RECOMBINATION AND CONDENSATION IN NOZZLES

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INTRODUCTION

Dissociated or evaporated species that do not recombine or condense to equilibrium values during expansion in the nozzle of a rocket or air-breathing engine may represent a large energy loss. Data and understanding on recombination and condensation rates are needed for prediction of jet- and rocket-engine performance. The problem is pertinent to a variety of propulsion systems, such as chemical rockets, hypersonic ramjets, jet engines with boron-type fuels, and nuclear rockets. Trends to higher operating temperatures, lower expansion pressures, and use of metals or their compounds in fuel, lead to the increasing importance of the chemical and physical processes in nozzles.

Broadly, there are three types of study that can be considered for evaluating nozzle performance.

First, there are simplified, or partial, analytical solutions. Penner(1) has described a method of estimating whether flow is near equilibrium or near frozen. The method cannot predict performance if the reaction rates are neither very fast nor very slow. Bray(2) describes a method of calculating for chemical equilibrium down the nozzle to a freezing point and for frozen composition thereafter; excellent experimental verification has come from Wegener for $2NO_2 \rightleftarrows N_2O_4$ as a diluent during expansion of nitrogen in a supersonic nozzle(3). Also, there is a question as to the applicability of reaction rate constants derived from equilibrium considerations to conditions far from equilibrium. These methods and any similar ones need to be checked against experimental performance data for several systems.

Second, the application of rate data to evaluate nozzle performance can be accomplished by solving a set of differential equations relating the flow, thermodynamics, and kinetics of the system. One difficulty in the rigorous approach is the mathematical complexity of including a number of processes. Just for example, assume that the hydrogen–air system requires consideration of four elementary reactions and seven species as follows:

$$1 \cdot H_2 + OH \rightleftarrows H_2O + H$$

$$2 \cdot H + O_2 \rightleftarrows OH + O$$

$$3 \cdot H_2 + O \rightleftarrows OH + H$$

$$4 \cdot H + H + M \rightleftarrows H_2 + M$$

Then 24 simultaneous differential equations must be programmed. However, the solution of any reasonable system appears possible if the kinetic data are known. The input data include equilibrium constants as functions of temperature and the equilibrium composition at the inlet, rate constants as functions of temperature, and the stepwise reaction mechanism. Simplifying assumptions such as treating the flow as one-dimensional and only considering those reactions which contribute substantially to the energy and neglecting minor species or assigning frozen flow or equilibrium flow to certain species can be introduced.

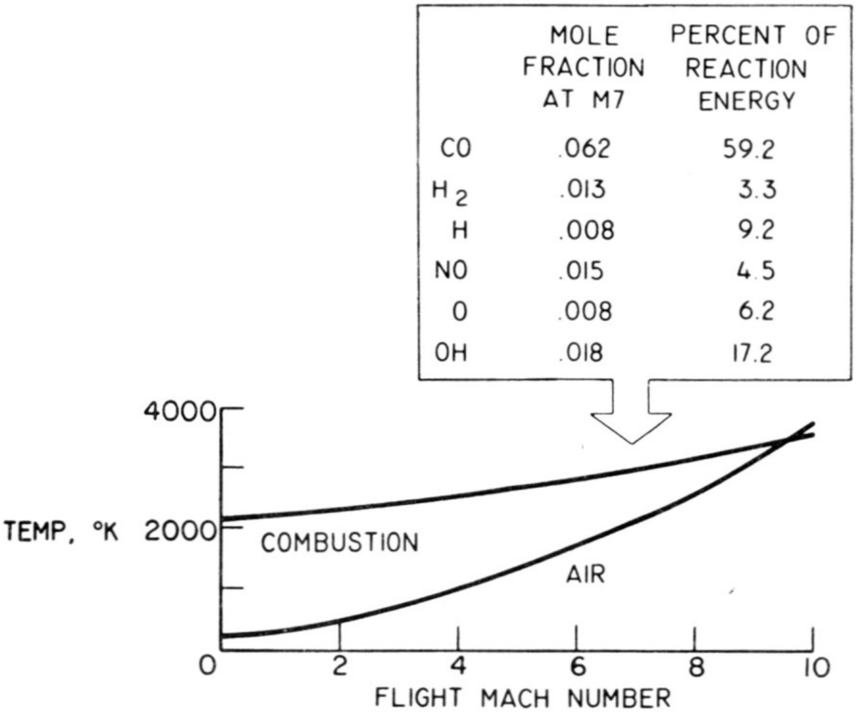
Another major difficulty is that the reactions and the reaction paths for excited states may be different from those for the usual, isolated, simplified reactions taken one at a time. In fact, Shuler(4) has pointed out that a serious perturbation of the initial, equilibrium, Maxwell-Boltzmann distribution in a reacting system may have a large influence on the ensuing rate of the reaction. For reactions with small activation energies (i.e. $E/kT < 5$), large perturbations of the initial energy distribution occur. Atomic reactions such as those occurring in the short reaction times available in nozzle qualify as $E/kT < 5$. The effect on chemical kinetics is yet unknown.

As a third method of studying recombination and condensation, direct measurements can be made of nozzle performance. Sufficient care must be given to instrumentation and technique to permit analysis of any observed losses.

This paper presents the effect of recombination on performance, some implications to design, and current data and analyses of certain systems. The examples used illustrate the several methods of predicting performance. The paper is not a complete summary of the field, but does highlight some important systems. In particular, data and analyses are presented for hydrocarbon–air, hydrogen–air, jet fuel–oxygen, hydrogen–fluorine, hydrogen, and boron hydride–air.

HYPERSONIC RAMJET

Hydrocarbon-air—Figure 1 shows the increase in total air temperature with flight Mach number for a hypersonic ramjet and the corresponding combustion temperature for stoicheiometric burning of jet fuel in this heated stream. Increasing dissociation at the higher temperatures prevents the combustion temperature from rising proportionately with the inlet air temperature, and, in fact, near Mach 10 no temperature rise at all will occur with the hydrocarbon fuel, although the fuel adds energy to the stream. The tabulation accompanying the graph at Mach 7 is for 100,000 feet and a diffuser kinetic-energy efficiency of 0.875; it shows the fraction of dissociated species and the energy distribution among them if they were to be converted to nitrogen, carbon dioxide, and gaseous water.



	MOLE FRACTION AT M7	PERCENT OF REACTION ENERGY
CO	.062	59.2
H_2	.013	3.3
H	.008	9.2
NO	.015	4.5
O	.008	6.2
OH	.018	17.2

FIG. 1. Combustion of hydrocarbon in ramjet. Stoicheiometric; $\eta_{KE}=0.875$.

Figure 2 shows the net jet thrust per pound of air that would result from expanding the combustion products of hydrocarbon and air in a ramjet operating at the pressure level provided by a diffuser kinetic-energy efficiency of 0.875 at 100,000 feet. This pressure is just over 10 atmospheres at a flight Mach number of 10 and is about 1 atmosphere at Mach 5. Two extremes of performance were calculated, equilibrium and frozen. Equilibrium performance results if all dissociated species react instantaneously to any change of state during the expansion process; frozen performance results if the products that expand have exactly the same composition as they do in the combustion chamber. Since, from

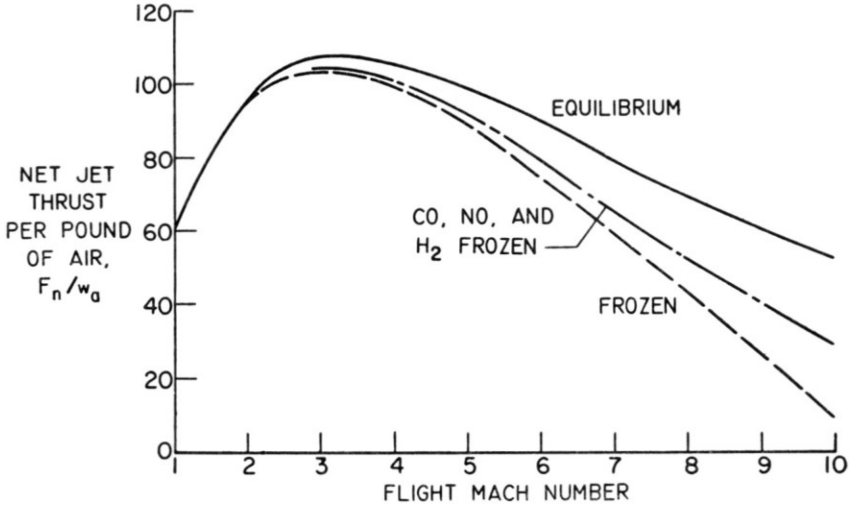


FIG. 2. Theoretical performance of hypersonic ramjet. Altitude, 100,000 ft; η_{KE}, 0.875; fuel, hydrocarbon (stoicheiometric).

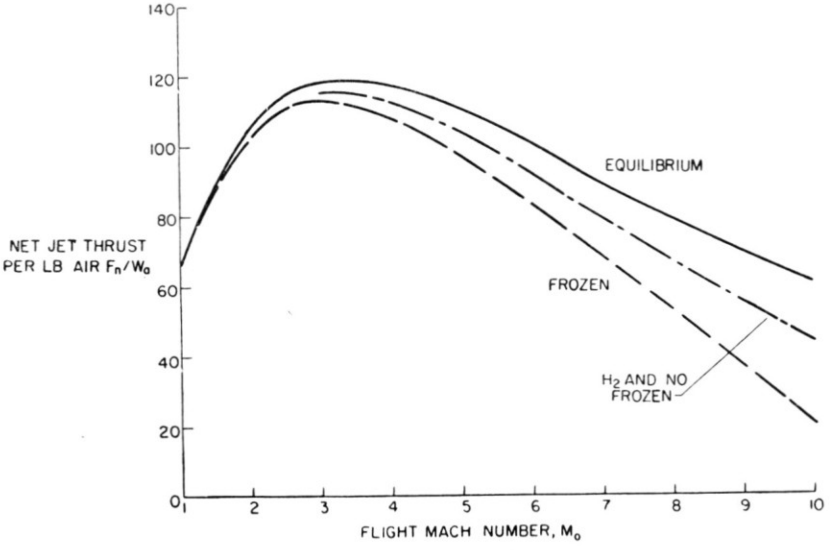


FIG. 3. Hydrogen plus air. Stoicheiometric.

Mach 7 to Mach 10, the net jet thrust for frozen flow decreases from 3/4 to 1/5 of that for equilibrium flow, it can readily be surmised that the thrust margin between the equilibrium- and frozen-expansion processes may be the difference between an operative and a nonoperative system at high flight Mach numbers. In any case, a considerable difference in fuel economy is indicated between the two extremes of flow.

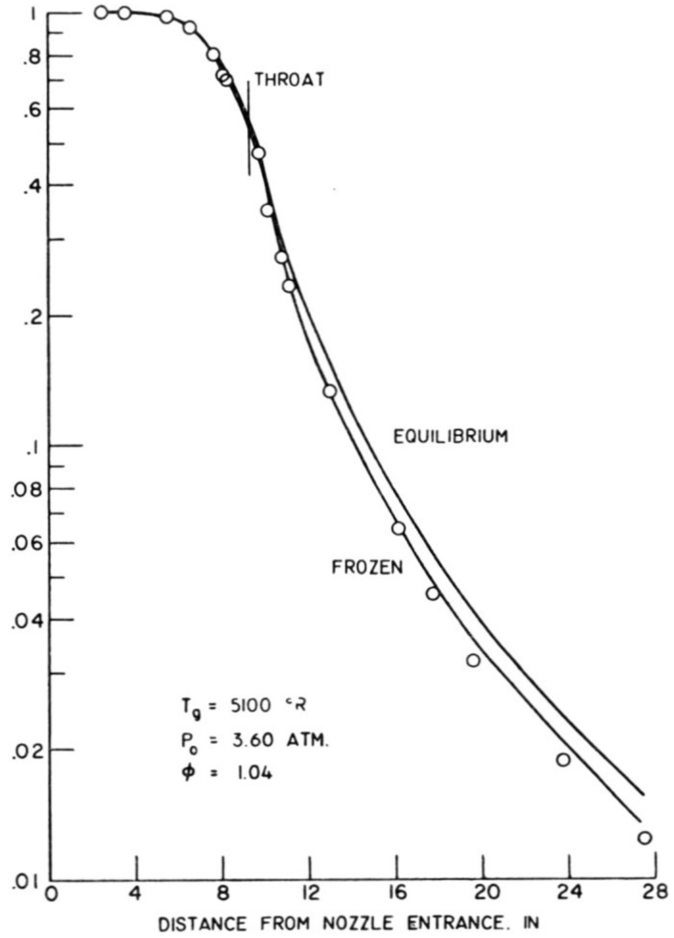


FIG. 4. Expansion of hydrogen–air combustion products.

It is impossible to describe the reaction paths and the reaction rates for these dissociated species; neither the chemistry nor the rates of the possible steps are all known in sufficient detail. An intermediate line has been shown for an assumption that carbon monoxide, nitric oxide, and hydrogen remain in their composition corresponding to combustion chamber conditions, it being assumed that atomic recombinations and disappearance of hydroxyl will be fast(5). Some experiments(6,7) have shown that these reactions may not be fast enough to equilibrate, however, and performance would then appear between the frozen and intermediate lines of Fig. 2.

Solution of one-dimensional flow equations for a system consisting of CO, O_2, CO_2, H_2O, and N_2 was performed by Reynolds and Baldwin(8)

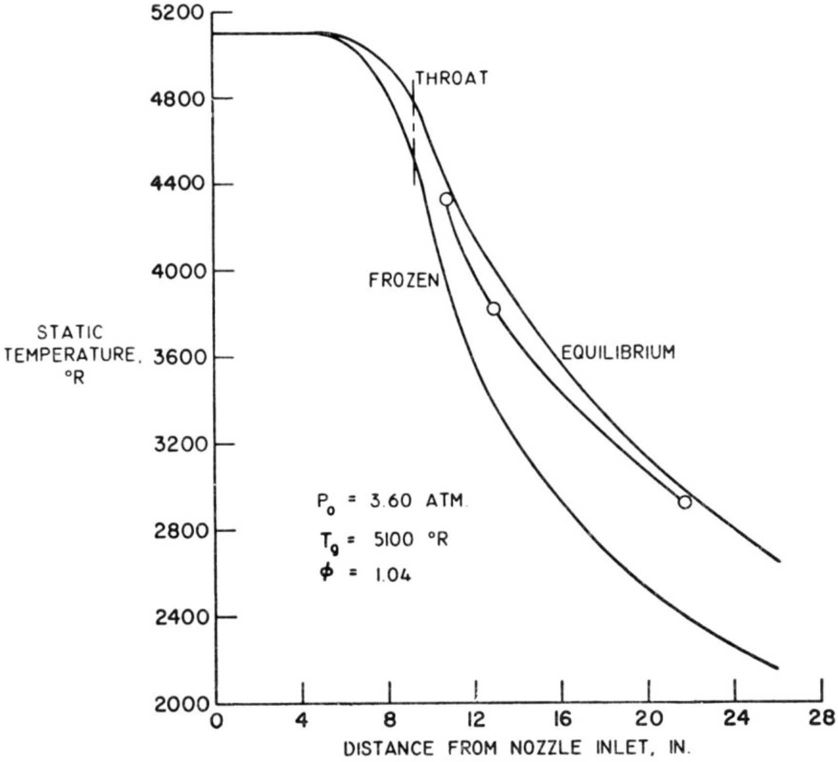


FIG. 5. Static temperature deviations from equilibrium.

with a reaction rate relation for $CO + 1/2\ O_2 \rightarrow CO_2$ from(9). Results indicate that flow is close to frozen throughout the nozzle at Mach 4; at Mach 7, only about 15 per cent of the CO has reacted, and even at Mach 10, where temperature and pressure are much higher, only about half of the CO has reacted. Even tenfold increases in nozzle length or rate constant left the process well short of equilibrium flow. Therefore, these curves provide a reasonable illustration of the magnitude of the recombination problem for a hypersonic ramjet with hydrocarbon fuel.

Hydrogen–air—Hydrogen may be used in hypersonic ramjet engines. Figure 3 shows the reduction in net jet thrust per pound of air for various flight Mach numbers if recombination fails to occur. An intermediate line assumes that atomic recombination of hydrogen–oxygen and disappearance of hydroxyl radicals are all instantaneously fast.

Experiments are under way at the NASA Lewis Center under Lezberg and Lancashire(10) to ascertain the effects of recombination reactions on nozzle performance. The work provides an example of a direct determination. Hydrogen at concentrations up to 1.26 times stoichiometric is burned in air that has been heated to 3400° R. Combustion gases are then expanded through a conical nozzle with a 3.1 inch diameter throat and a 9.5 to 1 expansion ratio. Deviations from equilibrium flow are determined from nozzle wall static pressures and from static-temperature measurements using the sodium D-line reveals method.

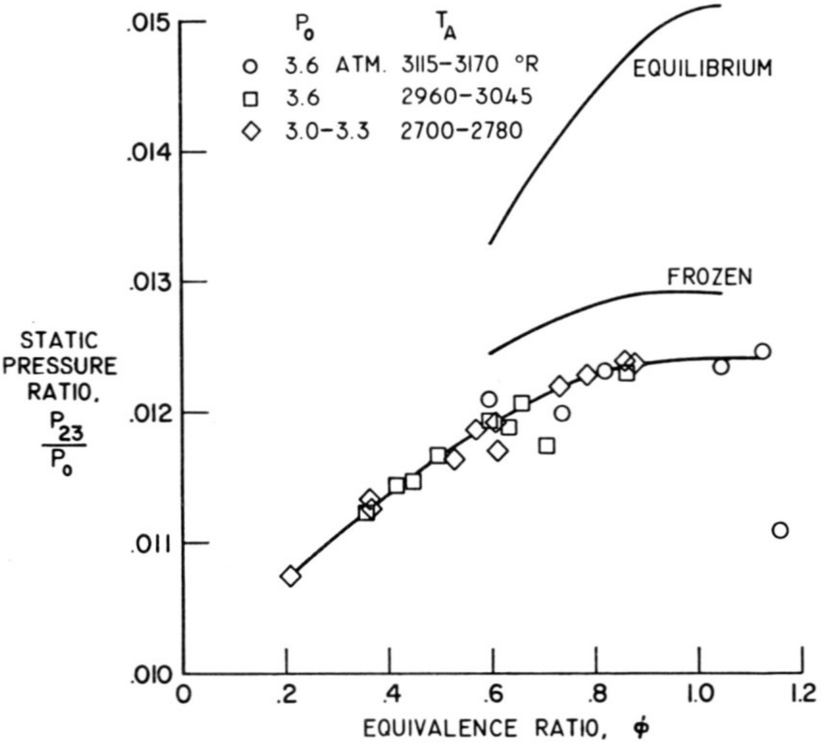


FIG. 6. Effect of equivalence ratio on nozzle exit pressure ratio.

Wall static pressures along the nozzle are plotted in Fig. 4. The calculated curves are for area ratios from cold-flow calibrations. The calibration includes three-dimensional effects and a cold boundary layer. Corrections for momentum losses to heat transfer have not been considered in the calculated area ratio–pressure ratio curves; these corrections may be expected to shift the higher area ratio end of the curves to the left. Static temperatures as observed are plotted in Fig. 5 along with the static temperatures computed for the equilibrium and frozen flow cases. There may be errors in the temperature observations; any temperature fluctuation in the sodium-colored portion of the light path such as might accompany a concentration fluctuation will be weighted almost entirely to the high side. Pressure ratios at the nozzle exit (Fig. 6) indicate frozen flow, but again, corrections for momentum losses due to heat transfer may put the experimental data somewhat above the prediction for frozen flow. Also, Browne$^{(11)}$ has used kinetic data for the disappearance of OH$^{(6)}$ to incorporate reaction rates into the isentropic flow equations for a nozzle. Results for the hydrogen–air system predict that only about 20 to 40 per cent of the enthalpy that is thermodynamically available from recombination would appear in typical nozzles.

The work so far indicates that the hydrogen–air system will perform at only slightly above the prediction for frozen flow.

LIQUID-PROPELLANT ROCKETS

General considerations—Figure 7 illustrates a typical distribution of energy for rocket combustion gases. The illustration is for stoicheiometric hydrogen and oxygen. In the chamber these are 40 atmospheres, and 3500° K; at the nozzle exist, these conditions are 1 atmosphere and 2500° K.

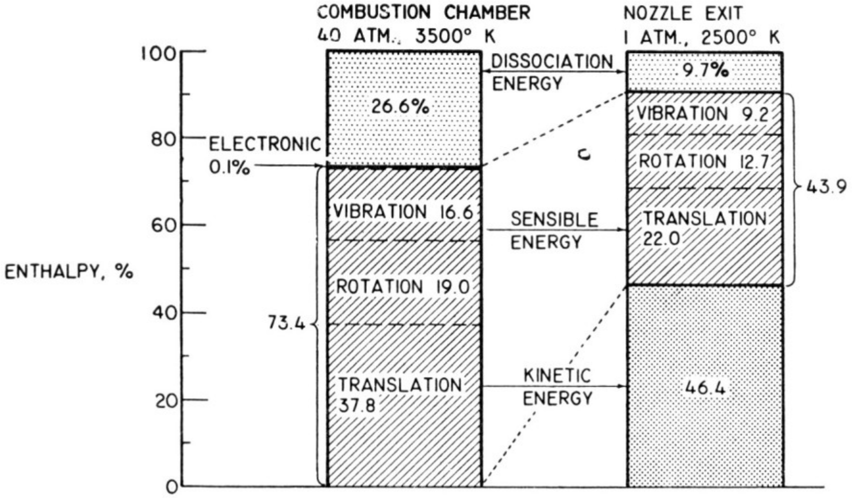


FIG. 7. Energy distribution in rocket gases.
$H_2(l)+{}^1/_2\ O_2(l) — H_2O(g) + 54{,}400$ cal/mole.

Tie-up of energy in electronic levels is generally negligible, performance continues to increase well past pressure ratios of 50 to 100 (Fig. 8)

Hydrogen–Fluorine—The extent to which equilibrium performance is approached for a propellant has a major influence on the overall design of the propulsion system. This point can be discussed from Fig. 9 for the case of the hydrogen fluorine rocket. In this example, differences between frozen and equilibrium performance are large. Furthermore, this propellant may become technologically important.

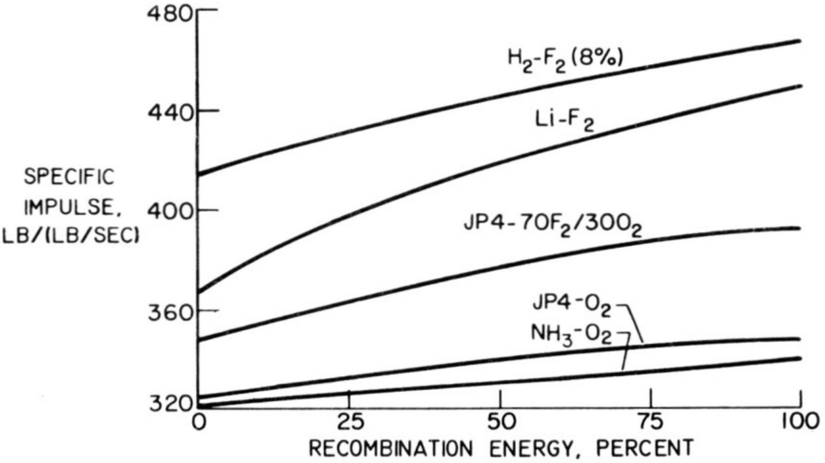


FIG. 8. Effect of recombination on specific impulse of several rocket propellants. Pressure ratio, 1000.

In the figure the specific impulse for various percentages of fuel in total propellant is plotted for three different pressure ratios for combustion at 600 lb/in^2 (13). The solid curves assume instantaneous adjustment of equilibrium in the nozzle; the dashed, frozen. The combustion gases are about $^1/_3$ dissociated at stoichiometric (i.e. at 5 per cent fuel). If, at high pressure ratios, equilibrium performance is obtained, the

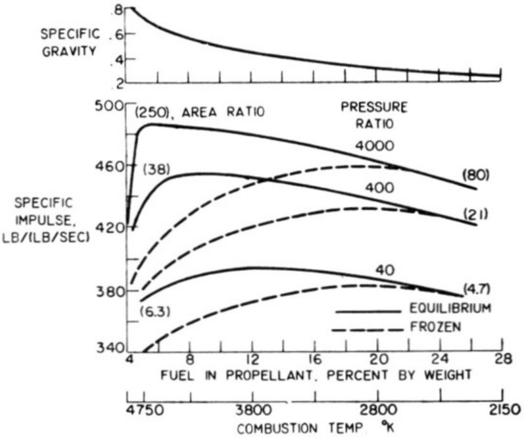


FIG. 9. Theoretical performance of H_2–F_2.

maximum specific impulse is higher than for frozen by 25 units. But more significantly, perhaps, the maximum specific impulse comes at about 6 or 7 percent fuel instead of at about 20 per cent.

Several design features that affect payload or velocity increment are favorably influenced. The density of the system has more than doubled, leading to larger propellant mass ratios in the system because of the smaller tanks and lines required. With only $^1/_3$ as much liquid hydrogen there is less of an insulation problem on the system. Also, analyses indicate that with $^1/_3$ as much liquid hydrogen the energy required for the turbopump is reduced approximately 50 per cent; the corresponding savings in propellant could go into payload or velocity increment(14).

On the other hand, combustion temperature is almost 2000°K higher near stoichiometric and there is only about $^1/_3$ as much fuel to cool with; these factors affect the coolant pressure drop and design of the cooling passages for the rocket. If equilibrium processes are followed and if lean combustion mixtures are used, larger area ratio nozzles are needed for complete expansion for a given pressure ratio than for either rich mixtures or frozen flow. Hence it is evident from an overall point of view that a reliable prediction of the extent to which the combustion products hydrogen and fluorine equilibrate in the nozzle is essential to several aspects of both engine and vehicle design.

Results of direct measurements of the performance of hydrogen-fluorine in rocket engines with large expansion ratio nozzles are not available. A prediction of performance might be made from examining the chemistry involved. Three exothermic reactions are important in the nozzle expansion; F_2 concentration is very small and so omitted.

$$\text{(a)}\ H + H + M \rightarrow H_2 + M \qquad -103\ \text{kcal/mole}$$

$$\text{(b)}\ H + F + M \rightarrow HF + M \qquad -134\ \text{kcal/mole}$$

$$\text{(c)}\ H_2 + F \rightarrow HF + H \qquad -31\ \text{kcal/mole}$$

From equilibrium concentrations in the rocket chamber(13) it is seen that (a) must be the predominant reaction in the nozzle for fuel-rich mixtures, and (b), for near stoichiometric mixtures.

Weight per cent fuel	Combustion temperature at 600 psia, °K	Mole fraction				
		F	F_2	H	H_2	HF
9.59	4090	0.011	0	0.143	0.242	0.604
5.04 (St.)	4740	0.170	0	0.119	0.026	0.685

As discussed below for the nuclear rocket, reaction (a) may be fast enough to produce near-equilibrium flow through most of the nozzle.

There are no rate data for reaction (b). According to Penner(15), reaction (b) will be too slow to equilibrate, but can go via paths that are fast enough to equilibrate. This conclusion is based on activation energies computed by Eyring(16).

Although the reactions in a hydrogen–fluorine flame are not identical with those of recombination in a nozzle, some reactions are common to both situations. It may be instructive, therefore, to consider briefly the chemical reaction rate of hydrogen and fluorine relative to other propellants. Reactivities are derived in(17) from observed flame speeds and calculated thermal conductivities. The results show hydrogen–fluorine flames to have chemical rates about two orders of magnitude greater than hydrogen–oxygen flames and several orders of magnitude greater than hydrocarbon–oxygen or hydrocarbon–air flames.

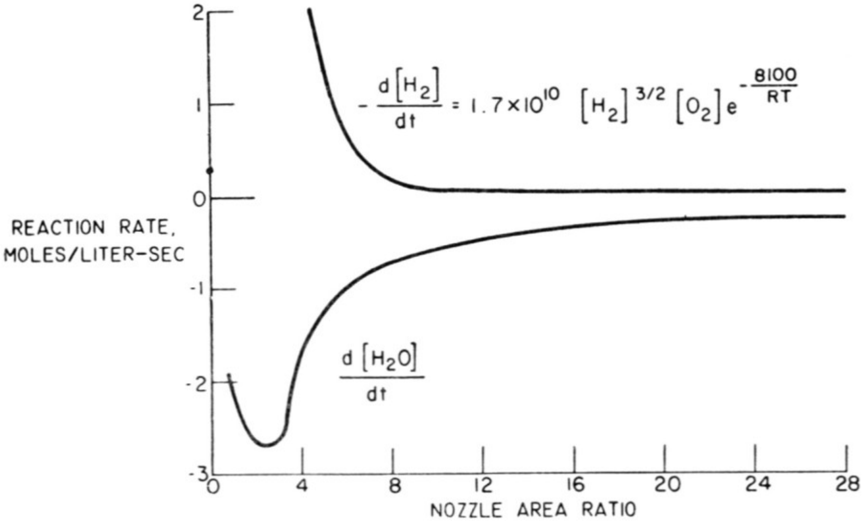


FIG. 10. Estimated recombination rate in H_2–O_2 nozzle. Stoichiometric; 300 lb/in²; 3440°K.

Thus, from admittedly inadequate evidence, it can be stated that hydrogen–fluorine will probably perform at near-equilibrium conditions, a conclusion already reached in(1).

Hydrogen–oxygen—Neither direct performance measurements with nozzles of significantly high area ratio nor rigorous calculations are available for this important system. Fine(18) has observed the disappearance of H_2 downstream of lean hydrogen–air flames, however, and therefrom deduced a rate constant and a reaction order

$$-\frac{d[H_2]}{dt} = 1.7\times 10^{10}[H_2]^{3/2}[O_2]\,e^{-\frac{81000}{RT}}, \text{ moles/sec.}$$

Whether this equation will apply to a fuel-rich hydrogen–oxygen rocket and over a wide range of pressures is a moot point. However, Fig. 10 compares a plot of this reaction rate, which can also be considered a rate of formation of water, with the rate of formation of water that corresponds to equilibrium flow along the nozzle. For the case illustrated, the stoichiometric mixture, temperature and pressure decrease from 3440° K and 300 lb/in^2 at nozzle entrance.

The relaxation times for vibrational excitation of simple species are generally one or two orders of magnitude less than the dwell time in nozzles(12). Also, the energy changes during expansion are usually modest. Vibration does not appear to cause significant losses in nozzle performance.

Rotational degrees of freedom equilibrate within a few molecular collisions for most common gases. No hold-up of energy in rotational excitation need be considered for the rocket case. Clearly the major problem is dissociation energy; equilibrium calculations predict that it should only be about 10 per cent at the nozzle exit compared to 27 per cent at the nozzle entrance.

The effect of recombination energies on performance has been tabulated for a number of rocket propellants and the results shown in Table 1. Several problems arise in identifying possible sources of energy loss in chemical rockets. Key among these are that unknown species may be formed, that thermal data are frequently missing, and, as far as rates are concerned, that neither the specific reaction paths nor the rates that go with these mechanisms are known.

The effect of recombination on specific impulse is plotted in Fig. 8 for several rocket propellants; one end of the curve assumes instantaneous adjustment of equilibria throughout the nozzle, the other end no readjustment at all, and various fractions of the recombination energy that could be available in the nozzle process are intermediate.

From Table 1 it is evident that the difference between frozen and equilibrium specific impulse for many propellants is only a few per cent. For a few high-temperature reactions the difference may be as high as 9 or 10 per cent; for example, the fluorine systems with their high combustion temperatures are in this category. The difference between frozen and equilibrium where H_2O is about one-third dissociated, to 2200° K and 1.5 lb/in^2 at an area ratio of 25 where equilibrium conditions indicate 94 per cent water. The chemical rate is always well above the rate required to maintain equilibrium, and the implication is that hydrogen–oxygen rockets should perform at near-equilibrium conditions.

Jet Fuel–Liquid oxygen—Fortini, Hendrix, and Huff(19) have measured the performance of a 1000-pound-thrust rocket engine having a nozzle

TABLE 1

Some Important Recombination Reactions

($P_c = 300$–600 psia; $P/P = 20$–40)

System	Propellants	Difference between frozen and equilibrium specific impulse, %	Recombination reactions	Approx. distribution energy among reactions, %
H, O	H_2—O_2	11–15 (depends on O/F)	$2H \rightarrow H_2$	10
H, O, N	NH_3—O_2	4	$H_2 + 1/2\ O_2 \rightarrow H_2O$	50
	$N_2H_4-O_2$	5	$OH + 1/2\ H_2 \rightarrow H_2O$	30
C, N, O	C_2N_2-Air	0		No dissociation
			$C + O \rightarrow CO$	50
	$C_2N_2-O_2$	1	$N + N \rightarrow N_2$	50
H, F	H_2-F_2	11	*Stoicheiometric*	
H, F, N	NH_2-F_2	11	$H + F \rightarrow HF$	80–85
	$N_2H_4-F_2$	9	$1/2H_2 + F \rightarrow HF$	15–20
			Fuel Rich	
			$2H \rightarrow H_2$	100
C, H, O	JP-4-O_2	7	$2H \rightarrow H_2$	5
			$OH + 1/2\ H_2 \rightarrow H_2O$	24
			$20 \rightarrow O_2$	8
			$CO + 1/2\ O_2 - CO_2$ (similar to Reynolds' results for CHON)	61
Li, F	Li-F_2	10	$Li + F \rightarrow LiF$ (no polymerization considered)	100
H, O, B	$B_5H_9-O_2$	The changes in composition can be accounted for by reactions on right, but it is questionable if they are to be considered for kinetic studies 2–3	$2H \rightarrow H_2$	43
	Fuel rich		$2BO \rightarrow B_2O_2$	29
			$3BO \rightarrow B_2O_2 + B(s)$	28
H, F, B	$B_5H_9-F_2$		$H + F \rightarrow HF$	17
			$BF + 2F \rightarrow BF_3$	60
			$2F \rightarrow F_2$	
C	NH_4ClO_4, Al	3–4	Overall reactions C	1.4–0.2
H	Hydrocarbon		involving these H	13.7–0.6
O			elements. Most O	46.6–49.6
N			important N	0–0.3
Cl			reactions are Cl	9.8–2.7
Al			Al, AlO, $Al_2O, O_2 \rightarrow$ Al	28.5–46.6
			$Al_2O_3(1)$—$Al_2O_3(s)$	

area ratio of 48 and operating at a chamber pressure of 600 pounds per square inch absolute. The rocket nozzle was fitted with a closed rocket ejector which utilized the exhaust gases as the pumping fluid. Consequently, data could be obtained at various pressure ratios. Figure 11 is a plot of these data for pressure ratios of 390, 750 and 930. The observed C* performance of this engine was about 93 per cent of the equilibrium value and 96 per cent of the frozen value. Figure 11 indicates no recovery of recombination energy. It should be pointed out, however, that the flow in the actual nozzle is neither isentropic nor axially discharged as is assumed for the ideal nozzles of the theoretical curves.

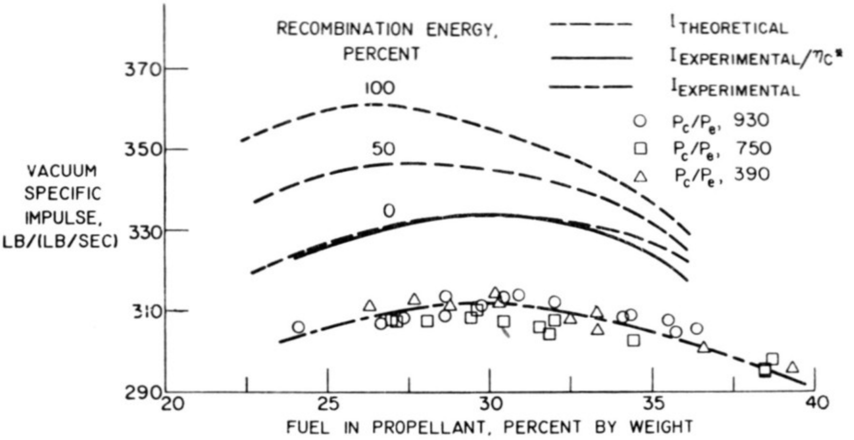


FIG. 11. Recombination in JP-4–O_2 rocket nozzle. Area ratio, 48; P_c, 600 psia.

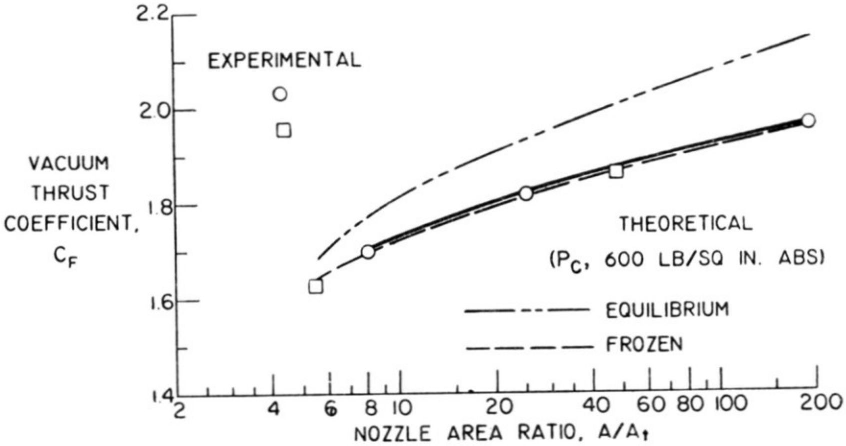


FIG. 12. Vacuum thrust coefficients for JP-4–O_2 rockets.

Another way of examining the performance of the nozzle is to compare the thrust coefficient with theoretical values. Average experimental values of C_f for several nozzles including the 48 : 1 nozzle (Fig. 11) are shown on Fig. 12 for maximum specific impulse. The data have been corrected for the pressure drop across the combustion chamber using the momentum relations. All of the measured values of C_f including those for area ratios as large as 200 are approximately equal to the value for theoretical frozen expansion. Again it should be noted that the experimental nozzles are not ideal contours. In fact, measured pressure distribution along the nozzle with an area ratio of 200 indicated that overexpansion was occurring near the nozzle throat and was followed by compression waves. These compression shocks resulted in lowered nozzle performance. Nozzles with more rounded throats performed at higher C_f values than the prediction for frozen. Thus in spite of the appearance of these particular data, the jet-fuel–liquid-oxygen rocket nozzle is expected to perform above the prediction for frozen flow, with exact values depending on nozzle design.

NUCLEAR ROCKET

The theoretical performance of heated hydrogen is presented in Fig. 13[(20)]. Several observations pertinent to design and performance of nuclear rockets are apparent from thermodynamic considerations alone. First of all, significant performance improvements from the enthalpy added by dissociation of hydrogen occur only above 2200° K for low chamber pressures, and only above 3000° K for chamber pressures greater than

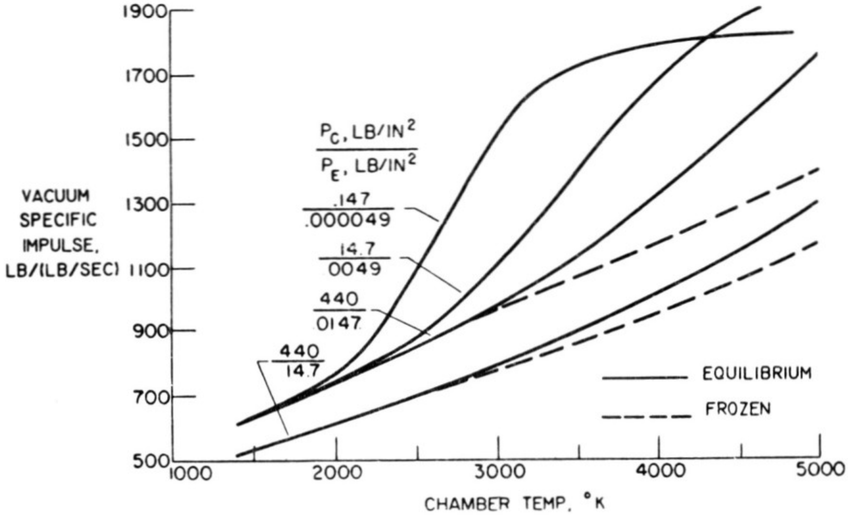


FIG. 13. Theoretical performance of heated H_2.

50 lb/in^2. Dissociation is not significant below these temperatures. Performance gains from dissociation are greater for lower chamber pressures and high expansion ratios. At very low pressures and high temperatures, however, the equilibrium state at the nozzle exit produces extensive dissociation. Hence, the energy gained by dissociation in the chamber cannot be regained in the nozzle. It follows that the highest performance will be obtained for intermediate pressures.

The question is the extent to which recombination occurs in the flow of dissociated hydrogen from a nozzle. Approximate methods, such as Penner's(1) can be used. A deficit of actual temperature from equilibrium temperature corresponding to a concentration is calculated from a combination of specific reaction constant, residence time in the nozzle, and the concentration of species. If this deficit is small (i.e. $\leqslant 20°\text{K}$), near-equilibrium flow will obtain. Also, from gas cooling rate in the nozzle, the temperature dependence of equilibrium constants, and reaction time, a temperature drop through the nozzle can be calculated. If this temperature drop is approximately 100 times the equilibrium temperature drop, then near-frozen flow will result. Table 2 lists the concentrations of hydrogen atoms needed to produce either near-equilibrium or near-frozen flow, according to(1), for two stipulated conditions and for several overall rate constants for

$$H+H+M \rightarrow H_2+M$$

Best current information on the rate constant is that it is about 10^{15} cm^6/mole^2-sec, based both on extrapolation of room-temperature data with temperature dependence like bromine atom recombination(21) and

TABLE 2

Nozzle Flow Criteria For $H+H \rightarrow H_2$(1)

(DeLaval Nozzle; cooling rate, 3×10^{7} °K/sec)

	Nozzle entrance; 3000°K, 20 atm		Nozzle exit; 2000°K, 1 atm	
Equilibrium (H) mole fraction (20)	35×10^{-2}		1.62×10^{-2}	
Mole fraction required for rate constants	For near-frozen	For near-equilibrium	For near-frozen	For near-equilibrium
10_{17} (1)	$\leqslant 0.0012 \times 10^{-3}$	$\leqslant 0.2 \times 10^{-3}$	$\leqslant 0.015 \times 10^{-3}$	37×10^{-3}
10_{16} (28)	0.012×10^{-3}	2×10^{-3}	0.15×10^{-3}	370×10^{-3}
10_{15} (7,21)	0.12×10^{-3}	20×10^{-3}	1.5×10^{-3}	$3{,}700 \times 10^{-3}$
10_{14} (22)	1.2×10^{-3}	200×10^{-3}	15×10^{-3}	$37{,}000 \times 10^{-3}$

on shock-tube data(7). The table only shows that the flow will not be frozen at the nozzle entrance and for rate constants larger than 10^{15} it will be near equilibrium; at the nozzle exit the flow will not be near equilibrium, and if the rate constant is smaller than 10^{15} it will be near frozen.

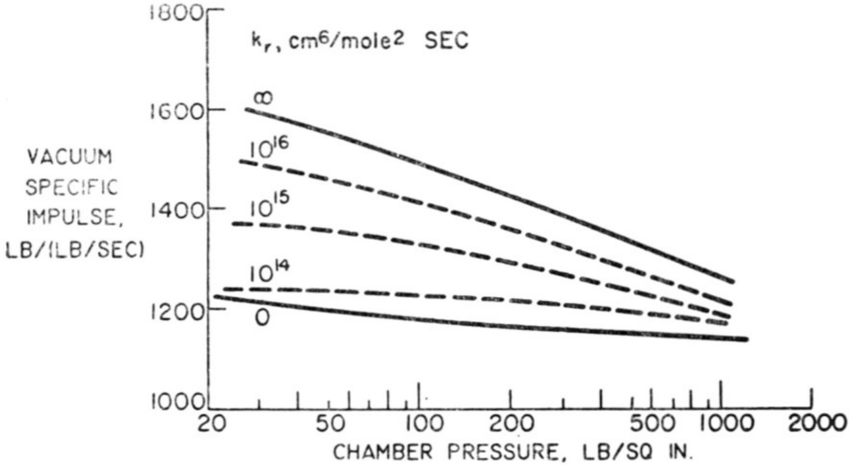


FIG. 14. Effect of specific recombination rate on hydrogen rocket performance T_c, 4000°K; nozzle throat diameter, 10 in., area ratio, 100 (from Hall *et al.*).

Detailed numerical solutions to specific finite-rate nozzle flows have been obtained by others(22,23,24). Exact numerical solutions(24) produced an approximate method of analysis which was applied to a range of pressures, temperatures, and nozzle sizes(25). An interpolation from these calculations is plotted in Fig. 14 for illustrative purposes. It develops that for hydrogen the probable recombination rate falls in the range where the effect of rate on specific impulse is the greatest; that is, at rates faster than 10^{17} cm^6/mole^2-sec, near equilibrium performance would be predicted; near frozen performance requires rates much slower than 10^{14} cm^6/mole^2-sec. Precise measurements of this rate constant at conditions corresponding to those to be encountered in nuclear rockets are required.

CONDENSATION

General—If metals or their compounds are used in fuels or propellants, condensation of certain combustion products may occur during adiabatic expansion. Heat will be released and the moles of gas will be decreased. Flow parameters for a condensible vapor under equilibrium conditions can be calculated. Losses usually result if condensibles fail to condense instantaneously throughout expansion in the nozzle. To predict the magnitude of these losses requires knowledge of the rate of condensation, or nucleation, and these rates are not generally known for the substances and conditions of concern in rockets and jet engines.

In addition, if a condensed phase is present during all or part of the expansion, losses will occur if the particle velocities lag the gas velocities during flow, or if the particles fail to reach temperature equilibrium with the expanding gas. Altman and Carter(26) have shown that, for practical purposes, both hydrodynamic and thermodynamic equilibrium in two-phase flow in typical nozzle situations require particles of 10^{-4}-cm diameter, or less.

Pentaborane–Air—Branstetter and Setze of NASA Lewis Research Center have studied the behaviour of pentaborane-air combustion products flowing through a 7-inch-long convergent-divergent nozzle. Figure 15 presents the observed air specific impulse, that is, the stream thrust per unit air flow at the nozzle throat. Below an equivalence ratio of about 0.4, or a nozzle entrance temperature of 1800° K, the data follow the expected expansion for condensed products. At equivalence ratios above 0.64, or entrance temperatures above 2150° K, the data indicate completely vaporized boron oxides. For equivalence ratios between 0.48 and 0.58, about 2100° K, fairly abrupt condensation of boron oxide was noted from wall static pressures ahead of the nozzle throat. It appears that transition from all-vapor to two-phase flow occurs at a lower temperature than the equilibrium flow model predicts. The significance to performance is that, at equivalence ratios of about 0.55, the increase in fuel flow needed to produce a 1-per cent increase in thrust must be about 4 times the requirement at equivalence ratios of about 0.4.

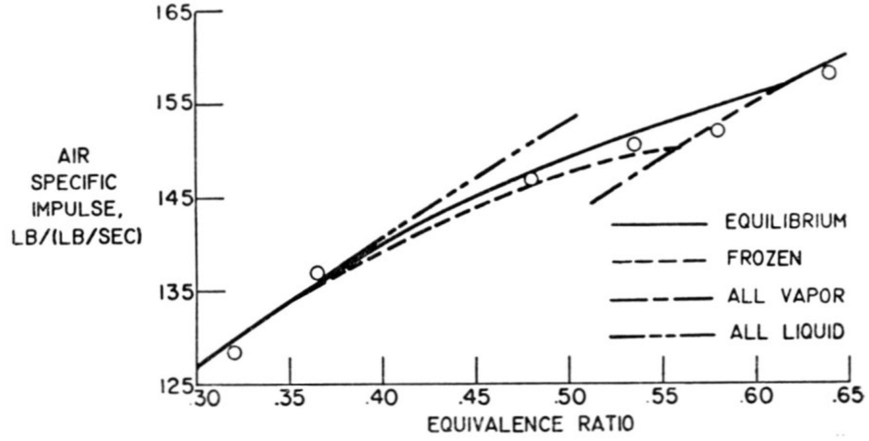


FIG. 15. Performance of pentaborane–air. Combustor pressure, 3 atm.

As far as particle size of the condensed phase is concerned, some theoretical considerations, as well as some experimental measurements of particle sizes in samples from a jet-engine-type combustor operating on pentaborane(27), show boron oxide particles to be less than 2×10^{-5} cm in diameter. This size is sufficiently small to ensure velocity and temperature equilibrium with the stream.

CONCLUDING REMARKS

Because of the inherent complexity of the mechanisms involved, there are very few systems for which recombination or condensation rates can be accurately predicted by calculations with fundamental rate equations and data. Even for such kinetically straightforward systems as heated hydrogen, hydrogen–fluorine, hydrogen–oxygen, or hydrogen–air there is a need for rate data of the temperatures and pressures that are encountered in engines. Of the examples cited herein, estimates from rate data indicate that hydrogen–fluorine and hydrogen–oxygen rockets should perform near equilibrium; jet-fuel–air engines, near frozen; and hydrogen nuclear rockets, intermediate, depending on the magnitude of the rate constant. Direct observations of nozzle performance indicate intermediate, but toward frozen, performance for jet-fuel–oxygen, hydrogen–air, and pentaborane–air.

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