Experimental study of fluoride complexes of metals and metalloids 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 to 250°C. This method was applied to study fluoride complexes of the third group elements: Ga, B. Fluoride complexes of this elements was research only at low temperature. Gallium fluoride complexes was researched [1] at 20°C and boron fluoride complexes was researched at 25-80°C [2]. Adding of gallium and boron in the solution increases the solubility of fluorite, wich can be determine by weight loss method. Fluorite solubility was researched in acid solutions with variable concentrations of $B(OH)_3$ to study the stability of boron fluoride complexes. Stability of gallium fluoride complexes was researched in the same way using $Ga(ClO_4)_3$. Program OptimA was used for calculating the Gibbs free energies from the experimental data [3]. pK values of the reactions (1), (2) for GaF_2^+ at 88, 155, 200, 250°C are 10.06±0.1, 17.09±0.1 19.29±0.1 and for $B(OH)F_3^-$ at 80, 155, 210°C are 13.6±0.02, 13.99±0.02, 15.00±0.03, respectively.

$$GaF_2^+ = Ga^{3+} + 2F^- \quad (1)$$
$$B(OH)F_3^- + 2H_2O = B(OH)^\circ_3 + 3F^- + 2H^+ \quad (2)$$

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