

Role of Hydrogen/Air Chemistry in Nozzle Performance for a Hypersonic Propulsion System

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A computer model for describing quasi-one-dimensional flow of a gas mixture with area change and finite-rate chemical reactions was used to study the role of hydrogen/air chemistry in nozzle performance for a hypersonic propulsion system. The important results obtained for a typical nozzle at a Mach 18 flight condition are as follows: 1) finite-rate chemistry should not be neglected in nozzle performance simulations because beneficial chemical processes persist throughout the entire nozzle length; 2) termolecular recombination reactions represent the principal chemical contribution to nozzle performance; 3) intermediate HNO species have little effect on hydrogen radical recombination; and 4) nitrogen oxides are not involved directly in the hydrogen radical recombination process but rather they provide a source of oxygen for recombination. In addition, the study shows that any major reduction in the detailed reaction mechanism used here may lead to incorrect simulations of nozzle performance.

Introduction

THE development of an air-breathing propulsion system for a hypersonic flight vehicle will depend heavily on computational fluid dynamic (CFD) simulations of the system performance. Since these CFD simulations involve complex supersonic reacting flow problems which can even strain the capacity of current supercomputers, any simplifications which do not affect the accuracy of the finite-rate chemical mechanisms are highly desirable. For example, results of a previous study of an air inlet for high Mach number flight conditions have shown that the finite-rate air chemistry can be decoupled from the fluid dynamics because significant dissociation of the air and production of nitrogen oxides will occur only in a small portion of the airflow captured by the inlet and located near its surfaces.¹ Accordingly, the present study was directed at understanding the finite-rate chemistry of hydrogen and air in the nozzle section with the objective of developing a chemical kinetic mechanism which will provide efficient use of computers for nozzle CFD simulations. In particular, this study has concentrated on the following aspects of the chemical processes in the nozzle section: 1) identifying the dominant reaction paths for radical species recombination; 2) understanding the reasons for chemical inefficiencies or limitations in the nozzle; 3) establishing the basis for a reduced chemical kinetic mechanism for nozzle simulations; and 4) determining the correct inlet conditions (i.e., combustor exit conditions) to be used for nozzle performance simulations.

Performance simulations for rocket engines and ramjets are usually based on the assumption that the gas composition in the nozzle is chemically frozen at either the combustor exit condition or the nozzle throat condition because the expansion process is very rapid.² For a hypersonic propulsion system, however, the high Mach number at the nozzle inlet pro-

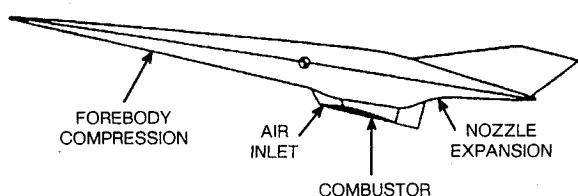
duces shallow wave angles which require a long nozzle that must be integrated with the airframe as shown in the schematic³ in Fig. 1. Unlike the nozzles for rocket engines and ramjets, this gradual expansion process should result in recovery of a significant fraction of the thermal energy from dissociated species present at the combustor exit. Therefore, performance simulations of nozzles for hypersonic propulsion systems should include finite-rate chemical kinetics.

Method of Approach

The basic approach to this study was to model the nozzle expansion process in sufficient detail to adequately simulate the pressure/temperature history in the nozzle, and thereby be able to isolate the role of chemical reaction mechanisms. In this regard, a computer model was developed based on the CHEMKIN code⁴ for describing quasi-one-dimensional flow of a gas mixture with area change, and simultaneous gas phase chemical reactions. Since the emphasis of this study was on nozzle chemistry, this model neglects effects due to mixing, diffusion, viscosity, and shock waves. The computer code performed a simultaneous solution of the set of first-order, ordinary differential equations which govern fluid flow, thermodynamic properties, and chemical species concentrations. The equations used for conservation of mass, momentum, energy, species and the equation of state are as follows:

$$\frac{1}{\rho} \frac{d\rho}{dx} + \frac{1}{A} \frac{dA}{dx} + \frac{1}{v} \frac{dv}{dx} = 0 \quad (1)$$

$$\rho v \frac{dv}{dx} + \frac{dp}{dx} = 0 \quad (2)$$



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Fig. 1 Schematic representation of the scramjet propulsion system.

Table 1 Hydrogen-air reaction mechanism

Reaction	<i>A</i>	<i>n</i>	<i>E</i>
1. $H_2 + O_2 = OH + OH$	5.50E + 13	0.0	5.78E + 4
2. $H + O_2 = O + OH$	1.20E + 17	-0.91	1.65E + 4
3. $H_2 + O = H + OH$	1.50E + 07	2.0	7.55E + 3
4. $OH + OH = O + H_2O$	3.40E + 13	0.0	5.02E + 3
5. $OH + H_2 = H + H_2O$	1.00E + 08	1.6	3.30E + 3
6. $H_2O_2 + OH + H_2O + HO_2$	7.00E + 12	0.0	1.43E + 3
7. $HO_2 + O = O_2 + OH$	2.00E + 13	0.0	0.0
8. $H + HO_2 = OH + OH$	1.50E + 14	0.0	1.00E + 3
9. $H + HO_2 = H_2O + O$	3.00E + 13	0.0	0.0
10. $H + HO_2 = H_2 + O_2$	2.50E + 13	0.0	6.93E + 2
11. $OH + HO_2 = H_2O + O_2$	2.00E + 13	0.0	0.0
12. $HO_2 + HO_2 = H_2O_2 + O_2$	2.00E + 12	0.0	0.0
13. $HO_2 + H = H_2O_2 + H$	7.30E + 11	0.0	1.87E + 4
14. $O + O + M = O_2 + M$ ($M = AR$) $O_2/0.0/N_2/0.0/H_2/3.67/N_2O/4.38$	1.00E + 17	-1.0	0.0
15. $O + O + O_2 = O_2 + O_2$ ($M = O_2$)	7.98E + 19	-1.5	0.0
16. $O + O + N_2 = O_2 + N_2$ ($M = N_2$)	6.17E + 15	-0.5	0.0
17. $H_2 + M = H + H + M$ ($M = AR$) $H_2/6.0/H_2/4.0/H_2O/15.0/N_2/1.2$	2.20E + 14	0.0	9.60E + 4
18. $H + O + M = OH + M$ ($M = N_2$) $H_2O/5.0$	6.00E + 16	-0.6	0.0
19. $OH + OH + M = H_2O_2 + M$ ($M = N_2$) $H_2O/6.0/H_2O_2/6.0/O_2/0.8$	1.30E + 22	-2.0	0.0
20. $H + OH + M = H_2O + M$ ($M = N_2, O_2$) $H_2O/6.3/H/2.0$	2.20E + 22	-2.0	0.0
21. $H + O_2 + M = HO_2 + M$ ($M = N_2, O_2$) $H_2/2.5/H_2O/16.0$	6.42E + 18	-1.0	0.0
22. $H + H_2O_2 = H_2O + OH$	1.00E + 13	0.0	3.59E + 3
23. $O + H_2O_2 = OH + HO_2$	2.80E + 13	0.0	6.41E + 3
24. $NO + M = N + O + M$ ($M = AR, N_2, O_2$) $N/20/NO/20/O/20$	4.00E + 20	-1.5	1.50E + 5
25. $N_2O + M = N_2 + O + M$ ($M = AR$) $N_2/1.22/O_2/1.22/N_2O/5.56$	6.92E + 23	-2.5	6.50E + 4
26. $NO_2 + M = NO + O + M$ ($M = AR$) $H_2O/6.1/NO/2.9/N_2/1.4/O_2/1.0/N_2O/2.1$	1.10E + 16	0.0	6.56E + 4
27. $N_2 + M = N + N + M$ ($M = N_2$) $AR/0.4/N/6.0/H_2/2.0/H_2O/1.4$	3.72E + 21	-1.6	2.25E + 5
28. $N_2 + O = NO + N$	1.82E + 14	0.0	7.62E + 4
29. $NO + O = N + O_2$	3.80E + 09	1.0	4.14E + 4
30. $N_2O + O = NO + NO$	6.92E + 13	0.0	2.66E + 4
31. $N_2O + O = N_2 + O_2$	1.00E + 14	0.0	2.80E + 4
32. $NO_2 + O = NO + O_2$	1.00E + 13	0.0	6.00E + 2
33. $NO_2 + N = NO + NO$	4.00E + 12	0.0	0.0
34. $NO_2 + N = N_2O + O$	5.00E + 12	0.0	0.0
35. $N_2O + N = N_2 + NO$	1.00E + 13	0.0	1.99E + 4
36. $NO + N_2O = N_2 + NO_2$	1.00E + 14	0.0	4.97E + 4
37. $NO_2 + NO_2 = NO + NO + O_2$	2.00E + 12	0.0	2.68E + 4
38. $HNO + O = NO + OH$	5.01E + 11	0.5	1.99E + 3
39. $N_2O + OH = N_2 + HO_2$	6.31E + 11	0.0	9.93E + 3
40. $HNO + OH = NO + H_2O$	1.26E + 12	0.5	1.99E + 3
41. $N + HO_2 + NO + OH$	1.00E + 13	0.0	1.99E + 3
42. $NO + HO_2 = HNO + O_2$	1.99E + 11	0.0	1.99E + 3
43. $NO + HO_2 = NO_2 + OH$	2.09E + 12	0.0	-4.77E + 2
44. $HNO + HO_2 = NO + H_2O_2$	3.16E + 11	0.5	1.99E + 3
45. $NO + H = N + OH$	2.63E + 14	0.0	5.04E + 4
46. $NO_2 + H = NO + OH$	3.47E + 14	0.0	1.47E + 3
47. $N_2O + H = N_2 + OH$	7.59E + 13	0.0	1.51E + 4
48. $HNO + H = NO + H_2$	1.26E + 13	0.0	3.97E + 3
49. $H + NO + M = HNO + M$ ($M = AR$) $H/1.86/N_2O/2.21/H_2O/6.15$	2.92E + 15	0.0	-5.96E + 2

Rate coefficients are in the form $k = AT^n \exp(-E/RT)$. Units are moles, cubic centimeters, seconds, Kelvins, and calories/mole.

Chaperone efficiencies are shown after each three-body reaction for species if not equal to unity.

$$\rho v \bar{c}_p \frac{dT}{dx} + \sum_{i=1}^N h_i \dot{\omega}_i W_i + \rho v^2 \frac{dV}{dx} = 0 \quad (3)$$

$$\rho v \frac{dY_i}{dx} = \dot{\omega}_i W_i \quad (4)$$

$$\frac{1}{p} \frac{dp}{dx} + \frac{1}{\bar{W}} \frac{d\bar{W}}{dx} = \frac{1}{\rho} \frac{dp}{dx} + \frac{1}{T} \frac{dT}{dx} \quad (5)$$

where x is the distance, ρ is the mass density, A is the cross-sectional area of the nozzle, v is the velocity, p is the pressure,

c_p is the specific heat at constant pressure, i denotes each chemical species, N is the total number of species, h is the specific enthalpy, $\dot{\omega}$ is the net molar production rate of the species, W is the molecular weight, Y_i is the mass fraction of the species, and

$$\bar{c}_p = \sum_{i=1}^N y_i c_{pi}$$

$$\bar{W} = 1 / \sum_{i=1}^N [y_i/W_i]$$

The chemical rate computations for a specified reaction mechanism, including thermochemical properties, were generated by the CHEMKIN code⁴ and the governing conservation equations were specified by a new subroutine called NOZZLE which was developed for this study. Solution of the set of simultaneous differential equations as a function of nozzle position was performed by means of a computer code which is based on the Gear method.⁵ This code has been found to be highly reliable for the solution of a very wide range of stiff initial value problems.

Reaction Mechanism

The detailed reaction mechanism adopted for this nozzle chemistry study was compiled from acknowledged sources of rate data for high temperature chemical reaction of hydrogen, oxygen, and nitrogen.⁶⁻¹⁰ This reaction mechanism (shown in Table 1) was chosen to cover mixture compositions with either fuel or air in excess, as well as stoichiometric mixtures, and to treat the variations in gas temperature and pressure expected during the nozzle expansion process. In addition to the oxidation of hydrogen, the reversible conversion of atmospheric nitrogen to NO_x species were included in this reaction mechanism. And, because of the importance of considering all possible reactions which can potentially contribute to radical recombination of intermediate hydrogen species, recombination reactions involving NO and HNO also have been included in the mechanism. In the most detailed form shown in Table 1, this reaction mechanism consists of 49 reaction steps which involve 14 species (H_2 , O_2 , N_2 , H , N , O , OH , HO_2 , H_2O , H_2O_2 , NO , N_2O , NO_2 , and HNO). To assess the importance of specific reactions and species, several variations to this mechanism have also been considered in this study.

Sample Problem

As the basis for this assessment of the role of chemistry in nozzle performance, a representative nozzle problem was formulated from thermochemical cycle analyses for a typical hypersonic flight vehicle. To emphasize the importance of

Table 2 Inlet conditions and geometry used for quasi-one-dimensional nozzle chemistry study

Nozzle inlet conditions ^a	
<i>M</i>	= 4.0
<i>V</i>	= 5364 m/s
ϕ	= 1.85
<i>T</i>	= 3072 K
<i>P</i>	= 1.0 atm
<i>I</i>	= 574.4 s
[H]	= 0.87059E - 01
[N]	= 0.14647E - 04
[O]	= 0.80033E - 02
[OH]	= 0.30143E - 01
[H_2]	= 0.20225E + 00
[O_2]	= 0.31803E - 02
[H_2O]	= 0.19909E + 00
[HO_2]	= 0.44573E - 05
[H_2O_2]	= 0.23341E - 06
[NO]	= 0.50908E - 02
[N_2]	= 0.46517E + 00
[NO_2]	= 0.30478E - 06
[N_2O]	= 0.19957E - 06
[HNO]	= 0.10668E - 05
Nozzle geometry	
Angle	= 12.431 deg
Length	= 844.1 cm
Area ratio	= 47.7:1

^aUnits of concentrations are in mole fractions.

finite-rate chemistry to nozzle performance, a hypersonic flight condition corresponding to Mach 18 was chosen for this nozzle problem. The results of a previous study of engine performance for this condition indicated that the gas mixture at the combustor exit is hydrogen rich, the temperature is approximately 3000 K, and the gas velocity is high. As a result, high concentrations of radical species exist at the nozzle inlet and nozzle residence times are comparable to reaction times.

Although nozzle performance depends on both the nozzle contour and the overall expansion ratio, the latter has been shown to be the more important geometrical parameter.¹¹ Whereas, the rate of expansion can be affected by the nozzle contour, a constant angle nozzle with a typical overall area ratio of 50:1 was chosen for the sample problem since the main emphasis of this study is on the importance of chemistry to nozzle performance. The nozzle geometry and inlet conditions used as a sample problem for this study are summarized in Table 2.

The gas mixture composition chosen for the nozzle inlet was taken from the results of a previous study of combustor chemistry which showed that chemical equilibrium is not achieved at the combustor exit at hypersonic speeds of the order of Mach 18. It should be noted from these nozzle inlet conditions that a large fraction of the energy conversion in the combustor has gone into dissociation of the hydrogen fuel and air. Clearly, the gas mixture is oxygen poor and the production of additional water and thermal energy will depend on the finite-rate chemistry which takes place in the nozzle. Although no reference is available at this time for the previous study from which these nozzle inlet conditions were taken, no reference is actually necessary since these conditions are generic for the subject hypersonic propulsion systems.

Results and Discussion

The results of the nozzle chemistry study for several variations of the chemical reaction mechanism are summarized in Table 3. Different quantities can be used to measure the relative performance of the nozzle expansion process. Therefore, several quantities which indicate nozzle performance are given in Table 3. For the purpose of weighing the effects of chemical processes on nozzle performance, the ratios of specific impulse at the nozzle exit are probably more relevant than quantities such as velocity or water concentration because they relate directly to vehicle performance. The two impulse ratios given in Table 3 are defined as follows: C_n is the ratio of the actual change in impulse produced by the nozzle to the change in impulse for equilibrium chemistry throughout the nozzle, and C_s is the ratio of the actual impulse at the nozzle exit to the exit impulse for equilibrium chemistry throughout the nozzle. Both C_n and C_s equal unity for the case of equilibrium chemistry throughout the nozzle. Similarly, the minimum values of both C_n and C_s occur for the case of frozen chemistry throughout the nozzle. As expected, the values of C_n and C_s for the cases of finite-rate chemistry lie between the values for the cases of equilibrium and frozen chemistry. On an absolute basis, there is not a significant difference between the values of C_n and C_s for the various cases. However, any improvement in C_n and C_s should be considered worthwhile because of the acute sensitivity of vehicle performance to specific impulse.

It is clear from the results in Table 3 that nozzle performance, i.e., C_n or C_s , depends on the extent of chemical reaction as well as the fluid dynamic expansion process. The predictions in Fig. 2 of specific impulse *I*, vs distance for the two limiting cases (equilibrium and frozen chemistry) and the case for detailed chemistry, clearly show that the contribution of chemical reaction to the increase in impulse persists throughout the entire nozzle length. The chemical processes do not reach a frozen state at any point along the nozzle expansion considered here. Similarly, the chemical processes do not attain a chemical equilibrium state anywhere in the nozzle. In other words, these results show clearly that finite-

Table 3 Summary of results of nozzle chemistry study: Nozzle exit conditions for various reaction mechanisms

Case description	V, m/s	T, K	P, atm	[H ₂ O] ^a	I, s	C _n	C _s
Detailed chemistry	6165	1133	0.0066	0.2447	637.5	0.889	0.988
Equilibrium chemistry	6215	1578	0.0087	0.2617	645.4	1.000	1.000
Frozen chemistry	6141	925	0.0055	0.1991	633.7	0.835	0.982
Detailed w/o HNO reactions	6164	1128	0.0066	0.2446	637.4	0.887	0.988
Detailed w/o nitrogen reactions	6156	1126	0.0066	0.2441	636.6	0.876	0.986
Detailed w/1 mole % NO added	6168	1150	0.0067	0.2467	638.1	0.897	0.989
Detailed w/recombination rate constants enhanced 3×	6179	1233	0.0071	0.2489	639.6	0.918	0.991
Detailed w/recombination rate constants reduced 3×	6146	1055	0.0062	0.2414	635.1	0.855	0.984
Detailed w/o H ₂ O ₂ reactions	6150	1146	0.0067	0.2459	636.2	0.870	0.986
Detailed w/o H ₂ O ₂ and HNO reactions	6158	1141	0.0066	0.2457	636.9	0.880	0.987
Detailed w/o HO ₂ , H ₂ O ₂ , HNO, NO ₂ , and N ₂ O reactions	6154	1106	0.0065	0.2435	636.3	0.872	0.986
Above w/recombination rate constants tuned	6162	1145	0.0067	0.2457	637.3	0.886	0.987
Above w/o NO reactions	6162	1145	0.0067	0.2457	637.3	0.886	0.987

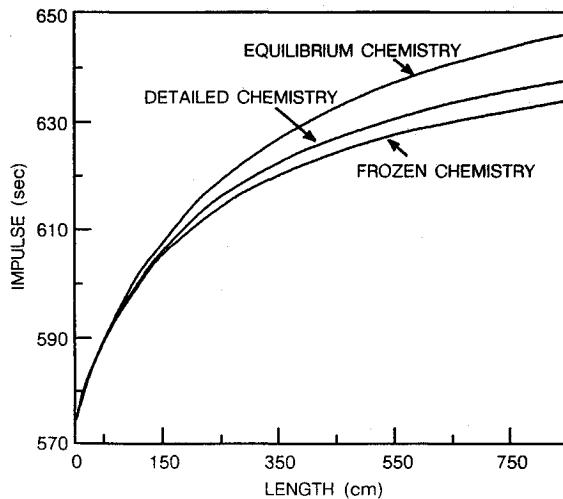
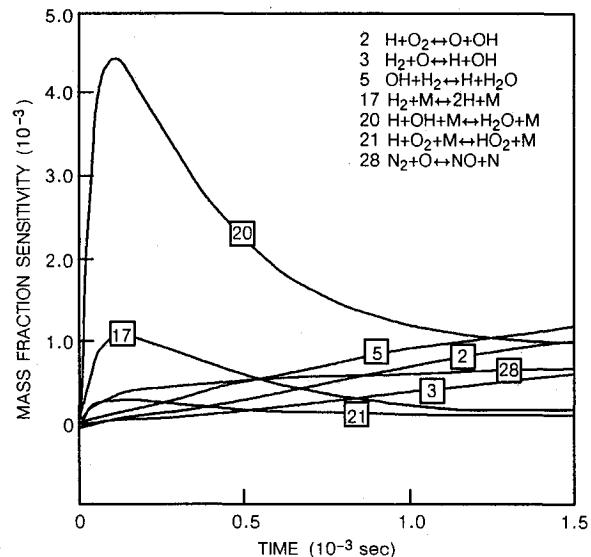
^aUnits of concentrations are in mole fractions.C_n = Ratio of actual change in impulse to change for equilibrium chemistry.C_s = Ratio of actual exit impulse for equilibrium chemistry.

Fig. 2 Effect of chemical reaction mechanism on nozzle performance.

rate chemistry cannot be neglected in nozzle performance simulations.

The results in Table 3 also show that the termolecular recombination reactions exert the greatest influence on the chemical contribution to nozzle performance as measured by the change in impulse or its ratios. These recombination reactions, in order of importance as they are listed in Table 1, are reactions 20, 17, and 21. Reaction 20, however, is by far the most important recombination path which contributes to nozzle performance. This conclusion was substantiated by a sensitivity analysis of the nozzle expansion process. The key results of this analysis are shown in Fig. 3 as the sensitivity coefficients for the production of water with respect to the rate constants for the most important reactions. Figure 3 shows conclusively that the termolecular reactions 20, 17, and 21 are the major pathways for radical recombination. This figure also shows that for the later period of the nozzle expansion process, the chain branching reactions 2 and 3, the chain propagation reaction 5, and even the main NO formation reaction 28 become important pathways for the formation of water. Presumably, the reverse of reaction 28 provides oxygen which is needed for the formation of water as well as some heat release.

With regard to the possibility of using a reduced kinetic mechanism for simulations of nozzle performance, variations to the detailed kinetic mechanism were studied. Prior to this study, reactions involving HNO in a catalytic mechanism in-

Fig. 3 Sensitivity of H₂O concentration to reaction rates during nozzle expansion process.

volving reactions 38, 40, and 49 were thought to assist radical recombination. However, the results in Table 3 show that the HNO reactions contribute very little to the radical recombination process. On the other hand, according to the results in Table 3, nitrogen reactions appear to play a more significant role in radical recombination. Table 3 shows that adding additional NO to the gas mixture serves to improve nozzle performance by increasing recombination. Apparently, the nitrogen reactions are not involved directly in the recombination of hydrogen radicals, but rather, the nitrogen reactions provide a source of oxygen from the NO_x species needed for radical recombination. This result is quite logical for these hydrogen-rich/oxygen-poor conditions, and it reinforces the importance of properly evaluating the combustor exit conditions rather than using chemical equilibrium at the combustor exit for the nozzle inlet conditions.

In the quest for a reduced kinetic mechanism one must be very careful to avoid simplifications which neglect important reaction paths. For example, Table 3 shows clearly that all simplifications to the detailed chemical kinetic mechanism which neglect reactions involving intermediate species (i.e., HO₂, H₂O₂, HNO, NO₂, and N₂O) show various reductions in nozzle performance. These erroneous simplifications effectively prevent certain species from participating in the re-

action mechanism as well as eliminating important reaction pathways. Table 3 also shows, however, that the elimination of species and reaction pathways as a result of simplifications to the chemical kinetic mechanism can be compensated for by "tuning" the termolecular recombination reactions to produce essentially the same result as the detailed kinetic mechanism. Despite this encouraging result, one should be cautious of such arbitrary simplifications to chemical kinetic modeling because this approach usually does not provide a general kinetic mechanism which is applicable to a range of conditions. Furthermore, as an indication of the crude nature of this approach, Table 3 also shows that the NO_x reactions in this reduced kinetic mechanism have no effect on nozzle chemistry.

During the course of this study an unusual characteristic of radical recombination chemistry during nozzle expansion processes became evident. In a nozzle expansion process, as temperature and pressure both decrease, the effect of decreasing temperature is to shift the chemical equilibrium toward products and away from radical species whereas the effect of decreasing pressure has the opposite effect on species equilibrium concentrations. Lowering both temperature and pressure has the additional conflicting effects on termolecular recombination rates because of the resultant effect of density on the collision rate. These characteristics of nozzle chemistry are well understood and documented in the literature. However, an unusual characteristic of nozzle chemistry was noted during this study by the results shown in Table 3 for those cases which represent an enhancement of recombination rates. These cases show that increasing radical recombination results in a higher temperature throughout the nozzle while pressure is only slightly increased. The net effect of this temperature increase is to shift the equilibrium composition away from stable products and toward radical species but, more importantly, the net rates of the termolecular recombination reactions decrease with increased temperature. Ironically, the chemistry of hydrogen radical recombination in a nozzle is a self-limiting process because of this resultant effect of increased temperature. As an indication of how much recombination chemistry is self-limited, the results in Table 3 for the equilibrium chemistry case required an artificial increase of the recombination rate constants of four orders of magnitude.

Summary

The principal results and conclusions of this study regarding the importance of chemical processes to nozzle performance are as follows:

1) Although the increase in impulse due to chemical processes in the nozzle is small compared to the contribution from acceleration of the gas, the effect of chemistry on nozzle performance is significant.

2) Finite-rate chemistry should not be neglected in nozzle performance simulations because beneficial chemical reaction processes persist throughout the entire nozzle length.

3) The termolecular reactions for hydrogen radical recombination exert the greatest influence on the chemical contribution to nozzle performance.

4) Reactions involving HNO have little effect on hydrogen radical recombination.

5) Nitrogen reactions are not involved directly in hydrogen radical recombination, but rather, they provide oxygen from the NO_x species for radical recombination.

6) For these hydrogen-rich/oxygen-poor conditions, the use of chemical equilibrium for nozzle inlet conditions may lead to errors in nozzle performance simulations.

7) The chemistry of hydrogen radical recombination in a nozzle is a self-limiting process because of the effect of temperature on equilibrium and recombination reaction rates.

8) Reduced chemical kinetic mechanisms, such as the tuned mechanism cited in this study, should be used cautiously for predicting nozzle chemistry. Inasmuch as predictions from these mechanisms may appear reasonable for limited conditions, such results are only fortuitous and there is no reason to believe that reduced chemical kinetic mechanisms will simulate all of the important reaction pathways for more general conditions.

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