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AN INVESTIGATION OF NONEQUILIBRIUM EFFECTS ON COMBUSTION IN SUPERSONIC STREAMS

A Thesis

Submitted to the Faculty

of

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NOMENCLATURE

Symbol	
E	activation energy
k	reaction rate constant
K	equilibrium constant
M	effective third body concentration
P	pressure, atmospheres
R	universal gas constant
T	temperature, ^{o}K
X	third body mole fraction
Greek Symbol	
η	species mole fraction
ϕ	equivalence ratio
τ_{ID}	ignition delay time, microseconds
τ_{R}	reaction time, microseconds

ABSTRACT

Bryce, Charles Alexander, Ph.D., Purdue University, January 1969. An Investigation of Nonequilibrium Effects on Combustion in Supersonic Streams. Major Professor: Bruce A. Reese.

The mixing and subsequent combustion of two high temperature gas streams flowing at supersonic velocities is of interest because of its application to SCRAMJET development. In most of the ground facilities employed in the development of SCRAMJET components and engines, the flowing gas stream is not in complete thermal and chemical equilibrium. Therefore, the flow does not completely simulate the actual flight conditions experienced by the SCRAMJET engine. Comprehensive theoretical and experimental research results are needed so that the performance characteristics of full-scale vehicles may be predicted from the results of model tests obtained in a nonequilibrium environment.

This research program is a theoretical and experimental investigation of the effect of nonequilibrium conditions upon the performance of combustors employing supersonic flows. Calculations and experiments are made regarding the effects on the combustion of hydrogen of the nonequilibrium species obtained experimentally using vitiated air. The objective of the program is to determine the difference in combustion performance between vitiated air and heated air under identical operating conditions.

In the experimental phase of the research, a gas generator burning nitrogen tetroxide and hydrazine plus nitrogen diluent is employed to produce the vitiated air. The vitiated air has approximately 19 percent by weight of water, replacing an equal volume of nitrogen in real air, 26 percent oxygen and 55 percent nitrogen. The stagnation temperature (2200°K) and the stagnation pressure (1000 psia) of the experimental conditions simulate a flight Mach number of $M_\infty = 6.5$ at an altitude of approximately 80,000 feet. The gas generator products expand through a converging-diverging nozzle to a supersonic combustor where heated hydrogen is introduced and supersonic burning occurs. Hydrogen is introduced into the combustor through an annulus at a velocity corresponding to sonic conditions. Injection is parallel to the mainstream gases to minimize shock interactions, thereby simplifying the analysis of both the theoretical and experimental results.

Analysis of the inlet conditions and subsequent combustion process necessitates the use of finite-rate chemistry calculations to determine (1) the composition of the entering streams and (2) the composition variation with time during ignition. A finite-rate, reacting gas program is used to determine the nonequilibrium inlet conditions to the combustor. Ignition delays are then calculated using a one-dimensional, reacting gas program which assumes constant temperature during the delay period. Results of this program are verified extensively against existing data for ignition delays in real air and hydrogen. The analysis for vitiated air at

the specific experimental conditions investigated showed the hydrogen would ignite approximately 1.5 inches downstream of the injection station. It also showed that if both streams were in chemical equilibrium prior to mixing, the ignition would take place approximately twelve inches downstream of the injector. Thus the nonequilibrium free-radical content of the incoming streams tends to accelerate the combustion process to a significant degree.

In the experimental program, the ignition lag length was determined visually from photographs of the exhaust flow. These pictures showed the hydrogen ignition took place about five inches downstream from the injection station. This length is reasonably close to that predicted by the analytical program for the case of nonequilibrium inlet conditions.

Results of this program show that the nonequilibrium free-radical content from a vitiated air source will cause early hydrogen ignition in a supersonic combustion mode. An analysis of heated air expanded from a high temperature source to test section conditions also indicates there is sufficient free-radical content in the incoming flow to cause early ignition. Therefore, neither vitiated air or heated air will simulate free-flight supersonic combustion performance in the regime where ignition delay times are rate-controlling.

INTRODUCTION

Until recently the flight regime of approximately a Mach number of five and above was considered to be the exclusive province of rocket jet propulsion (1).* Exploratory experiments, however, have demonstrated that the air-breathing ramjet engine utilizing supersonic combustion offers the potential of conducting flights in the hypersonic regime, from a Mach number of seven to above twelve at a fuel-specific impulse which is approximately five times that obtainable from a rocket engine burning liquid hydrogen and oxygen. To exploit the attractive potentialities of hypersonic flight with ramjet engine propulsion, it is essential that the technology associated with the supersonic combustion ramjet be advanced from its present status by a broad expansion of the research and development pertinent to that technology.

Research pertinent to the supersonic combustion process has been conducted for approximately ten years (2). In general, the research has been of an "exploratory" nature, and the principal effort, in several instances, has been directed to the single objective of achieving the combustion of a fuel in supersonic airstream (3, 4). Some research has been conducted to obtain an insight into the flow and fuel-air mixing problems (5). Other

---

* Number in parentheses indicate references in the Bibliography

investigators have been concerned with the theoretical analysis of the reaction kinetics of the hydrogen-air system and the correlation of the calculated results with experimental data (6).

Test facilities for investigating the supersonic combustion process normally employ ceramic heaters to heat the air prior to entering the combustion zone. These heaters are expensive to construct and operate. Another means of obtaining high temperature air for this type of testing is to use vitiated air. The term "vitiated air" as employed here really implies a synthetic mixture of gases having the same percent oxygen as real air. If vitiated air can simulate completely the combustion environment of heated air or if its effects are predictable, then a considerable amount of combustion development could be conducted very inexpensively.

This research program is a theoretical and experimental investigation of the effects of nonequilibrium conditions . . . thermal and chemical . . . upon the performance of combustors employing supersonic flows. Specifically, the effects of ionized species, free radicals, atoms, etc., upon the combustion process are determined. Calculations and experiments are made regarding the effects on the combustion of hydrogen of the nonequilibrium species obtained experimentally using vitiated air. The objective of the program is to determine the difference between the combustor performance with vitiated air and that which would occur if the combustor were operated at the same flowrate, stagnation temperature and pressure with heated air.

Scope of Present Investigation

In the supersonic burning of hydrogen there is a finite distance required for mixing and subsequent combustion of the two gas streams. If the combustor is operated at a high static temperature ($T > 1200^{\circ}K$) the reaction times for combustion are sufficiently fast that mixing becomes the rate controlling factor in determining the duct length.(2). At low static temperatures, corresponding to low flight Mach numbers, reaction times are slow and the reaction rate determines the duct length. The present investigation is in the latter regime where reaction times are significantly longer than mixing times. Therefore, the primary emphasis is on defining the effect of vitiated air on the ignition delay characteristics with supersonic combustion. In the experimental phase of the research, a gas generator burning nitrogen tetroxide and hydrazine plus nitrogen diluent is employed to produce the vitiated air. The vitiated air has approximately 19 percent by weight water, replacing a corresponding volume of nitrogen in real air, 26 percent oxygen and 55 percent nitrogen. The stagnation temperature ($2200^{\circ}K$) and the stagnation pressure (1000 psia) of the experimental conditions simulate a flight Mach number of $M_{\infty} = 6.5$ at an altitude of approximately 80,000 feet. The gas generator products expand through a converging-diverging nozzle to a supersonic combustor where heated hydrogen is introduced and supersonic burning occurs. Hydrogen is introduced into the combustor through an annulus surrounding the air

stream at a velocity corresponding to sonic conditions. Injection is parallel to the mainstream gases to minimize shock interactions, thereby simplifying the analysis of both the theoretical and experimental results.

The purpose of the program is to investigate both analytically and experimentally the effects of vitiated air upon the performance of a combustor employing supersonic flows. Analysis of the inlet conditions and subsequent combustion process necessitates the use of finite-rate chemistry calculations to determine (1) the composition of the entering streams and (2) the composition variation with time during the ignition and combustion process. A comparison of the analysis and experiments with vitiated air against analytical results for real air is used to illustrate the degree of simulation that can be achieved.

This program represents the initial phase of a much broader investigation of the effects of vitiated air on supersonic combustor performance. An additional analytical and experimental program is now under way to examine the effect of vitiated air on overall combustion efficiency as influenced by the mixing and heat release within the combustor. The follow-on effort will employ the hardware and instrumentation developed in this phase of the program to perform a series of sophisticated experiments to determine the distribution of temperature, pressure, and gas composition at the exit plane of the supersonic combustor.

Review of Pertinent Literature

The majority of the literature published concerning supersonic combustion has been classified for security purposes. The classified literature has been reviewed, but only the unclassified reports will be considered herein. Of the unclassified information available, the author was unable to find any reports which dealt specifically with the effect of vitiation on supersonic combustion. However, there are several articles concerning ignition delay in supersonic flows for hydrogen and real air. The unclassified articles considered most significant for comparison with the results of present programs are discussed in the following paragraphs.

Ferri (Ref. 2)

This is a review paper which summarizes primarily the work conducted by the General Applied Science Laboratories on supersonic burning prior to 1964. In examining ignition delay, GASL developed a computer program to solve the conservation equations for a reacting flow system. Species considered in this program were H, H_2, O, O_2, OH, H_2O and M, where M represents a third body. The assumption is made that the forward and backward rate constants are related by the equilibrium constant. Eight reactions, four bimolecular and four recombination (third body), were considered pertinent to hydrogen-air combustion. Starting conditions required for the analysis included the initial chemical composition of the

mixture and static temperature, pressure and velocity. To simplify the analysis the static pressure was assumed constant throughout the combustion process although the program was capable of handling a prescribed variation in static pressure.

Results of the analysis showed the bimolecular reactions dominate the ignition delay region and that these reactions take place at essentially constant temperature. In the ignition delay region free radicals increase to their peak concentrations. Ferri defines the ignition delay period as the time required to reach peak concentration for the hydrogen radical. During the latter portion of the induction period the free radicals begin to disappear. The heat release associated with the disappearance of the free radicals produces a rapid temperature rise to the final combustion temperature. The latter period is designated the reaction time.

From the analysis and a correlation of data from references 7 and 8, Ferri suggests the following simplified expression for calculating the ignition delay time. *

$$\tau_{ID} = \frac{8 \times 10^{-3}}{P} e^{9600/T}$$

Based on the results of the numerical analysis, the following empirical expression was formed to define the reaction time.

---

* The symbols are defined in the Nomenclature.

$$\tau_R = \frac{e^{-1.12T/1000}}{P^{1.7}}$$

One may observe from the above equation that the total reaction time is inversely proportional to temperature and pressure with temperature having the more significant effect. Thus, with high initial static temperatures ($T > 1200^{\circ}K$), reaction times are almost negligible and mixing becomes the rate controlling mechanism in supersonic combustion. But in the low temperature regime ($T < 1100^{\circ}K$) the overall reaction time is rate controlling and the mixing times can be neglected.

Nicholls, Adamson, and Morrison (Ref. 9)

Previous experiments by the first author showed a distinct separation between the flame front and shock front for standing detonation waves with hydrogen-air mixtures. The distance between the flame front and shock front is said to represent the ignition lag length. In the referenced article the authors developed a simplified relation for the time delay based on solving the differential equations for the kinetics (assuming the hydrodynamic variables constant).

Nine reactions, five bimolecular and four third body, are considered pertinent to the delay zone and these only proceed in the forward direction. Species considered were H, H_2, O, O_2, OH, H_2O, and M. The rate equations were written and terms

were eliminated which were considered sufficiently small. This resulted in three linear equations written in terms of O, OH, and H and these equations could be solved explicitly after the introduction of a linear transformation. The solutions were expressions which described the free radical concentrations as a function of time. Selecting as their criteria for ignition delay the inflection point in the atomic hydrogen versus time curve, the following expression was obtained for the induction period.

$$\tau_{ID} = \frac{RT}{2\,\eta_{O_2} PA_6}\, e^{E_{6/RT}} \ln\left[\frac{\eta_{O_2}^2 \cdot k_6}{\eta_{H_2} k_2 + \eta_{H_2} \eta_{O_2} k_5}\right]$$

where: $k_6 = \frac{PA_6}{RT}\, e^{-E_{6/RT}}$ is the forward reaction rate equation of the rate controlling reaction ($O_2 + H \xrightarrow{k_6} OH + O$). The authors conclusions regarding the ignition delay time for this system are:

(1) τ decreases with increasing pressure and increasing temperature because of the exponential term.

(2) τ is primarily dependent on reaction (6), a chain branching reaction usually consider controlling in the $H_2 - O_2$ system.

(3) τ decreases slightly with initial oxygen content, the log term being small.

(4) τ is weakly dependent on the initial H_2 concentration.

Brokaw (Ref. 10)

In this article, the differential equations governing the rate of change of free-radical concentration during the induction period were solved explicitly assuming constant temperature and negligible depletion of reactants. The reactions considered were as follows:

$$OH + H_2 \xrightarrow{k_1} H_2O + H$$

$$H + O_2 \xrightarrow{k_2} OH + O$$

$$O + H_2 \xrightarrow{k_3} OH + H$$

$$H + O_2 + M \xrightarrow{k_6} HO_2 + M$$

$$HO_2 + H_2 \xrightarrow{k_{11}} H_2O_2 + H$$

The first three are the standard bimolecular reactions considered with the H_2 - O_2 system while the latter two were felt to be significant at low temperatures. Employing only the forward reaction rates and eliminating the initiation rates, Brokaw solved, simultaneously, the equations for the growth of free radicals with time.

Three types of solutions were obtained and these tended to correspond qualitatively to the three explosion limits of the H_2 - O_2 system. The region of short ignition delays is of interest for application to supersonic combustion. Here Brokaw obtained an approximate analytical solution for the ignition delay in hydrogen-air flow systems. This solution assumes the induction period ends when the concentration of the OH radical reaches 10^{-6} moles/liter (suggested in Reference 11). The results of this

method are shown to compare favorably with the more sophisticated numerical methods of Momtchiloff, et al. (7) and Belles and Lauver (12).

Brokaw indicated the importance of considering the HO_2 species for finding ignition delays at low temperatures. The three bimolecular reactions produce free radicals while the third-body reactions inhibit the build up of atomic hydrogen. This effect results in an increase in ignition delay period over that predicted by neglecting the latter two reactions. Of particular significance to applications with vitiated air and hydrogen combustion is the fact that water vapor is an effective third body. This is illustrated by the reaction rate expression given for k_6.

$$k_6 = 3.27 \times 10^{15} \left(X_{H_2} + 0.35X_{O_2} + 0.43X_{N_2} + 0.2X_{AR} + 14.3X_{H_2O} + \ldots\right) T^{-1.92} \frac{(\text{liters})^2}{(\text{mole})^2 \text{ sec}}$$

where: X represents the mole fraction of the various third bodies. Since water vapor is an effective third body and tends to promote reaction 6, the overall effect should be to increase the ignition delay for hydrogen burning in vitiated air as compared to hydrogen burning in real air.

Momtchiloff, Taback, and Buswell (Ref. 7)

This article describes the development of a computer program for calculating ignition delays in hypersonic ramjets. The

program combines the reaction rate equations with the one-dimensional gas dynamics equations to form a series of simultaneous non-linear differential equations. Numerical methods were employed to obtain solutions for hydrogen-air flowing in an adiabatic, frictionless duct.

Starting conditions for the analysis were: (a) each stream is defined by its equilibrium composition at the local static temperature and pressure, and (b) instantaneous mixing is assumed to occur at the duct entrance. The assumption of instantaneous mixing is justified by their results which show that equivalance ratio has a very small effect on ignition delay in the range, $0.25 < \phi < 2.5$. A total of ten reactions are included in their program, six bimolecular and four third body. Species considered are O, O_2, H, H_2, OH, H_2O, N, N_2 and NO. This was the first attempt to include the effect of nitrogen reactions on the combustion process. However, their conclusion was that the nitrogen reactions are relatively unimportant at reactant temperature below $4000^{\circ}R$.

Several ignition criteria were examined by Momchiloff, et. al., to show their effect on the theoretical delay time. The criteria considered were: (1) time for OH radical to reach 10^{-6} moles/liter, (2) time at the intersection of the slopes for the initial and maximum temperature rise, (3) time for the temperature to reach 5% above the initial temperature, and (4) when the slope of the temperature versus time curve reaches 10^{6} degrees

R/second. Results of this comparison showed the relative magnitudes of the delay times for different ignition criteria were within a factor of two over a wide range of initial temperatures. The first criterion for hydroxyl concentration was somewhat arbitrarily selected for defining the ignition period.

In order to substantiate their analytical technique, a comparison was made with experimental delay time data. This comparison is shown as Figure 1. The authors rationalize that the large difference shown for Das Gupta's (13) data is partly due to mixing time being included in the delay period and they also question the experimental accuracy of Nicholls' (8) data. In general, the comparison tends to substantiate the validity of the analytical procedure. As a final comment, the authors note that by a simple adjustment to the initial concentrations, one could predict the effect of simulated air on ignition delay.

Rhodes (Ref. 17)

This is the first author to suggest that nonequilibrium, free-radical concentration may have a significant effect on ignition delay with supersonic combustion. Examining the four bimolecular reactions which govern the rate of growth of free-radicals, the author shows the ignition delay was primarily controlled by the reaction rate for:

$$O_2 + H \rightarrow OH + O$$

After several simplications, an expression was derived for the

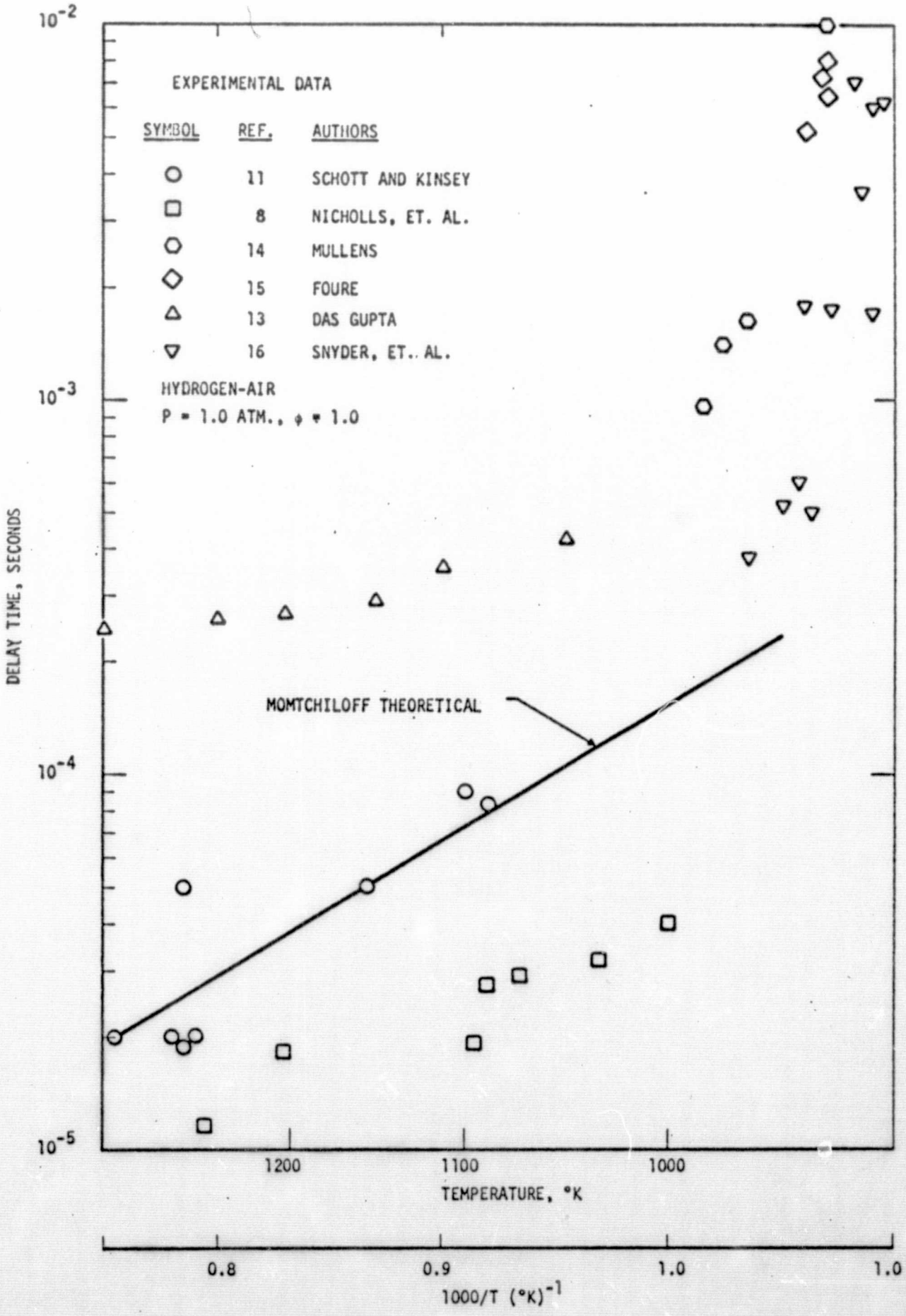


FIGURE 1 MOMTCHILOFF'S ANALYSIS COMPARED WITH EXPERIMENTAL RESULTS

initial rate of reaction in terms of the rate controlling reaction and the free-radical concentration. Rhodes then correlates the delay time (from the complete kinetics program of GASL) against the initial rate of reaction expression and found it conveniently plotted as a straight line on log-log coordinates. From this plot, the following expression was obtained for the ignition delay in terms of the initial free radical concentration:

$$\tau_{ID} = \frac{1.27 \times 10^{-3}}{P^{4/3}} \left[\frac{T}{X_{O_2}{}_o \; X_{FR}{}_o} \right]^{1/3} e^{3020/T}$$

where: $$[X_{FR}]_o = [X_H]_o + [X_{OH}]_o + 2[X_O]_o$$

From the above expression it may be noted that an order of magnitude increase in free-radical content for the incoming stream will reduce the delay time by a factor of two. There are two conditions in this equation which are somewhat inconsistent with other ignition lag correlations; one is the pressure dependence to the four-thirds power and the other is the rather significant effect of initial oxygen content. Since the author claims this method will only predict times within a factor of two, these anomalies are not sufficient to invalidate the overall correlation.

The most significant conclusion that can be drawn from this article is that nonequilibrium, free-radical species can affect induction time in supersonic combustion. In ground test facilities

heated air is expanded from a high temperature to a supersonic test section where hydrogen is added and combustion takes place. During the expansion process some recombination freezing will occur and the excess free radicals in the incoming air will cause ignition to take place sooner than expected. The same effect will be seen in ground testing with vitiated or synthetic air as the primary fluid. However, a free-flight system may incur an increased ignition delay because the free-radical concentrations produced by the inlet compression may be less than the corresponding equilibrium values.

Snyder, Robertson, Zanders, and Skinner (Ref. 16)

This report contains the results of an extensive experimental investigation of ignition delay for hydrogen-air mixtures. The work was conducted using shock tube techniques. Induction times were found by taking the difference between the time to peak pressure for the reflected shock and the time of sharp rise in ultraviolet emission at a specific axial location. Experimental conditions were varied over the following ranges: equivalence ratio ($0.5 \leq \phi \leq 1.0$), test section pressure ($1.5 \leq P \leq 130$ psia), and temperature ($800 < T < 1100^{\circ}K$). The effect of several contaminants on the induction characteristic of hydrogen-air were also studied. Additives investigated experimentally included water vapor, nitric oxide, nitrogen dioxide and ammonia.

Experimental results for the undiluted mixtures were utilized as an input to a nonlinear regression program and the following

equation is presented as a best fit to the data.

$$\tau_{ID} = \frac{7.92 \times 10^{-5} e^{15.950/T}}{(P)^{0.4}_{\phi}}$$

Limits for application of this expression are fuel concentrations less than stoichiometric and temperatures between 800 and 1100°K.

Some interesting results were obtained from the experiments investigating the effect of contaminants on the ignition reaction. Water vapor, nitric oxide, and nitrogen dioxide were found to reduce the ignition delay, while ammonia had essentially no effect. Water vapor was added in concentrations of 10, 15, and 20 mole percent in experiments at equivalence ratios of 0.5 and 1.0. At the lower equivalence ratio, the induction time was reduced by almost an order of magnitude. A plot of the experimental data illustrating the reduction in delay time with 15 mole percent water vapor is shown as Figure 2, which presents delay time as a function temperature. A similar effect was shown at higher temperature ($\sim$ 1000°K) for the equivalence ratio of 1.0 experiments but a slight inhibiting effect was found in the low temperature region.

Results from the nitric oxide experiments (also shown on Figure 2) were much more dramatic. The addition of only 0.5 mole percent NO resulted in a reduction in induction time of approximately two orders of magnitude. Nitrogen dioxide exhibited essentially the same magnitude reduction. Several different concentrations

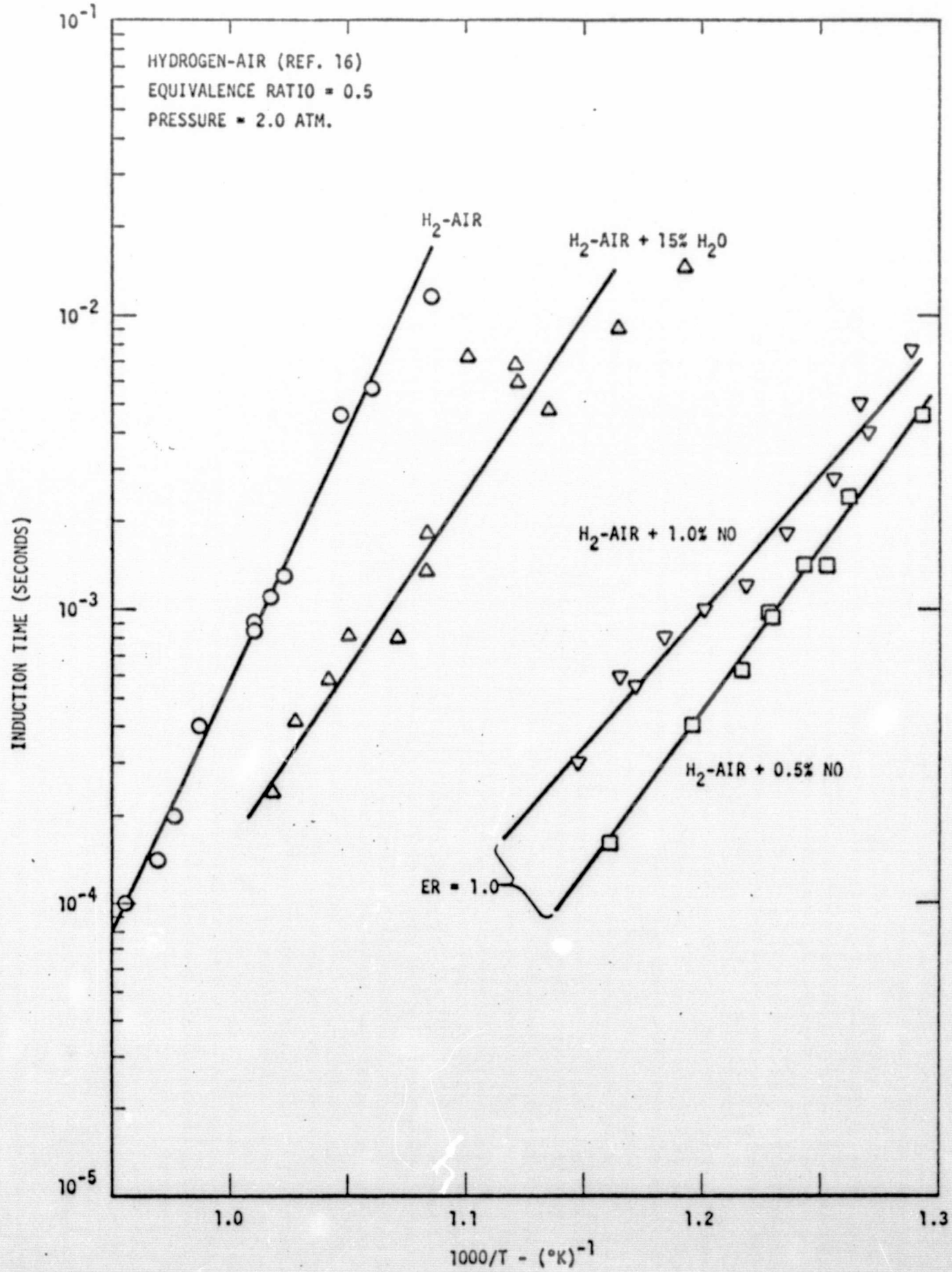


FIGURE 2 EFFECT OF CONTAMINANTS ON INDUCTION TIMES

were examined in the nitric oxide experiments ranging from 0.1 to 8.0 mole percent. Significant reductions (at least one order of magnitude) were found in each case with the peak reduction occurring in the neighborhood of 0.5 mole percent. This indicates that nitric oxide catalyzes the hydrogen-air reaction. Ground test facilities using heated air or synthetic air can have an appreciable quantity of NO entering the supersonic test section. Therefore induction times for ground testing may be considerably shorter than that experienced under the corresponding free-flight conditions.

ANALYTICAL PROGRAM

Most of the theoretical and experimental work concerning the combustion of hydrogen and air is based on the assumption that complete thermal and chemical equilibrium exists at the combustor inlet. In the shock tube work of Schott and Kinsey (11) and the standing detonation wave work of Nichols (8), the combined streams are assumed in equilibrium immediately downstream of the shock front. With this type of experiments, the assumption of equilibrium starting conditions may be justified on the basis that the agreement between analysis and experiments is reasonably good.

For certain cases of shock induced combustion, Rubins (18) has shown the possible existence of deviations from thermal equilibrium. In these cases, the different modes of energy storage are not in equilibrium, resulting in a translational temperature overshoot. By accounting for the overshoot in the reaction rate expression, they are still able to predict ignition delays for shock-induced combustion of hydrogen-air using the assumption of chemical equilibrium as a starting condition for finite-rate calculation. Therefore, most ignition delay data for hydrogen-air can be described theoretically by assuming (1) that the premixed gases are in chemical equilibrium just prior to ignition or (2) that each stream exists at its corresponding equilibrium state prior to mixing. The latter assumption applies to combustion without shocks where the two gases are initially

mixed at the combustor entrance.

An ideal supersonic combustion (ISSC) program was employed to determine the operating conditions of the gas generator and to size the gas generator, test section, and combustor exit. This program combines the one-dimensional gas dynamic equations with the equilibrium thermochemical relations to: (1) determine the products of combustion in the gas generator, (2) isentropically expand the products (shifting equilibrium) to the test section entrance, (3) calculate the properties of hydrogen at the injection station, and (4) calculate the results of mixing and burning the two streams at constant pressure.

A finite rate reacting gas (FRRG) program was used to determine the nonequilibrium free-radical concentrations in the vitiated air as it enters the combustor. This program integrates the one-dimensional gas dynamic relations for a chemically reacting flow system throughout the expansion process. Reaction rates used with the FRRG program were identical to those used in the ignition lag program (discussed below) for situations where the same reactions were found to be applicable.

Induction times were determined by a simplified ignition lag (SIL) program. This program solves the species reaction rate relations, assuming constant pressure and temperature, using a matrix technique. The validity of this program is established by a comparison of the program results against existing experimental induction data for heated air. This comparison requires that the SIL

program be run with initial species concentration data from the ISSC program because of the nature of the experimental results.

There is an abundance of reaction rate data for the hydrogen-oxygen system. A fairly up-to-date source of reaction rate information is provided in a study conducted by TRW (Ref. 19). This study attempts to identify the significant reactions which affect the kinetic performance of typical liquid propellant systems. After identification of important reactions, a summary was made of existing rate date and the degree of uncertainty was established. In general, the bimolecular reaction rates seemed reasonable, and, the third-body reaction rates do not include an activation energy term. This omission would not significantly affect rocket performance predictions based on kinetics calculations; however, it could make some difference in the species concentration determinations when attempting to establish the free-radical content. After initially beginning the analysis utilizing the TRW reaction rates, it was decided to change to a more consistent set of rate expressions. The rates selected for the final analysis were supplied by E. A. Lezberg of NASA Lewis Research Center. The general agreement of these rates with those employed by other authors (Refs. 2, 7, and 19) is considered acceptable, since uncertainties of at least one order of magnitude are quite common with reaction rate data.

Description of Computer Programs

The computer programs used in the analytical effort are discussed in the following paragraphs. The discussion includes (1)

basic assumptions, (2) program description, (3) input requirements, (4) output results, and (5) limitations.

Ideal Supersonic Combustion (ISSC) Program

Ideal performance calculations are useful, in many instances, for determining the maximum theoretical performance that can be derived for different propellant combinations. This program performs the basic thermochemical calculations necessary to design the gas generator assembly as well as the supersonic combustion test section. When making thermochemical calculations assuming shifting equilibrium conditions the following assumptions are made:

(1) Chemical equilibrium is maintained both in the combustor and during the expansion process.

(2) The combustion products behave as an ideal gas mixture.

(3) The expansion processes are adiabatic and reversible (isentropic).

(4) The reactants burn to completion at a specified pressure.

(5) Supersonic combustion takes place adiabatically and at constant pressure.

The program combines the one-dimensional conservation equations for an ideal gas with the equilibrium thermochemical relations to compute the combustion and expansion processes. Specifically, the program first computes conditions in the primary combustor and then expands these gases (shifting equilibrium) to various area ratios which may be chosen as inputs to the program. The secondary stream

is heated hydrogen with a temperature which corresponds to the input enthalpy of the reactants. Equilibrium dissociation is maintained as this stream is expanded to a pressure corresponding to that at which mixing takes place. Then both streams are mixed and burned at constant pressure. The latter step represents the supersonic combustion process. Provision is made for additional isentropic expansions and for calculation of the equilibrium stagnation pressure and temperature of the combined stream.

In the calculations for the production of vitiated air for these experiments, the required flow rates of nitrogen tetroxide, hydrazine, and nitrogen are a function of the desired chamber temperature. The flows are proportioned such that the vitiated air has the same volume percent oxygen as real air. Calculations of the flow rate requirements for setting the operational conditions of experimental hardware were made utilizing the equilibrium themochemical program. Typical results are shown on Figure 3 which presents gas generator operating conditions as a function of chamber temperature. The final selection of a design operating condition is discussed in the section titled Experimental Program.

The ISSC program can also be operated with the characteristics of heated air serving as input to the program as the primary gas stream. It is then possible to compare the ideal supersonic combustion performance of vitiated air and heated air. The equilibrium species concentrations for the test section entrance as

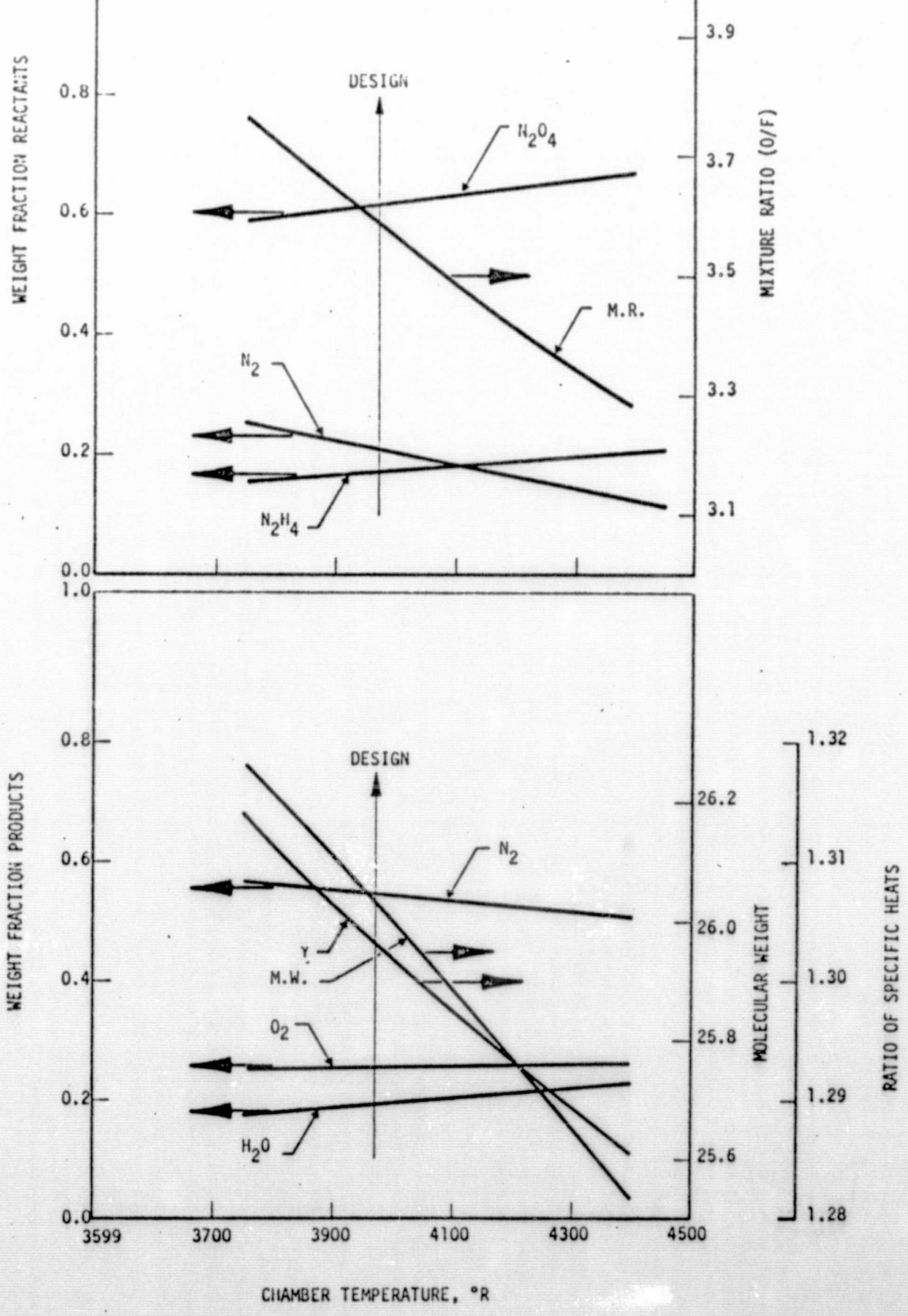


FIGURE 3 GAS GENERATOR OPERATING CONDITIONS

determined by this program are used as input to the ignition lag program. It is thus possible to determine ignition lag for equilibrium inlet conditions for comparison with the nonequilibrium conditions generated by the following computer program.

Finite Rate Reacting Gas (FRRG) Program

This computer program was developed by TRW Systems for NASA (MSC) under Contract NAS-4358. Inputs to the program included reaction rate information, nozzle geometry, propellant data (i.e., moles of fuel and oxidizer plus their heats of formation). The program solves the equations for inviscid, one-dimensional flow of a reacting gas mixture. The following assumptions are made when deriving the conservation equations:

(1) The expansion process is adiabatic.

(2) All species behave as ideal gases.

(3) Viscous effects are neglected.

(4) All internal modes of energy storage are in equilibrium.

The reaction rate parameters employed in the FRRG program are listed in Table 1. Only the constants for the forward rate expression are used as input to the program. The reverse reaction rates are computed internally from the forward rate and equilibrium constant (based on molar concentrations) by the following relation:

$$k_b(j) = k_f(j) / K_c(j)$$

There is some question as to the applications of this relation to three-body reactions, but it is known to be a good assumption for

TABLE 1

REACTION RATES FOR FRRG PROGRAM

J	Reaction	A(J), gr. cm. units	B(J), kcal/mole	N(J)
1	$H_2O + M \rightleftharpoons OH + H + M$	1.9×10^{18}	119.9	-1.278
2	$H_2 + M \rightleftharpoons H + H + M$	3.2×10^{16}	102.9	-1.5
3	$N_2 + M \rightleftharpoons N + N + M$	1.0×10^{18}	-	-1.0
4	$NO + M \rightleftharpoons N + O + M$	6.0×10^{16}	-	-0.5
5	$OH + M \rightleftharpoons O + H + M$	2.0×10^{18}	-	-1.0
6	$O_2 + M \rightleftharpoons O + O + M$	3.59×10^{17}	118.0	-2.5
7	$H_2O + H \rightleftharpoons H_2 + OH$	1.43×10^{14}	20.94	-
8	$H_2O + O \rightleftharpoons OH + OH$	2.9×10^{14}	18.7	-
9	$H_2 + O \rightleftharpoons OH + H$	4.0×10^{13}	10.2	-
10	$H_2 + O_2 \rightleftharpoons OH + OH$	2.5×10^{12}	38.9	-
11	$N_2 + O \rightleftharpoons NO + N$	1.5×10^{13}	-	-
12	$N_2 + O_2 \rightleftharpoons NO + NO$	1.0×10^{13}	79.5	-2.5
13	$NO + H \rightleftharpoons OH + N$	5.3×10^{11}	5.62	0.5
14	$NO + O \rightleftharpoons O_2 + N$	1.8×10^{8}	6.0	1.5
15	$O_2 + H \rightleftharpoons OH + O$	1.0×10^{14}	16.0	-

Where: $k_f(J) = A(J)\ T^{N(J)}\ e^{-B(J)/RT}$ and $k_b(J) = k_f(J)/K_c(J)$

bimolecular reactions. near equilibrium.

Numerical integration of the governing equations is accomplished using an implicit integration scheme. The advantage of this method is that it permits stable integration for step sizes of the same order of magnitude as the physical dimensions (nozzle throat size) for any flow condition (either near equilibrium or frozen). A similar program was developed earlier by Zupink, et al. (20) of United Aircraft. However, this program employs explicit intergration methods which are unstable unless the step size is of order of the characteristic relaxation distance. For near equilibrium flows the relaxation distance becomes very small and explicit integration methods require excessive computer time. In addition a first guess as to the initial step size to be utilized in the combustion chamber is required as input to the United Aircraft program. Because of these limitations it was decided to conduct all further analysis of nonequilibrium flows using the TRW program.

The FRRG program calculates the nonequilibrium species concentrations at specified area ratios in the nozzle. Since the one-dimensional flow equations are used in this program, the concentrations are assumed uniform at each axial location. A check was made as to the validity of the one-dimensional flow assumptions for the nozzle configuration employed in the experimental program. Results from a two-dimensional, axisymmetric flow program (also developed by TRW Systems), which employs the method of characteristics for chemically reacting gases, were used for this comparison.

The species concentrations at the nozzle exit were essentially identical for the two programs. Since the one-dimensional program uses about one-third less computer time than the two-dimensional program, additional sophistication of the latter program was not deemed necessary.

Results from the FRRG program are shown in Figure 4 which presents species concentrations as a function of temperature. As can be seen from the figure there is a significant difference in free-radical concentrations at the nozzle exit when finite rate chemistry is considered. For equilibrium flows the free-radical concentrations at the nozzle exit are quite small. However, the FRRG program predicts these concentrations are from two to ten orders of magnitude greater than their corresponding equilibrium values. These differences can be explained as follows. Free-radical recombination requires a third body to absorb the heat released by the reaction. The probability for three body collisions is quite small, so that termolecular reaction times become greater than the gas residence times. This effect is termed "recombination freezing", a subject which has received considerable attention in the past several years (Ref. 21). In general, the concentration changes within regions of rapid acceleration of the gas stream are governed by the bimolecular reaction rates which are several orders of magnitude faster than the termolecular rates.

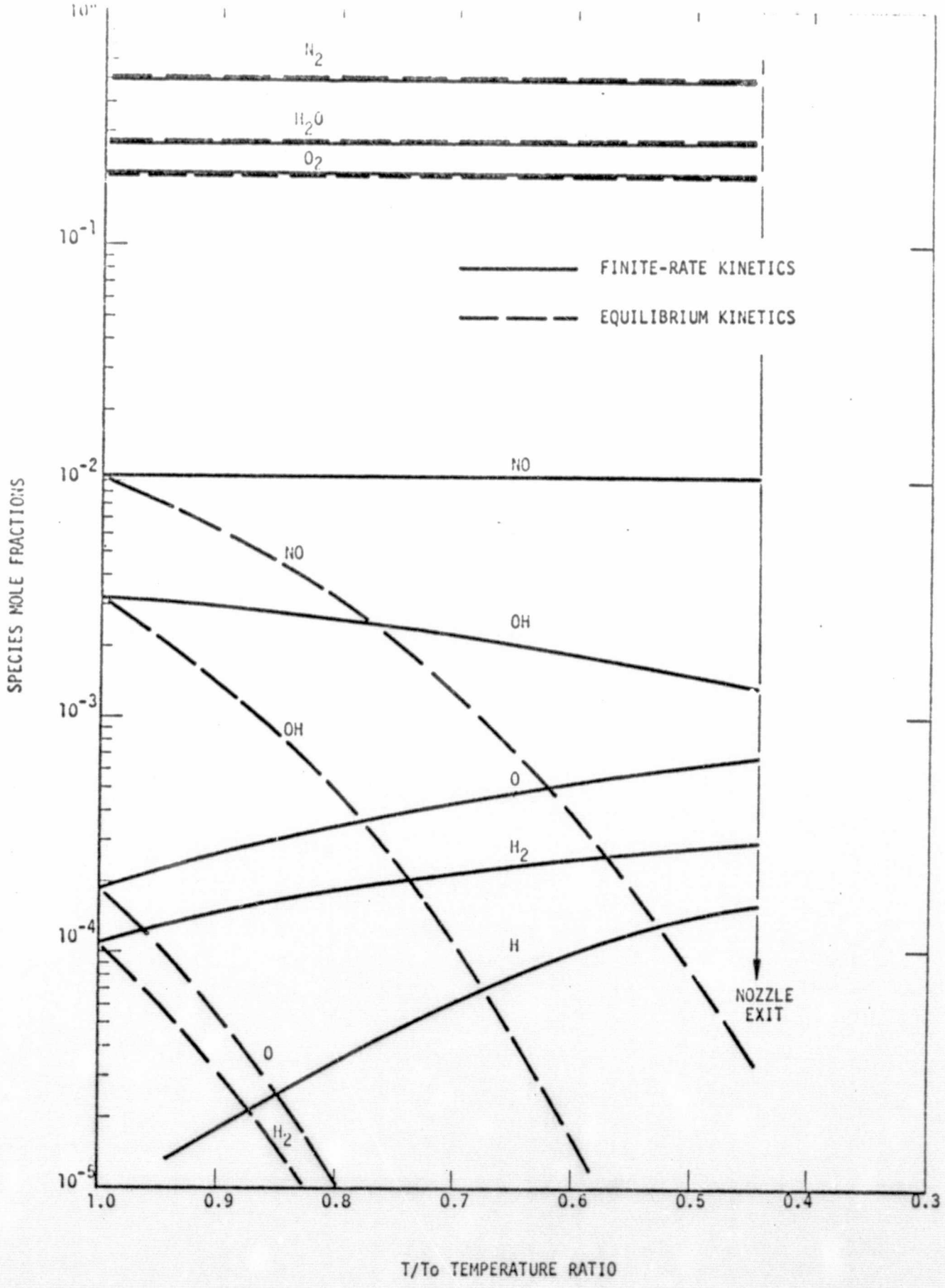


FIGURE 4 EQUILIBRIUM AND FINITE-RATE COMPOSITIONS FOR G.G. PRODUCTS

Simplified Ignition Lag (SIL) Program

The complete combustion process is assumed to occur in two steps as illustrated on Figure 5, which describes schematically the ignition model. During the induction period free-radicals are exponentially produced by: (1) the initial chain iniating steps and (2) the chain-branching mechanisms of the bimolecular reactions. Throughout this period the temperature remains essentially constant because certain reactions are slightly exothermic and others endothermic. Towards the end of the induction period the free radicals begin to recombine exothermically and the temperature starts to rise exponentially. The period of rapid temperature increase is termed the reaction time. In the temperature regime of interest in this investigation, the reaction times are much shorter than the induction period. Therefore, the analytical effort is directed toward evaluating the effect of vitiation on the induction period.

The ignition model employed assumes the temperature is constant throughout the induction period. This simplification along with the assumption of constant pressure makes it possible to neglect the hydrodynamic equations and to solve the differential equations describing the reaction kinetics. The approach is to write the equations governing the rate of growth of free-radicals and to solve these for species concentrations as a function of time using standard matrix techniques. The computer program is a simplification of a more general program developed by GASL. A source deck for the SIL program was supplied by E. A. Lezberg of NASA

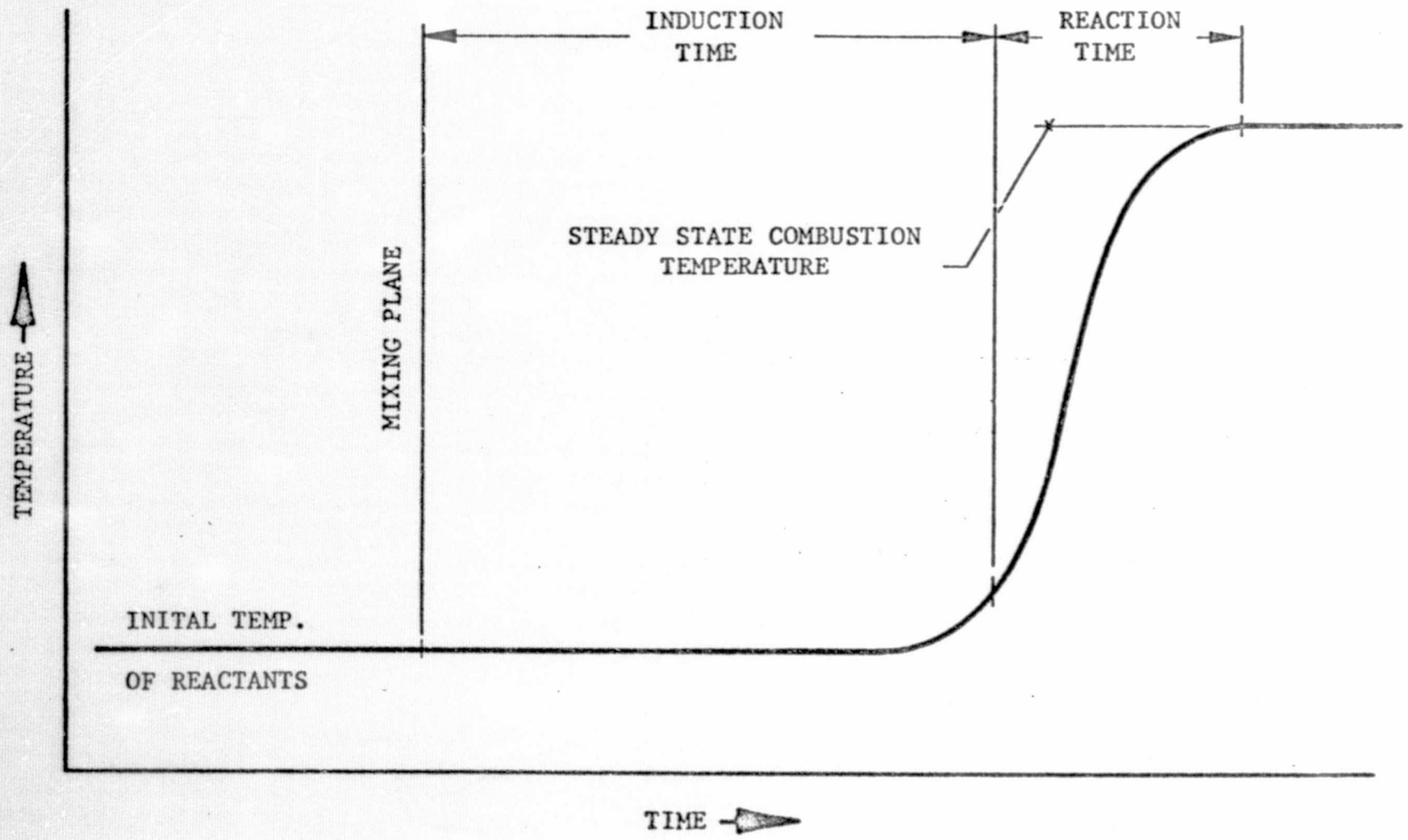


FIGURE 5 SCHEMATIC OF THE IGNITION MODEL

Lewis Research Center. The Lewis modifications to the program included the constant temperature simplification and the inclusion of several additional hydrogen and oxygen reactions which may be important to the ignition kinetics at temperatures below 1000°K. A list of reaction rate expressions and rate constants employed in the program is presented in Table 2.

A total of nine species are considered by the program. These are: H, O, H_2O, H_2, O_2, OH, N_2, HO_2, and H_2O_2. The latter two species enter into a chain-breaking step which tends to lengthen the induction period. Inclusion of these species in the induction analysis should result in a more favorable comparison of experimental and theoretical ignition delays at low temperatures.

Fifteen reactions are included in the SIL program. One of the advantages of this program is that a large number of reactions can be considered without significantly increasing the computing time. One limitation of this program is that it fails to include any NO or NO_2 reactions. The analysis of Momtchiloff indicated these reactions were comparatively unimportant below 4000° Rankine. However, the experimental results of Skinner indicated that both NO and NO_2 have a catalytic effect on the induction process. This effect tends to reduce delay times by an order of magnitude. Since the mechanism which accelerates the reaction is not understood at this time, it is not possible to include any NO or NO_2 reactions in a manner that would be meaningful.

TABLE 2

REACTION RATES FOR SIL PROGRAM

J	Reaction	A(J), gr. cm. units	B(J), kcal mole	N(J)
1	$H + O_2 \rightleftharpoons OH + O$	1.0×10^{14}	16.0	-
-1		4.16×10^{11}	-1.22	0.41
2	$O + H_2 \rightleftharpoons H + OH$	4.0×10^{13}	10.2	-
-2		1.85×10^{13}	8.39	-
3	$H_2 + OH \rightleftharpoons H + H_2O$	2.3×10^{13}	5.2	-
-3		1.43×10^{14}	20.94	-
4	$O + H_2O \rightleftharpoons OH + OH$	2.9×10^{14}	18.7	-
-4		2.03×10^{13}	1.13	0.26
5	$H_2 + M \rightleftharpoons 2H + M$	3.16×10^{16}	102.9	-1.5
-5		9.18×10^{15}	-0.97	-1.5
6	$H_2O + M \rightleftharpoons OH + H + M$	1.86×10^{18}	119.9	-1.278
-6		7.5×10^{16}	-	-1.0
7	$O_2 + M \rightleftharpoons 2O + M$	3.59×10^{17}	118.0	-2.5
-7		8.94×10^{15}	-1.57	-2.074
8	$H + O_2 + M \rightleftharpoons HO_2 + M$	4.3×10^{15}	-1.28	-
-8		8.91×10^{15}	46.12	-0.28
9	$H_2 + HO_2 \rightleftharpoons H_2O_2 + H$	2.0×10^{13}	23.72	-
-9		1.0×10^{14}	9.82	-
10	$H_2 + O_2 \rightleftharpoons OH + OH$	2.5×10^{12}	38.95	-
-10		4.77×10^{10}	19.87	-
11	$H_2O_2 + M \rightleftharpoons 2OH + M$	3.95×10^{17}	46.3	-
-11		0.0	-	-
12	$H + HO_2 \rightleftharpoons OH + OH$	1.6×10^{14}	-	-
-12		0.0	-	-
13	$HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2$	1.4×10^{13}	-	-
-13		0.0	-	-
14	$H + H_2O_2 \rightleftharpoons H_2O + OH$	1.0×10^{14}	7.01	-
-14		0.0	-	-
15	$OH + H_2O_2 \rightleftharpoons H_2O + HO_2$	2.0×10^{13}	2.64	-
-15		0.0	-	-

where: $k(J) = A(J)\, T^{N(J)}\, e^{-B(J)/RT}$

Results from the SIL program are the species concentrations as a function of time. Ignition lag is determined from the semilog plot of the hydroxyl radical concentration against time. The induction period is characterized by the region of essentially constant exponential growth of free-radical concentrations. The end of the induction period is considered to be the time when the hydroxyl concentration deviates from constant exponent growth. This definition for the end of induction is recommended by Hersch (22). Other methods for defining the end of the induction period were considered in this study. The following comparison illustrates the variation in ignition delay periods for different methods of defining the end of induction.

Definition of End of Induction	Reference	Delay Time
(1) End of exponential growth of (OH)	22	39 μsec
(2) OH concentration of 10^{-9} gram-moles/cm^3	11	30 μsec
(3) Hydrogen concentration = 1/2 $(H_2)_o$	17	47 μsec
(4) End of exponential growth of (H)	9	40 μsec

This comparison for heated air and hydrogen at 1200°K and one atmosphere pressure is shown on Figure 6, which presents the OH and H radical concentrations plus the hydrogen weight fraction as a function of time. Starting conditions assume each stream is in chemical equilibrium prior to mixing and an equivalence ratio of one for the combined streams. The comparative times indicate the method of defining the end of induction has some effect on the calculated delay times. However, Hersch (22) is able to show that method (2) is

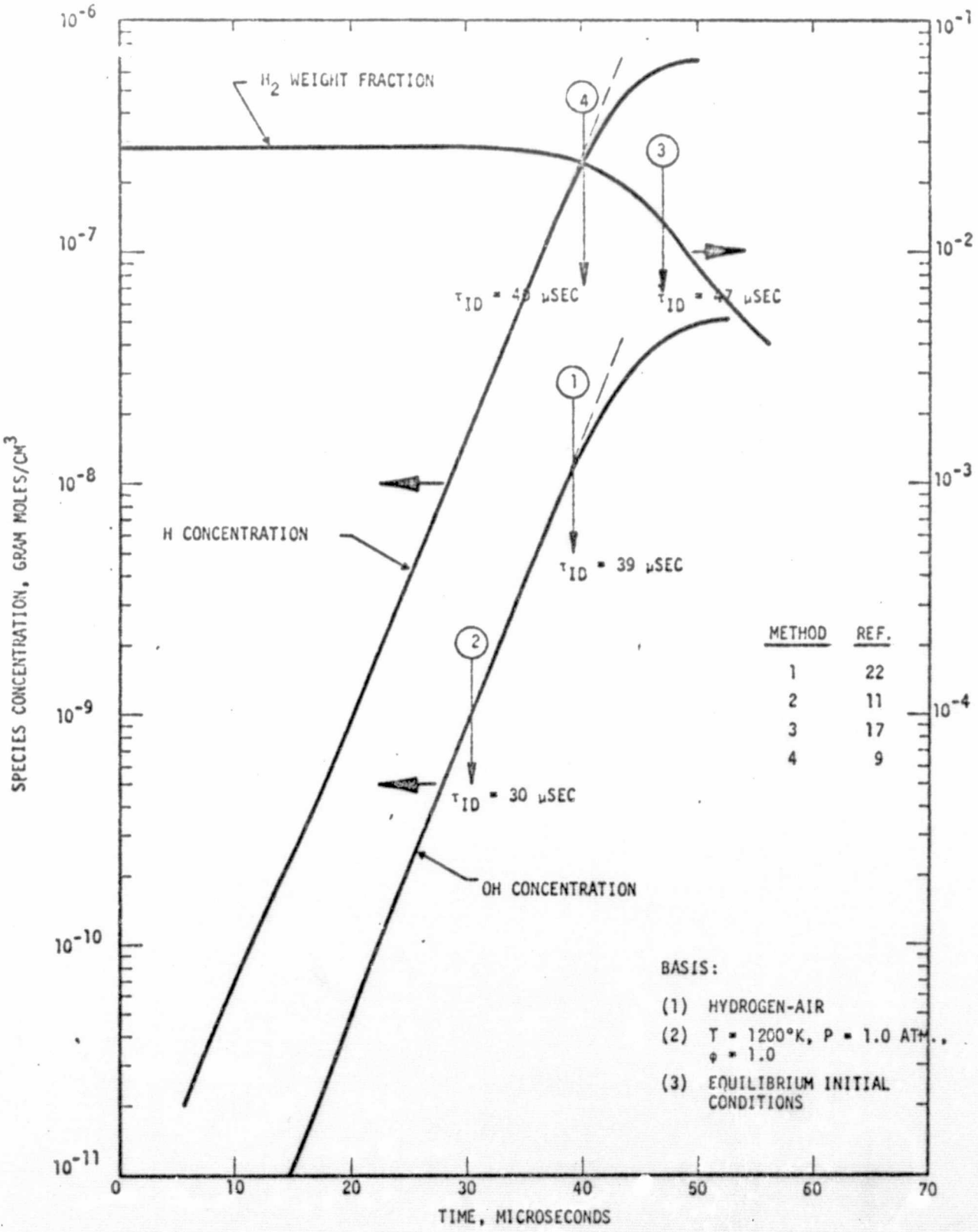


FIGURE 6 DEFINITIONS OF THE INDUCTION PERIOD

only a reasonable approximation of the delay period for temperatures greater than 1500°K. At the same time, method (3) is simply an approximation suggested by Rhodes (17). Methods (1) and (4) yield essentially identical delay time so that both methods appear applicable. Hersch was able to compare method (1) with a detailed analytical model which included the temperature variations during the postinduction period. Conclusions from this comparison were that method (1) was a reasonably good approximation to the induction limit over a wide range of initial temperatures ($1200 \leq T_i \leq 2500°K$). Therefore, this method was finally selected as most appropriate for application to the SIL program results.

When examining the results from the Lewis version of the SIL program, one modification was incorporated into the program. This modification is a revision of the method of defining the effective concentration of third-body species that enter into the three-body reaction rates. Brokaw (10) suggests that the third body expression in reaction 8 on Table 2 is a strong function of water vapor content of the reacting species. He showed the relative third body efficiencies are given by the following expression:

$$[M] = X_{H_2} + 0.35X_{O_2} + 0.43X_{N_2} + 0.2X_{Ar} + 14.3X_{H_2O}$$

where: X is the mole fraction of each third body. In the Lewis version of the SIL program, the relative efficiency of water vapor was reduced from 14.3 to 6.0. When the Lewis version of the SIL program was utilized to calculate the effect of 10 percent water

vapor content in the air on ignition delays at 1000°K an anomalous result was obtained: the ignition delay for hydrogen and air plus 10 percent water was six times longer than the corresponding dry air case. The magnitude of this difference is shown on Figure 7 which again presents OH concentration as a function of time. Also shown on this figure is the effect of further reducing the third body contribution of water vapor. The third body expression used in this comparison is as follows:

$$[M] = X_{H_2} + 0.35X_{O_2} + 0.43X_{N_2} + 0.2X_{Ar} + X_{H_2O}$$

When this expression for the third-body terms was employed in the SIL program the difference in delay times of hydrogen-air and hydrogen-air plus 10 percent water vapor is reduced to 15 micro-seconds.

The results on Figure 7 show that the third-body term may have a significant effect on delay times. This effect is quite pronounced under the following circumstances:

(1) when relatively large concentrations of water vapor are present in the initial reactants;

(2) when the initial temperature of reactants is low ($T < 1100°K$).

Further examination of the effect of the third body term revealed that it had absolutely no effect when applied to dry air over a temperature range of 950 to 1200°K. One reason why this term has no effect for dry air is that the third-body term acts to reduce the

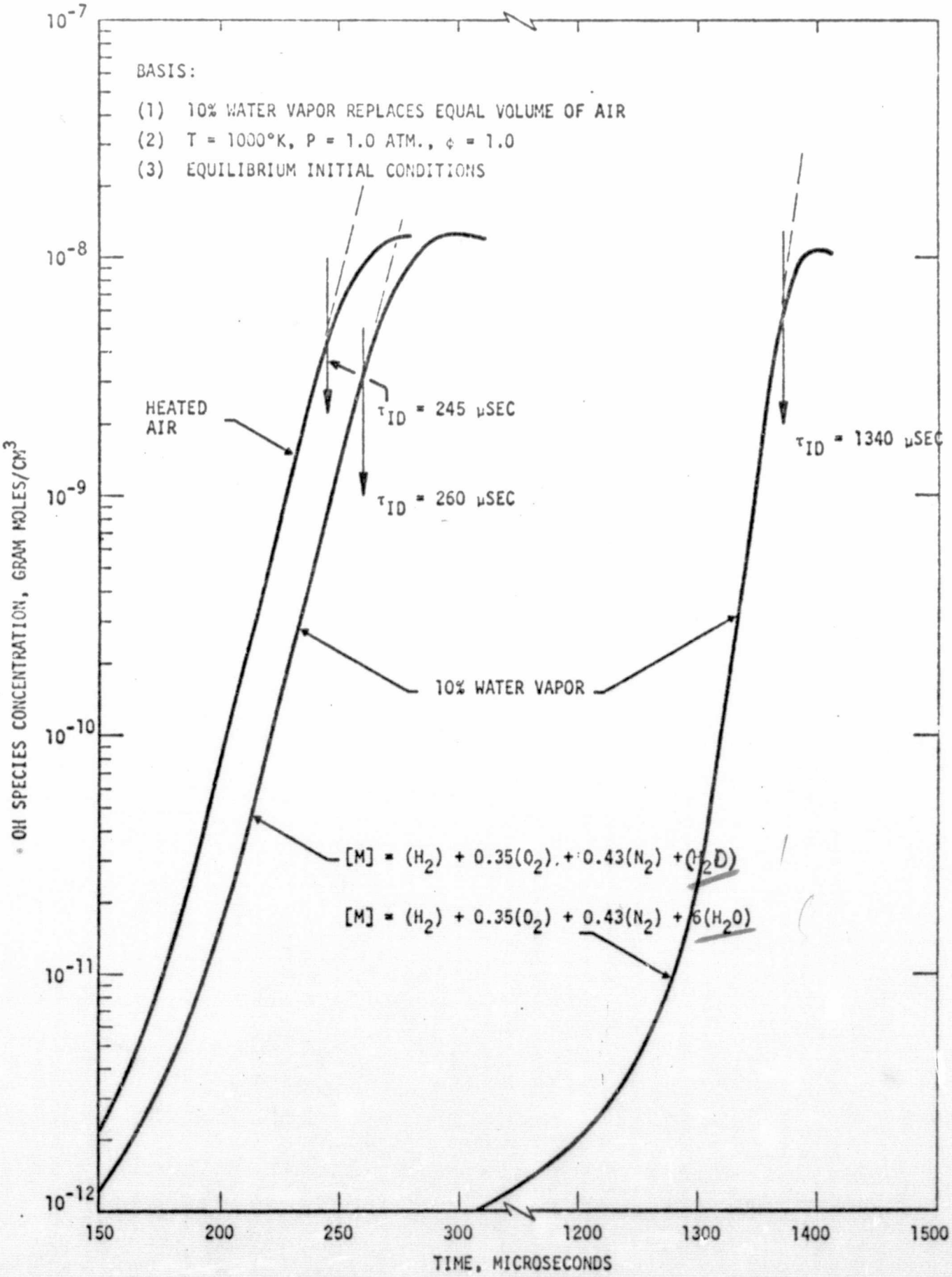


FIGURE 7 THIRD BODY EFFECTS ON DELAY TIMES

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build up of free radicals during the early part of the induction period. Water vapor does not appear in significant concentrations until the latter part of the induction period where the bimolecular reactions predominate the induction process. Thus the overall influence of the contribution of the effective water vapor concentration in the third-body expression is insignificant when applied to an initial mixture of hydrogen and uncontaminated air.

When this same type of comparison was made at 1200°K, the following results were obtained:

Initial Composition	Third-Body	Delay Time
(1) Hydrogen/Heated Air	M_1 or M_2	39 μsec
(2) Hydrogen/Air + 10% H_2O	M_1	36 μsec
(3) Hydrogen/Air + 10% H_2O	M_2	34 μsec

Where: $M_1 = X_{H_2} + 0.35X_{O_2} + 0.43X_{N_2} + 6X_{H_2O}$

$M_2 = X_{H_2} + 0.35X_{O_2} + 0.43X_{N_2} + X_{H_2O}$

These results indicate the effective water vapor concentration in the third-body term yields an almost negligible difference in delay times at temperatures of 1200°K or higher.

Experimental data of Snyder, et. al. (16) showed that water vapor in the initial air resulted in a slight reduction in delay times over the corresponding case for hydrogen and uncontaminated air. When the SIL program was modified to employ $[M_2]$ as the third body term, the agreement with Snyder's experimental results, while not entirely satisfactory, is considerably better than that shown by the Lewis version of the program. Obviously better agreement

between theoretical and experimental induction times could be obtained by further reducing the effective concentration of water vapor in the third-body term. However, there is no theoretical and very little experimental justification for making the effective concentration less than unity. Consequently the third-body term defined by $[M_2]$ was employed for all subsequent calculations using the SIL program.

Typical results from the SIL program are shown on Figures 8 through 13 which present OH radical concentration as a function of time. The results presented on these figures are discussed in the next section which is an extensive verification of the simplified induction model employed in the computer analysis.

Verification of the Simplified Ignition Lag Program

Before applying the SIL program to the analysis of ignition lag with vitiated air, it is first necessary to establish the validity of the program results. Since most of the theoretical and analytical work on ignition lag is concerned with real air and hydrogen, the verification is made for these gases. Initially, a base case was selected for making this comparison. Temperature for the base case is 1200°K, pressure is one atmosphere, and equivalence ratio is one. As a starting condition, both streams are assumed to be in chemical equilibrium at the assigned temperature and pressure prior to mixing. The combined stream is no longer in chemical equilibrium.

Results from the SIL program for the base case species are shown on Figure 8, which presents the OH radical concentration as a function of time. The induction period is defined by the end of the constant exponential growth for the OH radical. An induction time of 39 microseconds is obtained for the base case conditions. Several approximate relations for determining ignition delays are discussed in the review of literature. A summary of the equations presented by the different authors is given in Table 3 along with the range of temperatures over which they apply. These approximate relations are used to calculate the ignition lag for the base case conditions and the delay times are also shown on Figure 8. (Note that the empirical expression of Skinner does not apply above 1100°K). The relation of Ferri predicts much shorter delay times than the SIL program, while Rhodes predicts a considerably longer induction period. There is a relatively close agreement between Nicholls' result and that of the SIL program.

The effect of peripheral reactions and different reaction rate data are illustrated on Figure 9, which presents OH concentration as a function of time. Here the same starting conditions are applied to each case, but only the first nine reactions shown in Table 1 are considered. The latter six reactions on this table were expected to show minor effect on the induction time for the base case conditions. The difference between nine and fifteen reactions (using identical rate data for corresponding reactions) only amounts to eight microseconds variation in delay time.

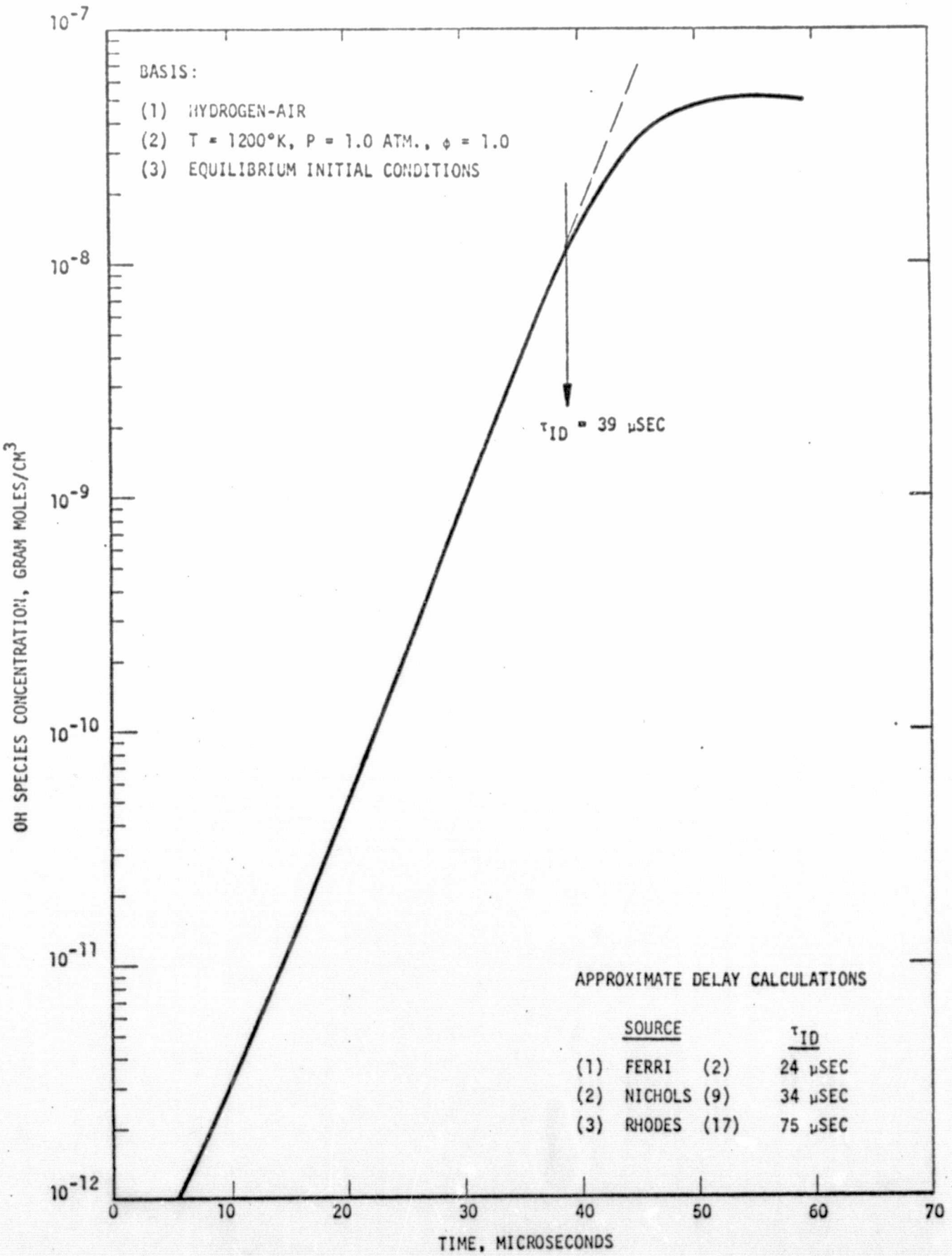


FIGURE 8 IGNITION DELAY FOR BASE CASE SPECIES

TABLE 3

APPROXIMATE LAG THEORIES

(1) Ferri:

$$\tau_{ID} = \frac{8 \times 10^{-3}}{P} e^{9600/T}$$

(2) Nicholls: $(1100° \leq T \leq 2000°K)$

$$\tau_{ID} = \frac{4.1 \times 10^{-7} T}{\eta_{O_2} P} e^{8.05/T} \ln \left[\frac{\eta_{O_2}^2 k_6}{\eta_{H_2} k_2 + \eta_{O_2} \eta_{H_2} k_5} \right]$$

(3) Skinner: $(800 \leq T \leq 1100°K)$

$$\tau_{ID} = \frac{7.92 \times 10^{-3}}{P^{0.4} \phi} e^{15.950/T}$$

(4) Rhodes: $(800 \leq T \leq 1800°K)$

$$\tau_{ID} = \frac{1.27 \times 10^{-3}}{P^{4/3}} \left[\frac{T}{[X_{O_2}]_o [X_{FR}]_o} \right]^{1/3}$$

$$[X_{FR}]_o = [X_H]_o + [X_{OH}]_o + 2[X_O]_o$$

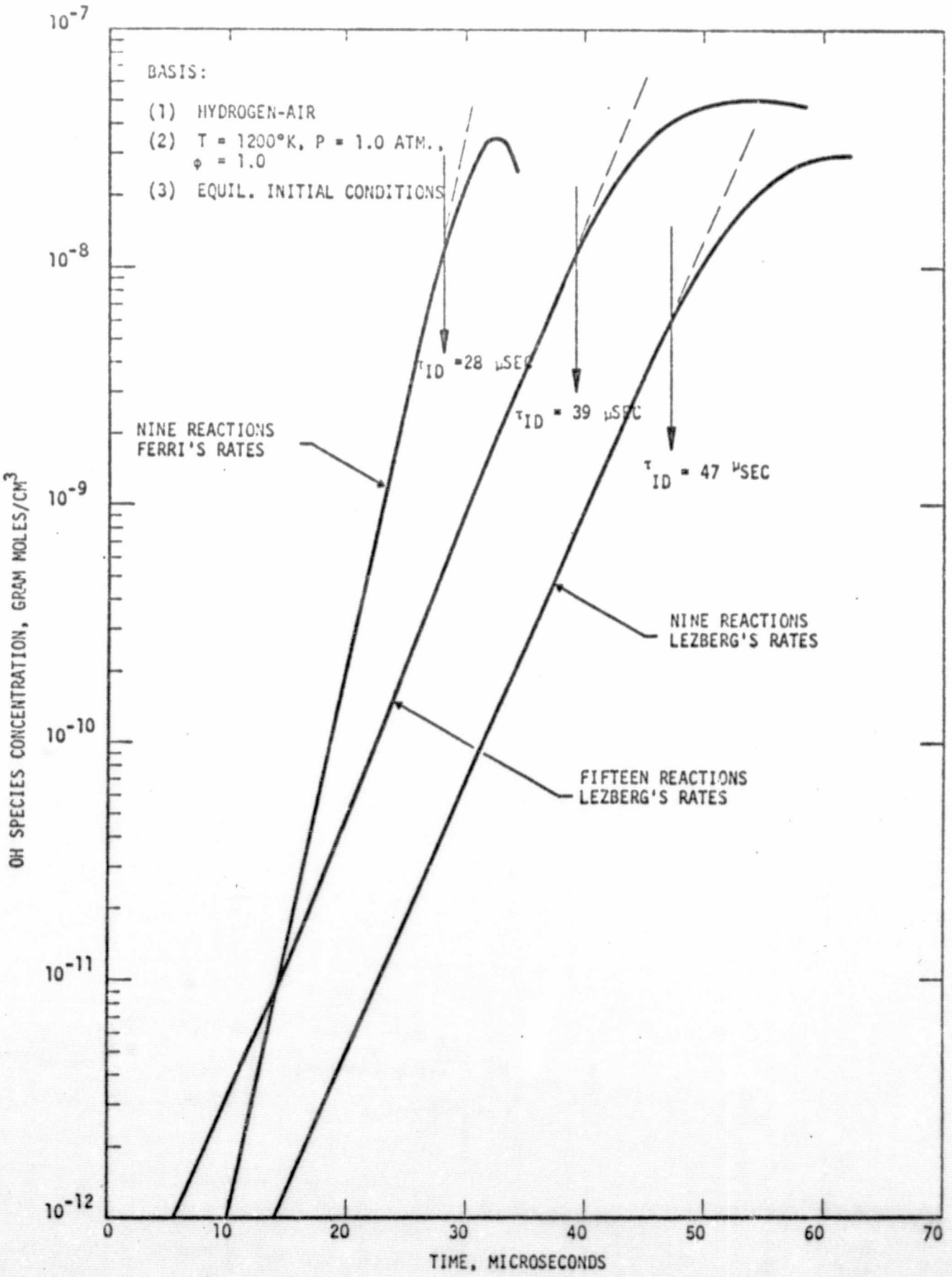


FIGURE 9 EFFECT OF REACTIONS AND RATE DATA ON DELAY TIMES

However, this represents a 20 percent variation in induction period so that the latter six reactions are more important than originally anticipated. When the reaction rates of Ferri were used in the nine reaction system a considerable decrease in delay time is evidenced (47 μ sec → 28 μ sec). In general, the forward reaction rates employed by Ferri are faster than those shown on Table 2, so that a reduction in delay time is not surprising. However, the magnitude of the difference shown here is hardly significant in terms of induction lengths for supersonic combustion. Even with gas velocities of 10,000 feet per second, the difference in induction distances is still less than 3 inches.

The effect of temperature on induction times is shown on Figure 10, in which hydroxyl radical concentrations as a function of time are shown at three separate temperature levels. Starting conditions for each case assume the heated air and hydrogen streams are in chemical equilibrium prior to mixing at constant temperature and pressure. The results show that a hundred degrees reduction in temperature over the base case, just about doubles the induction time. However, a further reduction of the same magnitude, results in a factor of six difference in induction time over the base case. The effect of initial temperature is best illustrated by plotting the induction times against the reciprocal of temperature on semi-log coordinates. This type of information is presented and discussed later in this section.

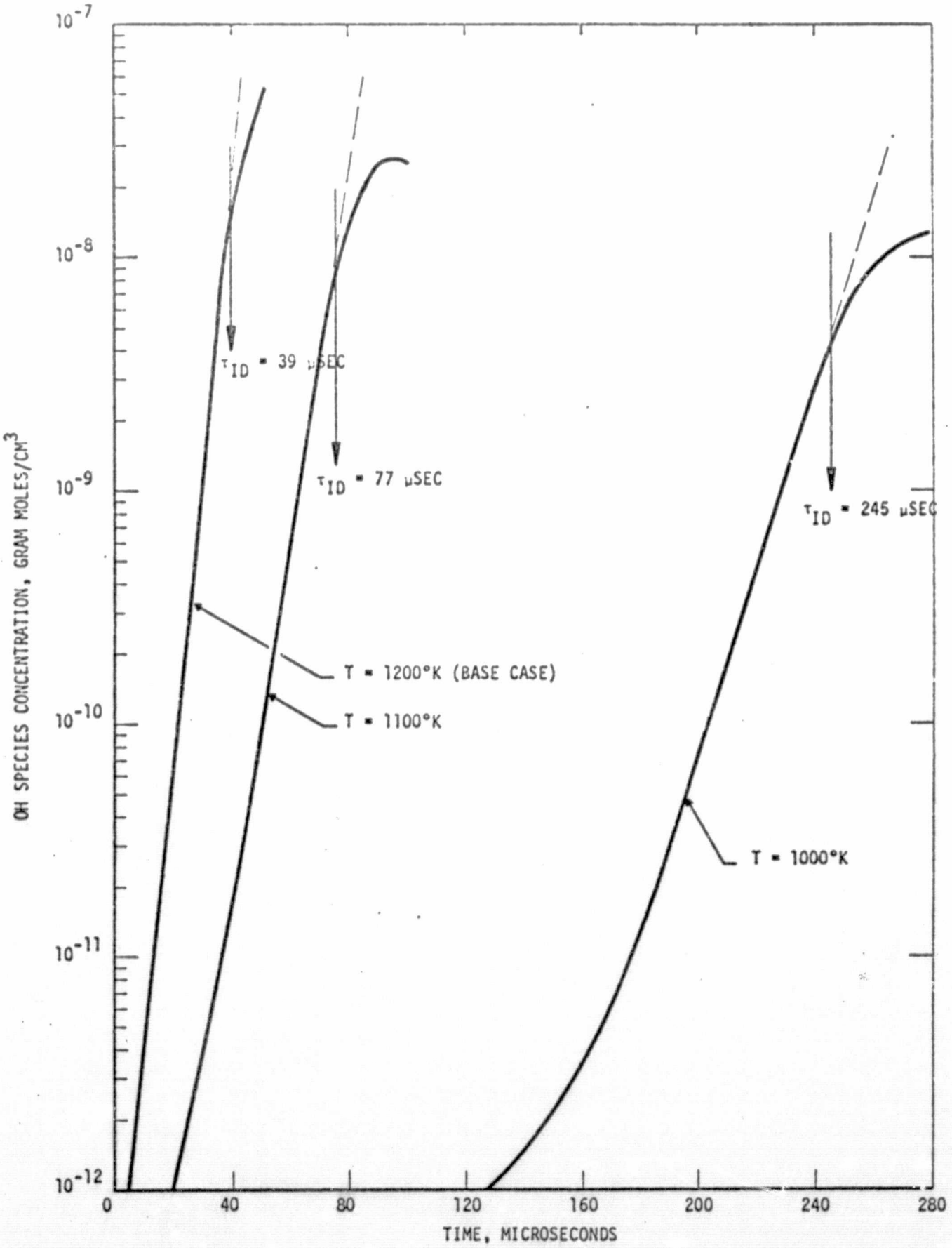


FIGURE 10 EFFECT OF TEMPERATURE ON INDUCTION TIMES

Figure 11 illustrates the effect of equivalence ratio on induction times for the base case species concentration. Three values for equivalence ratio are presented on this figure. The results show that equivalence ratio has a very small effect on induction times in the range ($0.2 \leq \phi \leq 1.0$). Momtchiloff obtained similar results in a theoretical and experimental comparison of the effect of equivalence ratio on delay times. The analytical model of the induction process assumes instantaneous mixing for the two streams. This assumption is justified on the basis that local mixture ratio variations during the actual mixing process have essentially no effect on induction time.

The effect of pressure on ignition delay is illustrated on Figure 12, which again presents OH concentrations as a function of time. Higher pressure in the combustor tends to decrease ignition delays; the delay time being inversely proportional to the pressure. In this constant temperature comparison, two combustor pressures are examined with the starting condition for each case being the equilibrium species concentrations prior to mixing. At two atmospheres pressure the delay time is 21 microseconds compared with 39 microseconds at one atmosphere pressure. Relating the delay time to the inverse of pressure yields an exponent of 0.9 on pressure. The theoretical work of Momtchiloff report this exponent is 1.09 at the same temperature conditions. Experimental data from Schott and Kinsey indicates this exponent is 1.0, while Das Gupta reports an average value of 0.9. The agreement of the

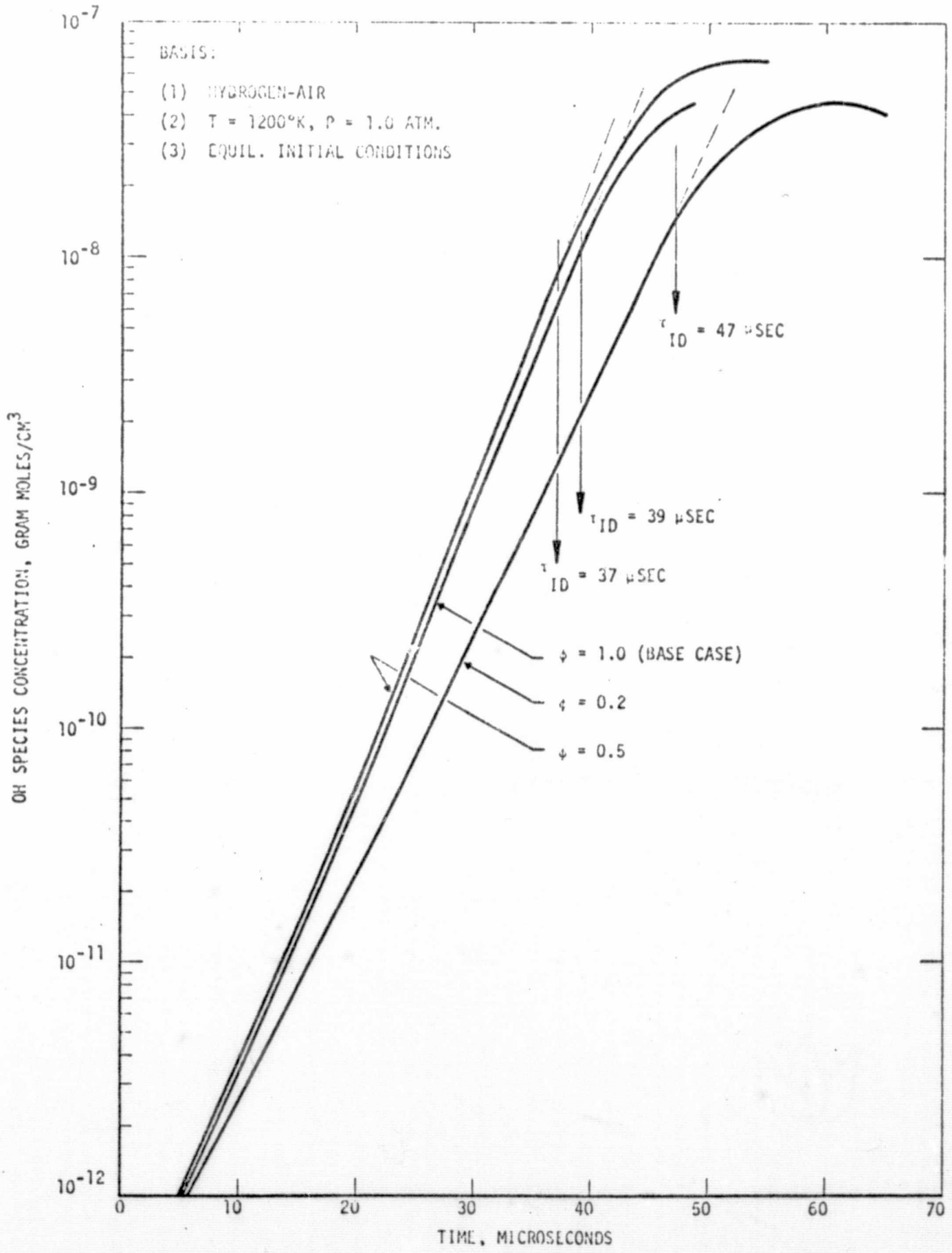


FIGURE 11 EFFECT OF EQUIVALENCE RATIO ON DELAY TIMES

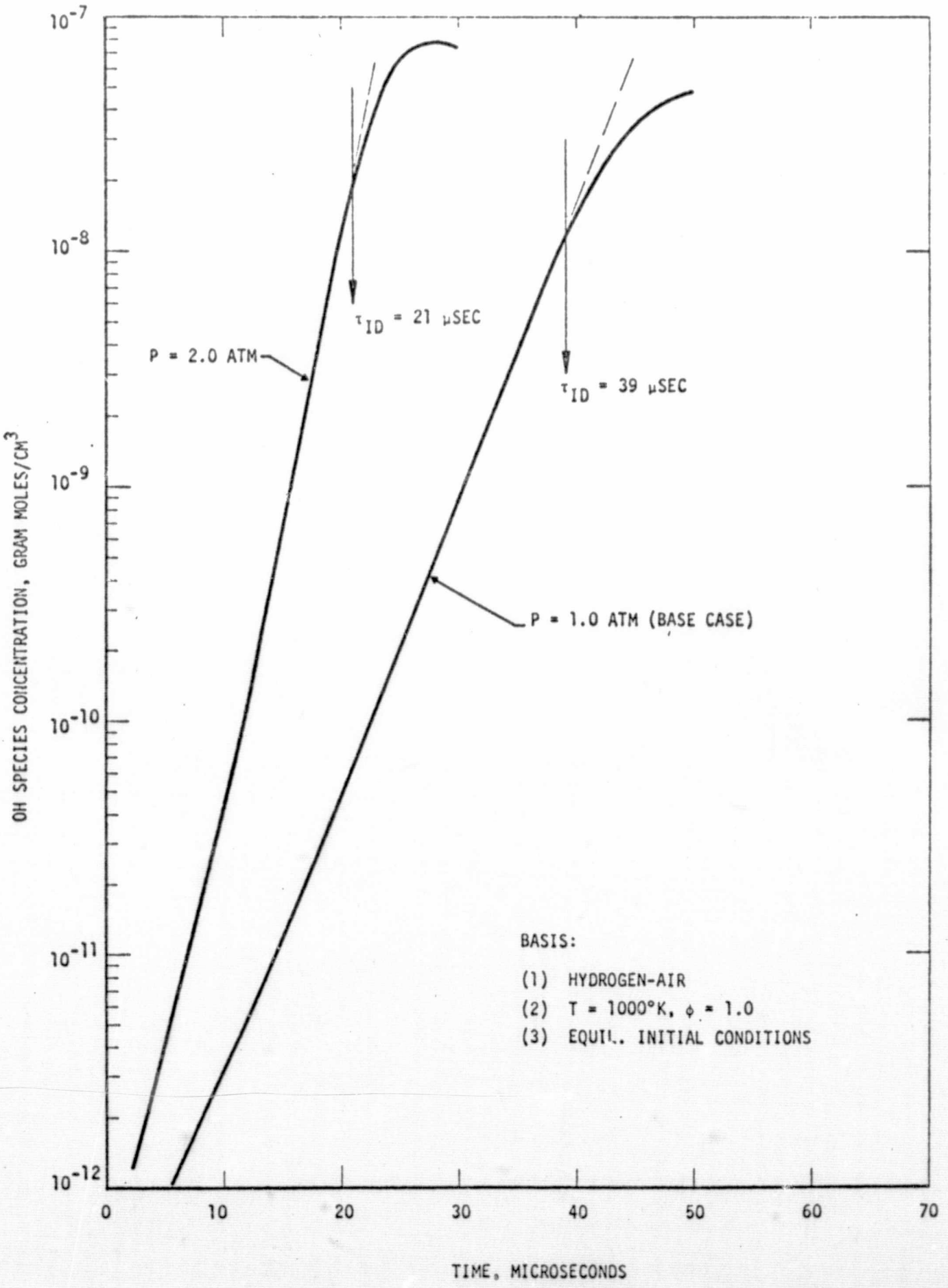


FIGURE 12 EFFECT OF PRESSURE ON INDUCTION TIMES

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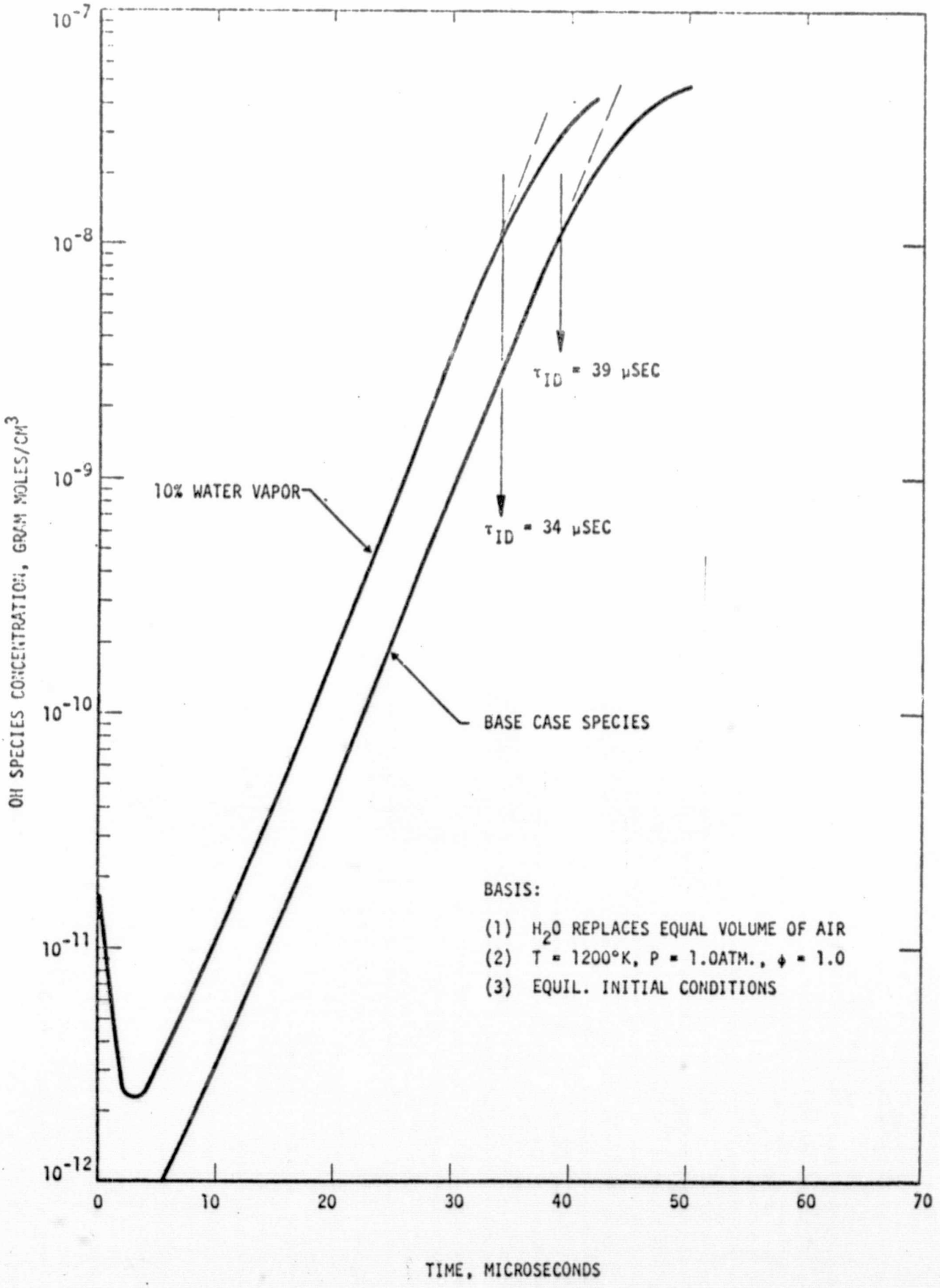


FIGURE 13 EFFECT OF WATER VAPOR ON INDUCTION TIMES

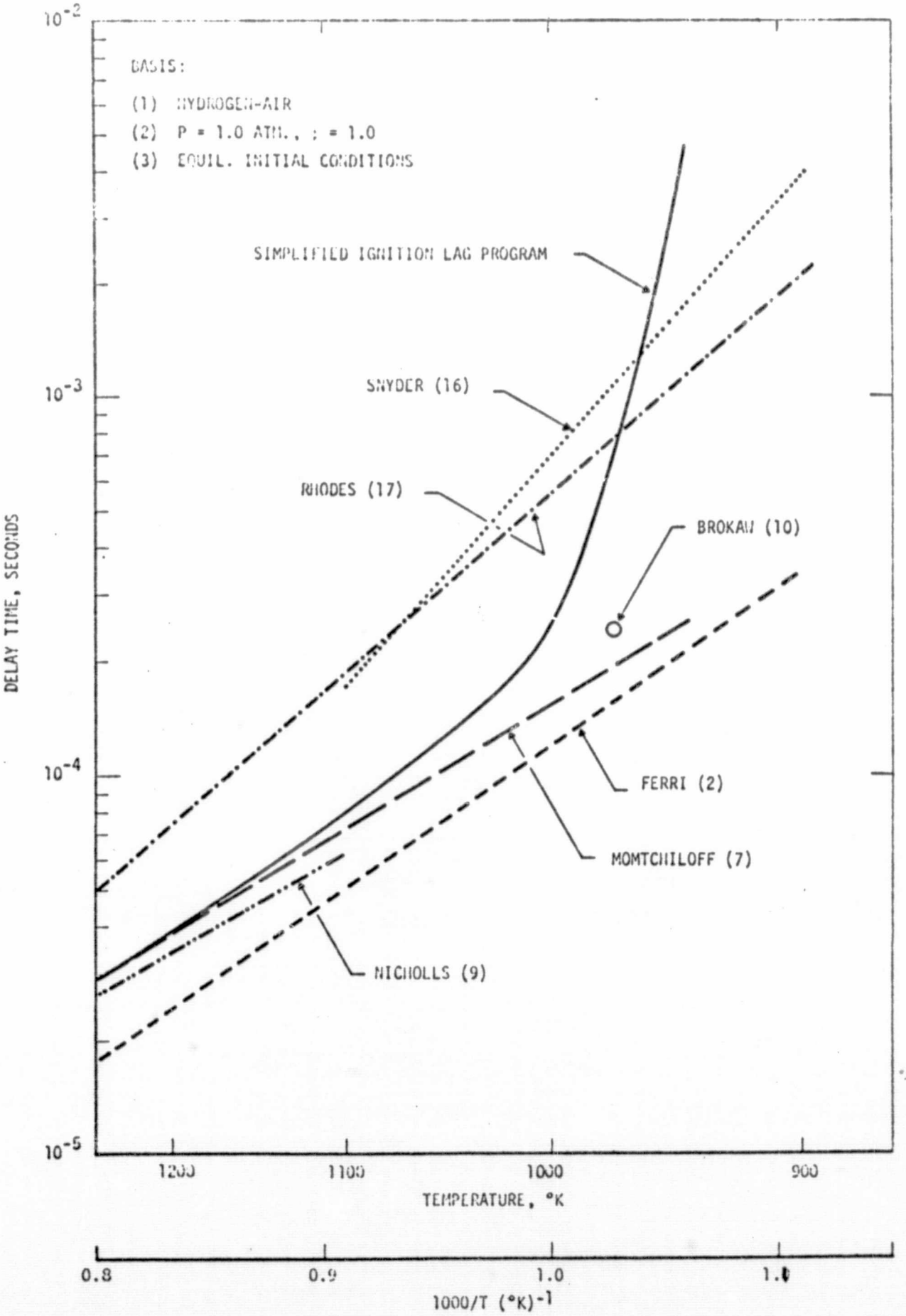


FIGURE 14 IGNITION DELAY TIMES FOR DIFFERENT CORRELATIONS

chemical equilibrium prior to mixing. The correlations shown here are terminated at their respective temperature range of application. Note that most of the correlation presented are plotted as a straight line on this figure. Even the sophisticated analytical model employed by Momtchiloff (7) yields a straight line in these coordinates. However, the SIL program results deviate considerably from straight line behavior, especially at low temperatures. The reason is that the SIL program includes the effect of the HO_2 species on the ignition times. This species has often been observed in hydrogen-oxygen flames as an intermediate product that disappears rapidly as the reaction progresses. Brokaw (10) is the only other author to include this species and the point shown on Figure 14 includes his postulated mechanism by which the HO_2 species influences the delay time.

In the high temperature range ($T \rightarrow 1000^{\circ}K$) the SIL program results agree reasonably well with the approximate lag calculations of Nicholls (9) and Ferri (2). It agrees even better with the more detailed theoretical analysis of Momtchiloff (7). At $950^{\circ}K$ the simplified model agrees with the empirical relations of Snyder (16) and Rhodes (17). Momtchiloff's analysis does not include the effect of HO_2 on induction times. This may explain the large differences between Momtchiloff's results and those of the SIL program in the low temperature range.

A comparison of the SIL program results with experimental data for ignition delay at low temperatures is made on Figure 15. Above

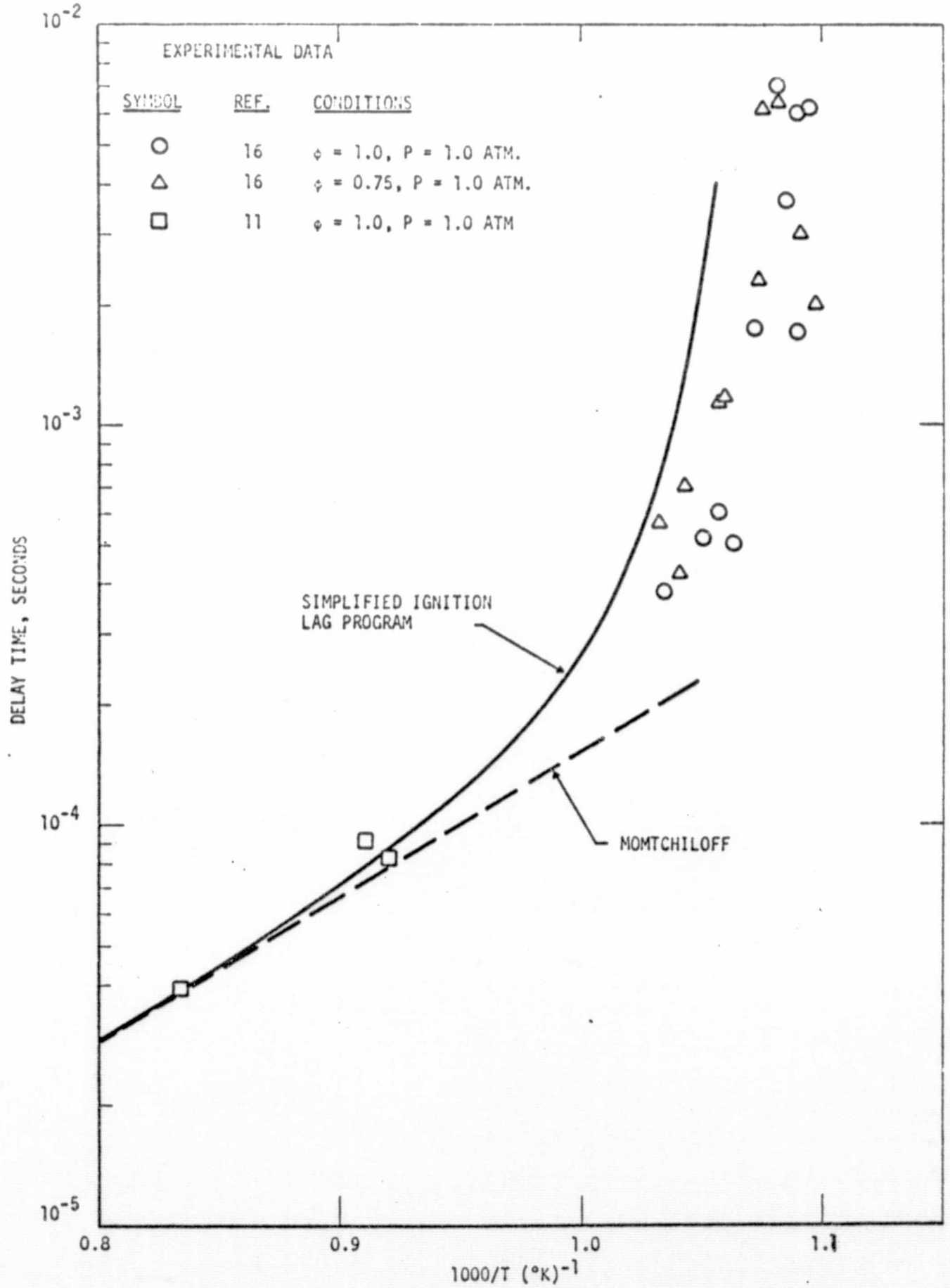


FIGURE 15 COMPARISON OF ANALYTICAL AND EXPERIMENTAL RESULTS

1000°K the SIL program predicts delays close to those of Momtchiloff (7), who was able to justify his theoretical model with experimental results as shown previously on Figure 1. The low temperature experimental results of Snyder (16) show very poor agreement with Momtchiloff's analysis. However, the SIL program results follow the basic trend of Snyder's shock tube data even though the agreement is not entirely satisfactory. The fact is that the SIL program consistently predicts longer delays than were found experimentally for the test conditions indicated on Figure 15. (Snyder's empirical relation used on the previous figure represents a correlation of all his data by a nonlinear regression program). However, the general agreement of the SIL program with experimental data tends to support the arguement that ignition delays increase significantly at low temperatures due to the self-inhibition of the reactions by HO_2 formation.

In summary, examination of the ignition model employed in the SIL program has shown that most of the relevant parameters influencing induction times are predicted with a reasonable degree of accuracy. The assumption of starting conditions where both streams are in chemical equilibrium is an essential part of this effort because:

(1) The experimental data used for comparison with the program results were obtained under conditions where equilibrium species concentrations at the combustor inlet is a reasonable approximation.

(2) Most of the theoretical approaches for calculating ignition delays employ the assumption of chemical equilibrium as a starting condition.

In the next section, the effect of nonequilibrium starting conditions is examined using the SIL program, and an analysis is made to show the effect of vitiated air on ignition delays in supersonic combustion.

Analysis for Vitiated Air

The vitiated air composition is made up of the products of combustion in the gas generator. A combination of nitrogen tetroxide, hydrazine and nitrogen serve as reactants for the gas generator. In the ignition lag experiments described in the Experimental Program Section, the design mixture ratio of reactants is such that the theoretical flame temperature is 2200°K at a chamber pressure of 600 psia. The products of combustion are expanded to atmospheric pressure (14.7 psia) where hydrogen is injected parallel to the mainstream gases. Injection velocity for the hydrogen corresponds to sonic condition and mixing and combustion takes place at constant pressure. A complete analytical description of this system has not been made in the present program. A model has been made which incorporated the following simplifying assumptions into the analysis in order to obtain a qualitative answer to the effect of vitiation on ignition lags.

(1) All viscous effects are neglected.

(2) Instantaneous mixing of the mainstream gases and hydrogen

at the point of injection.

(3) Constant temperature and pressure are assumed to exist throughout the induction period.

Of these three assumptions only the second is believed to be of significance. In the follow-on phase of the program it is anticipated that the model will be modified to include the effects of mixing.

The nonequilibrium composition of the vitiated air at the entrance to the supersonic test section is calculated utilizing the finite-rate reacting gas (FRRG) program. Computed composition changes during the expansion were shown previously on Figure 4. The hydrogen stream at the test section entrance is assumed to have a free-radical composition corresponding to stagnation conditions in the hydrogen manifold. The recombination of atomic hydrogen is a relatively slow three-body reaction and the assumption of frozen flow is quite reasonable for the temperatures and pressures employed in the experimental program. The vitiated air and hydrogen streams are mixed at constant pressure and the resulting species concentrations are input as initial conditions into the simplified ignition lag (SIL) program.

The SIL program results for vitiated air and hydrogen are shown on Figure 16, which present the OH radical concentration as a function of time. These results indicate the induction period for vitiated air and hydrogen may be as short as 20 microseconds. Under the experimental conditions of this program, ignition should occur less

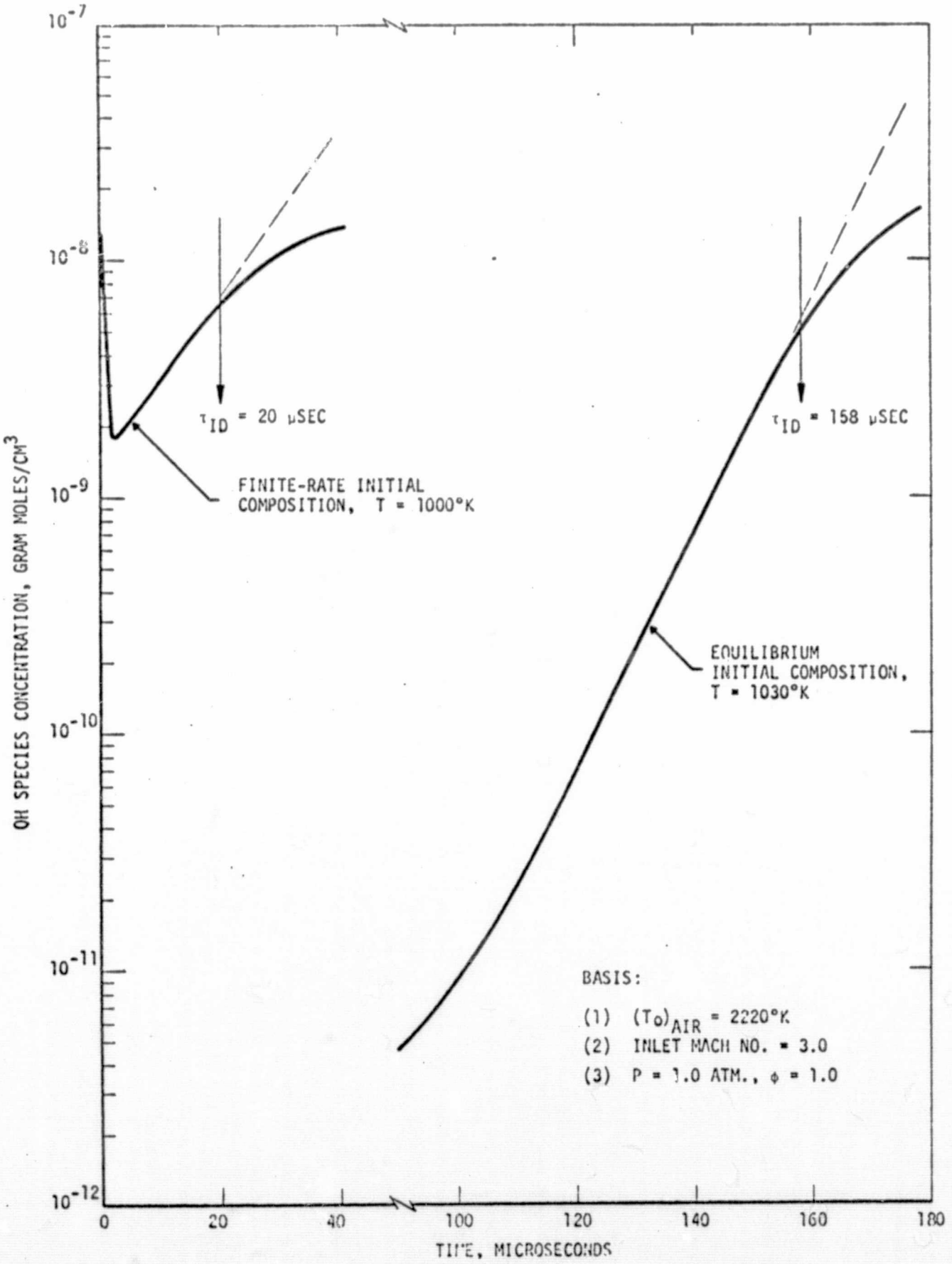


FIGURE 16 IGNITION DELAY FOR VITIATED AIR/HYDROGEN

than 1.5 inches downstream of the test section entrance. However, mixing times are neglected in this analysis, so that the actual distance to the ignition front may be located somewhat further downstream than predicted by the SIL program.

Figure 16 also includes the delay time calculated assuming chemical equilibrium for both the vitiated air and hydrogen stream prior to mixing. Notice the test section temperature is 1030°K for that case compared to 1000°K for the previous calculation assuming finite rate chemistry. Both the finite rate and equilibrium calculations are started at the same temperature and pressure in the gas generator. The heat release associated with additional recombination of free-radicals when assuming chemical equilibrium results in higher temperatures throughout the expansion process. An induction time of 158 microseconds was determined for vitiated air and hydrogen utilizing the assumption of equilibrium initial conditions. This delay corresponds to a distance of approximately 11.5 inches downstream of the test section entrance for the ignition front.

A comparison was also made to show the effect of employing heated air to perform the same type experiments. Conditions at the inlet to the supersonic test section (i.e., temperature, pressure and equivalence ratio) are identical to those employed in the vitiated air analysis.

The SIL program results for heated air and hydrogen are shown on Figure 17, which again presents OH radical concentration as a function of time. An induction time of 30 microseconds was obtained

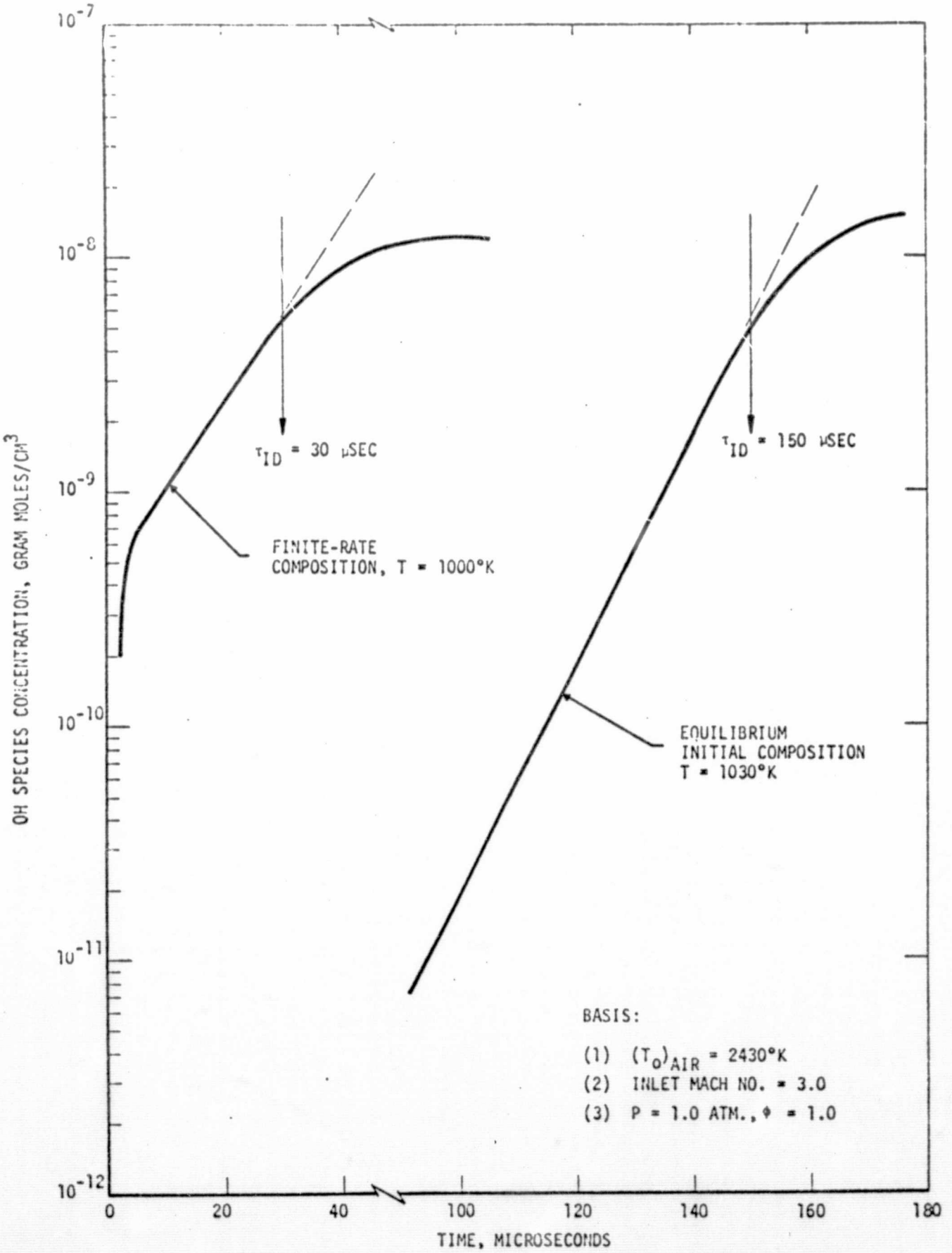


FIGURE 17 IGNITION DELAY FOR HEATED AIR/HYDROGEN

for nonequilibrium inlet conditions to the supersonic test section. This delay time corresponds to a flame front location of 2.2 inches downstream of the test section inlet. When equilibrium initial conditions were assumed for the heated air and hydrogen the delay time increased to 150 microseconds. This induction time corresponds to a lag length of 10.8 inches.

A comparison of the vitiated air and heated air analytical results indicates that vitiated air does, to some extent, simulate heated air from the standpoint that the ignition lag lengths are almost equal. For nonequilibrium inlet conditions, the free-radical content of the vitiated air and hydrogen is present in sufficient quantity to cause the ignition to be almost spontaneous. Heated air contains no hydroxyl radical at the test section inlet, but the nonequilibrium concentrations of atomic hydrogen and oxygen are sufficient to cause rapid build-up of hydroxyl radical through the bimolecular reactions. Again the ignition is almost spontaneous. Another factor which has not been included in this analysis is the effect of NO and/or NO_2 content on the ignition delay. These species have been shown to have a catalytic effect on the ignition process. Nonequilibrium inlet conditions for both the vitiated air and heated air have enough NO present to catalyze the induction process. This further tends to substantiate the argument that the use of heated air or vitiated air for ground testing of supersonic combustion with hydrogen will yield extremely short ignition delays under the conditions investigated. This may mean

that mixing will be rate-controlled such that the distance between the test section entrance and the flame front may represent for the most part the mixing length.

Supersonic combustion under free-flight conditions may correspond more closely to equilibrium initial conditions. In that event neither heated air nor vitiated air can be used to simulate supersonic combustion performance under free-flight conditions in the regime where reaction times are rate-controlling.

EXPERIMENTAL PROGRAM

The experimental program discussed in this report was concerned with the ignition lag effects with vitiated air. A follow-on effort is now underway in which the effects of vitiated air on overall combustion efficiency will be investigated. Most of the hardware for both programs was designed and fabricated in this phase of the program. Therefore, some of the hardware described herein is not actually utilized for the purpose of obtaining ignition lag information, but will be employed in the follow-on program.

Sizing of the experimental apparatus was based on the criteria that the supersonic test section should be large enough to minimize scale effects and small enough so that test costs were not prohibitive. It was also desirable that the design conditions simulate a flight regime in which the SCRAMJET vehicle might be expected to operate; however, this regime should be chosen so that ignition delay times could be readily measured.

Design conditions selected for the gas generator were: chamber pressure = 1000 psia, chamber temperature = 2200°K and flow rate = 15 pounds/second. The design operating conditions for the gas generator and supersonic combustor are shown schematically on Figure 18. These conditions approximately simulate a flight Mach number of 6.5 at an altitude of 80,000 feet, a regime that should be of interest for SCRAMJET application. The equipment size and

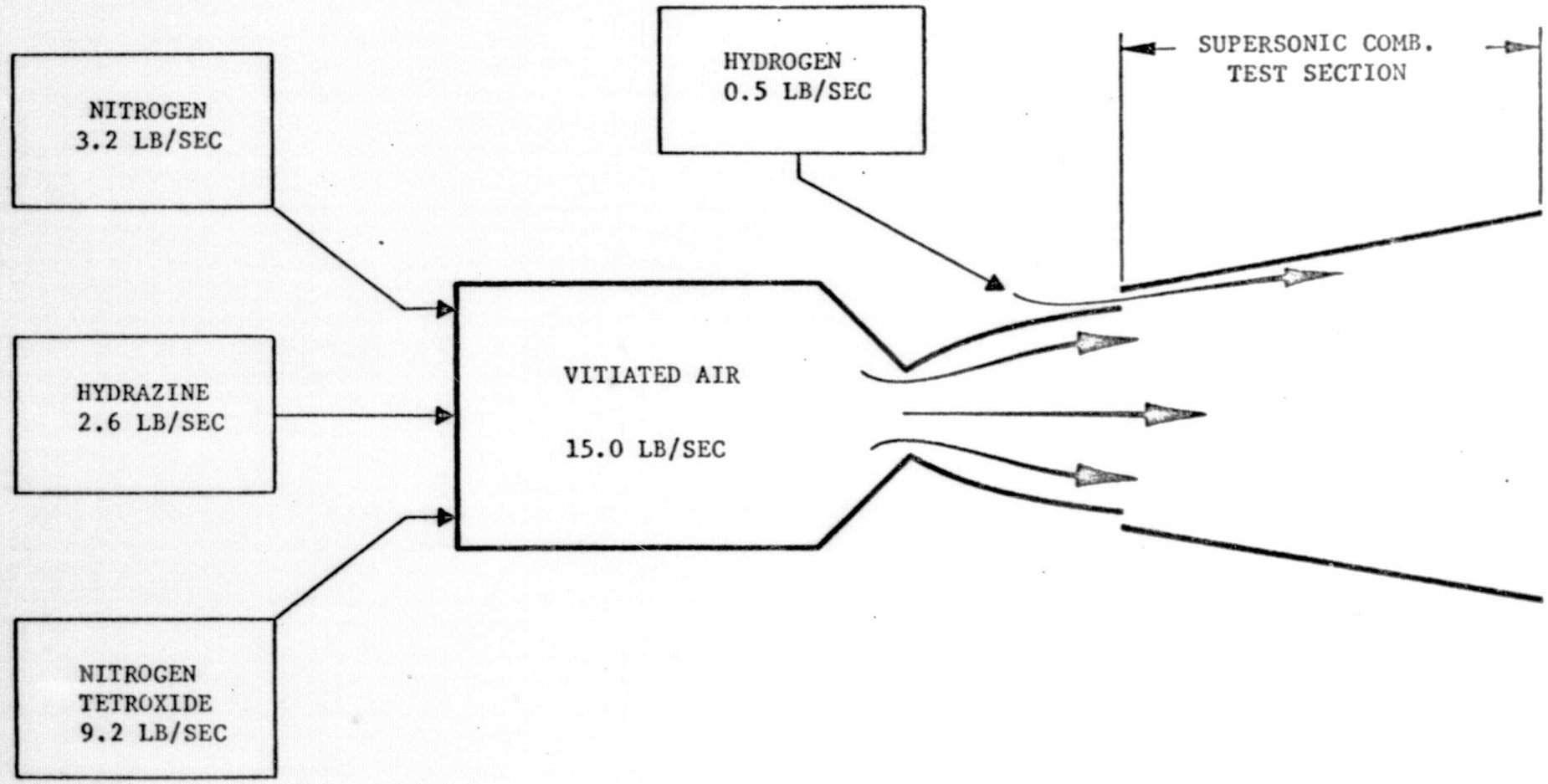


FIGURE 18 SCHEMATIC OF EXPERIMENTAL SET-UP

propellant flow rates were well within the limits of the existing research facilities at the Jet Propulsion Center, Purdue University.

In the ignition lag experiments, the gas generator gases and hydrogen stream were expanded to atmospheric pressure. The combined streams were permitted to mix and burn in an unconfined manner as a free jet. The absence of a confining wall made it possible to visually observe the flame front and determine the induction distance. A solid wall near the reaction zone often catalyzes the combustion process by either surface reactions or through a temperature increase due to viscous dissipation (23). In addition the flow pattern (recirculation) becomes more complex. By examining ignition in a free-jet, the ignition lag effects should be theoretically predicable providing the reaction mechanism is selected properly.

Design pressure for the supersonic test section is 25 psia. Since the ignition lag study was conducted with the test section at 14.7 psia, the gas generator was operated at less than design chamber pressure for these experiments. Chamber pressure in the gas generator was set at 600 psia for the ignition lag experiments, while the basic hardware remained unchanged except that the supersonic test section was removed.

The experimental data reported here is divided into two parts. The first part discusses the gas generator experiments made for the purpose of balancing propellant flow rates, establishing combustion efficiency in the gas generator, and verifying the performance of

the optical system. A limited number of experiments are reported in the second part where the full supersonic combustion system was operated to determine ignition lag lengths with vitiated air. The follow-on program will first extend the experimental results for ignition delay times and then examine combustion efficiencies for vitiated air and hydrogen.

Description of Hardware

In this section, the main elements of the experimental hardware are discussed briefly under separate headings.

Gas Generator

The components of the gas generator include an injector, two chambers, a turbulence ring and a nozzle. An assembly drawing of the gas generator components is presented as Figure 19. The chamber temperature in the gas generator is 2200°K and the walls of the nozzle and chambers are uncooled. However, the hot surfaces are coated with a high temperature ceramic material (zirconium oxide) which forms a thermal barrier between the stainless steel wall and the chamber gases. The coating material is flame-sprayed on the wall in four separate layers. The bottom layer is a bonding coat of nickel-aluminide. Each succeeding layer contains a larger amount of zirconium oxide (mixed with nickel-aluminide) until the top coat which is pure zirconium oxide. Some problems were experienced in attempting to coat the throat of the nozzle. After roughening the inner surface with a coarse file and hand manipulating the flame spray rig, it was possible to obtain a

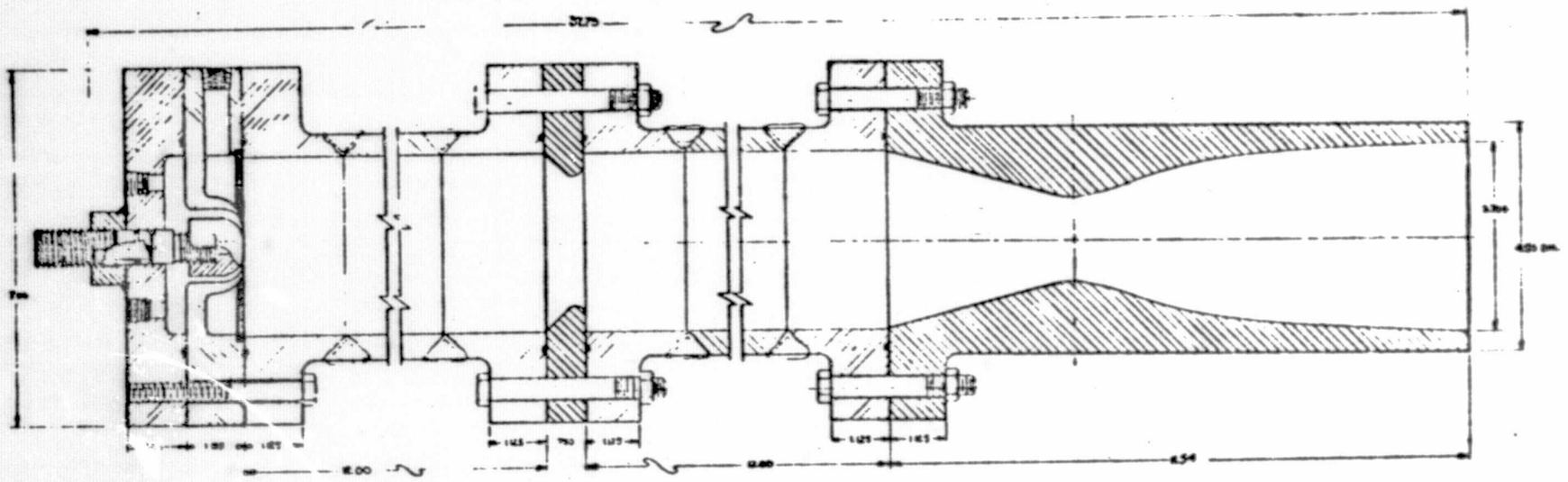


FIGURE 19 GAS GENERATOR ASSEMBLY

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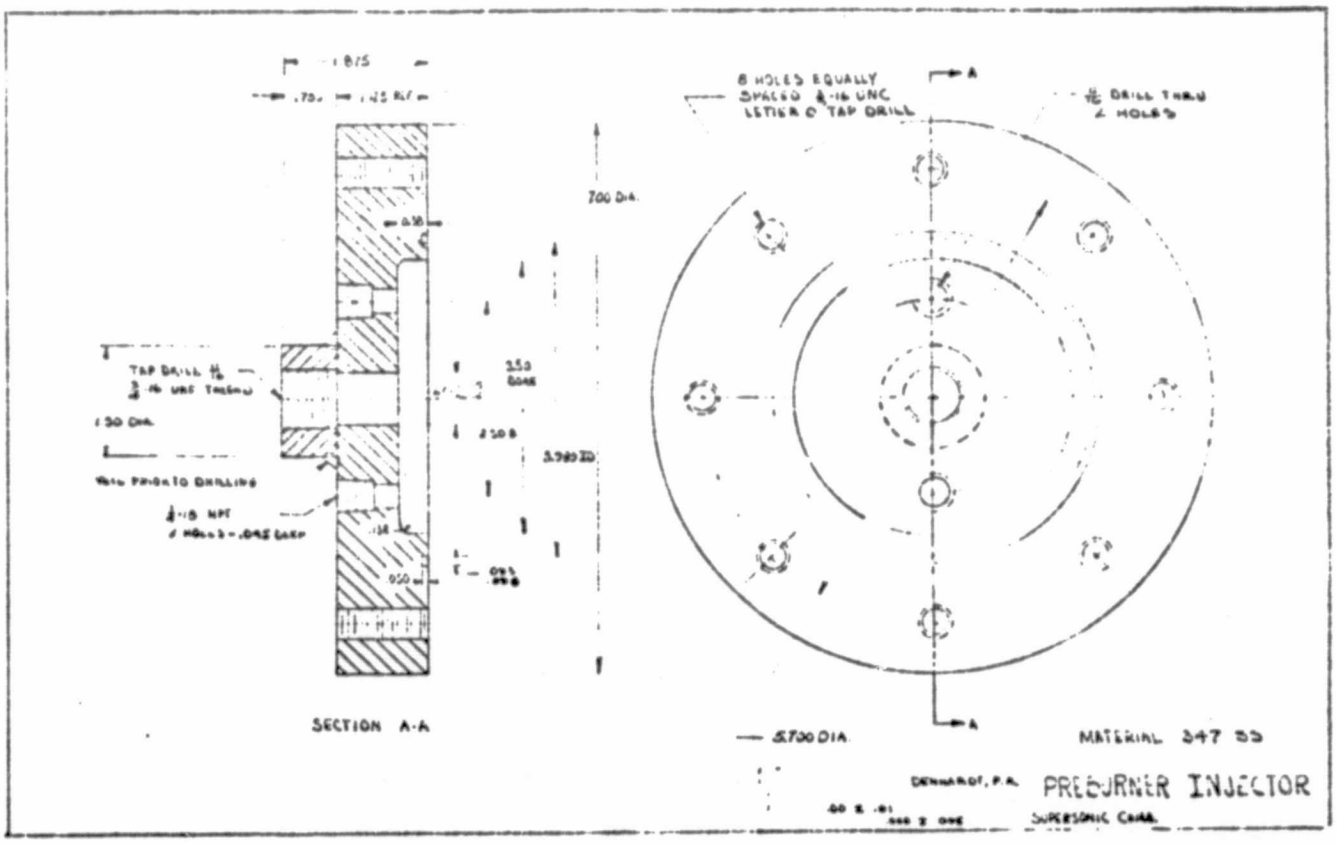
reasonably good coating in the nozzle throat region.

The components of the gas generator assembly were made from type 347, stainless steel. This material has relatively good heat resisting qualities and is compatible with both nitrogen tetroxide and hydrazine. The chambers were flanged on both ends with "O" ring grooves on the sealing surfaces. Material for the "O" rings was Viton A manufactured by Parker Seal Company. The seals were replaced each time the engine was disassembled; they did not show any signs of a leakage.

The two chamber sections were separated by a turbulence ring. The purpose of the turbulence ring was to promote mixing in the hot gases to insure a relatively uniform exhaust stream. It also was coated with zirconium oxide on the inner surface as a thermal barrier against the combustion gases.

The gas generator injector has three separate elements, two of which are shown as Figure 20. The upper half of this figure shows the oxidizer inlet housing with a pintle retainer along the center-line. The lower portion of Figure 20 shows the nitrogen inlet which has a porous metal face in the area exposed to the combustion gases. The diluent nitrogen is introduced into the combustion chamber through a porous metal surface and thus serves to cool the entire injector face. The injector pintle serves to introduce the hydrazine into a combustion chamber and together with the nitrogen inlet housing forms an annulus for injecting the oxidizer. A close-up photograph of the injector face and pintle is presented in

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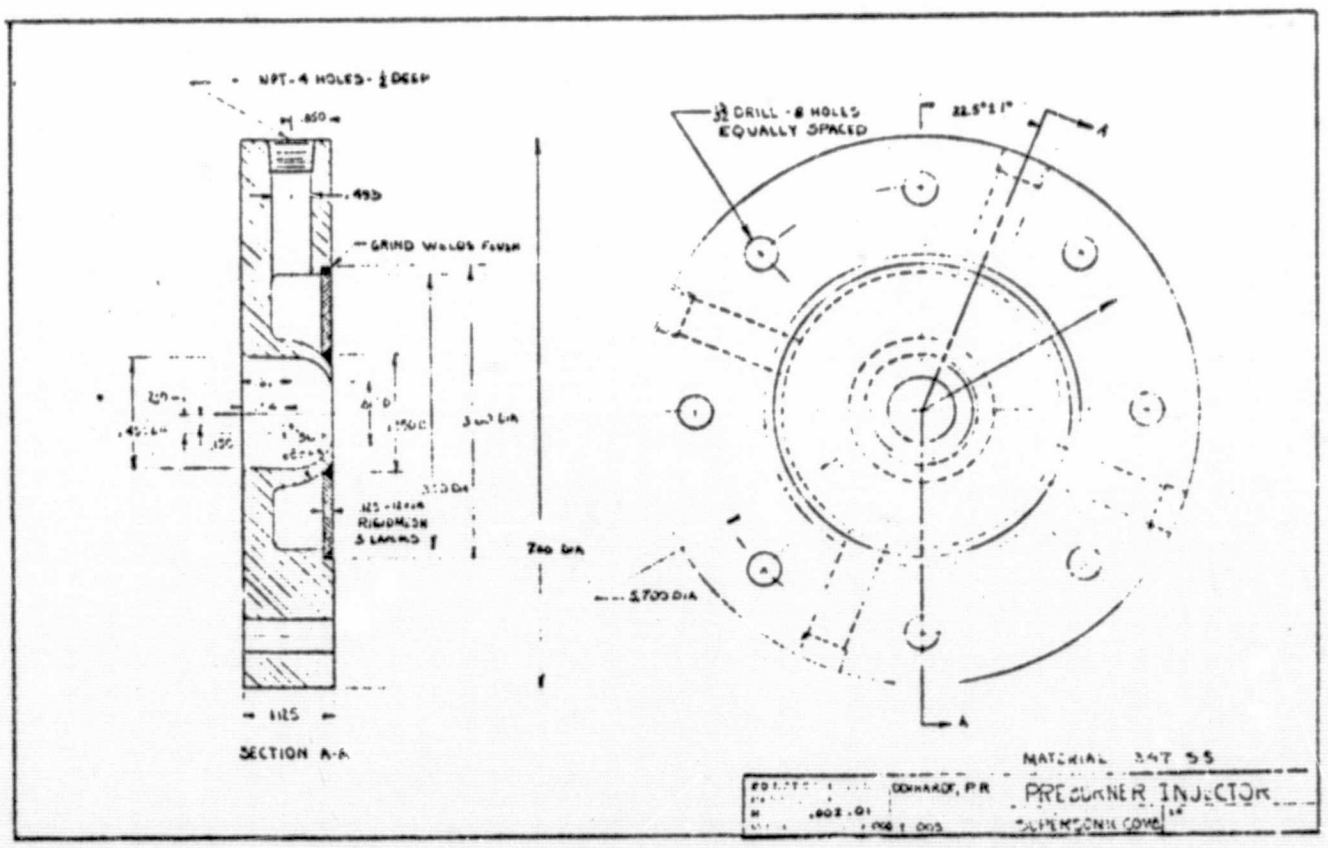


FIGURE 20 GAS GENERATOR INJECTOR

Figure 21. The pintle contains ten hydrazine injection parts of 1/16 in. diameter. The width of the annular passage for the oxidizer can be varied by turning the pintle assembly in or out. This feature permits some adjustment of the injector pressure drop to help avoid low frequency combustion instability problems.

The gas generator nozzle was designed for uniform, parallel flow across the exit plane. Design of the exit contour was accomplished by utilizing a computer program which solves the two-dimensional, axisymmetric flow relations by the method of characteristics. This program requires as input: (1) the gas properties, (2) the upstream and downstream blend radii, (3) the throat radius and (4) the design Mach number. A start line is calculated in the nozzle throat region using Sauer's method. A solution to the flow in the kernal is run out to the point where the Mach number on the axis corresponds to the design value. Then the exit characteristic is generated assuming the flow angle is zero. The exit characteristic is terminated when the mass flow equals that computed for the start line. A complete wall contour is calculated by solving the characteristic relations in the previously undefined region. A plot showing the complete characteristic network for the parallel flow nozzle is presented in Figure 22. This is a cross-sectional view of the nozzle exit section divided at the centerline. The computer program assumes constant values for the ratio of specific heats and for the molecular weight of the mixture. This assumption, while

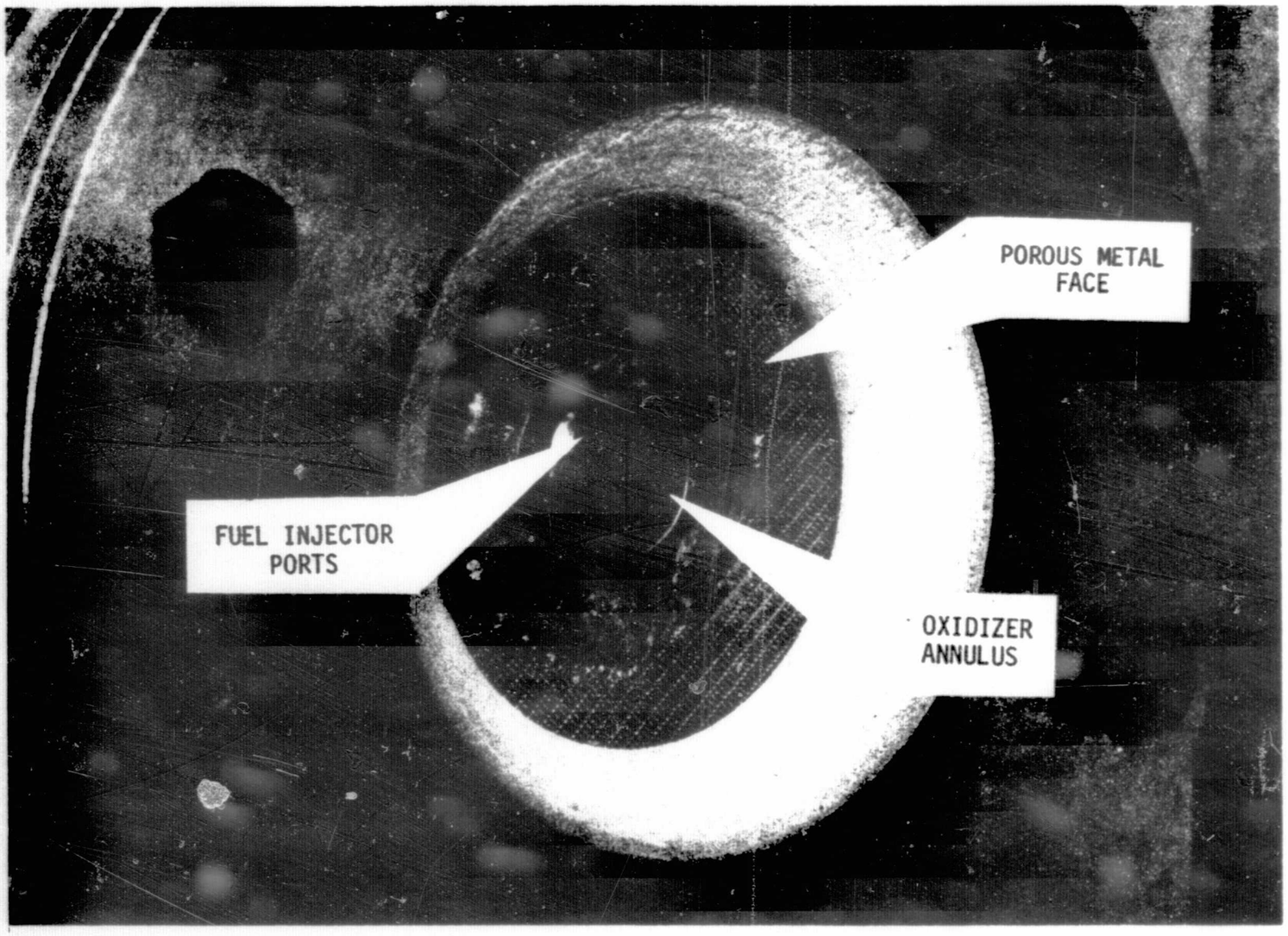


FIGURE 21 INJECTOR FACE AND PINTLE

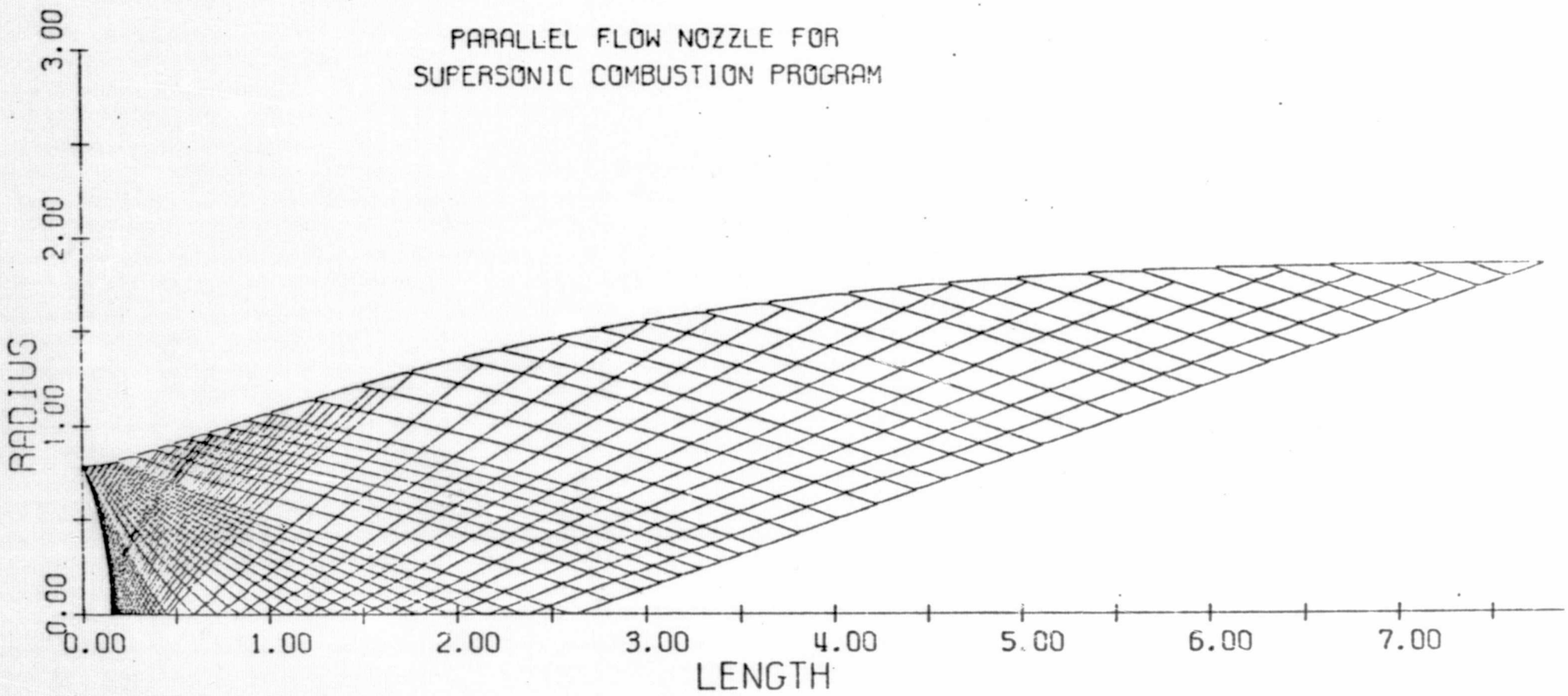


FIGURE 22 CHARACTERISTIC NETWORK FOR PARALLEL FLOW NOZZLE

esthetically displeasing, yields a good approximation to the contour coordinates calculated for real gas conditions. The parallel flow nozzle had a throat diameter of 1.596 in. and an overall area ratio of 5.38.

Hydrogen Heater

The hydrogen heater was designed and fabricated by Thermal Transfer Corporation of Monroeville, Pennsylvania. This unit consists of a large stainless steel coil which is heated by convection and radiation from the combustion products of three propane burners. A photograph of the installation of the hydrogen heater is presented in Figure 23. The heater is located outside the test cell perimeter as a safety precaution. Design specifications on the hydrogen heater are presented in the following tabulation:

Hydrogen Heater Specifications

Total Heat Input	BTU/HR	20.0×10^6
Design Operating Pressure	PSIG	325
Excess Combustion Air	%	50
Waste Gas Volume	S.C.F.M.	3,190
W. G. Temp.-entry	^{o}F	2,700
exit	^{o}F	1,400
Thermal Efficiency	%	30
Hydrogen Flow	#/sec	0.5
Hydrogen Temp.-entry	^{o}F	70
-exit	^{o}F	1040

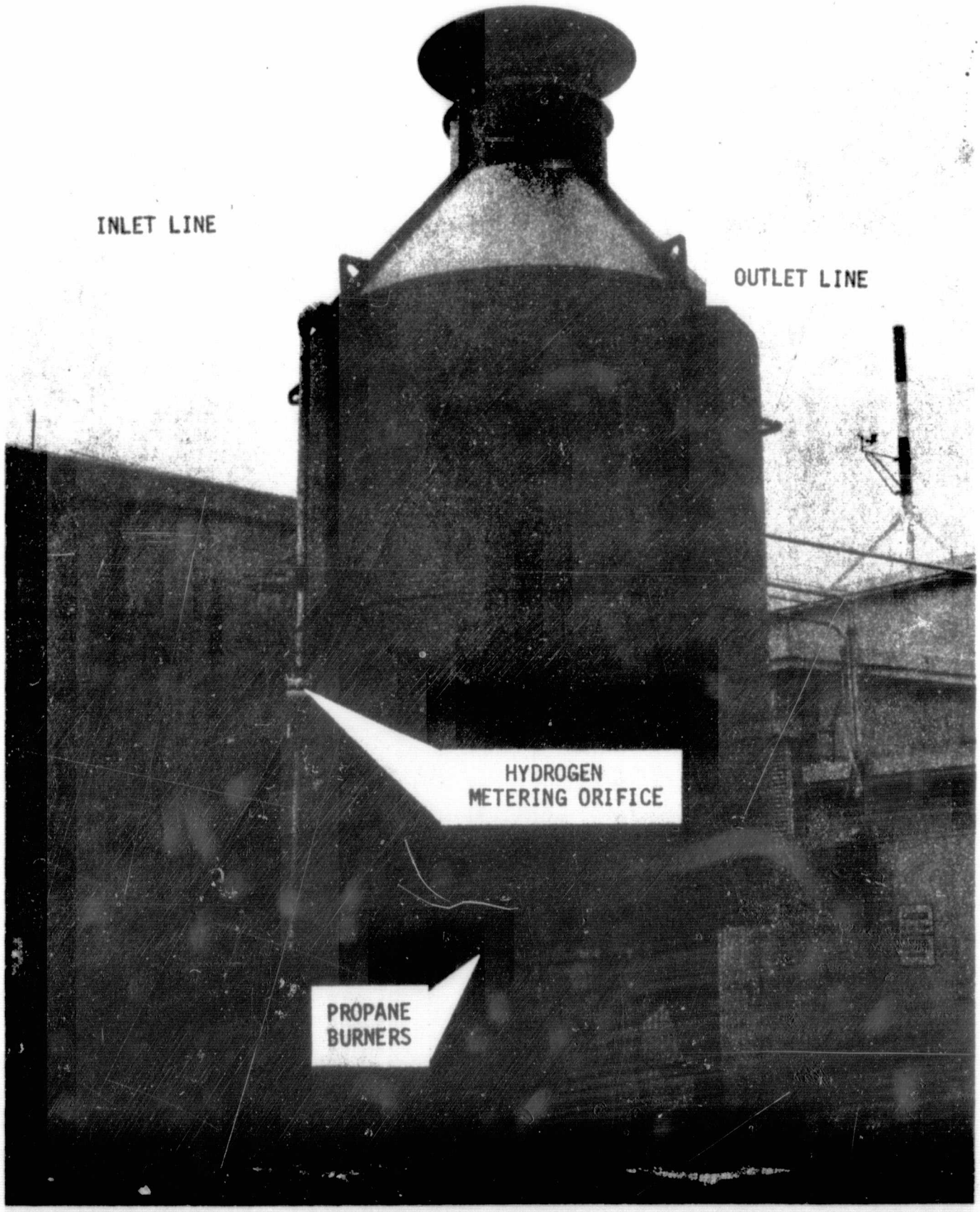


FIGURE 23 HYDROGEN HEATER INSTALLATION

The combustion system for the heater consists of a main shut-off valve, which can be operated either manually or automatically, and a multiple National Airoil burner arrangement equipped with spark ignited pilots. A flame safety system shuts off fuel to the burners in the event of excessive temperatures measured on the tube wall or in the exhaust stack gases. The heater is relatively simple to operate and performed quite well in the limited number of experiments conducted to date.

Supersonic Test Section

Three separate components make up the supersonic test section. These are (1) a hydrogen manifold, (2) a constant area mixing section, and (3) a divergent supersonic combustor. The latter two components are not employed in the experiments reported here.

Design details of the hydrogen manifold are presented on Figure 24, which is a photoreduction of the fabrication drawing. The manifold was machined from a single billet of type 347, stainless steel. After careful alignment, the manifold was welded to the exit section of the parallel flow nozzle. The mating of the hydrogen manifold and nozzle exit section is such that an annulus is formed between them. The hydrogen is expanded to sonic conditions as it passes through the annulus. A photograph showing an aft view of the hydrogen manifold is presented as Figure 25. The exit lip of the parallel flow nozzle is approximately a tenth of an inch width. This dimension was made as small as possible to

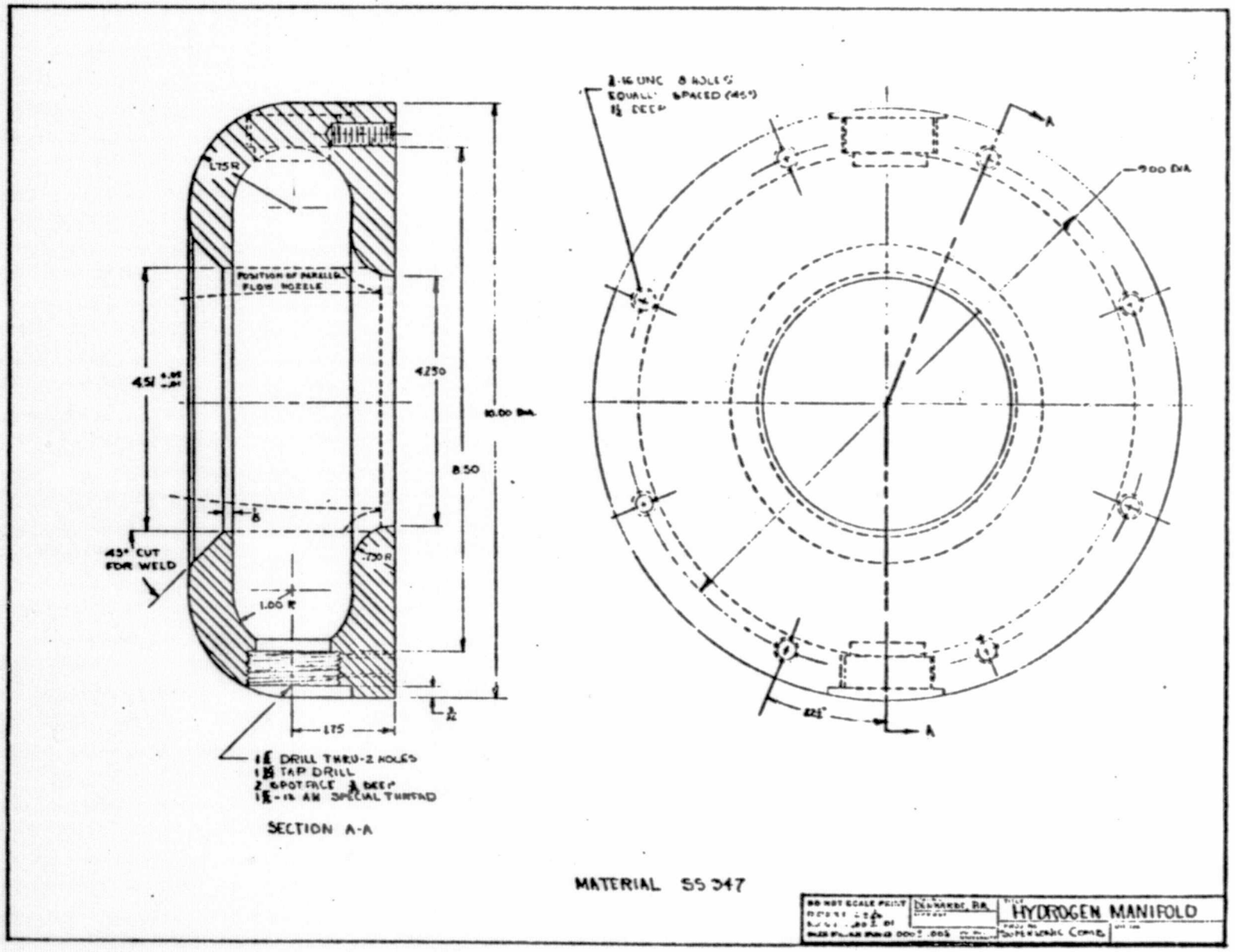


FIGURE 24 HYDROGEN MANIFOLD

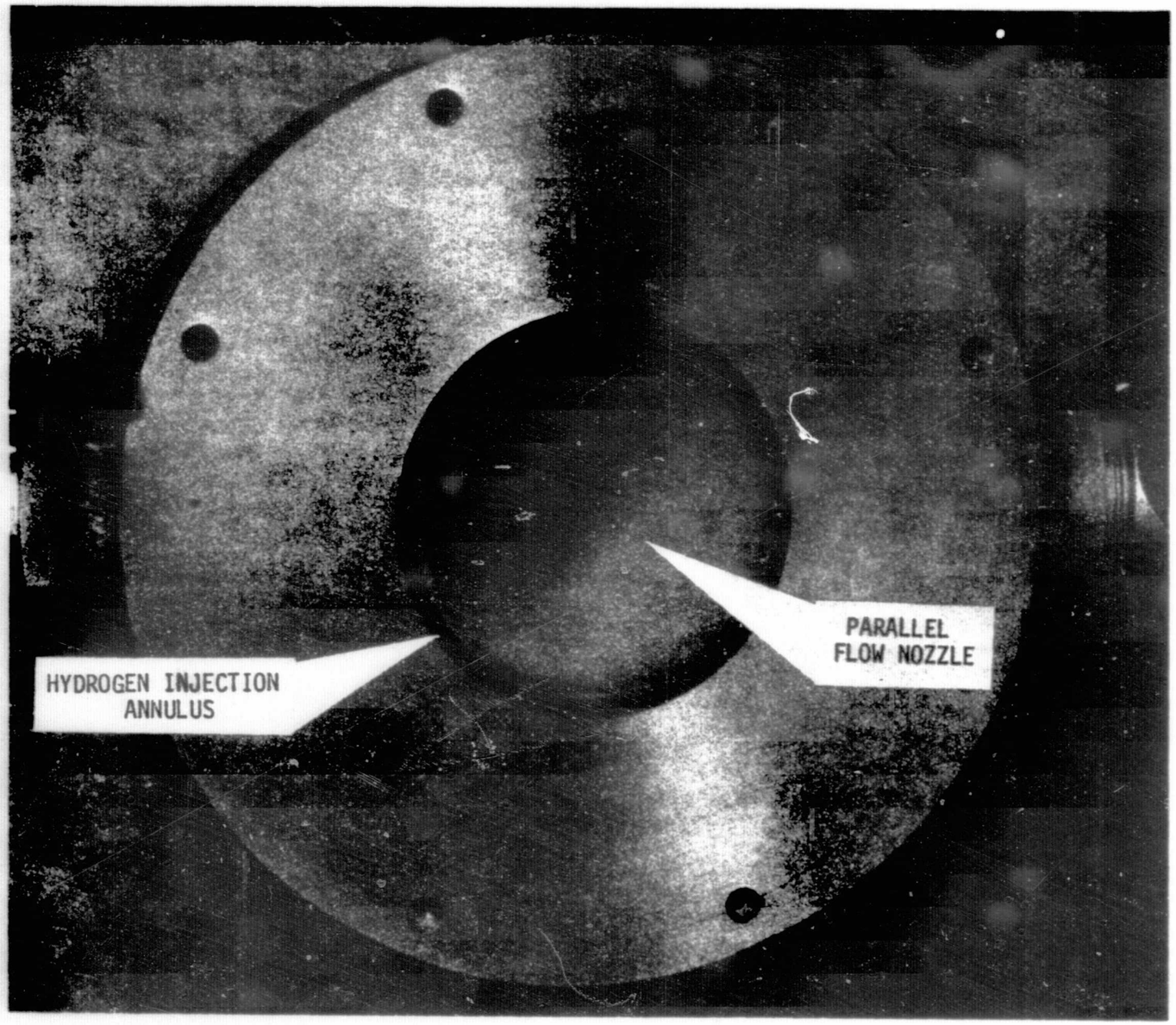


FIGURE 25 AFT VIEW OF HYDROGEN MANIFOLD

minimize flow recirculation problems in this area but large enough to maintain some structual strength.

The constant area mixing section has an inside diameter of 4.25 inches and is 5.0 inches long. Type 347, stainless steel, is the material from which mixing section and combustor section are fabricated, and the inner walls are coated with zirconium oxide to protect the metal from the hot gases. The combustor section has a conical shaped wall which diverges at a 5 degree half angle. Overall length of the combustor is 12.75 inches and the exit diameter is 6.37 inches. An aft view of the entire supersonic test section assembly is presented in Figure 26.

Description of Instrumentation

The basic instrumentation employed in the experimental program is summarized in Table 4. This tabulation includes all the pressure transducers, flow meters, and thermocouples utilized in the ignition lag experiments. A photocon transducer was employed in a few of the gas generator performance evaluations to determine whether the system exhibited any high frequency pressure oscillations. During these experiments the photocon data indicated there were no stability problems with the system. In an attempt to extend the run durations from three seconds to six seconds, the photocon transducer burned up and all later testing was conducted without obtaining any high frequency data. A photograph showing the photocon installation after the mishap is presented as Figure 27. Most of the damage occurred within the parallel flow

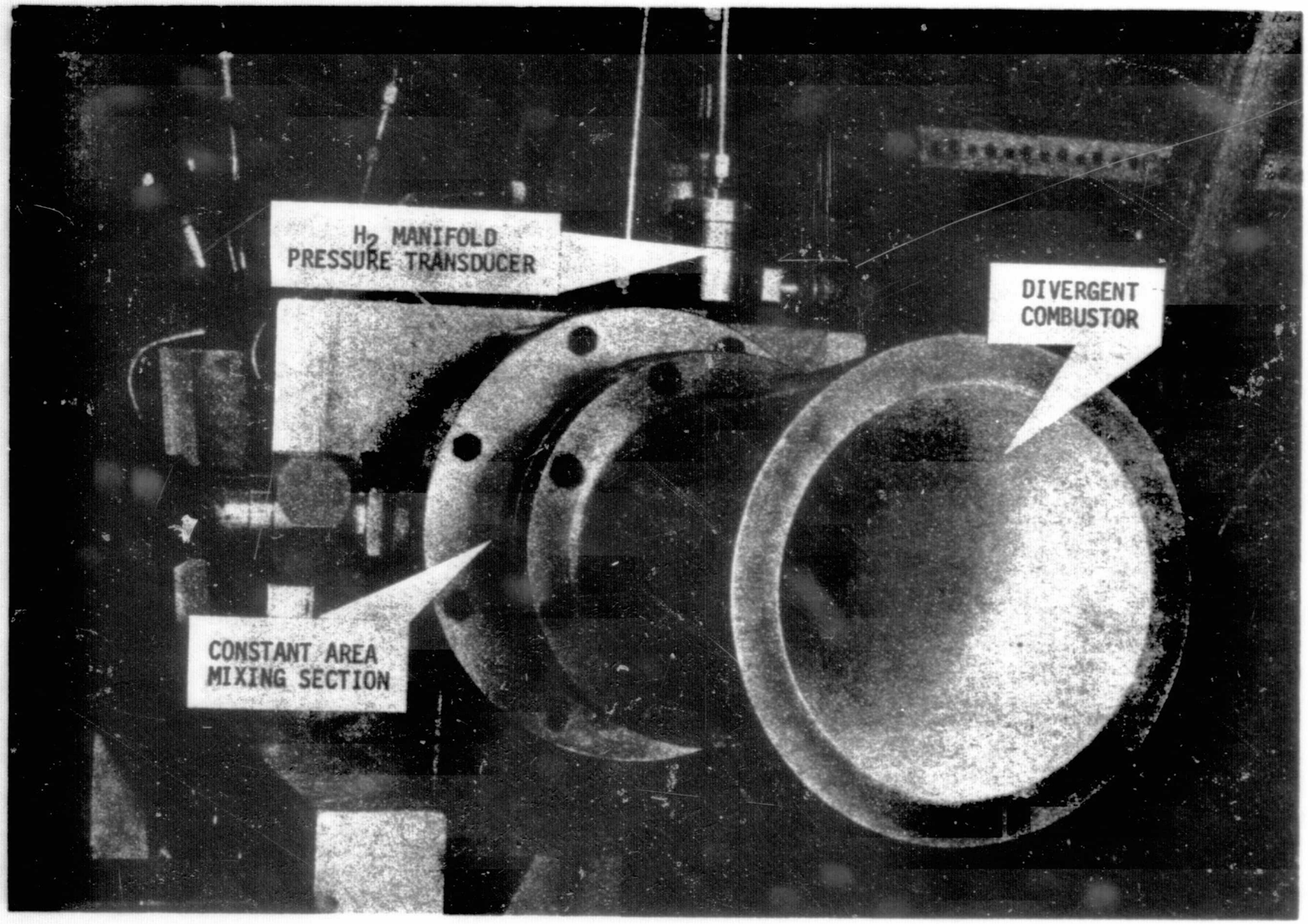


FIGURE 26 AFT VIEW OF SUPERSONIC COMBUSTOR TEST SECTION

TABLE 4

INSTRUMENTATION SUMMARY

Parameter to be Measured	Instrument Manufacturers and Model Number	Operating Range	Recording Instrument
1. G.G. Chamber Pressure	Tabor, 206-DB	0-1500 psig	Strip Chart & Oscillograph
2. N_2 Line Pressure	Tabor, 206	0-2000 psig	Strip Chart
3. N_2 Orifice Diff. Pressure	Tabor, 2102	±150 psid	Strip Chart
4. Fuel Tank Pressure	Tabor, 2301	0-2000 psig	Strip Chart
5. Oxidizer Tank Pressure	Tabor, 250	0-5000 psig	Strip Chart
6. H_2 Manifold Pressure	Tabor, 254	0-50 psia	Oscillograph
7. H_2 Line Pressure	Tabor, 217	0-200 psig	Oscillograph
8. H_2 Orifice Diff. Pressure	Tabor, 2102	±100 psid	Oscillograph
9. G.G. Chamber Pressure	Photocon, 352A	0-5000 psig	Oscillograph & Digital Tape
10. Fuel Flow	Pottermeter, 3/4-5550	0-30 gpm	Strip Chart
11. Oxidizer Flow	Pottermeter, 2-1/2=5971	0-400 gpm	Strip Chart
12. Gas Temperatures for N_2 Manifold	Iron-Constantan Thermocouples	0-1500°F	Strip Chart & Oscillograph

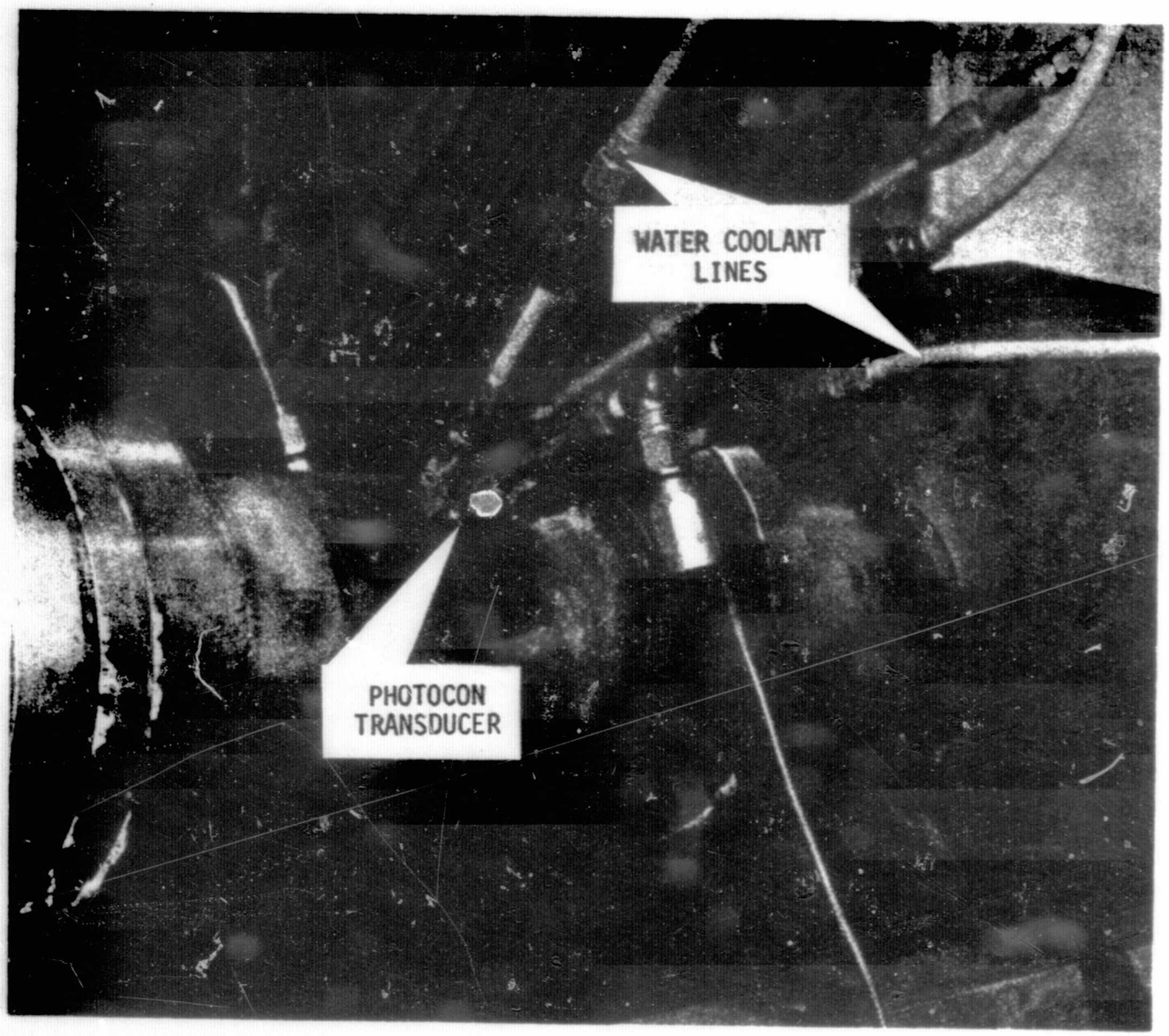


FIGURE 27 PHOTOCON INSTALLATION

nozzle although the inner wall of the combustor showed signs of local melting and erosion.

In the combustion efficiency experiments, which will be conducted in a later program, the static temperature profile across the supersonic combustor exit will be measured optically utilizing an intensity comparison scheme. The apparatus for making these measurements was developed in the present program. Several preliminary experiments were run to evaluate the basic concept and to prove the system would operate in the test environment. In these experiments, the optical system was operated in conjunction with the gas generator and employed to measure the static temperature of the vitiated air exhausting from the parallel flow nozzle. A photograph showing the placement of the optical system for the check-out experiments is presented on Figure 28.

The optical system consists of a modified sodium line, reversal pyrometer mounted on a base which moved vertically to permit the pyrometer to scan the hot gases across the plane of the combustor exit. Light from a tungsten strip lamp is focused on the center of the exhaust stream. The light beam is mechanically chopped at a rate of 120 times per minute by a four blade element driven by synchronous motor. The chopper is located between the strip lamp and first condensing lens. The resultant light beam is then focused by a second condensing lens on the entrance slit of a monochromator where the intensity of the Sodium D-line is measured by a photomultiplier tube. Two intensity levels

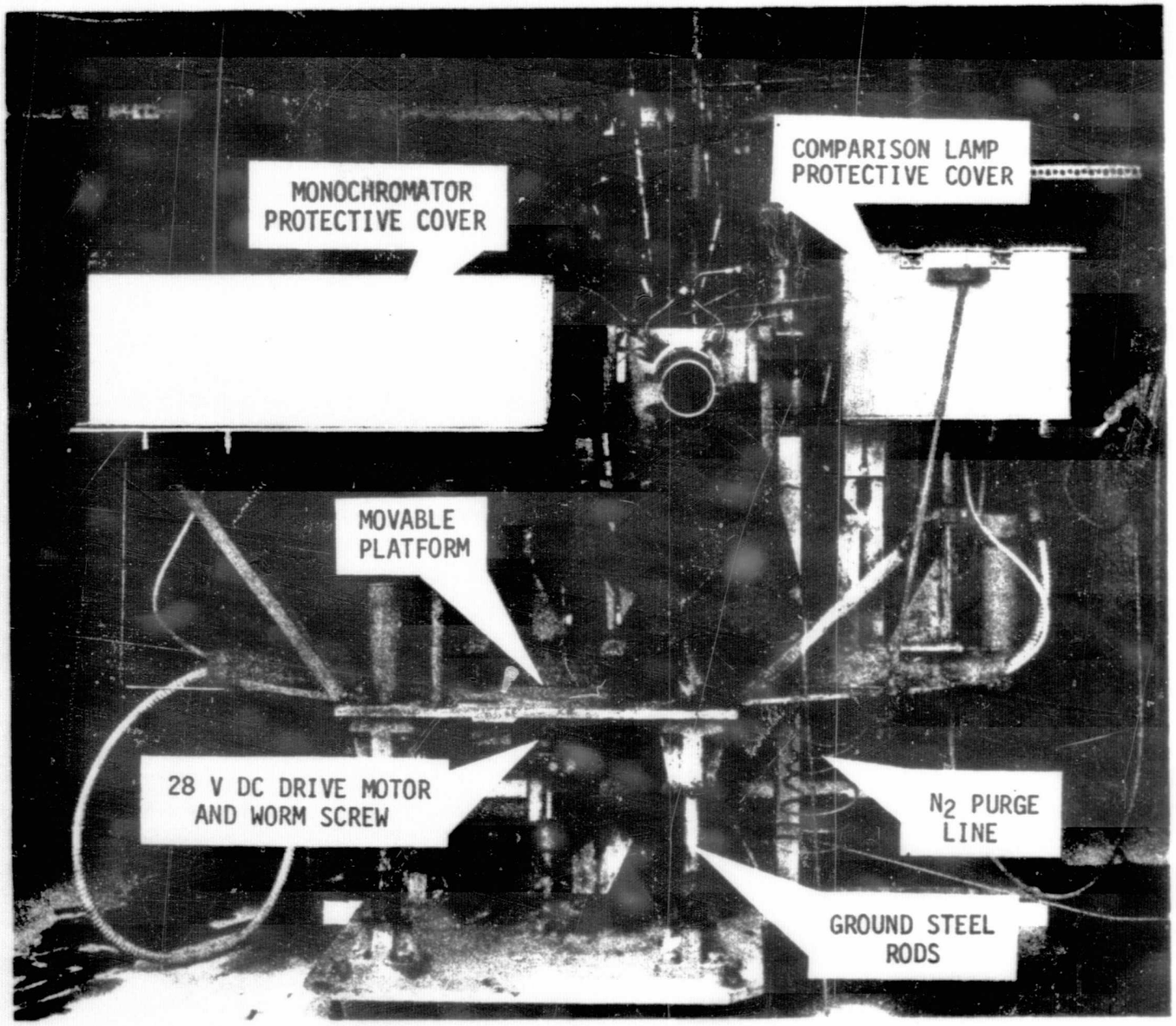


FIGURE 28 PYROMETER HOUSING AND TRAVERSAL MECHANISM

are observed, one with flame plus strip lamp and the other with the flame alone. Since the tungsten strip lamp has been calibrated such that its temperature as a function of voltage supplied (at the wavelength of the Sodium-D line) is known, the different intensity levels will permit a calculation of the line of sight average temperature of the flame.

The entire lamp-lens-monochromator assembly is moved vertically utilizing a d.c. motor and worm screw combination to 14 scanning stations during a single test firing. These 14 line of sight intensity measurements are then converted mathematically to a radial intensity-to-temperature profile using the Abel integral transform technique. Additional details concerning the mathematical procedure used to calculate the temperature profile can be found in reference 24 along with a comprehensive description of the optical system designed for this program.

To more completely describe combustor performance from experimental results, a thorough knowledge of the spatial distribution of pressure and specie concentration in the combustor exit plane is required. From these properties and the temperature profile, certain performance parameters can be defined by comparison with the parameters that would result from ideal process. The technique involves measuring as many properties as possible and determining the others through iteration of the integral equations of flow.

The instrumentation to be used in the combustor exit plane

is shown in Figure 29 and is a modified version of a probe assembly used at the Applied Physics Laboratory of John Hopkins University. Six pitot total pressure probes and six gas sampling probes are made from concentric pairs of tubes in which water in the annulus is discharged overboard approximately 3/32" downstream of the probe tip. The inner tube of the gas sampling probe has a sharp lip and a 12:1 internal area expansion which has the purpose of partially quenching any chemical reactions inside the tube. Due to the low pressure at which the manifold will be maintained, the external shock will be swallowed by the sampling probe. The gas samples will then pass to a set of six valved storage bottles. The samples will be analyzed by means of a Bendix Time of Flight Mass Spectrometer.

The complete probe assembly and associated collection equipment were fabricated in the present program. Experimental evaluations of the probe assembly will be accomplished in the overall combustion efficiency program.

Experimental Results

The experimental program is broken down into two phases. In the first phase, the gas generator was developed to a point where it could be operated with a high degree of reliability. It was also necessary to demonstrate that the gas generator would operate at high combustion efficiencies ($\eta_c \geq 96\%$) in order that the gas composition and state properties can be calculated

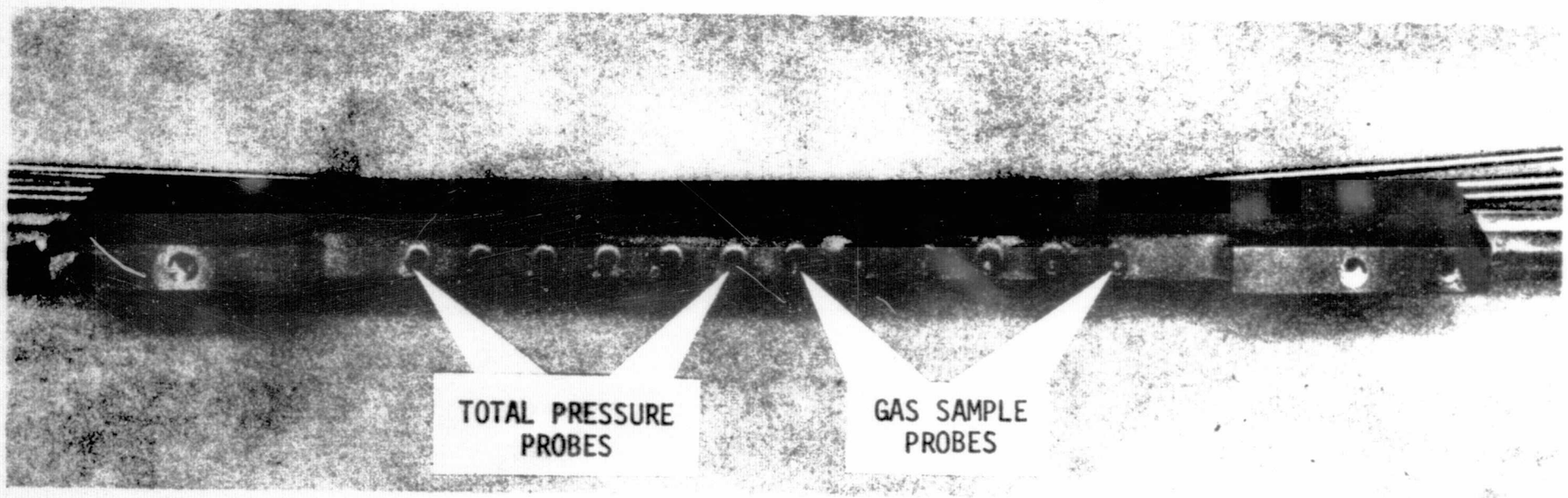


FIGURE 29 TOTAL PRESSURE AND GAS SAMPLE PROBE

by theoretical techniques. For this reason, the gas generator had a large characteristic length ($L^* \sim 120$) and a turbulence ring to promote mixing and complete combustion of the exhaust products. After the gas generator was operating satisfactorily, the supersonic combustion experiments were undertaken. This constituted the second phase of the experimental program. Results from each phase of the experimental program are discussed separately in the following sections.

Gas Generator Experiments

The purpose of the initial experiments was to balance the propellant flows by establishing line and injector resistances. This information is employed to set the propellant tank pressures for the desired flow rates of each propellant. The fuel employed for the first eight gas generator experiments was a 50/50 blend of hydrazine and unsymmetrical dimethylhydrazine. As a propellant, the 50/50 blend is much easier and safer to handle than pure hydrazine. It also has better thermal stability and shock sensitivity characteristics than hydrazine. These factors were demonstrated quite vividly during the first series of experiments that employed pure hydrazine as a fuel. Just how this was demonstrated is discussed later.

A summary of the performance results from the first eight gas generator experiments is presented in Table 5. This tabulation includes propellant tank pressures and flow rates, chamber

TABLE 5

GAS GENERATOR EXPERIMENTS (A)

Propellants: N_2O_4/50% N_2H_4 - 50% UDMH/N_2

Run No.	1	2	3	4	5	6	7	8
Date	12/14/67	12/14/67	12/14/67	1/26/68	1/26/68	1/26/68	1/30/68	1/30/68
Oxidizer System								
Tank Pressure (psig)	1413	1340	1313	1565	1820	1870	2150	2370
Flow Rate (lb/sec)	9.16*	8.41*	8.21	6.18	7.33	7.33	8.90	10.0
Fuel System								
Tank Pressure (psig)	1750	1610	1620	1460	1490	1760	2090	2140
Flow Rate (lb/sec)	3.31	3.56	--	1.83*	1.86	2.24	2.53	2.62
Nitrogen System								
Line Pressure (psig)	1516	1640	1620	1580	1546	1760	1620	1624
Differentail Pressure	100.5	111.0	112.0	--	82.5	100.5	103.0	96.0
Flow Rate (lb/sec)	3.14	3.42	3.42	2.84*	2.80	3.35	3.27	3.18
Chamber Conditions								
Chamber Pressure(psia)	915	925	905	795	805	908	990	1035
Flow Rate(lb/sec)	15.61	15.39	--	10.85	11.99	12.93	14.7	15.8
C* (measured)	3770	--	--	--	--	--	--	--
C* (theoretical)	4640	4680	--	4210	4130	4260	4330	4300
C* Efficiency	0.812	0.827	--	1.10	1.047	1.062	1.00	0.979
Purpose	Balance System			Balance System and Check Out Optical Instrumentation				
	Oxidizer flometer did not function	Recording pen dry on oxide. scale flow record	Fuel flow went off	Fuel flow recorder spanned incorrectly				
	← Fuel swirler worked out of position in these expirements →			Nitrogen differential pressure had wrong polarity				

*Flow rates calculated from line resistances.

pressure, a measured characteristic velocity (C*), and a C* efficiency. The theoretical characteristic velocity employed to determine the C* efficiency was calculated from an equilibrium thermochemistry computer program. Performance for the first three tests was quite low, indicating problems with the gas generator injector. The gas generator was disassembled and the problem was found to be the fuel swirler in the injector pintle. The initial design of the fuel injection system had a single port with a twisted ribbon of stainless steel in the injector pintle. This swirler was press fit in place before installation. During the first three tests, the swirler worked loose and had actually moved about one-half inch away from the port exit. Prior to reassembling the gas generator, the swirler was again wedged in place and a retaining washer added to ensure the swirler would remain in place.

Performance for the latter five experiments, shown in Table 5, was quite good, approaching 100 percent C* efficiency in all cases. The fact that some of the values reported are greater than 100 percent C* efficiency may be due to (1) an error in the theoretical C* calculation, (2) discrepancies in the flow rate measurements, and/or (3) an error in the chamber pressure reading. Since the primary purpose of these experiments was to balance the propellant flow system employing the 50/50 fuel blend, a detailed analysis of the performance discrepancies was not undertaken. However, every attempt was made to keep

TABLE 6

GAS GENERATOR EXPERIMENTS (b)

Propellants: $N_2O_4/N_2H_4/N_2$

Run No. / Date	9 2/22/68	10 3/5/68	11 3/19/68	12 3/26/68	13 3/26/68	14 3/26/68	15 4/4/68	16 4/29/68	17 4/10/68	18 4/29/68	19 5/22/68	20 5/22/68	21 5/23/68	22 5/23/68	23 5/23/68
Oxidizer System															
Tank pressure (psig)	2230	2050	2050	1980	1775	1410	1600	1500	1450	1420	800	760	760	870	770
Flow rate (lb/sec)	11.57	9.58	3.09	15.25	12.06	21.45	10.82	8.50	—	8.88	5.35	4.67	3.55	6.69	3.55
Fuel System															
Tank pressure (psig)	1905	1380	1480	1235	1340	1300	1320	1.40	1430	1300	785	794	820	760	8.5
Flow rate (lb/sec)	—	—	3.57	2.30	2.73	—	2.22	2.61	3.61	2.24	1.73	1.82	1.95	1.42	2.0
Nitrogen System															
Line pressure (psig)	1650	1640	1660	1666	1670	1660	1660	1660	1630	1610	985	970	968	957	947
Differential pressure	139.3	135.0	102.0	102.0	90.0	147.0	112.5	97.5	120.0	104.3	64.5	55.5	51.0	58.0	50.2
Flow rate (lb/sec)	3.76	3.50	3.3	3.37	2.94	3.95	3.45	3.25	3.52	3.22	2.08	1.95	1.86	1.99	1.81
Chamber Conditions															
Chamber pressure (psia)	170	173	911	990	1105	225	971	1090	615	942	625	630	630	585	630
Flow rate (lb/sec)	—	—	9.96	20.92	17.73	—	16.49	14.36	—	14.34	9.16	8.49	7.36	10.10	7.36
C* (measured)	—	—	5150	2670	3510	—	3320	4280	—	3700	3850	4180	4810	3260	4930
C* (theoretical)	—	—	4581	3990	4030	—	3817	4192	—	3964	4320	4610	4620	3890	4670
C* efficiency	—	—	1.12	0.75	0.872	—	0.87	1.02	—	0.933	0.89	0.905	1.04	0.839	1.057
Purpose	← Balance System for Hydrazine and Optical Instrumentation Checkout →														
Remarks	Fuel line ruptured at ignition	Fuel line ruptured at ignition. Changed fuel pintle for next test	Oxid. line resistances indicate error in flow reading			Oxid. line ruptured on prefire purge			Fuel tank ran dry						Burned out nozzle

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level of almost 200 psia to the fuel valve opening. Since the nitrogen purge pressure to the fuel line was less than 150 psia, the purge system may not have been completely effective in eliminating oxidizer blow back into the fuel line. A high pressure nitrogen purge system was installed for the next run and this eliminated any further fuel line mishaps.

The second fuel line explosion with hydrazine destroyed the swirler in the injector pintle. It was decided to redesign the pintle and eliminate the swirler in light of earlier problems. The new design incorporated ten small drilled ports in the pintle for fuel injection. This design is described in the previous section (Description of Hardware). The remaining gas generator experiments employed the multiport pintle design for the fuel injection system.

An oxidizer line ruptured during Run No. 14. The mishap occurred during the prefire purge before any of the main control valves had opened. A brief report was heard during the prefire purge, but it appeared to come from the gas generator chamber. However, when the main control valves opened, the chamber pressure failed to rise as expected, causing an automatic shutdown. Post fire inspection showed two of the four oxidizer inlet lines and check valves had blown apart. These two lines has low spots in them which were difficult to purge completely. New lines were added with the low spots eliminated to permit a complete flushing of the oxidizer inlet lines. No further propellant

line problems were encountered in the experiments.

The gas generator experiments up to and including Run No. 18 were operated at a chamber pressure of approximately 1000 psia. This corresponds to the design condition for the combustion efficiency experiments to be conducted in the follow-on program. A sufficient number of experiments were conducted to assure that the gas generator could be operated under design conditions and at a high performance level. Runs 16 and 18, shown in Table 6, correspond closely to the design operating condition. The average performance in these two experiments was sufficiently high to proceed to the next program objective.

The chamber pressure for the gas generator in the ignition lag experiments is 600 psia. This pressure level permits the gas generator exhaust products to expand to ambient pressure at the exit of the parallel flow nozzle. Runs 19 through 23 were conducted to balance the propellant flows and demonstrate combustor performance at the pressure level of the ignition lag experiments. After the first three runs in this series (19 through 21), the performance potential had been established and it was decided to attempt to extend the firing duration of the gas generator. Prior to Run 22, the firing durations were limited to approximately one second of steady-state operation. This was sufficient to obtain the necessary performance data. However, the optical system traversal mechanism requires about five seconds of steady-state operation for one complete

traversal of the exhaust stream. Therefore, a decision was made to progressively extend the firing durations for the next few experiments.

In Run No. 22, the steady-state firing duration was extended to three seconds. Then with Run No. 23, an attempt was made to extend the firing duration to six seconds. The firing was manually shut down in four seconds when problems were observed on the monitor from the remote TV camera. Postfire inspection revealed that the nozzle, chamber, and turbulence ring had sustained extensive damage. The damage consisted of severe burning and/or erosion of the hot-side walls, particularly in the nozzle throat region. These components had to be replaced prior to the next series of experiments. Two factors most likely contributed to this mishap. The first problem was that the gas generator operated off mixture ratio. The oxidizer-to-fuel ratio was much closer to stoichiometric than at design conditions resulting in a higher combustion temperature than anticipated. The uncooled hardware was designed to operate for approximately ten seconds at 2200°K chamber temperature. At the conditions encountered in Run 23, the chamber temperature was estimated to be about 230°K hotter than design conditions. Thus, the off-mixture ratio condition was certainly a factor contributing to the hardware damage. The other possible problem area that may have contributed to the mishap is related to the nozzle hardware. In one of the early gas generator tests, the nozzle throat started to erode. The eroded area was machined out with

a lathe and an insert fabricated to match the throat contour. The insert was coated with zirconium oxide and potted in place with a high temperature sealant. This insert had sustained several firings prior to Run 23. Postfire evidence indicates the hot gas worked its way behind the nozzle insert, thus causing rapid destruction of the nozzle hardware. The combined effects of these two factors was probably sufficient to cause the failure in this experiment. During the time required to fabricate new gas generator hardware, the hydrogen system was installed and preparations made for the supersonic combustion experiments to follow.

Several attempts were made to check out the optical system in the gas generator experiments. The thought behind the system checkout was that the relatively uniform temperature of the gas generator exhaust stream could be employed to establish the instrument precision of the optical pyrometer. Then using an optical system traversal of the exhaust stream to obtain a radiancy profile, a check could be made on the accuracy of the integral inversion technique for finding the temperature profile. These experiments met with limited success because the static temperature ($\sim 1000^{\circ}K$) at the nozzle exit was too low to produce a usable signal with the instrumentation available.

The optical system employs a modified sodium line reversal technique to measure the gas temperature. Thermochemical calculations indicate the exhaust gas temperature of the gas generator is $1015^{\circ}K$. Under these conditions the dissociation

of sodium hydroxide is very small, but there still should be a measurable emission and adsorption in this range. During the majority of the experiments, the emission detected was obscured by the noise level of the recording instruments. The signal-to-noise ratio was continually improved as the experiments progressed and sufficient data was recorded in Run 22 for a temperature calculation. The calculated temperature from the radiation measurements was 1180°K (see Ref. 24 for details). This temperature was somewhat higher than predicted by equilibrium thermochemical calculations. The error was traced to an instability in the lamp power supply. At the current setting employed in this experiment, the lamp brightness temperature fluctuated as much as 190°K, based on observations made after the firing. This can be corrected by increasing the power to the comparison lamp until it reaches a stable operating level and then using filters to reduce the brightness temperature.

In summary, the optical system was used with limited success to measure the static temperature of the gas generator exhaust stream. The experiments proved the pyrometer could operate in the test environment and produce a usable signal at low gas radiancies.

Supersonic Combustion Experiments

The supersonic combustion experiments were directed toward determining the effect of vitiated air on the ignition lag times

when burning hydrogen. Mixing and subsequent combustion of the hydrogen took place with the gases flowing as a free-jet without any confining walls. The static pressure for both streams at the injection station was 14.7 psia in an attempt to minimize shock interactions in the exhaust gases due to the surrounding atmospheric conditions. By permitting the gases to mix and burn in an unconfined exhaust stream, the flame front could be visually observed and recorded photographically. A solid wall in the vicinity of the flame front can often have a catalytic effect of the ignition process. This effect of the wall would be a function of scale size of the experimental equipment. The absence of a confining duct should permit the experimentally determined flame front to be a function of the true chemical kinetics of the reacting system of gases. There is a possibility of induction of ambient air into the mixing region of the hydrogen and vitiated air which would reduce the effective temperature of the mixture (longer delay time). The magnitude of this effect will be established by two experiments: (a) the oxygen in the vitiated air will be eliminated and (b) partial confinement of the ignition region with a plexiglas duct.

The vitiated air enters the supersonic test section at Mach 2.9 with a static temperature of 1000°K and a static pressure of 14.7 psia. The hydrogen stream is heated to 840°K in a stored energy heater, which burns propane to heat a large stainless steel coil. Injection conditions for the hydrogen are Mach 1.0 with a static temperature of 700°K and a static pressure of 14.7 psia. The relative velcoity ratio for the two streams at injection conditions was 1.08 (hydrogen/vitiated air).

These experiments had relatively large difference in static temp-

eratures for the hydrogen (700°K) and vitiated air system (1000°K) at test section conditions. The relative temperature difference for these two streams makes it difficult to establish a mean temperature of the gases prior to ignition. Injection of both streams at essentially the same temperature would eliminate this problem. If the hydrogen system was designed for a static temperature at injection equivalent to the vitiated air temperature, the heater would have to be designed to operate at 1200°K. The 840°K limit on the total temperature for the hydrogen was selected as a compromise to allow the use of relatively inexpensive materials in the construction of the hydrogen heater and the downstream hardware.

Operation of the full supersonic combustion experiments was considerably more complex than the gas generator alone. Safety is a primary concern when handling hydrogen. Precautions had to be taken to assure the gas generator products did not enter the hydrogen manifold at any time. A nitrogen purge system was employed to keep the hydrogen lines, heater, and manifold full of inert gas when the main hydrogen valve was shut off. This was accomplished by operating the main fuel valve for the hydrogen and the nitrogen purge valve off of the same pilot valve. Then when the main hydrogen valve is in the off-position, the nitrogen purge valve is open and when the hydrogen valve opens, the nitrogen purge valve closes. A separate valve located further upstream in the nitrogen purge line provides shut-off capability when the purge is not required.

Proper valve timing was essential for the supersonic combustion experiments. The main control valve for the hydrogen

system is a Jamesbury ball valve which is pneumatically actuated. This valve opens relatively slowly and is the last valve to open in the start sequence. The hydrogen valve is signaled to open by a pressure switch which indicates the gas generator has reached a satisfactory operating pressure level. Opening time for the main hydrogen valve is approximately one second. The time required to fill the heater, lines and manifold is also about one second, so that two seconds of steady state gas generator operation are necessary before the hydrogen reaches the supersonic test section. Thus for two seconds of steady-state operation of the supersonic combustor, the gas generator must be operated for at least four seconds. Previous experience with the uncooled gas generator had indicated that the structural capability of the hardware was marginal for four seconds of firing duration. If the coating material in the nozzle throat is adequately bonded to the steel wall, a firing duration of four seconds is not at all unreasonable.

There was approximately three months delay between the gas generator and the supersonic combustor experiments. This time was used to complete the installation and checkout of the hydrogen system and to refurbish the gas generator hardware. The delay between experiments, plus the fact that the gas generator had been completely disassembled, made it necessary to operate the gas generator alone prior to full supersonic combustion runs. Several checkout runs were made with just the gas generator operating. One or two runs would normally have been sufficient, but

a pressure switch caused several malfunction shutdowns and a solution to the problem was not readily apparent. It was finally resolved that the normally closed contacts of the pressure switch, which shuts down the gas generator when the chamber pressure is too high, were being opened by the test stand vibration during the start transient. The pressure switch was then isolated from the test stand vibrations and no further problems of this nature were experienced.

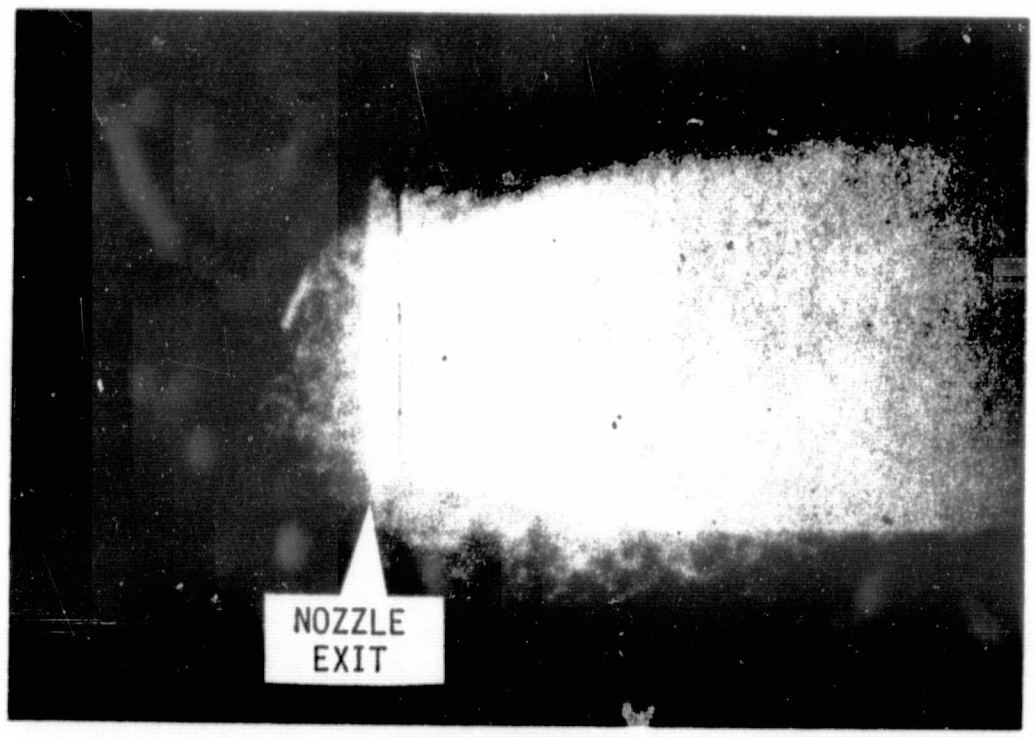
The nozzle was inspected after the gas generator checkout tests. There were several areas in the throat region where the coating had spalled away. A decision was made to proceed with the supersonic combustion experiments in spite of the obvious risk. In the first supersonic combustion experiment, the gas generator nozzle started to erode after a little more than three seconds of steady-state operation. The firing was shut-down normally by the sequencer after four seconds duration. Post-fire inspection revealed the gas generator nozzle has sustained severe erosion in the throat region. This prevented immediate resumption of the supersonic combustion experiments. However, there was sufficient worthwhile information obtained during the initial portion of the first experiment to draw some qualitative conclusions as to the effect of vitiation on supersonic combus-tion.

Because of the damage to the hardware in the first full supersonic combustion firing, it was decided to end this phase

of the program. A new nozzle had to be fabricated prior to the next firing. The revised program plans called for a redesign of the uncooled gas generator hardware and conducting this phase of the effort in the follow-on program. The new hardware will be fabricated out of copper with a heat sink design. This should provide sufficient wall cooling to allow longer firing durations.

In the one experimental firing that was conducted in this program, photographs were taken of the flame front location with supersonic burning. The photographs were obtained with a 16 mm motion picture camera using colored film. These pictures and the chamber pressure data indicated that the gas generator nozzle remained intact for about three seconds. During this time, the hydrogen system was in steady-state operation for about one second. A review of the motion picture frames taken during this operating period showed the hydrogen flame front had stabilized at about five inches downstream of the injector. An enlarged print of one of these frames is presented in Figure 30. In this figure the vitiated air stream and hydrogen are flowing from left-to-right. The hydrogen stream surrounds the primary flow in a symmetric pattern. The lower half of the flow is obscured by a part of the test stand so that the flame front can only be seen in the upper half of the photograph. The flame front is indicated by the spreading of the white portion of the photograph which is an indication of flame. A line is drawn on Figure 30 to indicate the beginning of the flame front in relation to the nozzle exit. The distance from the injection station to the flame front is approximately five inches. Thus the experimental ignition lag length for this experiment was five

(a) PRIOR TO HYDROGEN FLOW



(b) WITH HYDROGEN FLOW

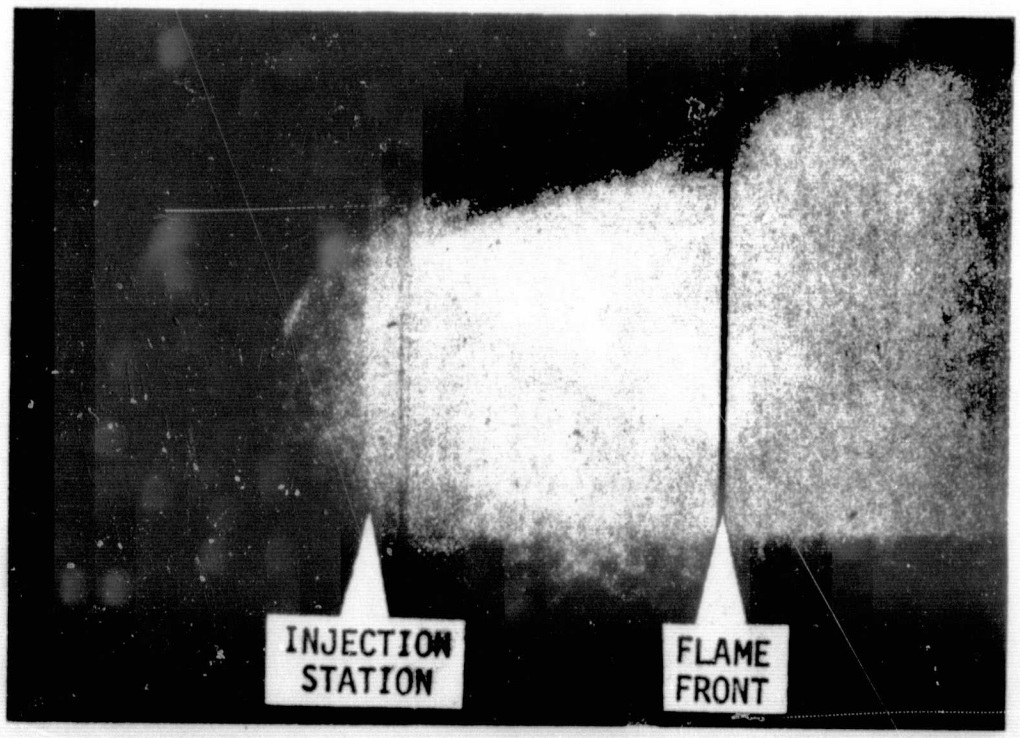


FIGURE 30 COMBUSTION OF HYDROGEN IN VITIATED AIR

inches, which corresponds to a delay time of almost 70 microseconds. This information constitutes the major results of the experimental supersonic combustion program. The follow-on effort will first extend the ignition lag results and then investigate the effect of vitiation of overall combustion efficiency.

DISCUSSION OF ANALYTICAL AND EXPERIMENTAL RESULTS

The ignition time for a reacting gas mixture is primarily determined by the number of free radicals present. At no time during the ignition and subsequent combustion process does the free-radical content become a large fraction of the total gas mixture. In the region of relatively long ignition delays, the ignition process can be accelerated significantly by small amounts of free radicals. An extensive analysis was undertaken to determine the effect of vitiation on the ignition delay characteristics of hydrogen. The analysis showed that the nonequilibrium free-radical content of the vitiated air system as it enters the supersonic combustor would result in very short ignition delay times. This effect is not entirely a function of the vitiated air composition but was shown to be related to the expansion process by which the gas is accelerated to test section conditions. In that sense, real air exhibits the similar effect on the ignition delay characteristics with hydrogen when the air is expanded to the supersonic test section Mach number from a high temperature source.

The results of the analytical program included a calculated ignition lag length of 1.5 inches for the vitiated air experiments. This calculation of the ignition delay assumes the hydrogen and vitiated air were instantaneously mixed at a constant temperature

of 1000°K and at an equivalence ratio of one. It also assumes nonequilibrium gas compositions for both streams prior to mixing. When equilibrium compositions were employed in these calculations, the ignition lag length was computed to be 11.5 inches. Therefore should the experimentally observed lag length be significantly less than 11.5 inches, the effects of the nonequilibrium inlet conditions will have been demonstrated.

In the experimental program, the hydrogen was heated to 830°K prior to injection and mixing with the vitiated air. Vitiated air conditions at the supersonic combustor inlet were a static temperature of 1000°K and a Mach number of 2.9. The two streams were introduced at a constant pressure of one atmosphere and permitted to mix as an unconfined flow system. The ignition lag length was determined visually from photographs of the exhaust flow. These pictures showed the hydrogen ignition took place approximately five inches downstream of the injection station. The measured lag length was reasonably close to that predicted by the analytical program assuming nonequilibrium inlet conditions to the combustor. This relative comparison of analytical and experimental results would seem to confirm the effects of nonequilibrium free-radical content on the ignition delay with supersonic combustion.

An additional analysis was undertaken to show even better agreement between the experimental and analytical program results. In the experimental program, the hydrogen and vitiated air entered

the supersonic combustor at different temperatures. This further complicates the analysis of the delay time, since a mean temperature for the reacting mixture must be defined before calculating the ignition lag. Mixing takes place continually as the two streams move downstream from the injection station. A combined mixing and reaction kinetics analysis is beyond the scope of the present program. However, by employing the gross oversimplification that the mean temperature is defined by average heat content of the combined streams, the ignition delay can be calculated with the SIL program. The initial heat content prior to mixing was determined using the actual static temperatures for the non-equilibrium inlet conditions. An equivalence ratio of one was employed for these calculations. The average temperature for the mixture was 940°K and the calculated lag length was 3.2 inches. This result does show better agreement with the experimental value of 5 inches than the previous analytical calculations. This comparison would seem to indicate that the effect of different static temperatures for the hydrogen and vitiated air streams should be accounted for in the analysis.

CONCLUSION

In the low temperature supersonic combustion regime, where the chemical reaction rates are slow, the use of vitiated air to simulate combustion phenomena for a SCRAMJET system will lead to erroneous results if the air entering the SCRAMJET combustor is near equilibrium conditions. When the vitiated air is expanded to the inlet conditions of the supersonic combustor, the nonequilibrium free-radical content of the incoming stream accelerates the reaction process. This causes ignition to occur much sooner than would be expected if the air entering the combustor of a free-flight SCRAMJET system were near equilibrium as far as free radical concentrations are concerned. While the vitiated air employed in this program was produced synthetically in a liquid rocket engine, similar effects would occur with any type vitiated air system. In fact real air, which is heated and subsequently expanded to the inlet condition of a supersonic combustor, will also undergo early ignition as compared to the equilibrium situation. Therefore direct ground simulation of supersonic combustion in the regime where reaction times are rate-controlling is difficult without a knowledge of the equilibrium conditions leaving the diffuse and may be impossible to achieve experimentally.

It must be pointed out that these conclusions only apply in the low temperature supersonic regime. Some SCRAMJET systems, which are designed to operate in the low Mach number regime, are designed with pilot flames or an hypergolic ignition source. The application of

vitiated air to simulate the supersonic combustion characteristics for these systems may not be a problem. Then in the higher temperature region, corresponding to high flight Mach numbers, mixing is rate-controlling and here it may be possible to employ vitiated air for ground simulation.

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APPENDIX

APPENDIX A

FACILITY DESCRIPTION

The experimental research program discussed herein was conducted in the Combustion Research Laboratory at the Jet Propulsion Center of Purdue University. This facility was designed for the purpose of investigating problems related to storable liquid rocket systems. The storable propellant capability made this facility readily adaptable to the requirements of the present program.

The Combustion Research Laboratory also has an extensive control room for remote operation of combustion experiments. The control room contains instruments for data recording (i.e., strip charts, oscillograph, and a 60 channel magnetic tape unit) and a flow system control panel with an automatic sequencer for the main propellant valves. A photograph of the main control panel is presented in Figure A-1. Any pneumatically operated valve in the facility can be operated off the main control panel. The sequencing unit is set-up to automatically open each valve at the proper time and to check for operating malfunctions. Since the control room services two test cells and four separate experiments, the instrumentation had to be shared.

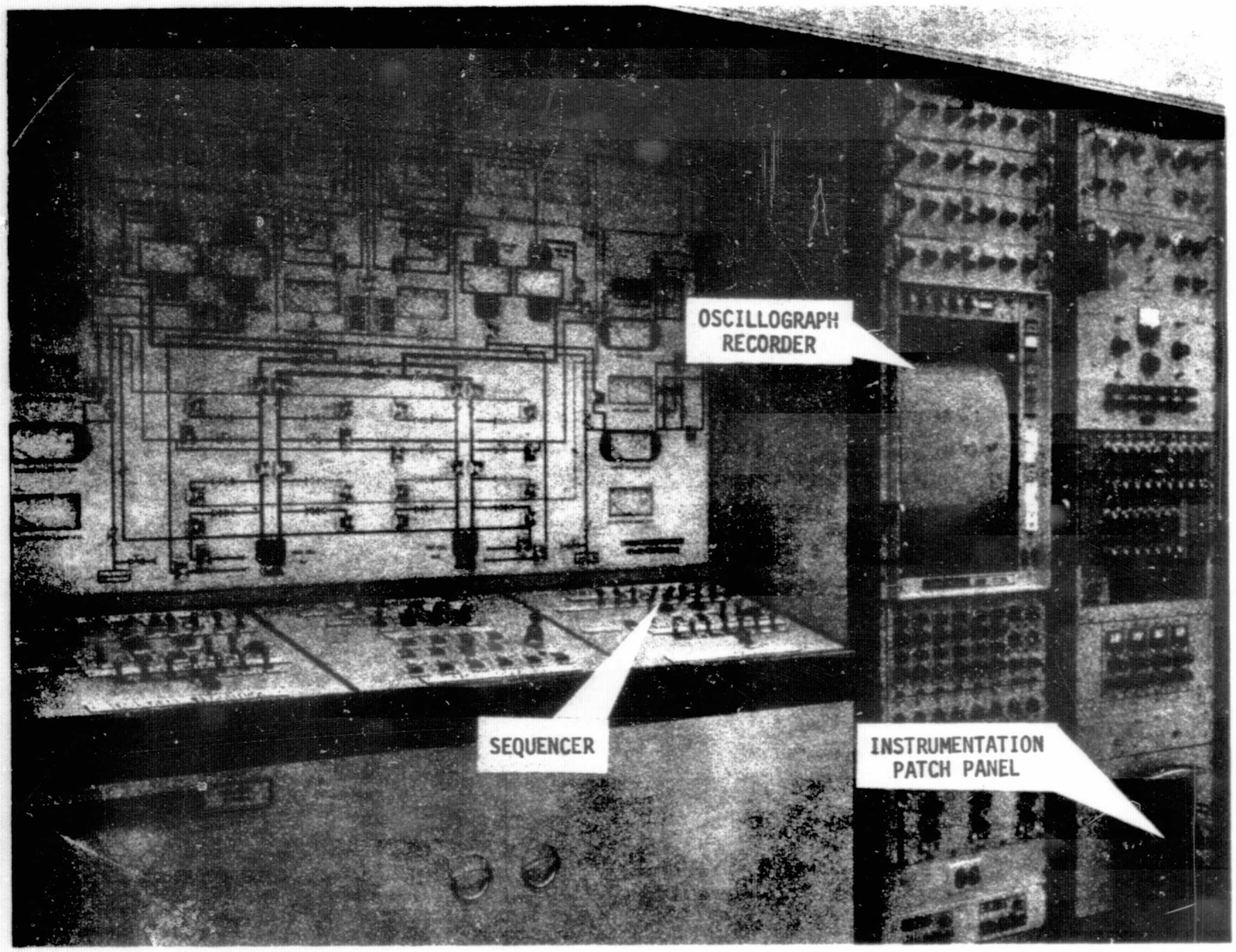


FIGURE A-1 MAIN CONTROL PANEL

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Each researcher was provided with a prewired instrumentation patch panel to provide rapid change over between different experiments.

The hydrogen heater was an addition made to the Combustion Research Facility specifically for this program. A separate control panel was also added for operating the hydrogen heater. A photograph showing the hydrogen control panel is presented as Figure A-2. The hydrogen heater is operated separately from the main flow control system. The heater is initially brought up to operating temperature prior to starting preparations for firing the gas generator. Flow of propane to the burners is controlled manually at the control panel. Two temperature controllers are provided for operating the hydrogen heater. One monitors tube wall temperature and the other the exhaust gas stack temperature. If either of these controls reaches a preset limit, the hydrogen heater is automatically shut down.

The propellant system in use at the Combustion Research Laboratory at the time of these experiments were nitrogen tetroxide and a 50/50 blend of hydrazine and unsymmetrical dimethylhydrazine. Since nitrogen tetroxide was employed in the present program, the existing oxidizer system was directly connected to the gas generator. A separate propellant supply system was added to handle the hydrazine fuel to avoid interference with other programs. High pressure nitrogen was

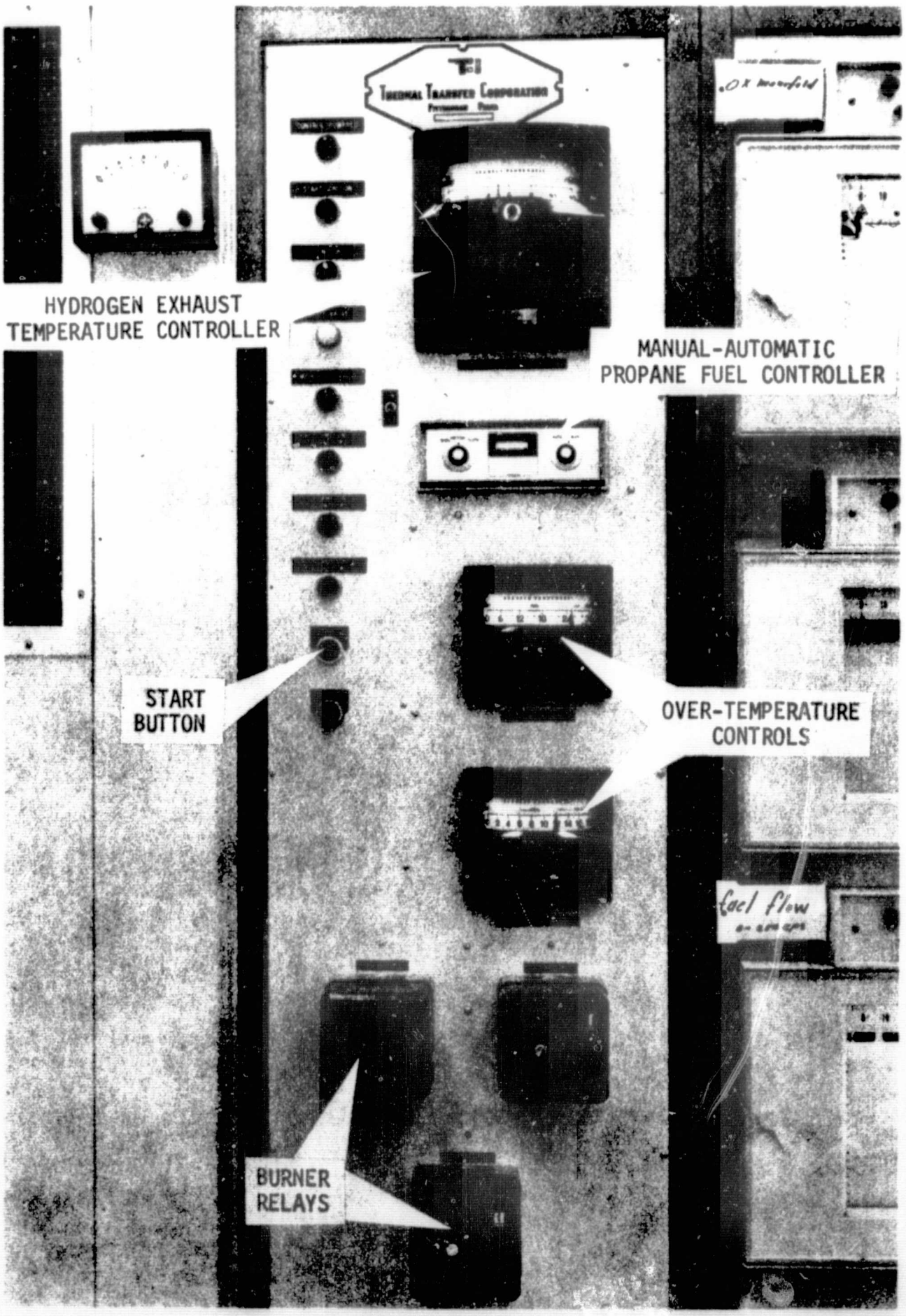


FIGURE A-2 HYDROGEN HEATER CONTROL PANEL

available at the test cell. Piping, valves and a regulator were added to provide the nitrogen diluent supply system. The hydrogen system was a new addition to this facility so that a complete system had to be installed for these experiments. A flow schematic of the propellant supply system for the supersonic combustion experiments is presented as Figure A-3. The dotted lines on this figure represent the facility fuel supply system which was not employed in this program.

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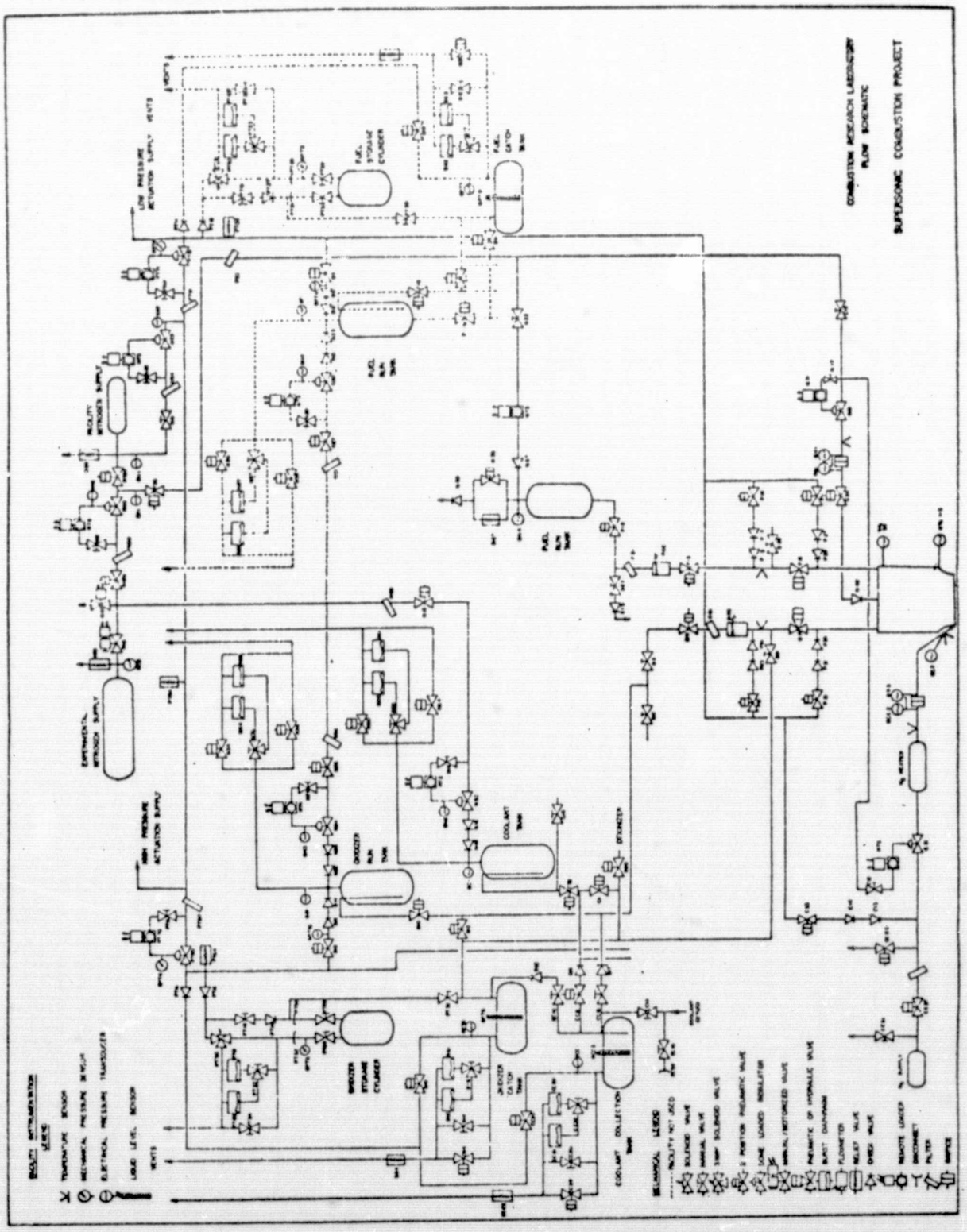


FIGURE A-3 FACILITY FLOW SCHEMATIC

VITA

Charles A. Bryce is a United States Citizen and was born in [redacted] on [redacted] He graduated from Glen-Nor High School in Glenolden, Pa. in June 1955.

After working for a year after graduating from high school, he attended Grove City College in Grove City, Pa. where he majored in Chemical Engineering. In June of 1955, he graduated from Grove City College with a B. S. degree with honors, Cum Laude. He then entered the University of Delaware to perform graduate work in Chemical Engineering. While there he performed research in heat transfer under a research fellowship. He graduated with an MSCHE degree in June of 1957.

Mr. Bryce then worked as a chemical process engineer with M. W. Kellog Co. in New York City for two years. In October 1958, he accepted a position of development engineer with Aerojet-General Corporation in Sacramento, California where he worked for three years in the Advanced Design Department of the Solid Rocket Plant. He then transferred to the Advanced Research and Technology Division of the Liquid Rocket Plant where he was employed as a supervisor of a Fluid Mechanics Section.

In September of 1965, he entered Purdue University to perform graduate work in Mechanical Engineering. There he was employed as a graduate research assistant at the Jet Propulsion Center conducting research in the area of supersonic combustion.