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Note

On some solid phase reactions of AgF and Ag_2F

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Although I highly appreciate that the authors of a recent paper on some solid phase reactions of silver fluorides[1] acknowledged my advice which was given at an early stage of the work, I feel forced to state that I do not agree with the conclusions of this paper.

In the mechanism given for the thermolysis of silver fluoride, the first step is the removal of the water. It is not proved, however, that the only product of the dehydration processes is water-free silver fluoride. There is also a possibility that silver oxide is formed as well. The amount of water in the silver fluoride was not determined, but according to the thermograms its quantity was considerable. It is quite arbitrary to state that the homolytic dissociation of silver fluoride occurs in such a broad temperature range as 90–520 °C at a heating rate of 4.7 °C min^{-1}. It is even more arbitrary to assume, that at 450 °C another process leading to the formation of Ag_2F and fluorine occurs, because for the decomposition temperature of Ag_2F the authors found a much lower temperature when investigating the thermolysis of silver subfluoride.

Moreover, the mechanism of the thermolysis of silver subfluoride seems to be contrary to fundamental laws of kinetics and thermodynamics.

According to the authors a very small part of silver subfluoride dissociates into silver and fluorine in the temperature range 270–340 °C. At 358 °C another reaction, leading to the formation of silver fluoride and fluorine, takes place. There are two evident questions: First, what is the reason that only a very small fraction of Ag_2F decomposes in a 70 °C temperature range? Second, which kind of kinetic barrier prevents the further decomposition between 340 and 358 °C? The strangest point of the mechanism is that at an even higher temperature silver subfluoride is again formed from AgF which then dissociates to metallic silver and elementary fluorine on further heating. As a whole, the given sequence of the reactions means a violation of the second law.

I think that the data presented in the paper are not sufficient for any sound mechanism to be postulated and further analytical determinations are necessary. It is my impression that the presence of oxygen and water may be responsible for the strange behaviour of the silver fluorides.

The findings on the solid phase reactions of the two silver fluorides with potassium halides are most interesting. However, in this case too, more analytical data were inevitably necessary to give a meaningful explanation.

REFERENCE

1 T. Flóra and I. Gaál, *Thermochim. Acta*, 7 (1973) 173.