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THERMAL DECOMPOSITION OF SOLID FLUORINE COMPOUNDS

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In solid state reactions migration of simple ions, atoms or electrons is generally assumed. This is of course true for reactions with simple halides, oxides etc., but difficulties arise in describing reaction mechanisms of systems with complex compounds like hexafluorosilicates, hexafluorophosphates, corresponding oxocompounds, etc. In these cases we suppose migration of collective particles like SiF_3^+ within the volume of the crystal and no diffusion of Si^{4+} or P^{5+} ions. To get some information on this field we studied thermal decomposition of solid fluorine compounds and the reaction of added substances during decomposition. The experimental results with hexafluorosilicates have been interpreted by reaction of species like SiF_3^+. Theoretical calculations show that such species are possible from an energetical point of view. Moisture complicates the investigations for hydrolytic side reactions which could not be totally excluded. Further experiments of topotactical decomposition reactions with phosphates showed no complication by moisture and confirm the assumption of migration of collective particles. The chemical experiments have been completed by high resolution NMR measurements. The results of our investigations correspond to the following postulate. Solid state reactions with complex compounds of central atoms having oxidation states $\sim$4 are characterized by migration of collective particles. In case of oxidation state 1 simple particles (ions, atoms) take part in the reaction. With oxidation states 2 and 3 a transition behaviour with respect to the kind of migrating particles is assumed.