Experimental study of fluoride complexes of zirconium and hafnium in hydrothermal solutions

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Fluoride complexes are difficult to study by traditional solubility method, because many elements are not form solid fluorides , or they are easy hydrolyzed. So, we developed a method to study the stability of fluoride complexes of metals and metalloids, based on increasing the fluorite solubility with the addition of these elements in the system. Experimental study of fluorite solubility in acidic solutions in the system CaF_2-HCl-HF-H_2O gave good agreement with the thermodynamic calculations.This method was applied to study fluoride complexes of Zr, Hf. Adding zirconium and hafnium in the solution increases the solubility of fluorite. For zirconium, the stability constants of the Zr $(OH)_3F$ *(aq)* and $Zr(OH)_2F_2$ *(aq)* complexes were determined in the works [1], and [2] at high temperatures. Fluoride complexes of hafnium was research only at room temperature [3]. Fluorite solubility was researched in acid solutions with variable concentrations of $ZrOCl_2$ to study the stability of zirconium fluoride complexes. Stability of hafnium fluoride complexes was researched in the same way using $HfO(NO_3)_{2^-}$. The slope of fluorite solubility dependence showed ZrF_6^{2-} and HfF_6^{2-} complexes. Program OptimA was used for calculating the Gibbs free energies from the experimental data [4]. pK values of the reactions (1), (2) were calculated.

$ZrF_6^{2-} = Zr^{4+} + 6F^-$ (1)
$HfF_6^{2-} = Hf^{4+} + 6F^-$ (2)

pK for reaction (1) were estimated at 90, 155, 205, 255°C 29.86±0.13, 34.03±0.062, 38.28±0.033, 40.94±0.079. pK for reaction (2) at 100, 150, 205 and 240°C were determined as 32.53±0.12, 33.70±0.030, 40.40±0.016, 41.7±0.022 respectively. Thermodynamic calculation showed that ZrF_6^{2-} is vary imprtant for zircon dissolution and recrystallization at hydrothermal conditions.

This work was supported by RFBR projects 18-35-00075.
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