AEDC-TR-67-177

3

cy 1

EXPERIMENTAL AND ANALYTICAL STUDY OF THE H_2-AIR REACTION KINETICS USING A STANDING-WAVE NORMAL SHOCK

Roger A. Strehlow, Consultant
and
Philip M. Rubins

ARO, Inc.

September 1967

This document has been approved for public release and sale; its distribution is unlimited.

ROCKET TEST FACILITY
ARNOLD ENGINEERING DEVELOPMENT CENTER
AIR FORCE SYSTEMS COMMAND
ARNOLD AIR FORCE STATION, TENNESSEE

NOTICES

ERRATA

AEDC-TR-67-177, September 1967

EXPERIMENTAL AND ANALYTICAL STUDY
OF THE HYDROGEN-AIR REACTION KINETICS
USING A STANDING-WAVE NORMAL SHOCK

Roger A. Strehlow and Philip M. Rubins, ARO, Inc.

Arnold Engineering Development Center
Air Force Systems Command
Arnold Air Force Station, Tennessee

Equation (10) on page 5 should read as follows:

$$\frac{\rho_2}{\rho_1} = \frac{\left(2h_2 - \frac{RT_2}{m_2}\right) - \left(2h_1 - \frac{RT_1}{m_1}\right)}{2RT_2/m_2} + \left[\left\{ \frac{\left(2h_2 - \frac{RT_2}{m_2}\right) - \left(2h_1 - \frac{RT_1}{m_1}\right)}{2RT_2/m_2} \right\}^2 + \frac{T_1 \; m_2}{T_2 \; m_1} \right]^{1/2}$$

AEDC-TR-67-177

EXPERIMENTAL AND ANALYTICAL STUDY OF THE H_2-AIR REACTION KINETICS USING A STANDING-WAVE NORMAL SHOCK

Roger A. Strehlow, Consultant
and
Philip M. Rubins
ARO, Inc.

Foreword

The work reported herein was sponsored by the USAF Office of Aerospace Research and by Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), Arnold Air Force Station, Tennessee, under Program Element 61445014, OAR Project 6952. Squadron Leader C. Holmes (RCAF) was the Air Force monitor of OAR Project 6952.

The report was given as a paper at the AIAA 3rd Propulsion Joint Specialist Conference, Washington, D.C., July 17-21, 1967, and is also identified as AIAA Paper No. 67-479. The research on this program was conducted from September 1965 to June 1967.

Professor R. A. Strehlow, Aeronautical and Astronautical Engineering Department, University of Illinois, was a technical consultant on subcontract to the project from September 1965 through June 1967.

This technical report has been reviewed and is approved.

Colin Holmes Squadron Leader, RCAF Directorate of Plans and Technology	Edward R. Feicht Colonel, USAF Director of Plans and Technology

Contents

Illustrations

Figure Page

Abstract

The design of a high speed airbreathing propulsion system (SCRAMJET) may depend on more precise information on chemical kinetics of the combustion processes than is now available, except for the very simplest reactions. An experimental method was devised whereby the macroscopic chemical reaction history can be traced from wall pressure measurements in a high speed reacting gas in a tube. The chemical reaction is started by means of a normal-shock compression at the tube entrance through which premixed fuel and air is heated to combustion temperature. The experiments were conducted with H_2 and vitiated air, and the data were compared with calculated pressure profiles using recent reaction kinetic information obtained from shock tubes. Good agreement between experiment and calculation was found when the flow was steady and no oscillations were present, indicating that the kinetics which govern the chemical reactions in shock tube experiments can be reproduced with the standing-wave experiment. Wall effects are evaluated. In addition, a semi-empirical analysis was made of the ignition delay and recombination, with the assumption that the two-body reactions are essentially in equilibrium during the slower recombination period. The mathematics of this approach is simple and is potentially useful with machine computations involving chemistry and mixing, or chemistry and aerodynamics. Finally, a short experiment with methane combustion in the tube produced similar phenomena, indicating that the method may be useful for determining rates of heat release for gases where little is known of the detailed kinetics.

Nomenclature

A	Cross section area
C_p	Specific heat at constant pressure
D	Tube diameter
F	Pressure correction factor (Eq. 30)
f	Coefficient of friction
f/a	Fuel-air mass ratio
H	Heat added from combustion
h	Enthalpy/unit mass
K	Chemical reaction equilibrium coefficient
k	Chemical reaction rate coefficient (appropriate units)
M	Mach number
M	Third body in chemical reactions
m	Molecular weight
mF	Mol fraction
N	Moles of gas per gram mixture for specific partial equilibrium state
N_f	Moles of gas per gram mixture at completion
N_i	Moles of gas per gram mixture at the start of chemical reaction (at the shock)
p	Pressure
Q	Heat transferred to the stream
R	Universal gas constant
Re	Reynolds number
r	Tube radius
T	Temperature
t	Time
u	Velocity
x	Distance in the tube along the direction of flow
φ_v	Equivalence ratio of vitiated air supply
φ_f	Equivalence ratio of unreacted fuel at the start of the chemical reaction

ξ	Extent of recombination, where $0 < \xi < 1$ as defined by Eq. (9)
γ	Specific heat ratio
ρ	Density
δ^*	Boundary layer displacement thickness
μ	Viscosity

Subscripts

a	Refers to air
comp	For compressible flow
f	Refer to fuel
inc	For incompressible flow
i,j	Refers to chemical species
mix	Refers to fuel and air mixture
t	At total or stagnation condition
w	At the wall
x	At a station x
1,2	With reference to the shock wave - 1 In front of the shock 2 Downstream of the shock
∞	Free stream

Introduction

The hypersonic ramjet with its need for supersonic combustion pronounces a need for extensive research to determine, much more precisely than heretofore, the details of the chemistry of combustion. For low altitudes where the combustor pressure is high and the chemical reaction fast, the reaction distance may be controlled by the mixing processes. However, as flight altitude increases, combustor pressure recedes, and detailed knowledge of the chemistry of combustion is needed, since the chemical reaction length may decide the engine length (Ref. 1).

There are other needs in high speed combustion; for example, a simplified mathematical description of the chemical reaction could be used to design a nozzle containing a reacting gas and using a method of characteristics with detailed chemistry, or analyze a mixing system in which the gas is reacting chemically at the same time. In addition, a means of studying overall reaction kinetics of other combustion systems than H_2-air is needed, where detailed kinetics are not currently understood and are considerably more complicated. If catalysts are added to extend the range of usable combustion for propulsion, the chemistry becomes even more complicated and incomprehensible.

In previous work at the Arnold Center (Ref. 2), an experimental method was demonstrated whereby a standing-wave normal shock was used to ignite an H_2-air mixture, and the resulting pressure change in a constant area tube was recorded from pressure taps in the tube and indicated the macroscopic combustion history in the flowing reacting gas. In the present work, (1) these experimental pressure profiles are compared with pressure profiles computed from recently proposed H_2-air reaction schemes and rates, and (2) a simplified mathematical model of the chemical reaction is developed, based on the assumption that partial equilibrium of the chemical processes exists during the recombination reactions.

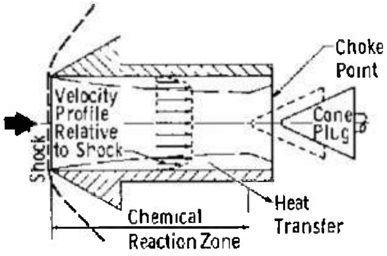
Theory

Theory of the Experimental Model

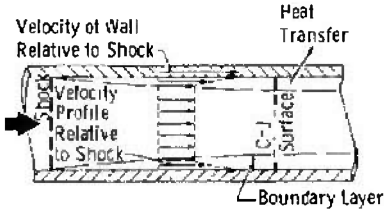
The purpose of the experiment is to produce a combustible mixture and suddenly heat it to ignition temperature by means of a steady standing-wave normal shock. Thus, the effect of chemical reaction in the flowing stream can be observed from steady-state wall static pressure measurements.

A standing-wave normal shock was first used by Nicholls (Ref. 3), later by Rhodes et al. (Ref. 4), and recently by Richmond (Ref. 5) as a means of observing ignition delay. Reasonable agreement was obtained with other ignition delay measurements, although a tube was not used to confine the flow downstream of the shock. In the present experiments, the normal shock is established at the entrance of a tube, such that ignition temperature is produced downstream of the shock and the flow is confined to a constant area (Fig. 1a). The chemical reaction may be considered to occur in one-dimensional stream tubes, irrespective of mixing, if the fuel profile and incoming gas properties are uniform and wall friction and heat transfer can be neglected. The effect of these factors on the experiment will be found in the section on discussion of results. This experimental model is very similar to the detonation wave in a tube, as shown in Fig. 1b. The principal phenomenological difference is in the boundary layer, in which the velocity is accelerating near the wall with respect to the wave in the shock tube, and decelerating with respect to the wave in the standing-wave experiment.

Whether the combustion zone is separated from the shock in a detonation wave has been debated (Refs. 6 and 7). However, the experiments at the Arnold Center with various methods of shock-induced combustion have shown a definite ignition delay zone in which the pressure measured just downstream of the shock corresponds with that which would exist if there were no combustion (Refs. 2 and 8). Hence, the present experiment produces a phenomenon that agrees with the Zel'dovich-von Neumann-Döring theory, where the shock wave produces an adiabatic pressure rise followed by heat generated from combustion. This process is shown in Fig. 2, where the peak compression point is denoted as the von Neumann spike (pt. B), constant area heat addition occurs on a Rayleigh line (B to C), and if sufficient heat is added under steady conditions, the thermal choking or Chapman-Jouguet point is reached.



a. Standing Wave Model



b. Shock Tube Detonation Wave Model

Fig. 1 Comparison of Shock Tube Detonation Wave Model with Standing Wave Model, Referenced to the Shock Wave

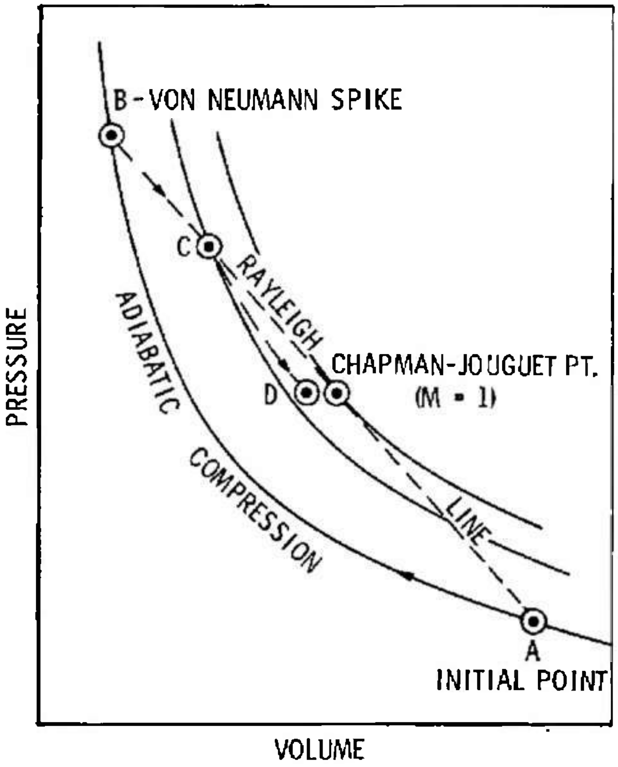


Fig. 2 Hugoniot Curve of Detonation Wave and Normal-Shock-Induced Combustion

Maintaining the shock exactly on the model lip is physically very difficult with heat release alone because slight variations in fuel concentration or airflow properties will cause fluctuations in the shock, resulting in spillage or swallowing. Therefore, the flow restricting cone plug was used to help maintain the shock-on-lip position. Thus the choke point was reached through a combination of chemical heat addition from point C to point D (Fig. 2) and flow restriction with the plug to reach the choking point at the exit at point E, probably with some continued chemical reaction.

Theory of the Chemical Model

The behavior of an inviscid quasi-one-dimensional reactive flow may be followed quite accurately by using numerical integration techniques on the set of equations which express the rate laws for the chemical transformations and the appropriate conservation equations describing the flow. Both the GASL (Ref. 9) and APL (Ref. 10) computer programs are examples of such an approach, and indeed comparisons made at the Arnold Center (Ref. 11) show that with identical kinetics these two programs yield essentially equivalent results. The difficulties with these programs are twofold. First, in order for this approach to yield accurate predictions for even the simplest flow situations one must know which reactions are important and one must have reasonably accurate rates for all the participating reactions. Second, this technique, while adequate for quasi-one-dimensional flows, is prohibitively time consuming in other more complicated situations; i.e., in a method of characteristics program or in a program which allows diffusive or turbulent mixing. In general, therefore, one must first explicitly prove the applicability of the kinetics used in any program of this type and then if possible find appropriate simplifications to the kinetic scheme (see for example Snow, Ref. 12, on the use of the steady-state approximation) to make the program tractable for the more general type of calculation.

H_2 Kinetics

In the case of the H_2-air reaction, various investigators have selected chemical reaction schemes and rates that appeared most probable based on the then current experimental evidence. Examples are the APL and GASL reactions and rates. Reaction histories computed from these two programs agree very well with each other and with the experimental data for the ignition delay period (Ref. 8). However, large differences appear between the APL and GASL predicted recombination (i.e., heat release) histories, and in their comparison to experiment (Ref. 2).

Recently, Getzinger (Ref. 13) has reported new rate constants for the recombination reactions and, in particular, has stated that only three reactions are important during recombination. Therefore, the APL computer program was modified to include only the following reactions:

1. The Shuffle reactions (Ref. 10):

1. $H_2O + H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2 + OH$

$$k_1 = 1.0 \times 10^{15} \exp(-25000/RT) \text{ cc/mole sec}$$

2. $H_2O + O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} OH + OH$

$$k_2 = 5.0 \times 10^{14} \exp(-18000/RT) \text{ cc/mole sec}$$

3. $H_2 + O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} OH + H$

$$k_3 = 7.0 \times 10^{12} \exp(-8500/RT) \text{ cc/mole sec and}$$

4. $O_2 + H \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} OH + O$

$$k_4 = 5.0 \times 10^{14} \exp(-18000/RT) \text{ cc/mole sec}$$

where R has units of cal/mole $^{\circ}K$, T is in $^{\circ}K$, and the reverse rates of these reactions are assumed to be related to the forward rates through use of the equilibrium constants,

$$k_{-m} = k_m/K_{p_m}$$

2. The recombination reactions (Ref. 13):

5. $H + H + M \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} H_2 + M$

$$k_5 = 4.0 \times 10^{14} \left[1 + 4(mF_{H_2O} + mF_{H_2})\right] \text{ cc}^2/\text{mole}^2 \text{ sec}$$

6. $H + OH + M \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} H_2O + M$

$$k_6 = 5.5 \times 10^{15} \text{ cc}^2/\text{mole}^2 \text{ sec and}$$

7. $H + O_2 + M \xrightarrow{k_7} HO_2 + M$

$$k_7 = 1.42 \times 10^{15}\left[1 - 4mF_{H_2} + 29mF_{H_2O}\right] \text{ cc}^2/\text{mole}^2 \text{ sec}$$

In the scheme that was employed, reactions (5) and (6) are assumed to be reversible with the reverse rates given by the expressions,

$$k_{-5} = k_5/(K_{p5}\ RT)$$

and

$$k_{-6} = k_6/(K_{p6}\ RT)$$

where the units on K_p are atmosphere, R has units of cc atm/mole $^{\circ}K$, and T is in $^{\circ}K$. Reaction (7) presents a problem in that it produces the new specie HO_2, which must either be included in the full scheme or handled in some other manner. The consensus at present (Ref. 13) is that, at high temperatures, this specie is quickly destroyed by reaction with reactive radicals. Therefore, HO_2 was not included as a specie in the kinetic scheme but was assumed to react rapidly with hydrogen atoms to produce two OH radicals through the process:

8. $H + HO_2 \rightarrow 2OH$

Therefore, reaction (7) is assumed to be irreversible and followed rapidly by reaction (8) to produce the overall stoichiometric change:

$$2H + O_2 \rightarrow 2OH$$

It should be added that initiation reactions such as $O_2 + M \rightarrow 2O + M$ were not included in this scheme although they are undoubtedly important to the early processes occurring in the induction zone (Ref. 14); all the comparisons reported herein were made for shock-induced combustion in vitiated air which already contained radicals (i.e., OH levels near 10^{-6} mols/mol mixture).

Numerical integration was started just downstream of the normal shock for all the calculations. The method of determining initial conditions for a specific calculation will be described later in this section.

The Partial Equilibrium Concept

Kaskan and Schott (Ref. 15) and Schott (Ref. 16) have discussed the requirements for partial equilibrium (PE) in a reacting system. In short, they define a PE state as one in which the available reversible reactions will not allow full equilibrium. They also point out that in certain cases one may treat a reacting system as having a partial equilibrium state if a number of reversible reactions, which are in themselves incapable of producing full equilibrium, are rapid while all other reactions are slow. Thus, depending on the difference in the relative rate of these two groups of reactions, the entire kinetic system may be more or less accurately modeled by assuming that the fast reactions define the relative concentrations of all the species and that the slow reactions simply drive this partial equilibrium (PE) system through a series of PE states toward full equilibrium.

In two significant papers, Schott and Bird (Ref. 17) and Getzinger and Schott

(Ref. 18) have shown that, at least in the range of temperatures from 2500 to 3200°R, the recombination kinetics of the hydrogen-oxygen system may be modeled quite adequately by using the PE approach. In their development of the concept, they assumed that the induction period of the reaction occurs without any simultaneous recombination and that at the end of the induction period, and thereafter, all shuffle reactions (i.e., the binary exchange reactions 1-4) remain in equilibrium while the recombination reactions simply change the extent of recombination. Since the shuffle or exchange reactions do not cause a change in the molecular weight of the system, they define the momentary PE state of the system through use of a single variable which represents the instantaneous value of the average molecular weight of the system. The same approach will be used here.

The PE Program

For this program, the initial composition of the vitiated mixture is defined in terms of three variables: φ_v, the vitiated stoichiometry; φ_f, the unreacted hydrogen stoichiometry at the normal shock wave: and ξ, the extent of recombination where

$$\xi = \frac{N_1 - N}{N_1 - N_f} \qquad (9)$$

and N_1 = moles per gram of mixture at the shock, N = moles per gram of mixture at any specific partial equilibrium state, and N_f = moles per gram of mixture if the recombination reactions were to go to full completion (i.e., to the point where the mixture contains only $H_2O + O_2$ + inerts for a lean mixture, or $H_2O + H_2$ + inerts for a rich mixture). It is further noted that the specification of φ_v, φ_f, ξ, and T completely describes the system because the partial equilibrium composition is determined by a set of three equilibrium equations, which are pressure independent (since they may be represented entirely by bimolecular exchange reactions). The program, therefore, contains a subroutine which calculates the partial equilibrium composition of the mixture for the set of variables (φ_v, φ_f, ξ, T). For this calculation, one must solve three non-linear equations in three unknowns. A three-variable Newton-Raphson method was employed in this subroutine to perform the calculation iteratively.

The remainder of the calculation was performed in the following manner. The experiment yielded the following properties of the fuel and vitiated air mixture before reaction: total temperature (T_t), total pressure (P_t), static pressure ahead of the normal shock (P_1), and static pressure immediately downstream of the lip shock (P_2). In addition, φ_f and φ_v could be determined from experimental measurements. Only two of the three experimentally measured pressures are needed to perform a calculation. The pressures (P_1 and P_2) were chosen, and P_{t2} was calculated for comparison with the experimental value.

In the program, an ideal gas assumption was used with real gas enthalpies. The enthalpies of the species were obtained from five-point curve fits to the JANAF tables (Ref. 14), and equilibrium constants were fitted to the equation ($\log K_p = A/T + B$) where A and B are constants. A subroutine was used to calculate the enthalpy (H), heat capacity ratio (γ), constant pressure heat capacity (C_p), and the molecular weight (m) of the mixture at a temperature (T) each time it was required.

The flow conditions upstream and downstream of the normal shock were calculated in the following manner: The stagnation enthalpy (H) was determined for the unreactive mixture. At this point, a series of temperatures lower than T_t were assumed successively until the calculated Mach number became greater than 1.5. Once two supersonic input flow values were obtained, a double-loop iterative calculation was used to adjust the incident temperature until the calculated value of P_2 P_1 for a normal shock equaled the experimental value. The shock calculation is described below. Stagnation pressure (P_{t2}) was then calculated, assuming unreactive isentropic stagnation for the flow downstream of the shock.

The shock calculation was performed by using the static enthalpy, static temperature, and molecular weight of the mixture at two stations (one upstream and one downstream of the shock) to determine the other property changes across the shock. To this purpose, one may solve the equations of conservation of mass, momentum, and energy for an ideal gas with variable molecular weight and real enthalpies to directly yield the density ratio between the two stations in terms of the above variables. The resulting equation is:

$$\frac{\rho_2}{\rho_1} = \frac{\left(2h_2 - \frac{RT_2}{m_2}\right) - \left(2h_1 - \frac{RT_1}{m_1}\right)}{2RT_2/m_2} + \left[\frac{\left(2h_2 - \frac{RT_2}{m_2}\right) - \left(2h_1 - \frac{RT_1}{m_1}\right)}{2RT_2/m_2} - \frac{T_1 m_2}{T_2 m_1}\right]^{1/2} \qquad (10)$$

The incident velocity may then be obtained by combining the mass and energy balance equations to yield

$$U_1 = \frac{\rho_2}{\rho_1}\left[\frac{2(h_2 - h_1)}{(\rho_2/\rho_1)^2 - 1}\right]^{1/2} \qquad (11)$$

The remaining flow and state variables may be calculated with this information. For the first shock calculation discussed, the shock was assumed to be unreactive, and therefore $m_2 = m_1$. This calculation was used to set initial values downstream of the shock wave for both the APL calculation with complete chemistry and the simplified partial equilibrium program.

In the PE program, the shock equations were solved iteratively for a series of assumed values of ξ, incremented from 0 to a value near 1. Thus all flow properties were uniquely determined for specific values of ξ. The only remaining problem concerns the distance between these stations. For $\xi = 0$ (the end of the induction zone), the approach of Rhodes (Ref. 20) was used as an approximation to calculate the induction delay time. For this purpose, the radical mole fractions were assumed to be in equilibrium in the vitiated mixture at the tunnel throat and were used as initial radical concentrations downstream of the shock with the assumption that the composition was frozen during expansion in the nozzle. These concentrations are quite low, and they were, therefore, not included in the overall stoichiometry of the system. A constant multiplying factor was included in the equation for the final concentrations so that the length of the induction zone could be adjusted if desired. It was found that setting this factor at 0.5 yielded the best correlation of all data. By using the induction time thus calculated, the length of the induction zone was found by multiplying it by the average flow velocity in the interval.

During recombination, the distance between stations (i) and (i + 1) having values of ξ which differ by $\Delta\xi$ was calculated by determining $d\xi/dt$ at each station, using the equation

$$\frac{d\xi}{dt} = \frac{\rho_2^2\, N}{(N_i - N_f)\, m^2}\, mF_H \left[\frac{k_5 mF_H}{2} + k_6 mF_{OH} + k_7 mF_{O_2}\right] \qquad (12)$$

The 1/2 in the k_5 factor arises because the concentration of hydrogen atom changes twice as rapidly as ξ in this equation and the original chemical notation is written in terms of H-atom concentration change. These values of $d\xi/dt$ are then used to determine the distance, from the equation

$$\Delta x = \Delta\xi (u_j + u_{j+1}) \Bigg/ \left[\left(\frac{d\xi}{dt}\right)_j + \left(\frac{d\xi}{dt}\right)_{j+1}\right] \qquad (13)$$

In the equation for $d\xi/dt$, it is assumed that the end state for the recombination process is a mixture in which $N = N_f$. This contention was checked in each calculation by calculating the full equilibrium concentrations through application of one of the recombination equilibrium constants. In all cases reported herein, $\xi > 0.99$ at equilibrium. Therefore, the neglect of reverse reactions in the equation for $d\xi/dt$ was satisfactory for comparisons.

This PE approach may also be used for other flow conditions. In the case of constant pressure flow, for example, the enthalpy per gram of mixture remains constant and the iterative procedure involves finding $T(\xi)$ such that $h(\xi) = h_{initial}$. The procedure is relatively simple because through the use of the PE concept the problem has been reduced to a single reaction coordinate (ξ) which is independent of pressure. Thus, this technique is also easily adaptable to a method-of-characteristics or mixing analysis.

<u>Equations Used in the Boundary Layer Corrections</u>.

The equations of conservation of mass, momentum, and energy can be used to calculate the equations for flow and chemical change in a duct (Ref. 21). By differentiating the equations, the "influence coefficient" may be calculated for the effects of variables on static pressure change in the flowing reacting mixture:

$$\frac{dP}{P} = \frac{-\gamma M^2}{1 - M^2}\frac{dQ}{C_pT} - \frac{\gamma M^2}{1 - M^2}\frac{dH}{C_pT} + \frac{\gamma M^2}{1 - M^2}\frac{dA}{A} - \frac{\gamma M^2[1 + (\gamma - 1)M^2]}{2(1 - M^2)}\frac{4f}{D}\,dx + \frac{\gamma M^2}{1 - M^2}\frac{dm}{m} \qquad (14)$$

The molecular weight term may be neglected since both the calculated and experimental data have molecular weight changes included. For undeveloped flow in a tube, the boundary layer growth can be considered in a similar manner to boundary layer on a flat plate where boundary layer displacement thickness includes heat transfer and frictional losses and can be treated as an effective area change. Equation (14) then reduces to:

$$\frac{dP}{P} = \frac{-\gamma M^2}{1 - M^2}\frac{dH}{C_pT} + \frac{\gamma M^2}{1 - M^2}\frac{dA}{A} \qquad (15)$$

where the dH term represents chemical heat release as calculated and the dA term the effective area change from friction and heat transfer. The term, dA/A can be evaluated from (see appendix)

$$\frac{dA}{A} \cong \left(\frac{\Delta A}{A}\right)_x = -\frac{2(\Delta\delta_x^*)}{r - 2\delta_x^*} \qquad (16)$$

where δ^* represents displacement thickness along the wall of the tube and the interior flow may be treated as an isentropic core (Ref. 22). The displacement thickness can be calculated for laminar or turbulent boundary layer; for example (Ref. 22),

$$\delta^*_{lam} = \frac{1.72x}{Re^{1/2}} \qquad (17)$$

Since transition is probable in the experiment, the end effect should lie somewhere between the laminar and turbulent case, although in either case, the effect will be shown to be small.

The gas properties used to determine Reynolds number were calculated from an H_2-air reaction kinetic computer program, where (1) the initial conditions at the start of the reaction were determined from the experimental measurements, (2) the chemistry was confined to a constant area process, and (3) the reactions and rates produced a computed pressure history which was a close approximation to the experimental pressure history. The tube was then divided into small increments (Δx) such that property changes were small in each increment, and the wall viscous and heat transfer effects on pressure were calculated for that increment with the assumption that small changes in the increment were negligible. Differential equations were used with the assumption that small increments were a satisfactory substitution for the differential term.

Three experimental boundary layer cases were considered:

1. No combustion and no heat transfer.
2. No combustion but some heat transfer.
3. Both combustion and heat transfer.

The pressure change measured for the cases 1 and 2 where no fuel was injected was compared with the calculated values. Agreement between the experimental and calculated values was used as justification for applying similar methods to the combustion with heat transfer data (case 3) in order to evaluate the extent of these effects. As will be discussed, the total effect was small (on the order of 1 percent).

Error Analysis

Effect of Change in Hydrogen Fuel Concentration on Temperature of the Mixture of Fuel and Air

From conservation of energy and the assumption that mean specific heat values are applicable,

$$T_{t_{mix}} \approx \frac{T_{t_a} + T_{t_f}\,(f/a)(C_{p_f}/C_{p_a})}{1 + (f/a)(C_{p_f}/C_{p_a})} \qquad (18)$$

By taking a first derivative and using increment values to approximate the differential,

$$\Delta T_{t_m} = \frac{C_{p_f}\,(T_{t_f} - T_{t_a})}{C_{p_a}\left[1 + \frac{C_{p_f}}{C_{p_a}}\,(f/a)\right]}\,\Delta(f/a) \qquad (19)$$

For typical experimental values of $f/a = 0.0016$, $\Delta(f/a) = 0.00016$ (10% error), $C_{p_f}/C_{p_a} \cong 13$, and $(T_{t_f} - T_{t_a}) = -1000^{\circ}R$, which yields $\Delta T_{t_{mix}} = -2^{\circ}R$. This is not large enough to affect the data or calculations by a measurable amount. For a 30-percent change in f/a ratio, $\Delta T_{t_{mix}} = -6^{\circ}R$. When the fuel concentration is about 0.3 equivalence ratio (E.R.), a 10-percent fuel concentration error will cause a $13^{\circ}R$ temperature error.

Pressure Measurement

From the approach discussed in Ref. 8, it is found that ignition delay is inversely proportional to pressure. Hence a 1-percent error in pressure will result in a 1-percent change in ignition delay. For recombination time, Ref. 9 indicates it is proportional to $p^{-1.7}$. Therefore, a 1-percent error in pressure will result in approximately 2-percent change in recombination time. Since the pressure measurement for most cases is within 1 percent, the effect of pressure error on the chemistry for the experimental cases discussed can be considered negligible.

Errors in Heat Transfer and Viscous Effects

The wall effects for the undeveloped flow in the tube is very small so that errors in calculation or measurements are second-order perturbations. However, at some conditions they can be of consequence. From Eq. (15), the effect of error in boundary layer thickness is represented by the equation

$$\frac{\Delta P}{P} \approx \frac{\gamma M}{1 - M^2}\,\frac{\Delta A}{A} = -\,\frac{2\gamma M}{1 - M^2}\,\frac{(\Delta\delta^*)}{(r - 2\delta^*)} \qquad (20)$$

where δ^* is determined for laminar or turbulent flow. For a typical case near the front of the tube, $M = 0.45$, $r = 0.45$ in., $\delta^* = 0.005$ in., and $\gamma = 1.3$, so that

$$\left.\frac{\Delta P}{P}\right]_{x \cong o} = 3.5(\Delta\delta^*) \qquad (21)$$

For an error of 10 percent in δ^* ($\Delta\delta^* = 0.0005$), then $\Delta P/P \cong 0.18$ percent, which can be neglected. However, as heat is added and Mach number increases to 0.8 near the end of the tube, with δ^* also increasing to 0.010, then $\Delta P/P \cong 12(\Delta\delta^*)$, and a 10-percent will result in a 1.2-percent error in $\Delta P/P$, or roughly of the same magnitude as from δ^*. From this analysis, it is concluded that errors in determining the wall boundary layer effects on pressure profile will be of negligible consequence for the fore parts of the tube, including the ignition delay and early recombination processes; however, as heat is added and the flow approaches $M = 1$, the wall effect errors may be of the same order or greater than that for the effect of the entire boundary layer displacement thickness.

Equipment and Procedures

The experiment consisted of heating air in a supersonic wind tunnel plenum to the ignition temperature of the fuel, or higher (Fig. 3). Heating was accomplished by means of a heat exchanger to about 1500°R and to higher temperature by burning hydrogen . Fuel was introduced into the vitiated air in either the supersonic portion of the tunnel or in the subsonic section just before the tunnel throat since in this section the static temperature was less than ignition temperature (Fig. 4). The possibility of preignition was greater when fuel was injected at the upstream point, but longer mixing lengths were obtained. Ignition of the fuel at the injector creates distinctive phenomena in the tunnel which are easily recognized. Emissions are observed upstream of the shock, and shock position is affected because tunnel Mach number is reduced. In addition, the combustion phenomena in the tube would not be observed, except as reignition of partially quenched reactions. These phenomena were not observed in the present experiments; hence preignition was not considered.

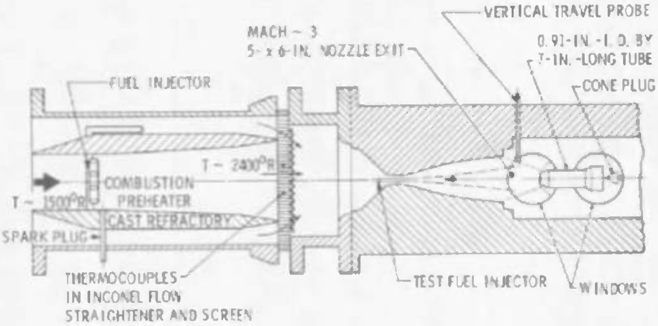


Fig. 3 Supersonic Combustion Tunnel with Standing-Wave Normal Shock Combustion Experiment

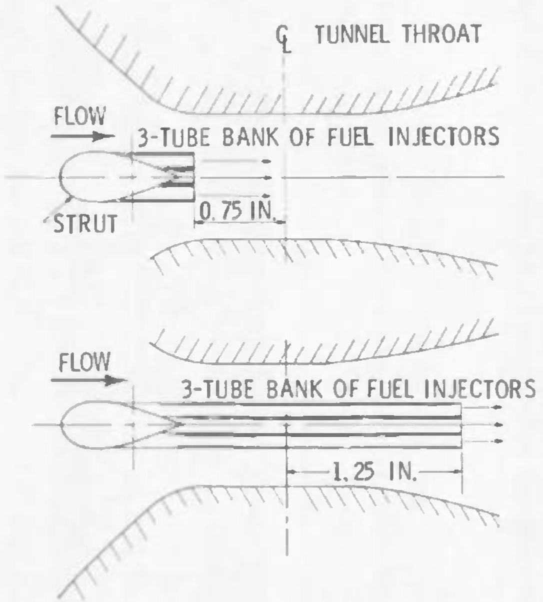


Fig. 4 Fuel Injector Configurations Used to Premix Fuel Entering the Combustion Tube

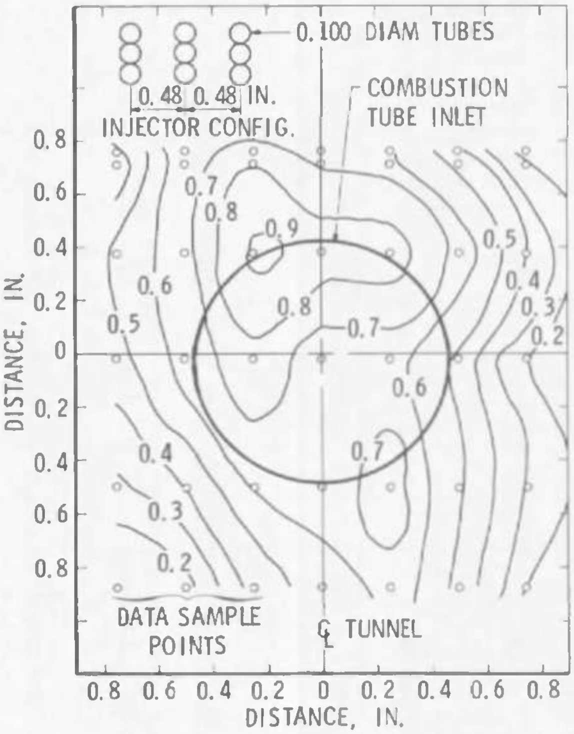
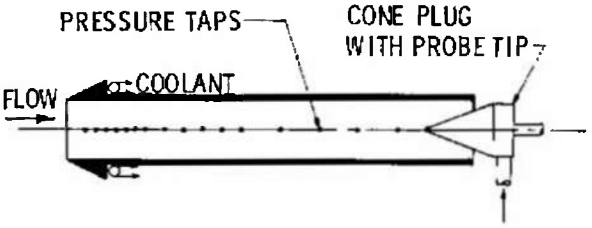


Fig. 5 Typical Fuel Concentration Distribution from a Multi-Point Fuel Injector with H_2 Fuel. Area Weighted Average Equivalence Ratio = 0.72; Center Point E.R. ≅ 0.65. Contour Lines Are for E.R. Values.

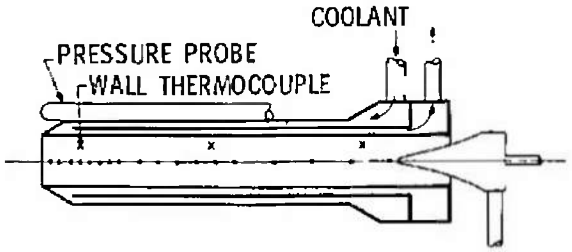
Several fuel injector designs were used in an attempt to obtain a fuel concentration uniformity of ±10 percent, but this effort was not very successful. A fuel distribution profile, using an area probing technique from a single point injector, was used to design a multiple point injector which was calculated to produce a nearly uniform profile. One of the better fuel distributions is shown in Fig. 5. It was concluded that, although the fuel profile from a single injection point can be measured, aerodynamic interference and construction problems arise in the process of designing multiple injection points to obtain a desired fuel pattern. Not the least of these is the drilling of small holes with predictable orifice coefficients that will inject the gas in self parallel streams. Alignment procedures were used before testing to check the orifice flow direction, using water injection, and to check the flow direction after installing the injectors in the tunnel, using air or nitrogen. These procedures allowed fuel profile uniformity to be improved. However, no design, manufacture, or installation procedure appeared to provide the desired fuel profile uniformity. Hence a portion of the results is concerned with analyzing the effects of nonuniform fuel profile.

The fuel mixture subsequently passed through the shock which was established at the combustion tube inlet, and at this point the temperature was increased to near stagnation temperature by the shock compression. The shock therefore constituted the ignition plane and a zero reference point for the reaction kinetics. The flow can then be considered one dimensional downstream of the shock if there is no spillover and mass flow is conserved. If chemical reactions are proceeding in the flow, the reactions can be considered as events in individual stream tubes, independent of the other stream tubes. (Translational temperature overshoot caused by vibrational relaxation was not considered in the analysis since the effects of this phenomenon on chemical reaction has not been well established and none of the experimental data show that it was a pressure measurable effect.) The changes in the gas properties were determined from wall static pressure measurements, and recorded on manometer tubes.

Two combustion tubes were used (Fig. 6). The thin-walled spray-cooled tube (Fig. 6a) was used first. Later a jacketed water-cooled tube was built, which included wall temperature thermocouples and cooling water temperature measurement (Fig. 6b). The large base area in this tube was the principal aerodynamic difference.



a. Spray-Cooled Combustion Tube



b. Jacketed Combustion Tube

Fig. 6 Diagram of Combustion Tubes (0.91-diam x 7-in. Long) Used for Normal-Shock Standing-Wave Experiments

The procedure for a specific set of test conditions consisted of: (1) Adjusting the flow constricting exit cone so that the normal shock rested as close to the lip as possible without swallowing, when no fuel was introduced. This provided a reference pressure profile which included friction and heat transfer and which would then be used to compare with data containing fuel chemistry, and (2) Injecting the desired fuel quantity and again adjusting the exit cone so that the normal shock rested as close as possible to the lip.

To obtain data with minimum spillover, the data were recorded for steady fuel and air flow, the only variable being the cone plug position. As the cone plug was retracted, data points were recorded until the shock could not be maintained on the lip. The point recorded just prior to shock swallowing was considered the best one. Schlieren photos were taken to verify the shock position.

Measurements

Measurements recorded consisted of:

Fuel Concentration Measurement

These were made by either (a) sampling the mixture in the region ahead of the combustion tube at several points in a plane perpendicular to the flow, and using a thermal conductivity gas analyzer to determine the unreacted hydrogen content, or (b) measuring total temperature profile in the heated air stream where cold hydrogen had been injected, so that hydrogen concentration was calculated as a function of its cooling effect. For the recording of combustion tube data, the area survey probe was removed, and a vertical traversing probe was used which measured total temperature, total pressure, and sampled the gas on a vertical centerline in front of the combustion tube.

Tunnel Flow Properties Measurements

These consisted of (a) pressure measurements to establish the tunnel operating conditions and (b) temperature recording to determine the stagnation temperature from the preheater and the amount of vitiation in the combustion preheater. A comparison of thermocouple data in the test section and in the straightening vanes showed good agreement; the straightening vane measurements were thereafter used. To calculate the concentration of free radicals in the test section, it was assumed that the vitiated air was in equilibrium at the tunnel throat and that the gas expanded with frozen composition to the test section (Refs. 2 and 8).

Combustion Tube Measurements

These consisted of 23 wall static pressure measurements in the tube (a) with swallowed shock to determine stream static pressure (using an average from several taps), (b) with shock-on-lip and no fuel to determine the static pressure behind a normal shock, and (c) with fuel and shock-on-lip to determine the change in pressure profile from chemical reaction. In addition, an actuated probe passing through the cone plug was used for some experiments to measure total pressure gradient and sample gases along the flow direction. Because of difficulties with the probe it was removed. For other experiments, the cone plug contained a sampling orifice in its tip. Equivalence ratio was determined from gas sample measurements from the cone plug. Where the centerpoint fuel concentration was not representative of the average, an adjustment was made in the calculations.

Discussion of Results

The primary measurement in the experiment was the wall static pressure drop caused by combustion and heat addition. The ignition delay and, in particular, the shape of the pressure curve during the recombination processes were important. In Figs. 7 and 8, experimental data at two pressure levels are compared with the calculated curves. The calculated curves were obtained using recent H_2-air reactions and rates (Ref. 18) and two computation procedures: (1) a modified IBM 7094 program based on the work of Westenberg and Favin (designated APL) (Ref. 10), and (2) a simplified "partial equilibrium" program described in the section on theory. As a further comparison, older rates proposed in Refs. 9 and 10 and tabulated in Table I for the same reactions were used in the computer program and also plotted in Fig 7. The experimental data appear to follow the trends of the more recent reactions and rate data proposed by Getzinger and Schott. The experimental data in Fig. 9 graphically show the effect of increasing tunnel temperature on the chemical reaction, particularly in the ignition delay region.

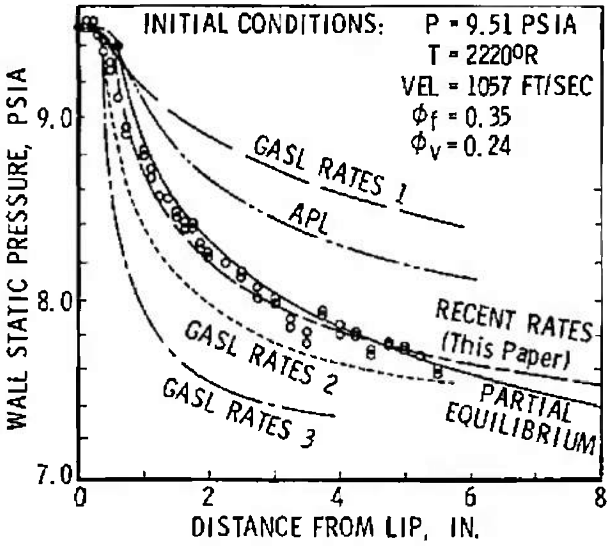


Fig. 7 Comparison of Various H_2-Air Pressure History Calculations with Experimental Data and the Partial Equilibrium Approximation, for an Initial Pressure of 9.51 psia.

Table I
Comparison of Some Reactions and Rates for the H_2-Air Reaction

Chemical Reaction	"Forward" Rate Equation		
	From Ref 9 (GASL)	From Ref 10 (APL)	Present Work
$H + O_2 \rightarrow OH + O$	$3 \times 10^{14} \exp(-8,810/T)$	$5 \times 10^{14} \exp(-18,000/RT)$	$5 \times 10^{14} \exp(-18,000/RT)$
$O + H_2 \rightarrow OH + H$	$3 \times 10^{14} \exp(-4,030/T)$	$7 \times 10^{12} \exp(-8,500/RT)$	$7 \times 10^{12} \exp(-8,500/RT)$
$2H + M \rightarrow H_2 + M$	$1 \times 10^{15} \times A$	$2 \times 10^{18}\, T^{-1}$	$4 \times 10^{14} \left[1 + \frac{4(F_{H_2} + F_{H_2O})}{\Sigma_i F_i}\right]$
$H + OH + M \rightarrow H_2O + M$	$1 \times 10^{16} \times B$	$3 \times 10^{19}\, T^{-1}$	5.5×10^{15}
$H + O + M \rightarrow OH + M$	$1 \times 10^{15} \times C$	$2 \times 10^{18}\, T^{-1}$	
$2O + M \rightarrow O_2 + M$	3×10^{14}	$2 \times 10^{18}\, T^{-1}$	
$H_2O + H \rightarrow OH + H_2$	$1.33 \times 10^{15} \exp(-10,950/T)$	$10^{15} \exp(-25,000/RT)$	$10^{15} \exp(-25,000/RT)$
$H_2O + O \rightarrow 2OH$	$3.12 \times 10^{15} \exp(-12,510/T)$	$5 \times 10^{14} \exp(-18,000/RT)$	$5 \times 10^{14} \exp(-18,000/RT)$
$H + O_2 + M \rightarrow HO_2 + M$ $HO_2 + H + M \rightarrow 2OH + M$ $\rightarrow 2H + O_2 + M \rightarrow 2OH + M$			$1.42 \times 10^{15} \left[1 + \frac{4F_{H_2} + 29F_{H_2O}}{\Sigma_i F_i}\right]$

$R_0 = 1.9846$ cal/gm°K
T = °K

Alternate Recombination Factors (GASL)

Factor	Rate 1	Rate 2	Rate 3
A	1	5	11.25
B	1	10	31.7
C	1	10	31.6

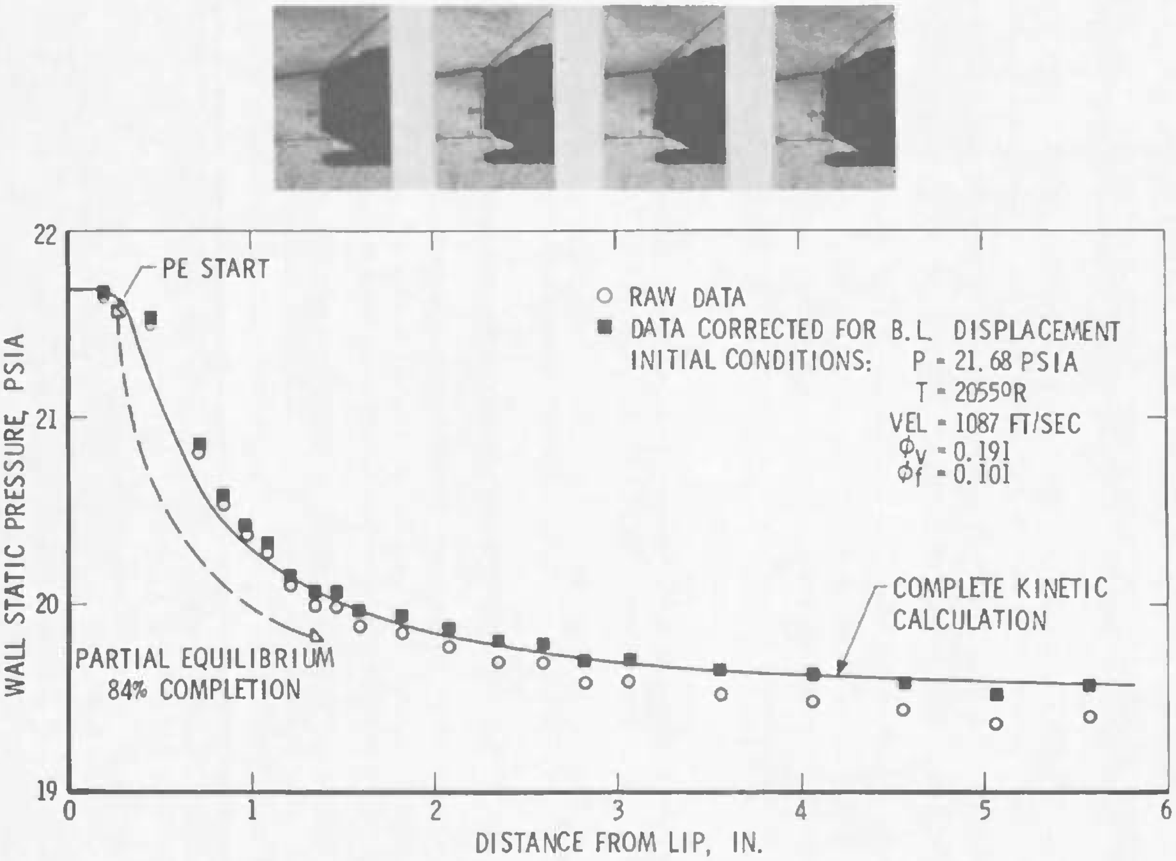


Fig. 8 Typical Experimental Pressure Profile for H_2-Air Combustion in a Tube When the Normal Shock Is Stable, and P = 21.58 psia; Comparisons to Calculated Curves with Complete Chemistry and with the Partial Equilibrium Assumption. Random Time Schlieren Photos Show Shock Stability.

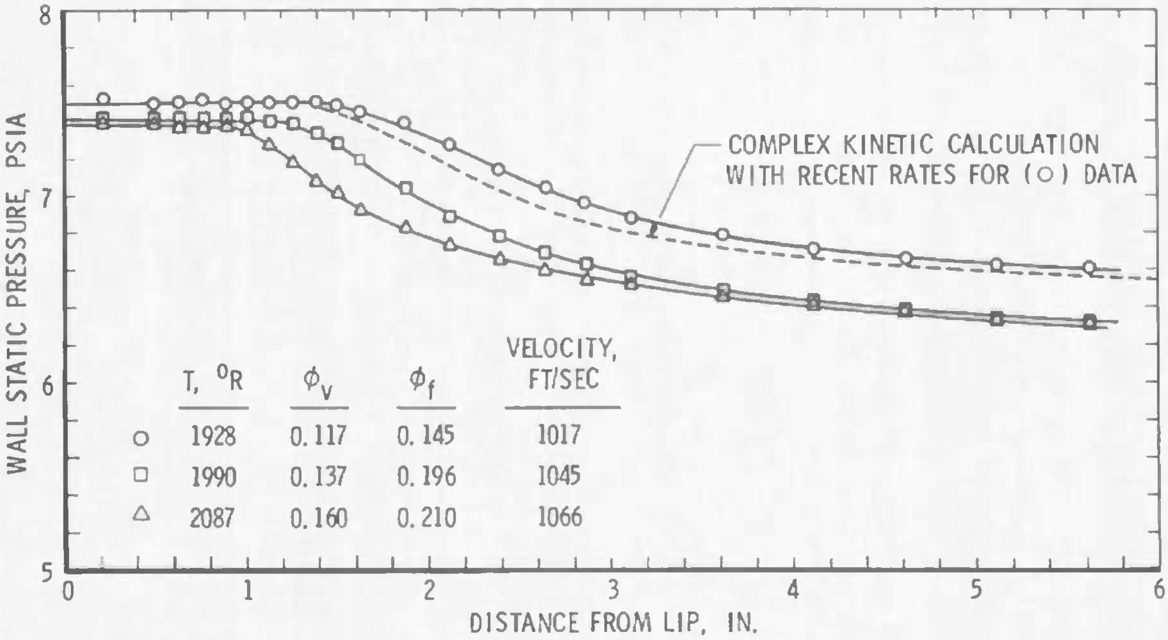


Fig. 9 Combustion Generated Pressure Profiles in the Combustion Tube, Using H_2 Fuel, and Showing the Effect of Increasing Temperature.

In addition, a short experiment was made with commercial methane (95 percent) to determine if the combustion characteristics of methane were such that similar recombination phenomena (i.e., static pressure change) could be observed in the tube. The pressure data clearly showed similar shaped pressure profiles to those from H_2-air reactions. Ignition delay determined for the experimental conditions ($T = 3100$ to 3200°R, $p = 0.65$ atm, $t_{i.d.} = 10^{-4}$ sec) was compared with shock tube results from Glass et al. (Ref. 23) and was found to be faster by a factor of 4 to 5. Preheater fuel required to obtain these high temperatures (E.R. = 0.45) produced relatively high free radical concentrations, 0.3 percent by volume (Ref. 24). These large amounts of free radicals and impurities could possibly affect ignition delay; however, no attempt was made to evaluate their effect at this time. The experiment did emphasize the need for unvitiated air in studying reaction kinetics of combustion processes for which there are little data on the detailed mechanisms.

As stated, the primary purpose of the work was to (1) correlate the measured pressure history from the chemical reaction in the tube with the pressure predicted by a chemical kinetic model, and (2) find an empirical or semi-empirical kinetic model which could be used to describe the chemical reaction as a close approximation to the actual case and yet be mathematically simple. Both of these objectives were accomplished to some degree. The limitations of the experiment, the limitations of the theory, extent to which the objectives were accomplished, and the problems which need solution for future work in kinetics experiments of this type will be examined in the following sections.

The range of conditions for the hydrogen reactions studied in the experiments included initial temperature of 1900 to 2300°R, initial pressure of 0.6 to 1.5 atm, and fuel equivalence ratio of 0.06 to 0.35.

Experiment and Theory and Their Limitations

Heat Release Compared with Theoretical Rayleigh Line Heat Addition

From the Zel'dovich-von Neumann-Döring theory of a shock wave followed by heat addition, one may calculate the gas flow properties just downstream of the normal shock from a knowledge of the upstream pressure, temperature, velocity and composition. For one-dimensional constant area flow, the quantity of heat that can be added to thermally choke the flow may be calculated. The free-stream Mach number for the tunnel is approximately 3.1. It follows that the Mach number downstream of the shock is approximately 0.45, and a total temperature rise of about 1300°R can be reached to thermally choke a flow when the initial static temperature is 2000°R. This temperature rise corresponds to an equivalence ratio for H_2-air of about 0.31, the upper limit of fuel addition for a completed chemical reaction. Obviously, higher equivalence ratios can be used if the reaction is not completed at the end of the tube, but, then, of course, less information on the reaction is obtained. About 80 to 90-percent reaction completion in the experiment is considered good for comparison of data with theoretical reaction kinetic schemes and rates. The amount of heat to thermally choke may be increased by raising the tunnel free-stream Mach number. For a Mach 5 free stream, choking equivalence ratio may be increased to 0.55; and a free-stream Mach number of 10 is needed to accommodate an E.R. of 1.0. In addition, a larger amount of heat may be added if the initial gas temperature is higher, the temperature ratio to choke being determined from Rayleigh line considerations. An infinite amount of heat may be added to a constant pressure combustion process without causing aerodynamic choking of the flow, even though the Mach number may decrease to 1.0 or less. However, the flow area must change very precisely in order to maintain the constant pressure, creating a difficult hardware problem. Other duct shapes may be usable for studying reaction kinetics, such as the expanding conical area. The selection of a configuration should be made such that the reaction does not quench nor restrict the entering mass flow.

Because of the Mach number and thermal choking limitation of the experimental model, the present approach is to correlate experimental and theoretical data for lean mixtures only. Later experiments may be used to verify the reactions for higher E.R.'s with a configuration which is not equivalence-ratio limited.

Wall Heat Transfer and Friction

The effects of wall heat transfer and friction were calculated by the method discussed in the theory section. Pressure data were obtained for the case where (1) no fuel was injected, (2) the shock was maintained on the lip, and (3) inlet air temperature was varied. Pressure profiles were then calculated for these cases for both laminar and turbulent boundary layers. A plot of the data and calculations is shown in Fig. 10. Since transition to turbulent flow is probable, it would be expected that the pressures measured at the end of the tube would lie between those calculated for laminar and turbulent flow. The accuracy of the data and the wall effects calculations is not such that laminar or turbulent boundary layer can be specified. The calculated effect is approximate and, for three typical experimental cases, was found to be approximately 1.0 percent at the end of the tube for laminar boundary layer and 1.5 percent for turbulent.

The region of ignition delay and initial recombination reactions is found in the first half of the tube. The boundary layer here is thin, and could be considered negligible or could be used to adjust the data.

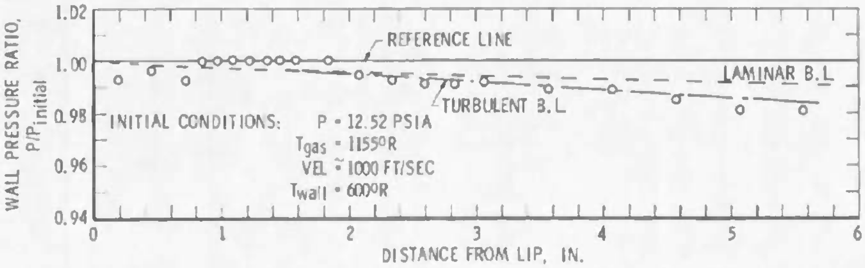


Fig. 10 Measured and Calculated Wall Viscous and Heat Transfer Pressure Effect in the Combustion Tube When No Fuel Was Present

In Fig. 8 is shown an experimental pressure profile that has been corrected for laminar boundary layer displacement thickness and wall heat transfer. The corrected values tend to more closely approximate the slope of the calculated pressure profile.

Fuel Concentration Nonuniformity

A typical fuel concentration map is shown in Fig. 5. For some data points, vertical traveling probe fuel profiles from traverses in front of the combustion tube showed even greater variation. It can be shown (Ref. 25) that the effect on wall static pressure of a one-dimensional flow with poor heat distribution in a tube of flowing gas is negligible, providing the pressure at any one station can be assumed to be constant across the duct. In addition, the computer programs with reaction kinetics can be used to establish that the kinetic history is not sensitive to fuel concentration for lean mixtures. It is suspected in the present case that constant pressure across the duct was not the case when fuel distribution was extremely asymmetric, and that this might explain the apparent "slow" recombination reactions obtained for a few data points, examples of which are shown in Figs. 11 and 12a. A simplified calculation of an extreme case where the fuel was assumed to be concentrated in 10 percent of the flow next to the wall and the pressure taps were located on the opposite wall indicated that a static pressure maximum lag in the tube might be as great as 0.2 inch near the start of the reactions, with a maximum of 0.4 inch as the flow approached M = 1. Since no fuel profile measurements showed a maldistribution of this extremity, the maximum effect calculated is not possible for steady-state conditions. However, it is possible that nonsteady fuel fluctuations may have an important effect on the pressure profile.

Expelled Shock at the Lip with Spillover

As the flow constricting cone plug is retracted during the experiment, the shock moves closer to the lip. The condition most closely approximating the theory occurs when the shock is very close to the tube inlet and spillover is negligible. When appreciable spillover is present, the data can not be used to correlate with the theoretical one-dimensional flow model with chemical reaction. Data of this type are shown in Fig. 11 and are discussed in Ref. 2.

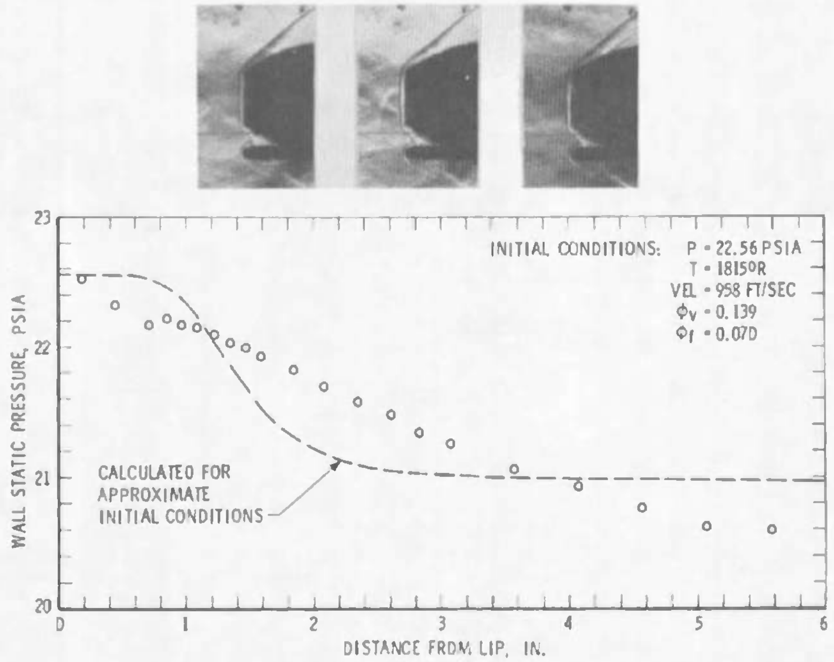
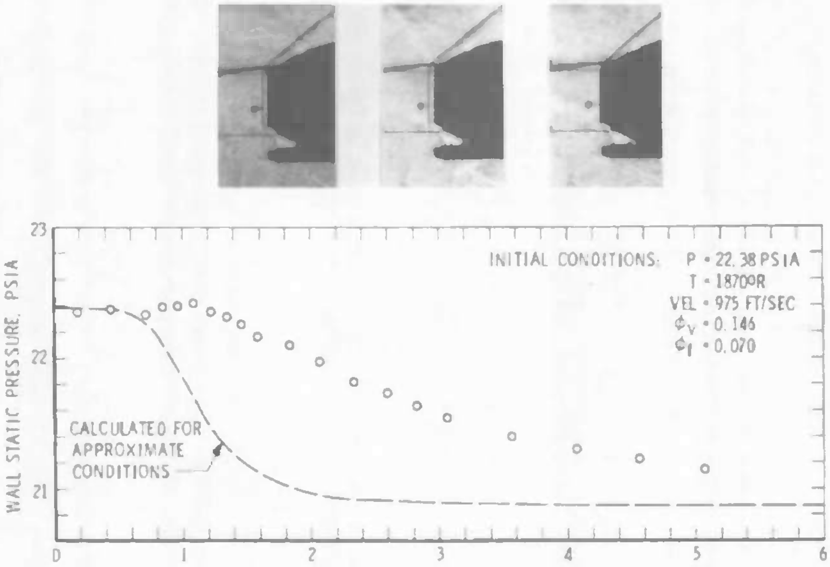
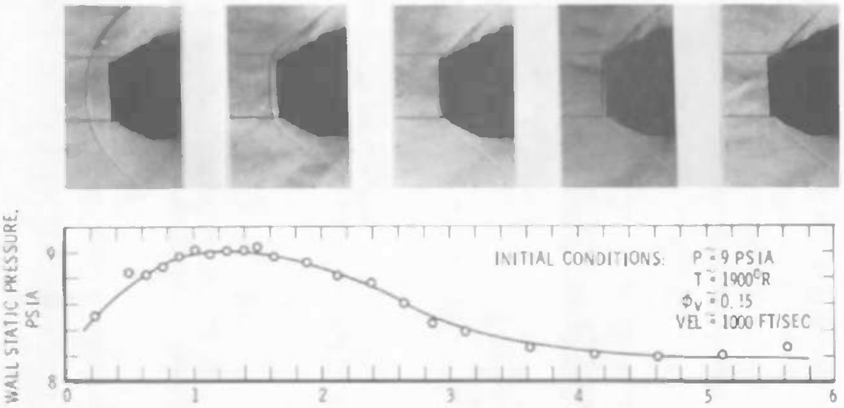


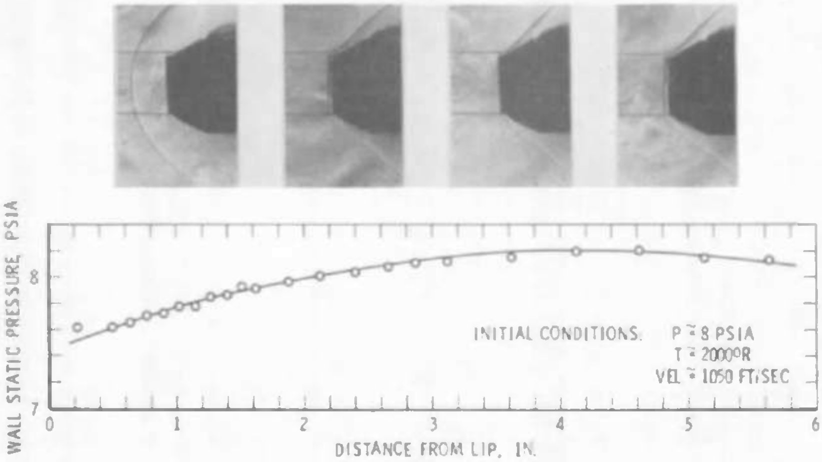
Fig. 11 Typical Combustion Tube Pressure Profile with Expelled Normal Shock, Compared to Calculated Pressure. Schlieren Photos Recorded at Random Time.



a. Small Oscillations



b. Larger Oscillations



c. Very Large Oscillations

Fig. 12 Combustion Tube Pressure Profile When Oscillations Are Observed. Random Time Schlieren Photos Show Shock Movement.

Shock Oscillation during Combustion

It was observed during the experiments that at some fuel flows the normal shock did not remain on the lip of the tube but oscillated in a fore and aft direction and at an unknown (not measured) frequency (Figs. 12a, b, c). The shock movement varied from fluctuations that were hardly perceptible to large movements covering nearly the full length of the tube out to about 1/2 inch in front of the lip. The magnitude of the movement appeared to be roughly proportional to fuel flow for a given set of flow conditions. The oscillations were first observed when the shock suddenly seemed to disappear. If the manometer board showed that the shock had not swallowed, it was noted that the oscillation produced a peculiar pressure profile which indicated a "slow" recombination history (Fig. 12a) or a pressure rise instead of a drop near the lip (Figs. 12b and 12c). Furthermore, from successive spark schlieren photos, the shock could be observed at various positions during the oscillation (Figs. 12a, b, c).

The wall pressure data were considered worthless for chemical kinetic studies when the oscillations were present. The pressure profile shown in Figs. 12b and c for an oscillating shock condition can be analyzed qualitatively if it is assumed that the pressure measured on the manometer tubes is a time-mean-average of the instantaneous pressures. This is shown in Fig. 13. When the shock is expelled, the lip pressure is high because of subsonic flow divergence behind the normal shock, and less pressure change from heat addition occurs; when the shock is swallowed, the low free-stream static pressure is sensed. The manometer tube registers a pressure which is some function of the duration of the pressure exposure time. In this analysis, it was assumed that the velocity of oscillation was relatively low compared with the chemical reaction speed, so that the effect of the oscillation on chemical reaction at any one stage of the cycle is small.

Several possible causes of the oscillations were investigated:

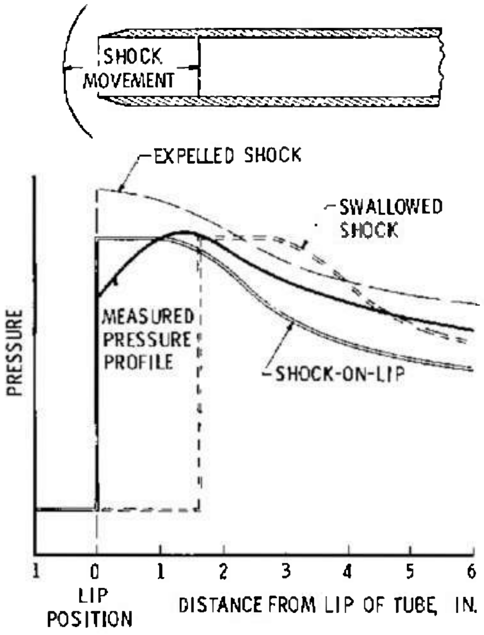


Fig. 13 Qualitative Analysis of Combustion Tube Pressure Profile during Oscillations

1. In the first experiments, a thin-walled spray-cooled tube was used, as compared with the thick-walled water-cooled tube in the later experiments (Fig. 6). Oscillation did not appear in the thin-walled tube until the combustion heat release approached that required for thermal choking. An analysis of the blunt base flow region was made to determine if the flow in this region was conducive to pressure fluctuations which might affect the choking flow area, then the mass flow, and hence the amount of flow spillover at the tube entrance.* This effect appears to be a possibility, but no definite conclusions could be drawn from the base flow analysis. However, since the base area was the principal difference between the two tube models, there is a strong possibility that the large base area plus a combination of exterior and interior aerodynamics were contributing factors.
2. Air stream profile nonuniformity was considered but could not be substantiated by pressure or temperature profile data in the air stream. Static pressure, total pressure, and total temperature measurements indicated very little nonuniformity and less than that observed in the thin-walled tube experiments.
3. Fuel profile nonuniformity was considered. From the one-dimensional flow analysis in Ref. 25, it was shown that nonuniform heat addition would produce the same static pressure change along the duct axis if the static pressure at any station were considered constant across the duct. However, as mentioned previously, nonuniform fuel distribution can result in some variation in pressure profile. It is conceivable that a fluctuating fuel concentration might trigger oscillating pressures. However, from total temperature measurements in the tunnel stream, there was no significant change in small temperature fluctuations when fuel was injected as compared with the no-fuel case. The thermocouple and potentiometer sensitivity was about 10 cps, so that only lower frequency fluctuations could be effectively sensed.
4. Boundary layer separation with resulting pressure rise, cooling of the gas near the wall, and inhibition of the chemical reaction was considered but could not be

---

*Analysis made by R. C. Bauer and J. Garner.

justified on the grounds that the pressure gradient in the tube is a favorable one and not conducive to separation.

5. Changes in reaction kinetic rates were considered as a possible result of changes in the reaction environment but could not be justified. Below $1800^{\circ}R$, a shift in the important chemical reactions may be expected, as will be the case for very rich mixtures (above E.R. = 4). Neither of these conditions existed in the experiment.

6. It is also possible that the oscillation may be the result of disturbances caused by the heat generating chemical reactions which may trigger either transverse or longitudinal wave oscillations. These phenomena are discussed by Strehlow and Fernandes (Ref. 26) for transverse waves and Fickett and Wood (Ref. 27) for longitudinal waves. Further investigations would be needed to ascertain the cause and characteristics of the oscillations.

Therefore, the only experimental effect to which the "slow" recombination history could be attributed was shock oscillations or inlet flow spillage. For one group of experimental data at the higher pressure level (90 psia in the plenum), some data points showed good agreement with the calculated pressure profile and others showed "slow" recombination and poor agreement. A careful examination of the data and the multiple photographs of the shock showed that the better correlations could be associated with little or no shock movement.

Limitations of the PE and Full Numerical Integration Models for the Reaction Zone

The APL program with the inclusion of recently determined kinetic rates appears to predict the observed pressure profiles quite well over the range of initial conditions studied in the current experiments. In addition, it is quite apparent from the results that the occurrence of HO_2 in the reaction scheme may be handled adequately by the technique used in this study over the range of experimental conditions.

One change was made in the APL program. As originally written, the program forced mass conservation at each step by calculating the rate of change of the hydrogen and oxygen atom concentrations from the net rate of change of the other species. It was noted that at the start of some calculations there were sporadic changes in the radical concentrations. Since the rate of formation of radicals is proportional to the radical concentrations, this method of handling the residuals could have led to these calculated instabilities. Therefore, the program was altered to carry the residuals in the species O_2 and H_2O. This change completely eliminated the instability.

The partial equilibrium program appeared to work satisfactorily at high temperatures and low pressures but did not yield as good an agreement at low temperatures and high pressures. In these lean mixtures, the rates of recombination reactions are primarily controlled by the hydrogen atom concentration, and this concentration was found to be very sensitive to the extent of recombination. An examination of the APL program results showed that the hydrogen atom concentration goes through a distinct maximum near the end of the induction zone. However, at high pressure and low temperature, this maximum is considerably lower than that predicted for $\xi = 0$ using the partial equilibrium program. Values of $(\xi)_{min}$ are plotted in Fig. 14 as a function of the shock pressure and temperature (P_2, T_2). The values of $(\xi)_{min}$ for this plot were determined by first running an APL and PE program for identical conditions. The output was when examined to find the maximum hydrogen atom concentration predicted by the APL program. This value was then used to determine an equivalent value of $(\xi)_{min}$ in the PE program. These are the values identified in Fig. 14 as $(\xi)_{min}$. In addition to these points, a reasonable set of constant $(\xi)_{min}$ lines are included to indicate trends. As $(\xi)_{min}$ increases, the agreement between the full numerical integration scheme and the PE scheme becomes progressively poorer, especially near the end of the induction zone. Typical plots of H-atom concentration versus time from the two programs are shown in Fig. 15.

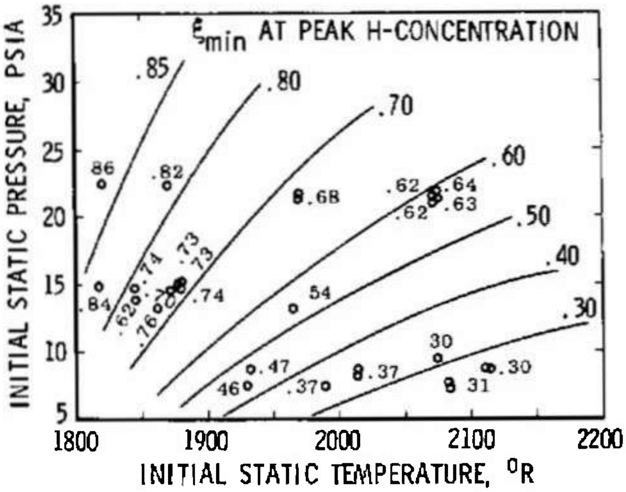


Fig. 14 Evaluation of H-Atom Concentration as a Measure of Ignition Delay, ξ_{min} Plotted as a Function of Initial Temperature and Pressure at the Peak H-Concentration. High Values of ξ_{min} Indicate H-Concentration Is Not a Good Indication of Ignition Delay.

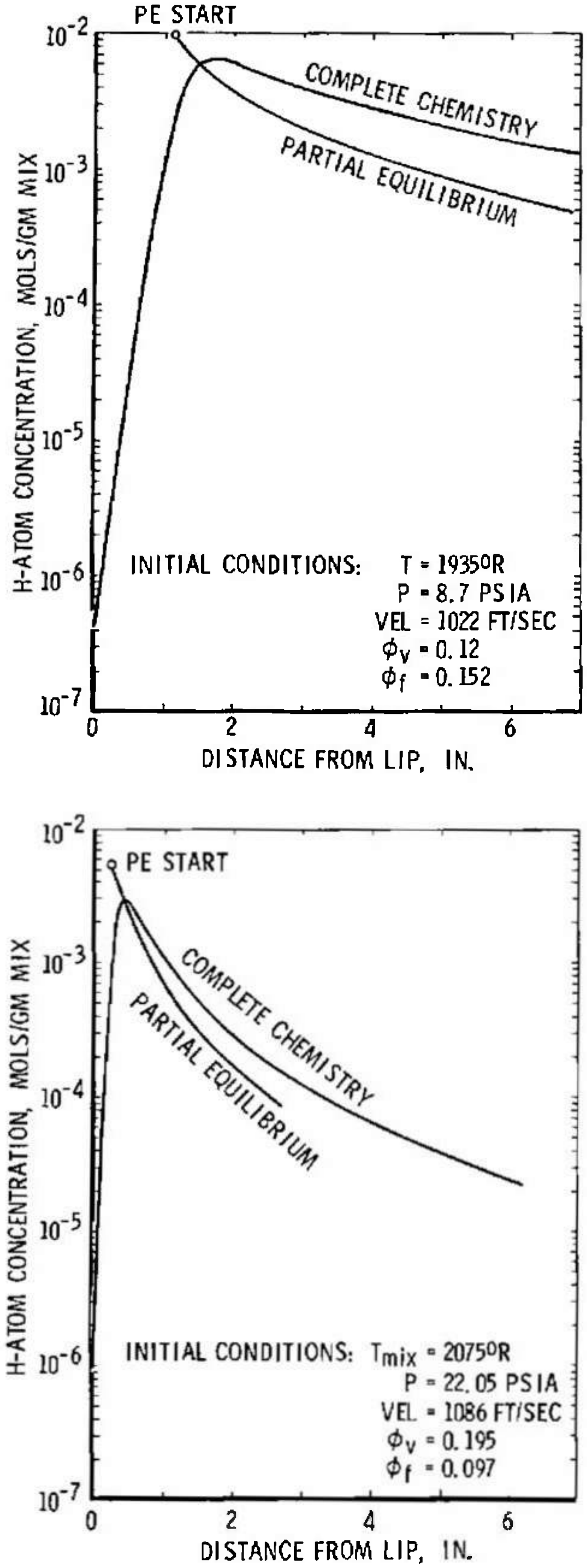


Fig. 15 Comparison of H-Atom Concentration for Complete Chemical Calculation and Partial Equilibrium Calculation

The PE program approximation to estimate the induction zone length appears to be reasonably good at high temperature and low pressure but probably should be modified at low temperature and high pressure where the recombination reactions occur to a significant extent before the exchange reactions reach equilibrium. This overlap of the induction zone and recombination zone represents a real limit to the utility of the PE model at low temperature and high pressure and warrants further investigation if a semi-empirical approach is desired for these conditions.

Extent of Accomplishment

Recently determined reactions for the H_2-air combustion and their rates were used to produce calculated theoretical curves of pressure history in a constant area duct. In general, the calculated pressure histories show better agreement with the experimental data than calculations using older proposed reactions and rates.

Since the new rates were taken from shock tube experiments, the experiments and analysis constitute a verification of the data obtained from the shock tube experiments.

The theory that partial equilibrium exists during recombination for reactions at low pressure and the higher temperatures appears to be a valid one. It was applied as a simplified kinetic scheme consisting of an ignition delay portion based on correlation of ignition delay data from H_2-air computer programs (Ref. 20), and a recombination portion based on three recombination reactions. The pressure profile calculated from the PE relations showed relatively close agreement with the full-scale reaction scheme computations using complicated mathematics and the experimental data (Fig. 7). The experiments were limited to lean mixtures up to E.R. = 0.35; however, theory and the work of others (Ref. 13) indicate that the PE assumption is valid from E.R. = 0.17 to 4.0. The graph in Fig. 14 indicates that, for lean mixtures, there is a high pressure and low temperature range that is not applicable to the PE approach. A different approach may be necessary in arriving at semi-empirical equations describing the recombination history for other fuels.

The initial gas composition included free radicals and products from the vitiation heating. Hence the current success in predicting the reaction history from a knowledge of the initial composition and free radicals provides a further information background for predicting the effect of contaminants entering a combustion chamber while the air is heated by vitiation. This is of particular interest to those interested in supersonic combustion ramjet ground test facilities where the means of achieving flight air temperature in the combustor may be by a vitiation process.

Problems for Future Work

With the assumption that the work accomplished so far justifies improving the method and extending its application to other combustion processes, these aspects deserve consideration:

1. To eliminate the effect of contaminants and free radicals on the reaction, at least in the initial stages of investigation, a nonvitiated air supply should be used. This can be accomplished for a fuel with an ignition temperature equal to or less than hydrogen by using an electric resistance heater (to 2500°R) or a storage heater.
2. Methods of improving the uniformity of the fuel profile should be developed so that the flow entering the shock is more nearly one dimensional.
3. Higher equivalence ratios can be run without thermal choking if the Mach number of the tunnel is increased. This will cause the Mach number downstream of the shock to be lower so that a larger heat release will be required to thermally choke the flow. Another method would be to let the combustion zone area expand; however, the constant area boundary condition is then lost. To establish a contour for another thermal heat release process, i.e., constant pressure, would not be impossible, but less likely to be as accurate as the constant area process. The amount of heat that could be added to a constant pressure process, however, would not be limited. Other methods would include expanding the flow area to prevent thermal choking, or increased initial temperature where the choking temperature ratio is fixed from Rayleigh line criteria.
4. Other fuels can be investigated experimentally, although, since much less is known about other combustion processes than H_2-air, the equations describing the reactions would likely contain more empiricism. A short test was made with commercial (95 percent) methane-air combustion in the existing tunnel, and although a high degree of vitiation was necessary to obtain combustion (approximately 3300°R tunnel plenum temperature), the shapes of the pressure profiles were similar to those obtained from hydrogen combustion.
5. If catalysts are mixed with the fuel or air, then it would be expected that their effect on the combustion process can be determined by changes in the pressure profile in the tube. Information of this type is of interest in supersonic ramjet combustion research, where the upper limits of flight altitude and Mach number may be restricted because of the time required for the combustion. Catalysts which speed the reaction may extend the range of operation in the flight envelope of these engines.
6. Because the presence of flow oscillations is incompatible with the one-dimensional flow analysis approach toward reaction kinetics, this effect should be removed. Fuel profile uniformity may be improved by using mixing theory, and the model may be redesigned to reduce the occurrence of oscillations. However, transverse and longitudinal oscillations observed in traveling detonation waves may also occur under similar circumstances in the standing wave, and it may be that the oscillations cannot be completely eliminated. Further studies of the phenomena may reveal ways of controlling it.

Comparison of Results with Shock Tube Experiments

From a one-dimensional flow, ideal gas, point of view, the detonation wave in a tube and the standing-wave normal-shock combustion are identical. From a physical point of view, there are several differences. Since data obtained from detonation experiments (Ref. 18) were used to correlate theoretical calculations with the standing wave experimental data, a comparison of the two phenomena is of interest.

Heat Transfer and Viscous Effects

Because the boundary layer for the detonation tube is accelerating with respect to the wave (Fig. 1), the friction term will be positive. Heat transfer will still be toward the wall if the wall is cold (Ref. 28). From Eq. (14), it can be seen that the two effects will be cumulative, rather than opposite and compensating as in the case of the standing wave, and the displacement boundary layer will be negative (expanding). These wall effects will also be influenced by tube diameter.

Shock Wave Stability

The standing-wave normal-shock stability depends on the steadiness of the entering flow and on the tendency of the shock wave to oscillate when combustion occurs. On the other hand, the flow entering the traveling detonation wave does not contain the turbulence that is characteristic of the flowing gas system, and gas mixture uniformity is easily obtained. However, transverse and longitudinal oscillations are observed in detonation experiments, and the one-dimensional analysis of reaction kinetics can not then be applied (Ref. 29). It is conceivable that a tunnel and tube model redesign for the standing-wave experiment could produce a relatively uniform flow and fuel mixture and reduce the base flow problems, thus reducing the probability of the oscillations. However, the standing-wave experiment may be subject to similar oscillation phenomena which have not been completely explored in the present experiments.

Experimental Measurements

Microsecond response time is needed for shock tube measurements, and for this reason, optical measurements are the most reliable. The shock tube equipment is relatively simple, but the measurement equipment and techniques become quite elaborate. On the other hand, the standing-wave combustion tube measurements may be made by relatively simple instruments, such as the manometer board; but the steady flow requirements create the need for relatively complicated equipment, such as large air and fuel supplies, air heaters, and controls.

Overall Kinetic Considerations

At the present stage of development of the standing-wave normal-shock combustion tube method, it does not appear to be a method for determining chemical reaction kinetic rates for individual reactions. The interactions between reactions and rates for a multicomponent reaction are too complicated. However, the method may have a distinct advantage in verifying heat release rates obtained from combinations of reactions and rates that were individually observed from other special experiments, or for determining heat release rates for complicated fuels, such as hydrocarbons, or mixtures of hydrocarbons, such as JP-4. As mentioned, a preliminary experiment with methane and vitiated air combustion demonstrated that the same type of pressure profile data can be obtained as with H_2-air. Also, the method can be used with much richer mixtures than the very dilute concentrations examined in the usual shock tube studies.

Conclusions

The experimental method of measuring pressure profile history of a chemically reacting high speed gas stream yields data which substantiate recent results reported from shock tube experiments on chemical reaction schemes and their rates for the H_2-air reaction. In addition, a mathematically simple method, based on the partial equilibrium concept, was devised for calculating the chemical reaction history for H_2-air, and the results were found to be in close approximation to the more complicated reaction schemes. The implication is that this partial equilibrium (PE) approach can be used in lieu of the full equations for the H_2-air system.

Experimental phenomena similar to those observed for the H_2-air reaction were also observed for the methane-air combustion, where the air supply was 45-percent vitiated during heating to approximately 3100°R. Ignition delay was calculated to be 4 to 5 times faster than measurements from other investigators. Rather large concentrations of free radicals from the combustion heated air supply may be an explanation for the differences. Thus, a nonvitiated air supply is highly desirable for combustion processes where the effects of free radicals are difficult to determine.

The close agreement of the experimental data and calculated data for the H_2-air system also implies that the experimental technique will prove to be satisfactory for the determination of heat release rates in other fuel-oxidizer systems. At present, it appears to be a useful steady-state technique which is capable of supplying empirical equations for the overall reaction.

Results of this type of experimental and analytical approach to analyze hydrocarbon fuel heat release should be applicable to the design of combustors for supersonic combustion ramjets. Another possible application is in simplifying computations involving simultaneous mixing and combustion or in simultaneous combustion in a method-of-characteristics net.

The method is not perfected, in that (1) the entering gas mixture was not uniform, and (2) shock oscillations were encountered at some conditions. Refinements could be made with further efforts. However, the technique appears promising to obtain heat release rate data for gaseous reactions where little or nothing is known of the reaction kinetic scheme or the reaction rates.

Acknowledgements

The authors acknowledge the efforts of Messrs. W. C. Armstrong and M. R. Reed in devising and modifying computer programs, Mr. J. H. Panesci in the design of the experimental hardware, Messrs. R. C. Bauer and C. Willbanks for their helpful suggestions, Messrs. L. Weller and C. Catalano and the Research Branch technicians for their fine cooperation in the experimental phase, and Miss Sandy Mercer in the typing of manuscripts.

References

1. Rubins, P. M. and Bauer, R. C. "A Hypersonic Ramjet Analysis with Premixed Fuel Combination." AIAA Second Propulsion Joint Specialist Conference, Paper No. 66-648, June 13-17, 1966.

2. Rubins, P. M. and Panesci, J. H. "Experimental Standing-Wave Shock-Induced Combustion for Determining Reaction Kinetic Histories." AIAA Propulsion Joint Specialist Conference, Paper No. 65-607, June 1965.

3. Nicholls, J. A. "Stabilization of Gaseous Detonation Waves with Emphasis on the Ignition Delay Zone." Air Force Off. Sci. Res. TN-60-442, June 1960.

4. Rhodes, R. P., Rubins, P. M. and Chriss, D. E. "The Effect of Heat Release on the Flow Parameters in Shock-Induced Combustion." AEDC-TDR-62-78, May 1962.

5. Richmond, J. K. and Shreeve, R. P. "New Techniques for Obtaining Kinetic

Data with Shock-Induced Combustion." AIAA 5th Aerospace Sciences Meeting, Paper No. 67-105, January 1967.

6. Hirschfelder, J. O. and Curtiss, C. F. "Theory of Detonation. I. Irreversible Unimolecular Reaction." *The Journal of Chemical Physics*, Volume 28, No. 6, June 1958, pages 1130-51.

7. Wood, W. W. "Existence of Detonations for Small Values of the Rate Parameter." *The Physics of Fluids*, Volume 4, No. 1, January 1961, pages 46-60.

8. Rubins, P. M. and Rhodes, R. P., Jr. "Shock-Induced Combustion with Oblique Shocks: Comparison of Experimental and Kinetic Calculations." *AIAA Journal*, Volume 1, No. 12, pages 2778-2784.

9. Pergament, H. S. "A Theoretical Analysis of Non-Equilibrium Hydrogen Air Reactions in Flow Systems." AIAA-ASME Hypersonic Ramjet Conference, Paper No. 53113, April 23-25, 1963.

10. Westenberg, A. A. and Favin, S. "Nozzle Flow with Complex Chemical Reaction." Johns Hopkins University, Applied Physics Lab., CM-1013, March 1962.

11. Rubins, P. M. "Comparison of Chemical History and Rates for the H_2-Air Reaction." *Journal of Spacecraft and Rockets*, Volume 3, No. 6, page 956, 1966.

12. Snow, R. H., "Chemical Kinetic Computer Program for Homogeneous and Free Radical System of Reaction," *Journal of Physical Chemistry*, 70, 2780, 1966.

13. Getzinger, R. W., "Shock Waves Study of Recombination in Near Stoichiometer Mixtures." Paper No. 11 presented at the 11th Combustion Symposium, Berkeley, California, August 1966.

14. Ripley, D. L. and Gardiner, W. C., Jr., "Shock Tube Study of the Hydrogen-Oxygen Reaction: II-Role of Exchange Initiation," *Journal of Chemical Physics*, 44, 2285, 1966.

15. Kaskan, W. E. and Schott, G. L., "Requirements Imposed by Stoichiometry in Disassociation-Recombination Reaction," *Combustion and Flame*, 6, 1962.

16. Schott, G. L., "Computation of Restricted Equilibrium by General Methods," *Journal of Chemical Physics*, 40, 2069, 1964.

17. Schott, G. L. and Bird, P. F., "Kinetics Studies of Hydroxyl Radicals in Shock Waves: IV-Recombination Rates in Rich Hydrogen-Oxygen Mixtures," *Journal of Chemical Physics*, 41, 2869, 1964.

18. Getzinger, R. W. and Schott, G. L., "Kinetic Studies of Hydroxyl Radicals in Shock Waves: V-Recombination via $H + O_2 + M \rightarrow HO_2 + M$ Reaction in Lean Hydrogen-Oxygen Mixtures," *Journal of Chemical Physics*, 43, 3237, 1965.

19. Dergazarian, T. E., et al., *JANAF Interim Thermochemical Tables*, The Dow Chemical Company, December 1960.

20. Rhodes, R. P., Jr. "The Effects of Non-Equilibrium Free-Radical Concentration on Ignition Delay Time in the Hydrogen-Oxygen System." AEDC-TDR-64-241, November 1964.

21. Shapiro, A. H., *The Dynamics and Thermodynamics of Compressible Fluid Flow*, Volume I, Ronald Press, 1952, page 219.

22. Shapiro, A. H. *The Dynamics and Thermodynamics of Compressible Fluid Flow*, Volume II, Ronald Press, 1953, page 1132.

23. Glass, G. P., Kistiakowsky, G. B., Michael, J. V., and Niki, H., "The Oxidation Reactions of Acetylene and Methane," *Tenth Symposium (International) on Combustion*, The Combustion Institute, 1965, pages 513-522.

24. Browne, W. G., and Warlick, D. L., "Properties of Combustion Gases, System: H_2-Air," General Electric Company, R62FPD-366, November 1962.

25. Rubins, P. M. and Cunningham, T. H. M., "Shock-Induced Combustion in a Constant Area Duct." *AIAA Journal of Spacecraft and Rockets*, April 1965, pages 199-205.

26. Strehlow, R. A. and Fernandes, F. D., "Transverse Waves in Detonations," *Combustion and Flame*, Vol. 9, 1965, pages 109-119.

27. Fickett, W. and Wood, W. W. "Flow Calculations for Pulsating One-Dimensional Detonations." *The Physics of Fluids*, Volume 9, No. 5, May 1966, pages 906-916.

28. Mirels, H., "Flow Nonuniformity in Shock Tubes Operating at Maximum Test Time," *Physics of Fluids*, Volume 9, October 1966, pages 1907-1912.

29. Barthel, H. O. and Strehlow, R. A., "Wave Propagation in One-Dimensional Reactive Flows." *The Physics of Fluid*, Volume 9, No. 10, page 1896, Oct. 1966.

Appendix

Analysis of the Effect of Wall Boundary Layer and Heat Transfer[1]

The general "influence coefficient" Eq. (14) for uniform flow in a constant area duct is assumed to be applicable to fully developed flow where heat transfer and friction exist. However, in the experiment using a normal shock at the entrance to a tube and unreacting gas, the boundary layer growth is very similar to that on a flat plate; therefore, the flow in the tube was treated as if boundary layer displacement thickness formed an effective area constriction in the constant area tube. Under these conditions, heat transfer to the cool walls serves to reduce the boundary layer thickness.

Thus the interior flow, excluding the displacement boundary layer, can be treated as isentropic when no combustion exists. From consideration of conservation of mass, the effective area (A_e) can be written in terms of the displacement thickness, δ^*:

$$\frac{A_e}{A_i} = 1 - 2\delta^*/r \qquad \text{(I-1)}$$

where A_i is the tube cross section area and r is the radius.

In the entrance region, the axial pressure gradient is relatively small and has negligible effect on the growth of the boundary layer; therefore, the boundary layer can be analyzed in the same manner as the boundary layer on a flat plate.[2]

If the laminar boundary layer equations for zero pressure gradient and Prandtl number of unity are transformed using the Illingworth-Levy transformation[3] variables and the viscosity is assumed to vary linearly with temperature, the momentum equation will be recognized as the incompressible flat plate equation of Blasius (see for example Dorrance[3]). The solution to the energy equation will be Crocco's integral.[3] The displacement thickness, by definition, is

$$\delta^* \equiv \int_0^{\delta} \left(1 - \frac{\rho u}{\rho_e u_e}\right) dy \qquad \text{(I-2)}$$

and under the transformation, it becomes

$$\delta^* = \frac{\sqrt{2\bar{x}}}{\rho_e u_e} \left[\int_0^{\eta_\delta} \frac{\rho_e}{\rho}\, d\eta - f(\eta_\delta) \right] \qquad \text{(I-3)}$$

where

$$\bar{x} = \int_0^x \rho_e u_e \mu_e \, dx$$

and

$$\eta = \frac{\rho_e u_e}{\sqrt{2\bar{x}}} \int_0^y \frac{\rho}{\rho_e}\, dy$$

where ρ is the density, u the axial velocity, μ the viscosity, x the distance from the leading edge of the tube, y the distance measured normal to the tube wall, δ* the boundary layer thickness, f(η) the Illingworth-Levy stream function variable, and the subscript (e) denotes the interface between the boundary layer and the isentropic core region. By using the perfect gas law and the Crocco relation, it can be shown that

$$\int_0^{\eta_\delta} \frac{\rho_e}{\rho}\, d\eta - f(\eta_\delta) = \left[\eta_\delta - f(\eta_\delta)\right] \frac{T_w}{T_e} + \left[f(\eta_\delta) - \int_0^{\eta_\delta} (f')^2 \, d\eta \right] \left(\frac{\gamma - 1}{2}\right) M_e^2 \qquad \text{(I-4)}$$

where T_w is the wall temperature of the tube, γ the ratio of specific heats, M_e the Mach number, and f′ the Illingworth-Levy non-dimensional axial velocity.

From the Blasius solution, it can be shown that

$$\eta_\delta - f(\eta_\delta) \cong 1.22$$

and

$$f(\eta_\delta) - \int_0^{\eta_\delta} (f')^2 \, d\eta \cong 0.47$$

Thus

$$\delta^* = \frac{\sqrt{2\bar{x}}}{\rho_e u_e} \left[1.22 \frac{T_w}{T_e} + 0.47 \left(\frac{\gamma - 1}{2}\right) M_e^2 \right] \qquad \text{(I-5)}$$

For low subsonic velocities, Eq. (I-5) becomes

$$\delta^* = \frac{1.73\sqrt{\bar{x}}}{\rho_e u_e} \frac{T_w}{T_e} \qquad \text{(I-6)}$$

and assuming ρ_e, u_e, and T_e constant, Eq. (I-6) can be simplified further to

$$\delta^* = \frac{1.73x}{\mathrm{Re}_x^{1/2}} \frac{T_w}{T_e} \qquad \text{(I-7)}$$

---

[1] Equations derived by C. Willbanks.

[2] Ref. Schlicting, H., "Boundary Layer Theory," 4th Ed., McGraw-Hill, 1960, p. 169.

[3] Ref. Dorrance, W. H., "Viscous Hypersonic Flow," McGraw-Hill, 1962, p. 30-33.

where

$$Re_x = \frac{\rho_i u_i x_i}{\mu_i}$$

The subscript (i) denotes conditions at the entrance to the tube. The assumption of constant p_e, u_e, and T_e is justifiable here because the correction term for boundary layer is small and also because these quantities do not change greatly from one end of the tube to the other.

Combining Eqs. (I-1) and (I-7) yields

$$\frac{A_e}{A_i} = 1 - \frac{3.46}{r} \frac{x}{Re_x^{1/2}} \frac{T_w}{T_e} \tag{I-8}$$

This area ratio can be used in conjunction with the isentropic flow relations to determine the pressure drop through the tube caused by friction and heat transfer.

Clearly, a similar analysis could be made for the turbulent boundary layer. Moreover, the case of a chemically reacting gas could be treated in an analogous manner, although the analysis would be complicated by the necessity of considering the heat release distribution in the tube.

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY *(Corporate author)* Arnold Engineering Development Center ARO, Inc., Operating Contractor Arnold Air Force Station, Tennessee	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP N/A

3 REPORT TITLE

EXPERIMENTAL AND ANALYTICAL STUDY OF THE H_2-AIR REACTION KINETICS USING A STANDING-WAVE NORMAL SHOCK

4 DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Final Report - September 1965 - June 1967

5. AUTHOR(S) *(First name, middle initial, last name)*

Roger A. Strehlow, Consultant, and Philip M. Rubins, ARO, Inc.

6 REPORT DATE September 1967	7a. TOTAL NO. OF PAGES 28	7b. NO. OF REFS 29

8a. CONTRACT OR GRANT NO. AF40(600)-1200 b. PROJECT NO OAR Project 6952 c. Program Glement 61445014 d.	9a. ORIGINATOR'S REPORT NUMBER(S) AEDC-TR-67-177 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)* AIAA Paper No. 67-479

10 DISTRIBUTION STATEMENT

This document has been approved for public release and sale; its distribution is unlimited.

11 SUPPLEMENTARY NOTES Available in DDC	12. SPONSORING MILITARY ACTIVITY USAF Office of Aerospace Research and Arnold Engineering Development Center, Air Force Systems Command

13 ABSTRACT

The design of a high speed airbreathing propulsion system (SCRAMJET) may depend on more precise information on chemical kinetics of the combustion processes than is now available, except for the very simplest reactions. An experimental method was devised whereby the macroscopic chemical reaction history can be traced from wall pressure measurements in a high speed reacting gas in a tube. The chemical reaction is started by means of a normal-shock compression at the tube entrance through which premixed fuel and air is heated to combustion temperature. The experiments were conducted with H_2 and vitiated air, and the data were compared with calculated pressure profiles using recent reaction kinetic information obtained from shock tubes. Good agreement between experiment and calculation was found when the flow was steady and no oscillations were present, indicating that the kinetics which govern the chemical reactions in shock tube experiments can be reproduced with the standing-wave experiment. Wall effects are evaluated. In addition, a semi-empirical analysis was made of the ignition delay and recombination, with the assumption that the two-body reactions are essentially in equilibrium during the slower recombination period. The mathematics of this approach is simple and is potentially useful with machine computations involving chemistry and mixing, or chemistry and aerodynamics. Finally, a short experiment with methane combustion in the tube produced similar phenomena, indicating that the method may be useful for determining rates of heat release for gases where little is known of the kinetics.

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
combustion						
kinetics						
1. airbreathing propulsion systems						
2-SCRAMJETS						
chemical reactions						
hydrogen						
air						
shock tubes						
pressure profiles						
oscillations						

2. Standing wave shocks.
& Scramjets -- Combustion.

16. 3.