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Uranium Hexafluoride Reduction with Hydrogen Atoms

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Abstract—The simulation of uranium hexafluoride reduction to uranium tetrafluoride by hydrogen and fluorine in flow has demonstrated that the high-capacity thermochemical atom generators designed for continuous-wave chemical lasers are promising for the industrial implementation of the continuous reduction process. Two variants of the reduction process are suggested: one uses a generator of H atoms and the other uses a generator of F atoms.

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The optimization of ^{235}U-depleted uranium hexafluoride conversion technologies has been stimulated by the challenging problem of the safe storage and utilization of this product. The total amount of this environmentally hazardous gas, which is a valuable raw material at the same time, has exceeded 1 million tons and is steadily increasing. Therefore, for a successful solution of the UF_6 utilization problem, the UF_6 processing rate should be ~1 mol/s or ~1 t/h over many hours.

A promising way of converting depleted uranium is by the so-called water-free UF_6 reduction with hydrogen to UF_4 or uranium metal according to the scheme

$$UF_6 + H_2 \longrightarrow UF_4(g) + 2HF - 4.2\ \text{kJ/mol}, \quad (I)$$

$$\searrow UF_4(g) + 2HF + 293\ \text{kJ/mol}, \quad (Ia)$$

$$UF_6 + 3H_2 \longrightarrow U(met) + 6HF - 548\ \text{kJ/mol}. \quad (II)$$

As is clear from reactions (I) and (II), the uranium hexafluoride molecule is so strong that its reduction to uranium metal with dihydrogen is very endothermic and its reduction to UF_4, which is the subject of this study, will be exothermic only if the resulting uranium tetrafluoride gas is condensed into solid particles. Furthermore, this reaction is rather slow: the activation energy of the rate-limiting step of UF_6 reduction is $E_a \sim$ 150–200 kJ/mol [1, 2]. Therefore, continuous combustion in a flow reactor can be carried out only if two conflicting requirements are simultaneously satisfied. On the one hand, the reaction temperature must be sufficiently high for molecular reduction to proceed at a high rate. On the other hand, this temperature must be low enough to allow the reaction products to aggregate into solid particles and thus ensure favorable energetics for the overall process (the boiling point of UF_4 is T_b = 1690 K [3]). For this reason, it is rather difficult to design a high-capacity burner for $UF_6 + H_2$ mixtures.

It was suggested to circumvent this difficulty by carrying out the reduction process in excess hydrogen and fluorine [4] or, in other words, to burn UF_6 in a fluorine–hydrogen flame. However, this method implies a marked increase in F_2 consumption and suffers from the following drawback: the $H_2 + F_2 \longrightarrow 2HF$ reaction is so fast that all of the fluorine burns out before UF_6 reduction takes place. This case can be considered as reaction (I) initiated at an elevated initial temperature. At the same time, it is well known for thermally neutral reactions such as reaction (I) with no cluster formation that, at equilibrium, the starting reactants and reaction products will be present in comparable amounts at any temperature. Therefore, it is generally impossible to achieve the desired deep conversion of UF_6 into UF_4 by this method. Thus, this approach also does not allow one to raise the final mixture temperature above the point at which UF_4 clustering begins (T_b).

PROBLEM FORMULATION

The method using H atoms in UF_6 reduction [5] is free of the above drawbacks. The mechanism of this process consists only of successive abstractions of fluorine atoms from UF_6 by H atoms:

$$\left.\begin{aligned} UF_6 + H &\longrightarrow UF_5 + HF + 287\ \text{kJ/mol},\\ UF_5 + H &\longrightarrow UF_4 + HF + 140\ \text{kJ/mol}.\end{aligned}\right\} \quad (III)$$

Both steps are very exothermic and proceed at rather high rates even at comparatively low temperatures. It is natural that the overall heat of UF_6 reduction with hydrogen atoms is higher than the heat of reaction (I) by the value of H_2 dissociation energy, which is 431 kJ/mol:

$$UF_6 + 2H \longrightarrow UF_4(g) + 2HF + 427 \text{ kJ/mol.} \quad (IV)$$

A specific feature of uranium hexafluoride reduction with hydrogen atoms is that a high relative concentration of these atoms is necessary: one should have at least 2 H atoms per UF_6 molecule. The hydrogen atom consumption in UF_6 reduction will be governed by the competition between reactions (III), initiated by these atoms, and the recombination reaction

$$H + H + M \longrightarrow H_2 + M + 431 \text{ kJ/mol.} \quad (V)$$

Uranium hexafluoride reduction with hydrogen atoms is accompanied by a considerable self-heating because of the high exothermicity of the reaction. As this takes place, reactions (III), which are characterized by rather high activation energies, are accelerated, while the rate of the recombination reaction (V) somewhat decreases with an increasing temperature. Therefore, even if the domination of the reduction reaction over the recombination reaction is achieved at a high conversion, there will in any case be a "cold" zone adjoining the reaction zone, where hydrogen atoms will be lost through recombination, heating the reaction mixture at the same time. Note an interesting fact facilitating the analysis of the problem: due to the coincidence of the heats of reactions (IV) and (V), heat evolution and the temperature profile in the reactor are independent of the reduction efficiency factor (the ratio of the recombination and reduction rates). Although the recombination reaction reduces the hydrogen atom consumption, it nevertheless exerts a beneficial effect, stabilizing the process conditions. Indeed, UF_6 reduction can be initiated at any temperature by adjusting the initial composition of the reaction mixture. At lower temperatures, the reaction will proceed in a similar way until the downstream temperature reaches an appropriate value owing to the partial recombination of hydrogen atoms.

Chemical generators of H atoms for continuous-wave chemical lasers (CWCLs) have already been designed and manufactured, making our suggestion all the more important for practice. These generators can operate at high temperatures in a fluorine or hydrogen fluoride atmosphere and have an output capacity sufficient for industrial UF_6 utilization [6].

These generators are based on the thermal dissociation of F_2 molecules (in which the F–F bond dissociation energy is as low as 37 kcal/mol) followed by the "quenching" of the resulting F atoms, their mixing with flowing dihydrogen, and the formation of H atoms via the fast chemical reaction

$$F + H_2 \longrightarrow HF + H + 134 \text{ kJ/mol.} \quad (VI)$$

Fluorine is usually heated by using the reaction $D_2 + F_2$ in excess F_2. However, deuterium is too expensive for the process suggested and can well be replaced with hydrogen, a cheaper gas.

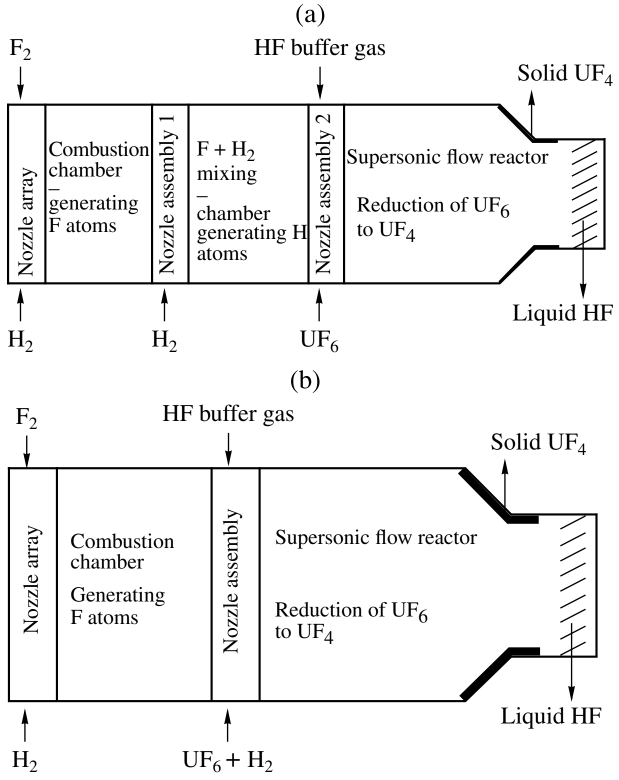

Fig. 1. Schematic diagrams of the UF_6 reduction reactors: (a) H generator and (b) F generator.

An important advantage of chemical atom generators is that they can operate at supersonic gas velocities, since, under these conditions, the heat released in the reaction zone cannot propagate upstream and, therefore, it is possible to maintain the nozzle assembly at a temperature low enough to prevent its disintegration.

Based on the CWCL operation practice, we will assume that the working gas of the thermochemical generator of F atoms is a hydrogen–fluorine mixture with $F_2 : H_2 = 3 : 1$, the dissociation of the excess fluorine is complete ($H_2 + 3F_2 \longrightarrow 2HF + 4F$), and 1/4 mol of H_2 and 3/4 mol of F_2 are spent for the formation of 1 mol of F atoms. One HF molecule per two fluorine atoms forms as ballast.

The schematic diagram of the reactor for UF_6 reduction with H atoms is presented in Fig. 1a. The left-hand part of the reactor (to the left of nozzle assembly 2) is similar in design to a CWCL. Next is the first mixing chamber, in which the fluorine atoms are mixed with H_2 and hydrogen atoms are generated via the fast reaction (VI). In the second chamber, the H atoms are mixed with UF_6. From the above, we deduce the following stoichiometric relationships: two hydrogen atoms are spent per reduced UF_6 molecule, resulting in three molecules of HF, which plays the role of an inert gas in this case.

A simpler reactor design is also possible (Fig. 1b). In this design, there is a single mixing chamber, in which the F atoms that have formed in the burner are mixed directly with UF_6 and, if necessary, with an inert gas. In this case, the chemical generator produces fluorine atoms, which are almost inert toward UF_6, and their fast reaction with dihydrogen (reaction (VI)) yields H atoms. This approach is in some respects more advantageous than use of a separate hydrogen atom generator. Indeed, the main cause of the wastage of hydrogen atoms is their recombination, which competes successfully with the desired reaction at high atom concentrations. In the first design (H generator), all of the hydrogen atoms necessary for the reduction reaction are formed before this reaction. In the other design (F generator), they result from the reaction between H_2 and F atoms and are simultaneously involved in UF_6 reduction. The latter reaction reduces the steady-state concentration of H atoms and, accordingly, the rate of their recombination. The recombination rate of F atoms,

$$F + F + M \longrightarrow F_2 + M$$

is two orders of magnitude lower that the rate of reaction (V). Although the cross recombination of active sites,

$$F + H + M \longrightarrow HF + M$$

is nearly as fast as reaction (V), the low rate of F recombination ensures some gain in the active species efficiency factor, and this gain can overbalance the adverse loss of F atoms through their attachment to uranium fluoride molecules [7, 8]:

$$UF_5 + F \longrightarrow UF_6^* \longrightarrow UF_6.$$

An obvious disadvantage of this design is the extra self-heating in the reaction zone caused by reaction (VI), whose heat is 134 kJ/mol. Furthermore, because this design uses a single mixer, it has a smaller number of controlled parameters and is, therefore, less flexible.

The need for a high-throughput process for the utilization of large amounts of UF_6 dictates that the gas-phase reduction of UF_6 should be designed as a closed cycle in which all of the final products should be either solid (like UF_4) or liquid (like HF condensed on cryopanels). Such a process can be carried out for stoichiometric mixtures not diluted with an inert gas and at product (HF) pressures well above the triple-point pressure ($P_{TP} \sim 12$ Torr).

In this case, the final adiabatic temperature of the mixture is $T_a = T_0 + \Delta T$, where T_0 is the initial temperature, and, because of the thermal neutrality of reaction (I), the temperature rise is $\Delta T = \Delta Q/C$ (here, ΔQ is the heat of the recombination of H atoms, and C is the heat capacity of the mixture). Taking the heat capacity of UF_6, HF, and H atoms to be 167, 29, and 21 kJ mol^{-1} K^{-1}, respectively, and neglecting the variation of the total heat capacity during the reaction, we obtain $\Delta T \sim 1500$ K. Therefore, even if the mixture is not preheated by heating the nozzle assembly, $T_a \sim 1800$ K. This implies that, if no diluent gas is used, the temperature rise during the reaction will prevent the condensation of the resulting UF_4. This circumstance substantially facilitates the analysis of the reduction process: it is unnecessary to include, in the reaction mechanism, cluster formation, growth, and disintegration, whose rate constants can be estimated, but only with a high degree of uncertainty.

The uranium hexafluoride reduction reaction is rather complicated: it takes place under essentially nonisothermic conditions, and the discrepancy between rate constants reported for its elementary steps is as large as several orders of magnitude (see, e.g., [9, 10]). Nevertheless, the simulation of this reaction seems to be very promising, for it is expected to elucidate the main features of UF_6 reduction, to bound the range of process conditions, and to reconcile the requirements imposed on the process parameters.

The consecutive reactions of uranium hexafluoride reduction with hydrogen atoms are always favorable steps. In the ideal case, the reduction is complete,

$$\eta = [UF_6]_{fin}/[UF_6]_0 \longrightarrow 0, \quad (1)$$

the desired-product selectivity is the highest possible,

$$\chi = [UF_4]_{fin}/[UF_6]_0 \longrightarrow 1, \quad (2)$$

the reactant consumption is the lowest possible,

$$[F]_0/[UF_4]_{fin} \longrightarrow 2, \quad (3)$$

and the length of the reaction zone is a few centimeters. Here, the subscripts 0 and fin stand for the initial and final conditions, respectively. Furthermore, because of the high yield of H atoms in the reaction between dihydrogen and F atoms, we set $[F]_0 = [H]_0$.

Obviously, in multiparametric optimization, it is necessary either to impose a special constraint on the parameters or to single out the most significant parameter and to optimize it under some constraints (e.g., inequality ones) imposed on the other parameters. In our calculations, we took the latter approach.

In mathematical modeling, we considered both reactor designs, namely, the H generator (in which the hydrogen atoms produced in a multinozzle mixer are mixed with UF_6 in another mixer) and the F generator (which has a single mixer in which the F atoms are mixed directly with a $UF_6 + H_2$ mixture).

We considered the following elementary reactions, including the reverse ones:

1. $H + H + UF_6 \longrightarrow H_2 + UF_6$, $\Delta H = -431.2$,
   $k_1 = 7 \times 10^{18} T^{-1}$,
2. $H + UF_6 \longrightarrow UF_5 + HF$, $\Delta H = -286.8$,
   $k_2 = 6 \times 10^{11} \exp(-29.3/RT)$,
3. $H + UF_5 \longrightarrow UF_4 + HF$, $\Delta H = -140.3$,
   $k_3 = 6 \times 10^{11} \exp(-50.2/RT)$,
4. $H + UF_4 \longrightarrow UF_3 + HF$, $\Delta H = 62.8$,

$k_4 = 6 \times 10^{11}\exp(-83.7/RT)$,

5. $H + UF_3 \longrightarrow UF_2 + HF$, $\Delta H = 43.1$,

$k_5 = 6 \times 10^{11}\exp(-83.7/RT)$,

6. $H + H + UF_4 \longrightarrow H_2 + UF_4$, $\Delta H = -431.2$,

$k_6 = 7 \times 10^{18}T^{-1}$,

7. $H + H + UF_5 \longrightarrow H_2 + UF_5$, $\Delta H = -431.2$,

$k_7 = 7 \times 10^{18}T^{-1}$,

8. $H + H + M \longrightarrow H_2 + M$, $\Delta H = -431.2$,

$k_8 = 2.3 \times 10^{18}T^{-1}$ $(M = HF, H_2)$,

9. $F + H_2 \longrightarrow HF + H$, $\Delta H = -134.0$,

$k_9 = 1.6 \times 10^{14}\exp(-6.7/RT)$,

10. $H + F_2 \longrightarrow HF + F$, $\Delta H = -410.3$,

$k_{10} = 1.6 \times 10^{14}\exp(-10/RT)$,

11. $F + H + M \longrightarrow HF + M$, $\Delta H = -565.2$,

$k_{11} \sim k_8$,

12. $F + H + UF_6 \longrightarrow HF + UF_6$, $\Delta H = -565.2$,

$k_{12} \sim k_1$,

13. $F + H + UF_5 \longrightarrow HF + UF_5$, $\Delta H = -565.2$,

$k_{13} \sim k_7$,

14. $F + H + UF_4 \longrightarrow HF + UF_4$, $\Delta H = -565.2$,

$k_{14} \sim k_6$.

The changes in enthalpy (kJ/mol) are taken from [3, 11, 12]. The rate constants k_i (in cm^3 mol^{-1} s^{-1} for bimolecular reactions and in cm^6 mol^{-2} s^{-1} for termolecular reactions) and the activation energies (kJ/mol) are taken from [6, 13]. The unknown rate constants were set to be equal to those of similar reactions. The rate constants of the reactions reverse to reactions (1)–(14) were calculated using the corresponding equilibrium constants.

We made the following simplifying assumptions in mathematical modeling: the mixing of reactants was considered to be instantaneous and perfect, the linear velocity of the flowing reactants was considered to be constant and was set at 200 m/s, and the temperature of the nozzle assembly was considered to be known. Diffusion and heat conduction were neglected. With these simplifications, the problem of determining the stationary concentration and temperature fields is reduced to the Cauchy problem for ordinary differential equations in which the independent variable is the axial coordinate and the initial conditions are the inlet concentrations and temperature. In greater detail, the model and computational procedure are described in the Appendix.

NUMERICAL EXPERIMENTS, RESULTS, AND DISCUSSION

The ultimate goal of our calculations was to determine the following quantities as a function of mixture stoichiometry and temperature:

(1) UF_6 conversion ($\eta = 1 - [UF_6]_{fin}/[UF_6]_0$),

(2) active species (H(F) atom) efficiency factor (which is defined as the number of U–F bonds broken by one H atom: $k = [HF]_{fin}/(2[H_2]_{fin} + [HF]_{fin})$, where $[HF]_{fin}$ is the number of HF molecules resulting from UF_6 reduction and $[H_2]_{fin}$ is the number of hydrogen molecules resulting from the recombination of H atoms), and

(3) the relative yield of the desired product, UF_4 ($\chi = [UF_4]_{fin}/[UF_6]_0$).

The initial concentration of uranium hexafluoride molecules $[UF_6]_0$ was taken to be 2×10^{17} cm^{-3}. The corresponding concentration of HF molecules at the reactor outlet was $\sim 10^{18}$ cm^{-3}. We considered the process kinetics after the mixing of the initial active mixture with UF_6. In most cases, the initial composition of the active mixture was $UF_6 : H : F : HF = 1 : \nu : 0 : 3/2\nu$, where $\nu \equiv [H]_0/[UF_6]_0$. It was assumed that 5/4 mol of H_2 and 3/4 mol of F_2 are consumed in the formation of 1 mol of H atoms, yielding 3/2 mol of HF.

The results of our calculations are presented in Figs. 2–6.

Figure 2 shows typical profiles of reactant and product concentrations. For the H generator, the extent of the reaction zone is ~3 cm. UF_5 forms initially, and its further reduction is incomplete under the conditions examined: the product contains ~15% UF_5. At the same time, the UF_6 conversion is complete even at short distances along the reaction zone: after the completion of the process, the mixture contains little, if any, uranium hexafluoride. The F generator is characterized by a greater self-heating because of the exothermic reaction (VI). With this design, the favorable reactions sooner begin to compete with the recombination of H atoms and, therefore, it is unnecessary to use H atoms in amounts larger than are dictated by the stoichiometric coefficients (Fig. 2 refers to the stoichiometric case).

As is mentioned above, the chemical generation of free atoms allows the chemical process to be accelerated and a nonequilibrium product composition to be obtained at some stage. Since we take into account the reverse of all reactions, the product composition at long distances along the reaction zone is equal to the equilibrium composition. The equilibrium concentrations, which are established at a distance of about 100 m, are $[UF_6] = 1 \times 10^{-10}$, $[UF_5] = 0.2 \times 10^{-2}$, $[UF_4] = 0.9$, $[UF_3] = 0.1$, and $[UF_2] = 0.4 \times 10^{-2}$ for the H generator and $[UF_6] = 3 \times 10^{-2}$, $[UF_5] = 6 \times 10^{-3}$, $[UF_4] = 0.9$, $[UF_3] = 0.1$, and $[UF_2] = 0.4 \times 10^{-2}$ for the F generator (all concentrations are relative to $[UF_6]_0 = 2 \times 10^{17}$ cm^{-3}). It is interesting that, even at equilibrium, the extent and selectivity of reduction are rather high. This fact, which

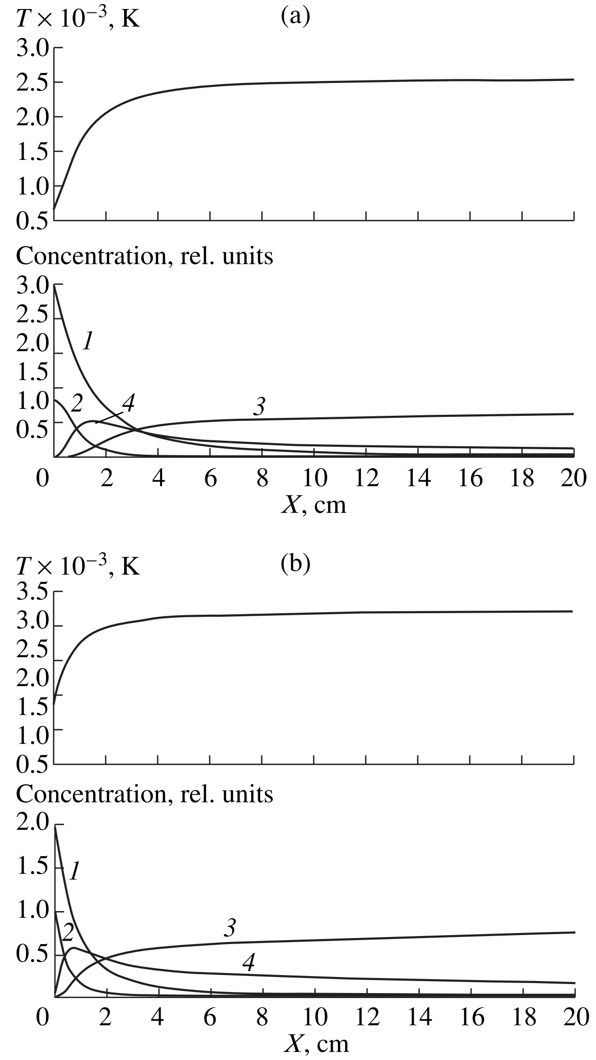

Fig. 2. Profiles of final mixture temperature (T) and of the relative concentrations of (*1*) H, (*2*) UF_6, (*3*) UF_4, and (*4*) UF_5 as a function of the axial coordinate X for the (a) H-generator- and (b) F-generator-type reactors. The flow velocity is 2×10^4 cm/s, the initial temperature is $T_0 = 600$ K, and the concentrations are relative to $[UF_6] = 2 \times 10^{17}$ cm^{-3}. The initial mixture composition is (a) $UF_6 : H : F : HF = 1 : \nu : 0 : 3/2\nu$ ($\nu \equiv [H]_0/[UF_6]_0 = 3$) and (b) $UF_6 : H : F : HF : H_2 = 1 : 0 : \nu : 1/2\nu : \nu$ ($\nu \equiv [F]_0/[UF_6]_0 = 2$).

was also mentioned in an earlier publication [1], is a consequence of the large change in entropy. In any case, the most significant inferences from this computational step are that UF_6 is reduced with H and F atoms at a high rate and that only small extra amounts of the reactants are required, particularly in the case of the F generator. The temperatures established during the reactions are so high that the lower fluorides UF_3 and UF_2 are present in the product mixture.

Figure 3 plots the main parameters of uranium hexafluoride reduction as a function of the relative H content ν_H and the relative F content ν_F for the H generator and F generator, respectively. The stoichiometric ν value for uranium tetrafluoride reduction is 2. Throughout the H and F concentration ranges examined, the final mixture temperature is well above the boiling point of UF_4, resulting only in a negligible product clustering. The conversion of UF_6 is complete once the stoichiometric requirement is satisfied. However, as is noted above, the highest concentration of the desired product UF_4 is reached at a relative H concentration of 3 and a relative F concentration of 2. As the atom concentration increases, the extent of UF_4 reduction to UF_3 and UF_2 increases and the concentration of UF_5 decreases down to zero. The endothermic reduction reactions yielding UF_3 and UF_2, which proceed at a high rate, stabilize the reaction temperature.

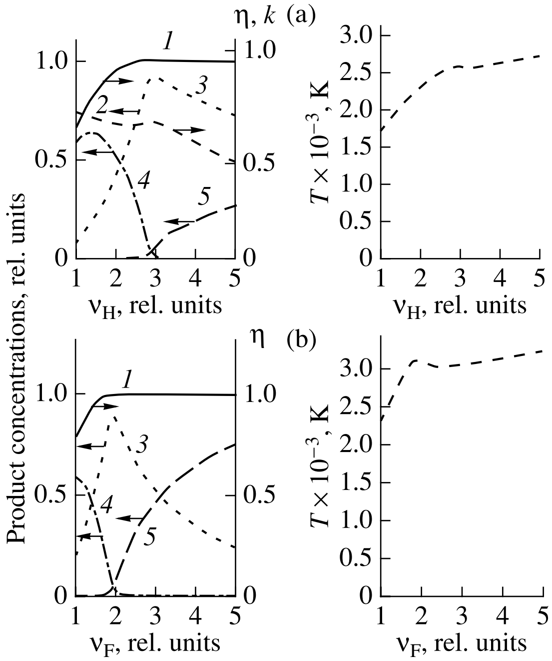

Fig. 3. (*1*) UF_6 conversion (η), (*2*) hydrogen atom efficiency factor (k), (*3–5*) the relative concentrations of (*3*) UF_4, (*4*) UF_5, and (*5*) $UF_3 + UF_2$, and the final temperature (T) versus the initial concentrations of hydrogen atoms (ν_H) and fluorine atoms (ν_F) for the (a) H generator and (b) F generator. (a) $UF_6 : H : F : HF = 1 : \nu : 0 : 3/2\nu$; $T_0 = 600$ K. (b) $UF_6 : H : F : HF : H_2 = 1 : 0 : \nu : 1/2\nu : \nu$; $T_0 = 600$ K. All concentrations are relative to $[UF_6]_0 = 2 \times 10^{17}$ cm^{-3}.

Figure 4 illustrates the effect of the initial mixture temperature on the reduction process for the H generator design. A decrease in T_0 is equivalent to a decrease in the relative H content of the mixture (some of the H atoms recombine to heat the mixture to a temperature at which the reduction process becomes effective). This stabilizing effect of atomic recombination is clearly illustrated by the results of a computer experiment presented in Fig. 5. In this experiment, we deliberately

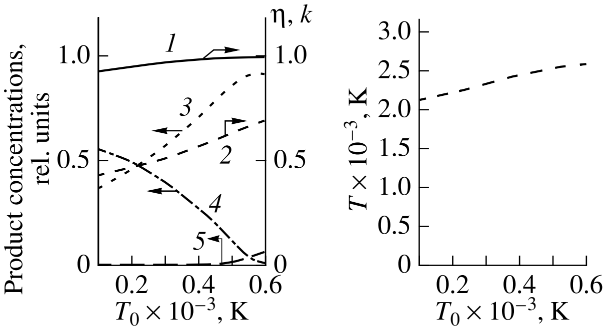

Fig. 4. (*1*) UF_6 conversion (η); (*2*) hydrogen atom efficiency factor (*k*); (*3–5*) the relative concentrations of (*3*) UF_4, (*4*) UF_5, and (*5*) $UF_3 + UF_2$; and the final temperature (*T*) versus the initial mixture temperature (T_0) at $\nu = 3$ for the H generator. All concentrations are relative to $[UF_6]_0 = 2 \times 10^{17}$ cm^{-3}.

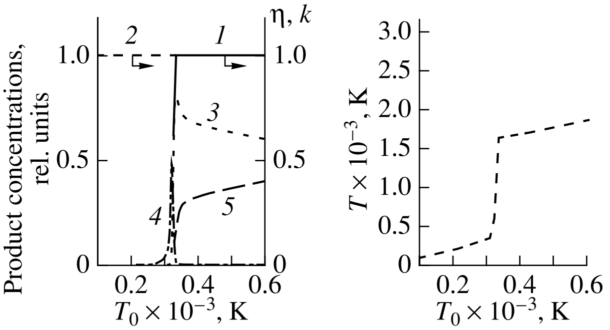

Fig. 5. Basic parameters of the UF_6 reduction process calculated as a function of initial temperature for the H generator with neglect of atomic recombination: (*1*) UF_6 conversion (η); (*2*) hydrogen atom efficiency factor (*k*); (*3–5*) the relative concentrations of UF_4, UF_5, and $UF_3 + UF_2$, respectively; and the final temperature (*T*). $\nu = 3$. All concentrations are relative to $[UF_6]_0 = 2 \times 10^{17}$ cm^{-3}.

excluded the recombination reactions. It might be expected that eliminating the waste of active species would only favor the desired process. In fact, sustained combustion in the case of the H generator is impossible for initial temperatures below 300 K, while the complete reaction network allows sustained combustion at any T_0.

A $\Delta\nu = 0.6$ increase in the initial atom concentration is estimated to be equivalent to a 300 K increase in the initial temperature of the mixture. The calculated data presented in Fig. 6 corroborate this simple estimate. The utilization of the heat of recombination of H atoms in the preheating of the mixture might seem to be very costly, because it would require extra amounts of molecular fluorine, an expensive and scarce gas. However, the power necessary to heat the gas flowing at a rate of ~1 mol/s by $\Delta T = 300$ K is estimated at $N \approx 80$ kW. At such a high power demand, any other heating method will hardly ensure the uniformity of temperature throughout the nozzle assembly.

Temperature is a rather important process parameter. Because of the large cross-sectional areas of the nozzle assembly and reactor, the process temperature can be controlled only by varying the composition of the gas mixture. In particular, the reaction temperature can be decreased (e.g., in order to suppress the deep reduction of UF_6 to UF_2 and UF_3) only by diluting the mixture with a buffer gas. This is generally in conflict with the requirement that no noncondensable gases should be present at the reactor outlet, and there is a single gas that can be used as the buffer. This gas is hydrogen fluoride, which is a reaction product at the same time. It can be liquefied and returned into the operating cycle. Furthermore, an extra amount of HF can serve to raise the outlet partial pressure above the triple-point pressure in order to maintain the steady-state pressure gradient responsible for the reactant flow. The simple kinetic analysis carried out in this study ignores the molecular reactions involving H_2 and the pyrolysis of UF_6 yielding fluorine atoms, reactions possible at the high temperatures established in the decomposition of UF_6 with hydrogen and fluorine atoms. These reactions are very favorable for the process, since they reduce the required flow rate of fluorine, which is the most critical reactant. Therefore, it is appropriate to simulate UF_6 reduction taking into account these reactions, although only rough estimates of their rate constants are available.

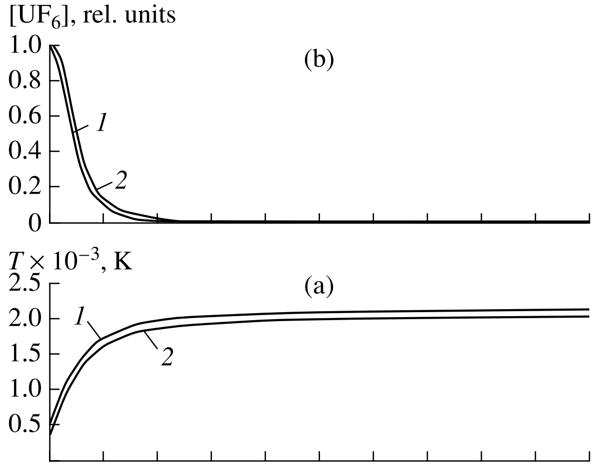

Fig. 6. (a) The final mixture temperature (*T*) and (b) relative UF_6 concentration versus the axial coordinate *X* for the H generator: (*1*) $\nu = 3$ and $T_0 = 600$ K; (*2*) $\nu = 3.6$ and $T_0 = 300$ K. The flow velocity is 2×10^4 cm/s, $UF_6 : H : F : HF = 1 : \nu : 0 : 3/2\nu$ ($\nu \equiv [H]_0/[UF_6]_0$). The concentration is relative to $[UF_6]_0 = 2 \times 10^{17}$ cm^{-3}.

APPENDIX

MATHEMATICAL MODEL AND COMPUTATIONAL PROCEDURE

Let us represent the chemical reactions examined in the following general symbolic form:

$$\sum_{i=1}^{m} \alpha_{ij} u_i \longleftrightarrow \sum_{i=1}^{m} \beta_{ij} u_i. \tag{A.1}$$

Let the overall reaction involve m substances with concentrations $u_1, \ldots, u_m$ (mol/cm^3) taking part in n elementary steps (in the process considered, $m = 10$ and $n = 16$). Here, α_{ij} and β_{ij} are nonnegative, integer, stoichiometric coefficients. We will assume that the rates of the chemical reactions obey the law of mass action and, for the forward and reverse reactions, are expressed as

$$\begin{aligned} w_j^+(u, T) &= k_j^+(T)\exp(-E_j^+/RT)u^{\alpha_{1j}}\ldots u^{\alpha_{mj}}, \\ w_j^-(u, T) &= k_j^-(T)\exp(-E_j^-/RT)u^{\beta_{1j}}\ldots u^{\beta_{mj}}, \end{aligned} \tag{A.2}$$

where $k_j^+(T) = k_j^+ T^{d_j}$, $k_j^-(T) = k_j^- T^{d_j}$, E_j^+, and E_j^- are the preexponential factors of the rate constants and activation energies for the forward and reverse reactions and d_j is the exponent in the preexponential factor for the jth reaction. Obviously, the following thermodynamic relationships are valid for all of the reactions:

$$k_j^+/k_j^- = V^{\sum_{i=1}^{m}(\alpha_{ij} - \beta_{ij})} \exp\left(\sum_{i=1}^{m}(\beta_{ij} - \alpha_{ij})s_i/R\right), \tag{A.3}$$

$$Q_j = \sum_{i=1}^{m}(\alpha_{ij} - \beta_{ij})h_i, \tag{A.4}$$

$$E_j^- - E_j^+ = Q_j, \tag{A.5}$$

where $V = 22400$ cm^3 is the molar gas volume under standard conditions and s_i and h_i are the specific entropies and enthalpies of the reactants and products, which are assumed to be constant. The factor standing before the exponential function in Eq. (A.3) converts molar volume units (which are given in thermodynamic handbooks) to cubic centimeters for reactions with a changing number of species. The above relationships, which express the equality of the chemical potentials of the reactants and products at equilibrium, are mathematically equivalent to the statement that, at any temperature T, the concentration set

$$u_i^*(T) = \exp(s_i/R - h_i/RT - \ln V) \tag{A.6}$$

is the detailed-balancing point, at which the rates of the forward and reverse reactions are equal to $w_j^+(u, T) = w_j^-(u, T)$ ($j = 1, \ldots, n$) and are positive. Furthermore, Eqs. (3A) and (4A) make the set of linear equations

$$\sum_{i=1}^{m}(\beta_{ij} - \alpha_{ij})x_i = b_j, \quad j = 1, \ldots, n$$

solvable for x_j in the cases of $b_j = \ln(k_j^+/k_j^-)$ and $b_j = Q_j$. This imposes a nontrivial constraint on the reaction parameters, since the rank of the stoichiometric matrix $\{\beta_{ij} - \alpha_{ij}\}_{ij}$ is incomplete because of the material balance equations.

We took into account these relationships directly when choosing kinetic parameters for the reactions listed in Table 1. The heats (Q_j) of these reactions were calculated from bond dissociation energy data [3, 11, 12], applying small (~5%) corrections lying within the confidence intervals to ensure the solvability of Eq. (A.4) for the enthalpies h_i. The thermodynamic functions necessary for calculating the rate constants and activation energies of reverse reactions, as well as the heat capacities and matched enthalpies of the reactants and products, are listed in Table 2. The temperature dependences of these quantities are neglected.

Consider a cylindrical reactor of length L in which the reactants flow with a steady-state velocity v along the X axis. Under steady-state conditions, the component concentrations and the mixture temperature in the reactor are functions of the coordinate X alone and the mass and energy conservation laws imply the following set of equations:

$$\begin{aligned} \frac{\mathrm{d}(\nu u_i(x))}{\mathrm{d}x} &= \sum_{j=1}^{n}(\beta_{ij} - \alpha_{ij})(w_j^+(u, T) - w_j^-(u, T)), \\ &\qquad i = 1, \ldots, m \\ \frac{\mathrm{d}(\nu c(u)T)}{\mathrm{d}x} &= \sum_{j=1}^{n} Q_j(w_j^+(u, T) - w_j^-(u, T)), \end{aligned} \tag{A.7}$$

where $c(u) = \sum_{i=1}^{m} c_i u_i$ is the total heat capacity of the system and c_i is the molar heat capacity of the ith component at a constant volume (in J mol^{-1} K^{-1}). The change of variables $x \longrightarrow t = x/v$ (t is the time taken by the flowing mixture to travel the distance between a nozzle and the point x) converts the set of equations (A.7), which describes steady-state profiles, to a set of ordinary differential equations of nonisothermal kinetics. Since the inlet concentrations and temperatures are preset, we deal with an initial-value Cauchy problem. The properties of the equations of chemical kinetics are well studied [14–16]. In particular, owing to the presence of a positive-material-balance vector in the system and the validity of the energy conservation law (Eq. (A.4)), the solution of Eq. (A.7) is defined at any $t \geq 0$ and is nonnegative and bounded. It is interesting that even a slight deviation from Eq. (A.4) (which can take place if

Table 1. Reactions included in the kinetic network and their parameters

No.	Reaction	Q_j	d_j	k_j^+	E_j^+	k_j^-	E_j^-
1	$H + H + UF_6 \longleftrightarrow H_2 + UF_6$	430.5	–1	7.0×10^{18}	0	4.480×10^{19}	430.5
2	$H + UF_6 \longleftrightarrow UF_5 + HF$	286.3	0	6.0×10^{11}	29.3	4.681×10^{8}	315.6
3	$H + UF_5 \longleftrightarrow UF_4 + HF$	140.0	0	6.0×10^{11}	50.2	1.364×10^{10}	190.2
4	$H + UF_4 \longleftrightarrow UF_3 + HF$	–62.7	0	6.0×10^{11}	83.6	4.075×10^{9}	20.9
5	$H + UF_3 \longleftrightarrow UF_2 + HF$	–43.1	0	6.0×10^{11}	83.6	2.901×10^{10}	40.5
6	$H + H + UF_4 \longleftrightarrow H_2 + UF_4$	430.5	–1	7.0×10^{18}	0	4.480×10^{19}	430.5
7	$H + H + UF_5 \longleftrightarrow H_2 + UF_5$	430.5	–1	7.0×10^{18}	0	4.480×10^{19}	430.5
8	$H + H + HF \longleftrightarrow H_2 + HF$	430.5	–1	2.3×10^{18}	0	1.470×10^{19}	430.5
9	$F + H_2 \longleftrightarrow HF + H$	133.8	0	1.6×10^{14}	6.7	1.774×10^{14}	140.5
10	$H + F_2 \longleftrightarrow HF + F$	409.6	0	1.6×10^{14}	10	2.634×10^{13}	419.6
11	$F + H + HF \longleftrightarrow HF + HF$	564.3	–1	2.3×10^{18}	0	1.632×10^{19}	564.3
12	$F + H + UF_6 \longleftrightarrow HF + UF_6$	564.3	–1	7.0×10^{18}	0	4.890×10^{19}	564.3
13	$F + H + UF_5 \longleftrightarrow HF + UF_5$	564.3	–1	7.0×10^{18}	0	4.890×10^{19}	564.3
14	$F + H + UF_4 \longleftrightarrow HF + UF_4$	564.3	–1	7.0×10^{18}	0	4.890×10^{19}	564.3
15	$H + H + H_2 \longleftrightarrow H_2 + H_2$	430.5	–1	2.3×10^{18}	0	1.470×10^{19}	430.5
16	$F + H + H_2 \longleftrightarrow HF + H_2$	564.3	–1	2.3×10^{18}	0	1.632×10^{19}	564.3

Note: Q_j, E_j^+, and E_j^- are, respectively, the heat and the activation energies of the forward and reverse reactions (kJ/mol); k_j^+ and k_j^- are the rate constants of the forward and reverse reactions (in $cm^3\ mol^{-1}\ s^{-1}$ for bimolecular reactions and in $cm^6\ mol^{-2}\ s^{-1}$ for termolecular reactions); and d_j is the exponent (T^{d_j}).

Table 2. Thermal and thermodynamic properties of the components [12]

Property	H	H_2	HF	UF_2	UF_3	UF_4	UF_5	UF_6	F	F_2
C_p, J mol^{-1} K^{-1}	20.7	28.8	29.1	117.2	117.2	117.2	166.2	166.2	22.8	31.4
S, J mol^{-1} K^{-1} (at 298 K)	114.7	130.6	173.8	298.1	332	349.6	377.2	376.8	158.7	203.1
H, J/mol	0	–430.5	–564.3	1936.6	1329.2	702.2	278	0	0	–154

Note: C_p is molar heat capacity, S is entropy, and H is matched enthalpy.

unmatched kinetic constants, either calculated or observed, are used) may lead to such solutions for Eq. (A.7) that an infinite temperature rise occurs in a finite time. Obviously, this is physically meaningless. In turn, condition (A.3) implies that any stationary point is a detailed-balancing point. This property, which was discovered by Zel'dovich [17] for reversible isothermic reactions, is also possessed by nonisothermic reactions, since the set of equations (A.7) has the same form when expressed in terms of the Gibbs free energy function

$$G(u, T) = \sum_{i=1}^{m} u_i(RT\ln u_i - Ts_i + h_i - RT + RT\ln V).$$

It can readily be checked that

$$w_j^+(u, T) = w_j(T)\exp(\langle \nabla_u G, \alpha_j \rangle),$$

$$\ldots w_j^-(u, T) = w_j(T)\exp(\langle \nabla_u G, \beta_j \rangle),$$

where $w_j(T) = k_j^+ T^{d_j} \exp(-E_j^+/RT)[u^*(T)]^{\alpha_j}$ is the reaction rate at the temperature T at the equilibrium point given by Eq. (A.6) and the brackets $\langle \ldots \rangle$ designate the scalar multiplication of the vectors that they include. Thus, the scalar multiplication of the first equations in the set of equations (A.7) by the gradient $\nabla_u G$ yields

$$\begin{aligned}&\langle \mathrm{d}u/\mathrm{d}t, \nabla_u G\rangle\\ &= \sum_{j=1}^{n} w_j(T)(\langle \beta_j, \nabla_u G\rangle - \langle \alpha_j, \nabla_u G\rangle)\\ &\times(\exp(\langle \alpha_j, \nabla_u G\rangle) - \exp(\langle \beta_j, \nabla_u G\rangle)).\end{aligned}$$

Since all terms on the right-hand side of this equation are nonpositive, the equality $\langle\beta_j, \nabla_u G\rangle = \langle\alpha_j, \nabla_u G\rangle$ must be true at the stationary point; that is, detailed balancing does take place at this point.

In the numerical solution of Eq. (A.7), we used a method known from the literature [15, 16] and a standard integration program to implement this method. This program is based on Euler's implicit difference scheme. The slow combinations are preliminarily singled out to improve the conditioning of the difference equations. A computational mesh consisting of points t is adapted by double calculation in order to achieve a closer approximation for abruptly changing unsteady-state processes. The implicit difference equations are solved by the Newton method. With this algorithm, the solutions of the differential equations (A.6) can be approximated with a relative accuracy of 10^{-3} in about 150 steps on the variable, adaptable mesh to obtain a stationary solution ($0 \text{ cm} \le x \le 10^6$ cm). Furthermore, this algorithm requires only a moderate computing power (~1 s per variant on an AMD K6-2/450 PC). The stationary solution of the Euler scheme is always the stationary solution of the set of equations (A.7); that is, it defines the chemical equilibrium in the system. The high degree of approximation achieved with this first-order implicit difference scheme is explained by the fact that, as applied to fast reactions, this scheme preserves the property of solution positiveness and the asymptotics inherent in the kinetic system [15]. By contrast, integrating the set of equations (A.7) using Gear's familiar program from the FORTRAN library IMSL [18], which implements a stiff, stable solver and is based on multistep implicit difference schemes of order 1 through 5 [19], leads to unreliable computations in the case considered. For typical computation conditions, we observed 20% deviations from the energy conservation law $c(u(x))T(x) - \sum_i h_i u_i(x) = \text{const}$. This is apparently explained by the fact that the difference schemes used in these computations break the special asymptotics inherent in kinetic equations.

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