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Abstract

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INVESTIGATION OF THE SYSTEM HF–HfF_4 –H_2O (SOLUBILITY ISOTHERM AT 25°C)

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The solubility relationships of potassium and ammonium fluoride salts of zirconium and hafnium, with the aim of separating the latter, were determined by Hevesy and co-workers (^{1}). Along with this, Hevesy and Wagner (^{2}) established a difference in the solubilities of zirconium and hafnium tetrafluorides in hydrofluoric acid and showed that the solubility of zirconium fluoride in 20 *M* HF is almost twice as high as the solubility of hafnium. Comparison of the nature of the solubility curves obtained by these authors with the solubility isotherm of the system HF–ZrF_4–H_2O (^{3}) leads to the conclusion that Hevesy and Wagner studied the solubility of $ZrF_4 \cdot 3H_2O$ within the range of HF concentrations where the indicated solid phase undergoes a chemical transformation.

Hevesy and Wagner did not note the fact of interaction of zirconium and hafnium fluorides with hydrofluoric acid; the solubility values were referred by them to the initial concentrations of hydrofluoric acid, without allowance for the change in HF concentration as a result of the reaction, which apparently distorted the difference in the solubilities of zirconium and hafnium obtained by Hevesy and Wagner.

The nature of the interaction of hafnium dioxide with hydrofluoric acid could be judged only on the basis of analogy with the behavior of zirconium fluorides in the system HF–ZrF_4–H_2O (^{3}). A similar investigation of the system involving hafnium fluorides is of interest both from the standpoint of determining the solubility of hafnium fluorides and of establishing the composition of the solid phases formed. In order to determine the actual difference in the solubilities of zirconium and hafnium fluorides, the distribution of the radioactive isotope Hf^{181} between the liquid and solid phases in the system HF–ZrF_4–H_2O was studied.

The method for investigating such systems has been described previously (^{3}). The temperature of the investigation was 25 ± 0.1°. The content of hydrofluoric acid was determined by the potentiometric method developed for solutions of zirconium fluoride (^{4}). At a molecular ratio HF : $HfO_2 < 4$, before titration a measured amount of hydrochloric acid and potassium fluoride was added. In this case, by the reaction
$6KF + 4HCl + HfO_2 = K_2HfF_6 + 4KCl + 2H_2O$, potassium hexafluorohafnate

was obtained, and the excess acid was titrated potentiometrically with alkali; the difference was recalculated as fluorine supplementing the Hf : F ratio to the value 1 : 4. Hafnium was determined by a gravimetric method. Hydrogen fluoride was first removed with sulfuric acid, after which hafnium hydroxide was precipitated with ammonia. After ignition, hafnium was weighed as HfO_2. The error in determining HF was $±2_{2}$ $±$1%.

Hafnium dioxide (purity 98.7%) was used as the starting substance. To obtain hafnium fluorides, the oxide was dissolved in hydrofluoric acid, the solution was evaporated, and the solid residue was used as a component of the system under study.

Table 1

Solubility in the $HF–HfF_4–H_2O$ system at 25°C

Liquid phase, wt. % HF	Liquid phase, wt. % HfO_2	Residue, wt. % HF	Residue, wt. % HfO_2	Composition of the solid phase	Liquid phase, wt. % HF	Liquid phase, wt. % HfO_2	Residue, wt. % HF	Residue, wt. % HfO_2	Composition of the solid phase
0,06	0,27	–	–		25,36	44,00	28,43	56,30	$HHfF_5 \cdot 2H_2O$ (B)
2,24	7,42	6,81	25,20	$Hf(OH)F_3 \cdot 0{,}75H_2O$	26,40	43,15	31,32	65,25	$HHfF_5 \cdot 2H_2O$ (B)
3,51	9,33	7,02	24,23	$Hf(OH)F_3 \cdot 0{,}75H_2O$	27,76	42,90	29,33	56,31	$HHfF_5 \cdot 2H_2O$ (B)
6,09	16,00	8,04	24,80	$Hf(OH)F_3 \cdot 0{,}75H_2O$	27,82	42,65	33,59	57,30	$HHfF_5 \cdot 2H_2O$ (B)
6,68	18,32	8,67	28,88	$Hf(OH)F_3 \cdot 0{,}75H_2O$	27,62	38,98	33,65	55,17	$HHfF_5 \cdot 2H_2O$ (B)
8,93	24,32	13,26	44,41	$Hf(OH)F_3 \cdot 0{,}75H_2O$	28,90	33,17	–	–	$H_2HfF_6 \cdot 2H_2O$
9,97	24,29	18,21	46,63	$Hf(OH)F_3 \cdot 0{,}75H_2O$	32,42	24,20	35,50	63,08	$H_2HfF_6 \cdot 2H_2O$
11,16	25,83	14,98	36,90	$Hf(OH)F_3 \cdot 0{,}75H_2O$	33,68	21,06	35,91	56,35	$H_2HfF_6 \cdot 2H_2O$
13,91	29,33	–	–	$HfF_4 \cdot 3H_2O$ (A)	35,03	18,26	–	–	$H_2HfF_6 \cdot 2H_2O$

Liquid phase, wt. % HF	Liquid phase, wt. % HfO_2	Residue, wt. % HF	Residue, wt. % HfO_2	Composition of the solid phase	Liquid phase, wt. % HF	Liquid phase, wt. % HfO_2	Residue, wt. % HF	Residue, wt. % HfO_2	Composition of the solid phase
14,78	30,24	18,93	45,03	$HfF_4 \cdot 3H_2O$ (A)	38,33	13,20	–	–	$H_2HfF_6 \cdot 2H_2O$
15,88	32,31	20,81	48,92	$HfF_4 \cdot 3H_2O$ (A)	41,95	7,98	–	–	$H_2HfF_6 \cdot 2H_2O$
20,50	37,67	–	–	$HfF_4 \cdot 3H_2O$ (A)	42,91	6,32	37,96	54,07	$H_2HfF_6 \cdot 2H_2O$
21,83	39,78	–	–	$HfF_4 \cdot 3H_2O$ (A)	43,64	5,90	37,79	52,83	$H_2HfF_6 \cdot 2H_2O$
21,96	40,67	23,35	51,86	$HfF_4 \cdot 3H_2O$ (A)	48,11	2,14	37,72	53,75	$H_2HfF_6 \cdot 2H_2O$
23,27	44,30	24,83	54,39	$HfF_4 \cdot 3H_2O$ (A)	52,75	0,52	42,77	37,92	$H_2HfF_6 \cdot 2H_2O$
24,68	45,61	27,66	59,91	A + B	59,22	0,17	43,25	44,48	$H_2HfF_6 \cdot 2H_2O$
24,68	44,60	30,75	63,62	A + B	66,80	0,062	51,36	30,44	$H_2HfF_6 \cdot 2H_2O$
					75,35	0,14	51,83	38,76	$H_2HfF_6 \cdot 2H_2O$

The data on solubility and on the composition of the residues are given in Table 1 and are presented on the triangular Gibbs diagram (Fig. 1). The initial section corresponds to the solubility of hafnium oxyfluoride in solutions from 0 to

Fig. 1. The HF—HfF_4—H_2O system (25° isotherm)

8,93% HF. The solubility in water is 0,27%, calculated as HfO_2. The composition of the solid phase corresponds to the conversion of hafnium oxide into the oxyfluoride $Hf(OH)F_3 \cdot 0{,}75H_2O$. With increasing HF concentration, the following is formed—

solid phase $HfF_4 \cdot 3H_2O$, which exists within the range 9.7-23.94% HF. The next small solubility branch corresponds to crystallization of the solid phase of composition $HHfF_5 \cdot 2H_2O$—the dihydrate of pentafluorohafnic acid. This acid, or its hydroxonium salt $(H_3O)HfF_5 \cdot H_2O$, separates in the form of thin plates similar to $HZrF_5 \cdot 4H_2O$ (5), within the range 24.68-27.76% HF. The observed considerable decrease in solubility is associated with the formation of the dihydrate of hexafluorohafnic acid, $H_2HfF_6 \cdot 2H_2O$. This solid phase dissolves incongruently; upon removal of the mother liquor its decomposition was observed. The study of the system was carried out up to a concentration of 75.35% HF.

To avoid errors associated with the determination of hydrogen fluoride in establishing the solubility values of zirconium and hafnium fluorides, a study was undertaken of the distribution of radioactive hafnium Hf^{181} between the liquid and solid phases in the system $HF—ZrF_4—H_2O$. Labeled hafnium dioxide was dissolved in hydrofluoric acid, and a certain quantity of the solution was introduced into a solution of zirconium tetrafluoride containing up to 0.05% HfO_2 as an impurity. Then the specific activity was determined, amounting to about 800 imp/min per 1 Zr. The solution was evaporated in a platinum dish, transferred to a Teflon vessel, and kept with stirring for 24 hours in a thermostat (25°). The contents of zirconium and hydrogen fluoride were determined in the solution. At the same time, six samples were taken for measuring the activity by β-decay, with a correction made for the decrease in activity during the experiments, taking into account the half-life of Hf^{181}, equal to 45 days. The discrepancy in the number of counts between parallel samples did not exceed 5%.

Table 2

Change in the distribution coefficient as a function of HF concentration

HF, wt. %	ZrF_4, wt. %	K	HF, wt. %	ZrF_4, wt. %	K
3.74	31.12	0.98	24.58	23.79	1.27
5.68	47.52	1.04	27.08	20.39	1.32
12.52	44.10	1.04	32.43	14.04	1.46
15.68	36.62	1.10	37.75	8.43	1.67
17.62	33.55	1.14	43.93	3.41	1.77
19.91	29.84	1.15	50.58	0.50	2.04

Table 2 gives the composition of a saturated solution of zirconium fluoride and the distribution coefficient of hafnium, i.e., the ratio of the specific activity of hafnium in the solution to the initial specific activity. Within the range of hydrogen fluoride concentrations corresponding to the existence of the solid phase $ZrF_4 \cdot 3H_2O$, no discrepancy is observed in the solubility of zirconium and hafnium fluorides. The greatest difference is reached under the conditions of crystallization of hexafluorozirconic acid, beginning at 15.68% HF. At an HF concentration of 50.58%, the solubility of hafnium fluoride is twice as high as the solubility of zirconium fluoride. Thus, in hydrofluoric-acid solutions an increased solubility of hafnium fluorides is maintained in comparison with zirconium fluorides, as is observed for the solubility of the potassium and ammonium fluoride salts of hafnium in aqueous solutions.

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