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SHOCK-INDUCED COMBUSTION WITH OBLIQUE SHOCKS, COMPARSION OF EXPERIMENT AND KINETIC CALCULATIONS

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Rocket Test Facility
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ARNOLD ENGINEERING DEVELOPMENT CENTER
AIR FORCE SYSTEMS COMMAND
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NOTICES

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FOREWORD

The authors wish to express their appreciation to Dr. Paul A. Libby, Mr. H. S. Pergament, and Mr. D. Magnus of the General Applied Science Laboratory for their help in adapting the kinetic reaction computer program developed at GASL for use in the work reported herein. Others who participated in the work were Don Chriss, test conductor on the experimental work; W. N. MacDermott, consultant on aerodynamic problems; Linn Weller, instrumentation designer; and Carl Catalano, who built most of the models and probes.

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ABSTRACT

Theoretical analyses made recently have shown the advantages of supersonic combustion for a hypersonic ramjet. The present work deals with experimental investigations of shock-induced H_2-air combustion in the constant pressure region aft of an oblique shock and with kinetic calculations for the H_2-air reaction. Quenched gaseous components for the early parts of the chemical reaction were analyzed to determine hydrogen molecule reaction rate, and a comparison was made of the experimental H_2 reaction rate with the current chemical kinetic computations. Agreement with one kinetic calculation for the H_2-air reaction at constant pressure was within the experimental error, indicating the possible use of kinetics to predict hypersonic ramjet combustion performance when shock-induced combustion is used. The concept of shock-induced combustion is defined and compared with the usual conditions where detonations are observed, and it is concluded that detonations are a special case of shock-induced combustion.

PUBLICATION REVIEW

This report has been reviewed and publication is approved.

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CONTENTS

ILLUSTRATIONS

NOMENCLATURE

a	Velocity of sound
a_2	Test zone fuel excess over E. R. = 1.0
C_p	Specific heat at constant pressure
C_p'	Specific heat at constant pressure neglecting vibrational energy
E_{vib}	Vibrational energy for a diatomic molecule
E. R.	Equivalence Ratio $= \frac{\text{Fuel Concentration}}{\text{Stoichiometric Fuel Concentration}}$
g	Dimensional constant, $32.2\ \text{ft-lb}_f/\text{lb}_m\text{-sec}^2$
(H_2)	Volume percent of H_2 in dry gas
M	Mach number
(O_2)	Volume percent of O_2 in dry gas
p	Static pressure
R	Universal gas constant
t	Relaxation time
T_o	Static temperature at reaction time = 0
V	Stream velocity
W	Mass
X	Mole fraction of a component
$X_{1,o}$	Mole fraction of component 1 at time = 0
x, y	Coordinates for probe location
y_1	Preheater equivalence ratio
y_2	Test zone fuel equivalence ratio
α	Wedge shock angle
γ	Specific heat ratio
δ	Wedge angle
ϵ	Hydrogen molecule percent reacted
η	Overall H_2 reaction "efficiency"
θ	Characteristic temperature for vibration $= h\nu/k$ where h = Boltzmann constant k = Planck constant ν = Frequency of vibration

τ	Reaction time

SUBSCRIPTS

o	Condition at time = 0, or reaction starting time
1, 2	Condition 1, 2, etc.
a	Air
f	Fuel
i	Each component of the test gas mixture
j	Each component of the preheater gas
p	At constant pressure
ph	Preheater
t	Stagnation condition
tf	Test fuel

1.0 INTRODUCTION

Interest in hypersonic ramjets flying at altitudes higher than 200, 000 ft has been such that many calculations have been made and designs proposed to convert this idea to reality (Refs. 1-6). However, a big stumbling block in achieving this reality has been the lack of experimental data on combustion in supersonic flow. The advantages of supersonic combustion for a hypersonic air breathing engine are well known, such as low static temperature in the engine, reduction of dissociation and recombination problems as the gases expand in the engine exhaust, and reduced diffuser losses.

At present, experimental supersonic combustion is being investigated from two points of view: one, from the standpoint of injecting gaseous fuel into a supersonic flow where the air and fuel are at a reacting temperature (diffusional burning), and second, by employing shock waves to increase premixed fuel and air temperature to a point where chemical reaction will start (shock-induced combustion).

Shock-induced combustion differs from "detonation" waves in that the chemical reaction behind the shock does not necessarily affect the shock. The usual concept of detonations is exemplified by those observed in constant area tubes, where the steady state condition is known as the Chapman-Jouget detonation. Shock-induced combustion implies that the fuel and air mixture is heated to a reacting temperature by shock compression, and thus applies to all conditions of shock followed by chemical heat release. The chemical reaction could proceed for conditions where constant static pressure, area, Mach number, or static temperature were maintained. Therefore, the constant area detonation observed in tubes is a special case of shock-induced combustion.

Previous work performed in the Rocket Test Facility (RTF), Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), consisted of studies of the chemical and aerodynamics effects in the region downstream of a normal shock formed by the intersection of two oblique shocks (Ref. 7 and Fig. 1a). The present work has been primarily concerned with chemical reactions at constant static pressure as they occur when combustible mixtures are passed through oblique shock waves (Fig. 1b) and with a comparison of the experimental results with available kinetic calculations.

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Thus, shock-heating was used as a mechanism for achieving reaction temperature of a fuel-air mixture, and the kinetics were then assumed to proceed in the various stream tubes as the mixture proceeded on its way.

A possible application of this effort would be to determine if these kinetics can be used to predict performance in a hypersonic ramjet using shock-induced combustion. Preliminary work has included a model using two oblique shocks with a constant area reaction zone as shown in Fig. 1c. This model was used to measure pressure rise as an indicator of temperature increase.

Because of the recent interest in supersonic combustion of hydrogen and air, several investigators have been concerned with the chemical kinetics of this particular reaction. Among them are Libby, Pergament, and Bloom (Ref. 8); Fowler (Ref. 9); and Momtchiloff, Taback, and Buswell (Ref. 10). The kinetic models of the calculations made by Libby, et al, and Momtchiloff, et al, assume that separate streams of hydrogen and air at a reacting temperature are suddenly mixed and start to react. This is very nearly what happens experimentally when pre-mixed fuel and air is suddenly raised to a reacting temperature upon passing through a shock wave. Since this similarity exists between experiment and kinetic models, it was found that their differences could be reconciled so that kinetic theory could be correlated with the experimental results.

The experimental program was limited to a determination of hydrogen molecule reaction only, so that the comparisons of experiment with kinetic calculation are also limited to that of the hydrogen reaction rate. Figure 2 is a combination spark schlieren and emission photograph of the experiment showing the oblique shock wave followed by emission in the reacting gas.

2.0 EXPERIMENTAL PROGRAM

2.1 TUNNEL

The experiments were carried out in a water-cooled, Mach number 3 tunnel, which has been fully described in a previous report (Ref. 7). Air was preheated to 1500°R with an indirect fired heat exchanger and further heated to a maximum of 3800°R with a hydrogen burning preheater, in which a portion of the oxygen was consumed (Fig. 3). The vitiated air entered the tunnel throat, expanded into the supersonic section, mixed with injected fuel, and then passed through an oblique shock wave formed by a 28-deg wedge. Fuel was injected from the trailing edge of a thin, 12-deg double wedge strut (Figs. 3 and 4). Static pressures were measured on the wedge surface, and stream pressures were measured from a total pressure probe. Figure 5 shows the 28-deg wedge and probe.

2.2 GAS SAMPLING

The total pressure probe was also used for gas sampling. Gas entered a small orifice, was cooled by sudden expansion to 1/6 of its original pressure, and then further cooled by contact with the cooled walls (Fig. 6). An analysis of the quenching process indicates that the gas will pass through the space between the normal shock and the probe tip in less than one microsecond. The combination of sudden expansion and wall cooling should render the gas substantially quenched in an additional one to three microseconds. Experiment does not refute this analysis because, if quenching had not occurred, zero or partial reaction completion would not have been measurable.

2.3 GAS ANALYSIS

The gas sample was dried and then analyzed in a continuous flow system for oxygen, by means of a magnetic susceptibility analyzer, and for hydrogen, with a thermal conductivity analyzer. Accuracy of analysis was ±1/2 percent of total gas volume. The net effect of this variation on the final calculation of hydrogen molecule consumption if ±9 percent, where 100 percent represents all of the hydrogen reacted (Ref. 7).

2.4 CALCULATION OF REACTION TIME

Reaction time was calculated by measuring the distance from the oblique shock wave to the probe and calculating velocity in the region downstream of the oblique shock; thus, time was determined from the shock to the probe. Distance was measured directly from schlieren photographs (assuming that the flow was parallel to the wedge surface). Velocity was calculated from the Mach number and the speed of sound in the region aft of the oblique shock. Mach number and the speed of sound were determined from gas composition, temperature, and pressure.

3.0 RESULTS AND DISCUSSION

3.1 APPLICATION OF A KINETIC MODEL TO THE EXPERIMENT

If it is assumed that the shock does act as a short duration compressor and if the gas temperature is increased by this compression to the point where chemical reactions are imminent, the region downstream of the shock may then be considered as a group of one-dimensional stream tubes in which the chemistry is proceeding. With steady flow aerodynamic conditions, such as constant pressure, the chemical reactions may then be followed as a function of distance traveled, or time elapsed. The chemical kinetics can then be evaluated independently of the flow.

The conversion of hydrogen molecule to H_2O, OH, and H is one of the first reactions in the kinetics of H_2 and air (Refs. 8, 9, 10), but appreciable temperature rise is not present for some time in the progression of the kinetic itinerary (Fig. 7). The process of the H_2-air reaction has been suggested by Schott and Kinsey (Ref. 11) and Duff (Ref. 12) to depend on the rates of the following reactions:

$$H_2 + OH = H_2O + H \tag{1}$$

$$H_2 + O = OH + H \tag{2}$$

$$O_2 + H = OH + O \tag{3}$$

$$O + H_2O = 2OH \tag{4}$$

$$H_2O + M = H + OH + M \tag{5}$$

$$H_2 + M = 2H + M \tag{6}$$

$$OH + M = O + H + M \tag{7}$$

$$O_2 + M = 2O + M \tag{8}$$

where M is any third body.

Several investigators have arrived at calculation procedures for analyzing the reaction kinetic processes of the H_2-air reaction using kinetic rate constants which are currently accepted. Among them are Libby (Ref. 8), who developed the calculation for a constant pressure process; Fowler (Ref. 9), for a constant density process; and Momtchiloff (Ref. 10), for a constant area process.

Libby's model for a constant pressure process fits our experimental conditions most nearly because the region downstream of an oblique shock is experimentally one of constant static pressure for small quantities of heat release. However, there are significant differences which must be accounted for in order to make a valid comparison. Libby's model assumes that two flowing streams of hydrogen and air, both in chemical equilibrium at a pre-set temperature, are instantaneously mixed and proceed to react. In the experiment, fuel is injected into preheated vitiated air, which flows at a static temperature less than ignition temperature, and the mixture is then passed through a shock wave where the temperature is suddenly raised to a value higher than necessary for chemical reactions to occur (Fig. 8).

The conditions which must be known to allow a comparison between Libby's kinetics and the shock-induced combustion experiment are:

1. The free radical content of the tunnel gas at the shock wave,
2. The degree of agreement between experimental pre-mixed shock-induced heating and the theoretical preheated, then mixed, chemical reaction,
3. The amount and duration of translational and rotational temperature "overshoot," and
4. The justification for the assumption of one-dimensional flow with kinetic reaction.

These conditions are discussed as follows:

3.1.1 Effect of Free Radicals

Free radical concentrations were calculated for the experiment by assuming gas composition and temperature at the preheater discharge at equilibrium, equilibrium flow to the throat, and frozen flow from the tunnel throat to the test section. The free radical concentrations were used as input data in the computer program developed by Libby, et al.

3.1.2 Effect of Pre-Mixed Shock Heating vs Mixing of Pre-Heated Gas

It is assumed that mixed fuel and air, suddenly heated, reacts the same as heated, un-mixed fuel and air, which are suddenly mixed. The mixed fuel and air, suddenly heated, is an experimentally realizable condition, whereas the theoretically suddenly mixed reacting mixture is not.

3.1.3 Shock Wave Translational and Rotational Temperature Overshoot

The static temperature overshoot caused by vibrational non-equilibrium downstream of the shock wave and the vibrational relaxation time were calculated for a typical test condition in order to evaluate this effect on the chemistry downstream of the shock.

Vibrational relaxation time is an exponential function (Ref. 13) and is defined as the time when the temperature reaches (1 - 1/e) of the difference between the initial and equilibrium value. For temperatures of 4000°R or less in air, the vibrational relaxation time of the oxygen molecule is predominant. A typical value for test conditions at 0.35 atm pressure is about 45 microseconds.

Translational and rotational temperature overshoot in a shock wave caused by non-equilibrium of vibrational energy was calculated from the following relationship (Ref. 14):

$$E_{vib} = RT \frac{\theta/T}{\exp(\theta/T) - 1} \tag{9}$$

where θ = characteristic temperature for vibration = $h\nu/k$.

For oxygen, $\theta = 4000°R$. For nitrogen, θ is 6000°R, but for mixtures at the lower temperatures, the gas behaves as if the effect of nitrogen is negligible. In order to ascertain the quantity of energy in the gas from vibrational non-equilibrium that will be transferred to the translational and rotational modes, the difference between the two vibrational energy levels before and after the shock may be expressed:

$$E_{vib_2} - E_{vib_1} = R\left[T_2 \frac{\theta/T_2}{\exp(\theta/T_2) - 1} - T_1 \frac{\theta/T_1}{\exp(\theta/T_1) - 1}\right] \tag{10}$$

Also, where $C_p' = 7/2\,R$ for the case where vibrational energy is neglected:

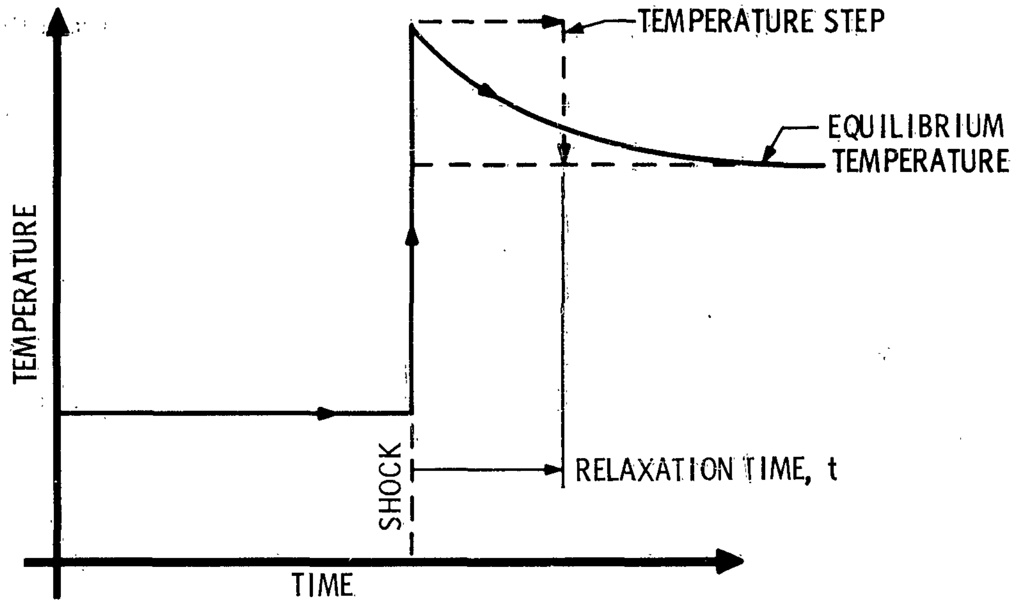
$$dE_{vib} = C_{vib}\, dT_{vib} = -C_p'\, dT \tag{11}$$

Therefore, the temperature overshoot (ΔT) may be written:

$$\Delta T = \frac{E_{vib_2} - E_{vib_1}}{C_p'} \tag{12}$$

If it is assumed that the reaction rate in a gas not in thermal equilibrium depends on the translational temperature (that is, the energy with which the molecules collide), the cumulative effect of translational temperature overshoot is to increase the rate of reaction for all the components. The input to the reaction kinetics computer program can be modified so that a step function is used to simulate the overshoot. Free radical concentrations recalculated at the end of the step may then be used as a starting point for a second computation and continued to the point of complete reaction.

For a typical tunnel condition, the calculated temperature overshoot is 150°R. Also, the relaxation time includes the major portion of the H_2 reaction. In Fig. 9 the typical condition in the tunnel for H_2 reaction is compared with the effect of a step function temperature overshoot of 150°R. The step change is shown in the schematic diagram on the following page.



3.1.4 Assumption of One-Dimensional Flow

Since the assumption of one-dimensional flow greatly simplifies the analysis of the experimental data, this question was examined further. The kinetics are considered to occur in a one-dimensional stream tube. Since the initial kinetic reactions are relatively insensitive to fuel concentration variations which may have been caused by turbulent mixing (Refs. 7, 8, 10), the one-dimensional flow model with superimposed kinetic reactions may be used with a reasonable degree of confidence.

3.2 COMPARISON OF KINETIC MODELS

The three kinetic calculations of Libby at constant pressure, Fowler at constant density, and Momtchiloff at constant area have been compared for the early portion of the kinetic processes, since at this point, there is little or no temperature rise: hence all three can be considered to be at constant pressure momentarily (Fig. 10). It is found that, for the H_2 reaction, the rates predicted by Fowler and Libby agree reasonably well, whereas that of Momtchiloff is slower by nearly a factor of 10. Momtchiloff used the kinetic rate constants from Bray (Ref. 15), Duff (Ref. 12), and other investigators; Fowler used kinetic rates from Schott and Kinsey (Refs. 11 and 16) and Duff (Ref. 12); and Libby employed the rates suggested by Schott (Ref. 16).

Figure 10 is a comparison of the three calculations for the initial reactions of hydrogen molecule. The relatively small disagreement between the Libby and Fowler calculations could be the result of different assumptions as to free radical concentrations at the start of the reactions, and partly in the use of somewhat different kinetic rate constants. The nearly order-of-magnitude difference of the Momtchiloff curve is probably the result of using different kinetic rate constants.

The model assumed by Libby has been discussed. That of Momtchiloff is similar, consisting of two streams flowing at a fixed temperature, suddenly mixed, and then reacting at constant area. Fowler's constant density model assumes pre-mixed gaseous hydrogen and air.

3.3 EFFECT OF VARIATION IN FREE RADICAL CONCENTRATION

To determine the effect of inexact evaluation of the free radical concentrations entering the reaction, the computer program was re-run with varying amounts of free radicals at the reaction starting time. Figures 11 through 13 show the effect of varying the total concentration of radicals from 0.10 to 10 times that calculated for a typical tunnel condition.

It is interesting to note that a large change in initial free radical concentration entering the reaction makes very little change in the overall reaction. For example, Figures 11 and 12 show that, in the region of rapid reaction, a reduction by a factor of 10 in initial free radicals slows the H_2 and H reaction by about 10 microseconds, and in the later part of the reactions also by 10 microseconds. If the initial free radicals are increased by a factor of 10, H_2 and H reaction is speeded up by 10 microseconds at first, and somewhat more as the reaction progresses. The temperature history (Fig. 13) is similar, being shifted by a few percent in time.

A second computer calculation was made using input data for a typical tunnel condition but eliminating all the free radicals at the reaction starting point except one. The purpose of this computation was to compare the relative effects of the initial OH, H, and O radicals on the reaction progress. Figures 14 through 16 show these effects as compared to the radical concentrations for a typical tunnel condition and for the hypothetical case where no radicals are present. It may be observed from the figures that the OH radical is the most effective, as might be expected from the kinetic relations, and also the one present in the greatest quantity. The initial OH radical, when present singly, has nearly the same effect on the reaction rate as the sum of OH, H, and O components.

Complete elimination of initial radicals at the reaction start creates a lag of 80 to 90 microseconds in the rate at which the free radicals form and recombine. This lag continues for the duration of the reaction time that was calculated, approximately 1000 microseconds.

This type analysis may make practical the use of high Mach number wind tunnels for testing air breathing engines where part of the air heating is, by necessity, secured from burning a portion of the available oxygen, and the effect of the products entering the engine on its performance must therefore be known.

3.4 FACTORS USED IN CORRELATING EXPERIMENTAL DATA WITH KINETICS

Since the experimental data were recorded at various inlet temperatures and pressures, a means of adjusting the results to a common reference level was needed. J. A. Nicholls's equation (Ref. 17) for ignition delay time as modified by Libby (Ref. 8) contains initial temperature, pressure, and concentrations:

$$\tau_d = \left[\frac{R\,T_o}{6X_{1,o}\,p \times 10^{14}}\right] \exp\left[\frac{15{,}860}{T_o}\right]\left[\ell n\,\frac{X_{1,o}}{X_{2,o}} + \ell n 3 + \frac{47{,}410}{T_o}\right] \tag{13}$$

Since the third bracketed term is roughly constant, the equation may be written:

$$\tau_d \sim \frac{T_o \exp\left[\frac{15{,}860}{T_o}\right]}{X_{1,o}\,p} \tag{14}$$

If it is assumed that the time (τ) for the hydrogen molecule to reach a specific concentration, in the initial portion of the chemical reaction, is the same function of the reaction initiating temperature and pressure as defined by Nicholls's derivation of the "ignition delay" (τ_d) equation, then the following equation may be written by taking a ratio at two conditions:

$$\frac{\tau_1}{\tau_2} = \left[\frac{T_{o_1}}{T_{o_2}}\right]\left[\frac{p_2}{p_1}\right]\exp\left[\frac{15{,}860}{T_{o_1}} - \frac{15{,}860}{T_{o_2}}\right] \tag{15}$$

This equation is an approximation but was found to be useful in adjusting experimental data for comparison with the kinetic calculations at a common starting temperature and pressure. It was used exclusively for the early parts of the reaction before significant change in temperature had occurred.

Figure 17 is a plot of kinetic calculated reaction time for 50 percent of the hydrogen molecule reacted compared to corrected values using Eq. (15). The deviations of equation values from kinetic calculation values are small.

3.5 COMPARISON OF EXPERIMENTAL OBLIQUE SHOCK DATA WITH THE KINETIC CALCULATION

After considering all of the foregoing implications of theory and experiment, the data were adjusted to a common reference inlet temperature and pressure; computer program results were obtained using inlet conditions typical of the tunnel operating condition; and both were plotted in Fig. 18. The kinetic calculation was for an equivalence ratio 0.4 but it was found, as previously noted, that the reaction is relatively insensitive to fuel concentration. In fact, it is apparent that fuel concentrations below the usually accepted combustible limit will react when the initial temperature is higher than reaction temperature.

The data agree with the Libby and Fowler kinetics within the experimental error and much closer than the agreement of all three kinetic calculations with each other. Curve "A" was calculated with Libby's method for no H radical recombination in the probe, and curve "B" represents the same calculation with complete recombination of H radicals after entering the probe to form H_2 only. The actual gas composition will likely lie between these extremes.

3.6 RESULTS OF CONSTANT AREA DUCT EXPERIMENTS

Static pressure measurements were made in the two-dimensional flow model (Fig. 1c) in an effort to detect temperature rise. From the one-dimensional flow theory, Rayleigh line heating in a supersonic flow should be approximated. The model was operated in a Mach number 3.0 stream and the flow diffused down to Mach number 1.5, at which point static pressure was 0.7 atmospheres. Some pressure rise was recorded within the 45 microseconds residence time in the model, indicating heat release. Further work is needed to explore the problems of shock-induced combustion within the confines of a controlled area duct.

4.0 CONCLUSIONS

Some conclusions may be drawn from an analysis of the foregoing:

1. The chemical kinetics of shock-induced combustion at constant static pressure, as measured thus far for the H_2 molecule reaction, agree with the constant pressure kinetic calculation method of Libby where the kinetic rate constants of Schott and Duff were used, within experimental error.

2. Based on this agreement, it appears reasonable that the complete chemistry, including heat release, should be predictable. Further work should be done to verify the later chemical reactions, in which heat release occurs.
3. Changing free radical concentration by a factor of 10 in the incoming gas, before the reaction starts, affects the reaction time and temperature history by only a few percent. This knowledge is significant in that small changes in free radical content from combustion heating of the gas may be ignored.
4. The effect of free radicals from a combustion-type preheater in a supersonic tunnel on a chemical reaction in an air breathing engine being tested should be predictable with the available kinetics, if hydrogen kinetics only are used.
5. The experiments have demonstrated that shock-induced reaction can be experimentally produced in a constant pressure field. By analyzing the flow conditions for detonation waves, it is found that the usual detonation wave observed occurs in a constant area duct. Since shock-induced combustion can theoretically occur for constant area, static temperature, static pressure, or Mach number, the constant area detonation may be regarded as a special case of shock-induced combustion.
6. The experiments indicate that the standing oblique shock wave is a means by which kinetics of chemical reactions may be examined with relatively inelaborate instrumentation.

It has been clearly demonstrated that the initiation of chemical reactions can be controlled by means of shock waves. This knowledge, plus additional information on the final stages of the reaction, should serve to promote the development of a hypersonic ramjet. Potentially, shock-induced combustion employed in a hypersonic ramjet offers control of the combustion processes over a wide range of flight and diffuser Mach numbers. Predictable kinetics will also aid in designing optimum nozzle lengths and contours.

Since shock-induced combustion pre-supposes the presence of fuel, the fuel must be injected at a point somewhere upstream of the reaction zone. It was not the intention of this work to develop fuel injectors for hypersonic ramjets, but the thin wedge used may serve as a basis for further study into this problem. Fuel distribution from the wedge can be studied both experimentally and theoretically, wedge pressure losses from shocks can be calculated, and, as suggested by M. Roy (Ref. 3), the wedge could possibly be incorporated as a part of the inlet diffuser of a hypersonic ramjet. Also, the fuel itself acts as a coolant for the metal injector wedge.

It is obvious that any complex reaction in aerothermochemistry can be more easily predicted if broken down into physically separable processes. Thus far, investigations at the AEDC indicate that this separation of injection, mixing, and combustion is feasible in supersonic flow. Sufficient measurements have been obtained in the initial stages of the H_2-air reaction to compare favorably with calculations based on reaction kinetics for similar conditions. On the basis of these initial results, it should be possible to proceed toward a more realistic prediction of the conditions necessary for heat release in shock-induced supersonic combustion, for the H_2-air system, that will generate thrust in a hypersonic air-breathing engine.

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APPENDIX I

CALCULATIONS BASED ON GAS ANALYSIS AND PROBE LOCATION DATA

GAS ANALYSIS

Reference 7 details the following equation to describe the chemical reaction in the preheater at 100 percent combustion efficiency, followed by partial reaction in the region aft of the shock wave:

$$2(y_1 + y_2 + a_2)H_2 + O_2 + 3.77N_2 \rightarrow \left[1 - (y_1 + y_2)\eta\right] O_2 + 2(y_1 + y_2)\eta\, H_2O + 2(y_1 + y_2)(1 - \eta)H_2 + 2a_2H_2 + 3.77N_2 \tag{I-1}$$

Fuel-air ratio and temperature from the preheater were calculated from gas samples in the tunnel test section, in which oxygen content was determined from dried gas. Assuming no test fuel (y_2 and $a_2 = 0$) and complete combustion of preheater fuel, preheater equivalence ratio may be derived from Equation (I-1):

$$y_1 = \frac{1 - 4.77(O_2)}{1 - (O_2)} \tag{I-2}$$

The H_2-Enthalpy chart of Powell and Browne (Ref. 18) was used to find temperature. It was assumed that mixing of preheater gases with unburned air diluted the combustion products and the temperature proportional to the dilution.

With y_1 known, a second sample with test fuel injected into the stream was analyzed for content of H_2 and O_2, again on a dry basis. From Equation (I-1), fuel concentration may be calculated:

$$(y_1 + y_2 + a_2) = \frac{1 - 4.77(O_2) + 0.88(H_2)}{1 - \left[(H_2) + (O_2)\right]} \tag{I-3}$$

and percent of H_2 that has reacted:

$$\epsilon = \frac{\eta(y_1 + y_2) - y_1}{y_2} \tag{I-4}$$

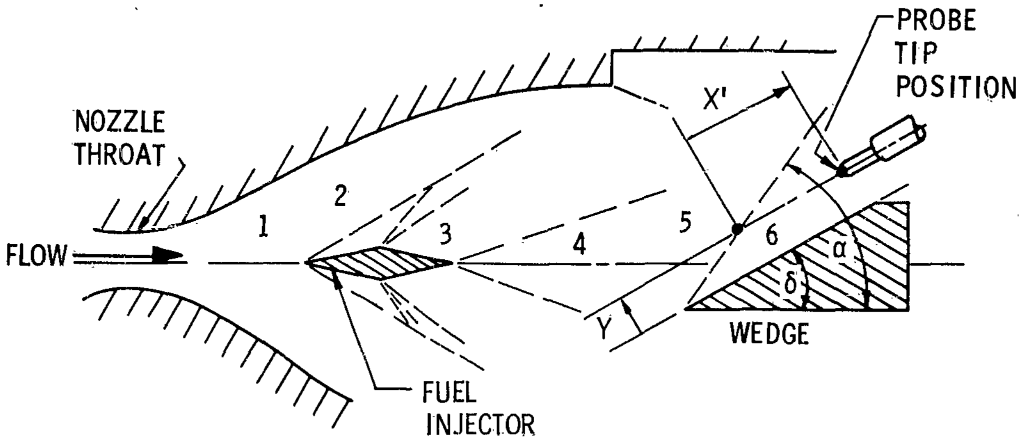
Since fuel injected into the supersonic stream was at a lower temperature than the stream, the fuel-air mixture temperature entering the shock wave was calculated from a heat balance:

$$T_{t_5} = (T_{t_1})_{corrected} = \frac{T_{t_1} + T_f \left(\frac{W_f}{W_a}\right)\left(\frac{C_{pf}}{C_{pa}}\right)}{1 + \left(\frac{W_f}{W_a}\right)\left(\frac{C_{pf}}{C_{pa}}\right)} \tag{I-5}$$

Fuel temperature was estimated to be 1200°R.

CALCULATIONS OF REACTION TIME

From a measurement of shock angle (α) and wedge angle (δ) from schlieren photos and using (T_{t_1}) corrected, an iteration procedure was used which established Mach number, γ, and static temperature T_6 aft of the shock wave.



Equations and tables for compressible flow were used from Refs. 19 and 20.

For the first estimated M_6:

$$\frac{T_6}{T_{t_6}} = \left(1 + \frac{\gamma_6 - 1}{2} M_6^2\right)^{-1} \quad \text{(I-6)}$$

using an approximate γ_6.

A revised T_6 and γ_6 were then calculated. A similar process was used for M_5, T_5, and γ_5, and an average $\gamma_{5,6}$ calculated from $\frac{\gamma_5 + \gamma_6}{2}$. This $\gamma_{5,6}$ was used in calculating values associated with the oblique shock, starting with M_5, and calculating M_6. Using the ratio,

$$\left(\frac{p}{p_t}\right)_6 = \left(1 + \frac{\gamma_6 - 1}{2} M_6^2\right)^{-\frac{\gamma_6}{\gamma_6 - 1}} \quad \text{(I-7)}$$

and the experimentally measured value of static pressure on the wedge (p_6), the total pressure (p_{t_6}) in the region of the wedge surface can be calculated.

To determine velocity of the gas from the shock wave aft, in the region of constant pressure, the defining relationship of Mach number was used:

$$M_6 = \frac{V_6}{a_6} \qquad \text{(I-8)}$$

and

$$V_6 = M_6 a_6 = M_6 \sqrt{\gamma_6 g R_6 T_6} \qquad \text{(I-9)}$$

Velocity was assumed constant in this region, since theoretically the flow is at constant pressure and experimentally it is also at constant pressure. The gas constant, R_6, was calculated from gas composition determinations (Fig. 13 of Ref. 7) for mean composition.

To determine the time from the shock wave to the probe position, the flow was assumed to be one-dimensional, so that streamlines at a distance y from the wedge surface at the point of entry into the oblique shock would also be at y distance at the probe position downstream. The distances x' were measured from schlieren photographs, so that time $(\tau) = x'/V_6$.

The assumption of one-dimensional flow and negligible diffusion of fuel is not exact, but considered sufficiently accurate for the data.

Calculations correcting τ for effects of temperature and pressure are discussed in the text of this report.

APPENDIX II

PROCEDURE FOR CALCULATING THE GAS FREE RADICAL COMPOSITION AT THE SHOCK WAVE

ASSUMPTIONS

The partly vitiated air coming from the preheater will be referred to as the preheater gas and the subscript (ph) will be used to identify the properties of this gas. The mixture of preheater gas and hydrogen will be referred to as the gas mixture with subscript (tf + ph) to identify it.

The initial assumptions are:

1. The preheater gas composition is in equilibrium at the throat of the nozzle and frozen from the nozzle downstream.
2. The static temperature of the preheater gas at the throat is 0.875 times the total temperature of the preheater gas in the test section. This number was based on an assumed γ_{ph} of 1.34 and a further temperature drop of 2 percent from mixing in the nozzle.
3. Dilution of free radicals by mixing in the nozzle was neglected.
4. The static to total temperature ratio on the downstream side of the shock was 0.75 based on a $\gamma = 1.34$ and an average value of the measured shock strength.
5. The combustion products leaving the preheater were in equilibrium, with all hydrogen fuel completely reacted.
6. The mass concentrations of the free radicals H, OH, and O were insignificant compared to the mass concentrations of the stable species H_2O, O_2, and N_2 in the preheater gas. Temperature also was independent of the free radical concentrations.
7. No reactions occurred between the wedge injected hydrogen and the preheater gas between injection and entry into the shock wave.

CALCULATION PROCEDURE

1. For preheater equivalence ratios of 0.2, 0.4, and 0.6, air inlet temperatures of 1500°R, and H_2 temperature of 600°R, $(T_t)_{ph}$, X_{H_2O}, and X_{N_2} were calculated, assuming no free radicals were present.

2. At a temperature of 0.75 T_t and a pressure of 1.35 atmospheres (throat conditions), X_O, X_H, and X_{OH} were calculated using tabulated equilibrium constants from Penner (Ref. 21), using Assumption No. 6 so that each species was calculated separately as a perturbation on the composition.

3. The composition of the preheater gas was plotted as a function of $(T_t)_{ph}$.

4. It was desired to operate the computer with input gas composition at the gas mixture reaction zone static temperatures of 1111, 1389, and 1667°K (2000, 2200, and 3000°R). The preheater gas total temperature necessary to produce these mixture temperatures was calculated as follows:

$$(T_t)_{ph+tf} = \frac{(T)_{ph+tf}}{0.75} \quad \text{(Assumption No. 4)} \qquad \text{(II-1)}$$

From the total enthalpy balance:

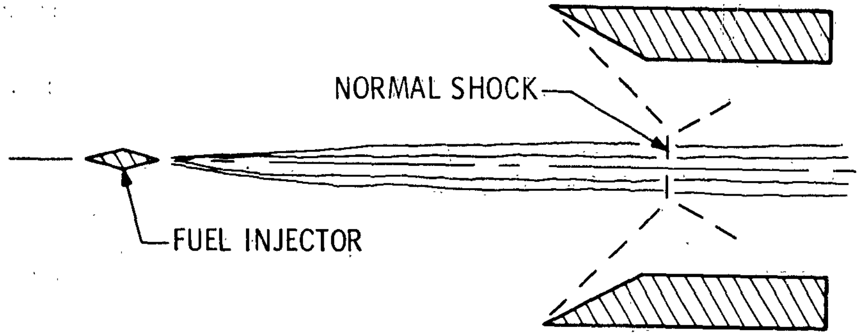
$$(T_t)_{ph} = \frac{(T_t)_{ph+tf}\, \Sigma\,(\text{moles } i)\, C_{p_i} + T_{tf}\,(\text{moles } H_2)\,(C_p)_{H_2}}{\Sigma\,(\text{moles } j)\, C_{p_j}} \qquad \text{(II-2)}$$

C_p values were those used in Ref. 8. A value of $(T_t)_{ph}$ was obtained for each $(T)_{ph+tf}$ and test fuel equivalence ratio desired.

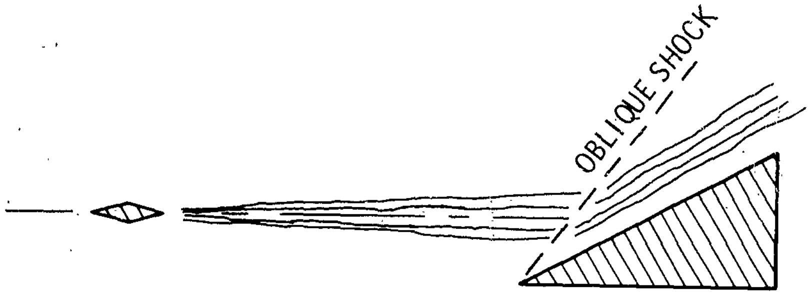
5. From the calculated $(T_t)_{ph}$, the preheater gas composition was obtained from the plot of composition vs $(T_t)_{ph}$ (Item 3).

6. The final composition for the computer input was obtained by adding the corresponding quantity of test fuel to the preheater gas and computing the resultant composition on a weight basis.

7. In addition, as required by the computer program, the stagnation enthalpy of each mixture was computed. The static enthalpy at $(T)_{tf+ph}$ behind the shock was also computed and the burner velocity calculated from the difference between the total and static enthalpy.



A. NORMAL SHOCK



B. OBLIQUE SHOCK (CONSTANT PRESSURE)

C. CONSTANT AREA, TWO-SHOCK MODEL

Fig. 1 Configurations for Supersonic Combustion Experiment

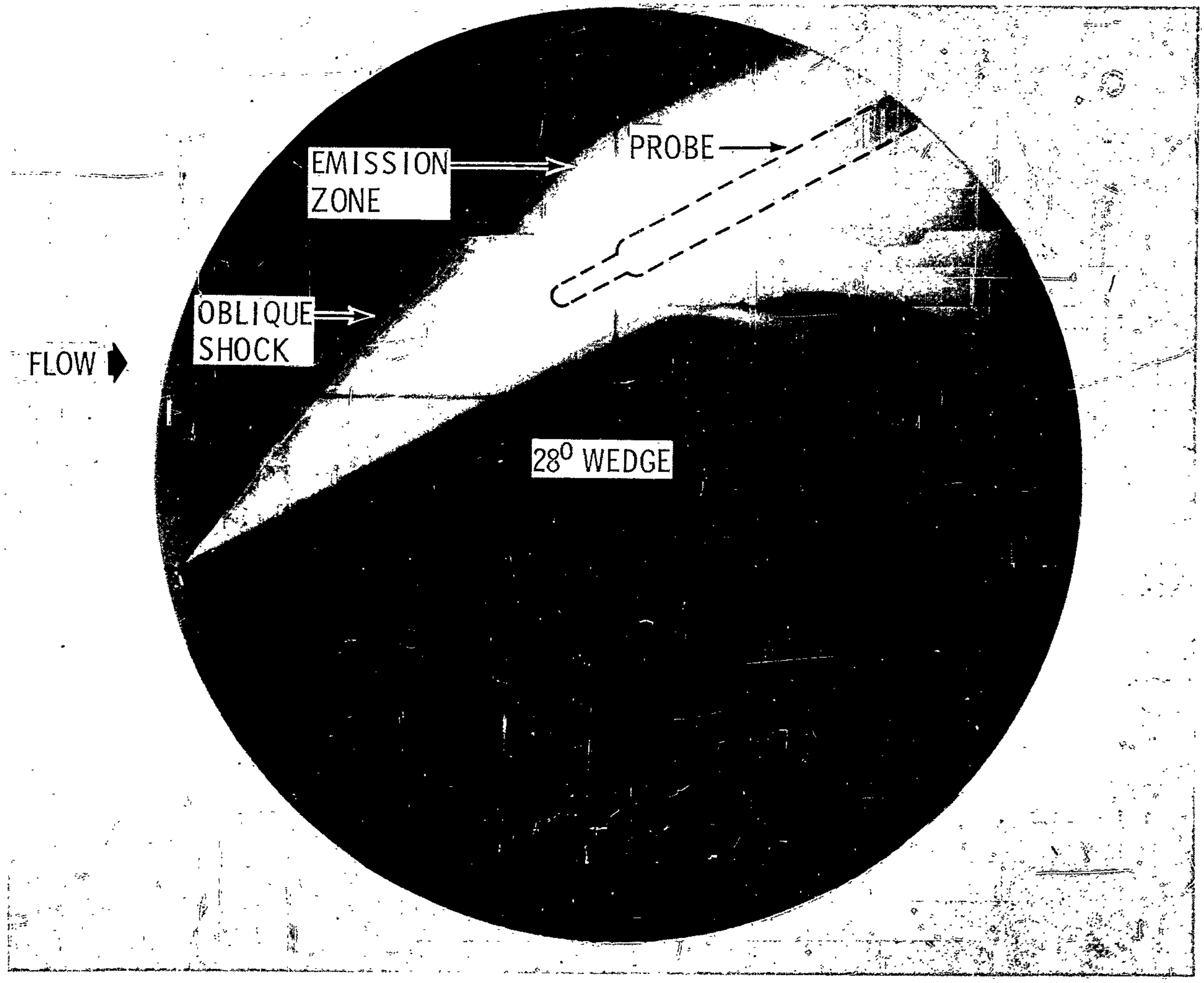


Fig. 2 Shock-Induced Combustion Aft of an Oblique Shock in a Mach Number 3 Stream

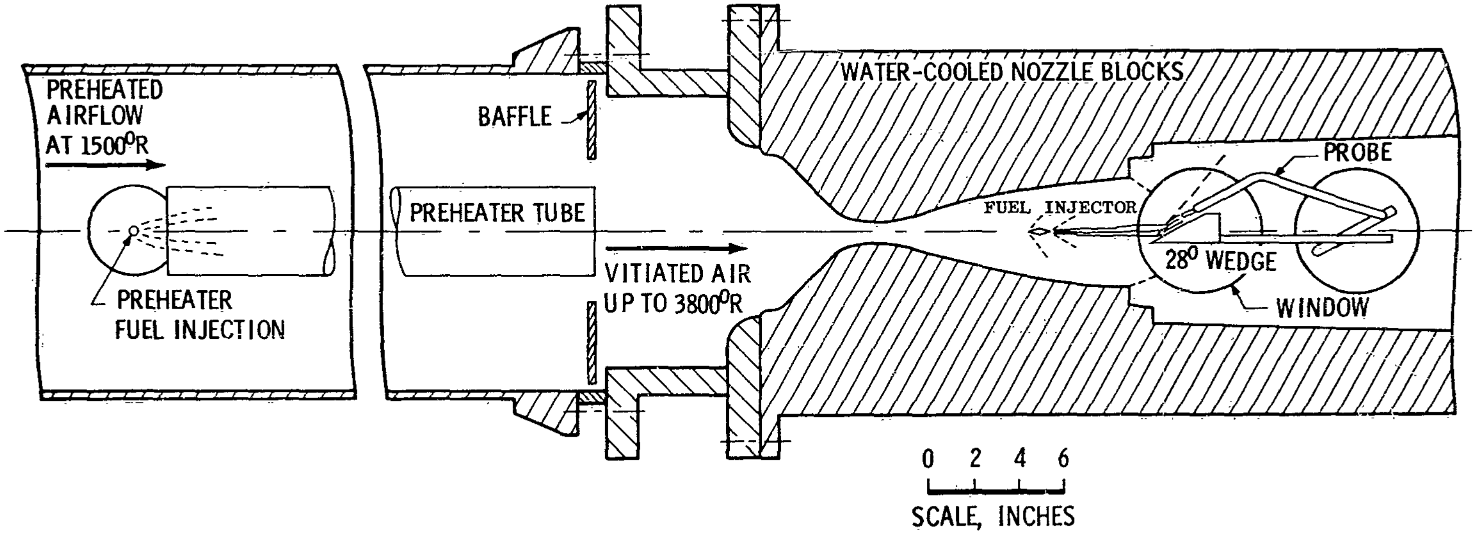


Fig. 3 Supersonic Combustion Tunnel and Oblique Shock Equipment

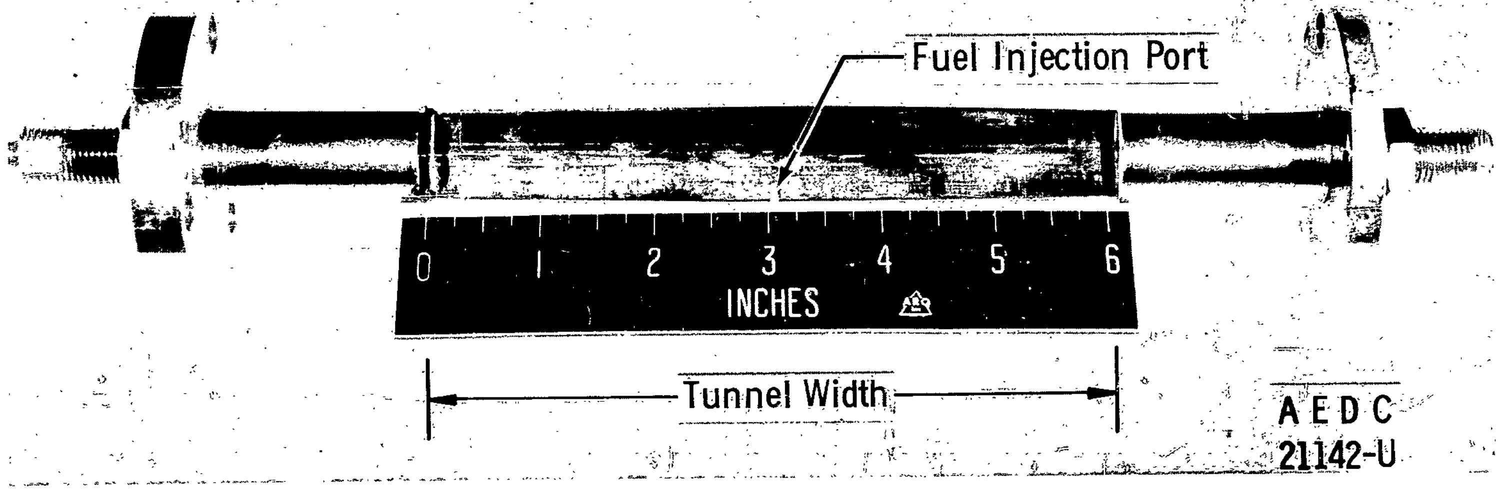


Fig. 4 Double-Wedge Fuel Injector, 12-deg Half Angle

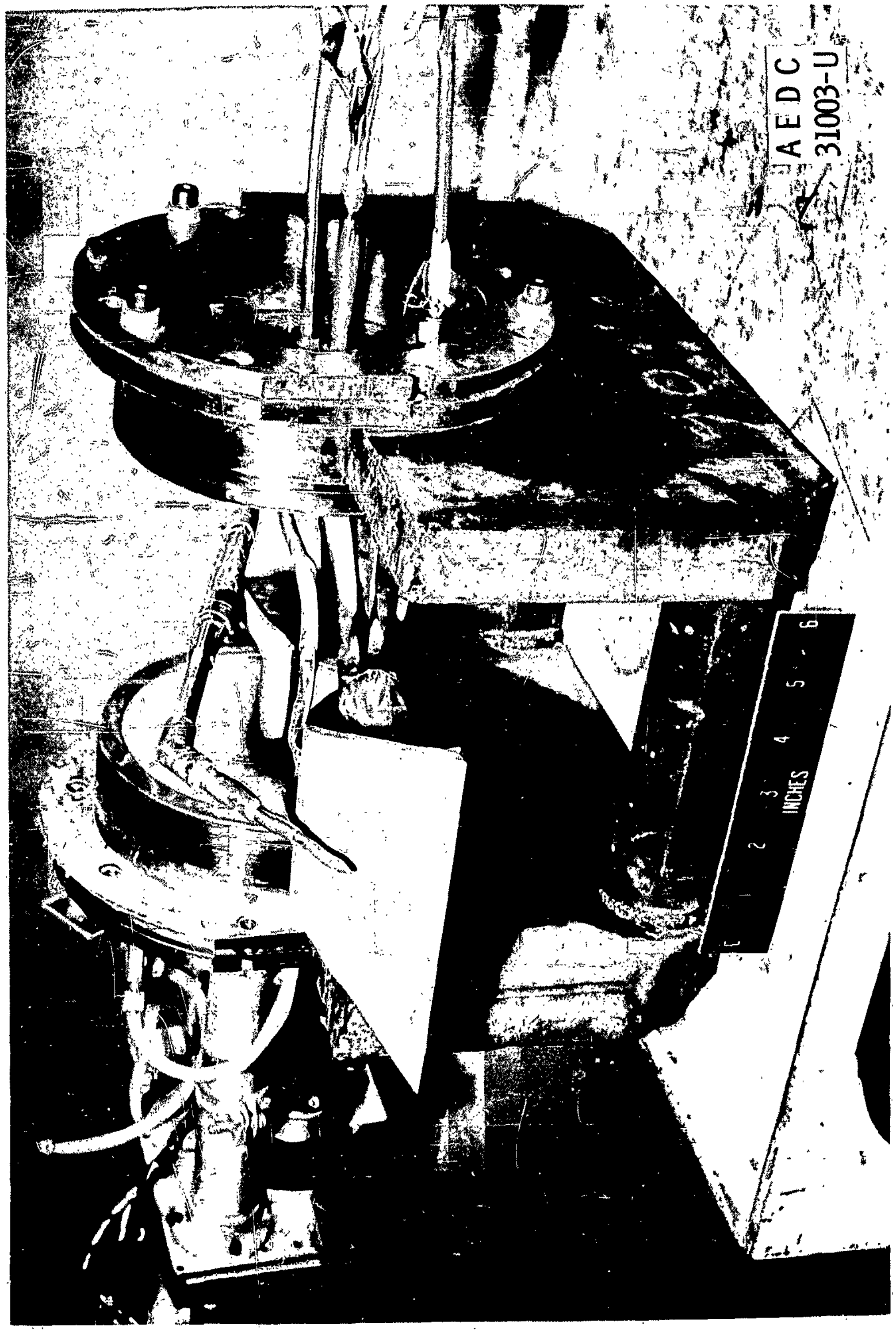


Fig. 5 Oblique-Shock Wedge and Probe for a 6-in. Wide Tunnel

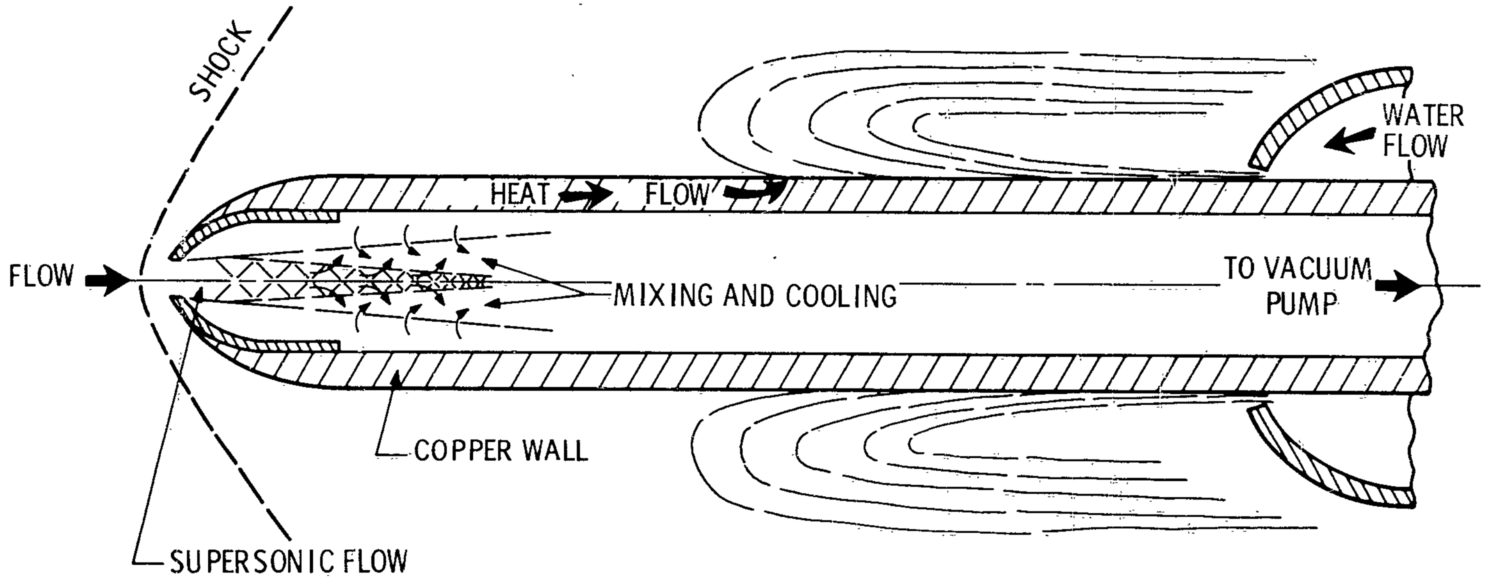


Fig. 6 Schematic of Gas Sampling Probe

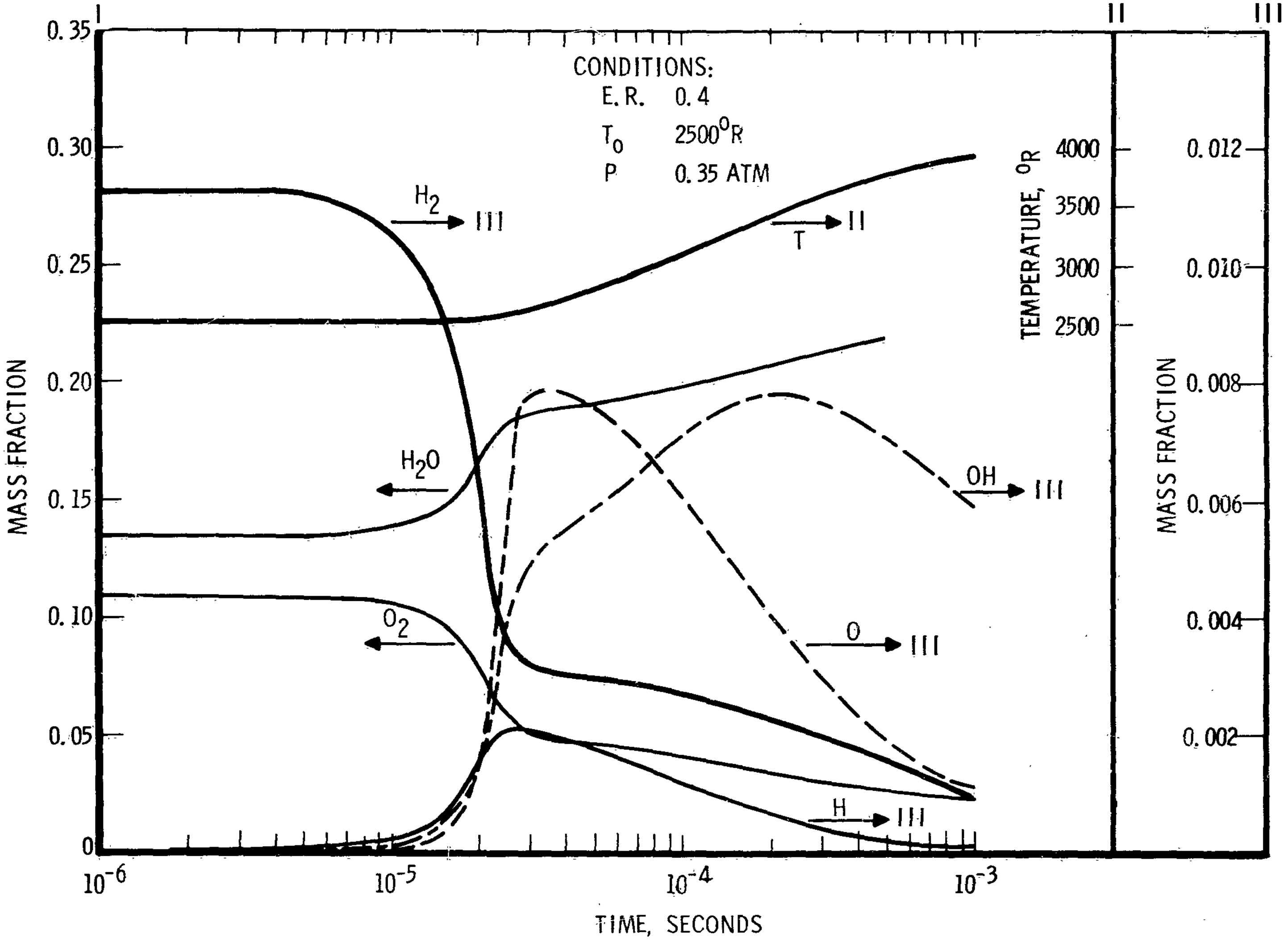
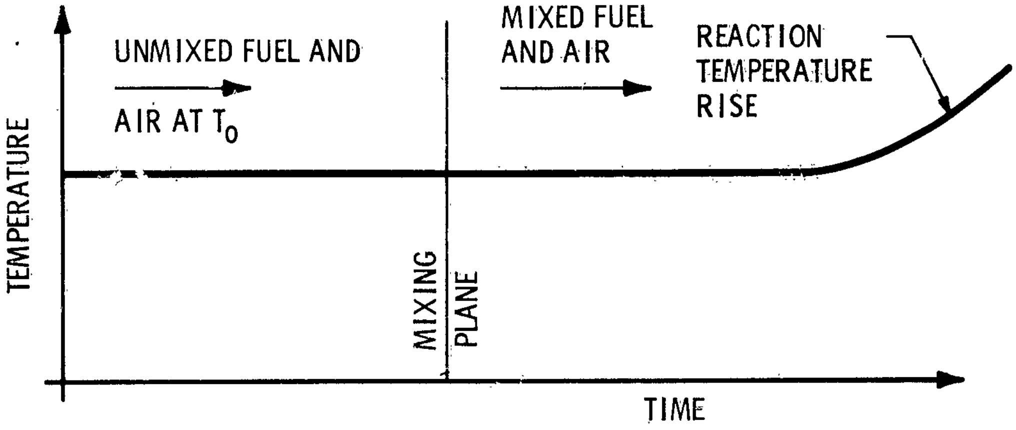
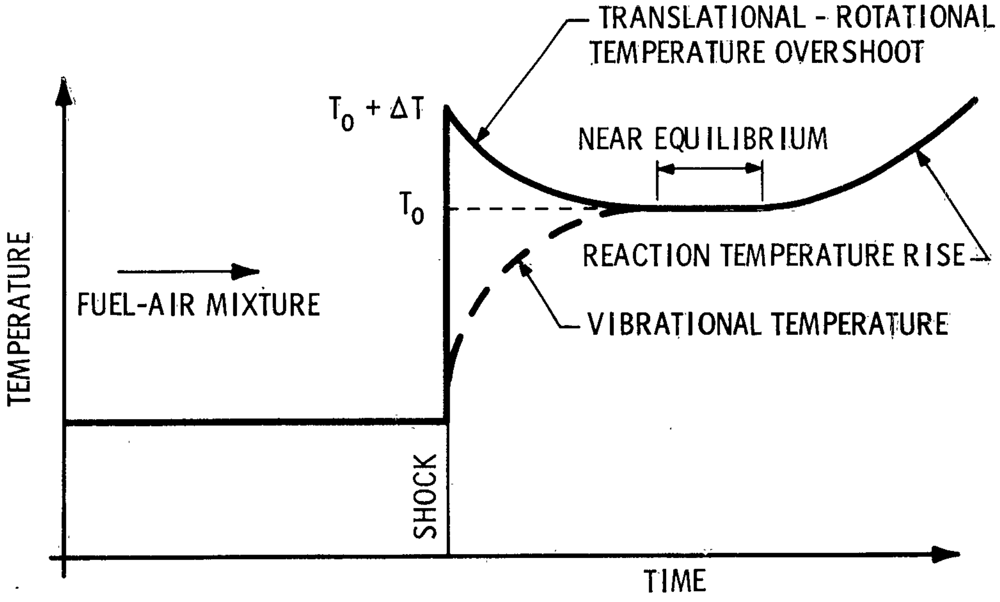


Fig. 7 Results of Kinetic Calculations for an H_2-Air Reaction Simulating Typical Test Conditions



LIBBY-MOMTCHILOFF KINETIC MODEL



SHOCK-INDUCED COMBUSTION MODEL

Fig. 8 Temperature-Time Curves Comparing Shock-Induced Combustion Model with Kinetic Models of Libby and Momtchiloff

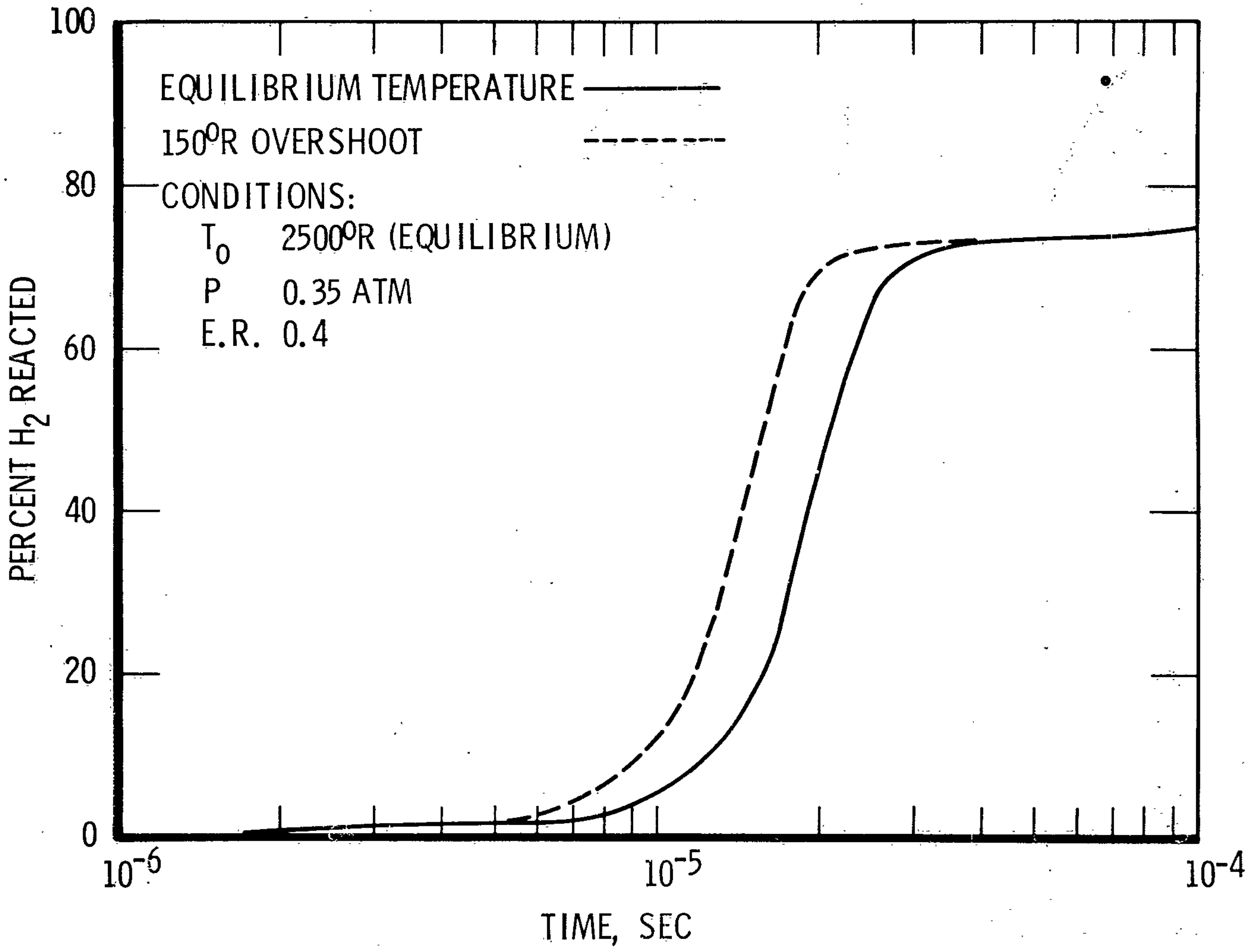


Fig. 9 Effect of Translational and Rotational Temperature Overshoot on H_2 Reaction Rate

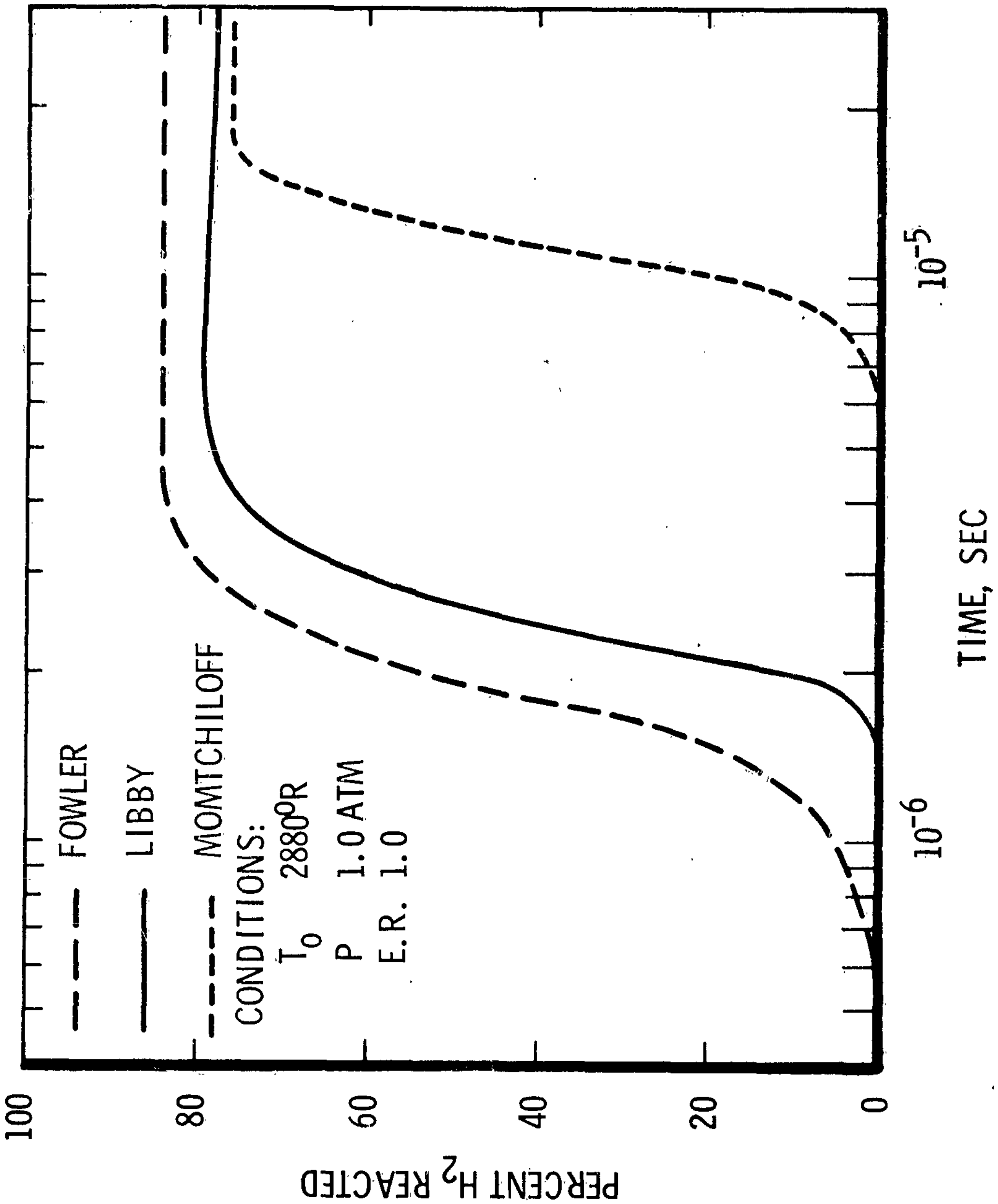


Fig. 10 Comparison of H_2 Reaction Rates for Various Kinetic Calculations

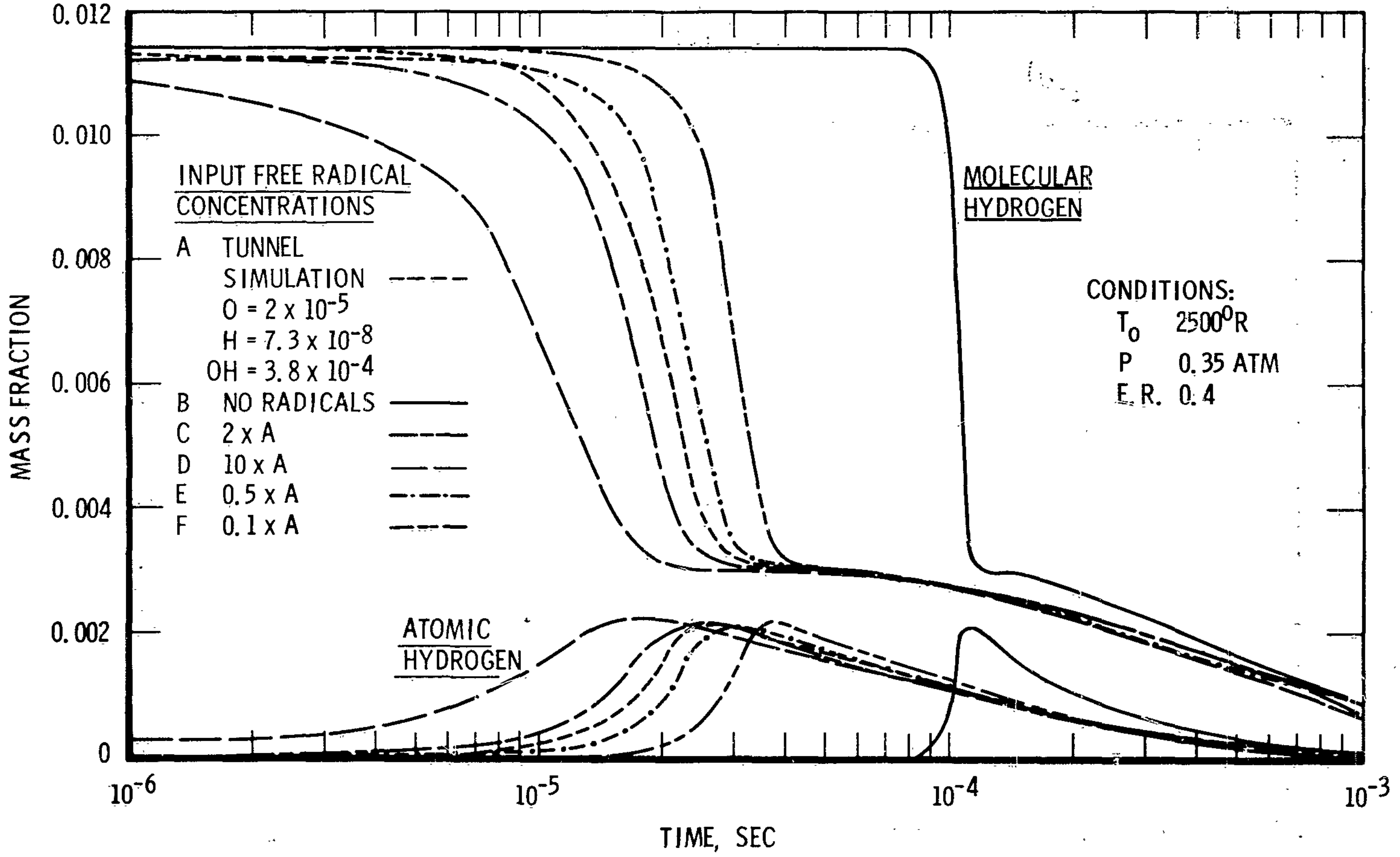


Fig. 11 Calculated Mass Fraction of H_2 and H vs Time with Large Changes in Input Free Radical Concentration

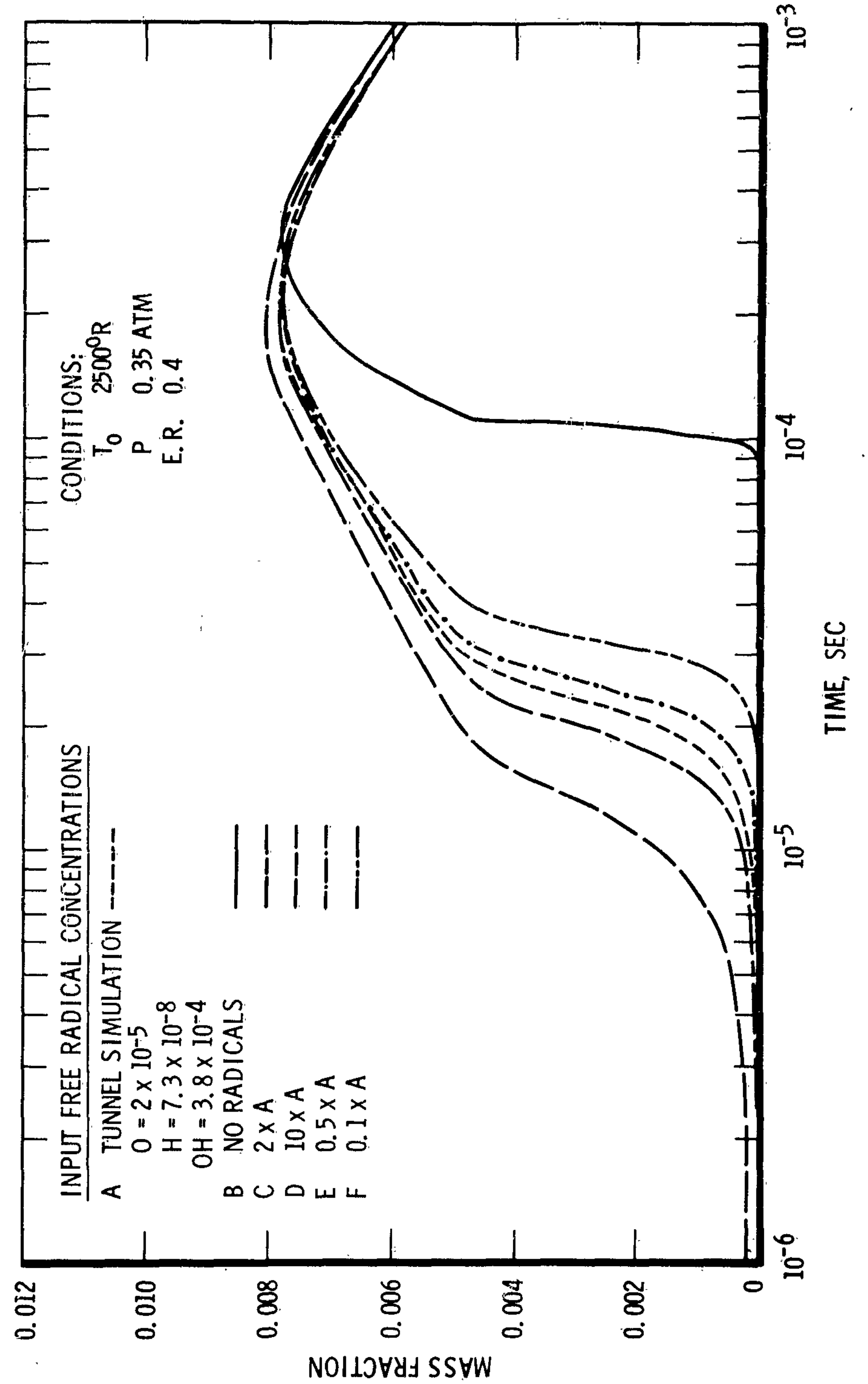


Fig. 12 Calculated Mass Fraction of OH vs Time for Large Changes in Input Free Radical Concentration

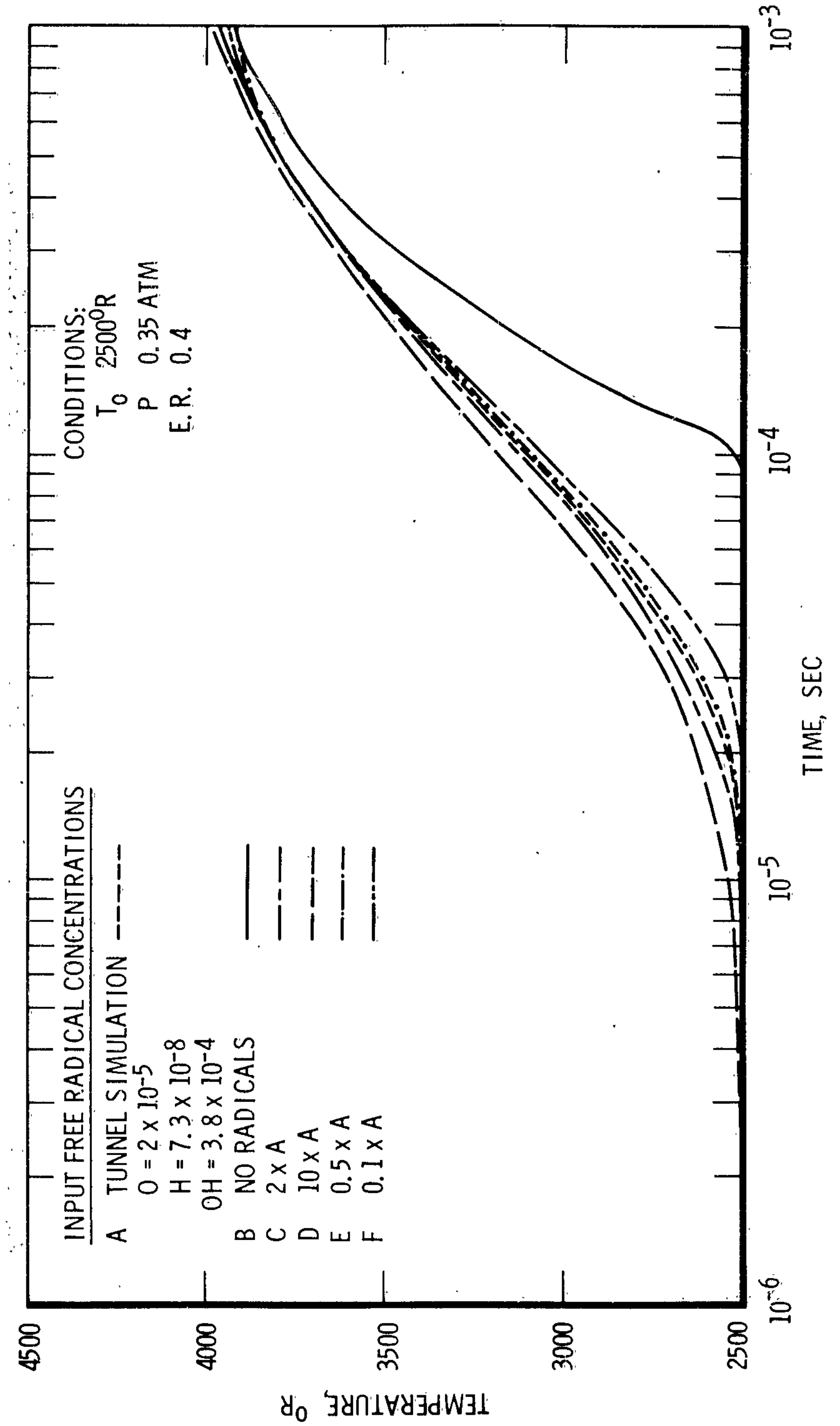


Fig. 13 Calculated Temperature vs Time for Large Changes in Input Free Radical Concentration

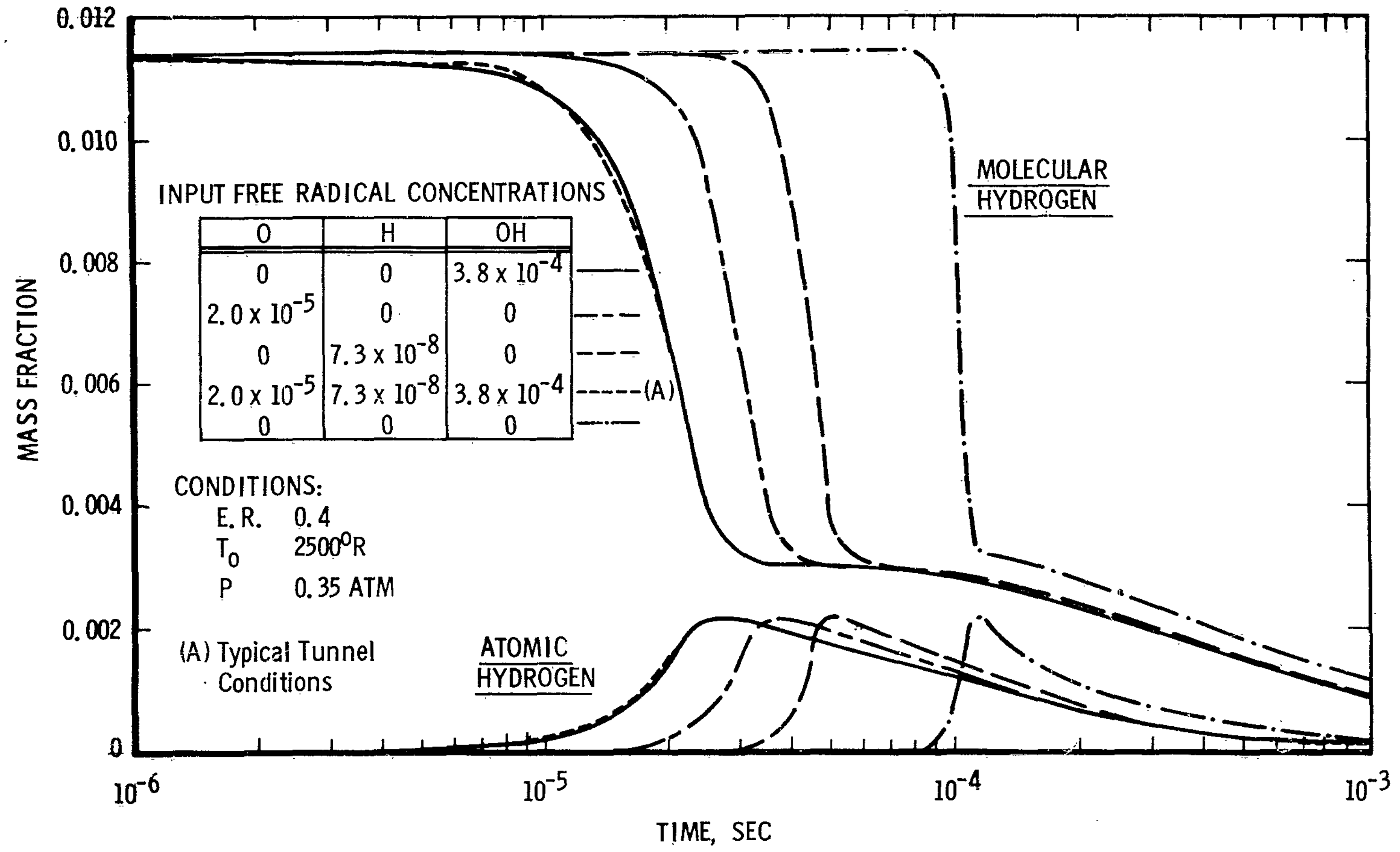


Fig. 14 Effect of Single Free Radical Concentration on Calculated Mass Fractions of H_2 and H vs Time for Conditions Simulating Tunnel Tests

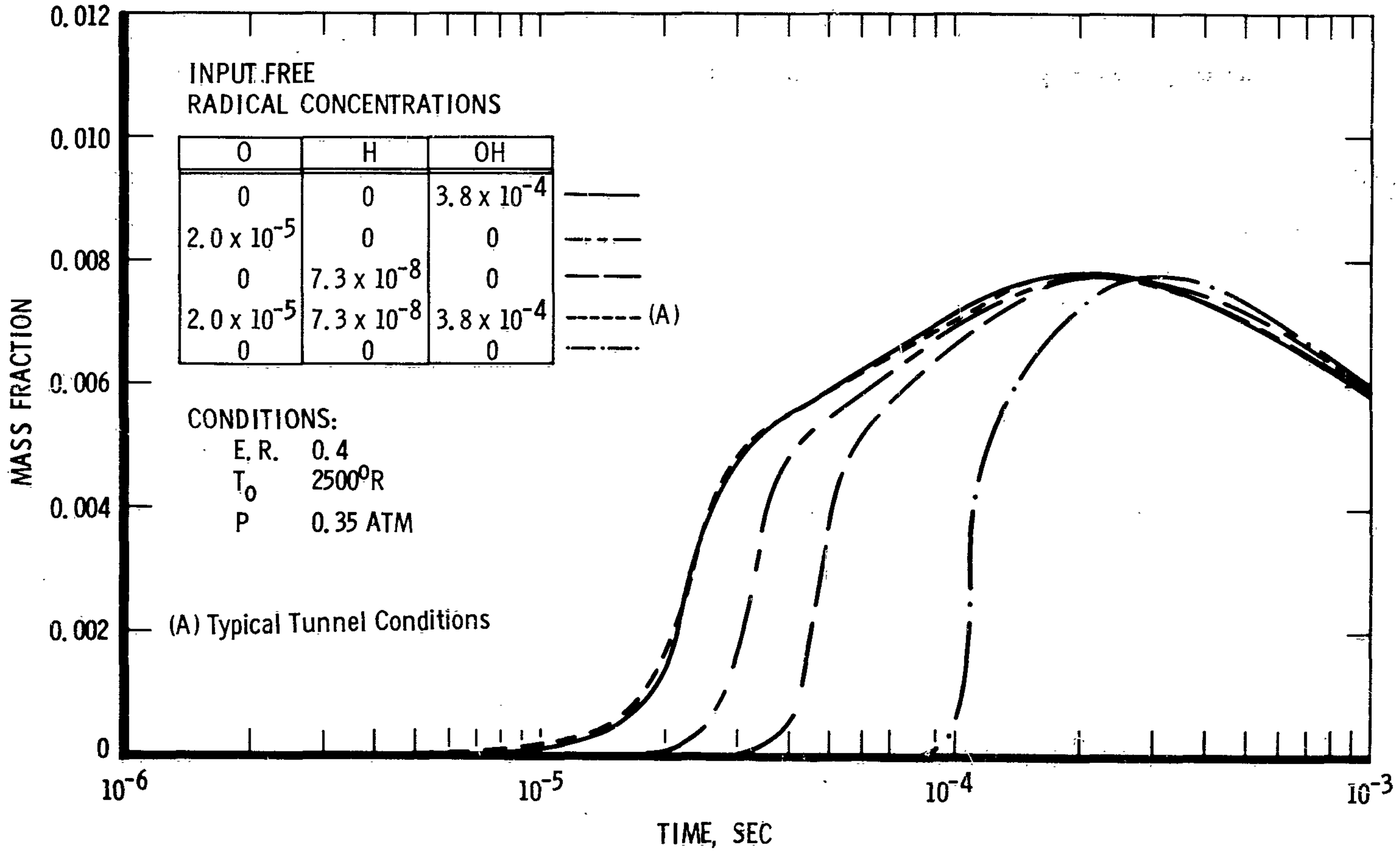


Fig. 15 Effect of Single Free Radical Concentration on Calculated Mass Fraction of OH vs Time for Conditions Simulating Tunnel Tests

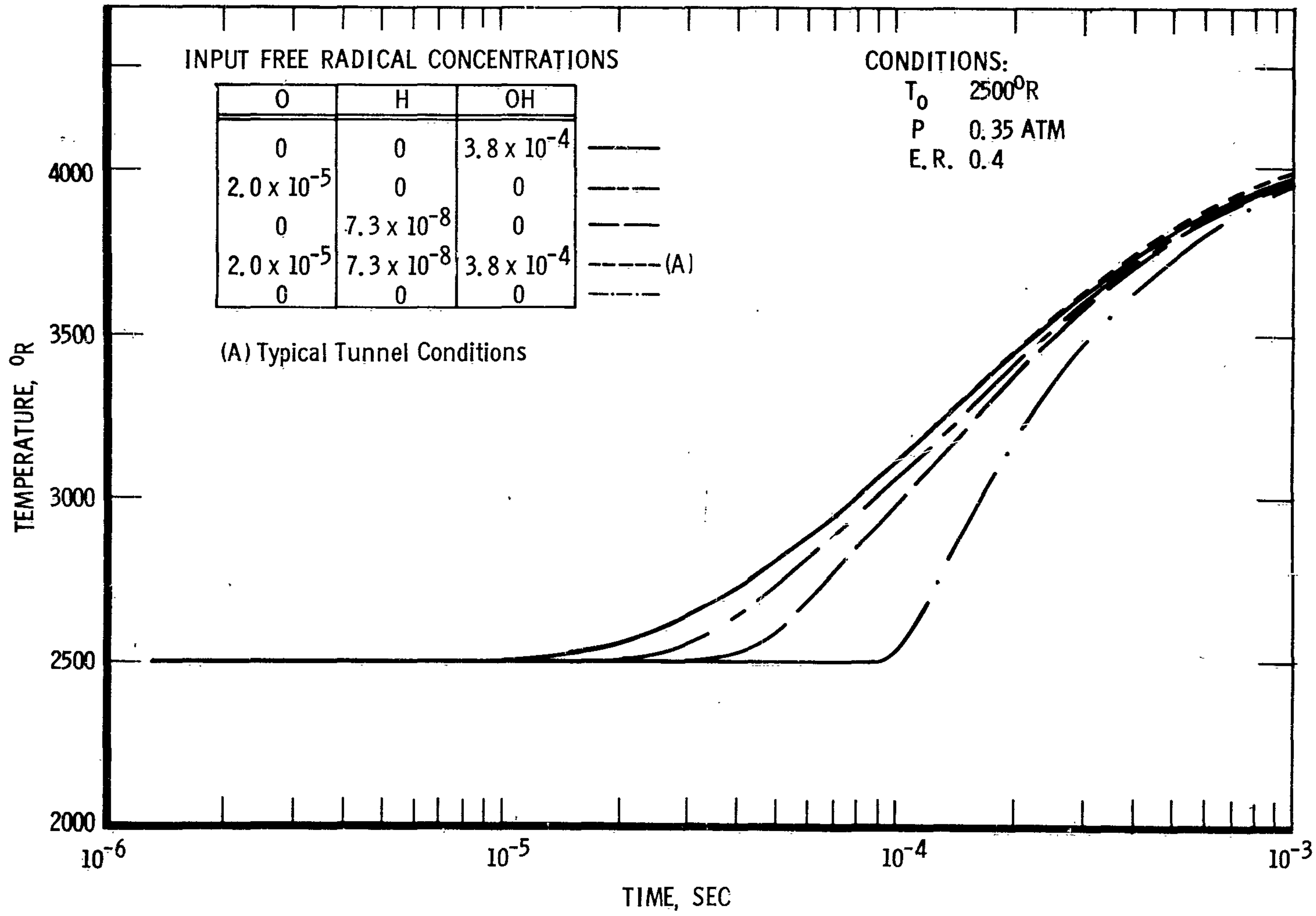


Fig. 16 Effect of Single Free Radical Concentration on Calculated Temperature vs Time for Conditions Simulating Tunnel Tests

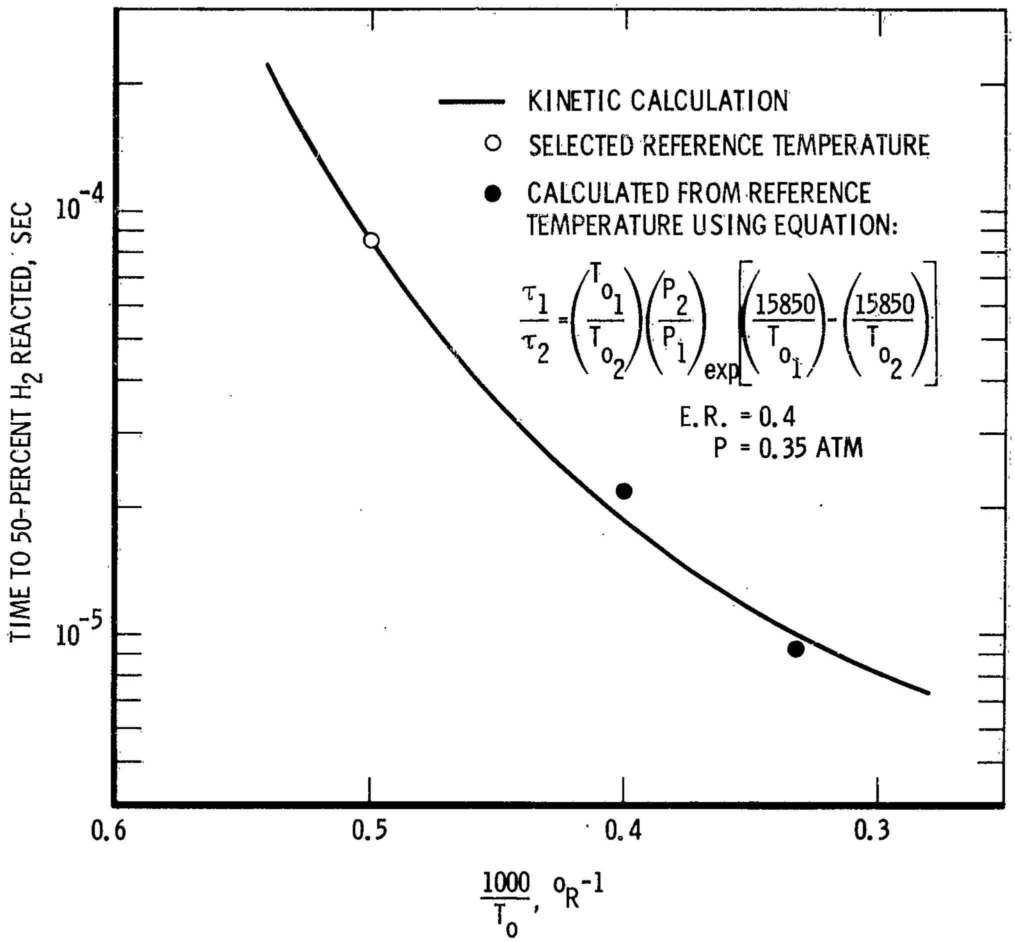


Fig. 17 Comparison of 50-percent H_2 Reaction Point for Kinetic Calculations and Correction Equation

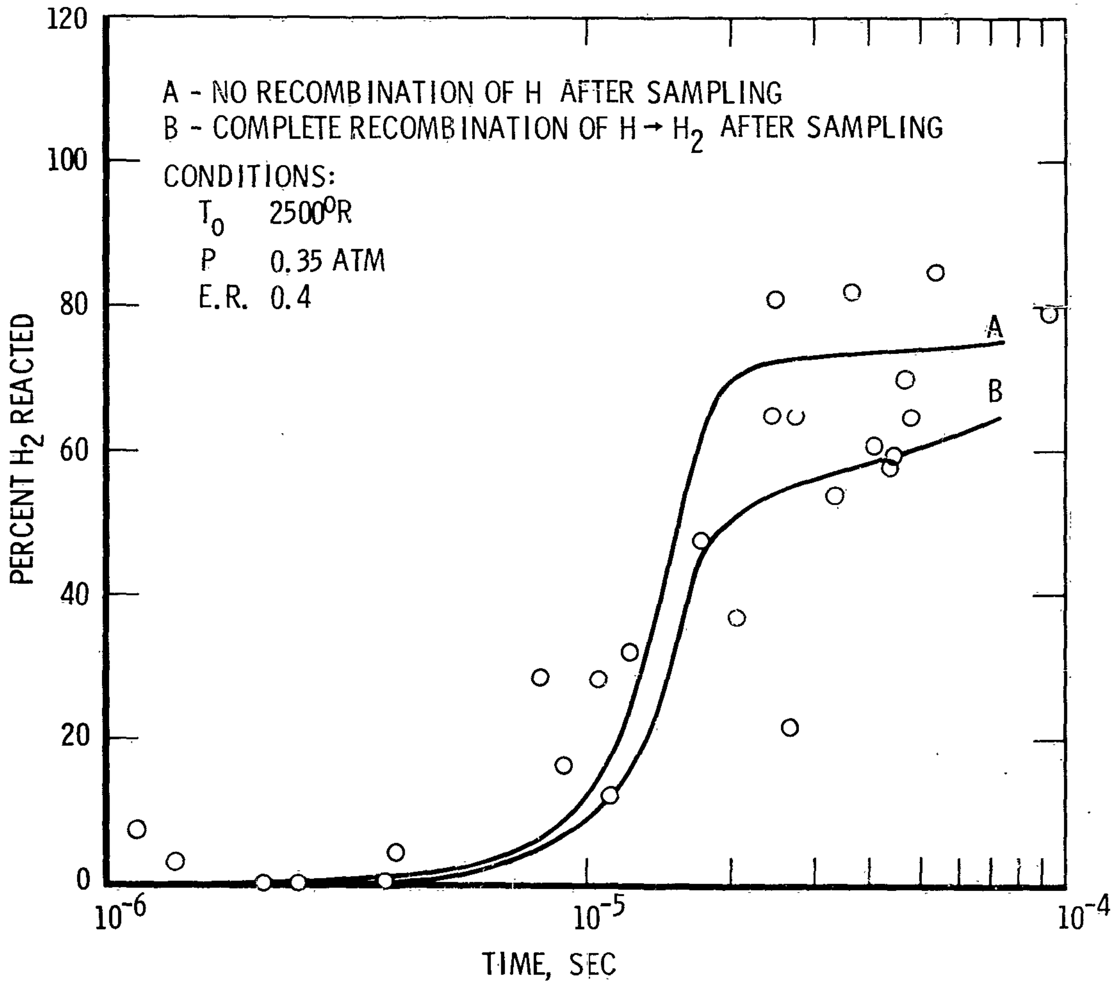


Fig. 18 Comparison of Kinetic Calculations and Experimental Data for H_2 Reaction in Vitiated Air

Arnold Engineering Development Center
Arnold Air Force Station, Tennessee
Rpt. No. AEDC-TDR-63-103. SHOCK-INDUCED COMBUSTION WITH OBLIQUE SHOCKS, COMPARISON OF EXPERIMENT AND KINETIC CALCULATIONS. June 1963.
49 p. incl 21 refs., illus.
Unclassified Report

Theoretical analyses made recently have shown the advantages of supersonic combustion for a hypersonic ramjet. The present work deals with experimental investigations of shock-induced H_2-air combustion in the constant pressure region aft of an oblique shock and with kinetic calculations for the H_2-air reaction. Quenched gaseous components for the early parts of the chemical reaction were analyzed to determine hydrogen molecule reaction rate, and a comparison was made of the experimental H_2 reaction rate with the current chemical kinetic computations. Agreement with one kinetic calculation for the H_2-air reaction at constant pressure was within the experimental error, indicating the possible use of kinetics to predict hypersonic ramjet combustion performance when shock-induced combustion is used. The concept of shock-induced combustion is defined and compared with the usual conditions where detonations are observed, and it is concluded that detonations are a special case of shock-induced combustion.

1. Ramjet engines
2. Combustion
3. Shock waves
4. Supersonic flow
5. Chemical reactions
6. Free radicals
7. Detonations

I. AFSC Program Area 801A, Project 6952, Task 695201
II. Contract AF 40(600)-1000
III. ARO, Inc., Arnold AF Sta, Tenn.
IV. P. M. Rubins and R. P. Rhodes, Jr.
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