# Physical Chemistry

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## Abstract

## Full Text

*Physical Chemistry*

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# ON THE SOLUBILITY AND COMPOSITION OF SOLID PHASES IN THE SYSTEM $HF–UO_3–H_2O$

It is known that when $UO_2$ (or $U_3O_8$) is dissolved in a stoichiometric amount of hydrofluoric acid, uranyl fluoride $UO_2F_2$ is formed ($^{1-3}$). This is the most commonly used method for preparing uranyl fluoride. In addition, there are indirect indications of the possible existence of a compound with a smaller amount of fluorine. In studying the phase diagram of the system $UO_2F_2–H_2O$ at 200° an area of solid solutions of $UO_2(OH)_2$ and a compound of presumed composition $UO_2(OH)F \cdot 0.5H_2O$ were found ($^4$). There is no single opinion concerning the interaction of $UO_2F_2$ with hydrofluoric acid. According to a study of the system $HF–UO_2F_2–H_2O$ carried out by Kunin ($^5$) by the isothermal-solubility method from 0 to 41.7% HF at 25°, one solid phase of composition $UO_2F_2 \cdot H_2O$ was found in the system. According to more

**Table 1**

Solubility in the system $HF–UO_3–H_2O$ at 20°

| Liquid phase, HF, wt. % | Liquid phase, $UO_3$, wt. % | Residue, HF, wt. % | Residue, $UO_3$, wt. % | Composition of the solid phase | Liquid phase, HF, wt. % | Liquid phase, $UO_3$, wt. % | Residue, HF, wt. % | Residue, $UO_3$, wt. % | Composition of the solid phase |
|---|---|---|---|---|---|---|---|---|---|
| 0,27 | 2,01 | 0,12 | 33,66 | $UO_3$ | 24,11 | 20,75 | 20,26 | 57,15 | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 0,30 | 3,00 | 0,13 | 30,88 | $UO_3$ | 25,10 | 18,27 | – | – | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 0,58 | 5,15 | 1,32 | 73,77 | $UO_3$ | 25,92 | 17,69 | 20,60 | 59,35 | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 0,73 | 5,79 | 2,48 | 85,62 | $UO_3$ | 32,02 | 12,25 | – | – | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 1,14 | 8,52 | 3,59 | 81,08 | $UO_3$ | 37,60 | 7,28 | 26,67 | 44,19 | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 2,41 | 17,28 | 2,81 | 62,30 | $UO_3$ | 40,99 | 6,04 | 33,74 | 26,42 | $H_2[UO_2F_4] \cdot 4H_2O$ |

| Liquid phase, HF, wt. % | Liquid phase, $UO_3$, wt. % | Residue, HF, wt. % | Residue, $UO_3$, wt. % | Composition of the solid phase | Liquid phase, HF, wt. % | Liquid phase, $UO_3$, wt. % | Residue, HF, wt. % | Residue, $UO_3$, wt. % | Composition of the solid phase |
|---|---|---|---|---|---|---|---|---|---|
| 2,44 | 18,53 | 4,75 | 66,22 | $UO_2(OH)F \cdot 0.5H_2O$ | 44,04 | 4,01 | – | – | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 3,24 | 22,60 | 4,41 | 66,95 | $UO_2(OH)F \cdot 0.5H_2O$ | 46,37 | 3,29 | 25,19 | 57,12 | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 4,35 | 31,77 | 6,24 | 64,61 | $UO_2(OH)F \cdot 0.5H_2O$ | 48,26 | 2,55 | – | – | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 5,36 | 37,92 | – | – | $UO_2(OH)F \cdot 0.5H_2O$ | 49,34 | 2,45 | – | – | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 5,88 | 43,17 | 6,28 | 67,89 | $UO_2(OH)F \cdot 0.5H_2O$ | 51,41 | 2,21 | 37,97 | 31,26 | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 7,10 | 50,14 | 6,28 | 67,03 | $UO_2(OH)F \cdot 0.5H_2O$ | 57,38 | 1,31 | 47,00 | 19,16 | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 7,01 | 51,83 | – | – | $UO_2(OH)F \cdot 0.5H_2O$ | 59,75 | 1,09 | 44,54 | 24,55 | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 7,48 | 54,11 | – | – | $UO_2(OH)F \cdot 0.5H_2O$ | 59,53 | 0,93 | 50,13 | 15,97 | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 8,14 | 57,46 | – | – | $UO_2(OH)F \cdot 0.5H_2O$ | 62,94 | 0,31 | – | – | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 7,57 | 57,56 | – | – | $UO_2(OH)F \cdot 0.5H_2O$ | 64,69 | 0,28 | 49,16 | 22,60 | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 8,39 | 62,50 | 6,65 | 79,56 | $UO_2(OH)F \cdot 0.5H_2O$ | 65,14 | 0,31 | – | – | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 8,31 | 60,07 | – | – | $UO_2F_2 \cdot 2H_2O$ | 65,17 | 0,52 | 55,87 | 15,88 | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 7,99 | 47,47 | – | – | $UO_2F_2 \cdot 2H_2O$ | 67,46 | 0,44 | 48,98 | 26,33 | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 9,73 | 37,19 | 10,81 | 64,74 | $UO_2F_2 \cdot 2H_2O$ | 70,11 | 0,38 | 55,77 | 19,13 | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 10,74 | 36,08 | – | – | $UO_2F_2 \cdot 2H_2O$ | 74,94 | 0,31 | 59,55 | 18,57 | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 14,78 | 30,64 | – | – | $UO_2F_2 \cdot 2H_2O$ | 76,52 | 0,13 | – | – | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 15,15 | 30,16 | – | – | $UO_2F_2 \cdot 2H_2O$ | 78,64 | 0,25 | 61,31 | 20,10 | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 16,79 | 29,71 | – | – | $UO_2F_2 \cdot 2H_2O$ | 82,53 | 0,19 | – | – | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 16,68 | 28,76 | 14,59 | 64,77 | $UO_2F_2 \cdot 2H_2O$ | 83,61 | 0,083 | – | – | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 15,95 | 28,47 | – | – | $UO_2F_2 \cdot 2H_2O$ | 84,23 | 0,111 | – | – | $H_2[UO_2F_4] \cdot 4H_2O$ |

Fig. 1. Solubility in the system HF—UO3—H2O at 20°

Figure 1: Fig. 1. Solubility in the system HF—UO3—H2O at 20°

| Liquid phase, HF, wt. % | Liquid phase, $UO_3$, wt. % | Residue, HF, wt. % | Residue, $UO_3$, wt. % | Composition of the solid phase | Liquid phase, HF, wt. % | Liquid phase, $UO_3$, wt. % | Residue, HF, wt. % | Residue, $UO_3$, wt. % | Composition of the solid phase |
|---|---|---|---|---|---|---|---|---|---|
| 19,37 | 26,26 | 16,08 | 52,46 | $UO_2F_2 \cdot 2H_2O$ | 91,40 | 0,030 | 76,07 | 14,11 | $H_2[UO_2F_4] \cdot 4H_2O$ |
| 21,98 | 22,84 | 17,39 | 50,33 | $UO_2F_2 \cdot 2H_2O$ | | | | | |
| 22,85 | 22,87 | 16,29 | 62,53 | $UO_2F_2 \cdot 2H_2O$ | | | | | |

recent data, uranyl fluoride forms only the dihydrate $UO_2F_2 \cdot 2H_2O$ ([4]). Arland and Larson ([6]) found that in the presence of fluoride ions, uranyl fluoride forms an anion of composition $[UO_2F_4]^{2-}$, and calculated its formation constant. However, Day and Powers ([7]) were unable to confirm

existence of such a compound. Meanwhile, as a result of studying the system HF—$PuO_2F_2$—$H_2O$, Alenchikova, Lipis, and Nikolaev ([8]) showed that the solid phases in the system are plutonyl fluoride dihydrate and the complex acid $H_2[PuO_2F_4] \cdot 4H_2O$. With respect to fluorides of other hexavalent elements, more remote in their properties from uranium and plutonium, it is known that chromium and molybdenum trioxides are fluorinated in an HF medium, giving $CrO_2F_2$ ([9]) and $MoO_2F_2 \cdot 2H_2O$ ([10]); moreover, in the case of molybdenyl fluoride a solid phase of composition $H_2MoO_2F_4 \cdot 1.5H_2O$ has also been isolated.

**Fig. 1.** Solubility in the system HF—$UO_3$—$H_2O$ at 20°

Thus, at the present time the interaction in the system involving uranyl fluoride and hydrogen fluoride has proved to be the least studied. This prompted us to investigate the system HF—$UO_3$—$H_2O$ by the method of isothermal solubility over a wide range of concentrations of hydrofluoric acid.

In the study we used uranic acid, prepared from uranium trioxide, which in turn was obtained by calcining $UO_2(NO_3)_2$ at 400°. Uranic acid and hydrofluoric acid of the required concentration were charged into Teflon vessels with lids and stirrers and placed in a thermostat at $20 \pm 0.1°$. After equilibrium had been reached, for which the solution with the solid phase was stirred for two days, samples of the liquid phase were taken and, after decanting the solution, the "residues." Large amounts of uranium were reduced with Zn amalgam and titrated with potassium permanganate in the presence of boric acid ([11]). At low uranium contents, a photometric method for determining uranium with hydrogen peroxide was used. Fluorine was first removed with sulfuric acid. Hydrofluoric acid was determined by alkalimetric titration. In the case of high acid concentrations, titration was carried out potentiometrically to the first potential jump, and at low contents—

in the presence of phenolphthalein, taking into account a correction factor introduced in the titration of uranyl salts and equal to 2.22 (11).

The results obtained in the study of the system $HF - UO_3 - H_2O$ are given in Table 1 and presented on the Gibbs diagram (Fig. 1).

The transformation of uranic acid is observed within the concentration range 0.58-0.73% HF. It is associated with the replacement of part of the oxygen in uranium oxide by fluorine and the formation of the compound $UO_2(OH)F \cdot 0.5H_2O$, which apparently is the dimer $U_2O_5F_2 \cdot 2H_2O$. The highest solubility attained in the system is 62.5% $UO_3$. The next solid phase is uranyl fluoride dihydrate $UO_2F_2 \cdot 2H_2O$, which exists up to a concentration of 22.85% HF. Further, at 24.11% HF, a new transformation of the solid phase occurs, caused by formation of the compound of composition $UO_2F_2 \cdot 2HF \cdot 4H_2O$. The crystallization region of this phase has been traced up to a concentration of 91.40% HF. Taking into account the existence of a solid phase of the same composition in the system with plutonyl fluoride, the latter compound should be represented as a complex acid of composition $H_2[UO_2F_4] \cdot 4H_2O$.

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*Note: Figure translations are in progress. See original paper for figures.*

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