

donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health for support of this research.

Funds to purchase the spectrophotometer were made available by the National Science Foundation under Grant No. 22611.

Solubility of Uranyl Fluoride in Hydrofluoric Acid-Nitric Acid Solutions at 25°¹

Leslie M. Ferris

Contribution from the Chemical Technology Division,
Oak Ridge National Laboratory, Oak Ridge, Tennessee. Received July 9, 1965

At 25° the solubility of UO_2F_2 in hydrofluoric acid solutions decreased from 4.82 to 0.15 *M* (60.1 to 3.5 wt. % UO_3) as the HF concentration increased from 0 to 28.4 *M* (0 to 47.4 wt. %). The equilibrium solid phase in this concentration range was $UO_2F_2 \cdot 2H_2O$. In HF- HNO_3 solutions the solubility decreased regularly with increasing hydrofluoric and nitric acid concentrations, but no change in equilibrium solid phase ($UO_2F_2 \cdot 2H_2O$) was noted.

Introduction

Studies of phase equilibria in the system UO_3 -HF- H_2O at 20 to 25° have been made previously,^{2,3} but no similar investigations in the system UO_3 -HF- HNO_3 - H_2O appear to have been made. In the present study, phase relationships in a portion of the system UO_3 -HF- H_2O at 25° were reinvestigated and some studies were made in the system UO_3 -HF- HNO_3 - H_2O .

Experimental Section

Uranyl fluoride was prepared by the reaction of UO_3 with hydrogen fluoride at about 300°. *Anal.* Calcd. for UO_2F_2 : U, 77.3; F, 12.3. Found: U, 75.7; F, 11.4; H_2O , 0.87. The X-ray diffraction pattern of the uranyl fluoride was identical with that reported by Zachariassen⁴; however, the low F:U atom ratio (1.88) suggests the presence of some unreacted UO_3 . All solutions were prepared from reagent grade acids and distilled water.

Excess UO_2F_2 was added to a series of hydrofluoric acid solutions varying in initial HF concentration from 0 to 28 *M* and to HF- HNO_3 solutions (4.68, 9.45, and 14.6 *M* HNO_3) that had HF concentrations as high as 9.3 *M*. Each sample was equilibrated at 25° for at least 10 days, although periodic analyses showed that equilibrium was reached in 4 days or less. After equilibration, samples of the saturated solutions

were obtained by centrifugation at 25° for density measurement and chemical analysis. Wet residues were drained as free of liquid as possible before dissolution in water and analysis.

Uranium was determined by Coulometric titration,⁵

Table I. Solubility of UO_2F_2 in HF- HNO_3 Solutions at 25°

Sample	Density, g./ml.	Concentration, <i>M</i>		
		HF ^a	HNO_3	U
1	2.2969	0.0	0.0	4.82
2	1.6879	1.42	0.0	2.45
3	1.5494	3.56	0.0	1.88
4	1.5029	5.34	0.0	1.69
5	1.4715	6.99	0.0	1.54
6	1.432	9.57	0.0	1.34
7	1.375	12.7	0.0	1.08
8	1.357	13.7	0.0	0.972
9	1.327	15.9	0.0	0.814
10	1.277	17.9	0.0	0.607
11	1.225	21.9	0.0	0.343
12	1.2103	28.4	0.0	0.149
13	1.4525	0.0 ^b	4.65	1.14
14	1.2315	1.86	4.74	0.248
15	1.2151	4.21	4.66	0.149
16	1.2165	5.88	4.74	0.113
17	1.2201	7.71	4.64	0.091
18	1.2264	9.32	4.66	0.075
			Av. 4.68	
19	1.3795	0.0	9.51	0.385
20	1.3009	1.73	9.25	0.056
21	1.3098	4.05	9.30	0.029
22	1.3080	5.63	9.33	0.025
23	1.3210	7.80	9.72	0.019
24	1.3259	9.02	9.62	0.018
			Av. 9.45	
25	1.4610	0.0	14.2	0.305
26	1.3947	1.58	14.4	0.029
27	1.4023	3.66	15.0	0.011
28	1.4018	5.62	14.7	0.0082
29	1.4070	7.88	14.9	0.0051
			Av. 14.6	

^a Defined as the total F concentration minus twice the uranium concentration. ^b HF concentration tabulated as 0 although the F:U atom ratio by analysis was only 1.79.

(1) This research was sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p. 570.

(3) Yu. A. Buslaev, N. S. Nikolaev, and I. V. Tananaev, *Dokl. Akad. Nauk SSSR*, **148**, 832 (1963).

(4) W. M. Zachariassen, *Acta Cryst.*, **1**, 277 (1948).

(5) W. D. Shults, "Uranium, Automatic Controlled Potential Coulometric Titration Method," Method No. 1 219225 and 9 00719225 (1-29-60), ORNL Master Analytical Manual, TID-7015, 1961, Suppl. 3.

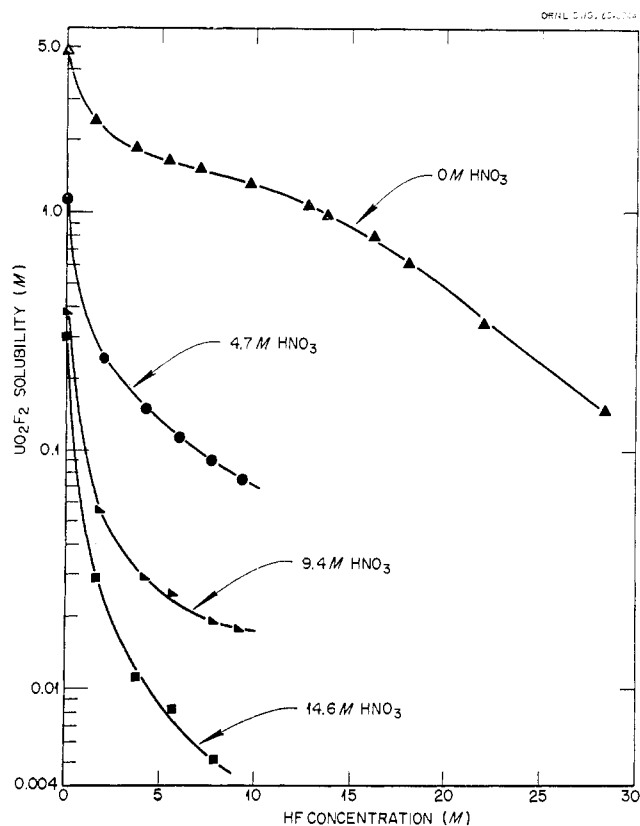


Figure 1. Solubility of UO_2F_2 in HF-HNO_3 solutions at 25° ; HF concentration defined as the total fluorine concentration minus twice the uranium concentration.

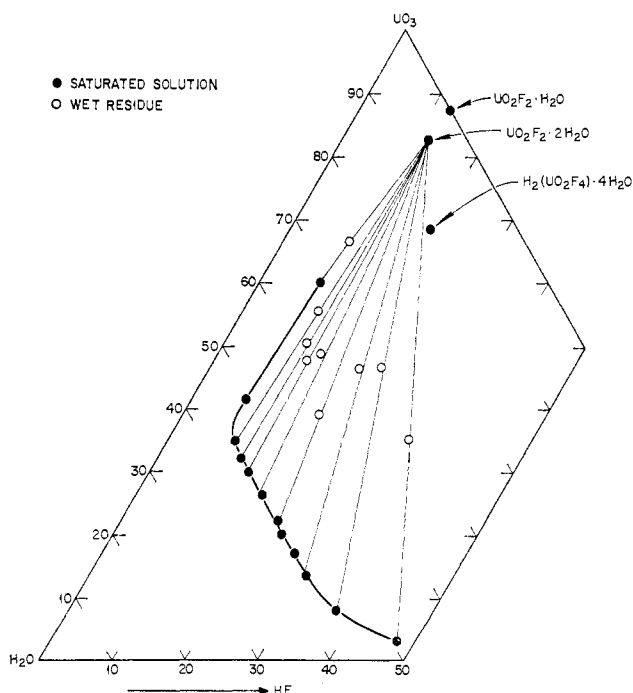


Figure 2. Portion of the system $\text{UO}_3\text{-HF-H}_2\text{O}$ at 25° ; compositions given in wt. %.

fluorine by pyrohydrolysis^{6,7} after drying the sample in the presence of an equimolar mixture of WO_3 and

(6) O. Menis, "Fluoride, Separation by Fusion Pyro Hydrolysis," Methods No. 1 00707 and 9 00651 (10-20-60), ORNL Master Analytical Manual, TID-7015, 1961, Suppl. 3.

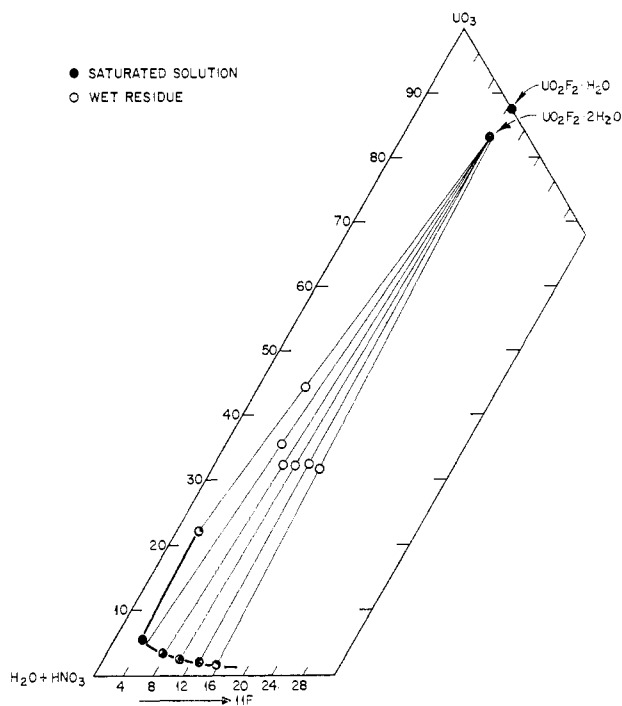


Figure 3. Portion of the $\text{UO}_3\text{-HNO}_3\text{-HF-H}_2\text{O}$ system at 25° ; nitric acid concentration 4.68 M (23.5 wt. %); compositions given in wt. %.

Na_2WO_4 , and nitrogen by a modified Kjeldahl procedure. X-Ray powder patterns were obtained with a Debye-Scherrer 114.59-mm. diameter camera using $\text{Cu K}\alpha$ radiation.

Results

The solubility of UO_2F_2 in hydrofluoric acid solutions at 25° decreased from 4.82 to 0.15 M as the HF concentration (defined as the total F concentration minus twice the uranium concentration) increased from 0 to 28.4 M (Table I, Figure 1). Application of Schreinemakers' wet residue method⁸ indicated that the solid phase at equilibrium was a hydrate of uranyl fluoride, probably $\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O}$, in the region investigated (Table II, Figure 2).

Table II. Portion of the System $\text{UO}_3\text{-HF-H}_2\text{O}$ at 25°

Sample	Compn. of satd. soln., wt. %		Compn. of wet residue, wt. %	
	UO_3	HF	UO_3	HF
1	60.1	8.44	66.8	9.00
2	41.5	7.49	57.4	9.71
3	34.7	9.45	55.8	10.2
4	32.1	11.6	50.7	11.2
5	30.0	13.7	48.0	12.4
6	26.7	17.1	49.1	14.0
7	22.4	21.6	39.3	18.5
8	20.5	23.1	33.8	19.9
9	17.5	26.4	32.2	22.2
10	13.6	29.9	46.7	20.5
11	8.02	36.9	48.4	22.1
30	8.09	36.6	46.6	23.7
12	3.52	47.4	35.4	32.7

(7) A. D. Hortoh, "Inorganic Fluoride, Thoron Indirect Spectrophotometric Method," Method No. 1 212810 and 9 00712810 (R. 8-12-54), ORNL Master Analytical Manual, TID-7015, 1958, Sect. 1.

(8) F. A. H. Schreinemakers, *Z. physik. Chem.*, 23, 417 (1897).

Table III. Portion of the System $\text{UO}_2\text{-HF-HNO}_3\text{-H}_2\text{O}$ at 25°

Sample	Av. HNO_3 concn., M	Compn. of satd. soln., wt. %				Compn. of wet residue, wt. %			
		UO_2	HF	HNO_3	HNO_3 + H_2O	UO_2	HF	HNO_3	HNO_3 + H_2O
13		22.2	2.81	20.2	74.8	44.4	6.48	11.1	49.2
14		5.77	3.83	24.2	90.4	35.6	7.49	13.3	56.9
15	4.68	3.50	7.42	24.2	89.1	32.6	9.12	15.0	58.3
16		2.66	10.0	24.6	87.3	32.2	11.0	15.1	56.8
17		2.14	13.0	24.0	84.9	32.6	12.5	13.2	54.9
18		1.75	15.4	23.9	82.8	31.7	14.4	12.8	53.8
				Av. 23.5					
19		7.98	1.03	43.4	91.0	53.3	6.93	16.8	39.8
20		1.23	2.83	44.8	95.9	33.8	7.30	24.1	58.9
21	9.45	0.63	6.27	44.8	93.1	27.8	8.51	27.8	63.6
22		0.55	8.70	45.0	90.8	23.1	10.4	27.2	66.5
23		0.42	11.9	46.4	87.7	27.3	12.7	28.2	60.0
24		0.40	13.7	45.7	85.9	32.9	14.2	20.3	52.9
				Av. 45.0					
25		5.97	0.81	61.2	93.2	45.2	5.82	24.6	49.0
26		0.59	2.35	65.3	97.1	26.9	6.22	40.8	66.9
27	14.6	0.23	5.26	67.2	94.5	27.9	7.61	39.3	64.5
28		0.17	8.04	66.0	91.8	24.8	7.80	43.2	67.4
29		0.10	11.2	66.5	88.7	23.8	12.0	44.3	64.3
				Av. 65.2					

The solubility of UO_2F_2 in HNO_3 -HF solutions at 25° decreased both with increasing HF and HNO_3 concentrations (Table I, Figure 1). Application of a modified wet residue technique⁹ considering the system as pseudoternary, the components being UO_2 , HF, and ($\text{HNO}_3 + \text{H}_2\text{O}$), indicated that the solid phase at equilibrium was either $\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O}$ or $\text{UO}_2\text{F}_2 \cdot \text{H}_2\text{O}$. Data are given in Table III, and a plot for the series that was 23.5 wt. % HNO_3 is shown in Figure 3.

X-Ray diffraction patterns were obtained for most of the wet residues from each series of samples, including those that contained no nitric acid. The residues were dried only by pressing between filter papers. The patterns each contained the same major lines and were essentially the same as the pattern for the dihydrate reported by Brooks, Garner, and Whitehead.¹⁰

Discussion

The values obtained in this study for the solubility of UO_2F_2 in hydrofluoric acid solutions are in agreement with those of Kunin at 25° , as reported by Katz and Rabinowitch,² and with those of Buslaev, Nikolaev, and Tananaev³ at 20° . However, the results of the various studies are not in complete agreement regarding the composition of the solid phase at equilibrium. It was shown in this study, primarily by X-ray diffraction analyses of the wet residues, that $\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O}$ was

(9) R. D. Thibodeau and M. Adelman, *Can. J. Chem.*, **41**, 531 (1963).
 (10) L. H. Brooks, E. V. Garner, and E. Whitehead, United Kingdom Atomic Energy Authority Report IGR-TN/CA-277, 1958.

the equilibrium solid phase in the UO_2F_2 -HF- H_2O system up to at least 28 M HF, and in the UO_2F_2 -HF- HNO_3 - H_2O system up to at least 9 M HF and/or 15 M HNO_3 . Use of Schreinemakers' wet residue method⁸ indicated that a hydrate of uranyl fluoride was the solid phase at equilibrium; however, it was difficult to distinguish between the mono- and dihydrates by this method, particularly in dilute HF solutions (Figure 2). Fortunately, the X-ray powder pattern of the dihydrate is different from the patterns of the anhydrous salt, the monohydrate, and the trihydrate.¹⁰ No lines unique to UO_2F_2 , $\text{UO}_2\text{F}_2 \cdot \text{H}_2\text{O}$ (which gives the same pattern as the anhydrous salt), or $\text{UO}_2\text{F}_2 \cdot 3\text{H}_2\text{O}$ were observed in the wet residue patterns. Buslaev, Nikolaev, and Tananaev,³ using the wet residue method, reported that at 20° the dihydrate was the solid phase in equilibrium with solutions containing up to about 25 wt. % HF and that the compound $\text{H}_2(\text{UO}_2\text{F}_4) \cdot 4\text{H}_2\text{O}$ existed at the higher HF concentrations. No evidence for the latter compound was found in this study. Kunin,² also using the wet residue method, concluded that $\text{UO}_2\text{F}_2 \cdot \text{H}_2\text{O}$ was the sole solid phase in the system up to about 42 wt. % (25 M) HF; however, Kunin's data can be extrapolated to the dihydrate composition with about the same confidence as to the monohydrate composition.

Acknowledgment. The author is indebted to J. F. Land for this technical assistance in this work. Analyses were provided by the ORNL Analytical Chemistry Division: chemical analyses under the supervision of W. R. Laing and X-ray analyses by R. L. Sherman.