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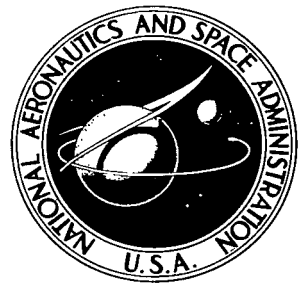

NONEQUILIBRIUM CALCULATIONS OF METHANE-FLUORINE — OXYGEN AND BUTENE-1-FLUORINE — OXYGEN ROCKET PERFORMANCE

by David A. Bittker

Lewis Research Center

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ABSTRACT

Equilibrium and kinetically limited performance, calculated using a one-dimensional model, are presented for methane and butene-1 rocket fuels combined with fluorine-oxygen mixtures for chamber pressures of 100 and 300 psia (6.895×10^5 and 2.069×10^6 N/m^2) and an oxidant-fuel ratio range of 2.5 to 6. Rate-controlling chemical reactions in the recombination process are identified and quantitatively rated in importance. Performance sensitivity to rate-constant uncertainty is studied in detail. It is shown that a one-dimensional kinetic flow model can be used to calculate performance in satisfactory agreement with the available experimental data and that no more than three reactions are rate controlling on the entire process.

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SUMMARY

Theoretical calculations of kinetically limited and equilibrium performance were carried out for the fuels methane and butene-1 combined with fluorine-oxygen mixtures. The nonequilibrium results, obtained using a one-dimensional flow model, agree satisfactorily with the available experimental results for a chamber pressure of 100 psia (6.895×10^5 N/m^2) and a contoured nozzle having an area ratio of 40. The oxidant-fuel ratios used ranged from 2.5 to 6 for oxidizers containing 54.3 to 91.4 weight percent fluorine.

Two rating factors were used to identify the important chemical reactions occurring in the nozzle and to quantitatively rank them in importance as rate-controlling steps in the recombination process. Performance sensitivity to rate-constant uncertainty was studied in detail for the important reactions. Results showed that performance is controlled mainly by three reactions, even though several others must be included in the complete mechanism: $H + H + M \rightleftarrows H_2 + M$, $H + F + M \rightleftarrows HF + M$, and $H + OH + M \rightleftarrows H_2O + M$.

The maximum kinetic performance for methane-fluorine - oxygen was 398 pound-seconds per pound (3903 (N)(sec)/kg) at 100 psia (6.895×10^5 N/m^2) chamber pressure using an oxidant containing 82.6 weight percent fluorine. For butene-1-fluorine - oxygen the maximum performance at this chamber pressure is 385 pound-seconds per pound (3776 (N)(sec)/kg) using an oxidant containing 70.4 weight percent fluorine.

INTRODUCTION

The rocket performance characteristics of propellant systems containing fluorine have been under investigation in recent years by several laboratories. Theoretical and experimental performance of the hydrogen-fluorine system has been reported in references 1 to 3. Although the high performance level of the hydrogen-fluorine system

makes it quite desirable for many missions, the practical problems of handling and storing liquid hydrogen have caused investigators to study the possibility of using less powerful, but more easily handled fuels combined with either fluorine, fluorine-oxygen mixtures, or the compound oxygen difluoride (OF_2). The types of fuels considered are the low-molecular-weight hydrocarbons (e.g., methane (CH_4), propane (C_3H_8) or Butene-1 (C_4H_8)), hydrazine (N_2H_4), and the reactive compound diborane (B_2H_6). Most of the possible combinations of the listed fuels and oxidizers are presently being considered for use as space-storable propellant systems. These are systems for which the propellants can be stored as liquids in outer space for long periods by using only insulating materials and heat shields.

Figure 1 compares the performance of several space-storable systems with that of the best earth-storable and cryogenic liquid propellants in use today. This figure pre-

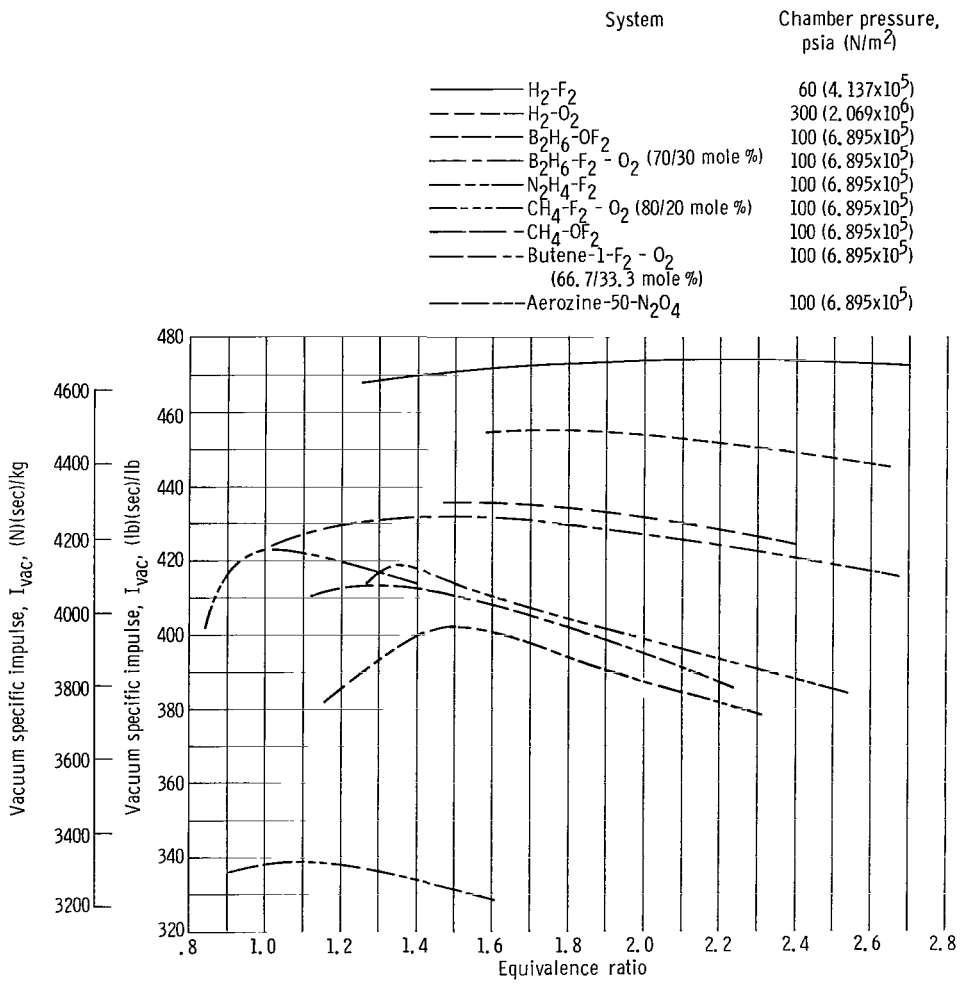

Figure 1. - Performance of rocket propellants. Equilibrium expansion to area ratio, 40.

sents equilibrium performance curves for six space-storable systems plus the hydrogen-fluorine, hydrogen-oxygen and Aerozine-50 - nitrogen tetroxide systems. Theoretical vacuum specific impulse is plotted as a function of equivalence ratio R defined by

$$R = \frac{\left(\frac{O}{F}\right)_{st}}{\left(\frac{O}{F}\right)} \tag{1}$$

(Symbols are defined in appendix A.) All calculations were performed using the method of Zeleznik and Gordon (ref. 4). It can be seen that the performance level of the space-storable propellants falls in the range of I_{vac} = 380 to 435 pound-seconds per pound ((lb)(sec)/lb) (3727 to 4266 (N)(sec)/kg)[1] or midway between the limits of today's highest and lowest energy systems.

Two of the most promising systems under investigation at present are fluorine-oxygen mixtures combined with methane or butene-1 as a fuel. Theoretical calculations for the methane combination were reported several years ago by Gordon and Kastner (ref. 5). Recent work on these two systems was reported in reference 6, which gives a limited number of experimental data on altitude performance and which also presents theoretical performance curves based on the full equilibrium expansion assumption. Reference 7 presents some theoretical performance calculations that consider the nonequilibrium (i.e., finite reaction rate) nozzle expansion losses for the methane fluorine - oxygen system. The purpose of the current work is to present extensive nonequilibrium theoretical performance calculations for the methane-fluorine - oxygen and butene-1-fluorine - oxygen systems. For each system, the results are compared with the limited experimental data available to determine how well the proposed mechanism and rates are able to predict the observed performance. The individual reactions in the proposed reaction mechanism are examined to determine which are most important to and controlling on the performance. The performance levels of both systems are compared with each other so that their capabilities can be evaluated by engine designers.

Conditions used for the methane-fluorine - oxygen system are chamber pressure, 100 and 300 psia (6.895×10^5 and 2.069×10^6 N/m^2); oxidant-fuel ratio O/F, 3 to 6; and weight percent fluorine in the oxidizer, 54.3 to 91.4. For the butene-1-fluorine - oxygen system the chamber pressure is 100 psia (6.895×10^5 N/m^2), O/F varies from 2.5 to 5, and percent fluorine in the oxidizer ranges from 54.3 to 82.6 weight percent.

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[1]The specific impulse unit, (N)(sec)/kg, is identical to m/sec inasmuch as 1 N is equal to 1 (kg)(m)/sec^2 in the SI system.

PROCEDURE

The complete investigation of rocket performance to be reported includes the following steps:

Equilibrium and Frozen Computations

These computations were performed to obtain the limiting theoretical performance and to determine the significant species present for each system and, also, the equilibrium starting conditions for the kinetic calculations. Computations showed that there was little or no effect on the results when certain trace species were purposely omitted from consideration. This fact allowed the selection of a set of significant species by using the criterion that omitting any species changes the equilibrium specific impulse by less than ±0.5 (lb)(sec)/lb (±4.9 (N)(sec)/kg) at an area ratio of 40.

Kinetically Limited Computations

With all significant species known, a reaction mechanism was then chosen for each of the systems under study. Many of the reactions were already known from previous investigations; details of the selection procedure are given in the following section. A set of "reference" rate-constant values was chosen for all the postulated chemical reactions after a survey of the available literature. These rate constants were used to obtain reference performance computations for all assigned conditions. The results of these calculations were analyzed to determine the most important reactions in each mechanism. Parametric rate variation studies were then made to find the effect of rate variations on performance.

The nozzle used for all the kinetically limited computations is identical to the one used for the experimental measurements reported in reference 6. It is a truncated perfect nozzle having a throat radius of 3 inches (7.62 cm) and an area ratio of 40. Thrust level is approximately 5000 pounds (22 240 N) at 100 psia (6.895×10^5 N/m^2) chamber pressure.

Comparison with Experimental Results

Experimental performance measurements for the methane - fluorine-oxygen system under altitude conditions are reported in reference 6. Table VI-2 of that report tabulates uncorrected I_{vac} and characteristic velocity efficiency η_{C^*}. In addition, the table lists

values of I_{vac} corrected for heat transfer, friction, and nozzle divergence losses, as well as values of η_{C*} corrected for heat transfer and momentum losses. The I_{vac} values were corrected for combustion inefficiency to obtain kinetically limited experimental specific impulse data that were compared with the computed theoretical results. The equation used is

$$I = \frac{(I_{vac})_{corr}}{(\eta_{C*})_{corr}} \tag{2}$$

THEORY AND INPUT DATA

Method for Kinetic Calculations

The problem of calculating kinetically limited rocket performance is part of the more general problem of calculating the progress of a complex set of chemical reactions in a flow system. One must solve the usual differential equations of fluid motion (conservation of mass, momentum, and energy) simultaneously with the equations for the changes of concentration due to chemical reaction. The particular system of equations used in the present work assumes one-dimensional flow of uniformly mixed, thermally perfect, reacting gases. The reactants are assumed to burn with 100 percent combustion efficiency in the chamber and all flow losses due to the effects of viscosity and other transport phenomena are neglected. The specific equations and computer program used for the computations were developed under NASA contract and are described in reference 8. They are the same as those used for the hydrogen-fluorine calculations described in reference 2. To perform these kinetic computations a set of reactions that accurately describe the chemical changes occurring in the flow system must be written. All reactions are considered reversible, and the law of microscopic reversibility is used to obtain the reverse rate constant for any reaction from its forward rate constant and equilibrium constant.

Reaction Mechanism and Species for Hydrocarbon-Fluorine - Oxygen System

Early theoretical work by Gordon and Wilkins (ref. 9) showed that the carbon atom combines preferentially with the oxygen atom and hydrogen with fluorine in a hydrocarbon-fluorine - oxygen combustion. The two major products of combustion are carbon monoxide (CO) and hydrogen fluoride (HF). Reference 9 also showed that best theoretical performance was obtained when the number of carbon atoms is the same as

the number of oxygen atoms in the mixture and the number of hydrogen atoms equals the number of fluorine atoms. This means that the carbon to hydrogen atom ratio of the fuel will be the same as the oxygen to fluorine atom ratio in the oxidant. For example, the following reaction can be written for the greatest performance of the methane-fluorine - oxygen system:

$$CH_4 + \frac{1}{2} O_2 + 2F_2 \rightarrow CO + 4HF \qquad (A)$$

This reaction has an oxidant containing 82.6 weight percent fluorine and an oxidant-fuel ratio of 5.75. For any other assigned oxidant composition the best performance will be obtained for one particular O/F value. A simple approximate method of calculating this value is also given in reference 9, and the equations are presented for reference in appendix B. Results of the present equilibrium calculations showed that two different sets of significant species are obtained as a function of the percent fluorine in the oxidant and the assigned O/F value. These variables control the atom ratios in the mixture. By using the oxygen to carbon atom ratio α defined in appendix B, the two species lists and corresponding chemical reaction mechanisms can be classified as follows:

Mechanism A: oxygen-to-carbon-atom ratio less than 1 (low O/F) and high fluorine-to-oxygen ratio. - For this situation CO is the only oxygen containing species, and the excess carbon atoms can combine with fluorine and hydrogen atoms. The complete list of significant species needed to satisfy the selection criterion described eariler is gaseous carbon (C), hydrogen atom (H), fluorine atom (F), carbon monoxide (CO), hydrogen fluoride (HF), difluoroacetylene (C_2F_2), acetylene (C_2H_2) and methylidyne radical (CH). No solid carbon or other condensed products were found. The reaction mechanism assumed for these species considers both CO and C_2F_2 as inerts and is as follows:

$$\left.\begin{array}{l} H + F + M \overset{k_1}{\rightleftharpoons} HF + M \\ \Delta H^{o}_{298} = -136 \text{ kcal/mole} \\ \qquad\quad = -569 \text{ kJ/mole} \end{array}\right\} \qquad (I)$$

$$\left.\begin{array}{l} H + H + M \overset{k_2}{\rightleftharpoons} H_2 + M \\ \Delta H^{o}_{298} = -104 \text{ kcal/mole} \\ \qquad\quad = -435 \text{ kJ/mole} \end{array}\right\} \qquad (II)$$

$$F + H_2 \overset{k_3}{\rightleftharpoons} HF + H$$

$$\Delta H^o_{298} = -32 \text{ kcal/mole} = -134 \text{ kJ/mole} \qquad \text{(III)}$$

$$CH + CH \overset{k_4}{\rightleftharpoons} C_2H_2$$

$$\Delta H^o_{298} = -231 \text{ kcal/mole} = -964 \text{ kJ/mole} \qquad \text{(IV)}$$

$$C + H + M \overset{k_5}{\rightleftharpoons} CH + M$$

$$\Delta H^o_{298} = -81 \text{ kcal/mole} = -339 \text{ kJ/mole} \qquad \text{(V)}$$

Mechanism B: oxygen-carbon ratio greater than one (high O/F) and low fluorine to oxygen ratio. - In this case there is excess oxygen present to combine with hydrogen atom as well as carbon. The fluorine forms only HF and no condensed species were found. The complete list of species is H, O, F, CO, CO_2, H_2, HF, O_2, OH, and H_2O. The reaction mechanism for these species consists of reactions I, II, and III plus the following:

$$CO + O + M \overset{k_6}{\rightleftharpoons} CO_2 + M$$

$$\Delta H^o_{298} = -127 \text{ kcal/mole} = -531 \text{ kJ/mole} \qquad \text{(VI)}$$

$$CO + OH \overset{k_7}{\rightleftharpoons} CO_2 + H$$

$$\Delta H^o_{298} = -25 \text{ kcal/mole} = -105 \text{ kJ/mole} \qquad \text{(VII)}$$

$$H + OH + M \overset{k_8}{\rightleftarrows} H_2O + M$$

$$\Delta H^o_{298} = -119 \text{ kcal/mole} = -498 \text{ kJ/mole} \qquad \text{(VIII)}$$

$$O + O + M \overset{k_9}{\rightleftarrows} O_2 + M$$

$$\Delta H^o_{298} = -119 \text{ kcal/mole} = -498 \text{ kJ/mole} \qquad \text{(IX)}$$

$$O + H + M \overset{k_{10}}{\rightleftarrows} OH + M$$

$$\Delta H^o_{298} = -102 \text{ kcal/mole} = -427 \text{ kJ/mole} \qquad \text{(X)}$$

$$H_2 + OH \overset{k_{11}}{\rightleftarrows} H_2O + H$$

$$\Delta H^o_{298} = -15 \text{ kcal/mole} = -63 \text{ kJ/mole} \qquad \text{(XI)}$$

$$H + O_2 \overset{k_{12}}{\rightleftarrows} OH + O$$

$$\Delta H^o_{298} = +17 \text{ kcal/mole} = +71 \text{ kJ/mole} \qquad \text{(XII)}$$

$$O + H_2 \overset{k_{13}}{\rightleftarrows} OH + H$$

$$\Delta H^o_{298} = +2 \text{ kcal/mole} = +8 \text{ kJ/mole} \qquad \text{(XIII)}$$

Experimental data are available for most of the chemical reactions written. After a survey of the current literature presenting both theoretical and experimental rate-constant data, the rate-constant expressions shown in table I were chosen as the set of values to be used. These rate constants will be referred to as the reference rates. It should be pointed out that, although the rate constants for reactions I, II, and III are taken from reference 2, they are not necessarily the "assigned" rates used in that work. In fact, only k_9 in table I is the same as the assigned rate constant of reference 2. The

TABLE I. - RATE CONSTANTS FOR METHANE-FLUORINE OXYGEN SYSTEM[a, b]

Reaction	Reaction number	Preexponential factor, A	Temperature exponent, n	Activation energy, E_a, cal/mole	Reference
$H+F+M \rightleftharpoons HF+M$	I	3.0×10^{19}	-1.0	0	2
$H+H+M \rightleftharpoons H_2+M$	II	7.5×10^{18}	-1.0	0	2
$F+H_2 \rightleftharpoons HF+H$	III	2.04×10^{13}	-.12	3 750.0	2
$CH+CH \rightleftharpoons C_2H_2$	IV	5×10^{11}	.5	6 000.0	16
$C+H+M \rightleftharpoons CH+M$	V	2×10^{16}	-.5	0	16
$CO+O+M \rightleftharpoons CO_2+M$	VI	7.0×10^{16}	-1.0	0	[c]15
$CO+OH \rightleftharpoons CO_2+H$	VII	3.1×10^{11}	0	600.0	17
$H+OH+M \rightleftharpoons H_2O+M$	VIII	4.5×10^{21}	-1.5	0	18
$O+O+M \rightleftharpoons O_2+M$	IX	8.15×10^{18}	-1.22	0	19
$O+H+M \rightleftharpoons OH+M$	X	4.0×10^{18}	-1.0	0	20
$H_2+OH \rightleftharpoons H_2O+H$	XI	2.3×10^{13}	0	5 200.0	17
$H+O_2 \rightleftharpoons OH+O$	XII	2.2×10^{14}	0	16 600.0	21
$O+H_2 \rightleftharpoons OH+H$	XIII	1.2×10^{13}	0	9 200.0	22
$F+OH \rightleftharpoons HF+O$	XIV	2.9×10^{12}	.68	200.0	11

[a]Rate constant expression is $k = AT^n \exp(-E_a/RT)$.

[b]Units of k are $cm^3/(mole)(sec)$ for two-body reactions and $cm^6/(mole^2)(sec)$ for three-body reactions.

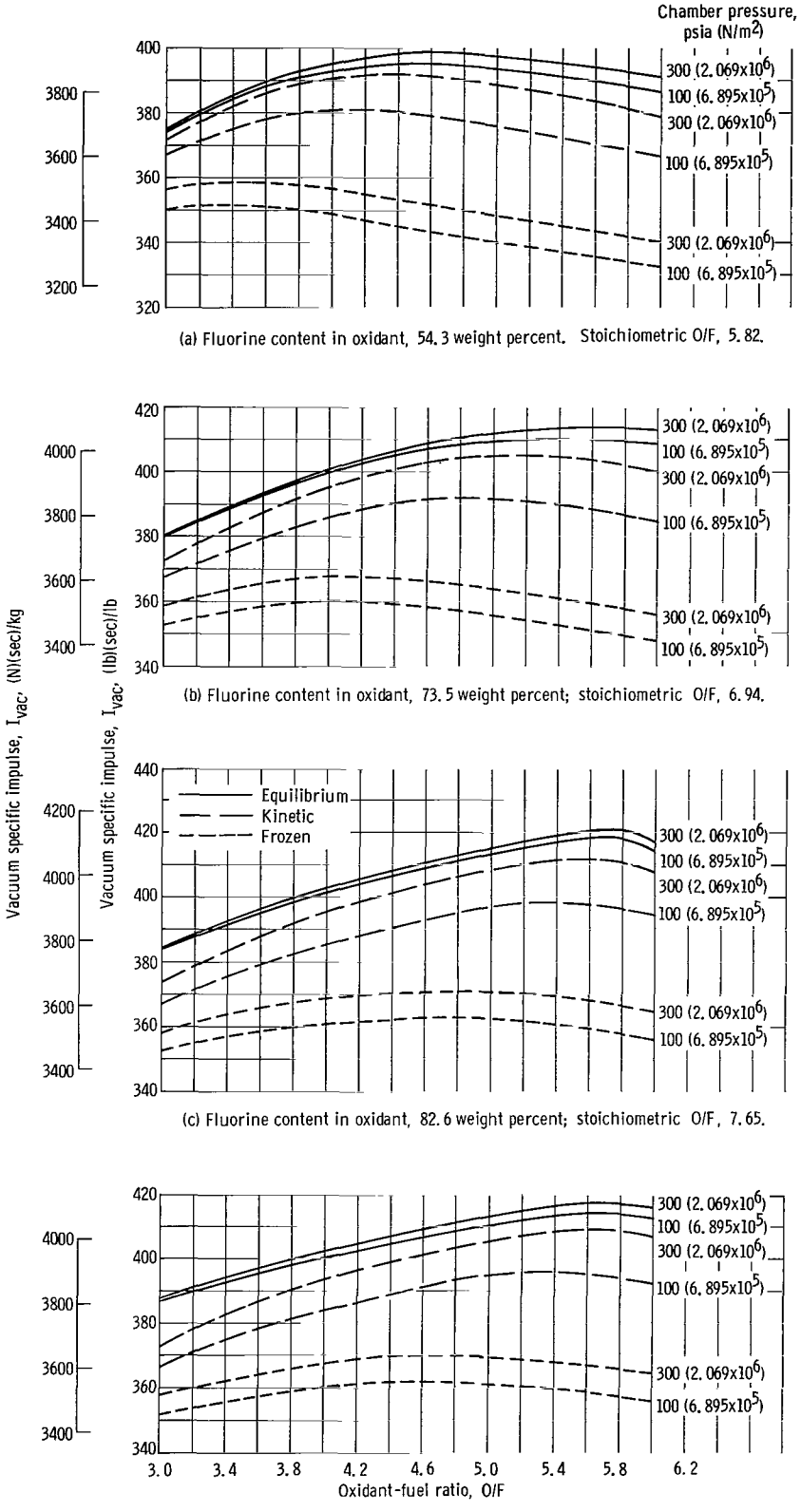
[c]Data from ref. 15 fitted to the equation $k = AT^{-1}$.

expressions for k_1 and k_3 given in table I are derived from recent experimental results (ref. 10) and are used in the present work as reference rate constants.

RESULTS AND DISCUSSION

Methane-Fluorine - Oxygen System

Performance results. - Kinetic performance has been calculated for a wide range of operating conditions. At chamber pressures of 100 and 300 psia (6.895×10^5 and 2.069×10^6



(a) Fluorine content in oxidant, 54.3 weight percent. Stoichiometric O/F, 5.82.

(b) Fluorine content in oxidant, 73.5 weight percent; stoichiometric O/F, 6.94.

(c) Fluorine content in oxidant, 82.6 weight percent; stoichiometric O/F, 7.65.

(d) Fluorine content in oxidant, 91.4 weight percent; stoichiometric O/F, 8.48.

Figure 2. - Methane-fluorine - oxygen performance. Area ratio, 40.

N/m^2) the oxidant-fuel ratio (O/F) was varied from 3 to 6 for four oxidants, containing 50, 70, 80, and 90 mole percent fluorine. Weight percents of fluorine in these oxidant mixtures were 54.3, 73.5, 82.6, and 91.4, respectively.

A complete summary of equilibrium, kinetic, and frozen performance is shown in figure 2. In these graphs the indicated stoichiometric O/F values are those for conversion to the final products HF, CO_2, and H_2O. The highest level of performance is shown with the oxidant containing 82.6 weight percent fluorine. Figure 2(c) shows that the maximum kinetic specific impulse is 398 (lb)(sec)/lb (3903 (N)(sec)/kg) at O/F = 5.1 for 100 psia (6.895×10^5 N/m^2) chamber pressure and 412 (lb)(sec)/lb (4040 (N)(sec)/kg) at O/F = 5.6 for 300 psia (2.069×10^6 N/m^2). To better visualize the effect of oxidant composition, performance has been plotted against percent fluorine in the oxidant for several O/F values in figure 3. Both the equilibrium results (fig. 3(a)) and the kinetic results

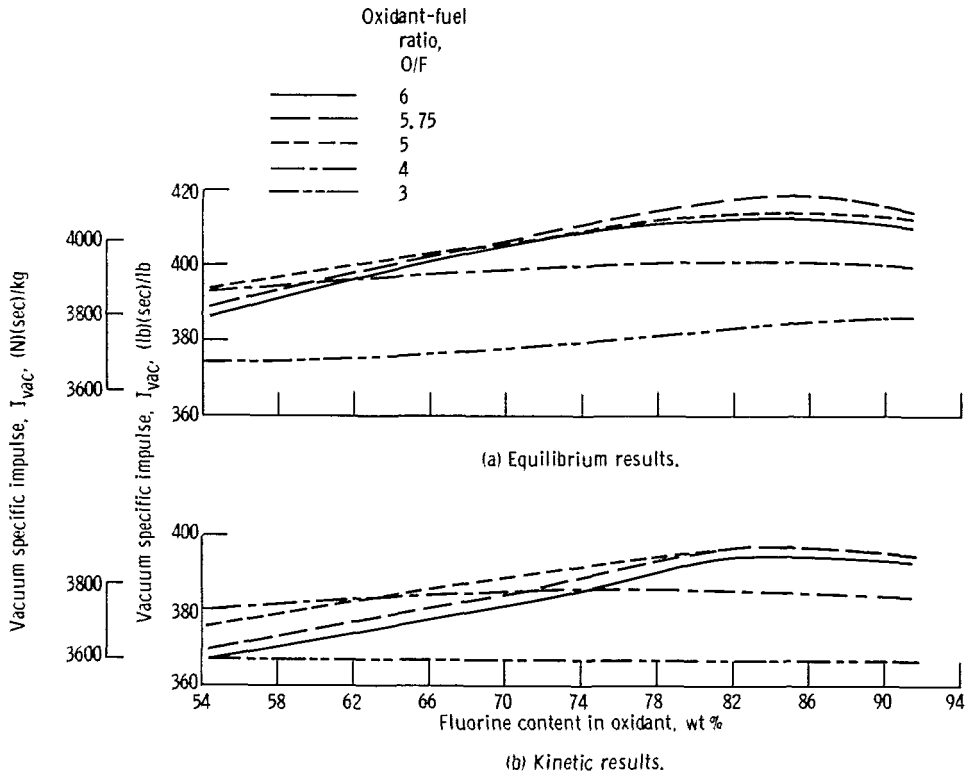


Figure 3. - Effect of oxidant composition on methane-fluorine - oxygen performance. Chamber pressure, 100 psia (6.895×10^{-5} N/m^2); final area ratio, 40.

(fig. 3(b)) show that highest performance is obtained for oxidants containing 82 to 86 percent fluorine. This fact agrees with reaction (A), written previously, and confirms the conclusion made from figure 2. It should be noticed that figure 2(c) shows maximum kinetic performance occurring at an O/F very close to 5 for low chamber pressure. This value is much lower than the O/F of 5.75 obtained from reaction (A). At the high

TABLE II. - IMPULSE RECOVERY PARAMETERS

FOR METHANE-OXYGEN-FLUORINE

[Oxidant-fuel ratio, 5.]

(a) U.S. Customary units

Fluorine content in oxidant, wt. %	Chamber pressure, P_c, psia			
	100	300	100	300
	Impulse recovery factor, F (a)		Impulse loss, $I_{eq} - I_k$, (lb)(sec)/lb	
54.3	0.660	0.817	18.2	9.1
73.5	.665	.852	18.0	7.1
82.6	.694	.850	15.5	6.7
91.4	.695	.838	14.8	7.0

(b) SI units

Fluorine content in oxidant, wt. %	Chamber pressure, P_c, N/m^2			
	6.895×10^5	2.069×10^6	6.895×10^5	2.069×10^6
	Impulse recovery factor, F		Impulse loss, $I_{eq} - I_R$, (N)(sec)/kg	
54.3	0.660	0.817	178	89
73.5	.665	.852	177	70
82.6	.694	.850	152	66
91.4	.695	.838	145	69

[a] $F = (I_k - I_{fr})/(I_{eq} - I_{fr})$.

chamber pressure, however, maximum performance occurs close to O/F = 5.75. One explanation of this behavior is the deviation from the assumption that the nozzle gas consists of only the species HF and CO. This assumption is good for an equilibrium condition but is much less valid for a nonequilibrium situation with much slower recombination rates for the formation of HF. The increase of these recombination rates with increased pressure explains why the kinetic performance curve for 300 psia (2.069×10^6 N/m^2) chamber pressure has its maximum at an O/F value closer to 5.75 than does the low-pressure curve. From the practical viewpoint, achieving maximum performance at a lower O/F means that less oxidant has to be carried along to perform a given mission.

The curves of figure 2 show that increasing the chamber pressure from 100 to 300 psia (6.895×10^5 to 2.069×10^6 N/m^2) has a small effect on equilibrium performance but

very significantly increases the reaction rate limited performance in all cases. This is because the largest effect of the pressure increase is to increase the rate of three-body collisions, and, thus, the overall rates of three-body recombination reactions. These are the reactions that release most of the energy into the expanding gases and are therefore rate controlling for kinetically limited performance. As a measure of performance losses due to finite reaction rates, we will use the impulse recovery parameter, defined by

$$F = \frac{I_k - I_{fr}}{I_{eq} - I_{fr}} \tag{3}$$

For comparison purposes the values of F are calculated for all the conditions in figure 2 at an O/F of 5. Results are given in table II and show quantitatively the percent-

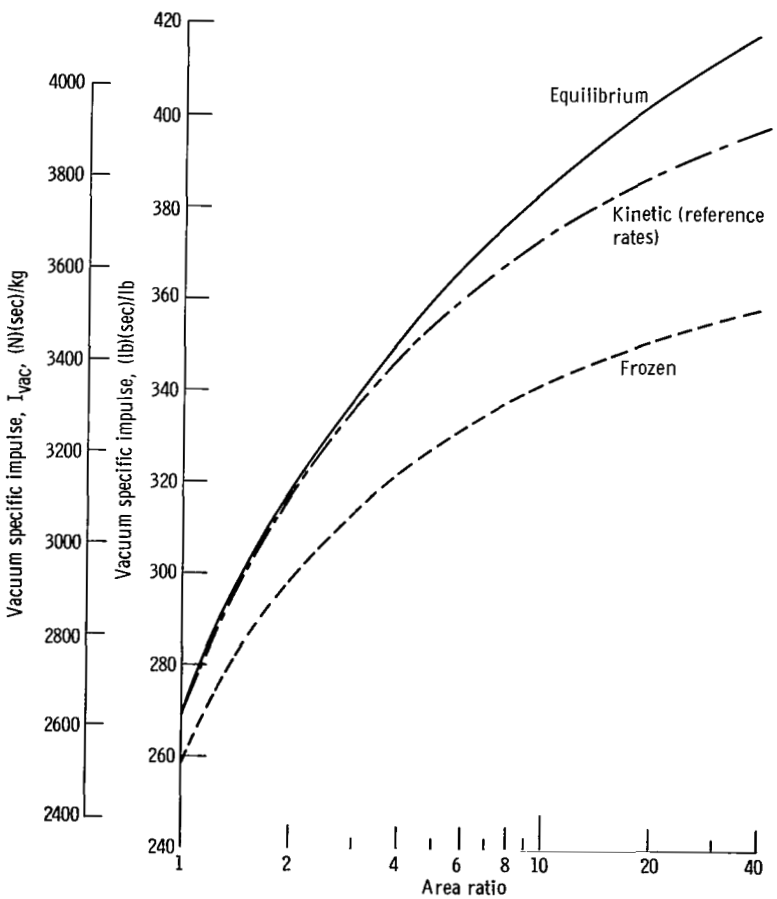


Figure 4. - Theoretical performance against nozzle area ratio for methane-fluorine - oxygen. Chamber pressure, 100 psia (6.895×10^5 N/m^2); oxidant-fuel ratio, 5.75; fluorine content in oxidizer, 82.6 weight percent.

age decrease of kinetic losses with increase in chamber pressure as well as the absolute performance loss $I_{eq} - I_k$. On an absolute basis, at O/F = 5, the kinetic loss $I_{eq} - I_k$ at a chamber pressure of 100 psia (6.895×10^5 N/m^2) is about twice the loss at 300 psia (2.069×10^6 N/m^2).

It is also of interest to see how the kinetic performance loss depends on position in the nozzle. A typical plot of the three types of theoretical performance as a function of supersonic nozzle area ratio is shown in figure 4. The 82.6 percent oxidizer is used at an O/F of 5.75 and a chamber pressure of 100 psia (6.895×10^5 N/m^2). At an area ratio of 2, the kinetic loss $I_{eq} - I_k$ is 1 impulse unit or less than 1/2 percent of the equilibrium value. A 1-percent loss in performance occurs at an area ratio of 3.5. For an area ratio of 40 the kinetic loss is about 20 impulse units or 5 percent of the equilibrium value.

Effect of reaction rate variation. - It is possible to obtain a qualitative idea about which reactions may be the most important in determining the calculated specific impulse by examining the changes in various species concentrations downstream of the rocket nozzle throat. Some typical examples of these concentration changes are shown in table III. Species mole fractions near the throat of the nozzle and at an expansion ratio of 40 are tabulated at O/F = 3 and 5.75 for two oxidizers.

For both oxidizers at O/F = 3, the only significant changes are a decrease in hydrogen atom concentration and an increase in molecular hydrogen concentration. At O/F = 5.75 both hydrogen and fluorine atom concentrations decrease, whereas HF increases. The molecular hydrogen concentration now decreases instead of increasing. From this information one might expect that the hydrogen atom recombination is most rate controlling at O/F = 3, but several possible reactions, for example, (I), (II), (III), and (XI), could be rate controlling at O/F = 5.75. A more systematic approach to measuring the importance of each chemical reaction has been suggested in reference 11, which assumes the importance of a reaction to be proportional to the net volumetric conversion rate, that is, the extent to which the reaction proceeds. The general formula for this quantity can be found in texts such as the work of Penner (ref. 12). The rating factor to be used is given by the formula

$$X_j = \frac{X_{v,j}}{\rho^2} \equiv \frac{k_{f,j} \prod_{i=1}^{N} c_i^{\nu_{ij}} - k_{b,j} \prod_{i=1}^{N} c_i^{\nu'_{ij}}}{\rho^2} \tag{4}$$

TABLE III. - COMPOSITION OF EXHAUST GAS FOR METHANE-FLUORINE - OXYGEN PROPELLANT

[Chamber pressure, 100 psia (6.895×10^5 N/m^2).]

(a) Fluorine content in oxidizer, 82.6 weight precent

Species	Oxidant fuel ratio			
	3		5.75	
	Throat	Area ratio, 40	Throat	Area ratio, 40
	Species mole fraction			
C	0.00009	0.00009	0.00011	0.00011
CO	.14158	.14339	.17971	.18687
C_2F_2	.05354	.05422	.00105	.00109
CH	.00003	.00004	.000001	.000003
C_2H_2	.01093	.01107	.000001	.000001
F	.00096	5.6×10^{-9}	.10380	.05527
H	.06673	.04307	.08858	.06625
H_2	.26783	.28301	.01294	.00005
HF	.45830	.46512	.61364	.69035

(b) Fluorine content in oxidizer, 73.5 weight percent

C	0.00001	0.00001	--------	--------
CO	.20796	.20998	0.17503	0.16749
CO_2	-------	--------	.00927	.02335
C_2F_2	.02231	.02253	--------	--------
CH	.00001	.00001	--------	--------
C_2H_2	.00405	.00409	--------	--------
F	.00070	1.0×10^{-10}	.05210	.00449
H	.05530	.03715	.07381	.07773
H_2	.26972	.28133	.01724	.00345
HF	.43993	.44491	.59595	.66654
H_2O	-------	--------	.00760	.00584
O	-------	--------	.04365	.03416
O_2	-------	--------	.00756	.01644
OH	-------	--------	.01779	.00051

TABLE IV. - REACTION RATING PARAMETERS FOR

METHANE-FLUORINE - OXYGEN FUEL

[Chamber pressure, 100 psia (6.895×10^5 N/m^2).]

(a) Fluorine content in oxidizer, 82.6 weight percent

Reaction number	Reaction	Mixture ratio							
		3				6			
		Reaction rating parameter							
		X_j	Rank	$X_{H,j}$	Rank	X_j	Rank	$X_{H,j}$	Rank
(II)	$H+H+M = H_2+M$	958.0	1	-99 610	1	239	3	-24 850	2
(I)	$H+F+M = HF+M$	56.1	2	-7627	2	1710	1	-232 600	1
(III)	$F+H_2 = HF+H$	22.9	3	-731	3	573	2	-18 350	3
(V)	$C+H+M = CH+M$	0.168	4	-1.36	4	-----	--	-------	--
(IV)	$CH+CH = C_2H_2$	8.9×10^{-6}	5	-2.06×10^{-3}	5	-----	--	-------	--
(VIII)	$H+OH+M = H_2O+M$	--------	--	----------	--	33.2	5	-3946	4
(X)	$O+H+M = OH+M$	--------	--	----------	--	9.85	7	-1004	5
(XI)	$H_2+OH = H_2O+H$	--------	--	----------	--	-34.1	4	+511	6
(VII)	$CO+OH = CO_2+H$	--------	--	----------	--	14.1	6	-353	7
(VI)	$CO+O+M = CO_2+M$	--------	--	----------	--	0.579	10	-74	8
(IX)	$O+O+M = O_2+M$	--------	--	----------	--	0.258	11	-31	9
(XII)	$H+O_2 = OH+O$	--------	--	----------	--	-1.38	9	-24	10
(XIII)	$O+H_2 = OH+H$	--------	--	----------	--	-9.14	8	-18	11

(b) Fluorine content in oxidizer, 73.5 weight percent

(II)	$H+H+M = H_2+M$	198	6	-20 590	4				
(I)	$H+F+M = HF+M$	916	1	-124 600	1				
(III)	$F+H_2 = HF+H$	769	2	-24 600	3				
(VIII)	$H+OH+M = H_2O+M$	476	3	-56 640	2				
(X)	$O+H+M = OH+M$	89.5	9	-9 129	5				
(XI)	$H_2+OH = H_2O+H$	-445	4	+6 675	6				
(VII)	$CO+OH = CO_2+H$	200	5	-5 000	7				
(VI)	$CO+O+M = CO_2+M$	5.5	11	-699	10				
(IX)	$O+O+M = O_2+M$	24.8	10	-2 951	8				
(XII)	$H+O_2 = OH+O$	-142	7	-2 414	9				
(XIII)	$O+H_2 = OH+H$	97	8	+194	11				

In this equation $X_{v,j}$ is the volumetric conversion rate for the j^{th} reaction

$$\sum_{i=1}^{N} \nu_{ij} M_i \underset{k_{b,j}}{\overset{k_{f,j}}{\rightleftarrows}} \sum_{i=1}^{N} \nu'_{ij} M_i$$

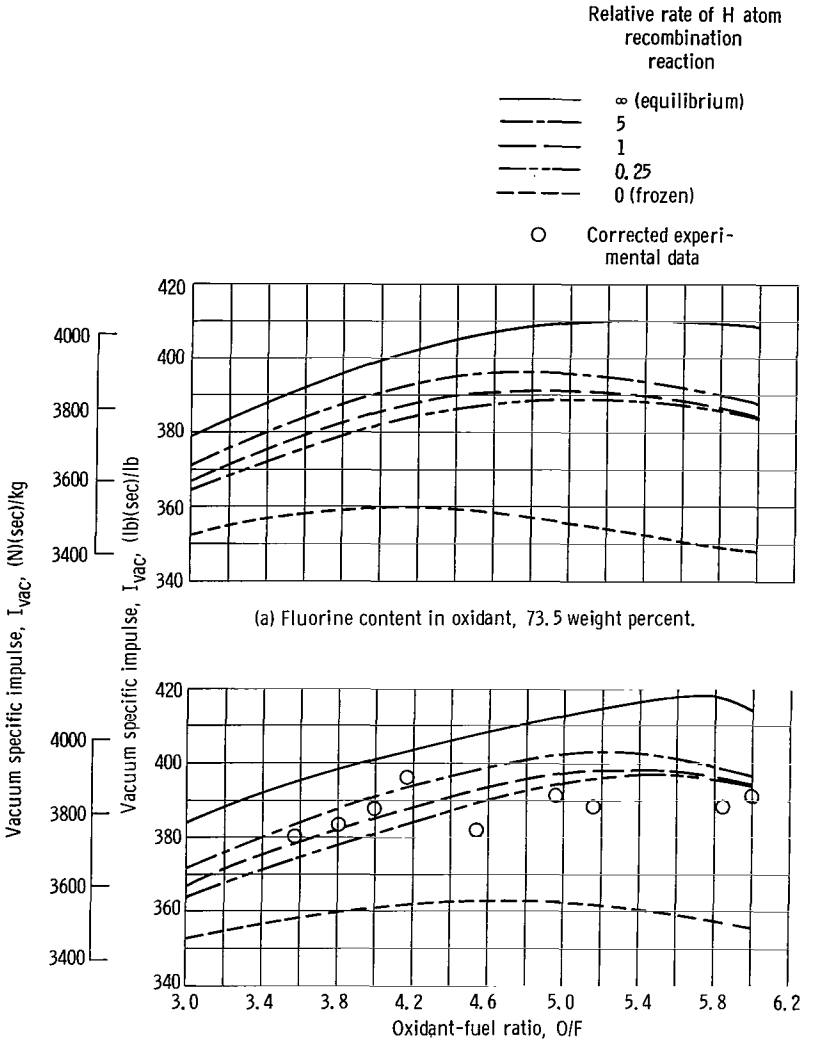
where M_i designates the i^{th} species in the reacting system. The sign of X_j indicates the direction in which the reaction is actually proceeding. A positive X_j means the reaction is actually producing products from reactants as written.

Performance, however, depends not only on a net reaction rate, but also on the amount of heat released into or absorbed from the system by each reaction. In the present work, therefore, a more meaningful parameter has also been used, namely,

$$X_{H,j} = X_j(\Delta H^o_{298}) \tag{5}$$

where ΔH^o_{298} is the molar heat of reaction at 298 K for the forward reaction as written. The units of ΔH^o_{298} are arbitrarily taken as kilocalories per mole. If the usual sign convention is used for ΔH^o_{298} (A negative sign means heat is released by the reaction.), then the sign of $X_{H,j}$ will always be negative if heat is released into the gas and positive if heat is absorbed from the gas. For example, if a reaction, as written, is exothermic, but actually proceeds in the reverse direction, X_j is negative and ΔH^o_{298} is negative. Then $X_{H,j}$ is positive, indicating that this reaction absorbs heat from the gas; therefore, $X_{H,j}$ gives both the magnitude and direction of the enthalpy change rate caused by a particular reaction.

Values for both rating parameters have been calculated for the reactions in the methane-fluorine - oxygen expansion for three conditions, and are given in table IV. These show that either X_j or $X_{H,j}$ selects reactions (I), (II), and either (III) or (VIII) as the most important at all operating conditions. To determine the actual sensitivity of performance to uncertainty in the rate-constant values for reactions (I), (II), and (III), rate variation calculations were performed in which each of the three reaction rates was individually changed. The rate variation factors were chosen to account for experimental uncertainties and third body efficiency effects. The effect of reaction II (the H atom recombination) on performance is shown in figure 5 for two oxidant compositions, 73.5 and 82.6 weight percent fluorine. The rate constant variation is from five times the reference value to one fourth of that value. It can be seen that either increasing or decreasing k_2 has a significant effect on performance over almost the entire range of O/F values for both oxidants. Even at O/F = 6, where the effect is smallest, increasing k_2 causes almost a 1 percent increase in specific impulse for both oxidants.

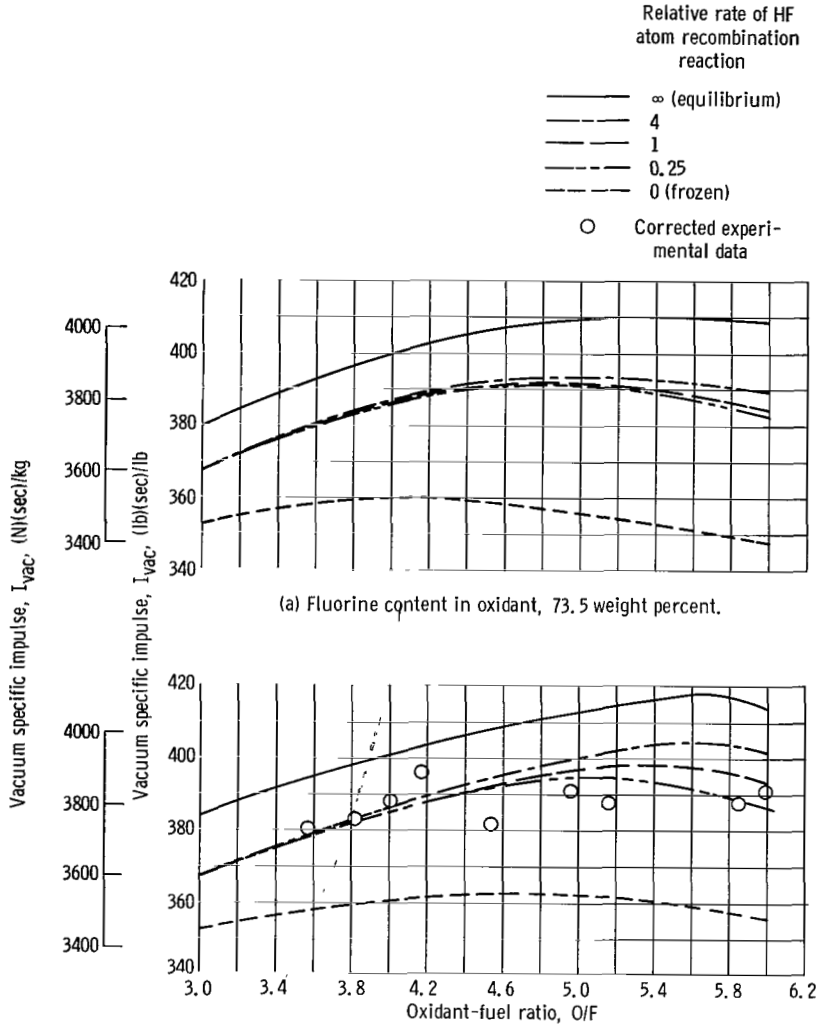


(a) Fluorine content in oxidant, 73.5 weight percent.

(b) Fluorine content in oxidant, 82.6 weight percent.

Figure 5. - Performance of methane-fluorine - oxygen: effect of hydrogen atom recombination rate. Chamber pressure, 100 psia (6.895×10^5 N/m^2); area ratio, 40.

The effect of changing only k_1, the rate constant for the H + F recombination reaction, is shown in figure 6 for the same conditions used in figure 5. For this reaction, k_1 was increased to four times the reference value and decreased to one-fourth of this value. The results in figure 6 show that changing k_1 has negligible effect on performance at O/F values less than 4, but it does have a significant effect at the higher O/F values. The maximum change is about 8 impulse units or 2 percent for the 82.6 weight percent fluorine oxidizer.



(a) Fluorine content in oxidant, 73.5 weight percent.

(b) Fluorine content in oxidant, 82.6 weight percent.

Figure 6. - Performance of methane-fluorine - oxygen: effect of hydrogen atom plus fluorine atom recombination rate. Chamber pressure, 100 psia (6.895×10^5 N/m^2); area ratio, 40.

Table V shows the effect of changing k_3 for the reaction $F + H_2 \rightleftarrows HF + H$. The value of k_3 was changed by factors of 10 and 0.1. The data in table V show that performance is much less sensitive to variation in the rate of reaction (III) than to variation of the rates of reactions (I) and (II). Neither of the rate changes causes more than a 0.6 unit change in specific impulse. Any change which is no greater than 0.5 impulse unit in magnitude was considered negligible in this work. From the last column in table V it is evident that removing reaction (III) entirely from the mechanism at low O/F values changes performance negligibly. Its removal has a quite significant effect at high

TABLE V. - EFFECT ON PERFORMANCE OF RATE

OF THE REACTION $F+H_2 \overset{k_3}{\rightleftarrows} HF+H$

Fluorine content in oxidant, wt. %	Oxidant-fuel ratio, O/F	Rate constant, k_3, equal to -			
		$^{a}k_R$	$5k_R$	$0.1\,k_R$	0
		Vacuum specific impulse, I_{vac}, (lb)(sec)/lb			
73.5	3.5	377.7	377.7	377.7	377.6
73.5	6	384.3	384.9	384.2	383.5
82.6	4.0	385.0	385.0	385.0	384.8
82.6	5.667	397.2	397.2	396.8	394.7

$^{a}k_R$ = Reference rate constant.

O/F, however, where the concentration of the fluorine atom is quite high. The matter of removing a reaction will be discussed further at the end of this section. It should be noticed from table IV that $X_{H,j}$ correctly predicts that performance should be more dependent on the rate of the $H + H + M \rightleftarrows H_2 + M$ reaction at high O/F than on the rate of $F + H_2 \rightleftarrows HF + H$, whereas X_j does not.

Table IV(b) shows that reaction (VIII), $H + OH + M \rightleftarrows H_2O + M$, should be important at high O/F for the 73.5-percent oxidizer. Inasmuch as this reaction is stated to have a rather large uncertainty in reference 11, the effect of its rate on performance was investigated for three conditions of high oxidant-fuel ratio. The results, as shown in table VI, agree with the information in table IV. Performance is sensitive to the rate constant of reaction (VIII) for the 73.5 weight percent oxidizer, but insensitive to k_8 for the 82.6 weight percent oxidizer. The value $k_8 = 0.10\,k_R$ is the rate constant suggested in reference 11 and is identical to the rate constant for $H + OH + Ar \rightleftarrows H_2O + Ar$ inferred

TABLE VI. - EFFECT ON PERFORMANCE OF RATE OF

THE REACTION $H+OH+M \overset{k_8}{\rightleftarrows} H_2O+M$

Fluorine content in oxidant, wt. %	Oxidant-fuel ratio, O/F	Rate constant, k_8, equal to -			
		$^{a}k_R$	$10\,k_R$	$0.1\,k_R$	0
		Vacuum specific impulse, I_{vac}, (lb)(sec)/kg			
73.5	5.667	387.8	397.5	385.3	384.9
73.5	6	384.3	393.4	382.5	382.2
82.6	6	394.1	394.9	393.9	393.8

$^{a}k_R$ = Reference rate constant.

from the experimental shock tube data reported in references 13 and 14. Our uncertainty limits for this reaction are considerably narrower than those estimated in reference 11. The data in table VI show that reaction (VIII) would, because of its rate-constant uncertainty, be an important reaction to consider, if an engine were operated at high O/F values with the 73.5 weight percent fluorine oxidant.

Rate variation calculations are also presented for reaction (VI) ($CO + O + M \rightleftarrows CO_2 + M$), which has very small X_j and $X_{H,j}$ factors but a large degree of uncertainty in its rate constant. The reference rate expression in table I was obtained by curve fitting the data of reference 15. Its numerical values are much lower, for a given temperature, than those given by the expression in reference 11. Consequently, rate variation factors of 200 and 0.5 were used to obtain the results shown in table VII. The data indi-

TABLE VII. - EFFECT ON PERFORMANCE OF VARIATION

OF RATE OF THE REACTION $CO+O+M \overset{k_6}{\rightleftarrows} CO_2+M$

[Oxidant fuel ratio, 6.]

Fluorine content in oxidant, wt. %	Rate constant, k_6, equal to -			
	$^{a}k_R$	200 k_R	0.5 k_R	0
	Vacuum specific impulse, I_{vac}, (lb)(sec)/lb			
73.5	384.3	387.9	384.7	384.7
82.6	394.1	394.0	394.0	394.0

$^{a}k_R$ = reference rate constant.

cate that performance is not sensitive to the value of k_6 when the 82.6 weight percent fluorine oxidant is used. Performance is affected by k_6, however, for the 73.5 weight percent fluorine oxidant. In comparing the k_6 expression in table I with the one given in reference 11, it was concluded that values from the table I may be slightly too low, because of third body efficiency effects, but that the reference 11 expression probably gives values that are much too high. In the high-temperature shock tube work of reference 15, care was taken to remove all traces of water, which is known to act as a catalyst and could be the cause for erroneously high rate constants for the CO + O recombination process previously reported.

Effect of reaction $F + OH \rightleftarrows HF + O$. - The work of reference 11 indicates that one reaction, which has not been considered herein, may be important and should be included in the reaction scheme for methane-fluorine - oxygen. This is the reaction

$$\left.\begin{array}{r} F + OH \overset{k_{14}}{\rightleftarrows} HF + O \\ H^{o}_{298} = -33 \text{ kcal/mole} \\ = -138 \text{ kJ/mole} \end{array}\right\} \qquad \text{(XIV)}$$

Calculations were made for two operating conditions at which this reaction should show its maximum effect. These are for the 73.5 and 82.6 weight percent fluorine oxidizer at O/F = 6 and a chamber pressure of 100 psia (6.895×10^5 N/m^2). Results are shown in table VIII. Because reaction (VI) affects the oxygen atom concentration, the computations were done for two values of k_6, namely, the reference value of table I and 200 times this

TABLE VIII. - PERFORMANCE CHANGE DUE TO THE REACTION $F+OH \overset{k_{14}}{\rightleftarrows} HF+O$

[Oxidant-fuel ratio, 6; chamber pressure, 100 psia (6.895×10^5 N/m^2).]

Rate constant for reaction (VI)	Fluorine content in oxidizer, wt. %	Vacuum specific impulse change, ΔI_{vac},[b] (lb)(sec)/lb	Case
[a] k_R	73.5	+0.23	1
	82.6	+.03	2
200 k_R	73.5	+0.51	3
	82.6	+.05	4

[a] Reference rate of constant.

[b] $\Delta I_{vac} = I_{vac}$ (with reaction (XIV)) - I_{vac} (without reaction (XIV)).

value. The conclusion from these results is that the addition of reaction XIV has negligible effect on performance for the two conditions investigated. The largest increase in I_{vac} caused by this reaction is 0.51 impulse unit, when the high rate for the $CO + O + M \rightleftarrows CO_2 + M$ reaction is used. The $X_{H,j}$ rating parameter values for cases 1 and 3 of table VIII are shown in table IX. It is seen that reaction (XIV) ranks last in importance if the reference value is used for k_6 and sixth out of 12 if the high k_6 value is used. Thus, even when reaction (XIV) ranks sixth out of 12, its addition to the mechanism changes specific impulse only by the assumed limit for an unimportant reaction.

TABLE IX. - REACTION RANKING PARAMETERS WITH THE

REACTION F+OH⇌HF+O INCLUDED IN MECHANISM

[Chamber pressure, 100 psia (6.895×10^5 N/m^2); oxidant-fuel ratio, 6; fluorine content in oxidant, 73.5 wt. %.]

Reaction number	Reaction	Case 1: $k_6 = k_R$		Case 3: $k_6 = 200\ k_R$	
		Reaction rating parameter, $X_{H,j}$	Rank	Reaction rating parameter, $X_{H,j}$	Rank
I	H+F+M⇌HF+M	-121 200	1	-87 970	1
VIII	H+OH+M⇌H_2O+M	-56 450	2	-40 920	3
II	H+H+M⇌H_2+M	-20 570	3	-14 840	4
III	F+H_2⇌HF+H	-17 330	4	-13 400	5
X	O+H+M⇌OH+M	-9 584	5	-6 942	8
XI	H_2+OH⇌H_2O+H	+6 771	6	+4 744	9
VII	CO+OH⇌CO_2+H	-4 723	7	+7 667	7
IX	O+O+M⇌O_2+M	-3 101	8	-2 248	11
XII	H+O_2⇌OH+O	-2 332	9	-2 292	10
VI	CO+O+M⇌CO_2+M	-726	10	-73 850	2
XIII	O+H_2⇌OH+H	+660	11	+508	12
XIV	F+OH⇌HF+O	-238	12	-12 070	6

In summary, rate variation calculations have shown that performance of the methane-fluorine - oxygen system is mainly controlled by the hydrogen atom recombination, the H + F recombination, and, under some conditions, the H + OH recombination. Next in importance is the reaction F + H_2 ⇌ HF + H. Although this reaction must usually be present, variation of its rate constant by one order of magnitude causes negligible change in computed specific impulse. This last result is consistent with the fact that bimolecular reactions are seldom rate controlling in the recombination process because of their high rates and relatively low heats of reaction. They generate the atomic and free radical species that participate in the rate-controlling three-body recombinations.

One more matter remains to be discussed. This is the question of when a reaction can be added to or removed from a mechanism without changing the computed performance significantly. An attempt to answer this question has been made by comparing the reactions in a given system with each other. To do this we use the following ratio for each reaction:

$$R_{H,j} = \left| \frac{X_{H,j}}{(X_{H,j})_{max}} \right| \tag{6}$$

Here $(X_{H,j})_{max}$ is the largest $X_{H,j}$ value for all the reactions in the mechanism. The smaller this ratio is for a given reaction, the less important it should be in determining performance. There ought to then be a limiting value of this ratio that has the following property: all reactions having $R_{H,j}$ values below this limiting value will change kinetic specific impulse by no more than ±0.05 (lb)(sec)/lb (4.9 (N)(sec)/kg) when added to or removed from a reaction mechanism. The three sets of $X_{H,j}$ values given in table IV were used to compute $R_{H,j}$ values for the three assumed conditions, and the results are shown in table X. Additional performance calculations were then made for these three cases and a few others not shown. Various reactions in the mechanism were systematically eliminated, starting with the least important ones, in an attempt to get an approximate value of the limiting $R_{H,j}$ ratio. These computations gave numbers between 0.015 and 0.025 as the limiting $R_{H,j}$ values. These few calculations cannot be used to establish a good quantitative criterion for identifying unimportant reactions. The results do give, however, an approximate guide to reaction importance. Any reaction with an $R_{H,j}$ value greater than about 0.02 should probably be included in a mechanism. However, reactions with $R_{H,j}$ less than about 0.02 may probably be eliminated without causing more than a ±0.5 (lb)(sec)/lb (4.9 (N)(sec)/kg) change in the computed kinetic specific impulse. It was found previously (table V) that the reaction $F + H_2 \rightleftharpoons HF + H$ could be dropped from consideration at low O/F but not at higher O/F values. This result is consistent with the observed change of $R_{H,j}$ with O/F shown in table X for this reaction. We may also determine whether $R_{H,j}$ values are consistent with the observation that the addition of reaction (XIV) ($F + OH \rightleftharpoons HF + O$) has no significant effect on computed performance. The information for cases 1 and 3 in tables VIII and IX gives the following $R_{H,j}$ values for reaction (XIV) and corresponding impulse changes ΔI_{vac} when this reaction is added to the original mechanism. For case 1, $R_{H,j} = 0.002$ and $\Delta I_{vac} = 0.23$ (lb)(sec)/lb (2.3 (N)(sec)/kg), and, for case 3, $R_{H,j} = 0.14$ and $\Delta I_{vac} = 0.51$ (lb)(sec)/lb (5.0 (N)(sec)/kg). Thus, case 1 gives a low ΔI_{vac} consistent with the $R_{H,j}$ value much lower than 0.02; case 3, however, gives a ΔI_{vac} smaller than would be expected for an $R_{H,j}$ value much larger than 0.02. It appears that the stated rule for reaction importance will indicate the inclusion of a reaction whose effect on performance is very close to our arbitrary limit for significant effect on performance. These computations have shown that reaction (XIV) might have to be considered under some assumed conditions, but not those used in the present work.

Comparison of experimental and theoretical results. - The experimental measurements reported in reference 6 were compared with the present theoretical nonequilibrium calculations after correction by the method described in the Procedure section. Two of the 11 test results given were not used, because they were stated to have error in the thrust measurement. The nine data points used are the same ones used for a similar comparison in reference 7 and shown in figure 123 of that work. The typical correction

TABLE X. - REACTION RATING PARAMETER RATIO[a] VALUES FOR METHANE-

FLUORINE - OXYGEN NOZZLE RECOMBINATION REACTIONS

[Chamber pressure, 100 psia (6.895×10^5 N/m^2).]

Reaction number	Reaction	Oxidant-fuel mixture ratio, O/F								
		3			6			6		
		Fluorine content in oxidant, wt. %								
		82.6			73.5			82.6		
		Reaction rating parameter, $X_{H,j}$	Reaction rating parameter ratio, $R_{H,j}$	Rank	Reaction rating parameter, $X_{H,j}$	Reaction rating parameter ratio, $R_{H,j}$	Rank	Reaction rating parameter, $X_{H,j}$	Reaction rating parameter ratio, $P_{H,j}$	Rank
I	H+F+M⇌HF+M	-7 627	0.0766	2	-124 600	1.000	1	-232 600	1.000	1
II	H+H+M⇌H_2+M	-99 610	1.000	1	-20 590	.165	4	-24 850	.107	2
III	F+H_2⇌HF+H	-731	.00734	3	-24 600	.197	3	-18 350	.0789	3
IV	CH+CH⇌C_2H_2	-2.1×10^{-3}	2.1×10^{-8}	5	--------	------	--	--------	-------	--
V	C+H+M⇌CH+M	-1.36	1.37×10^{-5}	4	--------	------	--	--------	-------	--
VI	CO+O+M⇌CO_2+M	---------	---------	--	-699	.0056	10	-74	.00032	8
VII	CO+OH⇌CO_2+H	---------	---------	--	-5 000	.0401	7	-353	.0015	7
VIII	H+OH+M⇌H_2O+M	---------	---------	--	-56 640	.455	2	-3 946	.0170	4
IX	O+O+M⇌O_2+M	---------	---------	--	-2 951	.0237	8	-31	.00013	9
X	O+H+M⇌OH+M	---------	---------	--	-9 129	.0733	5	-1 004	.0043	5
XI	H_2+OH⇌H_2O+H	---------	---------	--	+6 675	.0536	6	+511	.0022	6
XII	H+O_2⇌OH+O	---------	---------	--	-2 414	.0194	9	-24	.00010	10
XIII	O+H_2⇌OH+H	---------	---------	--	+194	.0016	11	-18	.00008	11

[a] $R_{H,j} = \left| \frac{X_{H,j}}{(X_{H,j})_{max}} \right|$

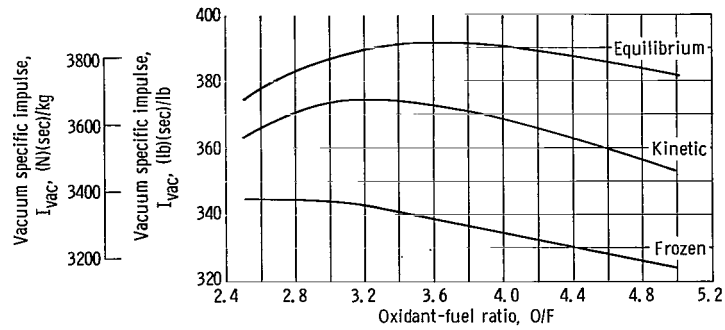
from the original experimental I_{vac} to the kinetically limited value is about 40 (lb)(sec)/lb (392 (N)(sec)/kg), in the present work. Of this total, the correction for combustion efficiency is approximately 35 (lb)(sec)/lb (lb (343 (N)(sec)/kg) and the remainder is the correction for heat transfer, friction, and nozzle divergence losses. The experimentally derived kinetic performance data are plotted as the circled points in figures 5(b) and 6(b). In figure 5(b) the computed curve using the reference rate constants gives the best agreement with the data points. However, in figure 6(b) a quantitative calculation had to be done to determine whether the data points are fitted better by the reference curve or the curve using the reduced rate constant for the H + F reaction. To measure the deviation from each of these two curves, the percentage standard deviation of the data points was calculated using the formula

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} \left\{ \frac{100(I - I_k)}{I_k} \right\}^2}{n}} \tag{7}$$

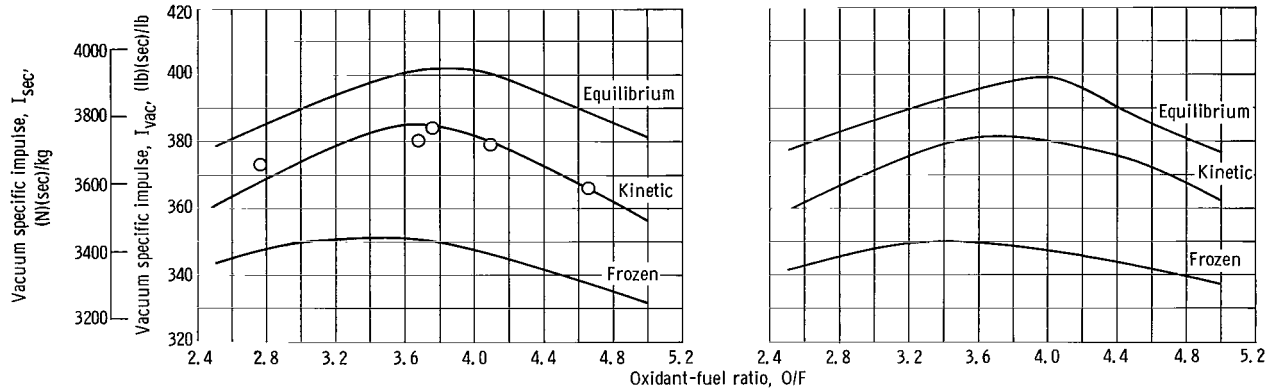
where I is the corrected experimental value and n is the number of data points. The value of σ for the curve using reference rates is 1.7 percent, while σ is 1.4 percent for the curve with the reduced value of k_1. This means that either set of rate constants gives a theoretical curve that matches the corrected experimental results to about the same accuracy. Therefore, using the reference rate constants presented herein has given a theoretical performance curve that agrees with a particular set of corrected experimental data to a percentage standard deviation of about $1\frac{1}{2}$ percent. The closeness of the agreement may be fortuitous, in view of experimental uncertainties as well as uncertainties in the method used to correct the experimental data. This method is simpler and less exact than the one used in reference 7; that work compares theoretical and corrected results which are both different from the results presented herein.

Butene-1-Fluorine - Oxygen System

The mechanisms and reference reaction rate constants given previously have been used to calculate the kinetic performance of the butene-1-fluorine - oxygen propellant system. The results are presented for a chamber pressure of 100 psia (6.895×10^5 N/m^2) and an O/F range of 2.5 to 5. For this combination, oxidant mixtures ranging from 54.3 to 82.6 weight percent fluorine were used. An oxidant having 70.4 weight



(a) Fluorine content in oxidant, 54.3 weight percent, stoichiometric O/F, 4.99.



(b) Fluorine content in oxidant, 70.4 weight percent, stoichiometric O/F, 5.76.

(c) Fluorine content in oxidant, 82.6 weight percent; stoichiometric O/F, 6.56.

Figure 7. - Butene-1-fluorine - oxygen performance. Chamber pressure, 100 psia (6.895×10^5 N/m); area ratio, 40.

percent fluorine corresponds to the chemical equation

$$C_4H_8 + 2O_2 + 4F_2 \rightarrow 4CO + 8HF \qquad (B)$$

which should give maximum performance. Figure 7 shows complete theoretical results (equilibrium, frozen, and kinetic) for three different oxidizers. In figure 8 the equilibrium and kinetic data are cross plotted to show the effect of oxidizer composition on performance. These curves show that the maximum kinetic performance of 385 pound-seconds per pound is obtained at an O/F value of 3.6 for an oxidizer containing about 70 weight percent fluorine, in agreement with reaction (B). A few experimental data points are reported in reference 6. These were corrected as described previously and are plotted in figure 7(b). Three of the points are in very good agreement with the computed curve, and the standard deviation of all the data points is 0.8, or about 1 percent.

A comparison of the performance of the methane fluorine - oxygen and butene-1-fluorine - oxygen systems is shown in figure 9. Kinetic and equilibrium curves are

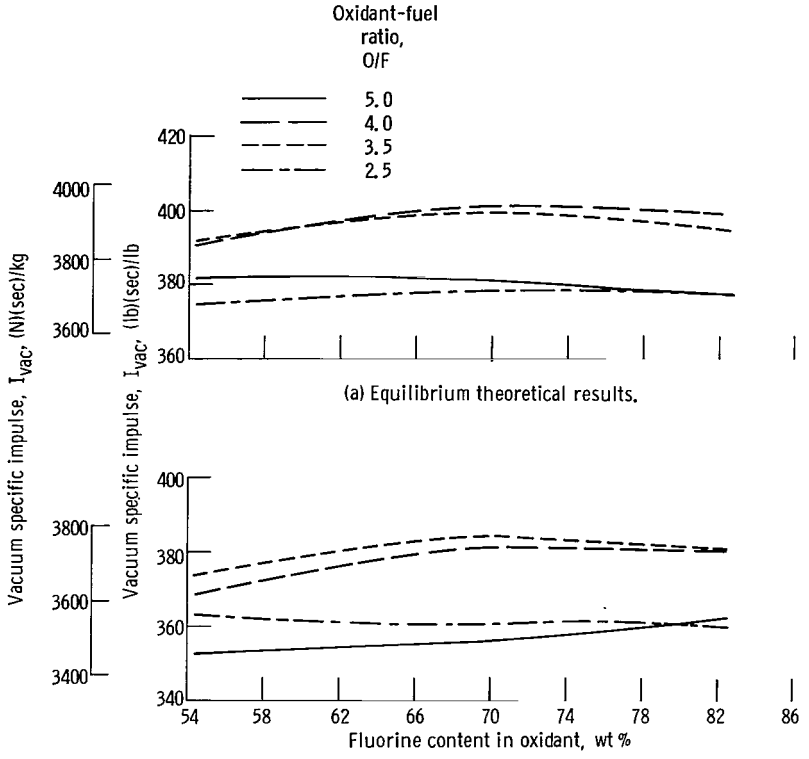


Figure 8. - Effect of oxidant composition on performance of butene-1-fluorine - oxygen. Chamber pressure, 100 psia (6.895x10^5 N/m^2); final area ratio, 40.

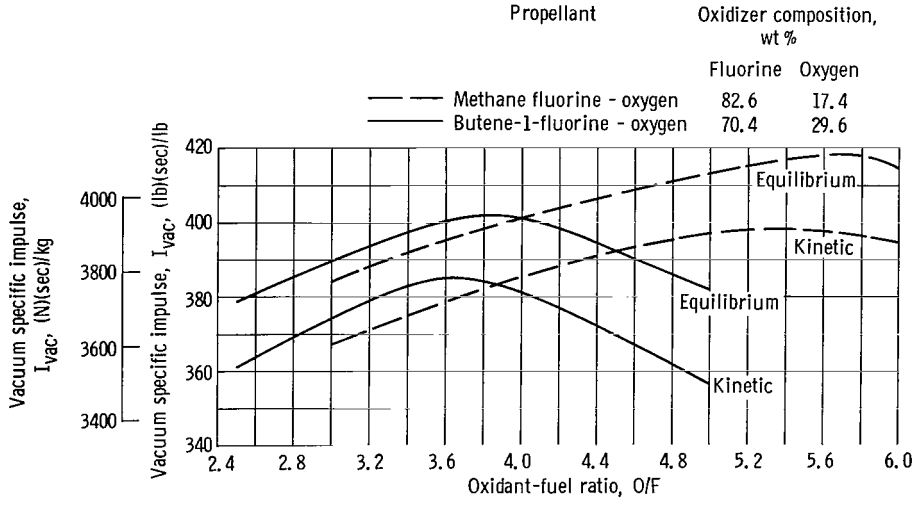


Figure 9. - Comparison of performance of methane-fluorine - oxygen and butene-1-fluorine - oxygen propellant systems. Chamber pressure, 100 psia (6.895x10^5 N/m^2); area ratio, 40.

plotted using the oxidizer that gives best performance for each system. The maximum kinetic specific impulse for butene-1 is about 385 (lb)(sec)/lb (3776 (N)(sec)/kg), whereas, for methane, it is 398 (lb)(sec)/lb (3903 (N)(sec)/kg). This comparison on the basis of specific impulse shows that methane is definitely superior to butene-1 when combined with the fluorine-oxygen oxidizer.

CONCLUDING REMARKS

Two general conclusions can be drawn from the results of the present work. First of all, three, or at most four, chemical reactions are really rate controlling in the overall recombination process of the multicomponent gas mixtures studied. Although a dozen or more individual reactions may actually occur, only the rate constants of a few three-body recombination processes have to be known to better than one order of magnitude uncertainty for computing kinetic rocket performance within an uncertainty of ±0.5 pound-seconds per pound (4.9 (N)(sec)/kg). Many other reactions must be present in the mechanism, but their rate constants can be changed in most cases by an order of magnitude or more without changing the computed specific impulse more than this uncertainty. The role of these reactions, which are the bimolecular processes, is primarily to maintain concentrations of the free radical and atomic species that combine in the rate-controlling reactions.

In the hydrocarbon-fluorine - oxygen systems studied herein, the rate controlling reactions are $H + H + M \rightleftarrows H_2 + M$, $H + F + M \rightleftarrows HF + M$, and, under a few conditions, $H + OH + M \rightleftarrows H_2O + M$. The bimolecular reaction occurring to the greatest extent is $F + H_2 \rightleftarrows HF + H$. However, performance is not significantly changed when its rate constant is changed from 1/10 to 10 times the reference value.

The other significant idea that emerges from this work is verification of the ability of a one-dimensional idealized flow model to calculate performance in good agreement with experiment when a selected set of reaction rate constants is used. This agreement was obtained in reference 2 for the hydrogen-fluorine system. In the present work, computed kinetic performance matches the corrected experimental results with a standard deviation of about $1\frac{1}{2}$ percent for the methane-fluorine - oxygen and 1 percent for the butene-1-fluorine - oxygen system. One should not conclude, however, that the one-dimensional theory will necessarily describe other systems equally well, because uncertainties still exist about the exact manner of correcting the experimental measurements.

SUMMARY OF RESULTS

Nonequilibrium rocket performance calculations have been performed for the methane-fluorine - oxygen and butene-1-fluorine - oxygen systems for chamber pressures from 100 to 300 psia (6.895×10^5 to 2.069×10^6 N/m^2) and oxidant-fuel weight ratios from 2.5 to 6. A truncated perfect nozzle profile with an area ratio of 40 was used. Computed equilibrium and nonequilibrium specific impulse are reported and have been compared with experimentally derived kinetic performance data. Two different rating parameters have been used to quantitatively rank all chemical reactions in order of their importance in controlling performance. The predictions of these parameters were checked by individual rate-variation calculations. The results of this investigation are as follows:

1. Theoretically computed performance using a one-dimensional theoretical model and a selected set of reaction rate constants agrees with "corrected" experimental data with a standard deviation of about $1\frac{1}{2}$ percent for methane and 1 percent for butene-1 combined with fluorine-oxygen mixtures.

2. Two rating parameters (X_j proportional to net reaction rate and $X_{H,j}$ proportional to net heat exchange rate), predict that the same four reactions are most significant for the conditions used. These are $H + H + M \rightleftarrows H_2 + M$, $H + F + M \rightleftarrows HF + M$, $H + OH + M \rightleftarrows H_2O + M$, and the bimolecular reaction $F + H_2 \rightleftarrows HF + H$. The parameter $X_{H,j}$ is somewhat better than X_j for quantitatively ranking the important reactions on the basis of performance change caused by uncertainty in each reaction rate constant.

3. The maximum theoretical nonequilibrium performance for methane-fluorine - oxygen is 398 pound-seconds per pound (3902 (N)(sec)/kg) at 100 psia (6.895×10^5 N/m^2) chamber pressure and an oxidant-fuel ratio O/F of 5.1 with the 82.6-weight-percent fluorine oxidizer. For butene-1-fluorine - oxygen, the maximum performance at 100 psia (6.895×10^5 N/m^2) and O/F = 3.6 is 385 pound-seconds per pound (3776 (N)(sec)/kg) using the 70.4-weight-percent oxidizer.

4. Calculated performance is most sensitive to the $H + H + M \rightleftarrows H_2 + M$ reaction rate at low O/F values for methane-fluorine - oxygen using both the 73.5 and 82.6 weight percent fluorine oxidizers. At high O/F values, the reactions $H + F + M \rightleftarrows HF + M$ and $H + OH + M \rightleftarrows H_2O + M$ are both rate determining for the 73.5 weight percent fluorine oxidizer. However, increasing the fluorine content to 82.6 weight percent at high O/F eliminates the water recombination as an important reaction in the mechanism.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, September 19, 1968,
129-01-02-01-22.

APPENDIX A

SYMBOLS

A	pre-exponential factor in rate constant expression
c_i	concentration of species i, (lb)(mole)/ft^3; (g)(mole)/cm^3
E_a	activation energy, cal/mole
F	impulse recovery factor defined by eq. (3)
ΔH^o_{298}	heat of reaction at 298 K, kcal/mole; kJ/mole
I	experimentally derived, kinetically limited vacuum specific impulse defined by eq. (2), (lb)(sec)/lb; ((N)(sec)/kg)
I_{eq}	theoretical equilibrium vacuum specific impulse, (lb)(sec)/lb; (N)(sec)/kg
I_{fr}	theoretical frozen vacuum specific impulse, (lb)(sec)/lb; (N)(sec)/kg
I_k	theoretical kinetically limited vacuum specific impulse, (lb)(sec)/lb; (N)(sec)/kg
I_{vac}	theoretical vacuum specific impulse, (lb)(sec)/lb; (N)(sec)/kg
$k_{b,j}$	reverse reaction rate constant for j^{th} reaction, cm^3/(mole)(sec) or cm^6/(mole)^2(sec)
$k_{f,j}$	forward reaction rate constant for the j^{th} reaction, cm^3/(mole)(sec) or cm^6/(mole)^2(sec)
M	third-body molecule in recombination reaction
O/F	assigned oxidant to fuel weight ratio
$(O/F)_{st}$	stoichiometric O/F value
P_c	chamber pressure, psia; N/m^2
R	assigned equivalence ratio = $(O/F)_{st}/(O/F)$
$R_{H,j}$	reaction rating parameter ratio = $\left\lvert \dfrac{X_{H,j}}{\left(X_{H,j}\right)_{max}} \right\rvert$
$X_{H,j}$	reaction rating parameter based on net enthalpy exchange rate for j^{th} reaction defined by eq. (5), (kcal)(ft^3)/(lb)(sec); (kg)(m^3)/(kg)(sec)
$\left(X_{H,j}\right)_{max}$	largest $X_{H,j}$ value for all reactions in a given mechanism

X_j reaction rating parameter based on net reaction rate for j^{th} reaction defined by eq. (4), (mole)(ft^3)/(lb)(sec); (mole)(m^3)/(kg)(sec)

$X_{v,j}$ volumetric conversion rate for j^{th} reaction, mole/(ft^3)(sec); mole/(m^3)(sec)

η_{C^*} characteristic velocity efficiency

ν_{ij} stoichiometric reaction coefficient for j^{th} chemical reaction

ν'_{ij} stoichiometric product coefficient for j^{th} chemical reaction

ρ gas density, lb/ft^3; g/cm^3

Subscripts:

corr corrected

APPENDIX B

CALCULATION OF CONDITIONS FOR MAXIMUM THEORETICAL PERFORMANCE OF HYDROCARBON-FLUORINE - OXYGEN PROPELLANT

The propellant formula is written using the notation of reference 9

$$CH_\gamma + \alpha(OF_\beta)$$

Then the oxidant-fuel ratio of this mixture is given by

$$\frac{O}{F} = \frac{\alpha(16 + 19\,\beta)}{12.011 + 1.008\,\gamma} \tag{B1}$$

Now, when it is assumed that the propellant composition is assigned, β and γ are known. We consider two cases for finding α.

(1) Fluorine-oxygen atom ratio less than or equal to hydrogen-carbon atom ratio ($\beta \leq \gamma$): The only products are assumed to be HF, CO, and H_2O. The hydrogen atom balance then requires that

$$\alpha = \frac{\gamma + 2}{\beta + 2} \tag{B2}$$

Thus, the complete propellant composition is known, and the oxidant-fuel ratio for maximum performance using a particular oxidant is

$$\left(\frac{O}{F}\right)_{max} = \frac{(\gamma + 2)(16 + 19\,\beta)}{(\beta + 2)(12.011 + 1.008\,\gamma)} \tag{B3}$$

Notice that α, the oxygen-carbon atom ratio, is greater than 1 and that this case corresponds to reaction mechanism B of this report.

(2) Fluorine-oxygen atom ratio greater than hydrogen-carbon atom ratio ($\beta > \gamma$): The final products are assumed to be carbon (C), HF, and CO. For this reaction the hydrogen and fluorine atom balances require that

$$\alpha = \frac{\gamma}{\beta} \tag{B4}$$

The complete propellant composition is now known and the oxidant-fuel ratio for maximum performance is given by

$$\left(\frac{O}{F}\right)_{max} = \frac{\gamma(16 + 19\,\beta)}{\beta(12.011 + 1.008\,\gamma)} \tag{B5}$$

For this case the oxygen-carbon atom ratio is less than 1 and this corresponds to reaction mechanism A.

It should be mentioned that equations (B3) and (B5) give $(O/F)_{max}$ values slightly different from those actually obtained from equilibrium computations. This is because small amounts of products other than those assumed are present in the gas mixture.

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