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RI 7785

Bureau of Mines Report of Investigations/ 1973

The K_2HfF_6-K_2ZrF_6-1.25 Percent HF System at 40° C With Other Solubility Curves From 25° to 70° C

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 7785

The K_2HfF_6-K_2ZrF_6-1.25 Percent HF System at 40° C With Other Solubility Curves From 25° to 70° C

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MARCH 3, 1849

UNITED STATES DEPARTMENT OF THE INTERIOR
Rogers C. B. Morton, Secretary

BUREAU OF MINES
Elburt F. Osborn, Director

This publication has been cataloged as follows:

Rhoads, Stanley C

The K_2HfF_6-K_2ZrF_6-1.25 percent HF system at 40° C with other solubility curves from 25° to 70° C. [Washington] U.S. Bureau of Mines [1973]

20 p., illus., tables. (U.S. Bureau of Mines. Report of investigations 7785)

1. Phase diagrams. 2. Hafnium. 3. Zirconium. 4. Fluorine. 5. Solubility. I. U.S. Bureau of Mines. II. Title. (Series)

TN23.U7 no. 7785 622.06173

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THE K_2HfF_6-K_2ZrF_6-1.25 PERCENT HF SYSTEM AT 40° C WITH OTHER SOLUBILITY CURVES FROM 25° TO 70° C

by

Stanley C. Rhoads[1]

ABSTRACT

The Bureau of Mines investigated the complete ternary system K_2HfF_6-K_2ZrF_6-1.25 weight-percent HF at 40° C. In addition, solubility curves have been established at 25°, 30°, 50°, 60°, and 70° C. These solubility data implemented a study of hafnium enrichment in feed solutions for liquid-liquid extraction processes. Selected K_2HfF_6-K_2ZrF_6-1.25 weight-percent HF mixtures were equilibrated in a constant temperature bath. Compositions of the equilibrated solutions and wet residues were established from combined hafnium and zirconium oxide and total fluorine analyses.

All solubility curves were essentially parallel on triangular coordinates. At 40° C, the solid phase of the K_2HfF_6-K_2ZrF_6-1.25 percent HF system is a series of solid solution hydrates with $K_2HfF_6 \cdot H_2O$ and $K_2ZrF_6 \cdot 3H_2O$ segments existing at the respective extremes. Since this system contains $K_2HfF_6 \cdot H_2O$ and $K_2ZrF_6 \cdot 3H_2O$ segments, it is not ideal for simple separation of high-purity K_2HfF_6 from K_2HfF_6-K_2ZrF_6 mixtures by recrystallization. However, it would be useful for producing hafnium-enriched feed solutions from zircon concentrates for liquid-liquid extraction of hafnium from zirconium.

INTRODUCTION

The concurrent recrystallization studies using the K_2HfF_6-K_2ZrF_6-1.25 weight-percent hydrofluoric acid system at 35° C showed that hafnium enrichment could be accomplished. Therefore, the Bureau of Mines studied the K_2HfF_6-K_2ZrF_6-1.25 weight-percent hydrofluoric acid system in this temperature range, specifically at 40° C. Equilibrium conditions for sample mixtures were attained in a constant temperature bath, and the equilibrium K_2HfF_6 and K_2ZrF_6 compositions of solutions and residues were calculated from fluorine and combined oxide contents. Since a complete evaluation of the system at several temperatures was beyond the time available for this investigation, the 40° C solubility diagram was determined first, followed by solubility curves at 25°, 30°, 50°, 60°, and 70° C.

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[1] Research chemist.

The only basic solubility values found in the literature for K_2ZrF_6 were reported by Missenden[2] in 1922. These solubility values were for K_2ZrF_6 containing unknown amounts of K_2HfF_6 in water instead of hydrofluoric acid solutions. From 1922 until 1950 no published data appeared. In 1950 Beaver[3] completed a separation report on the ammonium analogs of K_2HfF_6 and K_2ZrF_6, but no basic data were included. Such a lack of basic data hampered the development research involving this system.

ACKNOWLEDGMENTS

The author deeply appreciates the contribution to this study made by other employees of the Albany, Oreg., Metallurgy Research Center: The assistance of Jack L. Henry, research chemist, for the experimental and apparatus design; and the preparation of the excellent tube rotor design by Ralph Anderson, a former student trainee at the installation.

PROCEDURES AND APPARATUS

Preparation of Components

Three methods were considered for preparing K_2HfF_6. The best product was prepared by the reaction:

$$HfO_2 \cdot 5.28\ H_2O + 4HF + 2(KF \cdot 2H_2O) \rightarrow K_2HfF_6 + 11.28\ H_2O \tag{1}$$

At higher pH the basic salt K_3HfF_7 may form.[4] So an excess of hydrofluoric acid was used to promote the formation of K_2HfF_6. The K_2ZrF_6 preparation involved the following fusion reaction at 1,100° C:

$$ZrO_2 + K_2SiF_6 \rightarrow K_2ZrF_6 + SiO_2. \tag{2}$$

Leaching the minus 200-mesh product twice at 90° C with 1.2 weight-percent hydrofluoric acid removed K_2ZrF_6. Leaching was accomplished using a weight ratio of 4:1 for the dilute hydrofluoric acid-to-ground product. After the leach liquors were cooled to 25° C, the K_2ZrF_6 precipitate was filtered off and then vacuum dried overnight at 90° C. Analysis values for K_2HfF_6 and K_2ZrF_6 are in table 1. The 1.25 weight-percent hydrofluoric acid used was diluted 52 percent reagent grade. The diluted hydrofluoric acid percentage was determined by fluorine analysis.

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[2] Missenden, J. The Salts of Zirconium. Chem. News, No. 124, 1922, pp. 326-327.

[3] Beaver, W. W. Separation of Hafnium From Zirconium by Multiple Recrystallization of Ammonium Fluozirconates. AEC Final Tech. Rept. BBC-54, Aug. 28, 1950, 85 pp.

[4] Elger, Gerald W., Lloyd H. Banning, and Kenneth W. Moser. Producing Hafnium-Enriched Feed Solutions From Zircon. BuMines RI 6802, 1966, p. 10.

TABLE 1. - Analyses of K_2HfF_6 and K_2ZrF_6[1]

Sample	Percent				100 Zr, Zr + Hf	X-ray diffraction constituents	
	Al	Mg	Si	(Zr + Hf)O		Major	Minor
K_2HfF_6..........	<0.01	<0.001	<0.03	53.9	5.8	K_2HfF_6	None
K_2ZrF_6..........	<.3	<.01	<.1	42.3	98.9	K_2ZrF_6	None

[1] Significant percentages of other elements were not detected by spectrographic analyses.

Determining Solubility Curves

The Phase Rule

This study was done on mixtures at equilibrium since meaningful solubility data must be determined at equilibrium. The Phase Rule defines the condition of a system at equilibrium and thereby is applicable to this study. A mathematical expression of the Phase Rule is follows:

$$V = C - P + 2 \tag{3}$$

where V = Variance or degree of freedom of a system

C = number of components

P = number of phases

2 = temperature and pressure factors.

In this system, equilibria is attained at constant temperature and atmospheric pressure, which is considered to be constant. Hence for constant temperature and pressure, equation 3 becomes

$$V = C - P. \tag{4}$$

In this case a quarternary system is effectively reduced to a ternary system by knowing the hydrofluoric acid fluorine content. This system is better understood by examination of figure 1, which represents the quarternary system K_2HfF_6-K_2ZrF_6-HF-H_2O, the shaded triangle being the K_2HfF_6-K_2ZrF_6-1.25 weight-percent HF system.

For graphing purposes the altitudes of the equilateral triangle are divided into 100 equal segments following the Gibbs method. The corners are K_2HfF_6, K_2ZrF_6, and 1.25 weight-percent HF. Two mixed components are a point on their common side. A three component mixture is represented by a point within the triangle. The composition is defined by the perpendicular distance from each side of the triangle.

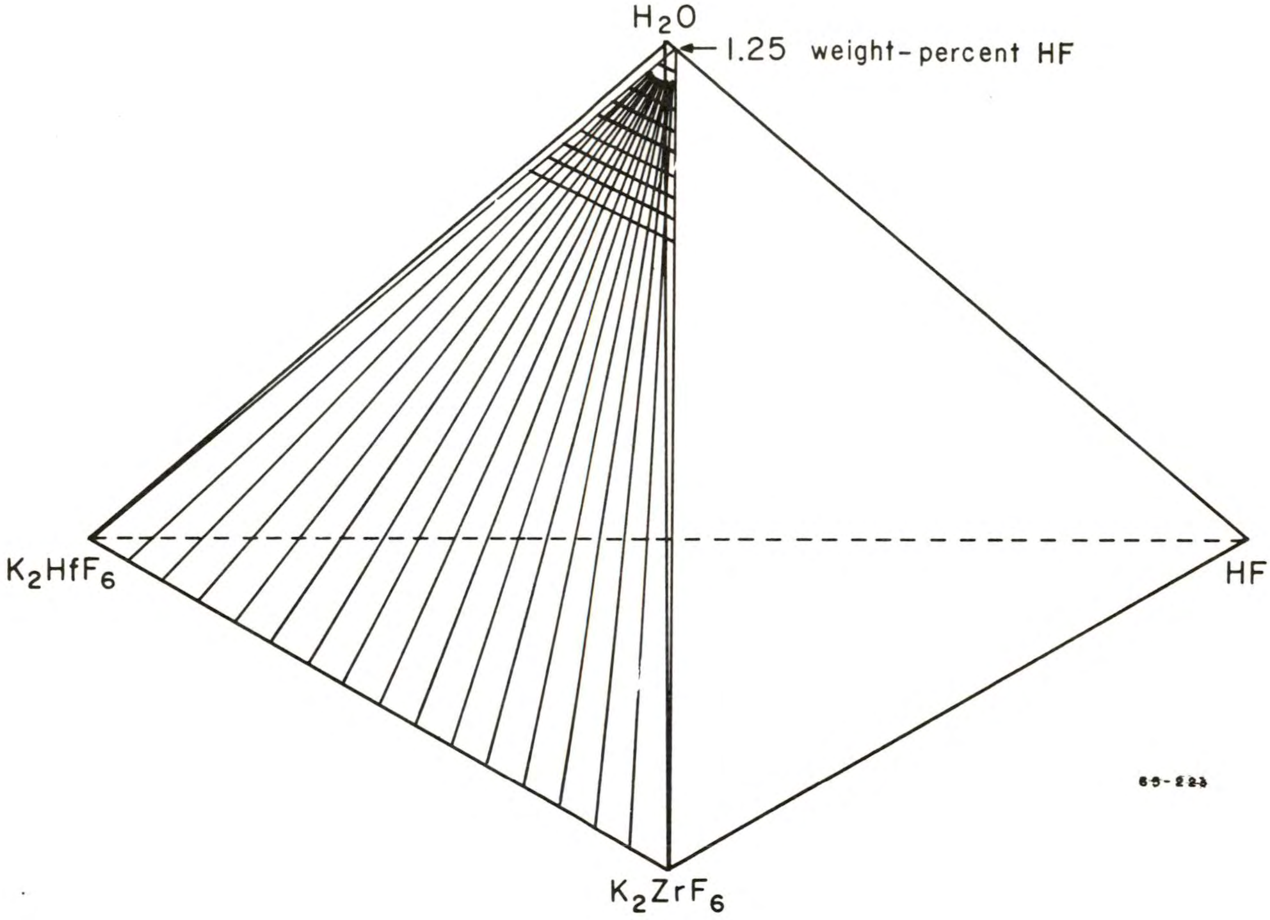

FIGURE 1. - The K_2HfF_6-K_2ZrF_6-1.25 weight-percent HF system.

Apparatus

To assure a constant temperature, continuous mixing, and no contamination of the equilibrium mixture, it was necessary to use a constant temperature bath, a tube rotor, polypropylene test tubes and stoppers, and Pyrex[5] caps.

Functionally, the constant temperature bath consisted of three parts: the plate glass tank, the control devices, and the tank insulation. The 28-inch-square tank was 24 inches deep and was filled to within 2 inches of the top with distilled water. A large mercury bulb thermostat, sensitive to ±0.005° C, maintained the constant temperatures by operating a 500-watt intermittent heater via a mercury relay. The temperature was adjusted by using continuous heaters of 100, 200, or 300 watts or by running cooling water through the cooling coils on the bottom of the bath. A uniform temperature throughout the bath was maintained with a 1,425-rpm circulating pump

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[5] Reference to trade names does not imply endorsement by the Bureau of Mines.

that drew water from the bottom and top of the tank and discharged it into the center of the tank. Continuous addition of distilled water to the tank maintained a uniform water level. The temperature range of the water bath was extended from 60° to 70° C by insulating the tank and cover with a two-layer aluminum foil blanket.

The tube rotor for continuous mixing was designed to provide minimum maintenance and problems. The design of the tube rotor in figure 2 was similar to one used by G. A. Louis.[6] The tube rotor was designed to hold and rotate 24 tubes in the water bath.

An improvised drive train turned the rotor 4 rpm. The drive train consisted of a 1/2 horsepower electric motor, a 1:66 reduction transmission, V-belt pulleys, V-belt, stainless steel sprockets, and stainless steel roller chain. The stainless steel sprockets and roller chain connected the tube rotor and transmission.

The water bath cover shown in figure 2 was assembled with bolts in two sections. The larger cover section supported the tube rotor so that it could be removed without disturbing the smaller section. Most of the control elements were mounted through the smaller section. When test tubes were placed in the stationary test tube rack, on the right in figure 2, the solid phase settled prior to sampling.

To avoid corrosion in the distilled water the tube rotor was fabricated from aluminum plate, stainless steel rod, and brass. The cover for the water bath was made from aluminum plate, the stationary tube rack from aluminum sheet. The tube rotor, bath cover, and stationary tube rack were protected by three coats of Amercoat. Most of the finish is in good condition after 2-1/2 years of service. The quality of the design can be appraised by two facts: the rotor functioned satisfactorily without modification, and no maintenance was required during the entire investigation. Initially, difficulties were encountered in obtaining rotor test tube clamps that would not corrode; however, this problem was overcome by using 600-volt ferrule-type brass fuse clips.

The three equilibrium mixture tube assemblies visible in figure 2 consist of a 100-ml polypropylene test tube closed with a hollow polypropylene stopper, a tapered neoprene sleeve around the test tube, and a Pyrex cap. This tube-sealing arrangement was used to avoid contamination and loss of equilibrium mixtures. Hydrofluoric acid control samples did not react with the polypropylene. These polypropylene test tubes proved to be entirely satisfactory. Tapered neoprene sleeves and Pyrex caps held the hollow stoppers in place and sealed off the space between the equilibrium mixture and the water bath. This space served as a check for leaks from the mixtures or bath. Tubes were identified by markings on the test tube and inside the Pyrex cap.

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[6] Louis, G. A. Phase Rule Study of the System $Al(SO_4)_3$-$ZnSO_4$-H_2O at 25° C. Available for consultation at Mackey Library, University of Nevada, Reno, Nev.

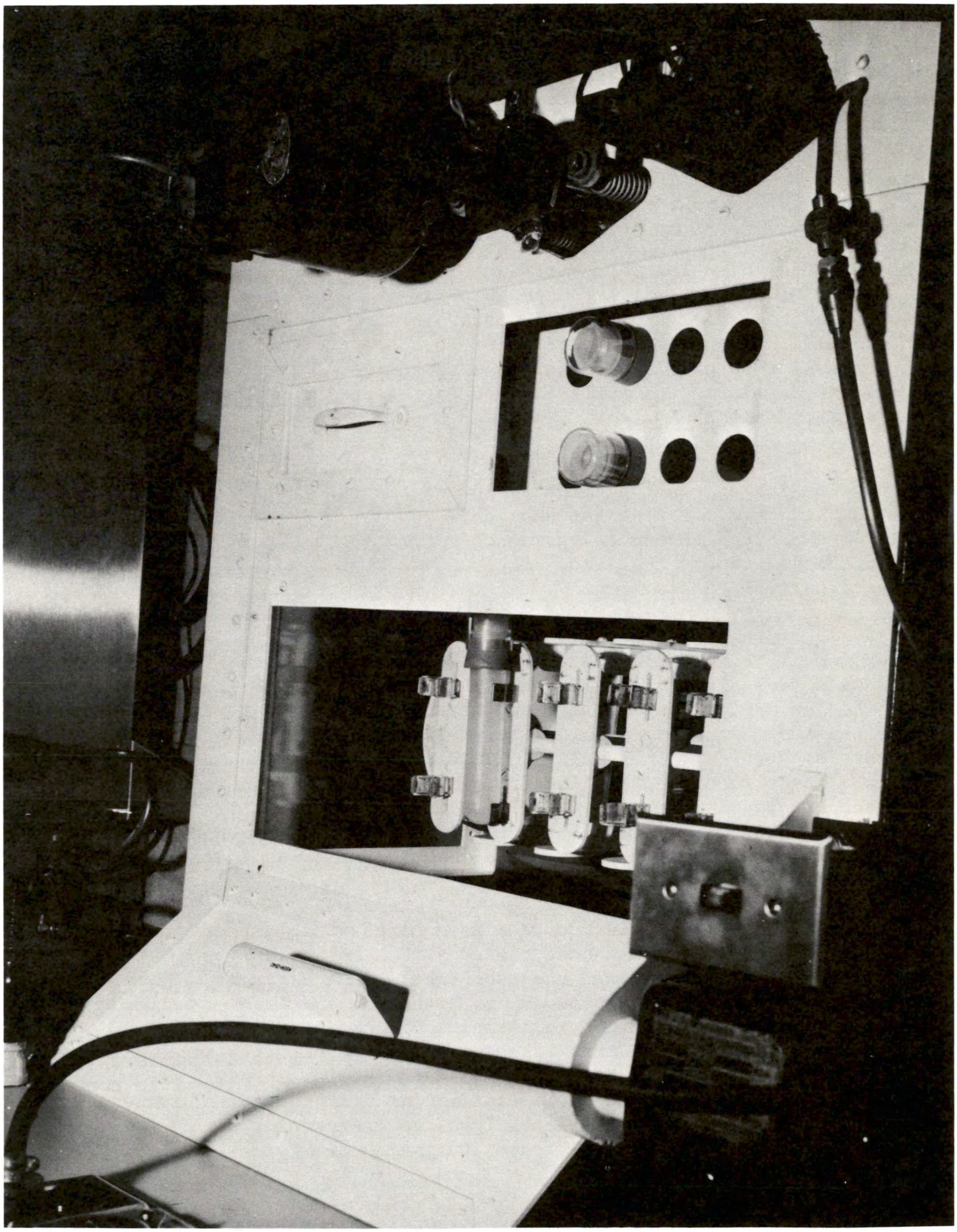

FIGURE 2. - Tube rotor and constant temperature bath.

Equilibrium Determination

The equilibrium determination consisted of mixture preparation and equilibration, sampling for analyses, analysis, and calculation of solution composition.

Mixture preparation and equilibration may be considered as one operation. First, predetermined weight-percentage ratios of K_2HfF_6 and K_2ZrF_6 were accurately weighed and added to each test tube. Subsequently, about 70 milliliters of 1.25 weight-percent hydrofluoric acid were added to each tube and the tube lightly stoppered. The required equilibrium temperature for the various mixtures was reached by dissolving the solid phase at elevated temperatures and placing the tube in a constant temperature bath, or by placing the tube containing the salts and HF solution directly into the stationary tube rack in the constant temperature bath. Equilibrium compositions attained were the same when equilibrium was obtained from unsaturated and supersaturated solutions. After the prepared tubes were placed in the constant temperature bath, thermal equilibrium was reached in about 30 minutes. Then the hollow stopper and Pyrex cap were firmly seated, and the tube assembly was placed on the rotor.

Chemical equilibrium was determined by successive duplicate fluorine analyses. By very careful fluorine analyses it was possible for successive duplicate fluorine analyses to agree within 0.08 percent. This accuracy was accepted as adequate for determining when a mixture reached equilibrium.

Sampling for analysis presented two problems: hydrofluoric acid attacked glass pipettes and weighing bottles, and precipitation of K_2HfF_6 and K_2ZrF_6 presented a problem during sampling and dilution. Both of these problems were overcome by using polypropylene pipettes and weighing bottles, heating pipettes to the test temperature before sampling, and proper dilution and weighing order. Samples for fluorine analysis were weighed and contained 0.03 to 0.08 grams of fluorine, and samples for hafnium zirconium oxide analyses were weighed and contained 0.5 to 1.0 grams of hafnium plus zirconium. These analyses were used to establish solid and liquid phase compositions.

Blake's[7] modified Willard and Winter method required phosphoric acid and 1:1 sulfuric acid using a distillation temperature range of 150° to 155° C to release fluorine, as HF, from hafnium and zirconium complexes. The only significant change from Blake's technique was improved distillation temperature control, achieved by monitoring the distillation temperature with a potentiometer. Since another acid fraction distilled from the mixture at about 160° C, the distillation temperature controls avoided possible contamination of the distillate by the higher boiling fraction. Sufficiently accurate distillation temperature control was obtained by using 0° to 600° C Pyrovane controllers set for a 3° to 5° C temperature range. The controllers and distillation apparatus are shown in figure 3.

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[7] Blake, H. E., Jr. Fluorine Analyses. BuMines RI 6314, 1963, 29 pp.

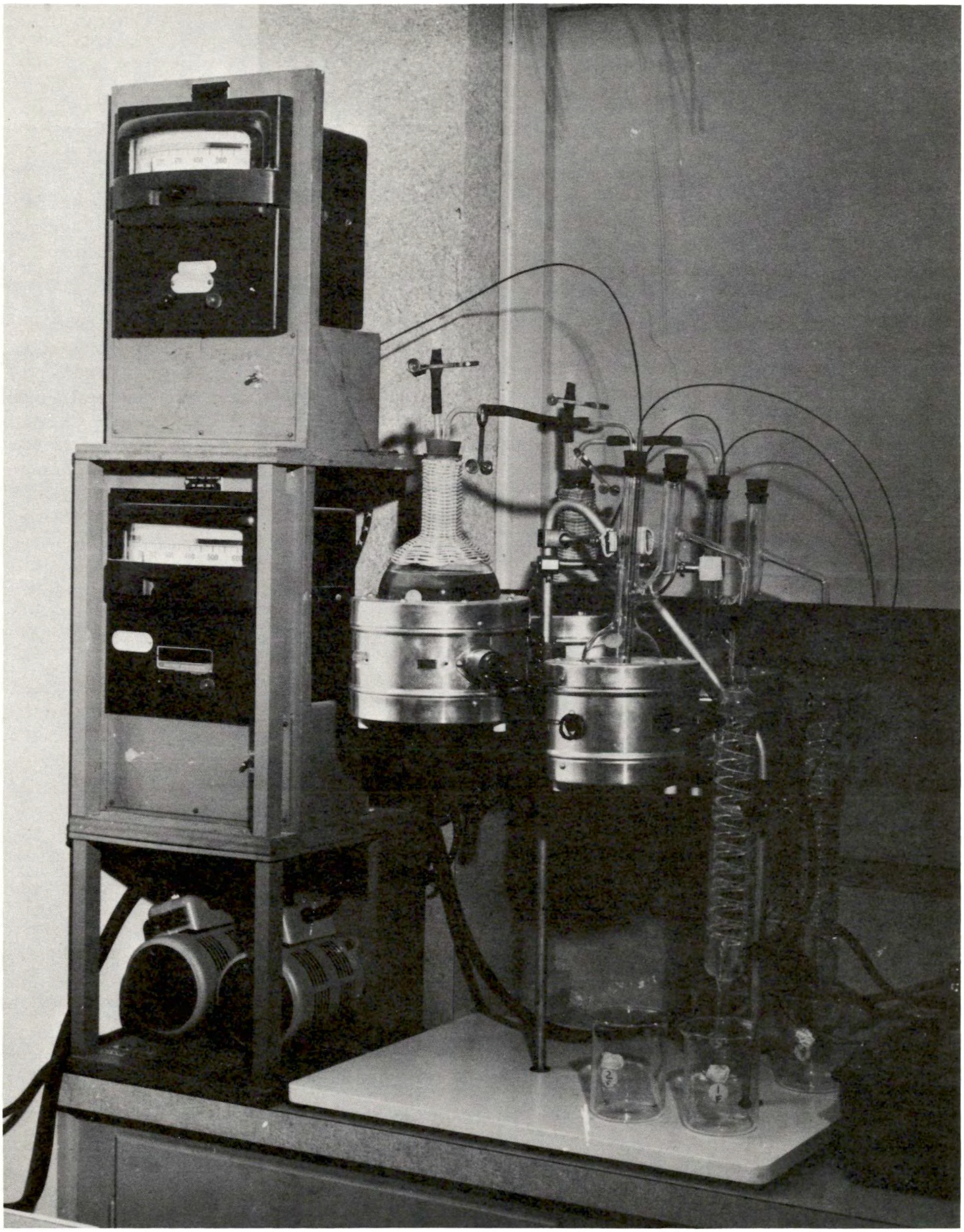

FIGURE 3. - Distillation apparatus.

The method used for hafnium-zirconium analysis involved fuming the sample with sulfuric acid to remove fluorine, precipitation of hydrous hafnium and zirconium oxides with ammonium hydroxide, dissolving that precipitate in dilute hydrochloric acid followed by reprecipitation of hafnium and zirconium as mandelates, and igniting those mandelates to their oxides. These analyses were performed in duplicate. Average combined oxide contents and fluorine contents were used to calculate compositions of equilibrated solutions.

Calculation of K_2HfF_6 and K_2ZrF_6 solution compositions were accomplished by nomographic extrapolation of hydrofluoric acid fluorine and subsequent calculation of the percent K_2HfF_6 and K_2ZrF_6 by simultaneous equations. To establish solubility curves these solution compositions were plotted on triangular coordinates. These plotted values were compared with hydrofluoric acid fluorine contents obtained by extrapolation.

Figure 4 is a scaled-down version of a 16- by 20-inch nomograph that was used to extrapolate the fluorine percentage of the hydrofluoric acid in solution samples at equilibrium. These percentages are based on 1.25 weight-percent hydrofluoric acid containing 1.18 percent fluorine, and 100 nomograph

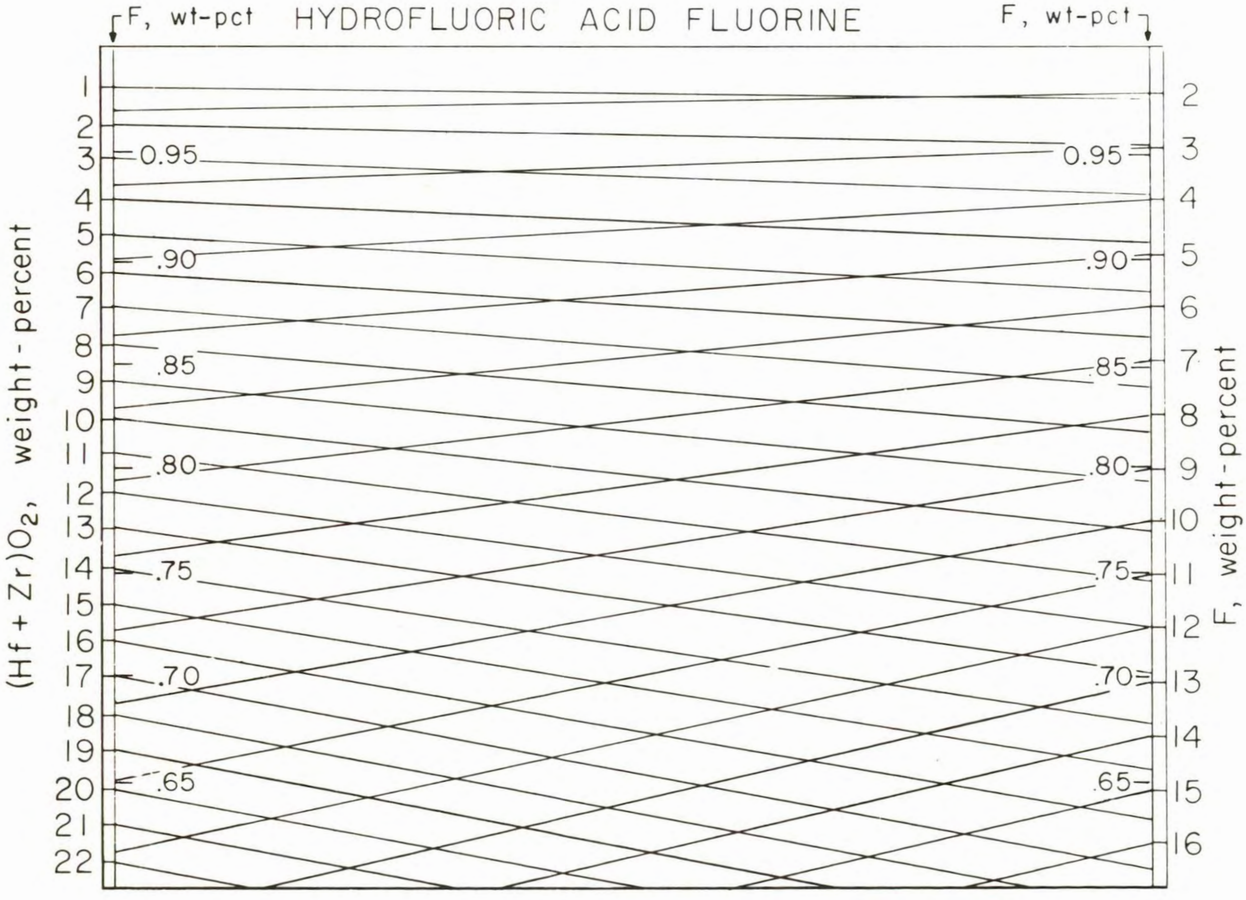

FIGURE 4. - Nomograph for hydrofluoric acid fluorine.

units equaling 1.18 percent fluorine. These nomographic extrapolations were accurate for obtaining hydrofluoric acid fluorine values, but would not provide accurate extrapolation values for K_2HfF_6 and K_2ZrF_6 contents.

The hydrofluoric acid fluorine was determined using the nomograph by (1) finding the intersection of the lines representing the total fluorine and $(Hf + Zr)O_2$ analysis values, (2) then projecting a line across the nomograph parallel to the horizontal axis to a vertical axis decimal scale, and (3) multiplying the extrapolated decimal factor by 1.18 to yield the hydrofluoric acid fluorine content.

Simultaneous equations were accurate for calculating K_2HfF_6 and K_2ZrF_6 weight-percents in solution. The K_2HfF_6 and K_2ZrF_6 percentages were calculated from total fluorine, hydrofluoric acid fluorine, and combined hafnium-zirconium oxides content. The simultaneous equations for calculating K_2HfF_6 and K_2ZrF_6 are as follows:

$$HfO_2/K_2HfF_6\ X + ZrO_2/K_2ZrF_6\ Y = \text{(weight-percent combined oxides), and} \quad (5)$$

$$6F/K_2HfF_6\ X + 6\ F/K_2ZrF_6\ Y = \text{(total weight-percent fluorine) minus (weight-percent HF fluorine),} \quad (6)$$

where X = weight-percent K_2HfF_6,

and Y = weight-percent K_2ZrF_6.

The two simultaneous equations reduce to:

$$0.2285\ X + 0.1749\ Y = 0.4023\ \text{(weight-percent combined oxides), and} \quad (7)$$

$$0.1337\ X + 0.1749\ Y = 0.4348\ [\text{(total weight-percent fluorine) minus (weight-percent HF fluorine)}]. \quad (8)$$

The calculated K_2HfF_6 and K_2ZrF_6 percentages were plotted on triangular coordinates and the percentage hydrofluoric acid fluorine determined for comparison with nomographically extrapolated percent hydrofluoric acid fluorine. For specific equilibrium conditions, K_2HfF_6 and K_2ZrF_6 solution compositions define points that, when connected, form a solubility curve.

Determination of a Solubility Diagram

A solubility diagram may be determined by tielines between corresponding solubility curve points and residue composition points projected to the residue composition points whether they are hydrous or anhydrous. The residue compositions were determined by Schreinmakers' method[8] of wet residues, and the isotherm was displayed on triangular coordinates. The wet residue is the solid equilibrium product that is wet with the equilibrated solution.

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[8] Schreinmakers, F. A. H. Graphische Ableitungen aus den Lösung-Isotherment eines Doppelsalzes und seiner Komponenten und nogliche Formen der Umwandlungs Kurve (Graphical Deductions From the Solution Isotherms of a Double Salt and Its Components). Z. Physik. Chem. No. 11, 1893, pp. 75-109.

Schreinmakers' wet residue method is illustrated in figure 5 with the composition of the liquid phase as point L, the wet residue composition as point W, and extrapolation of the tieline from point L through point W establishing the residue composition at point R. The wet residue analysis involved dissolving the wet residue, sampling the dissolved wet residue, analyzing for fluorine and hafnium-zirconium oxides in duplicate, and calculating wet-residue compositions. All sampling and dilutions were by weight. Solution and wet residue compositions were calculated by the same method.

The dry-residue composition was determined by plotting the compositions of the respective solutions and wet residues on triangular coordinates, and extending tielines from the respective solution points through the wet

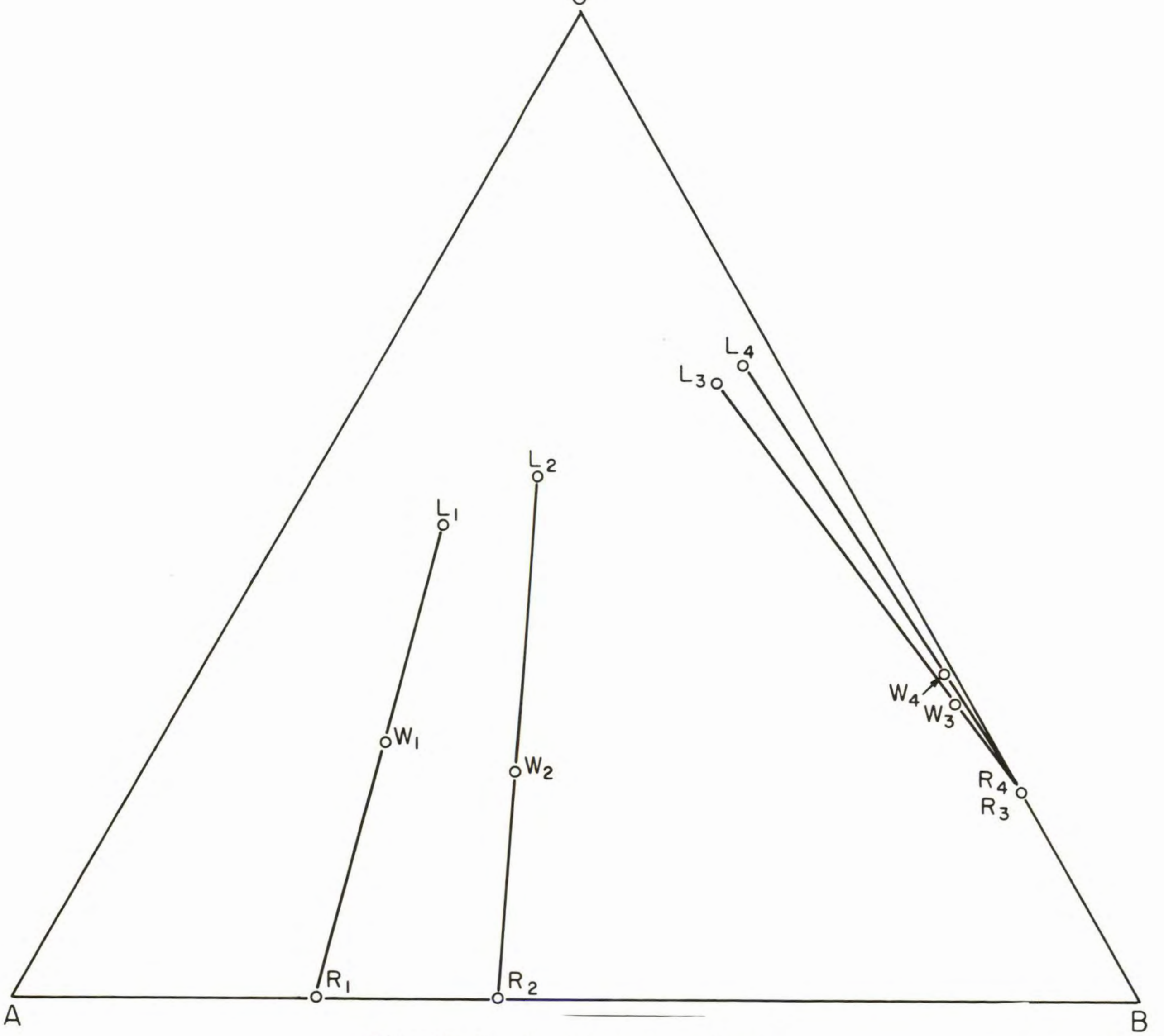

FIGURE 5. - Residue extrapolation.

residue points to a line connecting $K_2HfF_6 \cdot H_2O$ and $K_2ZrF_6 \cdot 3H_2O$. Intersection of a tieline with the line connecting $K_2HfF_6 \cdot H_2O$ and $K_2ZrF_6 \cdot 3H_2O$ defined the composition of the residual salt. Wet residue compositions were determined for this system at 40° C.

DATA AND DISCUSSION

The K_2HfF_6-K_2ZrF_6-1.25 Weight-Percent HF System at 40° C

This system was established by determining liquid and wet-residue compositions of a number of equilibrium mixtures. These compositions were calculated from total fluorine and total oxide contents for the various equilibrium mixtures. The liquid phase of the equilibrium mixtures were analyzed first to determine that equilibrium was established. Then the wet residues were analyzed.

The 40° C solubility curve shown in figure 6 is based on calculated experimental values in table 2 and establishes a solubility curve for this

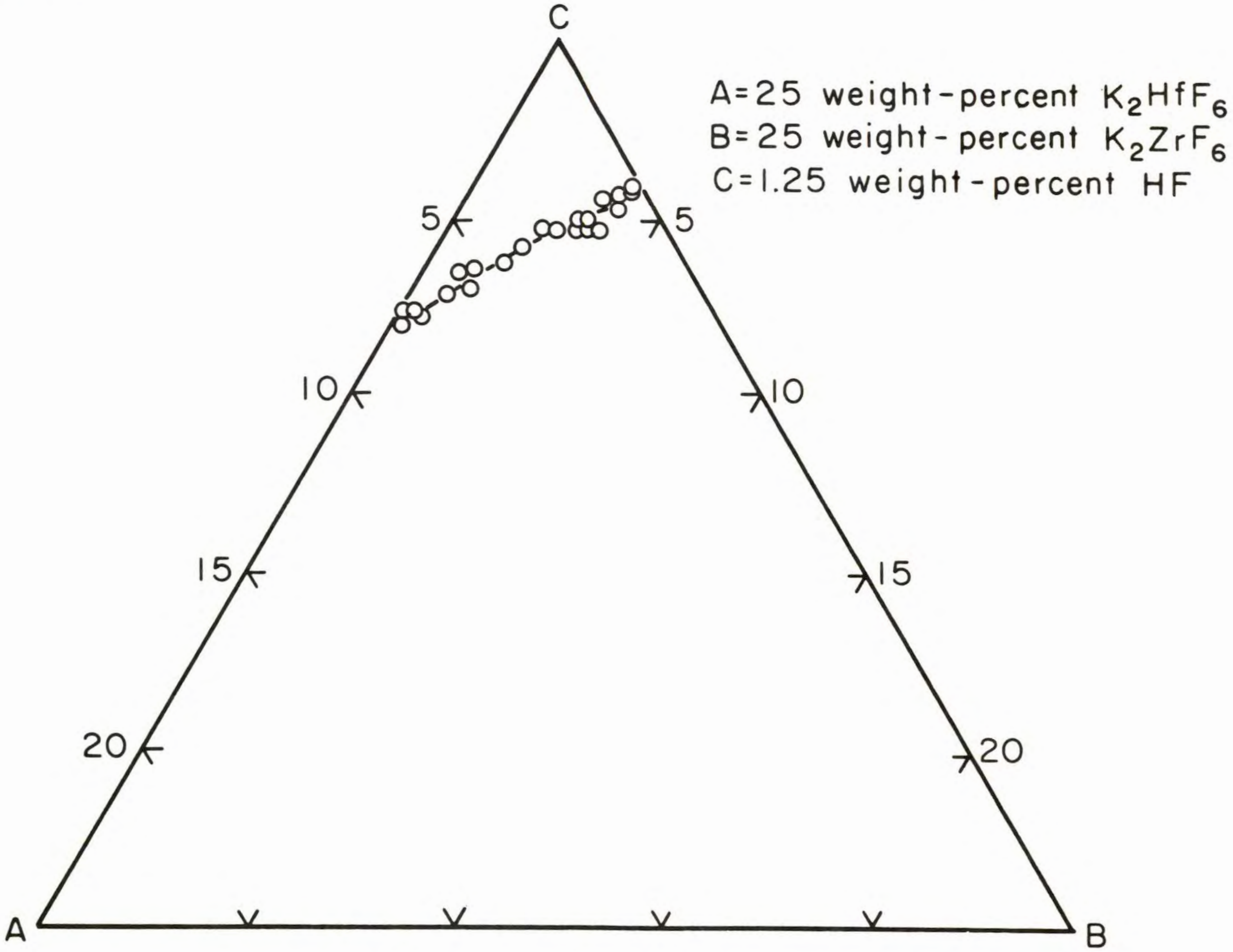

FIGURE 6. - The K_2HfF_6-K_2ZrF_6-1.25 weight-percent HF solubility curve at 40° C.

system at 40° C. Compositions on the solubility curve and compositions of corresponding wet residues were determined to establish tielines for the K_2HfF_6-K_2ZrF_6-1.25 weight-percent HF system at 40° C.

TABLE 2. - K_2HfF_6-K_2ZrF_6-1.25 weight-percent HF solubility data at 40° C

Sample tube No.	Weight-percent						
	Total F	$(Hf+Zr)O_2$ combined oxides	Nomograph, F from HF	Difference in F[1] from HF	Simultaneous equations: F from HF	Simultaneous equations: K_2HfF_6	Simultaneous equations: K_2ZrF_6
I:5	3.534	4.53	1.022	0.001	1.023	7.703	0.357
I:6	3.401	4.31	1.026	.001	1.027	7.397	.250
I:7	3.396	4.03	1.030	.002	1.032	6.251	1.103
I:8	3.094	3.54	1.041	.002	1.043	5.607	.818
I:9	2.980	2.73	1.050	.003	1.053	2.733	2.709
I:10	2.820	2.14	1.062	0	1.062	1.018	3.592
I:11	2.741	1.86	1.066	0	1.066	.211	4.003
I:12	1.113	0	1.113	-	-	-	-
I:13	3.570	4.606	1.021	.001	1.022	7.856	.331
I:14	3.383	4.327	1.026	.002	1.028	7.553	.086
I:15	3.436	4.307	1.026	.001	1.027	7.224	.469
I:16	3.405	3.907	1.030	.003	1.033	5.687	1.558
I:17	3.172	3.550	1.037	.003	1.040	5.273	1.277
I:18	3.183	3.371	1.042	.003	1.045	4.486	1.893
I:19	3.066	3.073	1.047	0	1.047	3.781	2.129
I:20	2.971	2.612	1.053	.003	1.050	2.288	3.019
I:21	2.984	2.582	1.053	.002	1.055	2.100	3.195
I:22	2.889	2.445	1.056	.001	1.057	1.968	3.052
I:23	2.975	2.539	1.054	.001	1.055	1.963	3.275
I:24	2.930	2.467	1.054	.002	1.056	1.865	3.238
I:25	2.911	2.485	1.055	.002	1.057	2.033	3.060
I:26	2.910	2.452	1.055	.001	1.056	1.897	3.162
I:27	2.923	2.495	1.055	.001	1.056	2.020	3.100
I:28	2.923	2.403	1.056	.001	1.057	1.634	3.392
I:29	2.899	2.433	1.057	.003	1.060	1.877	3.145
I:30	2.936	2.506	1.055	0	1.055	2.007	3.141
I:31	2.935	2.229	1.060	.001	1.061	.859	4.005
I:32	2.789	2.137	1.062	.001	1.063	1.148	3.416
I:33	2.822	2.069	1.064	.002	1.062	.717	3.822
I:34	2.810	2.033	1.064	0	1.064	.619	3.867
I:35	2.817	1.974	1.064	0	1.064	.337	4.100
I:36	2.808	1.894	1.065	.001	1.066	.433	3.792

[1] (Simultaneous equation fluorine) - (nomograph fluorine).

The wet-residue compositions shown in figure 7 are from calculated compositions presented in table 3. The tielines in figure 7 begin at specific solution compositions and extend through the corresponding wet-residue points to the hydrated residue compositions. These tielines indicate a system of continuous solid solutions except for a very small region of K_2ZrF_6/K_2HfF_6 ratios of more than 93:7 and a very small K_2HfF_6-rich region. The $K_2HfF_6 \cdot H_2O$

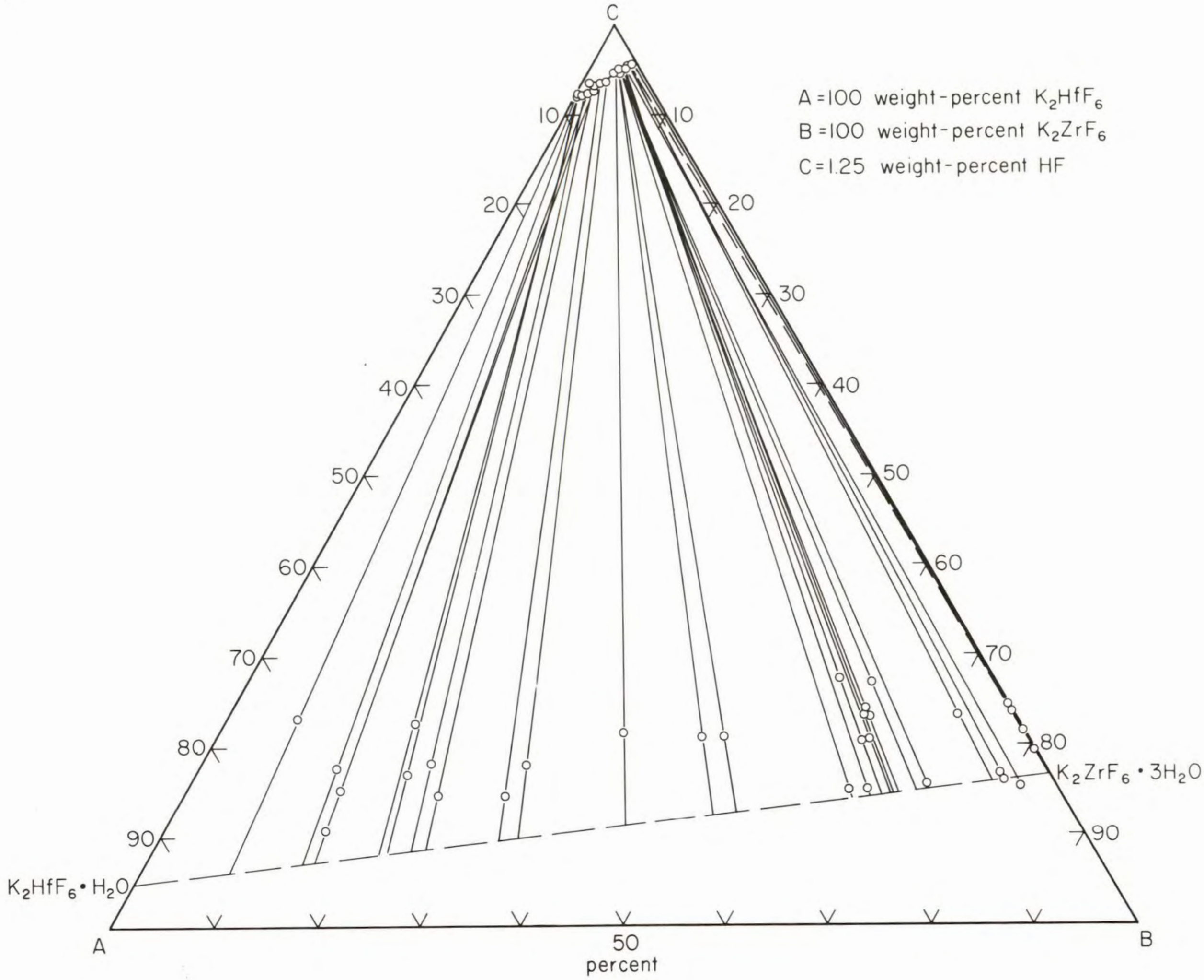

FIGURE 7. - The K_2HfF_6-K_2ZrF_6-1.25 weight-percent HF system at 40° C.

and $K_2ZrF_6 \cdot 3H_2O$ hydrates exist in this system at 40° C. This conclusion is based on two facts:

1. Differential thermal analysis (DTA) heating curve peaks (fig. 8) from 200° to 400° C do not occur in the corresponding cooling curves (fig. 9). This behavior is indicative of crystalline water of hydration.

2. Extrapolated tielines intersect the K_2ZrF_6-1.25 weight-percent HF side of the graph near $K_2ZrF_6 \cdot 3H_2O$ in figure 7.

The wet residue analyses and DTA peaks in figure 8 indicate that K_2ZrF_6 is a trihydrate and K_2HfF_6 is a monohydrate. The progression of DTA water of hydration peaks from 95 percent K_2HfF_6 5 percent K_2ZrF_6 to 3 percent K_2HfF_6 97 percent K_2ZrF_6 graphically illustrates the removal of crystalline hydrated water as the temperature increases. The DTA curves, the wet residue analyses, and the expected chemical similarity of hafnium and zirconium compounds indicate that the K_2HfF_6 hydrate does exist. Tielines from solution compositions through wet residue compositions did not indicate the K_2HfF_6 hydrate since the purest K_2HfF_6 available contained 5 percent K_2ZrF_6. The solid phase of this 40° C isotherm consists of continuous solid solution hydrates. Four other solubility curves were determined to see if the solubility curves were similar to the 40° C curve, and if time permitted, to complete one or more of these systems if significant differences were observed in these solubility curves.

TABLE 3. - K_2HfF_6-K_2ZrF_6-1.25 weight-percent HF wet residue data at 40° C

Sample tube No.	Weight-percent			
	Total F	$(Hf+Zr)O_2$ combined oxides	Simultaneous equations	
			K_2HfF_6	K_2ZrF_6
I:5	25.721	41.435	58.921	18.330
I:6	26.788	45.001	68.931	13.454
I:7	29.295	48.922	73.701	16.241
I:8	27.517	43.583	59.565	22.428
I:9	28.148	39.396	39.051	39.599
I:10	32.626	39.476	18.563	66.549
I:11	33.549	35.109	0.00	80.757
I:13	24.543	42.774	70.076	6.837
I:14	27.650	44.392	62.344	20.659
I:15	22.068	35.363	50.478	15.393
I:16	27.657	46.191	69.867	14.969
I:17	28.742	45.249	60.748	24.716
I:18	29.324	44.328	54.170	31.192
I:19	28.190	41.901	49.361	31.892
I:20	29.095	38.659	31.584	47.659
I:21	30.736	36.682	15.641	63.940
I:22	32.335	39.561	20.272	64.512
I:23	28.681	34.028	14.087	59.866
I:24	29.146	38.224	29.344	49.585
I:25	28.491	33.375	12.096	60.966
I:26	28.020	33.566	15.085	57.499
I:27	29.842	35.351	14.230	62.723
I:28	30.598	36.677	16.271	63.106
I:29	29.731	35.351	14.744	62.051
I:30	32.845	38.248	12.407	71.768
I:31	33.459	37.132	4.887	79.025
I:32	33.908	37.293	3.475	81.241
I:33	30.504	33.989	5.456	71.053
I:34	31.220	33.068	0.00	76.062
I:35	30.846	32.759	0.00	75.351
I:36	31.762	33.977	0.00	78.153

Solubility Curves at 25°, 30°, 50°, 60°, and 70° C

The solubility curves at 25°, 30°, 40°, 50°, 60°, and 70° C shown in figure 10 are from calculated analytical values in tables 2, 4, and 5 to 8. The solubility curves, which are essentially parallel at 25°, 30°, 40°, 50°, 60°, and 70° C, indicate temperature dependence in this system at these temperatures.

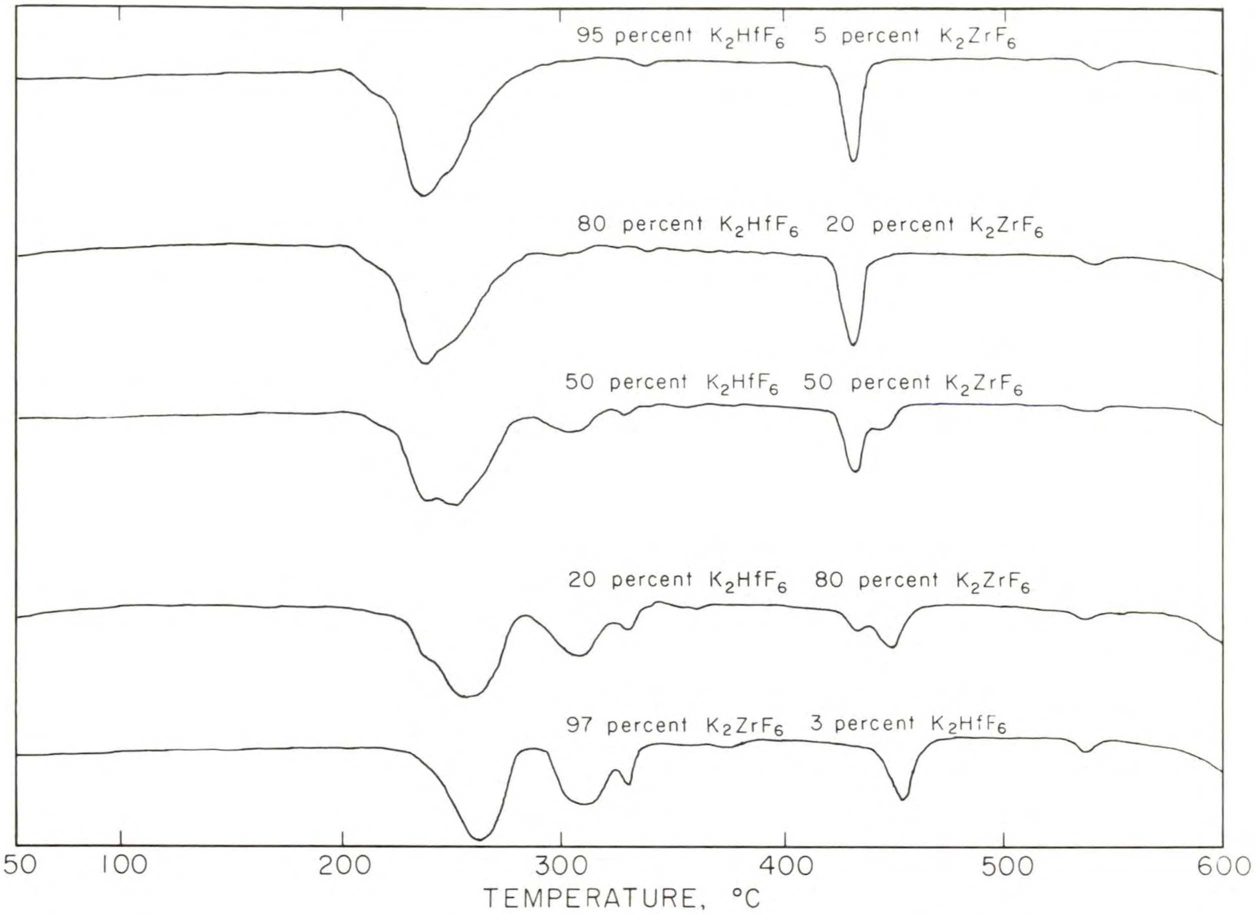

FIGURE 8. - Differential thermal analysis curves for K_2HfF_6 and K_2ZrF_6 mixtures, heating cycle.

TABLE 4. - K_2HfF_6-K_2ZrF_6-1.25 weight-percent HF solubility data at 25° C

Sample tube No.	Weight-percent						
	Total F	$(Hf+Zr)O_2$ combined oxides	Nomograph, F from HF	Difference in F[1] from HF	Simultaneous equations		
					F from HF	K_2HfF_6	K_2ZrF_6
IV:2	2.564	2.548	1.208	0.002	1.210	4.594	0.000
IV:3	2.619	2.502	1.208	.008	1.216	4.147	.338
IV:5	2.398	1.751	1.224	.001	1.225	2.045	1.355
IV:6	2.367	1.693	1.224	.002	1.222	1.942	1.357
IV:8	2.277	1.448	1.229	.003	1.232	1.338	1.583
IV:9	2.326	1.409	1.229	.002	1.231	.947	2.003
IV:11	2.260	1.227	1.232	.003	1.235	.492	2.180
IV:12	2.296	1.289	1.231	.003	1.234	.585	2.200
IV:14	2.239	1.046	1.235	.003	1.238	.00	2.406
IV:15	2.202	1.042	1.236	.002	1.238	.00	2.397
IV:16	1.267	-	1.267	-	-	-	-
IV:17	1.269	-	1.269	-	-	-	-

[1] (Simultaneous equation fluorine) - (nomograph fluorine).

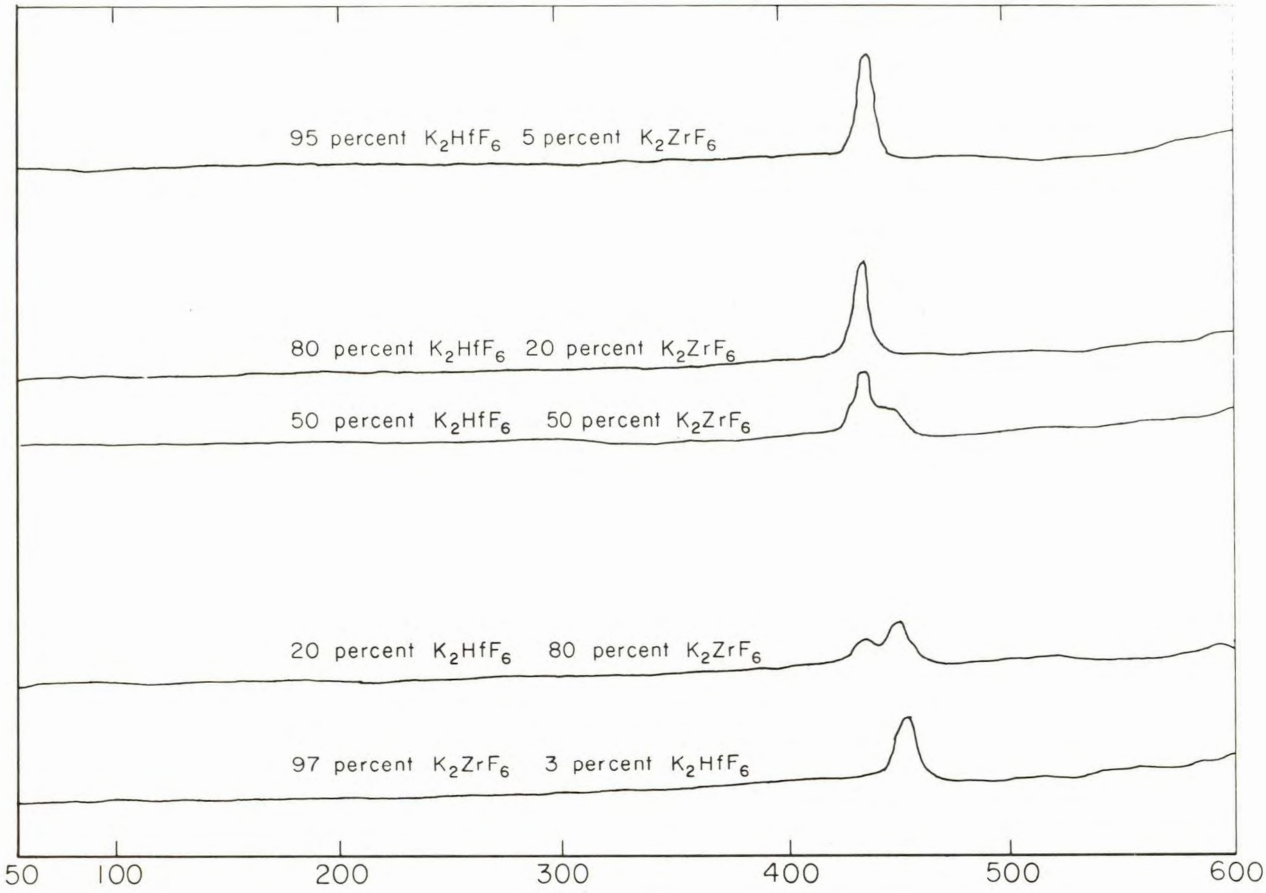

FIGURE 9. - Differential thermal analysis curves for K_2HfF_6 and K_2ZrF_6 mixtures, cooling cycle.

TABLE 5. - K_2HfF_6-K_2ZrF_6-1.25 weight-percent HF solubility data at 30° C

Sample tube No.	Weight-percent						
	Total F	$(Hf+Zr)O_2$ combined oxides	Nomograph, F from HF	Difference in F[1] from HF	Simultaneous equations		
					F from HF	K_2HfF_6	K_2ZrF_6
III:1	2.898	3.063	1.119	0.000	1.119	4.839	0.724
III:2	2.882	3.081	1.117	.004	1.121	4.980	.581
III:4	2.567	2.126	1.134	.000	1.134	2.449	1.690
III:5	2.608	2.209	1.132	.001	1.133	2.604	1.679
III:7	2.475	1.690	1.140	.003	1.143	1.049	2.517
III:8	2.402	1.793	1.140	.001	1.141	1.821	1.746
III:10	2.412	1.480	1.145	.000	1.145	.469	2.791
III:11	2.461	1.511	1.145	.001	1.146	.377	2.983
III:13	2.389	1.255	1.148	.002	1.150	.00	2.887
III:14	2.368	1.237	1.151	.000	1.151	.00	2.845
III:16	1.184	-	1.184	-	-	-	-

[1] (Simultaneous equation fluorine) - (nomograph fluorine).

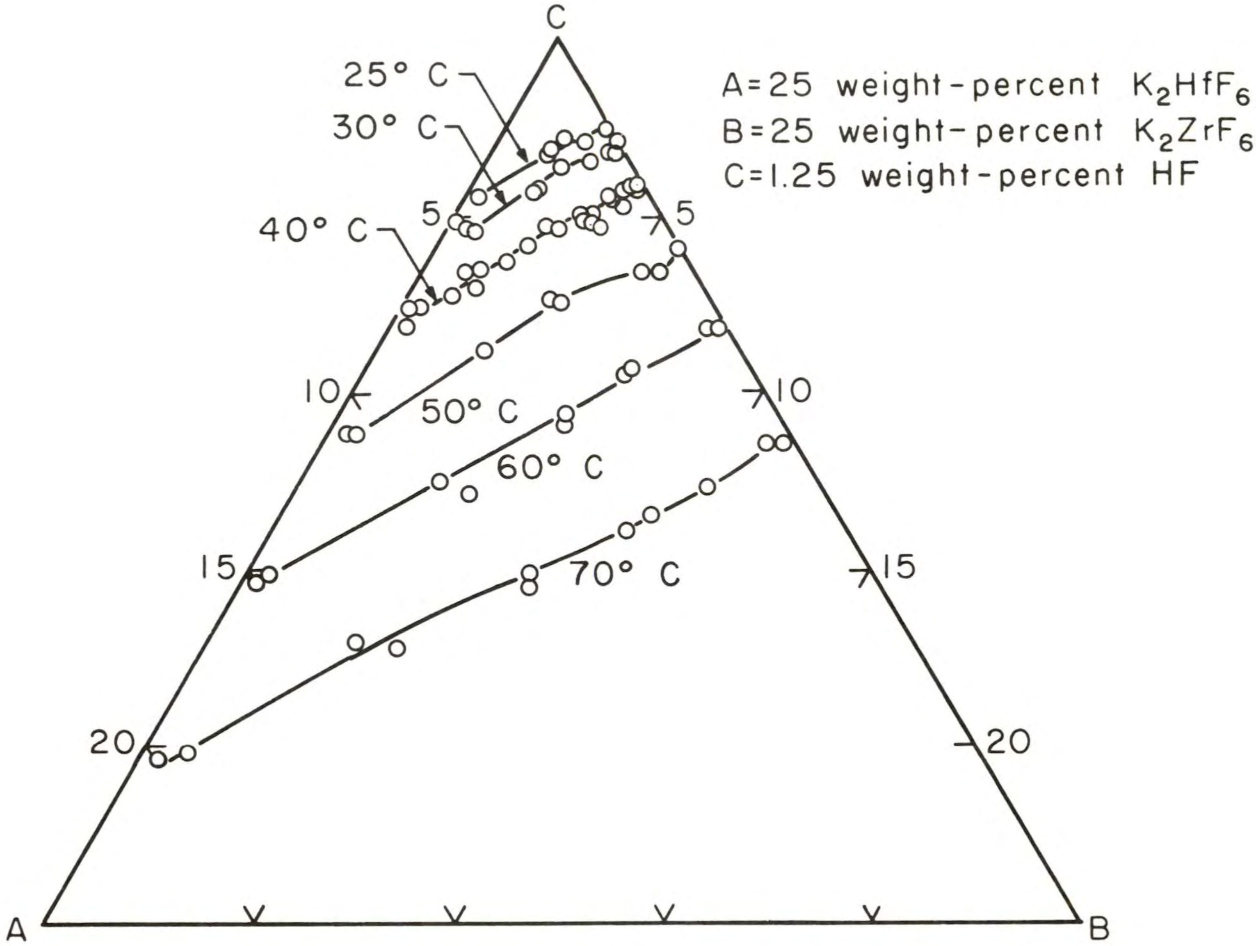

FIGURE 10. - Solubility curves at 25°, 30°, 40°, 50°, 60°, and 70° C for the K_2HfF_6-K_2ZrF_6-1.25 weight-percent HF system.

TABLE 6. - K_2HfF_6-K_2ZrF_6-1.25 weight-percent HF solubility data at 50° C

Sample tube No.	Weight-percent						
	Total F	$(Hf+Zr)O_2$ combined oxides	Nomograph, F from HF	Difference in F[1] from HF	Simultaneous equations		
					F from HF	K_2HfF_6	K_2ZrF_6
V:1	4.475	6.315	0.990	0.008	0.998	10.814	0.397
V:2	4.521	6.316	.992	.005	.997	10.617	.657
V:3	3.980	4.691	1.020	.003	1.023	6.331	2.519
V:4	4.034	4.725	1.021	.001	1.022	6.232	2.727
V:5	3.757	3.831	1.035	.005	1.040	3.773	3.882
V:6	3.721	3.704	1.037	.002	1.035	3.408	4.067
V:7	3.606	3.060	1.048	.001	1.049	1.253	5.401
V:8	3.646	3.029	1.048	.002	1.050	.939	5.741
V:9	3.486	2.553	1.056	.001	1.057	<.01	5.872
V:10	3.449	2.553	1.057	.000	1.057	<.01	5.872
V:11	1.100	-	1.100	-	-	-	-
V:12	1.145	-	1.145	-	-	-	-

[1] (Simultaneous equation fluorine) - (nomograph fluorine).

TABLE 7. - K_2HfF_6-K_2ZrF_6-1.25 weight-percent HF solubility data at 60° C

Sample tube No.	Weight-percent						
	Total F	$(Hf+Zr)O_2$ combined oxides	Nomograph, F from HF	Difference in F[1] from HF	Simultaneous equations		
					F from HF	K_2HfF_6	K_2ZrF_6
VI:1	5.741	8.665	1.008	0.006	1.014	15.063	0.252
VI:2	5.750	8.621	1.008	.006	1.014	14.836	.447
VI:3	5.244	6.721	1.040	.006	1.046	9.241	3.387
VI:4	5.385	6.711	1.039	.005	1.044	8.546	4.270
VI:5	4.955	5.484	1.062	.003	1.065	5.417	5.537
VI:6	4.900	5.400	1.063	.006	1.069	5.318	5.474
VI:7	4.607	4.569	1.080	.003	1.083	3.213	6.312
VI:8	4.589	4.524	1.081	.003	1.084	3.109	6.345
VI:9	4.375	3.595	1.098	.001	1.099	.226	7.974
VI:10	4.395	3.701	1.096	.002	1.098	.575	7.762
VI:11	1.206	-	1.206	-	-	-	-
VI:12	1.189	-	1.189	-	-	-	-

[1] (Simultaneous equation fluorine) - (nomograph fluorine).

TABLE 8. - K_2HfF_6-K_2ZrF_6-1.25 weight-percent HF solubility data at 70° C

Sample tube No.	Weight-percent						
	Total F	$(Hf+Zr)O_2$ combined oxides	Nomograph, F from HF	Difference in F[1] from HF	Simultaneous equations		
					F from HF	K_2HfF_6	K_2ZrF_6
VII:1	7.384	11.517	0.926	0.008	0.934	19.255	1.048
VII:2	7.269	11.561	.928	.006	.934	19.978	.492
VII:3	6.557	9.238	.967	.006	.973	13.564	3.528
VII:4	6.700	9.172	.966	.009	.975	12.625	4.604
VII:5	6.298	7.703	.992	.004	.996	8.353	6.805
VII:6	6.441	7.904	.987	.005	.992	8.527	7.040
VII:7	6.025	6.489	1.012	.004	1.016	4.544	8.989
VII:8	6.054	6.732	1.009	.004	1.013	5.430	8.392
VII:9	5.889	5.921	1.022	.003	1.025	2.804	9.956
VII:10	5.863	5.911	1.022	.003	1.025	2.881	9.833
VII:11	5.615	5.011	1.040	.002	1.042	.282	11.158
VII:12	5.566	5.065	1.039	.003	1.042	.731	10.695
VII:13	1.149	-	1.149	-	-	-	-
VII:14	1.200	-	1.200	-	-	-	-

[1] (Simultaneous equation fluorine) - (nomograph fluorine).

CONCLUSIONS

The K_2HfF_6-K_2ZrF_6-1.25 weight-percent HF system solid phase is comprised of continuous solid solution hydrates, except for the very small $K_2HfF_6 \cdot H_2O$- and $K_2ZrF_6 \cdot 6H_2O$-rich regions. The existence of these hydrates and the slope of the solubility curve connecting the hydrate solubility curves explains why hafnium enrichment can be obtained in recrystallization liquors of this system.

The parallel solubility curves were obtained for this system at 25°, 30°, 40°, 50°, 60°, and 70° C. Higher temperatures resulted in increased solubility.

Although these data indicate that hafnium enrichment is possible, this system is not suitable for separating high purity K_2HfF_6 from K_2HfF_6-K_2ZrF_6 mixtures.