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THEORETICAL NONEQUILIBRIUM PERFORMANCE OF OXYGEN DIFLUORIDE-DIBORANE ROCKET PROPELLANT

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ABSTRACT

Theoretical performance, both equilibrium and rate-limited, is presented for the oxygen difluoride-diborane propellant system. A one-dimensional kinetic flow model was used. The work also includes identification of the rate controlling chemical reactions in the recombination process. Reactions are quantitatively rated in importance and the sensitivity of performance to the uncertainty of individual rate constants is studied in detail. Results indicate that the hydrogen-atom recombination is the predominant reaction in the entire process as far as performance is concerned and that no reaction involving boron species has a significant effect on performance. The theoretical performance level of oxygen difluoride-diborane is significantly higher than that for the methane-fluorine/oxygen propellant, the most energetic of the hydrocarbon-fluorine/oxygen systems.

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SUMMARY

Theoretical computations have been performed for the oxygen difluoride-diborane propellant system to obtain both equilibrium and rate-limited theoretical performance over an oxidant-fuel ratio range of 2.7 to 4 at chamber pressures of 100 and 300 pounds per square inch absolute (68.95 and 206.9 N/sq cm). The performance limiting reactions in the recombination process were identified and quantitatively rated in importance A detailed study was also made to determine the sensitivity of vacuum specific impulse to individual uncertainties in the individual rate constant data. Finally, the theoretical performance of oxygen difluoride was compared with that for two hydrocarbon-fluorine/ oxygen systems.

Results of these computations showed that kinetically limited vacuum specific impulse at 100 psia (68.95 N/sq cm) chamber pressure ranged from 411 to 422 pound-seconds per pound (4030 to 4138 (N-sec)/kg) for oxygen difluoride-diborane. This is considerably higher than the maximum value 398 pound-seconds per pound (3903 (N-sec)/kg) for the methane-fluorine/oxygen system at the same chamber pressure. The most important reaction occurring in the nozzle is the hydrogen atom recombination process. Performance is very sensitive to uncertainty in the rate constant for this re- action over the entire O/F range. To a much smaller extent performance is also af- fected by uncertainties in the rate constant for the H + F and H + OH recombinations. No reaction involving boron species is rate controlling. In fact all such reactions can have at least one order of magnitude uncertainties in their rate constants without causing any change in the computed performance values. These results are in agreement with the predictions of the reaction rating parameter $X_{H, j}$, which gives both the magnitude and direction of the enthalpy change rate caused by a particular reaction.

INTRODUCTION

In the continuing development of new chemical rocket propellant systems interest has centered on fluorine containing combinations other than the hydrogen-fluorine system itself. For many missions a less energetic propellant than H_2-F_2, but one with fewer handling and storage problems, can be used. Several of these systems are termed "space storables," inasmuch as the constituents can be stored indefinitely as liquids in outer space with use of only insulating materials and heat shields. Examples of these space storable fuels are the light hydrocarbons (e.g., methane, propane, and butene-1) and also diborane (B_2H_6). These fuels are usually combined with fluorine/oxygen mixtures or oxygen difluoride (OF_2) as an oxidizer. A detailed study of the nonequilibrium performance of two hydrocarbon-fluorine/oxygen systems is given in reference 1. This work also presents equilibrium performance curves which compare several space-storable propellants with the best earth storable and cryogenic systems in use at the
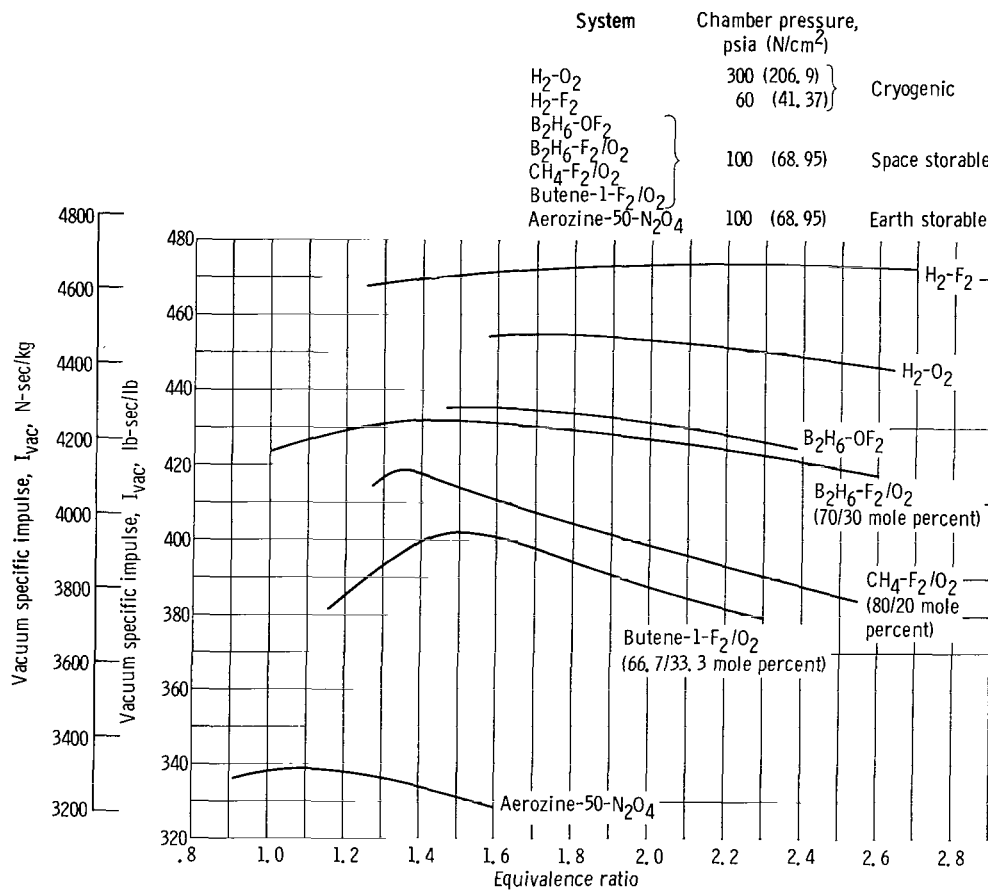

Figure 1. - Performance of rocket propellants assuming equilibrium expansion to area ratio of 40.

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present time. For reference purposes some of these curves are reproduced in figure 1. A similar comparison is shown in a recent NASA survey paper (ref. 16) which also gives a comprehensive discussion of the NASA space storable propulsion programs, including objectives and future goals. The hydrogen-fluorine and Aerozine-50-nitrogen tetroxide combinations are used as the current upper and lower performance limits. The space storable fuels shown are diborane, combined with oxygen difluoride and with oxygen/ fluorine mixtures, and the hydrocarbons methane and butene-1 combined with oxygen/ fluorine mixtures. These last two systems are the ones studied in reference 1. These equilibrium results show that diborane, with either OF_2 or oxygen/fluorine mixtures, has a higher performance level than methane, the most energetic hydrocarbon fuel. However, the best space storable system still has considerably less impulse than hydrogen-fluorine.

A study of the OF_2-diborane system was undertaken because of its favorable performance and because of renewed interest in it as a practical rocket propellant. The main effort was the computation of rate-limited performance and the identification of the important chemical reactions occurring during the nozzle expansion process. A method of quantitatively rating reactions in order of importance was given in reference 1 and has been used here. In addition we have studied the effect on computed specific impulse of changing individual rate constants over the range of their estimated uncertainty. A complete set of equilibrium, kinetic and frozen performance computations is presented for a wide range of operating conditions for the OF_2-diborane system. The calculations were made for chamber pressures of 100 and 300 psi (68.95 and 206.9 N/sq cm) and an oxidant-fuel ratio (O/F) range of 2.7 to 4. A comparison is also given of the rate-limited performance for OF_2-diborane with that for methane-fluorine/oxygen and butene-1 fluorine oxygen.

PROCEDURE

Equilibrium and Frozen Computations

Equilibrium and frozen computations were performed to obtain the starting conditions for the kinetically-limited computations. The necessary conditions are the significant species present at equilibrium in the convergent nozzle section, their concentrations, and the equilibrium values of the fluid dynamic variables, velocity, temperature, and either pressure or density. From these computations we also obtain the maximum and minimum values of theoretical performance for comparison with the rate-limited performance. The significant species were found by omitting several species which preliminary equilibrium calculations showed to be present with a mole fraction of less than

0.001. These trace species were dropped from consideration after it was verified that these omissions caused negligible change in all equilibrium performance results up to an expansion area ratio of 40 in the nozzle. A negligible change in vacuum specific impulse was arbitrarily taken as ±0.5 pound-second per pound (±4.9 (N-sec)/kg) or less. All equilibrium and frozen performance results presented in this report were computed using the method and program of Zeleznik and Gordon (ref. 3).

Kinetically-Limited Computations

After selecting the significant species present in the gas mixture entering the nozzle, a reaction mechanism was hypothesized for the complete nozzle recombination process. Then a set of "reference" rate constant expressions was selected by surveying the available literature. Many of these reactions are well known ones for which experimental rate constant data are available. Practically no experimental work has, however, been done on reactions of the boron containing species. Therefore, it was necessary not only to hypothesize the reactions which could occur, but also to calculate approximate theoretical rate constant expressions for these reactions. The details of the entire reaction and rate constant selection procedure are given in a subsequent section. Computations were made using these reference rates for all assigned experimental conditions to obtain a set of reference performance curves. These results also showed which reactions are important in determining kinetic performance. A detailed rate variation study was then done to determine the sensitivity of performance to individual rate constant variations. This type of study is especially important for the OF_2-diborane system since much of the rate constant data have large uncertainties.

THEORY AND INPUT DATA

Kinetic Flow Model and Equations

The problem of calculating chemical-rate limited rocket performance is just a particular example of the general problem of following the progress of several simultaneous chemical reactions in a flow system. One must solve a series of simultaneous differential equations consisting of fluid dynamic conservation equations coupled with the equations for the rates of change of species concentrations due to chemical reaction. The particular set of equations used for this work is based on the one dimensional flow of a uniform mixture of thermally perfect gases resulting from complete combustion of rocket propellants to chemical equilibrium in the chamber. All losses due to viscosity

and heat transfer are neglected. The specific system of equations used was first given in reference 2. It consists of the following $N + 3$ equations in the $N + 3$ unknowns V, T, and ρ, and the concentrations of the N chemical species. All symbols are defined in the appendix.

$$\frac{dV}{dx} = \frac{V}{\mathcal{M}^2 - 1}\left(\frac{1}{A}\frac{dA}{dx} - \mathcal{A}\right) \tag{1}$$

$$\frac{dT}{dx} = -T\left[\frac{(\gamma - 1)\mathcal{M}^2}{\mathcal{M}^2 - 1}\left(\frac{1}{A}\frac{dA}{dx} - \mathcal{A}\right) + \mathcal{B}\right] \tag{2}$$

$$\frac{d\rho}{dx} = -\rho\left[\frac{\mathcal{M}^2}{\mathcal{M}^2 - 1}\left(\frac{1}{A}\frac{dA}{dx} - \mathcal{A}\right) + \mathcal{A}\right] \tag{3}$$

$$\frac{d\alpha_i}{dx} = \frac{w_i r^*}{\rho V} \qquad i = 1, 2, \ldots, N \tag{4}$$

The auxiliary equations needed are

$$p = \frac{\rho RT}{M} \tag{5}$$

$$\mathcal{M}^2 = \frac{V^2 M}{\gamma RT} \tag{6}$$

$$\gamma = \frac{C_p}{C_p - \dfrac{R}{M}} \tag{7}$$

The $\mathcal{A}$ and $\mathcal{B}$ terms are given by

$$\mathcal{A} = \frac{r^* T}{pV}\sum_{i=1}^{N}\frac{R}{M_i}w_i - \mathcal{B} \tag{8}$$

$$\mathscr{D} = \left(\frac{\gamma - 1}{\gamma}\right)\frac{r^*}{pV} \sum_{i=1}^{N} h_i w_i$$

Equations (1) to (4) constitute a system of differential equations of the form

$$\frac{dy_i}{dx} = f_i(x, y_1, y_2, \ldots, y_n) \qquad i = 1, 2, \ldots, n \qquad (10)$$

The method of solution used for this system is the implicit numerical integration technique described by Tyson and Kliegel (ref. 4). This technique was used in a performance program written for NASA Manned Spacecraft Center. The present computations were performed with an extensively modified version of that program. As is customary in all flow-kinetic programs, chemical reactions are considered reversible and the law of microscopic reversibility is used to calculate the reverse reaction rate constant from the forward rate constant and the equilibrium constant for the reaction.

Reaction Mechanism and Species

Equilibrium flow computations showed that the following significant species are present in the expanding gas mixture for the OF_2-diborane propellant system.

$$B, \ O, \ H, \ F, \ BO, \ H_2, \ O_2, \ HF, \ H_2O, \ OH, \ BOF, \ BF, \ BO_2, \ BF_2$$
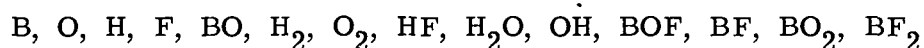
and BF_3.

The reactions selected for the complete reaction mechanism for the recombination process are listed in table I along with their heats of reaction at 298 K.

The reference rate constants selected for these reactions are given in table II. Those for reactions I to IX are identical to the rate constants used for the hydrocarbon-F_2/O_2 study reported in reference 1. These rate constant expressions are selected values based on an evaluation of all the available data. The rate constant expressions for the second group, which includes all other reactions, are theoretical estimates usually taken either from reference 5 or 14. The rate constants for reactions XI and XII, however, were calculated during the present work using the modified collision theory of C. Fredrick Hansen as detailed in reference 6. The accuracy of this second group of rate constants must be considered order of magnitude only. Therefore, the study of the effect of rate constant variation on performance is especially important for these reactions.

TABLE I. - CHEMICAL REACTIONS IN THE NOZZLE RECOMBINATION

PROCESS FOR THE OXYGEN DIFLUORIDE-DIBORANE

PROPELLANT SYSTEM

Reaction number	Reaction	Heat of reaction (forward direction), ΔH^O_{298}	
		kcal/mole	kJ/mole
I	$H + F + M \rightleftharpoons HF + M$	-136	-569
II	$H + H + M \rightleftharpoons H_2 + M$	-104	-435
III	$F + H_2 \rightleftharpoons HF + H$	-32	-134
IV	$H + OH + M \rightleftharpoons H_2O + M$	-119	-498
V	$O + H + M \rightleftharpoons OH + M$	-102	-427
VI	$H_2 + OH \rightleftharpoons H_2O + H$	-15	-63
VII	$H + O_2 \rightleftharpoons OH + O$	+17	+71
VIII	$O + H_2 \rightleftharpoons OH + H$	+2	+8
IX	$O + O + M \rightleftharpoons O_2 + M$	-119	-498
X	$F + OH \rightleftharpoons O + HF$	-33	-138
XI	$BO + F + M \rightleftharpoons BOF + M$	-169	-707
XII	$BF + O + M \rightleftharpoons BOF + M$	-160	-669
XIII	$BO + HF \rightleftharpoons BOF + H$	-33	-138
XIV	$BF + OH \rightleftharpoons BOF + H$	-58	-243
XV	$B + O + M \rightleftharpoons BO + M$	-189	-791
XVI	$B + F + M \rightleftharpoons BF + M$	-197	-824
XVII	$BF_2 + BO \rightleftharpoons BOF + BF$	-58	-243
XVIII	$BF_2 + H \rightleftharpoons HF + BF$	-25	-105
XIX	$O + BF \rightleftharpoons BO + F$	+8	+33
XX	$BF + BO_2 \rightleftharpoons BOF + BO$	-10	-42
XXI	$BF_2 + HF \rightleftharpoons BF_3 + H$	-18	-75
XXII	$BF + F + M \rightleftharpoons BF_2 + M$	-111	-464
XXIII	$BF_2 + F + M \rightleftharpoons BF_3 + M$	-154	-644
XXIV	$BO + O + M \rightleftharpoons BO_2 + M$	-150	-628
XXV	$BF + O_2 \rightleftharpoons BOF + O$	-41	-172

TABLE II. - REFERENCE REACTION RATE CONSTANTS[a,b]

Reaction number	Reaction	Preexponential factor, D	Temperature exponent, n	Activation energy, E_a, cal/mole	Reference
I	$H + F + M \rightleftharpoons HF + M$	3.0×10^{19}	-1.0	0	7
II	$H + H + M \rightleftharpoons H_2 + M$	7.5×10^{18}	-1.0	0	7
III	$F + H_2 \rightleftharpoons HF + H$	2.04×10^{13}	-.12	3 750	7
IV	$H + OH + M \rightleftharpoons H_2O + M$	4.5×10^{21}	-1.5	0	8
V	$O + H + M \rightleftharpoons OH + M$	4.0×10^{18}	-1.0	0	9
VI	$H_2 + OH \rightleftharpoons H_2O + H$	2.3×10^{13}	0	5 200	10
VII	$H + O_2 \rightleftharpoons OH + O$	2.2×10^{14}	0	16 600	11
VIII	$O + H_2 \rightleftharpoons OH + H$	4.0×10^{13}	0	10 200	12
IX	$O + O + M \rightleftharpoons O_2 + M$	8.15×10^{18}	-1.22	0	13
X	$F + OH \rightleftharpoons O + HF$	2.9×10^{12}	.68	200	14
XI	$BO + F + M \rightleftharpoons BOF + M$	2.5×10^{18}	-.77	-843	(c)
XII	$BF + O + M \rightleftharpoons BOF + M$	4.77×10^{18}	-.87	-443	(c)
XIII	$BO + HF \rightleftharpoons BOF + H$	1.0×10^{11}	.5	7 000	5
XIV	$BF + OH \rightleftharpoons BOF + H$	1.0×10^{11}	.5	6 000	5
XV	$B + O + M \rightleftharpoons BO + M$	3.0×10^{16}	-.5	0	5
XVI	$B + F + M \rightleftharpoons BF + M$	3.0×10^{16}	-.5	0	5
XVII	$BF_2 + BO \rightleftharpoons BOF + BF$	1.0×10^{11}	.5	6 000	5
XVIII	$BF_2 + H \rightleftharpoons HF + BF$	1.05×10^{11}	.5	6 663	14
XIX	$O + BF \rightleftharpoons BO + F$	5.3×10^{11}	.5	9 865	14
XX	$BF + BO_2 \rightleftharpoons BOF + BO$	1.05×10^{11}	.5	7 585	14
XXI	$BF_2 + HF \rightleftharpoons BF_3 + H$	1.05×10^{11}	.5	7 468	14
XXII	$BF + F + M \rightleftharpoons BF_2 + M$	1.0×10^{11}	.5	0	5
XXIII	$BF_2 + F + M \rightleftharpoons BF_3 + M$	1.0×10^{15}	-.5	0	14
XXIV	$BO + O + M \rightleftharpoons BO_2 + M$	1.0×10^{15}	-.5	0	14
XXV	$BF + O_2 \rightleftharpoons BOF + O$	6.96×10^{11}	.5	0	14

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

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

[c]Computed using the theory of ref. 6.

RESULTS AND DISCUSSION

Performance Results

Theoretical performance calculations were made for chamber pressures of 100 and 300 psi (68.95 and 206.9 N/sq cm) over the oxidant-fuel ratio range of 2.7 to 4, the ratios of greatest interest to engine designers. The stoichiometric equation for the complete consumption of all reactants is

$$3OF_2 + B_2H_6 \rightarrow 4HF + 2BOF + H_2O$$
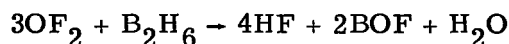
The stoichiometric O/F is 5.851 and therefore, engines using this propellant system operate in the fuel-rich region. Computed performance for the equilibrium, kinetically limited and frozen assumptions is given in figure 2 for the two chamber pressures. A typical 15° conical nozzle with throat area of 8.65 square inches (55.81 sq cm) and an expansion ratio of 40 was used for the kinetically limited computations. Thrust level is approximately 1500 pounds at 100 psi chamber pressure (6672 N at 68.95 N/sq cm). All computations are based on the latest experimental value of the heat of formation of oxygen difluoride (5.86 kcal/mole or 24.52 kJ/mole) reported by King and Armstrong in reference 15. Theoretical performance is moderately affected by changing O/F. Figure 2
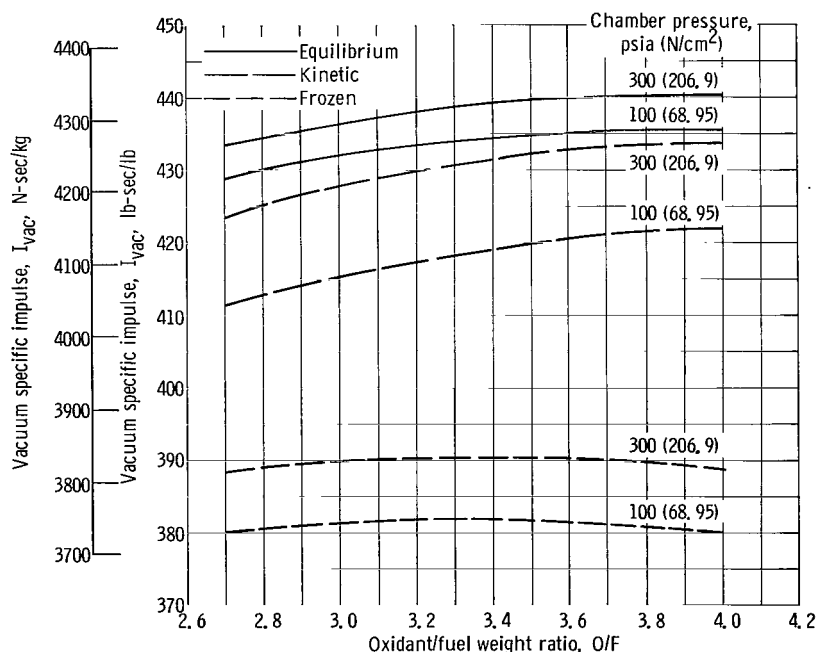

Figure 2. - Theoretical performance of oxygen difluoride-diborane.

shows that the kinetically limited performance increases steadily as O/F increases. Specific impulse ranges from 411 to 422 pound-seconds per pound (4030 to 4138 (N-sec)/kg) at a chamber pressure of 100 psia (68.95 N/sq cm). At the higher chamber pressure, the nonequilibrium specific impulse I_k is between 423 and 434 pound-seconds per pound (4148 and 4256 (N-sec)/kg). Increasing chamber pressure, therefore, increases I_k about 12 units or 3 percent. The kinetic impulse loss $I_{eq} - I_k$ is reduced from about 16 units (at 100 psia) to approximately 8 units by raising the chamber pressure. The increased molecular collision rate significantly speeds up the recombination reaction rates at the higher pressure.

The dependence of kinetic loss on position in the nozzle is shown in figure 3, where the three types of theoretical performance are plotted as a function of supersonic area ratio for a typical expansion. The assigned conditions are a chamber pressure of 100 psi
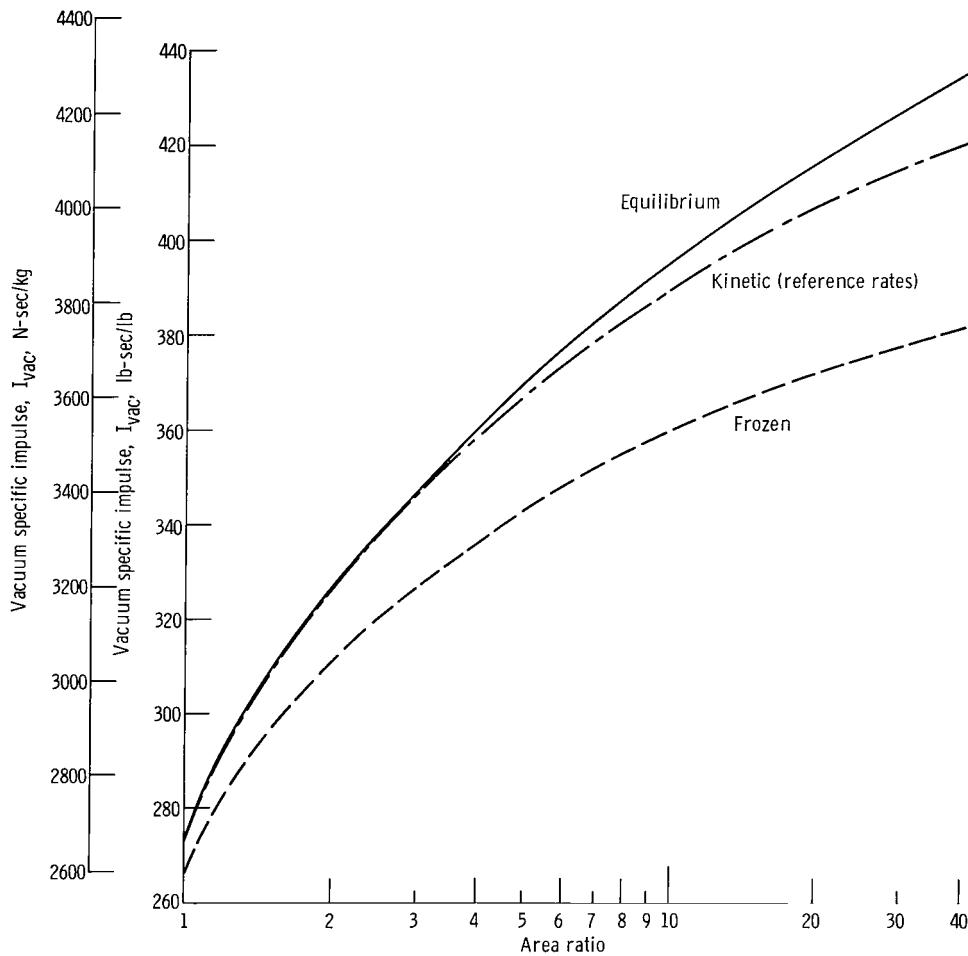

Figure 3. - Theoretical performance of oxygen difluoride-diborane plotted against area ratio. Chamber pressure, 100 pounds per square inch absolute (68.95 N/cm^2); oxidant-fuel ratio, 3.6.

and an oxidant-fuel ratio of 3. 6. The figure shows that kinetic specific impulse deviates from the equilibrium value by no more than one impulse unit up to an area ratio of 3. The deviation is 4 units or 1 percent of the equilibrium value at an area ratio of about 6. The kinetic loss at the final area ratio of 40 is 14 units or about 3 percent of the equilibrium specific impulse. In reference 1 a typical methane-fluorine/oxygen expansion at the same chamber pressure showed a 1 percent kinetic loss at an area ratio of 3. 5 and a total loss of 5 percent at area ratio 40. This single comparison, using the same chamber pressure, but different nozzles, indicates that the OF_2-diborane combination has significantly less kinetic loss than the methane-fluorine/oxygen system.

Effect of Reaction Rate Variation on Performance

A general idea about the relative importance of the many chemical reactions used in the assumed mechanism can be obtained from the changes in gas composition. Table III shows species mole fractions in the nozzle gases at the throat and at the end of the

TABLE III. - NOZZLE GAS COMPOSITION FOR THE

OXYGEN DIFLUORIDE-DIBORANE PROPELLANT

[Chamber pressure, 100 psia (68. 95 N/sq cm).]

Species	Oxidant fuel ratio			
	2. 7		40	
	Species mole fraction			
	Throat	Area ratio, 40	Throat	Area ratio, 40
B	0. 00101	0. 00106	0. 00036	0. 00038
BF	.09663	.10183	.02531	.00398
BF_2	.00656	.00032	.00355	3.6×10^{-5}
BF_3	.00168	.00368	.00105	.00031
BO	.01940	.00019	.02115	.00031
BO_2	.00126	1.5×10^{-6}	.00898	.00369
BOF	.20472	.23944	.21025	.27862
F	.00134	4.1×10^{-7}	.01951	6.4×10^{-5}
H	.20224	0. 14063	.28222	.25478
HF	.13774	.12673	.28968	.30551
H_2	.32477	.38589	.10986	.14382
H_2O	.00189	.00023	.00576	.00680
O	.00021	4.4×10^{-7}	.01306	.00106
OH	.00057	1.1×10^{-6}	.00898	.00061
O_2	4.7×10^{-7}	1.5×10^{-10}	.00027	1.9×10^{-5}

nozzle. For O/F = 2.7, the major species are BF, BOF, H, HF, and H_2. The significant changes among these species are the increase in BOF and H_2 mole fractions and the decrease in H and HF mole fractions. At O/F = 4, the major species are BOF, H, HF, and H_2. The same changes in H, BOF, and H_2 concentrations occur at O/F = 4 as did at O/F = 2.7. But HF concentration now increases between throat and nozzle exit instead of decreasing. So one would look for reactions that form H_2 and BOF and consume H as being the most rate controlling processes; however, a more quantitative and systematic procedure is needed to identify these reactions. The method to be used here was described in reference 1 and is a modification of the technique originally proposed in reference 14. A reaction rating parameter $X_{H,j}$ is used to quantitatively measure the importance of each individual reaction. It is proportional to the extent the reaction proceeds (i.e., the net volumetric conversion rate) and to the heat of reaction. The expression for $X_{H,j}$ is

$$X_{H,j} = X_j(\Delta H^O_{298}) \tag{11}$$

where X_j is a net reaction conversion rate parameter given by the equation

$$X_j = \frac{X_{v,j}}{\rho^2} = \frac{k_{fj}\prod_{i=1}^{N} c_i^{\nu_{ij}} - k_{bj}\prod_{i=1}^{N} c_i^{\nu'_{ij}}}{\rho^2} \tag{12}$$

The quantity $X_{v,j}$ is the net volumetric conversion rate for the general reaction:

$$\sum_{i=1}^{N} \nu_{ij}S_i \underset{k_{bj}}{\overset{k_{fj}}{\rightleftharpoons}} \sum_{i=1}^{N} \nu'_{ij}S_i \tag{13}$$

where S_i represents the name of the ith species in the system. The rating parameter $X_{H,j}$ measures the net enthalpy change rate caused by a particular reaction. A negative $X_{H,j}$ means that energy is released into the gas stream, while a positive value means that energy is absorbed due to the reaction. Calculated values of $X_{H,j}$ for the reactions under consideration are shown in table IV for two O/F values and a chamber pressure of 100 psia (68.95 N/sq cm). At O/F = 2.7 the hydrogen atom recombination appears to be much more important than any other reaction, since it releases the largest amount of energy into the reacting gases. This recombination reaction is also the most important one at the high O/F value of 4.0. But several other reactions now appear to be quite important in releasing energy. It should be noted that the H + OH recombination

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TABLE IV. - QUANTITATIVE RANKING OF REACTIONS FOR OF_2-B_2H_6 NOZZLE EXPANSION USING THE ENTHALPY EXCHANGE RATE PARAMETER $X_{H,j}$

[Chamber pressure, 100 psia (68.95 N/sq cm).]

Rank	Oxidant fuel ratio					
	2.7			4		
	Reaction	$X_{H,j}$	$R_{H,j}$	Reaction	$X_{H,j}$	$R_{H,j}$
1	$H + H + M \rightleftarrows H_2 + M$	-403 800	1.0000	$H + H + M \rightleftarrows H_2 + M$	-311 300	1.0000
2	$BO + HF \rightleftarrows BOF + H$	-60 850	.1507	$H + F + M \rightleftarrows HF + M$	-117 800	.3784
3	$H + F + M \rightleftarrows HF + M$	-14 130	.0350	$H + OH + M \rightleftarrows H_2O + M$	-101 900	.3273
4	$H + OH + M \rightleftarrows H_2O + M$	-12 410	.0307	$BO + HF \rightleftarrows BOF + H$	-100 800	.3238
5	$BF + OH \rightleftarrows BOF + H$	-10 120	.0251	$BF + OH \rightleftarrows BOF + H$	-24 670	.0792
6	$H_2 + OH \rightleftarrows H_2O + H$	+6 666	.0165	$F + H_2 \rightleftarrows HF + H$	-23 320	.0749
7	$BO + BF_2 \rightleftarrows BOF + BF$	-6 328	.0157	$H_2 + OH \rightleftarrows H_2O + H$	+16 200	.0520
8	$F + OH \rightleftarrows HF + O$	-2 229	.0055	$BF + O \rightleftarrows BO + F$	+11 370	.0365
9	$H + BF_2 \rightleftarrows HF + BF$	-1 971	.0050	$H + BF_2 \rightleftarrows HF + BF$	-8 423	.0271
10	$BO_2 + BF \rightleftarrows BOF + BO$	-1 835	.0045	$O + H + M \rightleftarrows OH + M$	-7 889	.0253
11	$BO + F + M \rightleftarrows BOF + M$	-1 131	.0028	$BO + F + M \rightleftarrows BOF + M$	-7 576	.0243
12	$BF_2 + HF \rightleftarrows BF_3 + H$	-1 089	.0027	$BF + O_2 \rightleftarrows BOF + O$	-6 183	.0199
13	$BF + O \rightleftarrows BO + F$	+1 022	.0025	$BF + O + M \rightleftarrows BOF + M$	-5 528	.0178
14	$F + H_2 \rightleftarrows HF + H$	-1 002	.0025	$F + OH \rightleftarrows HF + O$	+5 283	.0170
15	$BF + O + M \rightleftarrows BOF + M$	-789	.0020	$BO + BF_2 \rightleftarrows BOF + BF$	-3 994	.0128
16	$O + H + M \rightleftarrows OH + M$	-212	.0005	$BO_2 + BF \rightleftarrows BOF + BO$	-3 399	.0109
17	$O + H_2 \rightleftarrows OH + H$	-132	.0003	$O + H_2 \rightleftarrows OH + H$	+2 350	.0075
18	$BF + O_2 \rightleftarrows BOF + O$	+48	.0001	$H + O_2 \rightleftarrows OH + O$	-2 120	.0068
19	$H + O_2 \rightleftarrows OH + O$	-32	.0001	$BF_2 + HF \rightleftarrows BF_3 + H$	+1 946	.0063

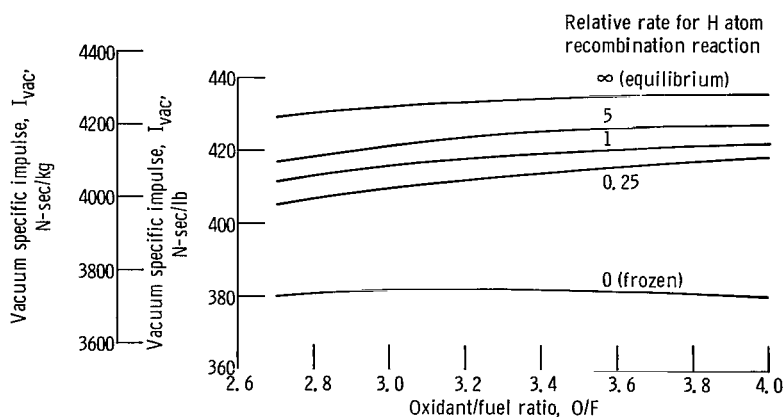Figure 4. - Effect of rate of $H + H + M \rightleftarrows H_2 + M$ reaction on performance of oxygen difluoride-diborane. Chamber pressure, 100 pounds per square inch absolute (68.95 N/cm^2); final expansion ratio, 40.

reaction has a very high $X_{H,j}$ value even though OH and H_2O are minor species. Its high specific rate constant and heat of reaction counterbalance the effect of the small concentrations to make its net energy release effect quite large.

The exact effect of each important reaction was determined by individually varying its specific rate constant over the range of its estimated uncertainty. The results of this variation for the H atom recombination are shown in figure 4. The value of k_2 was changed from five times to one fourth of the reference value. It is clear that variation of this rate constant has a large effect on specific impulse over the entire range of assigned conditions used. Changing the rate constant by its uncertainty changes performance by 3 to 6 pound-seconds per pound (29 to 58 (N-sec)/kg). The effect of changing other reaction rate constants is summarized in table V. Computations were made only at the highest and lowest O/F values for a chamber pressure of 100 psia (68.95 N/sq cm). The main conclusion from table V is that only two rate constants other than the one for the H + H reaction have a large enough uncertainty to effect performance by more than 0.5 pound-seconds per pound (4.9 (N-sec)/kg). These are the constants for $H + F + M \rightleftharpoons HF + M$ and $H + OH + M \rightleftharpoons H_2O + M$. This effect is only apparent in the high O/F region. Another fact brought out in these rate variation studies is that no reaction among boron-containing species is really rate controlling on the entire process. The two most important ones ($BO + HF \rightleftharpoons BOF + H$ and $BF + OH \rightleftharpoons BOF + H$) are low energy shuffle reactions, whose rate constant variation by one order of magnitude causes negligible change in performance. The two most energetic reactions involving the BOF species are not even among the first 10 significant reactions. These are the three-body recombinations of BO and F or BF and O to give BOF. A few rate variation computations were, however, made for these reactions to determine the effect if their rate constants were in error by two orders of magnitude. The results, shown in table V, indicate that the effect of both reactions would still be insignificant under these conditions.

The last column of table V shows the effect on performance of removing each reaction individually from the mechanism. Only for one reaction ($BO + HF \rightleftharpoons BOF + H$) does this removal cause a significant change in performance from the reference value. This fact does not mean, of course, that several of these reactions can be removed at the same time without changing our results. As in reference 1, we shall compare the reactions in a given mechanism with one another by using a ratio of $X_{H,j}$ values, namely:

$$R_{H,j} = \left| \frac{X_{H,j}}{\left(X_{H,j}\right)_{max}} \right| \tag{14}$$

In this equation $\left(X_{H,j}\right)_{max}$ is the largest value for all reactions considered. The smaller the $R_{H,j}$ value, the less important a reaction should be. Reference 1 shows

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TABLE V. - EFFECT OF REACTION RATE VARIATION ON PERFORMANCE OF

OXYGEN DIFLUORIDE-DIBORANE

[Chamber pressure, 100 psia (68.95 N/sq cm).]

Number	Reaction	Uncertainty factor		Oxidant fuel ratio, O/F	Rate constant			
		Maximum	Minimum		Reference	Maximum[a]	Minimum[b]	0
					Vacuum specific impulse			
I	$H + F + M \rightleftharpoons HF + M$	4	0.25	2.7	411.4	411.5	411.4	411.4
				4	422.0	422.7	421.9	421.8
IV	$H + OH + M \rightleftharpoons H_2O + M$	10	.10	2.7	411.4	411.7	411.4	411.4
				4	422.0	424.7	421.6	421.5
XIII	$BO + HF \rightleftharpoons BOF + H$	10	.10	2.7	411.4	411.5	411.1	410.4
				4	422.0	422.1	421.7	420.1
XIV	$BF + OH \rightleftharpoons BOF + H$	10	.10	2.7	411.4	411.5	411.4	411.4
				4	422.0	422.3	422.0	422.0
VI	$H_2 + OH \rightleftharpoons H_2O + H$	2	.5	2.7	411.4	411.4	411.4	411.2
				4	422.0	422.1	422.1	421.8
III	$F + H_2 \rightleftharpoons HF + H$	10	.10	2.7	411.4	411.4	411.4	411.4
				4	422.0	422.0	422.1	422.1
X	$F + OH \rightleftharpoons HF + O$	10	.10	2.7	411.4	411.5	411.5	411.5
				4	422.0	421.7	422.1	422.1
XIX	$BF + O \rightleftharpoons BO + F$	10	.10	2.7	411.4	411.5	411.4	411.4
				4	422.0	422.4	421.9	421.8
XI	$BO + F + M \rightleftharpoons BOF + M$	100	.01	2.7	411.4	411.6	411.4	-----
				4	422.0	422.5	422.1	-----
XII	$BF + O + M \rightleftharpoons BOF + M$	100	.01	2.7	411.4	411.5	411.4	-----
				4	422.0	422.5	422.1	-----

[a]Reference rate constant × maximum uncertainty factor.
[b]Reference rate constant × minimum uncertainty factor.

that all reactions with an $R_{H, j}$ of about 0.02 or less can be removed as a group from the hydrocarbon-fluorine/oxygen mechanism without changing kinetic specific impulse by more than the arbitrary limit of ±0.5 pound-second per pound. Reference 1 also shows that an individual reaction with an $R_{H, j}$ of 0.14 can be removed without changing performance more than this arbitrary limit. For the OF_2-diborane system the $R_{H, j}$ values in table IV and the information in table V show the following results. At O/F = 2.7, any reaction with $R_{H, j}$ less than or equal to 0.035 can be individually removed without significant change in performance. For O/F = 4, the reaction $H + F + M \rightleftharpoons HF + M$ with $R_{H, j}$ equal to 0.3782 can be removed with negligible change.

However, when the reaction $BO + HF \rightleftharpoons BOF + H$ with $R_{H,j}$ equal to 0.3238 is removed, specific impulse is decreased by 1.9 units. Consequently, $R_{H,j}$ is not a good measure of whether any single reaction can be removed and one must try to explain why a quite important reaction can be removed without effecting the computed performance.

One possible explanation is that specific impulse is more directly related to the total enthalpy change rate for the whole recombination process than to any single $X_{H,j}$ value. The total enthalpy change rate $X_{H,total}$ is the algebraic sum of the individual $X_{H,j}$ values:

$$X_{H,total} = \sum_{j=1}^{r} X_{H,j} \qquad (15)$$

where r is the number of reactions in the mechanism. The complete recombination process is always exothermic; therefore, $X_{H,total}$ will always be negative, since a negative $X_{H,j}$ indicates a net release of energy into the gas stream due to the particular reaction. Now it is possible that the mechanism shown in table I uses more reactions than are necessary to completely describe the recombination process. Therefore, if an important reaction is removed, the $X_{H,j}$ values for some of the other reactions may become more negative, so that the net effect is to change $X_{H,total}$ very little. That this is the case for the $H + F + M \rightleftharpoons HF + M$ reaction can be seen from the data in table VI. In this table, values of $X_{H,j}$ are shown for an assigned chamber pressure of 100 psia (68.95 N/sq cm) and O/F of 4 using three different reaction mechanisms. One is the complete set of reactions in table I. Mechanism A is all these reactions except reaction I, $H + F + M \rightleftharpoons HF + M$. Mechanism B is all the reactions of table I except reaction XIII, $BO + HF \rightleftharpoons BOF + H$. The values of $X_{H,total}$ are also shown for each mechanism. Comparing mechanism A with the complete mechanism shows that the $X_{H,j}$ values for several reactions (II, III, IV, and X) become significantly more negative when reaction I is not present. The total effect gives a value of $X_{H,total}$ which is only 1.5 percent less negative than the value for the complete mechanism. For mechanism B the removal of $BO + HF \rightleftharpoons BOF + H$ causes $X_{H,j}$ values for reactions XI, XIV, XVII, and XXV to become more negative, but causes the values for reactions X and XVIII to become more positive. The result of these changes is to make $X_{H,total}$ about 5 percent less negative than the value for the complete mechanism. Therefore, when the magnitude of $X_{H,total}$ decreases by 1.5 percent, specific impulse is negligibly changed (less than 0.5 impulse units). When the magnitude of $X_{H,total}$ decreases by 5 percent, specific impulse decreases by about 2 units, a nonnegligible change. This single comparison is not conclusive, but does indicate that the total enthalpy change rate is more important than any single $X_{H,j}$ value in estimating the effect of a mechanism change on

[Chamber pressure, 100 psia (68.95 N/sq cm); oxidant
fuel ratio, O/F = 4.]

Reaction number	Reaction	Enthalpy exchange rate parameter, $X_{H,j}$		
		Complete mechanism	Mechanism A	Mechanism B
II	$H + H + M \rightleftarrows H_2 + M$	-311 300	-369 800	-316 800
I	$H + F + M \rightleftarrows HF + M$	-117 800	0	-119 100
IV	$H + OH + M \rightleftarrows H_2O + M$	-101 900	-120 700	-105 600
XIII	$BO + HF \rightleftarrows BOF + H$	-100 800	-100 900	0
XIV	$BF + OH \rightleftarrows BOF + H$	-24 670	-24 550	-79 100
III	$F + H_2 \rightleftarrows HF + H$	-23 320	-35 490	-19 760
VI	$H_2 + OH \rightleftarrows H_2O + H$	+16 200	+19 140	+14 250
XIX	$BF + O \rightleftarrows BO + F$	+11 370	+11 240	-1 726
XVIII	$H + BF_2 \rightleftarrows HF + BF$	-8 423	-8 623	+3 295
V	$O + H + M \rightleftarrows OH + M$	-7 889	-9 445	-8 078
XI	$BO + F + M \rightleftarrows BOF + M$	-7 576	-8 957	-14 970
XXV	$BF + O_2 \rightleftarrows BOF + O$	-6 183	-6 765	-21 790
XII	$BF + O + M \rightleftarrows BOF + M$	-5 528	-6 336	-8 768
X	$F + OH \rightleftarrows HF + O$	+5 283	-11 130	+62 000
XVII	$BO + BF_2 \rightleftarrows BOF + BF$	-3 994	-4 031	-27 250
XX	$BO_2 + BF \rightleftarrows BOF + BO$	-3 399	-3 528	-2 384
VIII	$O + H_2 \rightleftarrows OH + H$	+2 350	+3 437	+2 399
VII	$H + O_2 \rightleftarrows OH + O$	-2 120	-2 543	-8 684
XXI	$BF_2 + HF \rightleftarrows BF_3 + H$	+1 946	+2 029	+1 291
	Sum of $X_{H,j}$'s	-687 700	-677 000	-650 800

performance. This idea is consistent with the interpretation of $X_{H, total}$ as an approximate indicator of the enthalpy release rate into the gas stream. $X_{H, total}$ is then related to the kinetic energy of the gas and therefore to specific impulse, which is proportional to the velocity of the gas stream.

It should be mentioned that only 19 reactions are listed in both tables IV and VI. The additional 6 reactions in table I were used during the calculations, but their contribution to $X_{H, total}$ and to computed performance is negligible, so they are omitted from the tables. Additional calculations showed that only the first 16 reactions listed in tables IV and VI are needed in order to compute kinetic specific impulse within our required uncertainty of ±0.5 pound-second per pound (4.9 (N-sec)/kg) for all assigned conditions. Only one of these is really rate controlling. This is the three-body recombination $H + H + M \rightleftarrows H_2 + M$. Performance is sensitive to rate constant uncertainties for

two other important recombinations, $H + F + M \rightleftharpoons HF + M$ and $H + OH + M \rightleftharpoons H_2O + M$. Most of the remaining reactions are rapid, low energy shuffle reactions which supply the free radical species that react in the three-body recombination processes. The most important reaction of this type is $BO + HF \rightleftharpoons BOF + H$, which generates hydrogen atoms.

Comparison with Hydrocarbon - Fluorine/Oxygen Propellants

In order to compare the most promising space storable propellant systems, theoretical performance curves are presented for three systems in figure 5. Equilibrium and kinetic results obtained in the present work for OF_2-diborane are shown along with those presented in reference 1 for the methane - F_2/O_2 and butene-1 - F_2/O_2 systems. The comparison is made at 100 psi chamber pressure (68.95 N/sq cm) and a nozzle expansion ratio of 40. The fluorine/oxygen mixture giving best performance was used for each of the hydrocarbon fuels. It must be noted that the actual nozzle area profiles are not the same for the hydrocarbon systems as for the OF_2-diborane propellant. This should not, however, have a significant effect on the comparison. Figure 5 shows that both equilibrium and kinetic curves for the latter system lie well above the corresponding curves for either hydrocarbon propellant. The kinetically-limited performance level for OF_2-diborane is 13 to 24 pound-seconds per pound (127 to 235 (N-sec)/kg) higher than the maximum kinetic specific impulse for methane-fluorine/oxygen. Moreover, the actual percentage kinetic loss is less for the OF_2-diborane system than for the others.
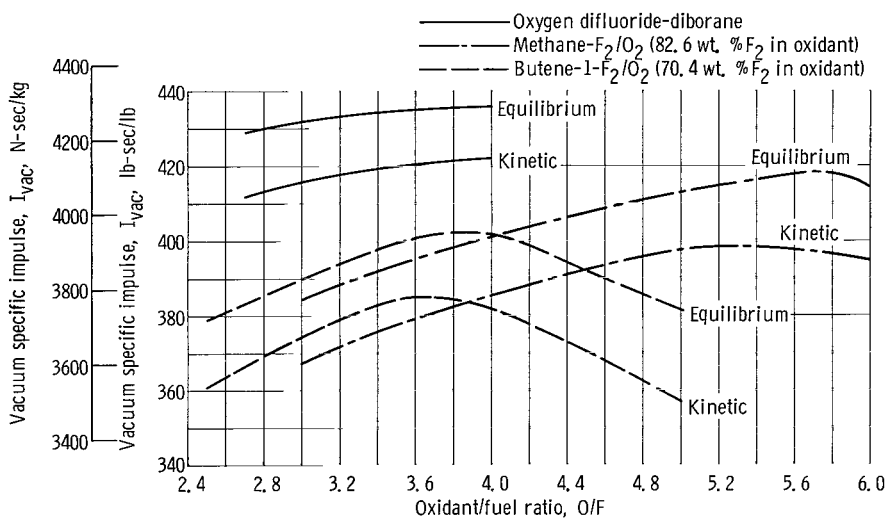

Figure 5. - Theoretical performance of "space storable" propellant systems. Chamber pressure, 100 pounds per square inch absolute (68.95 N/cm²); final expansion ratio, 40. (Reference values for all reaction rate constants.)

The ratio of kinetic to equilibrium specific impulse at the O/F value for peak kinetic performance is about 0.97 for OF_2-diborane and 0.96 for the other two systems. Therefore, the OF_2-diborane has higher kinetic performance not only because its equilibrium performance is higher, but also because its kinetic losses are smaller than for the hydrocarbon-fluorine/oxygen systems. This comparison shows the superiority of the OF_2-diborane system in terms of theoretically computed performance.

CONCLUDING REMARKS

The results of the present work have shown that OF_2-diborane nonequilibrium performance is sensitive to only 3 of the 25 possible reactions in the nozzle. Only the rate constants for the reactions

$$H + H + M \rightleftarrows H_2 + M$$

$$H + F + M \rightleftarrows HF + M$$

$$H + OH + M \rightleftarrows H_2O + M$$
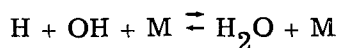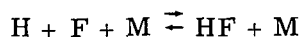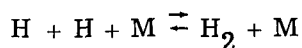
must be known to better than one order of magnitude accuracy to compute performance within an uncertainty of ±0.5 pound-second per pound. Thirteen additional reactions (including those of the boron compounds) must be in the mechanism, but their rate constants can be in error by one order of magnitude or more without changing specific impulse more than the stated uncertainty. The hydrogen atom recombination is really the one dominant reaction, inasmuch as computed performance is considerably more sensitive to this rate constant than to any other one. The OF_2-diborane system is one of the most complicated of the space storables studied so far. It contains more species and requires more chemical reactions than do the hydrocarbon-fluorine/oxygen systems. The latter systems have at least two dominant reactions (the H + H and H + F recombinations) whereas OF_2-diborane has only one.

The theoretical results shown here indicate that OF_2-diborane has higher specific impulse and smaller kinetic losses than the hydrocarbon-F_2/O_2 combinations. Unfortunately no experimental performance data were found for OF_2-diborane which were felt adequate for comparison with these computations. Therefore no comparison of experimental and theoretical results can be made. Uncertainty in the theoretical results can be due to other factors beyond any rate constant uncertainties. One of these is the value of the heat of formation of oxygen difluoride used to perform the equilibrium computations that are the starting point for obtaining the kinetic results. The current value

given by the J. A. N. A. F. Thermochemical tables for the heat of formation of $OF_2(g)$ at 298.15 K is ΔH^O_{298} = -4.39 kilocalories per mole (-18.4 kJ/mole). As stated previously we have used the value ΔH^O_{298} = 5.86 kilocalories per mole (24.52 kJ/mole) recently measured experimentally by King and Armstrong (ref. 15). This new value, higher by almost 10 kilocalories, increases the theoretical performance level for OF_2-diborane approximately 7 pound-seconds per pound (69 (N-sec)/kg). Therefore, this combination would still be more energetic than the hydrocarbon-F_2/O_2 combinations even if the value ΔH^O_{298} = -4.39 kilocalories per mole had been used for OF_2. The use of the recently reported higher heat of formation allows OF_2-diborane to compare even more favorably with other systems. Of course, this comparison has not considered any of the practical problems involved in using either type of propellant combination in a practical engine.

SUMMARY OF RESULTS

Theoretical computations have been performed for the oxygen difluoride-diborane propellant system to obtain both equilibrium and kinetically-limited performance at chamber pressures of 100 and 300 psia (68.95 and 206.9 N/sq cm) over an O/F range of 2.7 to 4. A study was also made to select the important chemical reactions occurring during the nozzle expansion and to evaluate the sensitivity of performance to individual variation in the rate constants of these reactions. The results of thie investigation are as follows:

1. Theoretical performance is moderately dependent on the assigned oxidant-fuel ratio. For the fuel-rich O/F range used, computed values of vacuum specific impulse increase steadily as O/F is increased. The kinetically limited values for 100 psi chamber pressure (68.95 N/sq cm) range from 411 to 422 pound-seconds per pound (4030 to 4138 (N-sec)/kg). At 300 psia (206.9N/sq cm), rate limited performance varies from 423 to 434 pound-seconds per pound (4148 to 4256 (N-sec)/kg).

2. The most important reaction occurring in the nozzle is the hydrogen atom recombination $H + H + M \rightleftharpoons H_2 + M$. Increasing or decreasing this reaction's rate constant by the estimated uncertainty changes computed specific impulse values by 3 to 6 pound-seconds per pound (29 to 58 (N-sec)/kg), or slightly more than 1 percent, over the entire O/F range used.

3. In the low oxidant-fuel ratio range performance is not significantly affected by any other reaction rate constant when these constants are changed within the limits of their estimated uncertainty.

4. In the high oxidant-fuel ratio range specific impulse is also affected by uncertainty in the $H + OH + M \rightleftharpoons H_2O + M$ and $H + F + M \rightleftharpoons HF + M$ rate constants. The effect

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is greater for the first reaction, since the uncertainty is greater for the H + OH recombination.

5. The results of the reaction-importance study are in good agreement with the predictions of the reaction rating parameter $X_{H,j}$, which measures the enthalpy change rate in the gas caused by the jth reaction.

6. Theoretical kinetic performance is not sensitive to one order of magnitude uncertainty in the rate constants for the reactions involving the boron-containing species, although many of these reactions must be present in the mechanism. The most important boron-containing reaction is $BO + HF \rightleftharpoons BOF + H$, which generates hydrogen atoms for the recombination reactions.

7. The kinetically-limited performance level for OF_2-diborane is 13 to 24 pound-seconds per pound (127 to 235 (N-sec)/kg) higher than the maximum vacuum specific impulse for methane-fluorine/oxygen, the most energetic of the hydrocarbon-fluorine-oxygen systems. The superiority of OF_2-diborane is due not only to the fact that its equilibrium performance is higher, but also to the fact that its kinetic losses are lower than those for the methane-fluorine/oxygen system.

Lewis Research Center,
    National Aeronautics and Space Administration,
        Cleveland, Ohio, October 25, 1968,
            129-01-06-01-22.

APPENDIX - SYMBOLS

A nozzle crossection area, length^2

$\mathscr{A}$ parameter defined in eq. (8)

$\mathscr{B}$ parameter defined in eq. (9)

C_p heat capacity of mixture based on fixed composition $= \displaystyle\sum_{i=1}^{N} \alpha_i \left(C_p\right)_i$, energy/(mass)(K)

$\left(C_p\right)_i$ heat capacity of species i, energy/(mass)(K)

c_i concentration of species i, mole/volume

E_a activation energy, cal/mole

h_i enthalpy of species i, energy/mass

I_{eq} theoretical equilibrium vacuum specific impulse, (lb-sec)/lb ((N-sec)/kg)

I_k theoretical rate limited vacuum specific impulse, (lb-sec)/lb ((N-sec)/kg)

I_{vac} theoretical vacuum specific impulse, (lb-sec)/lb ((N-sec)/kg)

M average molecular weight of mixture

M_i molecular weight of species i

$\mathscr{M}$ Mach number defined in eq. (6)

p pressure, force/area

R universal gas constant, energy/(mole)(K)

$R_{H,j}$ reaction rating ratio $= \left| X_{H,j} \middle/ \left(X_{H,j}\right)_{max} \right|$

r^* reference length

T temperature, K

V velocity, length/time

w_i production rate of species i, mass/(volume)(time)

$X_{H,j}$ reaction rating parameter defined by eq. (11)

$X_{H,total}$ net enthalpy change rate for complete nozzle expansion process, defined by eq. (15)

ΔH^o_{298} heat of reaction at 298 K for the forward reaction as written in table I, kcal/mole (kJ/mole)

X_j net conversion rate parameter for j^{th} reaction defined by eq. (12)

$X_{v,j}$ net volumetric conversion rate for j^{th} reaction defined by eq. (12)

x nondimensionalized distance coordinate = distance/$r*$

α_i mass fraction of species i

γ heat capacity ratio defined by eq. (7)

ν_{ij}, ν'_{ij} stoichiometric coefficients for species i in reaction j; see eq. (13)

ρ density, mass/volume

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