
3. The solubility of two different samples of basic zirconium trifluoride was determined in 1M, 6M, and 16M nitric acid at 25°C. Solubility was greatest at the intermediate acid concentration. These solutions were characterized by the slowness with which the solids and solution came to equilibrium.
4. Thermogravimetric analysis of zirconium tetrafluoride trihydrate showed a stoichiometric decomposition to the monohydrate at approximately 96°C. Upon further heating to 267°C the monohydrate lost both water and hydrogen fluoride. Both the zirconium tetrafluorides and their hydrolysis products can be converted into zirconia at 550°C without loss of zirconium.

II. INTRODUCTION

The dissolution of nuclear fuel elements is normally the initial step in preparing such materials for uranium recovery. Under certain conditions insoluble salts form when zirconium elements are dissolved in mixtures of hydrofluoric acid and other reagents; e.g., nitric acid, aluminum nitrate, or fluoboric acid. Under other conditions, such as concentration or prolonged standing, glasses or gels may appear.

The presence of solids in process streams is highly undesirable during chemical processing of reactor fuel elements by solvent extraction. The appearance of solids may also complicate the storage of waste solutions. According to present practice in the hydrofluoric acid process^[1], the plant operates within certain empirically defined stability ranges in order to obviate the difficulties caused by the presence of solids.

Although white solids have been observed in several investigations of the dissolution of zirconium^{[1][2]}, only limited systematic study of these insoluble zirconium salts has been made. The purpose of this investigation is to make a basic study of these solid phases with reference to the dissolution chemistry of zirconium. With the exception of a few experiments with fluoboric acid and a uranium-zirconium alloy the present study has been restricted to the system: zirconium fluoride-nitric acid.

III. EXPERIMENTAL

A. Analyses

Chemical analyses were performed by the Chemical Processing Plant Analytical Section under R. C. Shank. Considerable development work was required to perfect the necessary techniques. Other investigators have encountered similar difficulties with this type of material^{[3][4]}. It is felt that the results give the actual composition of the samples with a fair degree of accuracy, but the precision depends to some extent upon the nature of the sample.

Fluoride was determined by pyrohydrolysis with a current of moist oxygen in a quartz combustion tube, followed by titration of the liberated hydrofluoric acid with standard thorium nitrate or sodium hydroxide.

Zirconium was determined by amperometric titration of a sulfuric acid solution of the sample with cupferron.

Nitrate was determined by the Kjeldahl procedure, and water content computed by difference.

Analyses for the solubility measurements were made by pyrolyzing at 550°C the residues from evaporated samples of the saturated solutions.

The X-ray diffraction analyses were also performed by the Analytical Section. Powder diffraction patterns were obtained with a Geiger counter diffractometer using copper radiation with a nickel filter.

B. Zirconium Fluoride Monohydrate, $\text{ZrF}_4 \cdot \text{H}_2\text{O}$ *

Zirconium fluoride monohydrate constitutes the principal solid

*This formulation is used for convenience. To our knowledge single crystal studies have not yet indicated a choice between $\text{ZrF}_4 \cdot \text{H}_2\text{O}$ and $\text{ZrOF}_2 \cdot 2\text{HF}$.

phase formed when zirconium is dissolved in a mixture of concentrated nitric acid and dilute hydrofluoric acid. The salt is relatively insoluble in concentrated nitric acid, but forms rather slowly in the process of dissolution. If the dissolution is carried out at a rapid rate, the solution passes through the metastable region of fluoride-to-zirconium ratio from 6 to 2.5, zirconium nitrate complexes of higher solubility are formed, and precipitation does not take place. After the crystals of $\text{ZrF}_4 \cdot \text{H}_2\text{O}$ are once formed in a solution having a fluoride-to-zirconium ratio of approximately 4, there appears to be no tendency to exchange nitrate groups for fluoride groups between the solid and solution phases.

The compound crystallizes in well-defined octahedra. The solubility of $\text{ZrF}_4 \cdot \text{H}_2\text{O}$ in nitric acid has been determined from 0 to 80°C[5].

Table 1 summarizes the chemical analysis of ten samples of this compound. All gave the same X-ray diffraction pattern which was in agreement with previously reported work[6]. Single crystal studies have been described elsewhere[7]. Although there is appreciable variation in the chemical analysis of these samples, it is felt they represent relatively pure samples of monohydrated zirconium tetrafluoride on the basis of X-ray diffraction, solubility, thermogravimetric, and microscopic data.

The compound is non-hygroscopic and is very stable at temperatures up to 100°C. It undergoes slight degradation at 225°C with more rapid decomposition beginning at about 267°C. Analysis of the degradation product in air at 270°C indicated a fluoride-to-zirconium mole ratio of 3.5. Tananaev[4] observed a fluoride-to-zirconium ratio of 3 when the zirconium tetrafluoride monohydrate was decomposed at this temperature to the same ratio of weight loss. It required six days of heating at 265-320°C to convert $\text{ZrF}_4 \cdot \text{H}_2\text{O}$ into ZrOF_2 . The conversion was also accomplished in a water vapor atmosphere under similar conditions. It is completely converted to ZrO_2 in air at 550°C without loss of zirconium.

C. Zirconium Fluoride Trihydrate, $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$

The trihydrate degrades stoichiometrically into zirconium tetrafluoride monohydrate when heated to approximately 100°C. The dried product gives the same X-ray diffraction pattern as $\text{ZrF}_4 \cdot \text{H}_2\text{O}$ crystallized from concentrated nitric acid, but it is somewhat less stable to further thermal decomposition. $\text{ZrF}_4 \cdot \text{H}_2\text{O}$ readily undergoes a transformation to the $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$ in dilute nitric acid. The trihydrate has been crystallized from nitric acid solutions as concentrated as approximately 9M when the acid is saturated with ZrF_4 at higher temperatures and then allowed to cool to room temperature and stand for several days. Table 2 gives a summary of the chemical analyses for seven samples having essentially the same X-ray diffraction patterns and the same thermogravimetric characteristics. The average fluoride-to-zirconium ratio (3.65) is in reasonable agreement with the ratio (3.68) for the monohydrates in Table 1. It is felt that these compounds are fairly pure samples of zirconium tetrafluoride trihydrate.

TABLE 1
SUMMARY OF CHEMICAL ANALYSES OF $\text{ZrF}_4 \cdot \text{H}_2\text{O}$ SAMPLES
ALL HAVING THE SAME X-RAY DIFFRACTION PATTERNS

Sample No.	mg Zr/g	mg F/g	F/Zr	mg H_2O /mg	H_2O /Zr
64*	536	410	3.67	54	0.51
68*	499	348	3.35	153	0.55
70*	501	385	3.69	114	1.15
55*	500	381	3.97	87	0.88
69**	534	393	3.54	73	0.69
66**	490	386	3.78	124	1.28
61	530	381	3.45	89	0.85
81AB	498	405	3.90	97	0.99
94	505	400	3.80	95	0.95
Average $\pm \sigma$	510 $\pm$ 17	388 $\pm$ 17	3.68 $\pm$.20		

*,** Samples taken from same preparation

*** by difference

TABLE 2
CHEMICAL ANALYSES OF ZIRCONIUM TETRAFLUORIDE TRIHYDRATE

Sample No.	mg Zr/g	mg F/g	F/Zr	mg H_2O /g	H_2O /Zr
60*	382	323	4.06	295	3.91
65*	433	329	3.65	238	2.78
67*	435	330	3.64	235	2.74
57	458	275	2.88	267	2.95
74	424	348	3.94	238	2.84
75	430	337	3.77	233	2.75
59	454	344	3.64	202	2.25
Average $\pm \sigma$	431 $\pm$ 23	326 $\pm$ 23	3.65 $\pm$.34		2.89

* Samples taken from same preparation

** by difference

D. Zirconium Fluoride Hydrolysis Products

In attempting to measure the solubility of the monohydrates in dilute nitric acid it was found that crystalline solids (characterized by distinct X-ray patterns) are formed in neutral or dilute nitric acid

solutions of the tetrafluoride. Although these solids are crystalline and give sharp X-ray diffraction patterns they are physically quite different from the hydrated tetrafluorides. The hydrolysis products have a dendritic plate-like structure and are very bulky. Because of their bulkiness it is difficult to separate completely the occluded mother liquor, and some alteration may take place in their composition during the washing process.

Mellor[8] discussed a dihydrated zirconyl fluoride, $\text{ZrOF}_2 \cdot 2\text{H}_2\text{O}$ as a hydrolysis product of $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$. Zachariasen and Plettinger[3] observed two hydrolysis products, Zr_2OF_6 and ZrOF_2 . None of the solids removed from aqueous solution in this investigation corresponded to the zirconyl fluoride.

A summary of the analytical data for some of the products is given in Table 3. The fluoride-to-zirconium ratio in these compounds is approximately three. The difference between the sum of the zirconium plus the fluoride amounts to nearly two moles of water per mole of zirconium, which is considerably greater than represented by the Zr_2OF_6 compound suggested by Zachariasen.

Elevated temperatures enhance the hydrolysis and determine the product which precipitates. For example, three hydrolysis products (95, 212, and 58) which possess different X-ray diffraction patterns (Table 4) crystallize from solutions of low fluoride-to-zirconium ratio at temperatures of below 90°C , 65 - 100°C and above 95°C , respectively. It was found that the two former compounds could be converted to the latter by heating overnight in an oven at 100°C .

TABLE 3

SUMMARY OF ANALYSES OF HYDROLYSIS PRODUCTS OF ZrF_4

Sample No.	Preparation	Chem Analysis		Wt. Ratios		Mole Ratios		
		mgZr/g	mgF/g	Sample/Dried 100°C		Dry/ign	F/Zr	H ₂ O/Zr
58	1MHN0 ₃ , 55°C	565	350	1.00		1.43	2.97	0.76
73	1MHN0 ₃ , 65°C	489	324	1.09		1.43	3.18	1.97
92	1MHN0 ₃ , 80°C	489	322	1.09		1.42	3.15	1.96
93	2MHN0 ₃ , 80°C	505	329	1.06		1.43	3.13	1.68
95	1MHN0 ₃ , 80°C	487	329	1.10		1.43	3.26	1.93
208	1MHN0 ₃ , 80°C	507	314	1.05		1.44	2.97	1.79
119	1MHN0 ₃ , 80°C	511	327	1.03		1.42	3.07	1.61
211-P	1MHN0 ₃ , 80°C	367	271	1.04		1.43	3.53	4.99
212	1MHN0 ₃ , 80°C	476	328				3.31	2.08
124	H ₂ O, 25°C	506	296	1.10		1.42	2.81	1.98

Note: Nos. 58, 95, and 212 possess unique X-ray patterns; the others are combinations of these.

TABLE 4
HYDROLYSIS PRODUCT X-RAY DATA

(Cu K α Radiation, 1° Slit)

<u>COMPOUND 95</u>		<u>COMPOUND 212</u>		<u>COMPOUND 58</u>	
<u>D</u>	<u>I/I₁</u>	<u>d</u>	<u>I/I₁</u>	<u>d</u>	<u>I/I₁</u>
7.7	100	7.0	100	5.8	100
4.07	2	4.87	1	4.38	36
3.84	8	3.19	4	3.69	29
3.78	4	3.83	1	3.35	37
3.35	1	3.48	5	3.23	6
3.28	3	3.40	3	2.89	11
3.09	1	3.27	3	2.65	14
2.79	1	2.72	1	2.53	3
2.26	1	2.60	1	2.48	6
2.14	1	2.57	1	2.18	4
2.08	1	2.50	1	2.08	11
2.045	1	2.43	1	1.94	10
2.04	1	2.23	1	1.92	4
2.03	1	2.19	1	1.90	6
1.94	1	2.14	2	1.85	10
1.93	1	2.08	1	1.77	6
1.92	2	1.95	1	1.67	7
1.88	1	1.90	1		
1.81	1	1.88	1		
1.68	1	1.74	1		
1.67	1	1.71	1		
1.665	1	1.68	1		
1.64	1	1.67	1		
1.56	1	1.584	1		
1.53	1	1.580	1		
1.45	1				

The hydrolysis products do not lose appreciable weight on being dried at 100° C but come to constant weight. Decomposition at 500° C produces essentially the same ratio of weight change for the several different specimens. The X-ray diffraction patterns for the compounds as prepared show significant differences. On the basis of a fluoride-to-zirconium ratio of three and the thermal decomposition data, the formula for the common compound formed by drying would correspond to approximately $\text{ZrOHF}_3 \cdot 1/2\text{H}_2\text{O}$.

When these systems of zirconium tetrafluoride in dilute hydrofluoric and nitric acid are permitted to remain at 80° C for considerable time

they frequently turn to a stiff colloidal gel. It has not been determined whether this change represents a further hydrolysis to lower fluoride-to-zirconium ratio in the solid phase, a higher degree of hydration, or a polymerization of the solid species.

Limited solubility measurements have been completed with the hydrolysis products. Table 5 summarizes the observed solubility of two samples in 1M, 6M, and 16M nitric acid at 25°C. The data for one are graphically presented in Figure 1 to illustrate that the systems equilibrate slowly and require about two weeks' contact time to give reasonably constant composition of the solution phase. There was only slight change after four weeks. The fact that 6M acid shows greater solvent action perhaps indicates a reaction between the acid ions and the basic salt, which results in an ionic activity dependence not associated with the zirconium tetrafluoride system.

TABLE 5

SOLUBILITY OF BASIC ZIRCONIUM TRIFLUORIDE IN NITRIC ACID

Solid	Nitric Acid Conc.	Grams ZrO ₂ per liter at 25°C						
		Total continuous time, days						
		1	2	6	8	9	10	20
206	1M	15.6	23.4	35.1	38.4	39.2	40.0	42.7
208	1M	18.9	25.3	35.1	39.9	41.2	42.3	44.3
206	6M	20.1	28.0	43.3	50.5	51.9	52.7	55.4
208	6M	22.6	29.0	41.1	48.7	51.0	51.5	--
206	16M	6.7	7.6	9.5	10.4	10.6	10.7	14.1
208	16M	8.0	9.7	11.3	12.6	12.9	12.9	14.7

E. Zirconium - Fluoboric Acid Experiments

The aforementioned hydrolysis products were also produced by the reaction of zirconyl nitrate and fluoboric acid. Digestion at 50°C produced compound-95, while digestion at 80°C overnight resulted in the precipitation of essentially pure 212. Digestion at 100°C gave mixtures of compounds 212 and 58, thereby indicating that compound 58 is not merely a dry decomposition product of 212 and 95.

The reaction of zirconium hydroxide and fluoboric acid to produce boric acid demonstrated the great affinity of fluorine for zirconium.

F. Crystallization of Zirconium Nitrate in Fluoride Solutions

It is possible to dissolve zirconium rapidly in a mixture of concentrated nitric and dilute hydrofluoric acids to form solutions having a fluoride-to-zirconium mole ratio of less than one. In such a solution, containing 1.14M zirconium with fluoride-to-zirconium

FIGURE 1

SOLUBILITY OF BASIC ZIRCONIUM TRIFLUORIDE
IN NITRIC ACID AT 25°C (SOLID NO. 206)

ratio of 0.88, long needlelike crystals began to form after four or five weeks in a tightly sealed polyethylene bottle. The solid phase continued to crystallize for an additional three or four months. Another solution of similar composition had no solid phase present after standing for one month at room temperature, but after seeding with crystals from the first bottle the same type of solid phase continued to form for two or three months. Analysis of these solids showed a nitrate-to-zirconium ratio of approximately two but essentially no fluorine.

Crystalline salts began to appear from solutions such as that described above when they were slowly evaporated at about 80°C to a zirconium concentration of approximately 3M, fluoride concentration of 3M, and a nitrate concentration of 15M. The analyses of several samples of crystals removed from such solutions are given in Table 6. Traces of fluoride were detected in some of these specimens, but not in others. They gave X-ray diffraction patterns similar to that of a spectrographically-pure zirconium nitrate obtained from Mathey-Johnson Limited and also to that of a purified crystalline zirconium nitrate sample prepared in this laboratory. When the evaporation of these solutions is continued to dryness after removal of two or three crops of crystals, the dried residue consists of an unidentified solid phase and an extremely soluble amorphous glasslike material. This latter material can be dissolved in water and dried repeatedly without change in characteristics. (Sample No. 107 in Table 6 gives a chemical analysis of this material. These values are ambiguous, however, as they do not agree with other analyses). Cryoscopic measurements give an apparent molecular weight of approximately 400. The solid in aqueous solution is not appreciably absorbed by either cation or anion exchange resins. The aqueous solution is acidic (pH 2-3) but a precipitate is formed with dilute sulfuric or dilute hydrofluoric acid. Acetone salts out the solid phase from aqueous solution with apparently no change in properties. A mixture of 65 per cent of the dried solid and 35 per cent water is a very viscous clear mass.

TABLE 6

CRYSTALLINE AND NON-CRYSTALLINE SOLID ZIRCONIUM NITRATE SPECIES
FORMED IN THE ZIRCONIUM-HYDROFLUORIC ACID-NITRIC ACID SYSTEM

<u>Composition of Solid Phase as Millimoles/gram</u>				
<u>Sample No.</u>	<u>Zr</u>	<u>F</u>	<u>NO₃</u>	<u>H₂O by difference</u>
104	3.38±0.11	none	6.58±0.46	15.7
105	3.66±0.11	none	7.14±0.50	12.4
114	3.80±0.12	0.31	7.04±0.49	11.7
116	3.76±0.12	0.40	7.12±0.50	11.6
118	3.82±0.12	1.0	6.62±0.46	12.3
106	3.06±0.12	none	5.74±0.39	20.3
107	4.54	5.1	2.6	18.2*
107-S	4.52	2.84	3.35	18.1*

*Non-crystalline.

IV. DISCUSSION

At temperatures above 80°C, zirconium dissolves readily in mixtures of nitric and hydrofluoric acid. If the nitric acid concentration is greater than 8M and the hydrofluoric acid concentration less than 1.5M, stable solutions of relatively high zirconium concentration may be obtained with fluoride-to-zirconium mole ratios of less than two.

At higher hydrofluoric acid concentration and lower nitric acid concentration or lower temperatures, precipitates are likely to form. Because of the metastable nature of the solutions and effect of such factors as time of aging, degree of agitation, presence of minor impurities, rate of temperature change, and presence of crystal nuclei, it is difficult to predict the exact solution behavior. Sometimes solutions will remain clear for days or weeks before solids precipitate.

When the fluoride-to-zirconium mole ratio is maintained at a value of approximately 4, zirconium tetrafluoride separates from the nitric acid solution. The extent of precipitation, and whether the monohydrate or trihydrate or a mixture of the two separates, will depend largely upon the temperature and concentration of nitric acid. Lower nitric acid concentrations and lower temperatures favor the formation of the trihydrate, while higher temperatures and higher nitric acid concentrations favor the monohydrate. Zirconium tetrafluoride tends to hydrolyze into a basic trifluoride at nitric acid concentrations below about 4M. The hydrolysis is enhanced by higher temperatures. The extent of hydration of these compounds is a function of the temperature and composition of the solution phase.

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