PHYSICAL MATERIALS TECHNOLOGY

THE INTERACTION PROCESSES OF SILICON TETRAFLUORIDE AND HEXAFLUOROSILICATES WITH HYDROGEN-CONTAINING AND OXYGENATED SUBSTANCES: A THERMODYNAMIC ANALYSIS

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In the paper, the thermodynamic calculations have shown that at the temperatures above 1300 K, the main silicon-containing substance is silicon dioxide in the Si-F-H-O element system, and the main fluorine-containing one is hydrogen fluoride in the same system. The mentioned temperature was realized during the interaction reactions between silicon tetrafluoride, fluorosilicates and hydrogen-containing, oxygen-containing substances in the combustion mode. The high-temperature treatment of silicon tetrafluoride and fluorosilicates in the combustion mode can become the basis of industrial technology for hydrogen fluoride production.

Keywords: silicon tetrafluoride, hydrogen fluoride, silicon dioxide, thermodynamic equilibrium, Gibbs energy

ТЕРМОДИНАМИЧЕСКИЙ АНАЛИЗ ПРОЦЕССОВ ВЗАИМОДЕЙСТВИЯ ТЕТРАФТОРИДА КРЕМНИЯ И ГЕКСАФТОРСИЛИКАТОВ С ВОДОРОД- И КИСЛОРОДСОДЕРЖАЩИМИ ВЕЩЕСТВАМИ

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Термодинамическими расчетами показано, что в системе элементов Si-F-H-O при температуре выше 1300 K основным кремнийсодержащим веществом является диоксид кремния, а основным фторсодержащим − фторид водорода. Указанная температура реализуется при проведении реакций взаимодействия тетрафторида кремния и фторсиликатов с водородсодержащими и кислородсодержащими веществами в режиме горения. Высокотемпературная обработка тетрафторида кремния и фторсиликатов в режиме горения может стать основой промышленной технологии производства фторида водорода.

Ключевые слова: тетрафторид кремния, фторид водорода, диоксид кремния, термодинамическое равновесие, энергия Гиббса

Introduction

Hydrogen fluoride (HF) is the main fluorinating agent used in production of uranium fluorides in the nuclear fuel cycle, halocarbons, electron gases, etc. Production of anhydrous HF reaches 1.5 million tons per year [1, 2].

Hydrogen fluoride is obtained from fluorspar (natural CaF_2) by decomposition of sulfuric acid [1]:

$$CaF_{2\,sol} + H_2SO_{4\,liq} \rightarrow CaSO_{4\,sol} + 2HF_{gas}. \quad (1)$$

The subscripts here indicate the aggregate states of substances: solid (*sol*), liquid (*liq*) and gaseous (*gas*).

Only high-quality fluorspar with at least 95% content of the original material and a silicon dioxide admixture of not more than 1.5% is used to produce HF [1, 2].

The annual world production of fluorspar exceeds 4 million tons. The main producers are China (generating over 50% of the total world output), Mexico, Mongolia, and South Africa [1, 2].

The deposits of fluorspar in the Russian Federation are depleted, so fluorspar has to be imported. Therefore, developing alternative methods for producing hydrogen fluoride is an important task.

Production of wet-process phosphoric acid from fluorapatite, using the reaction

$$Ca_5(PO_4)_3F_{sol} + 5H_2SO_{4\,liq} \rightarrow 3H_3PO_{4\,liq} + \\ + 5CaSO_{4\,sol} + HF_{gas}, \quad (2)$$
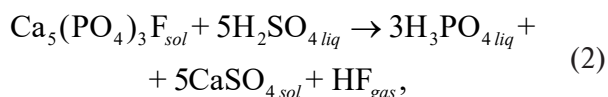
forms a substantial amount of hydrogen fluoride, which in turn forms silicon tetrafluoride SiF_4 reacting with silicon dioxide SiO_2 (an admixture in fluoroapatite):

$$SiO_{2\,sol} + 4HF_{gas} \leftrightarrow SiF_{4\,gas} + 2H_2O_{gas}. \quad (3)$$

Tetrafluoride is then hydrolyzed, and the obtained hexafluorosilicic acid H_2SiF_6 is neutralized, and solid fluorine-containing wastes are disposed to landfills.

The amount of these wastes generated in processing fluorapatite is about 2 million tons per year (in terms of fluorine content). Therefore, these wastes from processing fluoroapatite can serve as the main industrial source of fluorine.

There is a great number of chemical compounds in the Si-F-H-O system. Some of these compounds and data on their interaction with water, hydrogen and oxygen are given in Table 1 [3−13]. It follows from the data that the most stable compounds in the Si-F-H-O system are SiO_2, HF, SiF_4, H_2O; in addition, it can be seen that hydrogen fluoride can be obtained by hydrolysis of silicon tetrafluoride.

Determination of the temperature range

In order to determine the preferable temperature range for hydrolysis of silicon fluoride, we calculate the Gibbs energy change depending on temperature for the following process:
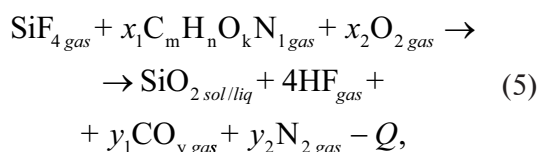
$$SiF_{4\,gas} + 2H_2O_{gas} \leftrightarrow SiO_{2\,sol} + 4HF_{gas}. \quad (4)$$

More than ten crystalline modifications of SiO_2 are known. The most stable of them are β-quartz, β-tridimite and β-cristobalite, whose melting points are 1550, 1680 and 1720 °C, respectively [4]. The heat capacities and other thermodynamic parameters of these crystalline modifications differ only slightly (by units of percent), so we performed further calculations for one modification, β-tridymite.

The procedure for calculating the Gibbs energy change is given in [14]. We approximated the temperature dependence of heat capacity by a first-degree polynomial. The calculation results are shown in Fig. 1.

Reaction (4) is reversible (↔); the forward reaction rate is equal to the reverse reaction rate at a temperature of 1170 K (referred to as critical, T_{cr}, for convenience from now on). Therefore, hydrogen fluoride can be obtained by hydrolysis of silicon fluoride at a temperature above T_{cr}, quickly cooling the products at temperatures below T_{cr}.

We propose to treat SiF_4 in flames of hydrogen-containing fuel and an oxygen-containing oxidizing agent for high-temperature hydrolysis:

$$SiF_{4\,gas} + x_1 C_m H_n O_k N_{l\,gas} + x_2 O_{2\,gas} \rightarrow$$

$$\rightarrow SiO_{2\,sol//liq} + 4HF_{gas} + \qquad (5)$$

$$+ y_1 CO_{y\,gas} + y_2 N_{2\,gas} - Q,$$

where $C_m H_n O_k N_l$ is the volatile hydrogen-containing substance, $m \geq 0$, $n > 0$, $k \geq 0$, $l \geq 0$; $nx_1 \geq 4$, $2x_2 > 2$, $y = 1$; 2; the standard enthalpy of formation is $Q \sim 10^2–10^3$ kJ; the adiabatic temperature of the reaction products is $T_{ad} > 10^3$ K.

Hydrogen, methane and ammonia can serve as hydrogen-containing fuel, and oxygen and air as an oxygen-containing oxidizing agent.

Table 1

Physico-chemical properties of silicon compounds

| Compound	Interaction with water	Characteristic reaction
SiF_4 Si_2F_6	$3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2[SiF_6]$ $(T = 100\ °C)$, $SiF_4 + 2H_2O \rightarrow SiO_2 + 4HF$ $(T > 800\ °C)$	$Si_2F_6 \rightarrow SiF_2 + SiF_4$ (700 °C)
H_2SiF_6	Exists in aqueous solution only	$H_2SiF_6 \rightarrow SiF_4 + HF$
H_3SiF H_2SiF_2 $HSiF_3$	$H_3SiF + H_2O \rightarrow 2HF + (SiH_3)_2O$	$2H_3SiF \rightarrow SiH_4 + H_2SiF_2$, $4HSiF_3 \rightarrow 3SiF_4 + Si + 2H_2$ (20 °C)
$SiH_4, Si_2H_6, Si_3H_8,$ $(SiH_{x)4}$	$SiH_4 + 2H_2O \rightarrow SiO_2 + 4H_2$, $Si_2H_6 + 4H_2O \rightarrow 2SiO_2 + 7H_2$	$SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$, $SiH_4 \rightarrow Si + 2H_2$ (400–1000 °C)
$H_2SiO_3\ H_4SiO_4$	Sparingly soluble	$H_2SiO_3 \rightarrow H_2O + SiO_2$
SiO, SiO_2	$SiO + H_2O \rightarrow SiO_2 + H_2$ $(T > 500\ °C)$	$SiO_2 + 2H_2 \rightarrow Si + 2H_2O$ (800 °C)
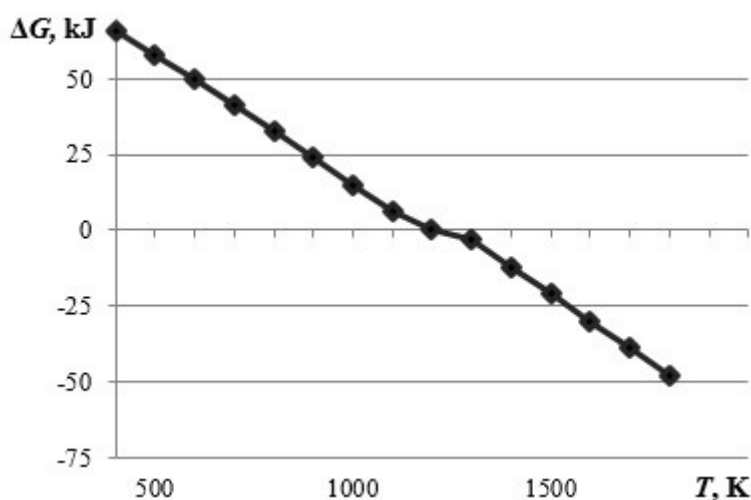
Fig. 1. Temperature dependence of Gibbs energy change for hydrolysis of silicon tetrafluoride (4)

The products of the process are a slightly dust-laden gas flow, i.e.,

$$V_{sol}/V \sim 10^{-5},$$

where V_{sol}, V are the volumes of the solid phase and all products of the process, respectively.

For this reason, the flow should be cooled in a convective heat exchanger of the double pipe type.
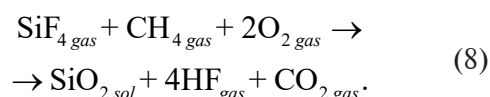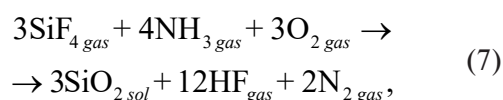
Table 2 shows the thermal enthalpies and adiabatic temperatures T_{ad} of the products for process (5). A nonhomogeneous flame loses up to 40% of the released energy due to thermal radiation [15]. In view of this, the temperatures T_{rad} of the reaction products given in Table 2 were calculated taking into account this loss.

Table 3 gives T_{ad} and T_{rad} depending on the initial temperature of the reagents for three crystalline modifications of SiO_2 for the process described by the reaction

$$SiF_{4\,gas} + 2H_{2\,gas} + O_{2\,gas} \rightarrow \\ \rightarrow SiO_{2\,sol/liq} + 4HF_{gas}. \quad (6)$$
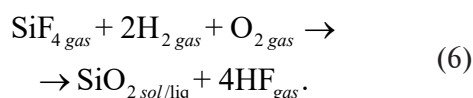
It follows from the data given in Table 3 that the values of T_{ad} and T_{rad} are significantly higher than the values of T_{cr} for all cases, so the preferable method for producing hydrogen fluoride from silicon tetrafluoride is by scheme (5). In addition, it is evident that T_{ad} and T_{rad} weakly depend on the structure of crystalline modification of SiO_2.

Fig. 2 shows the Gibbs energy change ΔG depending on temperature in the range of 300–1800 K for reactions (6)–(8) with the ratio of starting components corresponding to production of SiO_2 and HF:

$$3SiF_{4\,gas} + 4NH_{3\,gas} + 3O_{2\,gas} \rightarrow \\ \rightarrow 3SiO_{2\,sol} + 12HF_{gas} + 2N_{2\,gas}, \quad (7)$$

$$SiF_{4\,gas} + CH_{4\,gas} + 2O_{2\,gas} \rightarrow \\ \rightarrow SiO_{2\,sol} + 4HF_{gas} + CO_{2\,gas}. \quad (8)$$

It can be seen from Fig. 2 that the ΔG values are negative for the given processes, which means that processes (6)–(8) are not thermodynamically forbidden for this temperature range.

Table 2

Main thermal parameters for reactions occurring in interaction of silicon tetrafluoride with different compounds ($T_0 = 500$ K)

Reaction	$-Q$, kJ	T_{ad}	T_{rad}
		K	
$SiF_{4\,gas} + 2H_{2\,gas} + O_{2\,gas} \rightarrow SiO_{2\,sol/liq} + 4HF_{gas}$	384	2491	1843
$3SiF_{4\,gas} + 4NH_{3\,gas} + 3O_{2\,gas} \rightarrow \\ \rightarrow 3SiO_{2\,sol/liq} + 12HF_{gas} + 2N_{2\,gas}$	969	2083	1562
$SiF_{4\,gas} + CH_{4\,gas} + 2O_{2\,gas} \rightarrow \\ \rightarrow SiO_{2\,sol/liq} + 4HF_{gas} + CO_{2\,gas}$	703	3020	2214
$SiF_{4\,gas} + 2H_{2\,gas} + O_{2\,gas} + 4N_{2\,gas} \rightarrow \\ \rightarrow SiO_{2\,sol/liq} + 4HF_{gas} + 4N_{2\,gas}$	384	1836	1407
$3SiF_{4\,gas} + 4NH_{3\,gas} + 3O_{2\,gas} + 12N_{2\,gas} \rightarrow \\ \rightarrow 3SiO_{2\,sol/liq} + 12HF_{gas} + 14N_{2\,gas}$	969	1598	1248
$SiF_{4\,gas} + CH_{4\,gas} + 2O_{2\,gas} + 8N_{2\,gas} \rightarrow \\ \rightarrow SiO_{2\,sol/liq} + 4HF_{gas} + CO_{2\,gas} + 8N_{2\,gas}$	703	1982	1501

N o t a t i o n s : Q is the thermal effect; T_{ad} and T_{rad} are the adiabatic and radiation temperatures; T_0 is the temperature of the starting reagents.
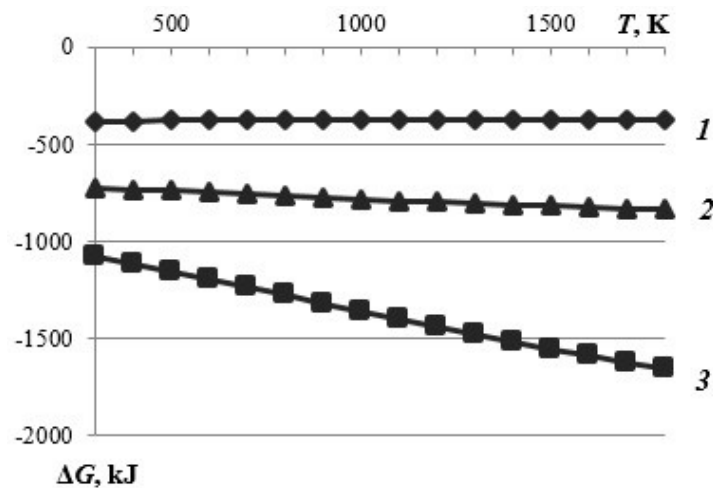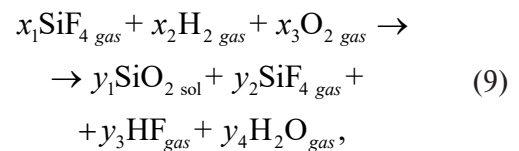
Fig. 2. Temperature dependences of Gibbs energy change
for reactions (6) (*1*), (7) (*2*) and (8) (*3*)

Fig. 3 shows the temperature dependences of the Gibbs energy change ΔG for β-quartz, β-tridymite, and β-cristobalite for process (6).

The Gibbs energy change in reaction (8) weakly depends on the structure of crystalline modification of SiO_2: the difference in ΔG does not exceed 5%.

As noted above, the most thermally stable elements in the Si-F-H-O system are SiO_2, SiF_4, H_2O and HF. The thermodynamically equilibrated composition of substances in this system was calculated by minimizing the Gibbs energy for the mixture, varying the concentration of the components with the given atomic ratio [16]:

$$x_1 SiF_{4\,gas} + x_2 H_{2\,gas} + x_3 O_{2\,gas} \rightarrow$$
$$\rightarrow y_1 SiO_{2\,sol} + y_2 SiF_{4\,gas} + \qquad (9)$$
$$+ y_3 HF_{gas} + y_4 H_2 O_{gas},$$

where x_i, y_i are the stoichiometric coefficients.

The atomic balance equations have the following form:

$$Si: y_1 + y_2 = x_1; \; H: 4y_2 + y_3 = 4x_1;$$
$$F: y_3 + 2y_4 = 2x_2; \; O: 2y_1 + y_4 = 2x_3. \qquad (10)$$

If we express y_2, y_3, y_4 in terms of x_1, x_2, x_3 and y_1, i.e.,

$$y_2 = x_1 - y_1; \; y_3 = 4y_1; \; y_4 = x_2 - 4y_1,$$
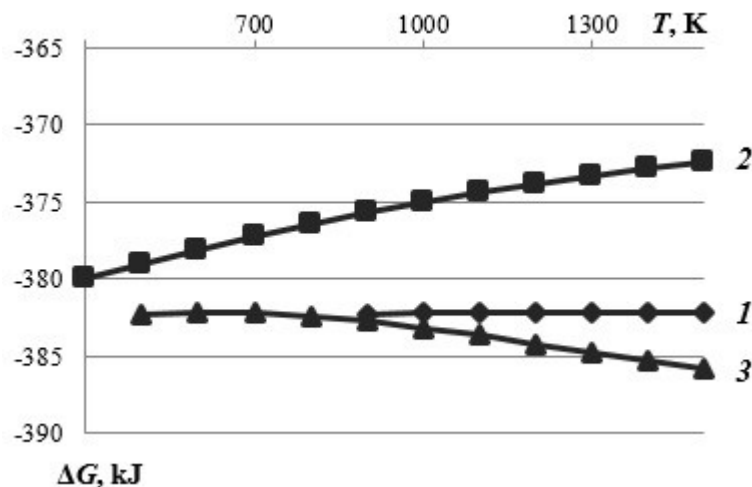
we obtain:

Fig. 3. Temperature dependences of Gibbs energy change for process (6),
for three crystalline modifications of silicon dioxide:
β-quartz (*1*), β-tridymite (*2*) and β-cristobalite (*3*)

**Temperature parameters of reaction (6)
depending on initial temperature of reagents
for different crystalline modifications of silicon dioxide**

T_0	T_{ad}	T_{rad}	T_{ad}	T_{rad}	T_{ad}	T_{rad}
	β-quartz		β-tridymite		β-cristobalite	
400	–	–	2544	1760	–	–
600	–	–	2886	2120	2812	2055
800	–	–	3226	2476	3161	2415
1000	3547	2803	3563	2829	3508	2773

Note. All temperatures are given in degrees Kelvin (K).

$$\sum G(x_1, x_2, y_1) = y_1 G(SiO_{2\,sol}) +$$
$$+ (x_1 - y_1)G(SiF_{4\,gas}) + \qquad (11)$$
$$+ 4y_1 G(HF_{gas}) + (x_2 - 4y_1)G(H_2O_{gas}).$$

Given fixed values of x_1, x_2, x_3, we varied y_1 in increments of 0.001, constructing a matrix and then selecting its minimum by comparison.

Fig. 4 shows the temperature dependences for the concentration of products of process (6) in a thermodynamically equilibrated mixture, calculated using the model we formulated [16].

SiO_2 is the main silicon-containing substance at temperatures above 1300 K, and HF is the main fluorine-containing substance; the concentration of SiF_4 does not exceed 3%, and that of H_2O does not exceed 8%.

**Calculations in the ASTRA
software package**

We have tested the model using the ASTRA software package, allowing to calculate the thermodynamically equilibrated composition by entropy maximization [17]. The calculated results for the Si-4F-4H-2O system are given in Table 4.

The results obtained with the ASTRA software package are in qualitative agreement with the calculated data on equilibrium compositions obtained by the method that we have developed.

The ASTRA package was also used to calculate the equilibrium compositions of substances in the Si-4F-C-4H-4O system. The calculated results are given in Table 5.
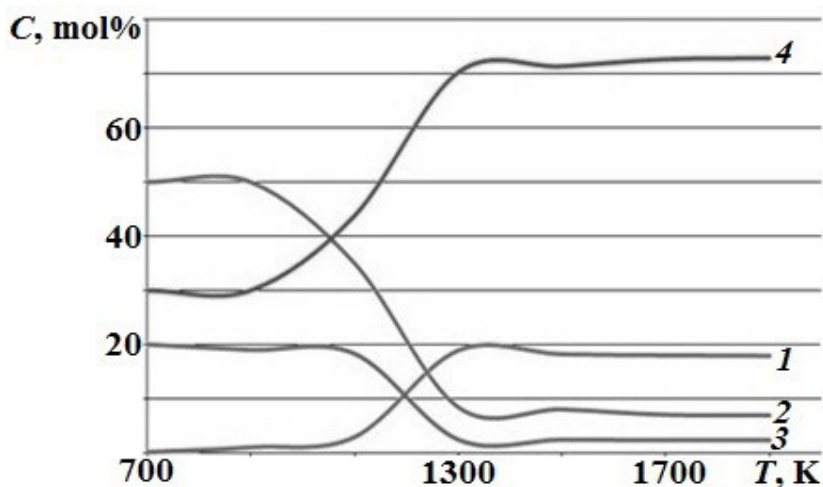

Fig. 4. SiO_2 (*1*), SiF_4 (*2*), H_2O (*3*) and HF (*4*) concentrations depending on temperature for Si-F-H-O system
(SiF_4-$2H_2$-O_2 mixture is thermodynamically equilibrated, i.e., $x_1 = x_3 = 1$, $x_2 = 2$)

Table 4

**Thermodynamic equilibrium
compositions of substances (mol.%)
in Si-4F-4H-2O system
depending on temperature**

T, K	H_2O	HF	SiO_2	SiF_4
500	64.5	2.2	0.5	32.5
700	57.3	10.8	2.7	28.9
900	46.1	24.3	6.1	23.3
1100	35.3	37.3	9.3	17.8
1300	26.9	47.4	11.9	13.6
1500	20.8	54.6	13.7	10.6
1700	16.7	59.6	14.9	8.5
1900	13.7	63.1	15.8	7.1

Notes. 1. The data given were calculated using the ASTRA software package. 2. The O_2 content was less than 0.2 mol.% at all temperatures.

Table 5

**Thermodynamic equilibrium
compositions of substances (mol.%)
in Si-4F-4H-1C-4O system
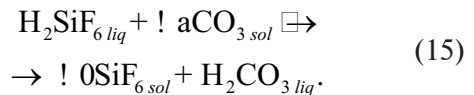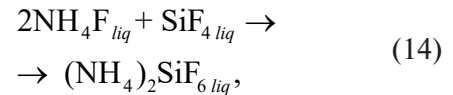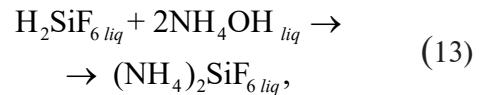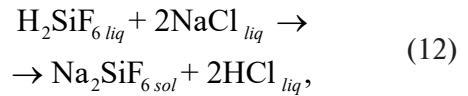depending on temperature**

T, K	H_2O	HF	CO_2	SiO_2	SiF_4
500	48.6	1.7	24.7	0.4	24.4
700	43.3	8.8	23.9	2.2	21.7
900	35.1	19.8	22.5	5.0	17.6
1100	27.0	30.6	21.1	7.6	13.5
1300	20.7	39.0	20.1	9.8	10.4
1500	16.1	45.1	19.3	11.3	8.1
1700	12.9	49.3	18.8	12.3	6.5
1900	10.6	52.3	18.2	13.1	5.4

Note. The data were calculated using the ASTRA software package.

Hydrogen fluoride is the main fluorine-containing substance at temperature above 1100 K in the Si-4F-4H-1C-4O system. Upon reaching 1900 K, the hydrogen fluoride content in the equilibrium mixture amounted to about 50 mol.%, and the silicon tetrafluoride content to about 5 mol.%.
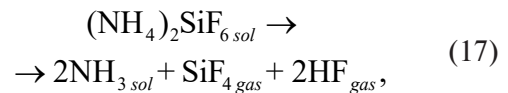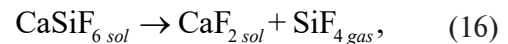
Thus, analyzing the calculated equilibrium compositions of the substances in Si-F-H-O and Si-F-H-C-O systems, we can assume that HF can be the main fluorine-containing substance for SiF_4 processed in flames of hydrogen-containing fuel with an oxygen-containing oxidizing agent at temperatures above 1300 K, and SiO_2 can be the main silicon-containing substance.

Metal and ammonium hexafluorosilicates can be obtained from aqueous solution of H_2SiF_6 and SiF_4 [18, 19]:

$$H_2SiF_{6\,liq} + 2NaCl_{\,liq} \rightarrow$$
$$\rightarrow Na_2SiF_{6\,sol} + 2HCl_{\,liq}, \qquad (12)$$

$$H_2SiF_{6\,liq} + 2NH_4OH_{\,liq} \rightarrow$$
$$\rightarrow (NH_4)_2SiF_{6\,liq}, \qquad (13)$$

$$2NH_4F_{\,liq} + SiF_{4\,liq} \rightarrow$$
$$\rightarrow (NH_4)_2SiF_{6\,liq}, \qquad (14)$$

$$H_2SiF_{6\,liq} + !\,aCO_{3\,sol} \boxdot\!\!\rightarrow$$
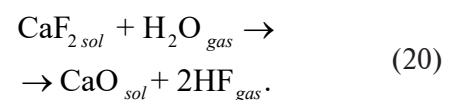$$\rightarrow !\,0SiF_{6\,sol} + H_2CO_{3\,liq}. \qquad (15)$$

Therefore, we considered whether it was thermodynamically possible to produce hydrogen fluoride from hexafluorosilicates in flames of hydrogen-containing fuel and an oxygen-containing oxidizing agent.

No data are available in literature on thermodynamic functions of the $CaSiF_6$, $(NH_4)_2SiF_6$, Na_2SiF_6 hexafluorosilicates; however, these salts are thermally unstable at temperatures above 370, 250 and 600 °C, respectively [7]:

$$CaSiF_{6\,sol} \rightarrow CaF_{2\,sol} + SiF_{4\,gas}, \qquad (16)$$

$$(NH_4)_2SiF_{6\,sol} \rightarrow$$
$$\rightarrow 2NH_{3\,sol} + SiF_{4\,gas} + 2HF_{\,gas}, \qquad (17)$$

$$Na_2SiF_{6\,sol} \rightarrow 2NaF_{\,sol} + SiF_{4\,gas}. \qquad (18)$$

For this reason, we performed further calculations for their decomposition products. The equations for hydrolysis of sodium and calcium fluorides have the form

$$NaF_{\,sol} + H_2O_{\,gas} \rightarrow$$
$$\rightarrow NaOH_{\,sol/liq} + HF_{\,gas}, \qquad (19)$$

$$CaF_{2\,sol} + H_2O_{\,gas} \rightarrow$$
$$\rightarrow CaO_{\,sol} + 2HF_{\,gas}. \qquad (20)$$

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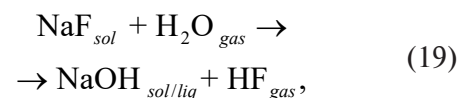
We calculated the Gibbs energy change as function of temperature for these reactions. We found (Fig. 5) that the Gibbs energy change for this reaction follows the inequality $\Delta G > 0$ in the entire temperature range considered. Consequently, reactions (19) and (20) are thermodynamically forbidden in the temperature range $T = 300-2000$ K.

The local maximum on curve *2* (Fig. 5) is due to the fact that the crystal lattice of calcium fluoride changes at a 1424 K, and this compound melts at 1691 K [5].

Table 6 gives the calculated standard enthalpies of formation, temperatures T_{ad} and T_{rad} for the interaction of products of thermal decomposition of hexafluorosilicates in flames of hydrogen-containing fuel and oxygen, with the ratio of the starting components corresponding to production of SiO_2 and HF at the initial temperature $T_0 = 500$ K. Hydrogen-containing fuel is contained in the molecule of hexafluorosilicate in case of ammonium hexafluorosilicate.

The values of T_{rad} in Table 6 significantly exceed the value of T_{cr} obtained for SiF_4 (see Fig. 1), and, therefore, hydrolysis of SiF_4 is thermodynamically possible in the given processes (see Table 6). Notably, sodium and calcium fluorides are not hydrolyzed in the temperature range $T = 300-2000$ K, so only 67% fluorine regeneration is possible from hexafluorosilicates of these elements.

Fig. 6 shows the Gibbs energy change ΔG depending on temperature in the range of $300-1800$ K for interaction of thermal decomposition products of hexafluorosilicates with hydrogen-containing substances and oxygen (all reactions in Table 6).
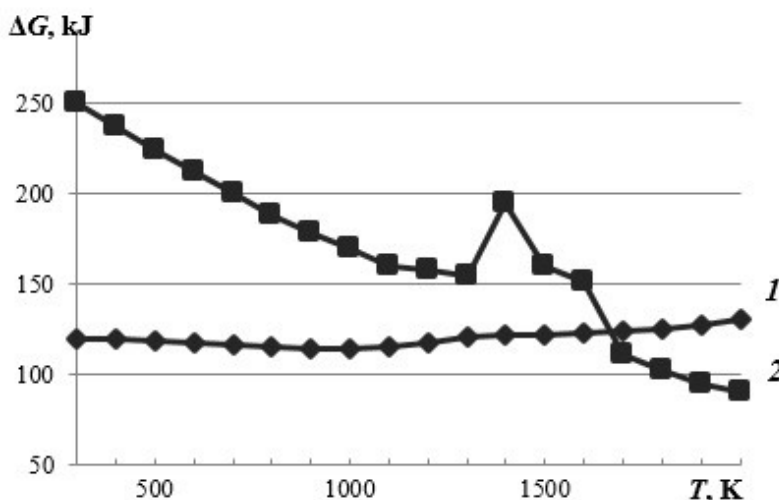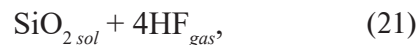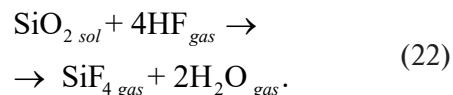
The Gibbs energy changes are negative in the given temperature range, therefore, all the reactions in Table 6 are not thermodynamically forbidden

As the dust-laden gas flow formed by combining the reagents

$$SiO_{2\,sol} + 4HF_{gas}, \qquad (21)$$

is cooled at temperatures below 1170 K, fluorination of SiO_2 occurs:

$$SiO_{2\,sol} + 4HF_{gas} \rightarrow$$
$$\rightarrow SiF_{4\,gas} + 2H_2O_{gas}. \qquad (22)$$

Because of this, flow (21) should be cooled at the highest rate possible.

Calculation of heat transfer parameters

Kinetic models for reaction (22) are not described in literature. It is thus impossible to give a quantitative assessment for the necessary cooling rate.

We made estimates for the characteristic cooling time of the dust-laden gas flow (21) and the parameters of the convective heat exchanger of the double pipe type with a thermostatically controlled wall for SiF_4 flow rates corresponding to the pilot and industrial-scale setups, based on the data from [20].

The Nusselt number for the dust-laden gas flow was calculated by the following relations:

$$Nu_i = 0.023\,\mathrm{Re}_i^{0.8}\,\mathrm{Pr}_i^{0.4} =$$
$$= Nu(1+\mu)^{0.8}(1-\beta)^{1.12}\left(\frac{1+C_{sol}\mu C_{gas}^{-1}}{1+\mu}\right)^{0.4}, \qquad (23)$$

Fig. 5. Temperature dependences of Gibbs energy change
for hydrolysis of sodium (*1*) and calcium (*2*) fluorides

Table 6

**Main thermal parameters for interaction
of thermal decomposition products of hexafluorosilicates
with different substances ($T_0 = 500$ K)**

Reaction	-Q, kJ	T_{ad}	T_{rad}
		K	
$SiF_{4\,gas} + 2NH_{3\,gas} + 2HF_{gas} + 1{,}5O_{2\,gas} \rightarrow$ $\rightarrow N_{2\,gas} + SiO_{2\,sol/liq} + 6HF_{gas} + H_2O_{gas}$	539	2211	1643
$2NaF_{sol} + SiF_{4\,gas} + CH_{4\,gas} + 2O_{2\,gas} \rightarrow$ $\rightarrow 2NaF_{sol} + SiO_{2\,sol/liq} + 4HF_{gas} + CO_{2\,gas}$	708	2354	1763
$CaF_{2\,sol} + SiF_{4\,gas} + CH_{4\,gas} + 2O_{2\,gas} \rightarrow$ $\rightarrow CaF_{2\,sol} + SiO_{2\,sol/liq} + 4HF_{gas} + CO_{2\,gas}$	708	2687	1978

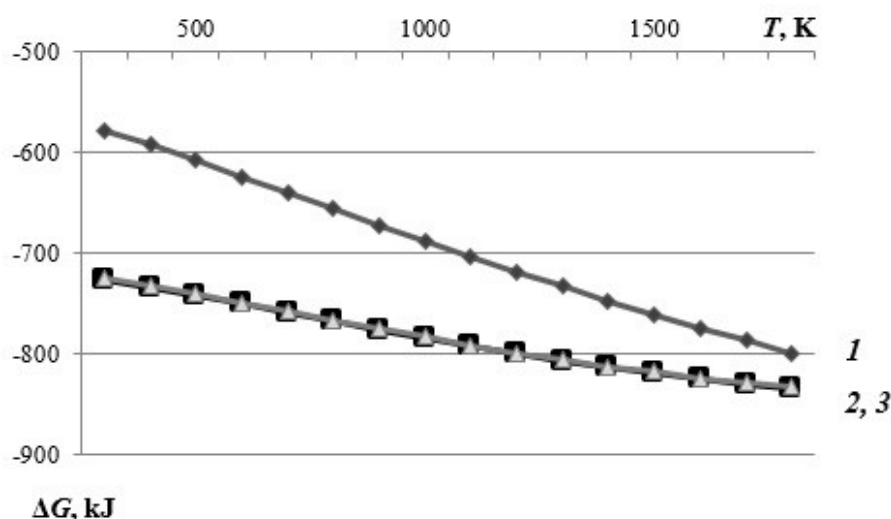The notations for the parameters are given in the caption to Table 2

Fig. 6. Temperature dependences of Gibbs energy change
for interaction of thermal decomposition products of hexafluorosilicates
with hydrogen-containing substances and oxygen
The numbers of the curves correspond to the numbers of reactions in Table 6

$$\mu = \frac{G_{sol}}{G_{gas}} = \frac{\beta}{1-\beta}\frac{\rho_{sol}V_{sol}}{\rho_{gas}V_{gas}},$$

$$\beta = \frac{F_{sol}}{F_s} = \frac{F_{sol}}{F_{sol}+F_{gas}} = \frac{\mu}{\left(\rho_{sol}V_{sol}\middle/\rho_{gas}V_{gas}\right)+\mu},$$ (24)

where G_{sol}, V_{sol} are the flow rate and velocity of the powder; G_{gas}, V_{gas} are the flow rate and velocity of gas; C_{sol}, C_{gas} are the heat capacities of the solid component and gas; ρ_{sol}, ρ_{gas} are the densities of the solid phase and gas, respectively; μ is the flow rate concentration; β is the volumetric concentration of the solid component; F_{sol}, F_{gas} are the volumes of the solid component and gas, respectively; F_s is the system volume.

Table 7 gives the cooling characteristics for slightly dusty ($\beta = 2 \cdot 10^{-5}$ at $T = 1100$ K) flow (21) at temperatures from 1100 to 500 K and for the heat exchanger depending on the SiF_4 flow rate and the diameter of the cylindrical heat exchanger.

It follows from the results given in Table 7 that the characteristic cooling time of the flow from 1170 to 500 K is of the order of 10^{-2} s provided that the diameter of the heat exchanger is of the order of tens of millimeters,

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Table 7

Characteristics of heat exchanger and slightly dust-laden flow (21) depending on heat exchanger diameter

D, mm	α, W·m^{-2}·K^{-1}	L, m	u, m/s	ΔP, kPa	t, s	Re	Re$_f$
20	382	0.68	81	1.47	0.02	16280	24635
30	184	0.94	36	0.29	0.05	10847	16413

N o t a t i o n s : D, L are the diameter and length of the heat exchanger, α is the heat transfer coefficient; u is the dust-laden gas flow velocity; ΔP, t are the pressure difference in the heat exchanger and the cooling time of the dust-laden gas flow with a decrease in temperature from 1170 to 500 K; Re, Re$_f$ are the Reynolds numbers for dust-laden gas flows. N o t e . The table gives the calculated data for silicon fluoride with the flow rate of 10 g/s (industrial value is 300 tons per year); the wall temperature of the heat exchanger T_{wall} = 100 ºC.

its length is of the order of units of meters, and the pressure difference in the heat exchanger is 1.5 kPa. The cooling time is 0.02 seconds for a heat exchanger diameter of 20 mm, so this diameter is considered to be optimal.

Main results and conclusions

Considering the regeneration of fluorine from fluorine-containing materials, we analyzed the existing methods for producing hydrogen fluoride. We have carried out thermodynamic calculations of adiabatic temperature, Gibbs energy change and the equilibrium composition of the reaction products of interaction of silicon tetrafluoride with hydrogen and oxygen-containing substances.

Analysis of the obtained simulation data allowed us to draw the following conclusions.

It is preferable to carry out hydrolysis of SiF$_4$ aimed at producing SiO$_2$ and HF at a temperature above 1170 K, followed by rapid cooling of the reaction products.

When SiF$_4$ is processed in flames of hydrogen-containing fuel (H$_2$, CH$_4$, NH$_3$) and an oxygen-containing oxidizing agent (oxygen, air), the temperature of the reaction products, taking into account thermal radiation of non-homogeneous flame, is significantly higher than 1170 K. The crystalline form of SiO$_2$ practically does not affect the adiabatic (T_{ad}) and radiation (T_{rad}) temperatures exceeding 1500 and 1200 K, respectively.

SiO$_2$ is the main silicon-containing substance at temperatures above 1300 K in an equilibrium mixture of substances of the Si-4F-4H-2O system, and HF is the main fluorine-containing substance. The content of SiF$_4$ is not more than 3%, of water not more than 8% (estimate by the Gibbs energy minimization method).

The results calculated using the ASTRA software package indicate that SiF$_4$ and H$_2$O contents in the equilibrium mixture at a temperature of 1900 K are 7% and 14%, respectively. Calculations for the Si-4F-1C-4H-4O system confirm that hydrogen fluoride is the main fluorine-containing substance at 1900 K, the SiF$_4$ content in an equilibrium mixture is about 5%, carbon dioxide content is 18% and water content is 10%.

HF and SiO$_2$ can be obtained in flames of hydrogen-containing fuel and an oxygen-containing oxidizing agent using CaSiF$_6$, Na$_2$SiF$_6$, (NH$_4$)$_2$SiF$_6$, etc., as starting materials: these processes are not forbidden thermodynamically, and the temperature of their products T_{rad} > 1170 K. Moreover, hydrolysis of calcium and sodium fluorides is thermodynamically forbidden in the temperature range T = 300--2000 K. Therefore, only 67% regeneration of fluorine is possible from sodium and calcium hexafluorosilicates.

The (SiO$_{sol}$ + 4HF$_{gas}$) flow is classified as slightly dusty, so it should be cooled in a convective heat exchanger of the double pipe type. The cooling time can amount to about 10^{-2} s in the temperature range from 1170 to 500 K.

Processing SiF$_4$ or fluorosilicates in flames of hydrogen-containing fuel and an oxygen-containing oxidizing agent may serve as the basis for producing hydrogen fluoride.

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