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N. S. Nikolaev and Yu. D. Shishkov

The Fluorination Reaction of Uranium Tetrafluoride with Chlorine Trifluoride

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Attempts are known to use halogen fluorides for the purpose of obtaining uranium hexafluoride (^{1}). It has been proposed to use uranium tetrafluoride and chlorine trifluoride as the initial reagents (^{2}). There is a report on the kinetics of the fluorination of uranium tetrafluoride by chlorine trifluoride (^{3}).

The present communication concerns an investigation of the chemistry of this reaction at temperatures above the boiling point of chlorine trifluoride—in the range 18-300°C. The method of investigation consisted in the action of ClF_3 on UF_4 for a specified interval of time at the temperatures under study. The experimental conditions included obtaining a homogeneous residue from the fluorination of the initial UF_4 sample. Chemical and X-ray phase analysis of the composition of this residue served as an indication of the intermediate phases through which the reaction proceeds. The yield of UF_6 served as the criterion of the intensity of the reaction. The experiments were carried out in a horizontal nickel cylindrical reactor. Volatile reaction products were collected by condensation in a system consisting of copper and quartz traps.

The experimental data are presented in the form of a diagram: yield of UF_6—temperature (see Fig. 1). From Fig. 1 it is evident that the reaction depends on temperature.

Three stages are observed: 1) a process occurring at temperatures up to 50°; 2) a process occurring at higher temperatures within the range up to 150°; 3) the last stage corresponds to temperatures above 150°.

The experimental limit in the present investigation was 300°. Analysis of the experimental data showed substantial differences in the chemical processes depending on the indicated temperature ranges. In the first stage, from room temperature to 50°, the reaction proceeds according to the scheme:

$$3UF_4 + 2ClF_3 \rightarrow 3UF_6 + Cl_2, \tag{1}$$

which, according to the observations of the authors, corresponds to a reaction in the condensed state. The intensity of this reaction increases with temperature and reaches a maximum at 50°. With a further increase in temperature, the yield of hexafluoride decreases.

However, already in experiments at temperatures somewhat below 50°, the composition of the nonvolatile residues differed from tetrafluoride in the direction of an increased fluorine content, and, as the temperature rose, the composition of the residue changed in the direction:

$$UF_4 \to U_4F_{17} \to U_2F_9.$$

Beginning at 100°, along with U_4F_{17} and U_2F_9, UF_5 begins to form in the nonvolatile residue. Thus, the processes occurring at temperatures above 50° can be represented by the schemes:

$$12UF_4 + ClF_3 \to 3U_4F_{17} + \frac{1}{2}Cl_2, \tag{2}$$

$$3U_4F_{17} + ClF_3 \to 6U_2F_9 + \frac{1}{2}Cl_2, \tag{3}$$

$$3U_2F_9 + ClF_3 \to 6UF_5 + \frac{1}{2}Cl_2. \tag{4}$$

Reactions according to schemes 2 and 3 are observed predominantly up to 100°, and at higher temperatures pentafluoride is formed.

Phase analysis of the residues at temperatures above 50° shows the presence of uranium tetrafluoride and U_2F_9, with a gradual increase in the amount of the latter compound as the temperature rises. In this case the composition of the residue is not identified as a chemical compound, and the formation of uranium hexafluoride should be attributed to fluorination of the unchanged portion of uranium tetrafluoride.

The descending branch of the curves in the diagram corresponds to a decrease in the amount of tetrafluoride in the solid residues and to the predominance in the latter of the U_2F_9 phase. This phase then begins to be fluorinated according to scheme (4), and, finally, at 150° an almost pure UF_5 phase is detected, reacting with chlorine trifluoride according to the scheme:

$$3UF_5 + ClF_3 \to 3UF_6 + \frac{1}{2}Cl_2. \tag{5}$$

The intensity of this reaction is considerably lower than that of reaction (1), which also explains the decrease in the yield of uranium hexafluoride as pentafluoride is formed. The minimum yield is at 150°. In this case the reaction of UF_6 formation proceeds entirely through uranium pentafluoride. A further increase

Fig. 1. Fluorination of uranium tetrafluoride by chlorine trifluoride. Duration of fluorination 1 hour. Weight of the initial UF_4 charge 20 g. Amount of ClF_3 passed (from bottom to top): 4, 5, 6, 7, 8, 10

Figure 1: Fig. 1. Fluorination of uranium tetrafluoride by chlorine trifluoride. Duration of fluorination 1 hour. Weight of the initial UF_4 charge 20 g. Amount of ClF_3 passed (from bottom to top): 4, 5, 6, 7, 8, 10

in temperature within the range of the present study is associated with an increase in the yield of uranium hexafluoride. This increase in yield was followed up to a temperature of 300° and is attributed to intensification of process (5) with increasing temperature.

Fig. 1. Fluorination of uranium tetrafluoride by chlorine trifluoride. Duration of fluorination 1 hour. Weight of the initial UF_4 charge 20 g. Amount of ClF_3 passed through (from bottom to top): 4, 5, 6, 7, 8, 10

Taking into account that fluorination by chlorine trifluoride represents a new process, it was important to compare it with the known reaction between gaseous fluorine and tetrafluoride ⁽⁴⁾ under conditions corresponding to our study. In this case no noticeable reaction was observed up to 50°. Some amounts of hexafluoride were observed only at temperatures above 150°; the intensity of fluorination by fluorine reached the intensity of the process with ClF_3, respectively, at a higher temperature, namely 350° for F_2, which corresponded to 300° for the reaction with ClF_3.

When comparing the processes of fluorination of uranium tetrafluoride by fluorine and by chlorine trifluoride, one may conclude that both processes differ comparatively sharply: when fluorine acts on uranium tetrafluoride at room temperature, formation of hexafluoride is excluded; meanwhile fluorination by chlorine trifluoride under the same conditions gives considerable yields of uranium hexafluoride; comparable yields in the reactions with fluorine and with chlorine trifluoride are observed at temperatures above 300°, but even here the intensity of the process with ClF_3 is noticeably higher. Thus, chlorine trifluoride is a more active reagent in fluorination processes than fluorine under the same conditions.

Earlier reports ⁽⁵⁾ interpreted reactions involving ClF_3 in accordance with the scheme

$$U + 3ClF_3 \rightarrow UF_6 + 3ClF, \tag{6}$$

hence, respectively,

$$UF_4 + ClF_3 \rightarrow UF_6 + ClF. \tag{7}$$

Our calculations of the equilibrium constants of the reaction according to this scheme and for the reaction according to equation (1) gave the following results:

$$K_{(1)} = \begin{cases} 4.4 \cdot 10^{94} & (\text{for } 25^\circ) \\ 1.4 \cdot 10^{56} & (\text{for } 300^\circ) \end{cases} \qquad K_{(7)} = \begin{cases} 3 \cdot 10^{34} & (\text{for } 25^\circ) \\ 1.6 \cdot 10^{21} & (\text{for } 300^\circ) \end{cases}$$

Considering that the exponents for both systems are very large, the authors do not think it possible to regard the calculated values as quantities that may have the significance of thermodynamic constants; however, their relative values show the predominance of reaction (1). In addition, in all experiments included in the present study, chlorine was the predominant component among the gaseous reaction products. Chlorine monofluoride was detected in vanishingly small amounts, and its formation is probably associated with side reactions.

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