SOME CONSIDERATIONS IN HYBRID COMBUSTION

by

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Certified by

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Chairman, Departmental Graduate Committee
वागर्थोऽनुक्रमं पृष्ठं को
ञगतं पितरीं वंदे
पार्वती परमेश्वरी।
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Kumar Nanjunda Rao Ramohalli

Submitted to the Department of Aeronautics and Astronautics in June 1971, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

This thesis concerns itself with theoretical and experimental investigations carried out to gain a better understanding of the fundamentals of hybrid combustion. A theory is developed to account for observed hybrid behavior. The theory is based on differences in polymer degradation behavior in inert and noninert environments.

A theoretical study of linear regression rate calculation through thermal depolymerization of polymeric fuels is carried out, with the size of the vaporizing particles specified through their vapor pressure. For the usual case of polymers characterized by constant activation energies, asymptotic techniques are used, in the limit of large reduced activation parameters \( \theta_a = E_T / R T_w \), to derive a closed form analytical solution that is very accurate in comparison with numerical results.

For the special case of PMMA, numerical results are obtained including explicitly the activation energy dependence on mean fragment length. Curves of linear regression rate \( \hat{t} \) vs. wall temperature \( T_w \) are obtained, and are found to correlate well with experimental hot plate data. The slope of this curve is found to be appreciably different from the slope of the \( \hat{t} \) vs. \( T_w \) curve obtained in typical hybrid boundary layer experiments, leading to the belief that there is a mismatch between the solid phase thermal degradation controlled regression rate, and the hybrid boundary layer controlled regression rate. It is observed that the intersect of the two curves is close to an \( \hat{t} \) from where pressure sensitivity begins to appear. It is hypothesized that in the high regression rate regime, subsurface thermal depolymerization is supplemented by surface depolymerization by reactive species, a mechanism that can explain the pressure sensitivity. In the absence of better data, chemical kinetic parameters for this surface attack are deduced from available experimental studies and it is confirmed that high \( \hat{t} \)'s can be accounted for through the present hypothesis.

Gas phase transport in an hybrid combustor turbulent boundary layer is considered in an order of magnitude way, with particular reference to turbulent eddy scale, molecular diffusion and chemical kinetics.
Experiments are conducted in a simulated superatmospheric pressure hybrid boundary layer with porous plate gaseous fuel injection. Time-average temperature and velocity ratio profiles are obtained across the boundary layer. Oxidizer concentration is measured by probe sampling near the wall. It is found that gas phase kinetics are not slow enough to be effective in controlling the hybrid regression rates.

It is argued that, under all conditions, a finite flux of unreacted oxidizer gas to the wall can exist through the mechanism of bulk turbulent eddy transport across the classical time averaged "flame-sheet." It is therefore concluded that the observed hybrid combustor behavior is due to surface oxidative (catalytic) depolymerization which aids thermal degradation in producing vaporizable fragments.

Thesis Supervisor: David B. Stickler
Title: Assistant Professor of Aeronautics and Astronautics
I consider myself fortunate in having had the opportunity of working with Professor D.B. Stickler, who, besides suggesting the problem, lent his time and effort at several stages of this investigation. His wit and humour brought cheer when spirits ran low. I thank him particularly for his presence on campus during the summer of 1969 and also for all the trouble he took arranging the trip to the XIII International Symposium on Combustion.

I express my deeply felt respectful gratitude to Professor Kerrebrock. I have benefitted immensely through his advice, kindness and unfailing encouragement. Association with him has been an education in itself.

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While most of this work was performed in building thirty one,
almost all of the original ideas evolved during my long walks along
the Charles. With this clarification, I hope that Longfellow will
not wince in his grave if I dedicate,

It is for this thou silent river
That my spirit leans to thee,
Thou hast been a generous giver
Take this idle song from me.
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<td>A</td>
<td>constant, used in plate heating calculations</td>
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<tr>
<td>B</td>
<td>constant, used in plate heating calculations</td>
</tr>
<tr>
<td>$B_{TD}$</td>
<td>Spalding's mass transfer number $[=2(\rho V_w)/(\rho U)_\infty c_f]$</td>
</tr>
<tr>
<td>CFS</td>
<td>pre-exponential constant for thermal degradation [sec.$^{-1}$]</td>
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<tr>
<td>CFS</td>
<td>critical fragment size, used by Rabinovitch [same as FSV, below]</td>
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<tr>
<td>$C_H$</td>
<td>stanton number $[= \dot{q}<em>w/c_p \Delta T/(\rho U)</em>\infty]$</td>
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<tr>
<td>c</td>
<td>specific heat of solid polymer [cal/gm.$^\circ$C]</td>
</tr>
<tr>
<td>$c_f$</td>
<td>twice the local skin friction coefficient $[= 2 \tau_w/(\rho U)_\infty^2]$</td>
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<tr>
<td>$c_p$</td>
<td>specific heat of gases at constant pressure [cal/gm.$^\circ$C]</td>
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<tr>
<td>D</td>
<td>diffusion coefficient [cm.$^2$/sec.]</td>
</tr>
<tr>
<td>D</td>
<td>energy for complete depolymerization to monomer [cal/gm]</td>
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<tr>
<td>$D^V$</td>
<td>local Damköhler number in the boundary-layer $[= (\text{characteristic time for chemical reactions})/(\text{characteristic time for molecular mixing of turbulent eddies})]$</td>
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<td>$E_{TD}$</td>
<td>activation energy for thermal depolymerization [cal/mole]</td>
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<td>F</td>
<td>non-dimensional blowing parameter $[= (\rho V)<em>w/(\rho U)</em>\infty]$</td>
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<tr>
<td>$F(n)$</td>
<td>spectrum function in turbulence [kinetic energy associated with turbulent eddies having wave-number distribution $\Delta n$ around $n$]</td>
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<td>FS</td>
<td>statistical mean fragment size of polymer at any plane [number of monomer units in a polymer chain]</td>
</tr>
<tr>
<td>FSV</td>
<td>statistical mean fragment size of polymer vaporizing [number of monomer units in a polymer chain]</td>
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<td>G</td>
<td>free-stream mass flow rate [lbm/sq.in.sec.]</td>
</tr>
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<td>h</td>
<td>non-dimensional heat of depolymerization $[= D/c(T_w - T_0)]$</td>
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<tr>
<td>I</td>
<td>a constant, defined in equation 3.4</td>
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<td>IB</td>
<td>inert band</td>
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<tr>
<td>k</td>
<td>thermal conductivity coefficient of the polymer [cal/cm.sec.$^\circ$C]</td>
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<tr>
<td>L</td>
<td>a thickness, used in several calculations [cm.]</td>
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<tr>
<td>$\ell$</td>
<td>a characteristic length scale [cm.]</td>
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<tr>
<td>$m$</td>
<td>molecular weight [gm/gm.mole]</td>
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$\mathcal{M}$  Mach number  [ratio of gas velocity to sonic velocity]

$\dot{m}_w^{\prime\prime}$  mass flow rate through the wall per unit area of injection  [gm./sq. cm.sec.  or  lbm/sq.in.sec.]

$N$  fractional number of back bone Carbon-Carbon bond in the polymer
[referred to the original number in the undegraded polymer]

$n$  index (i.e., power) on $G$ in the regression rate vs. $G$ curve

$n$  wave number in turbulence  [cm$^{-1}$]

$P$  always denotes the operating point

$p$  non-dimensional temperature gradient in the solid polymer  [see chapter II]

$p$  pressure  [psia, psig or atm]

$\dot{q}_w$  heat transfer rate to the wall by boundary-layer gas flow  [cal/sq. cm.sec.]

$R$  Reynolds number  [$\rho U x / \mu$]

$R$  Universal gas constant  [cal/gm.mole °C]

$R_t$  autocorrelation function for a turbulent eddy  [dimensionless]

$t$  linear regression rate of a polymeric fuel  [cm/sec.]

$S_b$  laminar flame speed in a gas of premixed reactants  [cm/sec. measured relative to burnt gases]

$s$  specific entropy  [cal/°C]

$T$  temperature  [°C, °F, °K or °R]

$t$  time coordinate  [sec.]

$t_0$  a characteristic time in turbulence  [sec.]

$U$  $x$ component of mean velocity of gases  [fps or cm/sec.]

$u'$  $x$ component of fluctuating turbulent velocity of gases  [fps or cm/sec]

$v$  $y$ component of mean velocity of gases  [fps or cm/sec.]

$v'$  $y$ component of fluctuating turbulent velocity of gases  [fps or cm/sec]

$x$  streamwise distance from leading edge  [cm or ft.]

$x$  distance coordinate into the polymer, measured from the wall  [cm]

$y$  boundary-layer vertical coordinate  [cm or ft.]

$y$  nondimensional distance coordinate within the solid polymer
Greek Symbols

\( \alpha \) thermal diffusivity in the solid polymer \([\text{cm}^2/\text{sec}]\)

\( \gamma \) ratio of the specific heats of the combustion gases

\( \delta \) time-averaged boundary layer thickness at a station \( x \) [cm]

\( \varepsilon \) small parameter used in the perturbation analysis

\( \varepsilon \) fraction of unmixed oxidizer in turbulent transport towards the wall

\( \xi \) dependent variable in the inner region

\( \eta \) independent variable in the inner region

\( \mu \) coefficient of viscosity of gases \([\text{lbm/ft}.\text{sec}]\)

\( \Theta \) constant activation energy parameter

\( \Theta_a \) reduced activation energy parameter \([\equiv E_{TD}/RT_w]\)

\( \Lambda, \chi \) regression rate eigenvalues in the intermediate steps

\( \lambda \) regression rate eigenvalue

\( \rho \) polymer density \([\text{gm/cm}^3]\)

\( \chi \) nondimensional temperature parameter \([\equiv (T_w - T_o)/T_w]\)

\( \tau \) nondimensional temperature variable \([\equiv (T - T_o)/(T_w - T_o)]\)

Subscripts and Superscripts

\( b \) high reaction rate zone (flame zone in older terminology) in the boundary layer

\( e \) edge of the boundary layer

\( o \) deep solid

SL Solid-Liquid interface

TD thermal degradation

\( w \) wall surface

ss stainless steel

ini initial

eqb equilibrium

\( \infty \) a reference state or the free stream
CHAPTER I

INTRODUCTION

1.1 General Introduction

It is a ponderable speculation that the punishment for Prometheus might have been substantially less severe, had Zeus paused to foresee the innumerable combustion problems that got introduced into our world that have caused immeasurable frustration to researchers in various branches of science and technology. Some of these problems, not necessarily confined to the bounds of our earth, have drawn a good deal of attention in recent years. The extensive literature available on solid and liquid propellant rockets renders a discussion of them unnecessary here. The hybrid rocket, characterized by the separate storage of fuel and oxidizer (one of them solid and the other liquid) offers the principal advantages of stop-start capability, ease of control and seemingly nonexistent combustion instability or detonation hazards. Although these, and other, potentialities of the hybrid rocket have been sufficiently recognized to warrant the extensive research effort that has been recently devoted to its development, resulting in successful test firings, it cannot yet be said that all phases of its operation have been understood clearly. The present effort, which was originally intended as an attempt at clarifying the controversial topic of pressure-sensitive combustion, appears at this stage to have emerged as a revision of several facets of hybrid combustion phenomenon.

1.2 The Problem

Simply stated, the problem is to predict the burning rate of the solid fuel as a function of oxidizer composition, flow rate and chamber pressure.
It is also of interest to find ways of improving any desired performance of the hybrid rocket. Our ability to solve the above problems depends on our understanding of the detailed processes involved in hybrid rocket operation. We evaluate such an understanding by our success at explaining observed phenomena. Since the investigations available in the literature (discussed in chapter IV.6) have been only partially successful at such a task, besides being mutually inconsistent, it is felt desirable to embark on the problem at a fundamental level. We focus our aim on a coherent unification of available studies.

To supplement our understanding of the fundamental processes, it is found necessary to solve the following constituent problems.

(i) Prediction of the burning rate of the solid polymeric fuel as a function of wall temperature, chamber pressure and other thermo-chemical data.

(ii) Evolution of a scientifically valid criterion for specifying the statistical mean fragment size of the polymer fragments at the wall, since this size enters as an important parameter in the problem.

(iii) Determination of the structure of the combusting turbulent boundary layer over the hybrid fuel; more specifically, theoretically accounting for the presence of appreciable oxidizer concentrations below the classical time-averaged flame zone located in the boundary layer.

(iv) Determination of the variation of oxidizer concentration at the wall, as a function of pressure and fluid dynamic parameters; in the absence of reliable theoretical predictions, a combustion tunnel facility is designed and built to make experimental
measurements.

In addition, it is also required to solve a multitude of secondary problems, both theoretical and experimental. Some of these are described in this report.

A study of the problems outlined above shows that it is possible to understand the reported behavior of hybrid combustion within the framework of a new theory developed here.

1.3 Thesis Synthesis

It is convenient to discuss the work under four major divisions which form the building blocks of the present developments on hybrid combustion.

(a) Solid Phase Theory

It is of interest to theoretically predict the linear regression rate of a solid polymeric fuel, considering only the condensed phase reactions. For this purpose, the solid phase is visualized as completely isolated from the gas phase. Equilibrium wall temperature is taken as a boundary condition to be determined by thermochemical energetics and mass balance between gas phase and condensed phase reaction rates. The statistical mean fragment size of the polymer leaving the surface (called the "Fragment Size Vaporizing," FSV, for short) is a parameter in the treatment. The requirement that the vapor pressure sum of all polymer fragments at the surface add up to the gas phase pressure is chosen as a means of removing the arbitrariness in the value of FSV.

As shown in figure 1.1, heat transfer by thermal conduction, bulk material heating and heat of depolymerization are considered in the energy balance. In view of extensive literature supporting it, the bond breaking kinetics in the polymer is modeled as a first order Arrhenius law. Bond loss due to kinetic bond breaking and bond supply due to bulk material
movement are included. Diffusion of bonds, that is, local movement of small polymer fragments through large ones is neglected.

The governing system of third order, coupled nonlinear differential equations is:

Energy:

\[
\frac{d}{dx} \left( k \frac{dT}{dx} \right) + \rho c_r \frac{dT}{dx} = D \rho N B_{TD} \exp(-E_{TD}/RT)
\]

\[x = 0: \ T = T_w \quad ; \quad x = \infty: \ T = T_0\]

Bond Conservation:

\[-\frac{dN}{dt} = N B_{TD} \exp(-E_{TD}/RT)\]

\[x = 0: \ N = N_w \quad ; \quad x = \infty: \ N = 1\]

In the above equations, \(T\) stands for temperature (°K), \(k\) for coefficient of thermal conductivity (cal/sec. cm °C), for specific heat (cal/gm °C), \(D\) for depolymerization energy to convert 1 gm of polymer to 1 gm of monomer (cal/gm), \(\rho\) for density (gm/cm\(^3\)), \(B_{TD}\) for the preexponential constant for thermal degradation (sec\(^{-1}\)), \(E_{TD}\) for activation energy for thermal degradation (cal/mole), \(R\) for universal gas constant (cal/gm mole °C), \(x\) for coordinate into the solid from the wall (cm), \(N\) for fractional bond number referred to that in the cold interior and \(N_w\) for the fractional bond number at the wall.

After we note the similarity between energy and bond conservation equations (in analogy with the problem of laminar flame propagation in premixed gases), it is possible to mathematically simplify the governing system of equations to a single first order nonlinear differential equation in which the nondimensional regression rate appears as an eigenvalue:
\[ pp' + p = \Lambda(h + p + \tau) \cdot \exp(-E_{TD}/RT) \]

\[ \tau = 0 : \ p = 0 ; \ \tau = 1 : \ p = -1 - h/FSV \]

In the above equations,

\[ \tau \equiv (T - T_0) / (T_w - T_0) \]

\[ p \equiv d\tau/dy \]

\[ y \equiv c\rho \tau x/k \]

\[ h \equiv k B_{TD}/\rho c\tau^2 \]

\[ FSV = \frac{1}{1 - N_w} \]

Noting the strong exponential decay of the bond breaking rate term as we go into the solid from the surface, the system is solved by neglecting the reaction rate term in the interior. Near the wall, the chemical reaction rate term cannot be neglected. The governing equation is solved including explicitly the reaction rate term. The solution is matched with the deep solid solution. The matching process determines the eigenvalue.

In a different terminology, the problem belongs to the class of singular perturbation problem and is solved by the method of inner and outer expansions. The solution, which predicts the linear regression rate of the polymer as a function of the surface temperature, the mean statistical fragment size of the polymer (FSV) at the wall interface and the thermochemical properties, is:

\[ \dot{r} = \left[ \frac{B_{TD} \cdot \exp(-E_{TD}/RT_w)}{\left(\frac{\rho c}{k}\right) \cdot \left(\frac{T_w - T_0}{T_w}\right) \cdot \left(\frac{E_{TD}}{RT_w}\right) \cdot \left[\left(\frac{D}{c(T_w - T_0)} + 1\right)\ln \frac{FSV}{FSV-1} - \frac{D}{c(T_w - T_0)FSV}\right]} \right]^{1/2} \]

We carefully note that the linear regression rate is proportional to the square root of the isothermal depolymerization rate at the wall temperature. This simple observation renders transparent a whole host of seemingly
inconsistent data in the literature. If an Arrhenius rate law is forced on experimental measurements of linear regression rates, an activation energy of one half that for isothermal depolymerization rate is predicted. Complete depolymerization to monomers is not allowed by the solution, which is consistent with our concept of a first order reaction. The accuracy of the solution is demonstrated by comparison with numerical solutions obtained for four extreme cases.

For the special case of plexiglas (PMMA), the governing equation is numerically integrated, including explicitly the reported activation energy variation with mean fragment size.

Choosing a polymer (plexiglas) on which extensive experimental test data is available, the theoretical predictions are compared with hot plate results. It is found that qualitative agreement is excellent. FSV values of 6-10 (molecular weight 600-1000) are found to match experimental data quantitatively. The vapor pressure criterion predicts FSV values of approximately 2-4 at the temperatures of interest. While it is possible that the discrepancy is due to various approximations in analysis and uncertainties in data, it is more probable that a different criterion is needed for the hot plate experiments, where the existence of clearly defined equilibrium between gas and condensed phases is doubtful. Further credence is lent to such a feeling by the successful application of the vapor pressure criterion to experiments where there is a clearly defined equilibrium between condensed and gas phases (described in chapter IV).

(b) Gas Phase Theory

A fundamental investigation of the turbulent combustion of nonpremixed gases is undertaken. The aim is the determination of the oxidizer specie profile in the hybrid boundary layer. A finite
concentration of oxidizer at the wall, if it exists, may cause surface catalytic degradation, for example.

Available studies on overall features of the hybrid boundary layer are reviewed with reference to fluid mechanics and heat transfer. Influence of the similarity parameters (Reynolds number, Stanton number and Spalding's mass transfer number) are indicated.

Essential concepts from fluid turbulence and chemical kinetics are briefly reviewed. It is pointed out that although turbulent transport gives gross mixing, molecular diffusion-mixing is an essential prerequisite for chemical reactions to occur in a nonpremixed system. Such an argument renders questionable the frequently used generalization of Burke-Schumann laminar diffusion flame model to turbulent diffusion flames. It is argued in the present work that oxidizer gas in its transport towards the wall escapes chemical reactions even during its passage through the time-averaged high temperature high reaction rate zone if the oxidizer does not mix with the fuel on the molecular scale. Turbulent combustion of nonpremixed gases is compared with the laminar situation in figure 1.2. Each type script represents a molecule (F - fuel, O - oxidizer). Entropy, Knudsen number, density, kinetic scheme of reaction and such other details are thought irrelevant for the purpose of mnemonics.

The importance of a new nondimensional group (called here as a Damköhler's fifth group $D^V$) defined as the ratio of the local molecular mixing rate to the chemical reaction rate at the same temperature with the reactants premixed, is highlighted. Recognizing that the molecular mixing rate is directly related to the local dissipation rate of turbulent mechanical energy into heat, the mixing rate is related to the dynamics of turbulent motion and the boundary layer mechanisms. Damköhler's fifth group
is computed in an order-of-magnitude way for the typical experiment of Wooldridge and Muzzy\textsuperscript{64} who determined the structure of the hybrid boundary layer in a simulated porous plate experiment at one atmosphere pressure. The experimental trend in the measured oxidizer profile is compared with the predictions of the present treatment. It is found that the comparisons are qualitatively satisfactory. Quantitative comparison is not attempted since such a comparison would be inconsistent with the nature of the present analysis.

Turbulent transport involves movement of macroscopic groups of fluid from above the reaction zone to below. The familiar expression for turbulent boundary layer transport,

\[
\text{oxidizer transport rate} \propto \frac{\text{free-stream mass flow rate}}{\text{Reynolds number}} \cdot \text{difference in concentration between free-stream and wall}
\]

i.e.,

\[
\dot{m}_{\text{ox}} \propto G \cdot R_x^{-2} \cdot (K_{\text{ox}_e} - K_{\text{ox}_w})
\]

needs modification. Allowance has to be made for the consumption of oxidizer in gas phase chemical reactions. When chemical reaction rates are high compared with mixing rates, the oxidizer consumption rate is essentially the mixing rate. A factor \(\varepsilon\) is introduced in the above expression to represent the fraction of oxidizer that gets consumed in chemical reactions; that is, the fraction that microscopically mixes with the fuel in presence of an ignition source. Thus,

\[
\dot{m}_{\text{ox}} \propto G \cdot R_x^{-2} \cdot (K_{\text{ox}_e} - K_{\text{ox}_w}) \cdot \varepsilon
\]

Since we do not expect pressure to affect mixing rates at a constant Reynolds number, it is seen that the subflame oxidizer partial pressure depends directly on the free-stream oxidizer partial pressure. Again a reference to figure 1.2 may aid visualization.

Within a reasonable range (one to fifty), the wall mass transfer number \(B\) is not expected to greatly influence the turbulence structure in the
outer parts of the boundary layer (near the free-stream). Since
turbulence structure in the outer parts of the boundary layer governs
the transport of oxidizer to subflame regions, variations in mass transfer
number B are thought not significant in determining this transport.
However, after reaching the subflame region, the diffusion of oxidizer
against wall injection, and hence the concentration at the wall are ex-
pected to depend strongly on parameter B.

(c) Theory of Hybrid Combustion

Unifying the solid phase and gas phase theories, an attempt is
made to understand the mechanism of hybrid combustion. The aim is to be
able to explain all of the reported data in a coherent way.

Comparison of theoretical solid phase solutions with experimental
data in noninert environments, such as in a typical hybrid rocket, shows
that there is both quantitative and qualitative disagreement. The regression
rate predictions (based on any reasonable criterion for FSV) are found
to fall short of experimental values by one to two orders of magnitude;
the slope of the regression rate versus inverse wall temperature curve
on the standard semilog plot is approximately twice that predicted by
solid phase theory, i.e., the activation energy appears to be higher by
a factor two.

It is hypothesized that in addition to subsurface thermal degra-
dation, polymer degradation at the surface by reactive species leads to
an increased local bond breaking rate. Recalling that the gas phase theory
(and experiments) indicate finite concentration of oxidizer at the wall,
oxidative degradation at the surface is postulated. Numbers computed
for oxidative degradation rates from such data as available tend to support
this view. (Energetics of the process of oxidative attack are treated as
small compared to either the energetics of combustion in the gas phase or the heat transfer to the wall. Bond breaking energy is, however, the same as in the subsurface solid.) Indirect evidence is available that oxidative degradation proceeds with an activation energy identical with that for "thermal" degradation of catalytically cured polymer, while the preexponential constant increases with additional cure catalyst which is a source of highly reactive free radicals. Thus, surface degradation by free radicals in an operating hybrid should indicate the activation energy for isothermal pyrolysis at the wall temperature, which is indeed what is observed in hybrid environments.

It is argued that when the heat transfer rate to the solid wall is increased by increasing the oxidizer mass flow rate in the free-stream, the regression rate increases till a point is reached at which the wall oxidizer concentration is no longer sufficient to complete the oxidative degradation. After such a point, any increase in free stream oxidizer mass flow rate results in a regression rate less than what the heat transfer theory would predict (for a constant "flame" temperature). Now, if the wall oxidizer concentration is increased, say by increasing the chamber pressure or by increasing the partial pressure of free-stream oxidizer, the regression rate should increase till limited by heat transfer rate again. All these arguments are shown to be completely in agreement with reported experimental data.

It is concluded that the rate controlling steps in the hybrid motor operation are, condensed phase kinetic bond breaking rate in the low mass flow rate (C) regime, and the surface oxidative bond breaking rate in the high mass flow rate regime, with the heat transfer to the wall always being a necessary but insufficient rate limiting factor.
It is pointed out that accurate wall temperature measurements in the various regimes of hybrid motor operation and data on oxidative degradation of polymers are badly needed to render the semiquantitative theory quantitatively predictive.

(d) Experiments in the simulated Hybrid Boundary Layer

Not a single experimental investigation has been found in the literature on the structure of hybrid boundary layers covering a range of pressures. Such an investigation is undertaken here.

A combustion tunnel facility is designed and built to simulate the hybrid boundary layer on a porous wall with gaseous fuel injection. The free-stream oxidizer mass flow rate \( (G) \) and the gas composition are variable over the range of typical hybrid rocket operation \( (0.01 \, \text{lbf/sq. in. sec. to } 1 \, \text{lbf/sq.in. sec.; composition – practically any gas}) \). The tunnel static pressure is variable from one to twenty atmospheres. Measurement of dynamic head, temperature and species concentrations across the boundary layer is the primary intent.

At the time of reporting, measurements have been made at one streamwise location for mass flow rates between 0.01 and 0.06 lbf/sq.in. sec. and pressures from two to four atmospheres. Time-averaged temperature and dynamic head profiles are obtained. Oxidizer concentration is measured by probe sampling near the wall. Gas analysis is through a chromatograph.

The experimental results lead us to the following conclusions.

(1) The temperature profiles are very similar to those at atmospheric pressures. This observation lends support to the present gas phase theory, besides questioning the validity of all gas phase kinetic control theories of hybrid combustion.
(i) Near the wall, the oxidizer concentration is finite. Precise statements on the quantitative support the measurements lend to hybrid combustion theory must await the availability of accurate data on polymer oxidative degradation and also the perfection of the present experimental technique. At the time of reporting, it can be said that the measurements lend an order-of-magnitude support.

(iii) Variation in static pressure, maintaining constant the oxidizer flow rate and the wall mass transfer number, has little effect on the wall oxidizer mole fraction, as was anticipated in the gas phase theory.

Finally, it is observed that some of the results obtained in this thesis, although motivated by hybrid combustion problems, have applications in a wide variety of fields that range from composite propellant burning to fire research.
CHAPTER II

SOLID PHASE THEORY

2.1 Introduction

From the theoretical point of view, the problem of hybrid combustion is different from that of say, solid propellant combustion, in that it is relatively simple to model the hybrid combustion process in order to compute the mass "burning" rate from two independent calculations. One of these is the much pursued \(^ {30,60,53,25}\) gas phase theory where, the heat transfer to the solid phase from the parallel gas flow on the surface is of primary interest and a determination of this heat transfer rate is used to predict the burn rate through the "heat of vaporization" of the solid. The other is the relatively unexplored \(^ {48,20}\) solid phase theory, where the linear regression rate of the solid is predicted, based on a study of the subsurface chemical kinetic depolymerization reactions, given the wall temperature of the solid. For a satisfactory comparison, the two predictions are each expected to match with experiments.

At this stage a doubt may arise as to the feasibility of such calculations. Quantitative accuracies of most present day calculations involving chemical kinetics data are difficult to assess. This is because uncertainties of several orders of magnitude in the values of the kinetics constants are frequent. However, in the field of polymer degradation, probably because of the relative simplicity of the kinetics, reproducible values of the kinetics constants appear to be available in the extensive literature on the subject \(^ {33a,14,61}\). The accuracies of the reported values appear to be sufficient to justify a theoretical calculation involving them.
The physics of the problem of polymer degradation is discussed in chapter II. Modeling and mathematical formulation is undertaken in section III. The nature of the problem posed is indicated in section IV, where analytical solutions are obtained for any general polymer characterized by a constant activation energy of depolymerization. For the special case of polymethylmethacrylate (PMMA, i.e., plexiglas) numerical solutions are obtained, including explicitly the reported\textsuperscript{14} variation in activation energy with degree of depolymerization. The accuracy of the results is discussed in the light of the assumptions in modeling and limitations of analysis. Comparison with experimental data in inert environments is undertaken in section V. Comparison with experimental data in an operating hybrid, is reserved for a later chapter (for reasons that will be apparent there).

It is a matter of observation that the results obtained in this chapter, although motivated by a rocket fuel combustion problem have applications in a wide variety of fields involving polymer chemistry, that range from fire research\textsuperscript{29} to biomechanics.*

2.2 Physics of the Problem

The first requirement of our study of any physical phenomenon is that we picture the essentials of the process in terms of simpler, well understood constituent processes. The availability of a system of very general conservation equations that include all conceived processes, and the argument that it should be possible to understand (in principle at least) any physical phenomenon through them, often lead to little beyond confusion as far as the utility of the study to an engineering application is concerned.

* Polymer degradation applied to skin burning is discussed by Stoll and Green, J. Appl. Physiol., 14, 373, (1959).
It is to be noted that the present analysis does not have for its aim, the detailed and refined treatment of the problem. Rather, it is the first attempt at a complex problem, where only the essentials are included. That is, a "zeroth order" treatment in familiar terminology. With this in mind we look for the simplest models for the constituent processes.

Experiments with thermocouples imbedded in the regressing solid fuel and order of magnitude calculations indicate that the worst case thermal depth (distance from the wall - normal to the wall - to achieve 1/e of the wall temperature) is no less than $10^{-4}$ cm, which is far greater than molecular dimensions. Since this depth is the smallest natural length scale in the problem, it would appear safe to assume a continuum model. This assumption is used throughout (see chapter IV for additional considerations).

Unless we are forced to abandon the idea, it is normal practice to assume that local thermodynamic equilibrium prevails at various spatial locations in the solid. This means a quantity like temperature has meaningful interpretation. If we further assume the material to be thermally perfect, other thermodynamic variables can be related to temperature.

We now isolate the solid completely from the gas flow (figure 1.1). The deep solid temperature is determined by experimental conditions. Let us assume that this value is the same as the ambient temperature ($T_0$), much lower than the wall temperature ($T_w$). At low temperatures, the polymer consists of large molecular chains, with chain weights usually around $10^5$ gm/gm mole. It is unlikely that such heavy molecules can enter and assume gaseous state at low temperatures. That such is the case can be seen in analogy with, say, straight chain hydrocarbons. Under normal conditions, methade ($\text{CH}_4$), ethane ($\text{C}_2\text{H}_6$) ...(low molecular weight) are gases; heptane ($\text{C}_7\text{H}_{16}$), octane ($\text{C}_8\text{H}_{18}$) ...(medium molecular weight) are liquids;
eicosane \((C_{21}H_{66})\), dicosane \((C_{22}H_{66})\) ... (high molecular weight) are solids. Expressed in another way, the vapor pressure of the large molecular weight polymer is very low.

When the molecular kinetic energy (temperature) is raised, the backbone bonds in the chain are broken. When the rate of temperature increase is so high that chemical equilibrium is not maintained. We are mainly interested in the bond breaking rate and not in the reverse bond making rate. Such a nonequilibrium situation is the general problem in the present case. Experimental evidence\(^{33c}\) supports the view that there is very little breakdown of the monomer while the polymer chain is broken at solid temperatures of interest to hybrid rockets motor operation. In conformity with the generally accepted practice (see later for a more detailed justification), I assume the primary mechanism of interest to be kinetic bond breaking.

In the analysis we use a Galilean transformation of reference frame to keep the wall surface stationary. Let us follow the changes in a "differential element" of the polymer as it moves from deep solid \((-\infty)\) to the surface (see figure 3.2). Heat transfer to the wall from the gas phase maintains the equilibrium wall temperature at \(T_w\), far above the deep solid temperature \(T_o\), determined by experimental conditions. The difference in temperature \((T_w - T_o)\) gives rise to a temperature gradient in the solid. The mechanism of thermal conductivity transfers heat into the solid down this temperature gradient. A temperature profile is established. Local thermodynamic equilibrium prevails. Chemical equilibrium is attempted but the reverse, bond making rate falls short of the forward bond breaking rate, except at stations very near the cold interior. The differential element starts with all of the polymer backbone bonds intact at the temperature \(T_o\).
As it moves through the temperature profile, the increasing temperature increases the bond breaking rate. The mean fragment size gets smaller and smaller till a temperature is reached when the mean fragment size is small enough to leave the solid surface. Let us call this Fragment Size Vaporizing, FSV for short. The temperature where this is reached is the wall temperature $T_w$. There is only one speed at which the element has to move from deep solid ($-\infty$) to wall (w), so that $T_w$ and FSV are reached simultaneously (at the stationary plane, wall). If the element moves faster, there has not been time enough for breaking the requisite number of bonds to bring FSV at $T_w$, so that larger fragments than FSV reach that plane. If the element moves slower, the polymer has spent time enough in the high temperature environment to have more than the requisite number of bonds broken so that fragments smaller than FSV reach the plane at $T_w$. The existence of an unique rate at which the polymer has to move to reach $T_w$ and FSV at the stationary plane, is typical of any eigenvalue problem. In the formulation, the regression rate appropriately appears as an eigenvalue.

Hence, given the wall temperature ($T_w$) and the deep solid temperature ($T_0$) we should be able to predict the linear regression rate of the solid as a function of FSV and other physicochemical properties entering the system. It is easy to anticipate the general trends in the solution. Large FSV leads to a high regression rate and a small FSV leads to a low regression rate, all other quantities held constant. Large FSV implies a small number of bonds to be broken from the initial polymer chain. To keep the total number of bonds broken the same to match endothermic heat transfer requirements under an established temperature profile, there is the larger mass "flow" rate. Extension of this argument to the small FSV
case should now be obvious.

2.3 **Mathematical Formulation**

The formulation is carried out under the requirement that various conservation equations and boundary conditions have to be satisfied.

The usual conservation equations of classical heat transfer in solids are generalized to include the effects of chemical kinetic bond breaking. Its effects are to bring in sinks (or sources) of heat and sinks (or sources) for polymer backbone bonds.

In addition to the assumptions of a continuum and local thermodynamic equilibrium, the following further assumptions are made:

(i) the field is one dimensional,

(ii) the regression is steady,

(iii) thermal diffusivity is constant,

(iv) diffusion of small fragments through large ones is absent,

(v) mechanical energy involved is negligible,

(vi) chemical reaction is of the single step irreversible Arrhenius type,

(vii) temperature gradient deep within the solid is zero,

(viii) phase changes need not be included in the analysis.

In the equations to follow, \( T \) stands for temperature (\(^\circ\)K), \( k \) for coefficient of thermal conductivity (cal/sec cm \(^\circ\)C), \( c \) for specific heat (cal/gm \(^\circ\)C), \( D \) for depolymerization energy to convert 1 gm of polymer to 1 gm of monomer (cal/gm), \( \rho \) for density (gm/cm\(^3\)), \( B_{TD} \) for the preexponential constant for thermal degradation (sec\(^{-1}\)), \( E_{TD} \) for activation energy for thermal degradation (cal/mole), \( R \) for universal gas constant (cal/gm mole \(^\circ\)C), \( N \) for the nondimensional bond number referred to the initial bond number, and \( x \) for the normal distance into the solid from the wall (cm).
Energy:

$$\frac{d}{dx} \left( k \frac{dT}{dx} \right) + \rho c \frac{dT}{dx} = D \rho N B_{TD} \exp(-E_{TD}/RT)$$  \hspace{1cm} (2.1)$$

$$x = 0 : \quad T = T_w \quad ; \quad x = \infty : \quad T = T_0$$  \hspace{1cm} (2.2)$$

Bond conservation:

$$- \frac{dN}{dT} = N B_{TD} \exp(-E_{TD}/RT)$$  \hspace{1cm} (2.3)$$

$$x = 0 : \quad N = N_w \quad ; \quad x = \infty : \quad N = 1$$  \hspace{1cm} (2.4)$$

We note the similarity of the equations to those governing laminar flame propagation in premixed gases. Following Spalding's treatment, we define

$$y \equiv c \rho f x / k$$

$$\tau \equiv (T - T_0) / (T_w - T_0)$$

These transform equations (2.1) and (2.3) into

$$\frac{d^2 \tau}{dy^2} + \frac{d\tau}{dy} = \frac{D k \rho N B_{TD} \exp(-E_{TD}/RT)}{(c \rho f)^2 (T_w - T_0)}$$  \hspace{1cm} (2.5)$$

$$\frac{dN}{d\tau} \cdot \frac{d\tau}{dy} = \frac{k N c \rho B_{TD} \exp(-E_{TD}/RT)}{(c \rho f)^2}$$  \hspace{1cm} (2.6)$$

Now we define,

$$p \equiv d\tau / dy$$

$$h \equiv D/c (T_w - T_0)$$

$$\Lambda \equiv k B_{TD} / (\rho c f^2)$$

leading to
\[ pp' + p = \Lambda \ h \ N \ \exp(-E_{TD}/RT) \tag{2.7} \]
\[ pN' = \Lambda \ N \ \exp(-E_{TD}/RT) \tag{2.8} \]
with

\[ \tau = 0 : \ p = 0, \ N = 1 \]
and

\[ \tau = 1 : \ p = p_w, \ N = N_w \]

where a prime denotes differentiation with respect to \( \tau \), and \( p_w \) and \( N_w \) are determined as follows.

Energy considerations at the wall surface lead to

heat supplied into the material = heat used to raise the temperature from \( T_0 \) to \( T_w \) + heat used up in bond breaking of chains

i.e.,

\[-k \frac{dT}{dx} = \dot{\rho}c(T_w - T_0) + D \rho \dot{\tau} / FSV \tag{2.9} \]

See chapter II.3.7 for a discussion of the effects of phase changes in the solid. At this stage an observation can be made regarding the interesting mathematical nature of the problem. We note that the boundary condition at the hot end is not known a priori but can only be specified in terms of the unknown eigenvalue \( \dot{\tau} \). In other words, the system of equations is such that the regression rate and the boundary condition are coupled and neither can be specified to start with. In the final solution both are determined simultaneously.

In terms of nondimensional variables, defined earlier, the wall energy
condition (2.9) may be written as

$$p_w = -1 - h/FSV$$  \hspace{1cm} (2.9a)

When the initial number of bonds per unit mass of polymer is large, it is easy to see that

$$N_w = 1 - 1/FSV$$  \hspace{1cm} (2.10)

Multiplying equation (2.8) by $h$ and subtracting the resulting equation from equation (2.7), we get an equation that can be integrated in closed form, leading (after the use of boundary conditions) to

$$N = (p + \tau + h)/h$$  \hspace{1cm} (2.11)

Substituting equation (2.11) in equation (2.7), we get

$$pp' + p = (h + p + \tau)\Lambda \exp(-E_{TD}/RT)$$  \hspace{1cm} (2.12)

Defining $\Theta_a \equiv E_{TD}/RT_w$, and $\chi \equiv (T_w - T_o)/T_w$, it is a matter of algebra to arrive at,

$$pp' + p = (h + p + \tau)\Lambda \exp\left(-\Theta_a/[1 - \chi (1 - \tau)]\right)$$  \hspace{1cm} (2.13)

$$\tau = 0 : p = 0 ; \quad \tau = 1 : p = -1 - h/FSV$$  \hspace{1cm} (2.14)

A solution of the system of equations (2.13) and (2.14) leads to the determination of the regression rate eigenvalue $\Lambda$ as a function of $FSV$, $\Theta_a$, $h$ and $\chi$.

2.4 Discussion of the Assumptions

2.4.1 One-dimensional Field

The essential physics in many problems can be analyzed on the basis of one-dimensional theories. This way, the advantage of dealing with ordinary, instead of partial differential equations can be had (when steady state is considered). Variations in two or more dimensions are present in
the hybrid rocket. There is a streamwise variation in the regression rate which may imply a streamwise variation in wall temperature. However, the variations are very slow, sufficiently far downstream of the leading edge because of the slow streamwise variation of skin friction/wall heat transfer in boundary layers. In laminar boundary layers, the variation is proportional to $x^{-0.5}$ and in turbulent boundary layers to $x^{-0.2}$. Essentially the variations scale like one of the boundary layer thicknesses (momentum $\theta$, energy $\delta$) which are much greater than the length relevant for temperature variations in the solid, a variation that is strongly exponential.

However, these arguments do not hold near the leading edge where, the streamwise variations are strong and theoretically the skin friction coefficient approaches infinity. The boundary layer assumption itself breaks down. Sufficiently close to leading edge there is a region where the streamwise variations in temperature may be just as important as the variations in the solid. A two dimensional treatment is definitely needed for such cases. In a practical hybrid a further problem is that the "leading edge" is the region close to oxidizer injection into the chamber so that the strongly coupled effects of droplet breaking, evaporation, surface melting, heterogeneous and gas phase chemical reactions in the highly stirred environment defy all notions of simple modeling. Reference (58) has a discussion of such problems.

2.4.2 Steady State Regression

In the turbulent boundary layer over the hybrid fuel, temperature and pressure fluctuate around a mean. The pressure fluctuation amplitude is normally small enough not to affect the mean fragment size at the surface. Such a conclusion is reached after noting the weak logarithmic dependence
of fragment size on pressure (see fig.4.3). Temperature fluctuations are caused by bulk motion of eddies at different temperatures. The lowest frequency fluctuations are caused by the largest eddies which occasionnally manage to reach the wall. The largest eddies have a length scale like the boundary-layer thickness (\(10^{-1}\) ft.). At a mean velocity of 100 fps, the time scale of interest is \(10^{-3}\) sec. The characteristic response time of the thermal profile in the polymer is like, \((\text{thermal diffusivity})/(\text{regression rate})^2\). For the quickest response case, this corresponds to \(10^{-3}/10^{-2}\), or \(10^{-1}\) sec. Hence it is reasonable to assume that the temperature profile in the polymer does not respond to wall temperature fluctuations due to turbulence. The assumption of steady wall temperature is realistic for the purposes of solid phase analysis.

2.4.3 Constant Thermal Diffusivity

Fourier's law of heat conduction is assumed to be valid. That is, the heat flux in the solid is proportional to the first gradient in temperature. Thermal conductivity coefficient is known to vary with temperature, and it would also seem probable that there is a dependence on the mean fragment size. The density and specific heat are also known to vary with temperature, hence the thermal diffusivity \(\alpha = k/\rho c\) varies. Mainly because of the lack of availability of precise variations of thermal diffusivity with temperature and fragment size (in the regimes of interest to hybrids) the present analysis considers \(\alpha\) to be a constant. After the results are obtained, a simple method of modifying the constant \(\alpha\) results is used. We are led to believe that such variations are not likely to modify the constant property results by factors important enough to alter the basic conclusions of the present study. However, when more precise numbers are needed for regression rate calculations, such variations have to be included in the analysis, if other data used in the analysis are available to a
consistent degree of precision.

2.4.4 Absence of Diffusion

As the fragments get smaller, it is conceivable that the small fragments assume velocities differing from the "mean" regression rate velocity. Such local movements may be grouped under "diffusion" effects. They cause, firstly, bond number transfer, i.e., the number of bonds still left unbroken in the small fragments add to the total number of bonds under consideration at the location they diffuse into. Secondly, they affect all of the molecular transport through the Onsager reciprocal relations. While it would be interesting to study such "real solid effects", they have been ignored in the present analysis mainly because of the desire to keep the analysis simple.

The resulting error is difficult to estimate unless some assumption is made regarding the diffusion. If we are interested mainly in monomer diffusion, we may try to define a Lewis number (≡ Dpc/k) as in the corresponding problem of laminar flame propagation in premixed gases. It is observed\textsuperscript{13} that the diffusion of organic molecules (benzene) through rubber appears to have a diffusion coefficient close to the thermal diffusivity at temperatures of interest to hybrids. The Lewis number, then, may be around unity for monomer diffusion through polymers. If this extrapolation is made, neglecting diffusion corresponds to putting diffusion coefficient and hence the Lewis number, identically equal to zero. The ratio of flame speed eigenvalue at a Lewis number of unity to that at a Lewis number zero, around the reduced activation energy parameters of interest is about 9.\textsuperscript{27} The close similarity of the present problem to that of laminar flame speeds indicates that the regression rate predictions probably have a maximum overestimation by a factor 3, if diffusion effects are important.
2.4.5. Mechanical Energy Involved is Negligible

The bulk volume expansion of the polymer with temperature increase involves a $p \Delta V$ work. The associated energy, for the typical case of Plexiglas, corresponds to around 2 CHU/ft$^3$. This is negligible compared to either the sensible enthalpy or the chemical enthalpy change in the same mass of polymer.

2.4.6 Chemical Reactions are of Single Step First Order Arrhenius Type

The kinetic bond breaking rate of a vast class of polymers is satisfactorily represented by our concept of "probability" of a reaction for a given number of random "tries". In any chain (say of a system of mutually linked spring-mass systems) we ask for the probability that an energy greater than a specified amount $E_1$ be accumulated in any one link. If this specified energy happens to be greater than that requisite to break the link, it may result in the rupture of the link. Whether such a rupture is permanent or not depends on whether a recombination is possible soon after the rupture. The accumulation in a link of the energy far greater than the mean is a "rare" event. The rate of occurrence of such rare events depends directly on the number of participants. From a knowledge of statistical mechanics it is easy to anticipate for the remaining probability factor, a form like $\exp(-E_1/E_2)$ at any mean energy $E_2$, equated to RT. (Equating $E_2$ to RT actually defines the thermodynamic temperature $T$). Now we are in a position to predict the local reaction rate at each temperature as

$$\frac{dN}{dT} = -N \cdot B \cdot \exp(-E_1/RT)$$

where $B$, ideally speaking, is the number of random tries per unit time per participant. It is a matter of experience that the above definition of $B$ does not lead to satisfactory agreement between theory and experiments.
Significant progress has been made in physically accounting for, and quantitatively removing this dilemma in chemical kinetics. For our purposes, it is safe to regard $B$ as an empirical factor. The reaction rate function depicted above belongs to the well known class of Arrhenius reaction rate function. In the present work such a first order Arrhenius reaction rate function is used to model the bond breaking kinetics.

A second look at some of the polymer degradation studies in the literature indicates that a slightly modified degradation kinetics scheme is more accurate. There appears to be sufficient justification to postulate that the degradation is actually brought about by reactive species distributed within the polymer matrix. The reactive radicals may originate from the cure catalyst, or they could be additional species intentionally added. (The cure catalyst forms the end group of a polymer chain.) As the concentration of the reactive radicals increases, there is a higher depolymerization rate at the same activation energy. (Now we see that the reaction scheme is actually second order.) The concentration effect of the free radical source may be mathematically absorbed in a modified pre-exponential factor, $B$. The modified kinetic scheme of polymer degradation has far reaching implications (see chapter IV).

There are polymers for the degradation of which, a more complicated reaction rate scheme (including chain reactions) is required. Chain reaction schemes require the determination of the rate limiting step after which the solution will be straightforward but laborious. In the present study, we are content with applications to polymers that obey a "first order" Arrhenius kinetic scheme only, since this class of polymers is quite large and covers most of the fuels used not only in hybrid rockets but in solid propellants as well.
2.4.7. Temperature Gradient Deep Within the Solid is Zero

The Arrhenius reaction rate scheme is such that the chemical reaction rate does not go to zero at the cold boundary. This is physically plausible also, since even at the lowest temperatures, a small fraction (very small though) of links in the chains do possess energies far above the mean and are thus able to undergo rupture. When the material starts from $-\infty$, as in the mathematical modeling, the finite regression rate allows infinite time for reactions so that any nonzero reaction rate leads to extremely tantalizing difficulties, identical with the time-honored cold boundary difficulties\(^{19}\) in the analysis of laminar flame propagation in premixed gases. The temperature gradient can be small but has to be finite, to take care of the heat transfer needs of maintaining the bond breaking rate at the low temperature, $T_o$.

Physically the resolution of the difficulty is simple. We do not allow infinite time for the reactions to occur. The polymer element starts from a finite distance. Consequently the temperature gradient will have to be artificially terminated near the cold boundary. Considering the strong exponential decay of the temperature profile, we note that the temperature gradient approaches zero at fairly short depths below the wall surface. Since we find also (see, for example, fig.2.6) that the temperature gradient at the cold boundary does not have a strong effect on the regression rate eigenvalue, the gradient is identically equated to zero at the cold boundary ($T = T_o$ boundary).

2.4.8. Phase Changes in the Solid

Under high regression rate conditions there is little evidence (experimentally) of any phase change before the fragments enter the vapor phase. Under low regression rate conditions phase changes may occur.
As a first approximation we may take it that the phase changes, when and if they occur, will be isothermal, (figure 2.3). Thus in the transformed plane (figure 2.4) the profile undergoes a step change. It is easy to see that such changes can be handled analytically after the regression rate is obtained without their inclusion. Such a procedure is undertaken in the development of the liquid layer (see section IV.5).

2.5.A Analytical Solutions

The system of equations (2.13) and (2.14) is highly nonlinear. At first sight we may be tempted not even to try for analytical solutions. However, it is possible to solve the system in a very elegant way through the powerful technique of Kaplun and Lagerström, lucidly described in Chapter III of Ashley and Landahl. The price we pay for success is rigour, although it is felt that a day will come when the price will go down.

In the limit of large $\Theta_a$ (i.e., small $T_w$) the reaction rate term is very small and most of the energy balance is between conduction and bulk material heating ("convection"). Mathematically, the right hand side of equation (13) is small and hence we may try to find the solution neglecting this term, which leads to

$$pp' + p = 0,$$ having

$$p = -\tau$$

(2.15)

as the solution, satisfying the boundary condition ($p = 0$) at the cold end. But this solution fails to satisfy the boundary condition at the hot end. The problem belongs to the class of "Singular Perturbation" problems and we need to consider the "inner" (wall) and "outer" (deep solid) regions separately, with consequent matching of the solutions.

We identify $1/\Theta_a \gamma$ as a convenient small parameter in the system (see equation 2.13). The asymptotic methods work best when the "small
parameter" used in the expansions is really small. Typical values of \( E_{TD} \) vary from 30 kcal/mole (Polymethyl acrylate) to 80 kcal/mole (Poly-tetrafluoroethylene). The highest reported values of \( T_w \) are around 800°K. Hence \( \Theta_a \equiv E_{TD}/RT_w \) varies from around 17 to 50. \( \chi \equiv (T_w - T_o)/T_w \) varies from about 0.5 to 0.7. Thus it is safe to say that values of \( \epsilon \), to be used in the analysis will rarely be higher than \( 10^{-1} \).

**Outer Solution**

It is easy to show formally that equation (2.15) represents the outer solution to all orders.

**Inner Solution**

A common error found in the literature is to assume that all of the reaction takes place at the surface only. The thermal depth is so small, it is argued, that it is as good as zero. But, smaller the depth, more has to take place in a shorter distance. That is, the gradients get very large. We cannot treat the reactions as taking place in a region of constant temperature, no matter how small the thickness is. No other single error seems to have caused greater confusion in the field of polymer degradation\(^{38,29}\). To examine the behaviour near the wall, where the gradients are very large, we write equation (2.13) as

\[
pp' + p = (h + p + \tau) \lambda \exp(-\Theta_a [1 + \chi(1 - \tau)])
\]  

(2.16)

Defining \( \chi \equiv \lambda \exp(-\Theta_a) \)

we get,

\[
pp' + p = (h + p + \tau) \chi \exp(-\Theta_a \chi(1 - \tau))
\]  

(2.17)

Taking \( \epsilon \equiv 1/\Theta \chi \) and defining inner variables

\[
\eta \equiv (1 - \tau)/\epsilon
\]

\[
\xi \equiv p + \tau
\]

along with \( \lambda \equiv \epsilon \chi \), we get from equation (2.17),
\[-(\xi - 1 + \epsilon \eta). \xi ' = (h + \tau). \lambda. \exp(-\eta) \quad (2.18)\]

where a prime denotes \( d/d\eta \). We also have [from equation (2.14) and the new definitions]

\[\eta = 0 : \quad \xi = -h/FSV \quad (2.19)\]

making the expansions

\[\xi = \xi_o + \epsilon \xi_1 + \epsilon^2 \xi_2 + \epsilon^3 \xi_3 + \ldots.,\]

\[\lambda = \lambda_o + \epsilon \lambda_1 + \epsilon^2 \lambda_2 + \epsilon^3 \lambda_3 + \ldots.,\]

and substituting them into equation (2.18) we get to zeroth order (the subscript \( o \) has been dropped here),

\[\xi' - \xi' \xi = (h + \xi). \lambda. \exp(-\eta) \quad (2.20)\]

This may be written,

\[\frac{d\xi}{h + \xi} - \frac{\xi d\xi}{h + \xi} = \lambda. \exp(-\eta). d\eta \quad (2.20A)\]

Equation (2.20A) integrates to,

\[\ln(h + \xi) - [\xi - h \ln(\xi + h)] = -\lambda. \exp(-\eta) + \text{(constant)} \quad (2.21)\]

Kaplun's matching theorem requires

\[
\begin{array}{c}
\text{Inner limit of the} \\
\text{Outer solution}
\end{array} = \begin{array}{c}
\text{Outer limit of the} \\
\text{Inner solution}
\end{array}
\]
\[ p^0_{\tau \rightarrow 1} = p^{i}_{\eta \rightarrow \infty} \]

which gives, \( \xi = 0 \) as \( \eta \rightarrow \infty \), yielding through equation (2.21)

\[
(\text{constant}) = (h + 1) \ln h \tag{2.22}
\]

Substituting into equation (2.21), we get

\[
(h + 1) \ln (h + \xi) - \xi = -\lambda \exp(-\eta) + (h + 1) \ln h \tag{2.23}
\]

Using the boundary condition at the hot end, namely \( \xi \equiv -h/F_{SV} \) on \( \eta = 0 \), we finally have

\[
\lambda = (h + 1) \ln \left( \frac{F_{SV}}{F_{SV} - 1} \right) - \frac{h}{F_{SV}} \tag{2.24}
\]

Retracing all the defined symbols that went into equation (2.24) we get:

\[
\dot{\xi} = \left[ \frac{B_{TD} \exp\left(-E_{TD}/RT_w\right)}{2\xi \cdot \left(\frac{T_w}{T_w} - \frac{T_o}{T_w}\right) \cdot \left(\frac{E_{TD}}{RT_w}\right) \cdot \left[\left(\frac{D}{c(T_w - T_o)} + 1\right) \ln \frac{F_{SV}}{F_{SV} - 1} - \frac{D}{c(T_w - T_o)F_{SV}}\right]} \right]^{1/2}
\]

(2.25)

The most important observation is to note the unmistakable square root dependence of linear regression rate on the isothermal depolymerization rate at wall temperature. If an Arrhenius rate law is forced on experimentally measured linear regression rates versus inverse wall temperature, an activation energy of one half that for isothermal depolymerization rate is predicted.

Complete depolymerization to monomers is not allowed by the solution, which is consistent with our concept of a first order reaction.

All the other parameters in the solution have only a weak influence on the regression rate.

Equation (2.24) is plotted on figure 2.5 for two representative
values of h. We note that such a plot has in it the solution for all
d polymers characterized by a constant activation energy.

Equation (2.25) has been plotted in figure 4.6 for representa-
tive values of the physio-chemical constants.

2.5.B Numerical Solutions for a General Polymer Characterized by

a Constant Activation Energy

The asymptotic methods must lead to very good accuracy in the
present case, as already discussed. However, as a matter of routine,
numerical solutions were obtained for comparison.

An arbitrary constant $E_{TD}$ of 32 kcal/mole was used (so long
as $\Theta_a$ is large, the value of $E_{TD}$ should not matter anyway, since the
Singular Perturbation solution indicates that $\lambda$ is not a function of $E_{TD}$).
Equation (2.13) subject to boundary condition (2.14) was integrated
numerically. Standard fourth order Runge-Kutta-Gill\textsuperscript{49} method was used.
Marching was from hot end to the cold end.

But for the usual, trivial oversights common to the initial
stages of any computer program, no difficulties were encountered in the
marching process. But considerable difficulties hurdled the logical
determination of the correct eigenvalue through the computer, even after
many runs with various alternative logic statements. The circumstances
under which the numerical solutions were being obtained did not permit
time-consuming computer experiments, so that the following foolproof,
if laborious, procedure was used. A set of trial $\lambda$'s with step increments
were fed into the computer. The marching was started at the hot end with
each of these $\lambda$'s and the value of $p$ at $= 0$ (i.e., at the end of marching)
was printed out for each case. This enabled the initial determination
of the range of \( \lambda \)'s in which the correct was buried. This range of \( \lambda \)'s with fine step increments between them was fed into the computer and the run was repeated. The resulting values of \( p_{\tau=0} \) were plotted against \( \lambda \). The correct eigenvalue is that for which \( p_{\tau=0} = 0 \). We note the practical consideration that in the computer the value of \( p \) at the cold boundary was not \( \tau = 0 \) but a finite value \( (\approx 10^{-2}) \). Hence the \( p \) will have to be evaluated at that point and not at \( \tau = 0 \). We recall that when we are so close to the cold boundary, \( p = -\tau \) for all purposes [equation (2.15)] so that the value of \( \tau \) which was being treated by the computer as being equivalent to zero, was equated to the value of \( p \). At this \( p \) the \( \lambda \) was taken to be exact. A typical plot is shown in figure (2.6).

In the fourth order Runge-Kutta-Gill method\(^{49} \), which is essentially a Taylor's series expansion method, the errors are like (step size)\(^5 \). The results with a step size of \( 10^{-2} \) should be extremely accurate in the present case, where there are no inflexion points in the \( p - \tau \) profile. Nevertheless, the standard step size check was used, again as a matter of routine. Numerical integrations were repeated for two extreme cases with step size halved. The results are shown in figure (2.6). The descriptancy in the eigenvalue \((<0.0001)\) due to step size effect was considered small enough not to require any further checks.

The numerical results are compared with the analytical solutions (i.e., predictions of equation 2.24) in Table I, for four extreme cases. The extreme cases were selected to be the two extreme wall temperatures reported, and the two values of FSV that are thought to be extreme limits. Very good accuracy of the analytical solution is evident. It is further pointed out that the regression rate \( \dot{r} \) is proportional to \( (\lambda)^{-1/2} \) so that the predictions through equation 2.25 will be even more accurate.
2.5.C The Special Case of Polymethylmethacrylate

Grassie and Melville in a thorough investigation of the depolymerization of polyvinyl compounds, have found that the apparent activation energy of PMMA varies with the degree of depolymerization. Their finding leads to

\[ E_{\text{TD}} = [31.5 + 10 X \text{(fractional conversion to monomer)}] \]

Noting that the fractional conversion to monomer at any point can be related to energy absorbed in excess of the solid heating term, \( c(T - T_0) \), at that point, it is easy to show, through nondimensional variables that,

\[
\text{fractional conversion to monomer} = \frac{p + \tau}{(p_w + 1) FSV} \tag{2.26}
\]

Since \( \Lambda \) in equation (2.13) is a very large number, it is convenient to write equation (2.13) as

\[
pp' + p = (h + p + \tau) \Lambda \exp(-\Theta) x \exp[\Theta - \frac{a}{1 - \chi(1 - \tau)}] \tag{2.27}
\]

where

\[
\Theta \equiv (31.5 + 10/FSV) \cdot 1000/RT_w \tag{2.28}
\]

Finally, defining \( \lambda \equiv \Lambda \exp(-\Theta) \), we get

\[
pp' + p = (h + p + \tau) \cdot \lambda \cdot \exp[\Theta - \frac{a}{1 - \chi(1 - \tau)}] \tag{2.29}
\]

Equation (2.29) subject to boundary conditions (2.14) was integrated numerically to determine the eigenvalue \( \lambda \) for different values of the parameters, \( T_w \) and FSV. A \( T_0 \) of 300°K was used throughout. Standard Runge-Kutta-Gill method (see section 2.5.A.) was employed. The results are displayed in figure (2.7). Numerical values of properties of polymer properties used were,
\[ B_{TD} = 3 \times 10^9 \text{ sec}^{-1} \]

\[ c = 0.35 \text{ cal/gm}^\circ \text{C} \]

\[ k = 5 \times 10^{-4} \text{ cal/cm sec}^\circ \text{C} \]

\[ \rho = 1.19 \text{ gm/cm}^3 \]

These are the values quoted in the literature.\(^{48}\) Consequent upon the vapor pressure criterion, the heat of depolymerization quoted in the literature will have to be interpreted carefully. \(D\) used here is computed on the basis of conversion of \(N\) (backbone carbon-carbon) single bonds to \(N - 1\) double bonds, which leads to \(D = 280 \text{ cal/gm} \).

Before closing the chapter, I would like to make the following observation. There are available in the literature, studies dealing with numerical integrations of the equations to determine regression rates of polymers. All of these methods use the integral (quadrature) procedure. Each polymer has to be treated separately and the procedures usually involve approximations of one form or another. Although the details of those computations are not disclosed in those papers,\(^{20,48}\) it is not difficult to estimate the possible expense involved. The present method of formulation, which has led to (a) accurate solutions for all constant \(E\) polymers, and (b) accurate solutions for PMMA with variable \(E\), involved, on the IBM 360 system at the Information Processing Center of M.I.T., a total computation fee of $47.68.
CHAPTER III

GAS PHASE THEORY

3.1 Introduction

It provides an interesting and instructive pastime to read the introductory statements in most of the theses, some of the research reports and a few of the journal articles that deal with fluid turbulence in pure or applied form. Eloquent statements on the inhospitality of this research field have been so numerous that I need not add some more here. In the present case, the situation is hardly likely to improve, as Lees points out, with the inclusion of mass addition, heterogeneous species and combustion. But, it is precisely for such a situation that an analysis is badly needed. Analogies with the simpler laminar flow situations have led in the past to erroneous conclusions.

The gross physical structure of the hybrid boundary layer is outlined in section 3.2. Such a recapitulation provides that basic framework for further analysis. The, often ignored, fine structure detail of nonpremixed, turbulent combustion of gases is developed in section 3.3. The picture developed is consistent with recent experimental observations. Based on some useful knowledge in much simpler situations, a treatment is given of a possible way to theoretically handle the problem. A solution is hindered by our lack of knowledge even of the simplest form of incompressible, isothermal, homogeneous, isotropic turbulence. A simple way, that I have not seen used before, is outlined to get some limiting solutions. It is concluded that a well organized research program is
needed to solve this challenging problem effectively.

3.2 Fluid Dynamics and Heat Transfer in the Hybrid Boundary Layer

The oxidizer gas flow over the burning fuel surface in a conventional hybrid rocket is at a Reynolds number high enough, and the flow is smooth enough for a boundary layer to be established over the wall.* The Reynolds number is usually sufficiently high for the boundary layer to be turbulent. Mass addition into the boundary layer from the wall renders the boundary layer unstable at Reynolds numbers lower than the Reynolds numbers in conventional zero mass addition boundary layers.

The vaporizing fuel from the wall is transported outward towards the free stream through turbulent diffusion and, at the same time, is convected downstream. Oxidizer from the free stream is transported toward the wall and mixes with the fuel [figure (3.1)]. The high reaction rate zone that is established stretches as an intermittent diffuse layer, occupying about one third of the boundary layer thickness, where high temperature eddies are more frequent than elsewhere in the boundary layer. These general features are confirmed both by Schlieren studies and by conventional probing. 10

There is an inherent stability mechanism for the spatial location of the high reaction rate region. If the zone gets too close to the wall, more fuel evaporates and the effect of increased wall mass transfer drives the reaction zone away from the wall. If the reaction zone moves too far outward, the decreased wall heat transfer causes less fuel to evaporate and the free stream momentum flattens the boundary layer, driving the reaction zone nearer the wall again.

It is not very probable that the heat of vaporization of the fuel

*Not applicable to some of the ONERA rocket motors.
has such a value that the heat transfer rate to the wall evaporates
exactly the requisite amount of fuel to burn in a stoichiometric ratio
with the oxidizer. In fact, many hybrid fuels have been known to burn
fuel-rich, implying that the heat of vaporization is smaller than what
we would like to have for efficient combustion. Moreover, it is ob-
served that a certain fraction of the evaporated fuel gets convected
downstream below the high reaction rate zone and never mixes with
oxidizer at high enough temperature for burning. Unless some arrange-
ment is made to burn this "escaped" fuel, at the end of the chamber,
say, the chemical enthalpy of this fraction of the fuel is lost.

Wall heat transfer rate in the hybrid rocket decreases (slowly)
with distance from the leading edge because of increasing Reynolds
number effects. Thus the burning rate should, and is known to, de-
crease with distance from the leading edge. If the flow port was of
constant area to start with, there will develop, in course of time, a
variable area port for flow of oxidizer. A streamwise pressure gradient
is, thus imposed on the boundary layer. In addition to the well known
effects of such pressure gradients, there is in the present case, the
possibility of a velocity "overshoot," i.e. the velocity at some locations
in the boundary layer assuming a value higher than the free stream velocity.
For the same axial pressure force, hot, low density gases in the high
reaction rate zone are accelerated much more than the cold, high density
gases elsewhere in the boundary layer. Such an overshoot has been ob-
served.23

In the combusting case, the thickness of the boundary layer increases
above that of the cold boundary layer. Such effects have been discussed
in the available literature.36 The relevant fluid dynamical variables
and parameters in the hybrid boundary layer have been the subject of extensive study by Marxman et al. Reynolds number of flow,

\[ R \equiv \frac{(\rho u)_x}{u} \]

plays an important role in determining the general characteristics of the viscous boundary layer. A non-dimensional group characteristic of the injection rate may be written as

\[ F \equiv \frac{(\rho v)_w}{(\rho u)_\infty} \]

i.e., the ratio of the wall mass injection rate per unit area of the wall to the rate of free stream mass flow per unit free stream area. F considers only the inertial effects. It is to be recognized that the "distortion" of the classical boundary layer properties due to injection depend also on the viscous effects. Hence a new similarity group incorporating the effects of injection and viscous effects is formed as

\[ B \equiv \frac{F}{(c_{f/2})} \]

The wall friction coefficient \( c_{f/2} \), instead of the Reynolds number, is used as a more direct representation of viscous effects. It has been demonstrated\(^{40,42,36} \) that B is indeed a very powerful similarity parameter in boundary layers with wall mass transfer. The effects due to combustion cause changes in density and velocity in the classical, boundary layer. A parameter

\[ \phi \equiv \frac{(\rho u)_b}{(\rho u)_\infty} \]

has been found to be useful\(^{60} \) in this connection. Parameter \( \phi \) represents the ratio of momentum at the high reaction rate zone to the free stream momentum. Finally, the assumption of similarity among the transport of enthalpy, momentum and specie in the boundary layer (Reynolds analogy)
leads to the familiar relation

$$C_H \ (\text{Stanton number, i.e., a heat transfer coefficient}) = \frac{c_f}{2} \ (\text{friction coefficient})$$

Information least explored in the hybrid boundary layer have been turbulence characteristics and species concentration profiles. Turbulence intensity plays a role in the transport and mixing, both of which are important in determining the reaction rate and the position of the reaction zone. Research on influence of combustion on turbulence has a long history.\(^5^7\) Available results are interesting but inconclusive. A first look at the very extensive literature on the subject,\(^5^4,^6^3\) seems to support the view that turbulence intensity is increased, slightly increased or unaffected depending on whether the flow is confined (duct), semiconfined (boundary layer) or unconfined (open jet). There is certainly much more in the problem than the above qualitative generalization.

The species profiles in a turbulent combusting boundary layer, provide us with the true picture of the nature of combustion, thereby hinting at proper models to base our analysis on. They also provide valuable clues as to possible mechanisms behind newly observed, intriguing experimental data. The only careful measurements reported are those of Wooldridge and Muzzy.\(^6^4\) They simulated the hybrid boundary layer with porous plate fuel injection at one atmosphere pressure and low mass flow rates. The reaction zone was found to be broad; considerable fractions of fuel and oxidizer were found on the oxidizer and fuel sides of the reaction zone respectively. The former observation prompts us to carefully reexamine the applicability of the Burke-Schumann flame sheet.
approximation so extensively used in almost all diffusion flame analyses. We also recognize the availability of oxidizer species at the fuel surface so that heterogeneous oxidation, or catalysis, cannot be ruled out.

The above account covers most of the characteristics peculiar to the hybrid boundary-layer. No attempt is made to describe the general turbulent boundary-layer 9,50,52, all the characteristics of which are, however, very relevant to the problem on hand.

3.3 Turbulent Combustion of Nonpremixed Gases

A detailed examination of the processes involved in the turbulent combustion of nonpremixed gases would be worthwhile. Aside from the intrinsic interest of the general problem, the results would have extensive applications in fields ranging from industrial furnaces to fire spread in forests. More immediately, the study would unveil the structure of the hybrid boundary-layer to better understand experimental measurements. Based on a postulated picture of the combustion process, it is argued that molecular mixing rate of reactants and chemical kinetic rate of combustion are the two rates of primary interest. The former is taken from turbulence theories and the latter from gross chemical kinetic studies. The general behaviour of the concentration profile of oxidizer is deduced and compared with experiments. It is concluded that even when chemical reaction rates are much higher than transport or mixing rates, it is possible to have significant concentrations of oxidizer on the fuel side (up to the wall) of the time-averaged high reaction rate zone, often referred to as the "turbulent flame" in the literature.

Literature on turbulent combustion of nonpremixed gases show that an extremely important feature is either assumed to be universally known
or only hinted at, if not ignored completely. The usual model of reactants diffusing against each other, and burning where stoichiometry permits, combustion has led to satisfactory results in laminar flow cases. Generalizations to turbulent flow, with an "eddy" diffusivity replacing laminar diffusion coefficient tend to be nonphysical. A brief review of the relevant details from turbulence and chemical kinetics is given below. Present thoughts on a possible theory of the combustion situation are also indicated.

Our concepts of fluid turbulence usually involve the postulate of the existence of macroscopic "groups" of fluid, distributed against the background continuum. (The word "continuum" is not used to denote the limit of Knudsen number tending to infinity; such a definition applies to all fluid elements under consideration. Rather, I use "continuum" to mean ungrouped fluid.) Fluid elements in a "group" have a property in common that distinguishes the group from the neighboring groups or the background continuum. This property is the vector velocity. The boundaries of a group are not well defined. The velocity gradually merges into that of the neighbors. Interpreted in terms of a correlation function there are no "sharp corners" present. These groups of fluid have come to be known as "eddies", in the extensive literature on turbulence. The size and distribution of these eddies in space and time is random, but under identical set of experimental conditions, extremely reproducible statistically, obviously implying an inherent stability mechanism in the time-averaged dynamics. The random velocity field does not correlate with the random pressure field in the sense of the Bernoulli equation, so that the velocity
fluctuations are not derived from the local pressure field. There is present a total pressure variation in the field - i.e., vorticity is a principal feature. Three dimensionality is another essential feature that goes frequently unemphasized. The eddies, in their motion from one location to another, transport mass, momentum energy and any extensive property of the fluid.

A particular (tagged) eddy undergoes changes in the course of time. In the absence of a driving source, an eddy breaks up into smaller eddies and the smaller into still smaller ones until a scale is reached below which the eddy loses its identity in the background continuum. This scale is far above the molecular scale, however. The smallest scale of turbulence is determined by viscous effects. The smallest eddy has a Reynolds number [defined as (length of the eddy) x (relative velocity)/(kinematic viscosity)] of the order unity. The scale of the larger eddies in the field, on the other hand, is the scale of the field itself (diameter of the pipe, width of the channel, thickness of the boundary layer, etc.; incidentally, an interesting exception that has remained surprisingly unexplored is the vortex chamber, where the largest scale of turbulence is far below the chamber diameter).

The mechanism of turbulence is dissipative. Mechanical energy in the motion of a large eddy finally enters molecular kinetic energy-heat. The local rate of dissipation is proportional to the local mixing rate. (Throughout this report, "mixing" is used to denote molecular mixing.) Molecular mixing, taking place at the smallest scale of turbulence, takes place at the rate at which the small eddies can be "prepared" from the large eddies, i.e., the breakup rate of large eddies. This breakup rate
is proportional to the rate of loss in correlation in any eddy. (I am presently revising this approach.)

The correlation function was shown by G. I. Taylor\textsuperscript{59} to be the Fourier transform of the spectrum function. The "spectrum function" is the distribution of energy among the various scales of eddies in equilibrium. The first step in understanding turbulence is thought to be the ability to predict, for the simplest form of homogeneous isotropic case, the spectrum function. If an analogy helps, we may recall the problem of spectrum function in black body radiation. (however, the mechanics of black body radiation is fortunately nondissipative.) For that part of the turbulence spectrum, sufficiently far removed from both sources and sinks (the "inertial subrange"), Kolmogoroff has given the limiting form

\[ F(n) \approx k_n^{-5/3} \]

at large Reynolds numbers, \([F(n)\) is the energy contained among eddies with frequency distribution of \(\Delta n\) around \(n; k_n\) is the associated wave number]. This law bears his name and also matches very well with experimental data. Near the scale of dissipating eddies, Heisenberg\textsuperscript{18} deduces a form like

\[ F(n) \approx k_n^{-7} \]

which again has been found to match experimental data. So far, a theoretical prediction of the complete spectrum function has not been available. For practical purposes, semiempirical forms for the correlation function are used frequently. In their tests on turbulent jet flames, Günther and Simon\textsuperscript{16} found that the form of the spectrum function was very little different from that in a cold jet. For the present purposes of an order-of-magnitude treatment of the problem, the above observation of Günther and Simon gives
me confidence to use for the hybrid case, correlation functions used in isothermal cases.

The conditions to be met in order that a successful chemical reaction may occur are governed by complex quantum mechanical phenomena and the details can be had by solving the time dependent Schrödinger equation for the matrix elements. Empirically, the concept of reactions occurring upon sufficiently energetic collisions of reactant molecules has led to satisfactory representation of experimental data over limited ranges of validity. Such empirical curve fit procedures are usually not representative of the detailed kinetic scheme of the transformation of reactants to products. They can, however, be thought of as depicting the gross kinetics, essential from the point of view of the experimenter. Whatever the procedure of arriving at the representation, the most important feature to note is that chemical reactions take place at a scale no higher than molecular.

Extraneous factors, among which heat transfer rate plays a prominent role, impose concentration limits of combustability and limits of ignition. Thus we note that even after the reactants mix at molecular level, whether combustion takes place or not is determined by these limits, availability of an ignition source of sufficient energy and by the absence of strong heat sinks.

Chemical reaction rates at high pressures (1 - 100 atm) as prevalent in hybrid rocket combustion chambers may be expected to be high, since reactants with simple chemical structure are employed often. Experiments on plexiglas burning indicate that characteristic chemical reaction times are not more than $10^{-4}$ to $10^{-5}$ sec. Laminar flame speed
measurements may be used to deduce the chemical reaction times (defined as the ratio of density of products to the mass production rate of products in unit volume), in premixed gases of simple hydrocarbons and air/oxygen. All such calculations indicate that chemical reaction times are much smaller than characteristic mixing times in the time averaged hybrid flame zone where the mean velocity is of the order of 100 fps.

With the above background, we turn our attention to the hybrid boundary layer combustion. Turbulent eddies give gross mixing, but chemical reactions can take place only on the molecular scale. Thus, chemical reactions follow an intimate molecular mixing of fuel and oxidizer in a zone several (hundred or a thousand) mean free paths thick. When chemical reaction times are much smaller than the mixing times, the actual combustion zone is limited to this "molecular diffusion band" around the periphery of the large eddies. The band separates zones of oxidizer-rich and fuel-rich eddies in the turbulence field. A probe actually draws alternate samples of fuel and oxidizer as the respective eddies happen to flow over the probe and the gas composition obtained in such an experiment should not be interpreted as implying the existence of such a uniform composition on molecular scale prior to entering the probe.17,62 As a crude mnemonic representation, figure (1.2) has been prepared. Entropy, density, Knudsen number and such details are thought irrelevant for the purposes of mnemonic representations.

With the above picture in mind we obtain an order of magnitude estimate of the oxidizer transport. We consider an eddy at the edge of the boundary layer \((y = 0)\) making its way toward the wall \((y = \delta)\). The correlation function drops from unity at \(y = 0\) to essentially zero at
y = δ. (This is true only for the largest eddies.) Assuming the standard, correlation function, \( R_t = e^{-t/\tau_0} \), we obtain the local mixing rate as it varies with y.

\[
\frac{dR_t}{dt} = -\frac{1}{\tau_0} e^{-t/\tau_0}
\]

(3.1)

The mixing length of the largest eddy is very nearly equal to \( \delta \).

Mixing length = \( \delta = \sqrt{\langle u'^2 \rangle} \int_0^\infty R_t \; dt = \sqrt{\langle u'^2 \rangle} \tau_0 \) which leads to

\[
\tau_0 = \delta/\sqrt{\langle u'^2 \rangle}
\]

The time it takes a fluid element to move across the boundary layer is approximately equal to the time it takes a fluid element to travel from the leading edge to that station at x. This shows that

\[
t = xy/\langle U_\infty \delta \rangle
\]

Hence, \( t/\tau_0 = \{x/\delta \} \{y/\delta \} \left[ \sqrt{\langle u'^2 \rangle} / U_\infty \right] \)

or

\[
\frac{\tau_{mix}}{\tau_{local}} = \frac{1}{\sqrt{\langle u'^2 \rangle} \exp\left[ -\frac{x}{\delta} \frac{y}{\delta} \frac{\sqrt{\langle u'^2 \rangle}}{U_\infty} \right]}
\]

(3.2)

\( \sqrt{\langle u'^2 \rangle} U_\infty \) can be put equal to the turbulence intensity level in the boundary layer.

From reference 36, we have

\[
\delta/x = \{[0.0281/I] [1 + B] [\ln (1 + B)/B]\} \cdot 8 \frac{R_x^{-2}}{x}
\]

(3.3)

Where,

\[
I = \frac{7(1 + 13 B/10 + 4 B^2/11)}{72 \ (1 + B/2)^2}
\]

(3.4)
If the local mass consumption rate of the reactants is given by \( \dot{m}'' \) gm/cm\(^3\) sec, the characteristic reaction time is \( \rho/\dot{m}'' \) sec.

If at some reference condition \( \dot{m}'' \) is known, this may be written,

\[
\tau_{\text{reaction}} \sim \tau_{\text{ref}} e^{+E/R (1/T - 1/T_{\text{ref}})}
\]

(3.5)

Now we define a Damköhler "fifth" group as,

\[
D^V \equiv \left[ \frac{\tau_{\text{reaction}}}{\tau_{\text{mix}}} \right]_{\text{local}}
\]

(3.5)

\[
D^V = \tau_{\text{ref}} e^{+E/R (1/T - 1/T_{\text{ref}})} \left[ \frac{Y}{\delta} \frac{K}{\delta} \left[ \sqrt{u'^2}/U_\infty \right] \right] e^{\frac{\nu}{\delta} \left[ \sqrt{u'^2}/U_\infty \right]}
\]

(3.7)

Even after recognizing the extreme simplification that went into equation (3.7), we find it instructive to compute \( D^V \) across the boundary layer. We read the experimental \( T \) at a selected \( y/\delta \) (at any station \( x \)) and calculate \( D^V \). When \( D^V \) exceeds unity, it is clear that any oxidizer that mixes further, reacts relatively slowly and hence the oxidizer concentration after that station is expected to undergo simple diffusion against wall injection.

We have selected the measurements by Wooldridge and Muzzy\(^{54}\) to test equation (3.7). Flame velocity measurements in hydrogen air mixtures by Rosenfeld and Sugden* suggest,

\[
\tau_{\text{chem}} = 1.25 \times 10^{-5} e^{32500 (1/T - 0.0007855)} \text{ sec}
\]

(3.8)

---

* Comb. & Flame, 8, 37, 1964.
For the boundary layer with mass injection and combustion found in reference 64 at a $B = 9.3$, we have,

$$\tau_{\text{mix local}} \approx 0.0667 e^{4.36 y/\delta}$$  \hspace{1cm} (3.9)

$$D^V \approx 18.75 \times 10^{-5} \frac{e^{32500(1/T - 0.007855)}}{e^{4.36 y/\delta}}$$  \hspace{1cm} (3.10)

Calculation of $D^V$ across the boundary layer (flame at $y = 0.8''$, wall $y = 0''$) indicates that below $y = 0.3'' - 0.4''$ effects of chemical reactions can be neglected. Now the problem reduces to one of diffusion of a trace species in a (laminar) "boundary layer" with wall injection. With reference to figure (9)\textsuperscript{64} we note that the predictions through equation (3.10) are not in bad disagreement with experiments.
CHAPTER IV

THEORY OF HYBRID COMBUSTION

4.1 Introduction

A critical survey of many available theories of hybrid combustion has been made by Green. The major failing of those, and subsequent theories, is that the efforts are generally isolated from each other. Each applies to a narrow facet of the problem. Only the work of Marxman et al. represents a detailed investigation of the many processes involved. Under the basic assumption that heat transfer to the solid wall from the gas phase is rate limiting, (and assuming a constant "heat of vaporization"), they succeeded in matching theory with experiments covering a range of operating conditions of pressure and mass flow rates. Essentially, the linear regression rate of fuel at any streamwise location is predicted as a power, n (n = 0.5 for laminar, and 0.8 for turbulent boundary layers), of the flow rate, with an independence on chamber pressure. Considerable departures from the predictions of the theory have been observed in certain experiments where pressure sensitivity appeared and also the power n approached zero. In the light of the previous two chapters, a careful examination of the combustion processes involved indicates that not only is it possible to account for the departures, but we may have to revise the early theories as well. The new theory which emerges in the process of noting differences in polymer degradation behaviour in inert and noninert environments, brings coherence into the fields of polymer degradation and hybrid combustion. So far all nonmetallized hybrid data available have been consistent with the present theory. Towards the end of the present chapter a brief
discussion is given of the limits of validity of several previous attempts at explaining the pressure sensitive behaviours. It is concluded that a thorough reexamination of associated fields involving polymer degradation, like composite propellant burning, may be necessary in the wake of the present developments.

4.2 The Role of FSV

It was noted in chapter II that the mean size of the fragments leaving the wall is an important parameter in the problem. We need a physically valid criterion for specifying FSV for a given set of conditions.

When there is quasi-equilibrium between the condensed phase and the gas phase at the interface it would appear natural to require that the vapor pressure sum of all fragments coming off the surface contribute to pressure at the interface. This assumption is not valid when there exist additional molecules in proportions significant enough to contribute to chamber pressure.

Most researchers in the field of rocket combustion either state explicitly or assume implicitly that degradation proceeds till monomers come off the surface. While in some experiments a large fraction of the material evaporated from a heated sample of polymer appear to be monomers, other experiments have been reported where clear evidence can be found of the presence of dimer, trimer and higher fragment sizes. Besides, even in the experiments where large fractions of monomers were found, it cannot be ruled out that the fragments while leaving the surface were much bigger, and subsequently underwent further depolymerization in the gas phase. At the time of writing, the status then is: there is clear evidence in many experiments of fragments larger than the monomer leaving the surface, while
there is no definite evidence in any experiment that only monomers leave
the surface. The importance of the question cannot be treated lightly,
because FSV plays a crucial role in the analysis of polymer regression rates;
and the regression rate calculation of polymers holds the key in many
problems involving degradation/burning of polymer solids, which is surely
a very vast field.

The nature of first order Arrhenius reaction rate functions does not
allow complete depolymerization to monomers. Hence if we require monomers
to come off the surface some artificiality will have to be introduced in
the system. In order to overcome the mathematical difficulty, Lengelle\textsuperscript{31}
specifies that 1/100 of the initial number of backbone bonds still remains
at the stage of vaporization (FSV = 1.01). Such a choice is purely arbitrary
and has no physical significance whatsoever. His predictions of the re-
gression rate for PMMA fall far short of experimental observations.

Rabinovitch\textsuperscript{48} uses an energy argument to arrive at a number for the
mean size of the vaporizing fragments. He specifies:

\[
\text{critical fragment size} = \frac{\text{backbone c-c bond energy}}{\text{latent heat of vaporization of monomer}}
\]

His argument is that degradation of polymer in the solid takes place till a
stage is reached when the heat supplied into the solid is more profitably
employed in allowing the polymer to evaporate than in breaking the backbone
c-c bonds. His argument gives a valid mathematical boundary condition at
the wall. A typical T-S diagram for a liquid is shown here. The latent
heat of vaporization decreases with increase of pressure. Hence, if such
thermodynamic diagrams are applicable to polymers, the CFS of Rabinovitch
increases with pressure. Such an increase is directly in conflict with the
There are some experimental conditions where a criterion on FSV different from the vapor pressure criterion seems necessary. A typical example is the familiar hot plate experiment where a strand (cylinder) of the polymer is pressed against a heated plate. It is strongly felt that a "mechanical strength" criterion is more appropriate for such experiments. As the polymer chains get shorter, due to degradation, there is a loss in mechanical rigidity of the solid. Soon a mean fragment size and temperature is reached at which the strength gets so low that appreciable flow may take place under a load. This is a promising area for further research in evaluating the numerous hot plate experiments that have been reported.\textsuperscript{47} The interpretations of surface temperature measured in such experiments, as affected by possible gas films, has been so thoroughly treated by Cantrell\textsuperscript{6a} that the next logical step would appear to be an evaluation of FSV.

4.3 \textbf{Comparisons of Theoretical Predictions with Experimental Data Obtained in Inert Environments}

Figure 4.2 has the plot of PMMA regression rates predicted by numerical results of chapter II. FSV is allowed to be a parameter. Experimental
points shown are those of Chaiken et al.\(^7\) where strands of 0.6 x 0.6 cm cross section were pressed against a hot plate with a force of 640gm, leading to a "pressure"-like 2.77atm abs. We note that the experimental data trend is very well predicted by the theory. FSV values of 6-10 are seen to match with experiments. The equilibrium vapor pressures of various higher fragment sizes of PMMA have not been found in the literature. The vapor pressures as a function of molecular weights and temperature were approximated by comparison with those for standard hydrocarbons of identical molecular weights. Standard values for the latter, taken from American Petroleum Institute data book\(^2\) are shown in figure 4.3. It is comforting to note that the values of monomer vapor pressure measured by Ivin\(^21\) agree well with those predicted for hydrocarbons.

Based on a study of figure 4.2 I draw the following conclusions.

(i) The results of the present theory match the experimental trends very well.

(ii) If an Arrhenius curve fit is attempted for experimental hot plate data, an apparent activation energy of E/2 would be predicted (as can also be seen from equation 2.25 of chapter II). Thus we understand at last the conflicting values of activation energy that are reported to be around 30kcal/mole for small samples depolymerized isothermally and 15kcal/mole for hot plate data.

(iii) The existence of a mean FSV larger than the monomer is very real.

(iv) Vapor pressure criterion for FSV determination in hot plate experiments is not unsatisfactory.

(v) Rabinovitch's CFS of 9 agrees well with experimental hot plate data.
4.4 Comparisons in Noninert Atmospheres and the Theory of Hybrid Combustion

Extensive theories of hybrid combustion developed by Marxman et al. use a constant surface temperature (for a constant "flame" temperature) and match the experimental line. It also appears experimentally that the surface temperature in an operating hybrid does not vary too much with \( i \), although the exact number for this surface temperature seems to vary a little from experiment to experiment. Marxman and Gilbert quote a value of 600°K, while House and Peck obtained more nearly 650°K - 700°K. McAlevy et al. measured the surface temperature and the regression rate of PMMA in an experiment where a jet of oxygen was squirted on the end of a polymer cylinder as shown here. This is a stagnation point laminar boundary layer combustion experiment quite similar to laminar flow hybrids. Such available data on regression rates for PMMA in noninert atmospheres are presented in figure 4.4. At the reported surface temperatures we note that FSV's like 30 (i.e. molecular weight 3000gm/gm mole) are needed to match experiments.
with degradation theory. That such large fragments can enter the gas phase is difficult to understand; firstly from just a feel for molecular weights of gases, and more scientifically, either through the vapor pressure criterion or through Rabinovitch's energy criterion. It would seem that an additional agency is needed at the surface to degrade the polymer pieces from values of around 30 to vaporizable fragments like 2-6. The only obvious agency appears to be surface attack by reactive species (i.e. free radicals, oxygen, fluorine, hydrogen fluoride ... etc.). At this juncture it is necessary to point out that most researchers in polymer degradation agree that oxidative degradation is a mechanism that influences degradation although they may not agree on precise numbers for the process. However, we have the important exception in McAlevy and Hansel who maintain, on the basis of their experimental finding, that oxygen in the environment plays no role whatever in the degradation of PMMA at 's comparable to hybrid 's. The apparent paradox is resolved below.

We recall from chapter III that wall oxidizer concentration in hybrid boundary layers has been found to be nonzero. Thus the postulate of catalytic oxidative surface degradation of polymer appears to be a logical one at this stage.

Precise values for the kinetic parameters in oxidative degradation have not been found in the literature. Reasonable values deduced from the work of Bresler et al lead to an expression like,

\[
\frac{dN}{dt} = -N 9.71 \times 10^{10} p_{ox} e^{-\frac{35000}{RT}}
\]

where \( p_{ox} \) is the partial pressure of oxygen (in psia) at the surface. Choosing a reasonable depth of \( 10^{-6} - 10^{-7} \) cm for the surface attack of
oxidizer, we satisfy ourselves that oxidative attack is indeed capable of degrading the polymer pieces from a large fragment size (=30) down to an FSV= 3 - 10. Such an oxidative degradation requires a partial pressure of oxidizer like 0.6 psia at the wall, which is the order of $p_{ox,w}$ we expect at about 10 atm chamber pressure.

If the present postulate of oxidative surface attack is correct, the surface temperature variation with regression rate must give evidence of an activation energy like 30-40 kcal/mole. The measured value is\textsuperscript{38} 37 kcal/mole. Based on the work of Grassie and Melville\textsuperscript{14} who observed an activation energy variation with fragment size, this value of 37 kcal/mole indicates a fragment size like 2. We note from fig.4.4 that a vapor pressure of 1 atm. is provided by fragments of about that size (=4) at those temperatures. We note a break (at point B in fig.4.4) in the slope of the experimental data of regression rate vs. inverse wall temperature where the vapor pressure line intersects the regression rate data. This aspect of the problem is discussed later in connexion with the "liquid layer". If the inverse surface temperature, inferred from thermocouple measurements inside the solid, is plotted against the regression rate, we should observe a slope that leads to an activation energy around 15 kcal/mole in the Arrhenius scheme. This is because subsurface reactions are purely thermal, and the $E_{TD}/2$ effect has already been discussed (equation 2.25). The measured values are\textsuperscript{38} around 15 kcal/mole.

The above discussed regression rate behaviour, replotted for convenience in fig.4.4A, is used to interpret the hybrid combustion behaviour as follows. Below the matching point P on the hybrid band, the heat transfer rate is insufficient to evaporate the polymer at a rate greater than $\dot{r}_l$. As G increases, $\dot{q}_w$ increases, and the operating point moves to P, where the
thermal degradation just brings FSV to the surface and these can enter the gas phase without further degradation. Now, if we increase the G, giving a higher $q_w$, we expect a higher $\dot{r}$. (This assumes that the gas-phase combustion temperature does not vary too much from 1 to 2, a reasonable assumption, following Cohen's experiments.) To establish this higher $\dot{r}$, the thermal theory requires a larger FSV than the vapor pressure (or Rabinovitch's) criterion allows to enter the gas phase. Unless an additional agency steps in to degrade the surface polymer pieces down to FSV at a rate fast enough to maintain the high $\dot{r}$, the $\dot{r}$ tends to equilibrate to a lower value on the "Inert Band." Since finite concentrations of reactive species are available at the wall surface, the additional needs of bond breaking are met for a while. However, as $G$ increases further, the increased need for reactive species at the wall is not met. Now if the chamber pressure is increased, the wall concentration of reactive species increases directly with free stream pressure (see chapter III) and the regression rate increases to the $G^n$ line.

The porous-tube data of McAlevy and Hansel is shown in figure 4.4. There are at least two different explanations that can be offered for their negative results. One is that, though their heat-transfer and regression rates were comparable to those of a hybrid, their surface temperature was much higher, bringing their point almost on the inert band below which oxidizer effects are not observable anyway. Second, they never really went to zero oxidizer concentration; the minimum value was apparently 9%.

The main conclusion of the present treatment is that the variation of $\dot{r}$ with pressure in the pressure-sensitive regime 3 is directly controlled by the wall-oxidizer concentration, which in turn depends on the transport...
parameters, $B$, $\rho o x_e$, and possibly $G$ also. (See pages 8 - 9).

**Low $i$ Behaviour**

At high regression rate (regime 3 in fig.4.4), the "Hybrid Band" is applicable to experiments since the "Inert Band" predictions fall short of observed regression rates. However, at low regression rates (regime 1) it appears that $T_w$ might be double valued (one on the "Hybrid" and the other on the "Inert", bands). The following explanation is capable of removing the difficulty.

As a polymer layer moves from deep solid interior to surface, we note that the average molecular weight decreases and the temperature increases. Both these favor loss in physical strength of the polymer. If the polymer spends considerable time in the high temperature environment (low $i$'s) it may soften to acquire low enough viscosity to affect the hybrid operation. As pointed out by McAlevy et al\(^{38}\), this layer may get squeezed out in a hot-plate experiment like that of Chaiken et al\(^{7}\). Whether this layer has the familiar fluid-dynamic significance to merit the usage "liquid layer" remains to be seen. Lieberherr\(^{32}\) has given an introductory treatment.

In the light of the above discussion we note the existence of a layer of low viscosity (on the wall) that gets progressively thinner as the $i$ increases. In the hot plate experiments\(^{7}\) the layer is absent and the wall temperature $T_w$ and the solid-"liquid" interface temperature $T_{SL}$ are equivalent, showing that the discussion on fig.4.4 needs no modification. I am fully aware of the crudeness of the argument, but feel that it not inconsistent with the nature of that experiment. The hybrid operating points have the behaviour shown in fig.4.5. At a regression rate $i_1$, the wall temperature is $T_{w1}$ and the fragment size there is FSV. At the solid-"liquid" interface SL, the temperature is $T_{SL1}$ and is lower than the wall temperature $T_w$ and the fragment size $FS_{SL}$ is bigger than FSV. The degradation
from $F_{SL}$ to FSV takes place as the layer moves from SL to wall through $T_{SL}$ to $T_w$. At a higher regression rate $\dot{r}_2$ the same explanation holds, as can be seen from figure 4.5. At $\dot{r}_3$, the "liquid" layer has disappeared completely and $T_{SL}$ and $T_w$ coincide.

4.5 The "Liquid" Layer

The following is a first attempt at getting a handle on the essentials of the postulate of the liquid layer on operating hybrid fuels. It is worth repeating that in a non crystalline solid, like PMMA, for example, there are no sharp distinctions between liquid and "solid" phases. Condensed phase can only be classified as liquidlike or solidlike. With this in mind, we calculate below the thickness of the liquidlike layer at various regimes of hybrid motor operation.

Molecular weight versus melting point correlation of straight chain hydrocarbons is presented in figure 4.6. An approximate curve fit expression is also indicated. (eq. 4.1)

As the polymer degradation proceeds from deep solid interior to the surface, the decreasing molecular weight, combined with increasing temperature, indicates that there may be a plane around which the "melting" of the polymer begins. For a specified fragment size vaporizing (FSV) and wall temperature ($T_w$), the regression rate is determined through equation

The solid-"liquid" interface temperature ("melting" point) $T_{SL}$ and the mean fragment size at this layer, $F_{SL}$, are related according to (see figure 4.5)

$$F_{SL} = \frac{12.2 \text{ molecular weight of monomer}}{0.010315 T_{SL}} \quad (4.1)$$
For a given regression rate, equation (2.25) may be looked upon as specifying a relation between the temperature and fragment size at any location (of course, only so long as the basic assumptions behind that equation are applicable). Hence eqns. (4.1) and (2.25) may be simultaneously solved for the unknowns $F_{\text{SL}}$ and $T_{\text{SL}}$ when once $\dot{r}$ is specified. It is convenient to solve the system graphically (as shown in figure 4.6).

We first ask for the temperature rise through the liquid layer when it exists. At any regression rate, say $\dot{r}_A$, a horizontal line (AB) is drawn. The wall temperature is specified, say at $\text{1}$. This fixes the operating point at $P_1$. The temperature of a polymer element starting from deep solid increases on the operating line AB from right to left. At the point where the melting point is met (M on the line AB), melting begins and the temperature of the element increases from M to $P_1$ in a liquid layer. This temperature rise is related to depth $x$, through the crude relation,

$$\tau = \exp(-\dot{r}.x/a)$$

If at the regression rate $\dot{r}_1$ the wall temperature had been lower than at $\text{1}$ (say at $\text{2}$), the operating point would be at $P_2$. Now, no liquid layer exists, because the melting point at M is not reached in the course of temperature increase of the element from deep solid value (far right on the line AB) up to the operating point $P_2$. The polymer sublimes.

The calculated thicknesses are presented in figure 4.7. Good qualitative agreement is observed between this figure and reported behaviour.\

Lieberherr has given an introductory treatment of the fluid-dynamical aspects of a liquid layer in ONERA hybrid rocket motors.

4.6 Previous Investigations

It is again convenient to group our discussions under the same four divisions as used in the introduction. The present work does not have for
its aim either a critical review or a detailed comparative study of previous investigations.

(a) **Solid Phase Theory**

Considerable literature exists on the problem of deflagration of double base propellants or gun powder. While the problems are similar, studies directly related to hybrid fuels appear to be only those of Houser and Peck and Rabinovitch. The work of Lengelle which appeared after my work was presented, is almost identical with chapter II.5a. Lengelle's work was discussed in parts already and no more mention will be made in the present chapter.

Houser and Peck start with the energy equation used in the present work. However, the factor N (number of bonds remaining at time t) is omitted in the kinetic term, probably due to an oversight. Thus the bond conservation equation is not invoked at all. Approximate integral procedure of Scala and Gilbert is employed to solve the equation by numerical quadrature. The results of Houser and Peck fall short of experimental regression rates by one to two orders of magnitude. Such a discrepancy is understandable, if it is required that the vaporizing fragment size be very small (nearly monomer). They conclude by suggesting oxidative degradation as one of the possible mechanisms that could explain the discrepancy.

Rabinovitch uses the bond conservation equation only. He approximates the temperature profile by neglecting the endothermic bond breaking contribution. The governing equation is solved by numerical quadrature. The major contribution of Rabinovitch is his unique postulate of a vaporizable fragment size larger than the monomer. While his way of specifying FSV
(in his terminology, CFS or critical fragment size) as

\[
CFS = \frac{c \cdot c \text{ bond energy}}{\text{heat of vaporization of monomer}}
\]

appears a little nonphysical, his predictions of linear regression rate agree with experimental data within a factor of two. Section IV.2 has some more discussion of his approach.

A survey of the literature on polymer degradation studies motivated by applications to rocket propellant combustion, reveals conflicting data accumulated over the past several years. The last paragraph of reference (38), written in 1968, is an aptly worded summary of the state of the art which has not improved much since then. Let us consider the typical example of plexiglas. All of the data mentioned below on the degradation/regression rate variation with surface temperatures have been interpreted within the framework of an Arrhenius reaction rate scheme on the standard semilog plot. Experiments on small samples (DTA, TGA) appear to indicate an activation energy around 30kcal/mole.\textsuperscript{33a,14} Simple extrapolations of these results to tests on degradation of polymers under temperature/heat transfer rates, similar to those of propellant combustion have led to inconsistent results [see reference (39)]. Experiments where a strand of the polymer is pressed against a heated plate at a rate determined by the linear regression rate, indicate an activation energy around 15kcal/mole.\textsuperscript{7}

When a jet of oxygen was squirted axially on a cylinder of plexiglas and ignited the surface regression rate variation with optically measured temperature indicated an activation energy around 35kcal/mole.\textsuperscript{38} Many of the available studies\textsuperscript{6,1} suggest that thermal degradation is influenced by the presence of a reactive/catalytic specie, like oxygen. However,
McAlevy & Hansel based on their "porous tube" experiments, where the "test gas" with varying percentages of oxygen was passed from one end through a bed of closely packed pellets of plexiglas exposed at the other end to the hot exhaust gases from a rocket (see figure 4.8), conclude that oxygen plays no role in the degradation of plexiglas at heat transfer rates comparable to propellant combustion heat transfer rates.

Early in the present program, it was felt that a resolution of these apparent conflicts may clarify the mechanism of hybrid combustion.

(b) Gas Phase Theory

Attempts at understanding the hybrid gas phase details through governing equations have been made in the past. The major drawback of all such efforts has been that physical processes are not examined in detail. Despite statements in the past of the nature of turbulent combustion of nonpremixed gases, no one appears to have considered such details in boundary layer combustion. Too recently to be included in the present thesis, Chung has been presenting a number of papers with ideas very close to our own on the topic. Future developments on the subject remains to be seen.
(c) Hybrid Combustion Theories

The reader is referred to Green\textsuperscript{15} for a discussion of early hybrid theories. Here we mention only the later theories, particularly those dealing with pressure-sensitive combustion, which has been observed below 9-10 atmospheres pressure.

Miller\textsuperscript{41}, Smoot and Price\textsuperscript{53} and Kosdon and Williams\textsuperscript{25} all assume that gas phase chemical reaction rates become comparable to turbulent transport rates as the chamber pressure is lowered. However, simple computation of numbers for the processes do not agree with their assumptions (see chapter III.3).

Wooldridge and Marxman\textsuperscript{65} obtain excellent agreement between their theory and experimental data by postulating that there is a competition between turbulent mixing rates and chemical rates in the hybrid boundary layer. At high pressures they expect the chemical reaction rates to be much higher than at low pressures. Essentially, gas phase chemical kinetic rate control is suggested at low (less than 10atm) pressures. For turbulent diffusion, a time like 100 milliseconds is quoted in general agreement with our own computations. However, a time like 10-100 milliseconds that Marxman\textsuperscript{37} quotes for chemical reactions, is a gross overestimate. He considers,

\[ \tau_{\text{reaction}} \sim \frac{l}{S_b} \]

where \( S_b \) is the laminar flame speed in premixed gases, and \( l \) is a characteristic length scale. His error results from the improper length scale he uses in the above expression. It is well known that the proper length scale \( l \) is the interfacial flame thickness (\( \sim 0.1 \)mm) and not an eddy scale or boundary layer thickness (\( \sim 10 \) to 100mm) as he states. The proper
choice of interfacial flame thickness results in a chemical reaction time scale like $10^{-4}$ sec which is completely in agreement with our own estimates.

It is most interesting to note that the mathematical treatment of Wooldridge and Marxman may be interpreted as a description of the present hybrid combustion theory (chapter IV). The turbulent mixing process is identical in the two theories and their treatment may be interpreted as the computation of unmixed oxidizer transport to the wall. Their chemical reaction times, with a best fit activation energy of 60 kcal/mole enters as the square root in the expression for regression rate [equation (5) of their paper], so that essentially they use an $E$ of 30 kcal/mole, which is approximately the activation energy I use for oxidative degradation. I conclude that Marxman and Wooldridge obtained essentially the right results, but based upon an erroneous physical model.

An extensive study of laminar flow hybrid combustion has been made by Omori. His work also includes references to Japanese work on the subject which are so rarely referred to in our literature that a detailed discussion of his work is felt worthwhile here.

Experiments on a laboratory scale hybrid rocket using polyethylene–90% hydrogen peroxide system and on a plexiglas–oxygen system are reported. Charge lengths of 44 cm and 66 cm were used. Inside diameter was 2.6 cm. Pressures of 10 to 30 atmospheres were employed. Mass flow rates of 0.1 to 0.4 lbm/sq.in.sec were used. Burning duration varied between 15 and 30 seconds. Experimental results show pressure dependent burning.

Porous plate, propane injection, 50% oxygen (rest nitrogen) hybrid operation at one atmosphere chamber pressure are also reported. Color Schlieren photographs were taken and the results interpreted to get
qualitative density and temperature profiles. A free stream velocity $V_\infty$ of 3fps was employed at an $F \equiv (\rho u)_w/(\rho U)_\infty$ of $6.8 \times 10^{-3}$. The temperature profile is consistent with other observations.\(^{43}\)

A detailed theoretical analysis, considering essentially the gas phase only, is also reported. The unique features being:

(i) variable surface temperature in the streamwise direction - ("non-equilibrium" evaporation, as he calls it),

(ii) two region combustion of fuel - surface combustion up to a "flame Detachment Point," followed by Burke-Schumann\(^5\) gas phase diffusion flame of the type used frequently.

Surface pyrolysis of fuel is assumed, and the pyrolysis rate is related to surface temperature by a rate equation that he determines through a hot plate test on polyethylene. (He obtains an $E \approx 20$ kcal/mole, Madorsky\(^{33a}\) quotes 63 kcal/mole.) For plexiglas, the data of Chaiken et al\(^7\) is used.

A modified Rayleigh analogy is used in solving the complicated coupled system of equations.

His results indicate that the surface temperature decreases continuously in the streamwise direction from the "Flame Detachment Point," which is very reasonable. The wall temperature increases from room temperature at leading edge to a maximum at the "Flame Detachment" (P.D.). He seems to imply that the pressure sensitivity is entirely due to the surface combustion upstream of the P.D. This distance is seen to decrease with increasing chamber pressure. Strong pressure dependence is predicted even at pressures like 60 atmospheres. The factor two disagreement between his theory and experiment is attributed to "three dimensionality" and "turbulence."
A few comments can be made on his work.

(i) The model of "Flame Detachment Point" is very realistic and is certainly needed for a clear understanding of the hybrid motor operation. (A similar proposal has been made by Waldman also.)

(ii) Variable surface temperatures can also be expected to pay an important role in a detailed consideration of hybrid motor design.

(iii) The skillful employment of Rayleigh analogy for solution of complex gas phase equations is commendable.

(iv) Maximum flame temperature increases with increasing distance from leading edge and "attains finally adiabatic flame temperature." This prediction does not seem physical, besides being in direct conflict with the experiments of Jones et al. 23

(v) Attributing the pressure sensitive behavior entirely to surface combustion over small length of fuel charge is questionable, particularly in view of the present developments.

(vi) His thought on his theory that "extension to the turbulent flow may be possible by employing equivalent transport coefficients for turbulent flow" may have to be revised.

(d) Experimental Investigations

Kulgein 26 studied the combusting turbulent boundary layer on a porous cylinder through which methane was injected and burned with air. Atmospheric pressure was employed. $G$ values were around 0.005 lbm/sq.in.sec and $B$ values approximately unity. He reports "a lack of evidence of any sort of reaction generated turbulence or that the experimentally demonstrated turbulence of the viscous layer by mass injection substantially affected the transport phenomena." It is difficult to extrapolate his results to hybrid situations.
Wooldridge and Muzzy\textsuperscript{64} report a porous plate fuel injection hybrid simulation experiment covering the range of B values of interest, and G values, of approximately 0.02 lbm/sq.in.sec. The experiments conducted at atmospheric pressure indicate finite concentration of oxygen in the sub "flame" region. Reaction zone is found to be broad.

Jones et al\textsuperscript{23} essentially repeated the experiments of Wooldridge and Muzzy\textsuperscript{64} for non zero pressure gradients. Only the temperature and dynamic head profiles were obtained. Velocity "overshoots" are observed for favorable pressure gradients.

Cohen\textsuperscript{10} measured the structure of the boundary layer over a burning plexiglas slab at one atmospheric pressure. Maximum temperature in the reaction zone was nearly independent of mass flow rate G. Oxygen was found below the time averaged "flame" zone.

In the literature no experiments have been found on high pressure hybrid boundary layer.
CHAPTER V

EXPERIMENTS IN THE SIMULATED HYBRID BOUNDARY LAYER

5.1 Introduction
We recall from chapters III and IV that an experimental investigation of the structure of the high pressure hybrid boundary layer would be very valuable. The present experimental investigations were planned to measure the time averaged dynamic head, temperature and oxidizer concentration profiles. The range of experimental conditions covered were planned to include those typical of pressure-dependent and pressure-independent hybrid motor operation. At the time of reporting, results have been obtained for ranges of free stream flow rate, \( G = 0.01 - 0.06 \text{ lbm/sq.in.sec} \) and B values of 2 to 50. These ranges include those of pressure-sensitive combustion noted by Smoot and Price\(^53\) and by Marxman et al.\(^35\) The oxidizer employed in the present investigation was air; fuel was a mixture of Hydrogen (37.5\% mole) and Nitrogen (62.5\% mole).

The oxidizer concentration was measured at one sub"flame" location in each run, mainly because of the lack of availability of a reliable method (with requisite time resolution) of oxygen concentration measurement in situ. The experimental facility which was designed, fabricated and assembled, exists at present in working condition for the remaining measurements to be made. The results obtained so far have indicated satisfactory boundary layer profiles - both cold and combusting. The measured oxygen concentrations are consistent with the gas phase theory (chapter III).

The experimental facility is briefly described in section 2. (The
details of design and construction are fully discussed in the appendices.) The instrumentation employed, method of calibration and accuracies expected are mentioned in section 3. Typical, raw and processed data are presented in section 4. The results are interpreted in section 5.

5.2 Experimental Facility

The experimental facility consists essentially of a combustion tunnel of square cross section with provision for varying the free stream mass flow rates and gas composition. The tunnel is designed for an operating pressure range of one to twenty atmospheres. The "fuel" can be either a solid fuel plate held as the top wall or a porous plate assembly through which a gaseous fuel can be injected uniformly into the tunnel.

As shown in figure (5.1), the free stream oxidizer gas is supplied from commercial gas bottles (A) through heavy wall copper pigtails (B) into a high pressure manifold (C). The gas is led through a pneumatically operated (see D) ball valve (E) to a metering orifice (F). The gas from the metering orifice supersonically enters a conical section (G) of gradually increasing internal cross sectional area. In this section, a shock is established depending for its strength on the pressure setting in the tunnel downstream. The gas then enters a conical enlarger section (H) at the end of which is placed a sintered stainless steel porous plate (I) backed by a perforated stainless steel plate (J). The gas now enters the leading section (K) just upstream of the tunnel. In this leading section (K) is placed a honeycomb flow straightener (L). At the end of this section (K) are placed two stainless steel woven screens (M1 and M2) spaced apart by an aluminum spacer (N). The tunnel (P) is essentially a long square (see later) duct, with a movable bottom wall (Q) for pressure
gradient adjustments. The top wall (S) is of a porous plate assembly through which a gaseous fuel is injected into the tunnel. The gases, after combusting exit smoothing into the exit section (T) in which there is provision for the insertion of a bluff body (U) which ensures proper mixing and combustion of unreacted gases. The exit of the gases from the section T is through an orifice plate (V) bolted to the tunnel with four weak bolts (W) designed to fail (as a safety relief) at pressures above the designed maximum. The gases are now led through a contraction section (X) where ambient air is injected and mixed like in an ejector. The final exit into the atmosphere is via a stainless steel flexible hose (Y) led out through the window.

The ignition of the gases in the tunnel is accomplished by a pilot ignitor mounted on one of the side walls of the tunnel. The hot exhaust gases from the pilot are injected supersonically at an angle as shown in figure A.3.2. The pilot operation lasts only about 4 seconds after injection of fuel starts, so that during the period of probing, starting about 5-10 seconds later, this extraneous hot gas injection should have little effect on the boundary layer characteristics, as indeed the results confirm. No "flame holder" was found necessary. However, as Kulgein comments on a similar experiment that he performed, the entire porous plate acts like a flame holder.

5.3 Instrumentation

5.3(a) Introduction

The quantities of primary interest are: time averaged dynamic head, temperature and specie concentration. These are measured at one streamwise location twenty-four inches from the "leading edge." The choice of this station was determined by boundary layer growth characteristics
(described in Appendix I). Many supplementary measurements are also necessary to determine the experimental conditions. As mentioned in figure (5.3) these are, pressure and temperatures of the oxidizer and fuel gases upstream of the metering orifices, the orifice areas, the pressure and temperature of hot gases just before exit, the porous wall temperature, and the area of the exit orifice that sets the tunnel pressure.

5.3(b) Dynamic Head

Conventional impact and static tubes are used for dynamic head measurements. Two, 0.028 inch outside diameter, stainless steel hypodermic tubes are bent to the required shape [see figure (5.4)] and are placed side by side. The impact tube nose is drawn out to an inside diameter of 0.009 inch. The front opening of the static tube is heated, sealed by Plastic deformation and ground hemispherical. Two, 0.004 inch diameter static pressure holes, spaced 90° apart on the circumference, are drilled into the side (bottom and port) of the static pressure tube. The holes are spaced eight diameters downstream from the leading end, according to standard practice. The impact and static tubes are placed inside the 0.23 inch diameter probe holder. Two, Jessall Strip-a-Tube 0.03 inch inside diameter plastic tubes approximately six inches long lead the pressure outputs into a 28 V D.C. Edcliff, 0-0.5 psid differential transducer. Stainless steel tube enlarger transition pieces are used in the connections [see figure (5.5)]. The output from the transducer [T] is carried via approximately 20 ft long shielded cable to an output "terminal box" [B] on the instrument panel [see figure (5.6)]. From here, the output is fed through shielded cables to the \( x \) channel of a Moseley 135-C, Hewlett-Packard, \( x-y \) plotter [D in figure (5.6)]. The gain
is usually adjusted to be 5 mV/inch of displacement.

The pressure transducer is calibrated against a standard inclined tube manometer [figure(5.7)]. Accuracy of the pressure reading is within ± 0.005 inch of water.

5.3.(c) Temperature

Conventional thermocouple probing is employed. OMEGA, CAIN-116E-12, chromel-alumel, stainless steel sheathed (1/16 inch outside diameter) is slightly modified as shown in figure (5.8). The exposed head of the thermocouple junction is broken and approximately 1/4 inch of the sheath is stripped off from the end. To obtain finer spatial resolution and to have good time response, 0.003 inch chromel and alumel bare wires are welded on to the respective leads. A new head is made, using the oxy-acetylene torch flame, with the 0.003 inch wires. The head position is adjusted to be approximately central between the two "prongs" of heavy leads. A length to diameter ratio of approximately twenty is allowed on either side of the head, to minimize axial temperature gradients.

The thermocouple is housed inside the probe holder. The output from the thermocouple is led through a shielded cable (soldered to the thermocouple leads) about 20 ft long, to the X channel of an Autograt (moseley) Model 135 x-y plotter [A in figure 5.6].

Charts (based on standard calibration) which indicate the thermocouple voltage output versus measured temperature are used as Calibration. Accuracy should be within ± 50°F.

5 5.3(d) Gas Sampling

After significant thought and careful consideration of various alternatives, it was decided to employ conventional probe sampling, as
representing the best compromise on reliability and development time. Two probes were specially designed and built. The one used in the experiments reported here, is described below.

Supersonic expansion is employed for rapid freezing of chemical reactions. Water cooling is employed both to reduce the total temperature of sample and to provide a "shield" against surrounding hot gases. As shown in figure (5.9), the probe consists of a 0.028 inch outside diameter, 0.014 inch inside diameter, stainless steel hypodermic tube (A) drawn out to an inside diameter of 0.009 inch at the entrance. One inch downstream of the tip a return circuit water cooling jacket is pressed onto the sampling tube. Water enters through a 0.045 inch outside diameter (0.047 inch inside diameter) stainless steel tube (B), in which is housed the 0.028 inch gas sampling tube (A). The return circuit for water is through an outer tube (C) of 0.095 inch outside diameter (0.077 inch inside diameter) housing the inner tube and the gas tube. Distilled water [contained in 5, in figure (5.2)] pressurized by filtered shop air [through 6, in figure (5.2)] approximately at 100 psig is used for water cooling. The entire sampling probe assembly is placed inside the probe holder. Exit from the sampling tube is led via Jessall Strip-a-Tube plastic tubing (I.D. 0.03 inch) to a three way ASCO, Red Hat, solenoid valve with a selector switch that controls the connexion of the input gas either to a vacuum pump or to a sampling bottle [S in figure (5.5)] evacuated before the start of each run. The vacuum as read on a vertical mercury manometer, was full atmospheric pressure of mercury. The leak rate observed with the bottle stopper closed
was negligible even after two hours. The time lag before pressurizing approximately to atmospheric pressure the evacuated sampling bottle with the gas sample, (after the vacuum pump was disconnected from the sampling bottle), was usually of the order of one minute.

During each run, the probe outlet is connected through the solonoid valve to the vacuum pump. Boundary layer gas at each probe location is thus being continuously drawn through the probe and ejected to atmosphere. When a desired position in the boundary layer is reached during the course of probe traverse, the probe movement is stopped by deenergizing the drive motor and the solonoid valve is energized to connect the probe outlet to the initially evacuated sampling bottle. After the desired time interval of sampling (usually 8 seconds) the solonoid valve is deenergized to close the sampling bottle and to communicate the probe outlet to the vacuum pump again. The remaining boundary layer traverse of the probe is completed for dynamic head and temperature profiles. (The final operation does not apply to wall samples, obviously.)

The quenching requirements of the probe in the low temperature, sub"flame" region are not very demanding. (We carefully note that this is not because of any existence of low temperature reactions in the usually understood way. Developments in chapter III show that the temperature measured by a thermocouple in the hybrid boundary layer is actually a time average of hot and cold eddy temperatures. The hot reacting eddies would be very near theoretical diffusion flame temperature and the quenching requirements for the hot eddies in the sub"flame" region would be just as severe as in the high temperature reaction zone. The advantage we have in the sub"flame" region is that considerable amounts of cold gas also
enters the probe, thus providing a natural scavenging action.

Since the velocity of the gases entering the probe is not equal to the velocity of the boundary layer gases at the same vertical plane, the "stream tube contraction" effect is present. The mass of gas entering the probe was flowing in a stream tube of cross sectional area equal to (area of the probe entrance) x (ratio of the stream tube areas at the two Mach numbers $M_1$ and $M_2$). A simple calculation reveals that the worst case stream tube area in the boundary layer is no more than 30 times the probe area, or the stream tube diameter is approximately 0.05 inch (worst case boundary layer thickness was approximately 1 inch). It is also slightly comforting to note that in a turbulent field, the effects of streamtube expansion are not so pronounced as in a laminar field.

5.3(d) **Supplementary Instrumentation**

Information regarding the overall behavior of each test are mass flow rates, and pressures and temperatures at various locations. The oxidizer mass flow rate is computed by measuring the supply manifold pressure through a CEC 84145, 0-5000 transducer [1 in figure (5.2)], the signal from which is fed through a bridge network [housed in N in figure (5.6)] into a CEC, 5-124 Recording Oscillograph [0 in figure (5.6)].
Fuel feed pressure is measured by a CEC 84145, 0-600 transducer [2 in figure (5.2)] and the output is fed to another channel of the oscillograph. The transducer is mounted just upstream of the fuel valve. Both the transducers are calibrated against a US Gauge Company, 0-3000 psig test gage [G in figure (5.6)] employing nitrogen bottle pressure.

The flow metering of both oxidizer gas and fuel gas is through choked orifices of known area. The oxidizer orifices are orifice plates held between two flanges with "O" rings providing sealing. The fuel orifice is drilled through a 1/4-20, hexagonal headed socket screw, screwed (with teflon tape around it) into the transition piece between the fuel valve and the base plate [figure

There is provision for oxidizer manifold temperature measurement by a Tungsten-Rhenium thermocouple, the output from which can be continuously recorded on the oscillograph. This measurement was not made in the runs reported. The porous plate temperature is measured by a Chromel-Alumel thermocouple [3 in figure (5.2)] the head of which makes contact with the top side of the bottom (wall) plate in the two plate assembly of tunnel wall [see figure (5.10)]. The interpretation of temperature measured is indicated later.

5.4 Raw and Processed Data

The experiments were conducted in the order of increasing complexity. The data are presented in the same order.

The dynamic head, as read on the x-y plotter, is shown in figure (5.11) for two initial runs. Run $^{23}_N$ was a plain isothermal boundary layer, while Run $^{24}_N$ had wall injection of cold nitrogen. Cold runs subsequent to the above, indicated much smoother profiles, as a typical example of which,
Figure (5.12) is presented. Raw data in figure (5.11) is converted to conventional $U/U_e$ versus $Y/Y_0.99$ plot and presented in figure (5.13). In figure (5.14) the same boundary layer profiles are presented on the standard plot of Coles. The skin friction coefficient (needed for the calculation of friction velocity, $U_f$) was determined by the empirical relation, $Y/2 = 0.03 R_n^{-0.12}$. It is found that another rule in the same family of empirical rules predicts the boundary layer thickness with an accuracy of 0.95. For the injection boundary layer, Stevenson's $S$ [defined in figure (5.14)] is used based on standard practice. The ratio of skin friction coefficient with blowing to that without was determined by the empirical relation of Spalding.

The rest of the data presented are of combusting runs. The outputs from the X-Y plotter recording the temperature are given. The displacement on the plotter is converted to temperature through a calibration chart prepared from the table giving the voltage output as a function of thermocouple head temperature above the cold junction for a Chromel-Alumel thermocouple.* The output of the X-Y plotter recording the pressure transducer voltage output is given. The velocity ratios are obtained from the graphs through the following expression.

$$\frac{U}{U_e} = \sqrt{\frac{\text{Chart displacement}}{(\text{Chart displacement})_e} \times \frac{M_e}{M} \times \frac{T}{T_e}}$$

$M$ denotes the mean molecular weight of the gases at any station, and the subscript $e$ stands for boundary layer edge. The above expression assumes linearity of chart displacement with pressure differential across the

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transducer, which is based on the calibration chart [figure (5.26)]. The molecular weight profile across the boundary layer was not measured in the present experiment. The mean molecular weight profile was computed for the experiment of Wooldridge and Muzzy$^{64}$ and was used as an approximate expression in the above equation at each corresponding nondimensional boundary layer location ($Y/\delta$). We recall that Wooldridge and Muzzy$^{64}$ used the same fuel composition as was used in the present experiments. I do not expect an error greater than $\pm 3\%$ in the velocity ratio, because of such an approach. The calculated velocity ratios are plotted on the same graph on which the experimental output was obtained on the X-Y plotter. I have tried to read a mean chart displacement needed for the calculations at discrete points although the data acquisition was continuous. The possible error in final $U/U_e$ resulting from such a procedure is difficult to state precisely. An estimated error bracket is indicated on the plots. The square root of fluctuation amplitudes in the dynamic head profiles, was included in the total-error estimation.

The following table has a summary of figures presented. These were chosen as a good statistical sample from among numerous data.

Figures (5.22) to (5.27) have the data obtained under the most carefully conducted experiments in the present series. A new thermocouple head was made with new wires, its positional stability tested with a high momentum jet of air, the porous plates were mounted with extra care, the bottom wall was rigidly held to give a calculated zero pressure gradient, and even small possible leaks around the periphery of the bottom wall were sealed. The reservoir pressure was adjusted at identical ($\pm 5$ psi) values at the start of each of the first three runs of equal duration. The
fourth run [figures (5.24) and (5.25)] with a slightly smaller reservoir initial pressure had a shorter duration to ensure identical dynamic head conditions during probe traverse. It was checked that the reservoir pressure at the end of the run was identical with those in the previous three runs. The fuel feed pressure was also adjusted at identical values (+ 2 psi) in each run.

The oxidizer mole concentrations indicated on the graphs are the ratios of oxygen peak to the total peak on the chart output from the chromatograph. The runs indicated in figures (5.22) to (5.25) were conducted allowing sufficient time for sample collection to reach nearly atmospheric pressure in the sampling bottle. The sample was injected into the chromatograph using a precision Hamilton hypodermic tube. The background gas in the chromatograph was Helium.

5.5 Interpretation of Experimental Data

5.5.1 Cold Runs

The thickness of the tip of the probe used for dynamic head measurements is comparable to the sublayer thickness in these experiments. Hence, an error of unknown magnitude is present in the dynamic head measurements at distances from the wall comparable to probe tip dimensions. The first two points in figures (5.13) and (5.14), marked with flagged symbols, are ruled out of the discussion.

The mean profiles conform very well to the generally accepted standards of turbulent boundary layers. A noticeable feature of all of the initial low dynamic head runs is the presence of fluctuations with frequencies of the order of ten cycles per second. These fluctuations are negligible in later cold runs [see figure (5.12)].
The interpretation of results is summarized below.

(i) The tunnel design is such that a standard boundary layer established in it.

(ii) The presence of fluctuations in some of the runs is not significant to mean flow characteristics. (Probably such fluctuations exist in many wind tunnels but go unnoticed only because of the method of measuring the dynamic head. A U tube manometer, for example would damp out these fluctuations in the final read out. The time response of instrumentation employed in the present experiments is such that these functions are easily detected.)

(iii) The cause of the fluctuations might very well be of nonfluid dynamical origin. The pressure transducer used in these runs was such that its output rarely exceeded the initial 5% of full scale. At such low loads, the vibrational unsteadiness of the strain gage diaphragm may be appreciable in comparison with its mean displacement.

(iv) Stevenson's method of correlating turbulent boundary layers with wall mass transfer appears satisfactory.

(v) The departures from Cole's plot of turbulent boundary layer characteristics are well within the experimental uncertainties.

(vi) Because of the blowdown operation, the dynamic head decreased continuously during every run. The variation in dynamic head is linear in reservoir pressure. In the present runs the total variations were of the order of 10% of the initial, although the variation during the probe traverse was usually less than 5%.

5.5.2 Combusting Runs

The accent in the following discussion will be on pressure
effects. Other features like differences between cold and combusting boundary layers have been the subject of previous discussions.\textsuperscript{23,64}

It is possible to directly carry over previous discussions on velocity profiles at one atmospheric pressure to the present velocity profiles at high pressures. This follows the observation of close similarity between high and low pressure velocity ratio profiles.

In figure (5.15), the velocity ratio appears similar to those measured by Wooldridge and Muzzy\textsuperscript{64} or Jones et al.\textsuperscript{23} I attribute the more pronounced kink near the high temperature region to an adverse pressure gradient. The bottom wall had been set to give a calculated zero pressure gradient boundary layer. But a later examination revealed a slight downward movement near the downstream end possibly as a result of the detonation, mentioned earlier. Such an adverse pressure gradient would decelerate the hot low density gases much more than the cold low density gases and the velocity profile is understandable. Again, a lack of any sort of reported data on adverse pressure gradient, hybrid boundary layers prevents a more conclusive comparison.

The temperature profile in figure (5.16) has the same qualitative features of those reported in the literature.\textsuperscript{64,23} Even at four times atmospheric pressure there is no evidence of any thinning of the reaction zone, which is just as broad as at atmospheric pressures. This observation, which is common in all of the present high pressure data is a very heartening support to the gas phase theory (chapter III), where it was argued that chemical kinetics in the gas phase could not be a rate limiting factor in hybrid boundary layers.

In the particular experiment reported in figure (5.16), the
peak temperature is seen closer to the wall (≤ 0.2 δ) than in the experiments of Wooldridge and Muzzy⁶⁴ (≥ 0.3 δ). Various factors like the (mentioned) adverse pressure gradient, slight uncertainties in the thermocouple head position, uncertainties in B calculation, can all be brought in to discuss this shift in position of maximum temperature point. However, I feel that the cold wall offers the real explanation. The plate heat up time is such that the equilibrium wall temperature had not been reached in that experimental run. The maximum temperature point in the boundary layer moves gradually outward as the wall heats up, as less of heat transfer is needed to maintain the wall temperature at its equilibrium value. That such is indeed the case can be seen later [figures (5.23) and (5.25)] where two runs were conducted in quick succession, the first one designed to bring the plate to equilibrium temperature, while the important data were taken during the second run.

Figure (5.17) has two dynamic head profiles obtained at a tunnel static pressure of 30 psia, all other conditions being identical with those of the run reported in figures (5.15) and (5.16). The extremely neat profiles are to be observed. Unfortunately, the delicate thermocouple head which had been in continuous use for many (thirty to forty) runs got broken during the first run under the high aerodynamic load, and no temperature profiles accompanied these dynamic head profiles. I have little doubt that very satisfactory boundary layers, with proper temperature profiles, existed in those runs.

The data in figure (5.18) indicate a very nearly zero pressure gradient boundary layer. The velocity profile is very similar to that measured by Jones et al.²³ Based on their results, the broken line
through the computed data points in figure (5.18) seems more reasonable
than the continuous line I drew initially.

The velocity ratio profiles have large uncertainty at positions
closer than \( y/\delta = 15\% \) near the wall. This results from the very low
dynamic head read by the transducer. The fluctuation amplitudes are
comparable to the mean. The sharp peak in the temperature profile
[figure (5.21)] is only indicative of the passage of a hot eddy over the
thermocouple and should not be interpreted to mean any narrowing of reaction
zone. The proper indication of the width of the reaction zone is the
temperature gradient on either side of the broad high temperature region.

Recalling that the data in figure (5.22) to (5.27) are obtained
under carefully controlled conditions, we make the first observation that
are
the temperature profiles almost identical in the runs at 40 and 50 psia.
Any small differences are attributed to experimental scatter. It is also
observed that the mean position of the high temperature zone is approxi-
mately a third of the temperature boundary layer thickness, which is
almost identical with observations of Wooldridge and Muzzy\(^{64}\) at one atmo-
sphere pressure. I interpret these as lending strong support to the earlier
assertion (chapter III) that under identical conditions of mass flow rate
(G) and wall injection rate (B), changes in chamber pressure should have
little effect on the structure of the hybrid boundary layer.

The variations in wall oxidizer concentration are within the sta-
tistical scatter of experimental data. In other words, within the limits
of accuracy of the present method of measurements, the oxidizer concen-
tration does not vary much with pressure variations. Although such an ob-
servation is completely consistent with the present development, the
temptation to make the claim of support from oxidizer measurements is resisted. This is mainly because the accuracy of the measured values has not been firmly established.

The oxidizer concentrations as read on the chromatograph read-out chart are higher than what may be expected based on previous experiments and also on theoretical considerations. The following explanations are offered for this measurement. (ten mole percent oxygen is taken as a typical indicated value.)

1) The chromatograph, with Helium gas as the background, does not sense Hydrogen at all. Hence 35 to 40 mole percent of the injected gas is not registered. (We recall that the wall injectant has 37.5 mole% of Hydrogen.) Thus a correction factor of approximately 0.65 is needed for the oxygen peak in the chromatograph. This brings the value down to

\[ 0.065 \]

(ii) Commercial air has in it 1% Argon which is not distinguished from oxygen in the chromatograph. This correction brings the value down to approximately

\[ 0.055 \]

(iii) The sonic probe used in the present investigation senses a much larger area than its 0.009 inch inside diameter inlet would suggest. At typical velocities of 30 fps near the probe center line, the stream-tube expansion effect (already discussed in section 5.3) gives a maximum diameter of 0.05 inch (five to ten percent of boundary layer thickness). Hence such a drawing of sample from a distance farther out from the wall, effectively indicates the composition not exactly at the wall. Previous
oxygen profile results at one atmosphere \(^6^4\) indicate an increase of oxygen concentration by a factor 1.5 to 2 over the wall concentration at distances of five to ten percent boundary layer thickness from the wall. Hence a factor of 1.5 may be introduced as a correction on the previous figure, leading to approximately \(0.035\).

(iv) The peak temperature in the present experiments were lower (by nearly 300°K) than in the experiments of Wooldridge and Muzzy \(^6^4\). Without a detailed knowledge of the chemical reaction rate and the structure of the boundary layer, it is difficult to get a precise correction factor due to this lower temperature. This is so because the temperature measured in the turbulent field is not the interfacial flame temperature which is of importance in chemical reaction rate calculations. Nevertheless we may expect more oxygen to reach the wall at lower maximum measured temperatures than at higher values.

(v) The reported value of nearly 0.5% oxygen mass fraction at the wall \(^6^4\) was at a wall mass transfer number, \(B\) of 9.3. (We remind ourselves that the \(B\) in the present experiments under discussion is 3.5.) The \(B\) variations are expected to affect momentum and species transport in a similar way, so that the empirical relation, for \(\frac{c_f}{c_{fo}}\) may be used for a crude estimation of the effects of change in \(B\) on wall oxidizer concentration. From figure (1) of reference 36, we note a factor 2.5 in \(c_f/c_{fo}\) if the \(B\) varies from about 9.3 to 3.5. Hence, directly extrapolating from the results of Wooldridge and Muzzy \(^6^4\) we may expect a concentration of approximately 1% oxygen at the wall in the present experiments, if all other variables are held the same.
(vi) Since the flame cannot reach the wall on both sides because of quenching some oxygen was thought to "leak" into the sub"flame" region. However the wall injection outward should impede any such "corner" effects. Besides the ratio of boundary layer thickness to tunnel lateral dimension is approximately the same in the present experiments as in both references 23 and 64. I do not expect the corner effect to be a significant difference in the two cases of atmospheric and superatmospheric pressures.

(vii) If either the relative scale or the intensity of turbulence is higher in the present tunnel, it is possible to anticipate a higher wall oxidizer transport. An important measurement that has not been made in the present tunnel is the turbulence intensity. From the fact that the mean profile looks very familiar, I expect that the turbulence intensity is less than 5%, (which is itself a very high number).
CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

The present work on nonmetallized hybrid combustion leads to the following conclusions.

(1) The problem of linear regression-rate calculation through thermal degradation of a polymeric fuel can be formulated as an eigenvalue problem in a manner that greatly simplifies analysis and numerical computations. For the usual case of a constant activation energy, asymptotic techniques can be used, in the limit of large reduced activation parameters \( \theta_a \equiv \frac{E_{TD}}{RT_w} \), to obtain a closed form analytical expression for the regression-rate eigenvalue that is found to be very accurate in comparison with numerical solutions. Though numbers have been checked with experimental data selecting one polymer (PMMA) for consideration, I have no reasons to doubt the validity of the theory for other polymers as well.

(2) The postulate of a vaporizing fragment size larger than the monomer, and specification of this size through vapor-pressure equilibrium criterion leads to numerical results that correlate well with experimental data in inert atmospheres. The regression rates observed in noninert environments, like hybrid experiments, are too high to be accounted for by thermal degradation alone. Wall-temperature variations with \( \dot{r} \) are different in inert and noninert environments.

(3) The hypothesis of depolymerization at the surface by reactive species (mostly in the role of catalysis) in addition to subsurface thermal degradation, is capable of accounting for the observed pressure sensitive behaviour.
(4) For both polymer degradation and hybrid combustion, all data available are consistent with the present theory.

(5) It is possible to have significant oxidizer concentrations below the classical time-averaged flame sheet, so that reactive species are available for surface attack. Since intimate molecular mixing of fuel and oxidizer is a prerequisite for chemical reactions to occur, the presence of oxidizer below the "flame" is possible even when chemical reaction times are much smaller than transport or mixing times in the "flame". An order of magnitude calculation for this process checks well with experimental data.

(6) It is feasible to make measurements across the simulated hybrid boundary-layer in the combustion tunnel designed and built for that purpose.

(7) There are no significant differences between the atmospheric pressure data and high pressure data in the temperature or velocity ratio profiles in the simulated hybrid boundary-layer. Chemical kinetics in the gas phase are not rate limiting in the hybrid operation at mass flow rates and pressures of interest.

(8) Measured oxidizer concentrations near the wall are sufficient to account for hybrid combustion behaviour in an order-of-magnitude way.

It is recommended that the following investigations be carried out as a continuation of the present work.

(1) The structure of the hybrid turbulent boundary-layer should be obtained theoretically, extending the simple approach outlined in chapter III.
An accurate solution to this problem, based on a physically valid model, will have applications far beyond the domain of rocket combustion.

(2) Surface temperatures and the statistical mean size of vaporizing fragments from a polymer must be accurately determined. The data will be of fundamental interest.

(3) Measurements must be made in the combustion tunnel facility for the remaining regimes of mass flow rates, pressure, wall injection rates and free stream gas composition.

(4) An instrument, optical or otherwise, must be developed for the determination of the molecular oxygen concentration in a gas. The sensor which must have fine spatial resolution must not lose its effectiveness in a high-temperature, reducing environment. The time resolution of the system should be better than a hundred milliseconds. The unavailability of such an instrument was badly felt during the present investigation.
APPENDIX I

DESIGN OF THE COMBUSTION TUNNEL

AI.1 Introduction

All the experimental study reported in this work was carried out in a combustion tunnel designed to give the boundary layer flow in which measurements are made. The primary intent, we recall, is to simulate as closely as practicable, the boundary layer in an actual hybrid rocket motor operating in the pressure-sensitive regime. A general description was given in chapter V [see figures (5.1) and (5.2)]. It was decided early in the program to operate the tunnel on the blowdown principle as this type of operation eliminates an expensive pressure regulator from the system. Since it was projected to use conventional probes with limited space resolution, it was desired to have a boundary layer thick enough to make meaningful measurements. In order to definitely have a boundary layer flow, and not a channel flow, the minimum cross sectional flow dimensions of the tunnel turned out to be large enough to necessitate high total mass flow rates. High mass flow rates of specially ordered compositions of oxidizer gas require that the tunnel operation time be as short as possible for economical reasons. Under these constraints, an unconventional tunnel design emerged through the design procedure.

AI.2 The Tunnel

The tunnel consists of a nominal 2 1/2 inch x 2 1/2 inch flow duct, 28 1/2 inch long. The length was determined by the choice of a suitable Reynolds number to make measurements at. The worst case (G = 0.01
B = 50) zero pressure-gradient boundary layer thickness was calculated
(based on conventional, empirical theory\textsuperscript{52}, with required modifications\textsuperscript{36} for the combusting case) to be one inch.

With reference to figure (5.1), the oxidizer gas is fed through the tunnel inlet and the exhaust gases leave the tunnel through a circular exit section in which there is provision for inserting a bluff body. The transition from the square tunnel to the circular exit section is arranged to be smooth. The purposes of the exit section are, (i) to allow a smooth exit from the boundary layer flow through a slight contraction ratio, (ii) to allow for mixing and burning of any unburnt fuel, and (iii) to provide a site for making gross thermodynamic measurements in the exhaust gases. The exhaust gases leave through a sonic orifice whose area sets the combustion tunnel operation pressure for any given mass flow rate of fuel and oxidizer. The top wall of the tunnel for the initial 2 inch has a leading edge piece and the last 2 1/2 inch has another exit piece, both welded across the side walls. The middle 24 inch of the top wall is of a porous plate through which is injected the fuel gas into the tunnel.* The bottom wall of the tunnel is movable and swings in the vertical plane about a pivot axis perpendicular to the oxidizer flow direction. The angular position of the bottom wall determines the streamwise variations in the cross sectional area of the tunnel. This arrangement is necessary for pressure gradient adjustments. The flow from the fixed inlet bottom wall piece to the movable bottom wall is arranged to be as smooth as possible. The movable bottom wall is pressure sealed along its periphery.

The side walls of the tunnel are made from 1 1/2 inch thick, \textsuperscript{304}

*The injection surface was chosen to be the top wall instead of the bottom wall. This choice was influenced by the reported successful experiments of Wooldridge and Muzzy\textsuperscript{64}.
stainless steel plates, ground flat on the inside. This thickness was chosen in order to minimize fabrication cost, to serve as a good heat sink for combustion runs, because of ruggedness (a detonation can never be ruled out in a N₂–H₂–O₂ gas system), and also to serve as good support for various mountings such as pilot burner, pressure taps etc. Stainless steel was chosen as the material to give long term corrosion-free service. The two side walls are welded to a square flange at the exit. The spacing between the two side walls is 2 1/2 inch throughout the length. The leading edge piece for the first 2 inch of tunnel top wall is welded to across the side walls and to the square flange and similarly the exit piece for the last 2 1/2 inch to the side walls and the rectangular flange. The remaining 24 inch of the tunnel top are left blank and a support step is cut in each side wall to hold the top porous wall.

The detonation pressures and velocities that are of interest are calculated below. The basic assumptions made in the calculations are not repeated here. See, for example, Williams. 63

As a worst case, an accumulation of hydrogen and air, without combustion, is assumed in the tunnel at high mass flow rates. Let us suppose the gases achieve a premixed state. A source of high local enthalpy is made available to this mixture (say, an accidental switching on of the pilot spark plug). It is of interest to know the pressure rise and the velocity of the detonation front. The following numbers are taken as representative.

Static pressure in the tunnel 250 psia
Oxidizer flow rate 1.0 lbm/in² sec
Fuel injection B = 20 (5% by mass, hydrogen)

Initial temperature approximately 1000°K.
The tunnel volume of 187.5 cubic inches holds a mass of 0.0333 lbm of explosive mixture under these conditions.

\[ G = (\rho u) = 144 \text{ lbm/ft}^2\text{sec} \]
\[ \rho = 0.3 \text{ lbm/ft}^3 \]
\[ u = 480 \text{ fps} \]

Heat release capability = 882.5 GHU/lbm of mixture (as a very conservative estimate the higher calorific value of hydrogen air mixture, 64,000 BTU/lbm, is used).

Using the notation in Williams\textsuperscript{63} (p. 26-27)

\[ p = \frac{p_\infty}{p_0} = \frac{p_\infty}{250} \]
\[ \alpha = \frac{q_0}{p_0} = 12.85 \]
\[ \mu = \frac{m^2}{p_0 p_\infty} = \frac{(\rho_0 v_0)^2}{p_0 p_\infty} = 1.92 \]

Final pressure, specific volume, Mach number, temperature, and velocity of detonation are presented in Table A.I.

I recall the occurrence of a detonation under fairly mild conditions (\( G \sim 0.05 \text{ lbm/in}^2\text{sec}, p = 1 \text{ atm}, B = 10 \)). The tunnel has not shown any visible damage.

\section*{AI.3 The Tunnel Inlet}

Oxidizer gas is fed through heavy wall copper pigtailed from ten compressed gas bottles into a high pressure manifold. The outlet of the gas from the manifold is through a pneumatically operated stainless steel ball valve. The gas issuing from the ball valve is metered through a sonic orifice. There is provision for interchanging different size sonic orifices. The supersonically flowing gas now passes through a 9 in long gradually
enlarging section in which the shock strength is determined by the desired operating pressure downstream, as set by the size of the exit orifice at the end of the tunnel. The post-shock subsonic gas is decelerated through a circular cross section, 6 in long, 6.25:1 area ratio diffuser. At the end of this diffuser section is placed a high pressure drop, sintered stainless steel screen, backed by a strong stainless steel perforated plate. Experience demonstrated a necessity for the latter. The oxidizer gas then enters a 12 in long, 2 1/2 in x 2 1/2 in aluminum inlet section in which is placed, approximately midway, a 1 in long, 1/8 in hexagonal honeycomb flow straightener. At the end of this 12 in long inlet section and before the main tunnel are placed two stainless steel screens apart by a 1/8 in thick aluminum spacer. The screens are woven from 0.005 in round wires with approximately fifty wires per inch.

In order to get the desired flow in the tunnel, the details of many of these "upstream" components were optimized based on fairly extensive tests, both cold and combusting. Such of those tests that are thought to be of general interest for experimentalists are briefly described below.

Initial probing (at atmospheric pressures) of tunnel flow revealed a highly distorted profile such as one that may be expected if the flow regime was between boundary layer and channel flow types. The "boundary layer" was obviously much thicker than what was predicted by the standard theory on which the tunnel design was based. It was suspected that initial disturbances may be causing such an artificial thickening. Appreciable wall nonuniformities had resulted across the initial star where the main flange had been welded to the side walls. Smoothing out these irregularities with a ceramic cement resulted in the establishment
of a satisfactory boundary layer profile.

Tunnel runs at high pressures revealed unacceptable fluctuations of such a magnitude that the flow could not be classified as anywhere near steady. Anchoring with a gradually diverging tube the shock in the flow section G which was originally a parallel tube, removed the unsteadiness almost entirely. (Apologies are tendered for the poor workmanship of the diverging tube. But I had to machine it under abnormal circumstances. Besides, it has been discovered since that the rough internal surface is better for our purposes than a very well machined smooth internal surface. The boundary layer is turbulent over the rough surface and resists shock induced separation much better than the laminar boundary layer in a smooth tube!)

The small fluctuation that remained in the dynamic head profile at this stage were almost completely eliminated by shifting to upstream of the honeycomb, the high pressure drop sintered stainless steel porous plate (I), which was originally downstream of the honeycomb.*

AI.4 The Porous Plates

The porous plates through which the fuel gas is injected into the tunnel constitute an important part of the experimental set up. They are intended to provide an uniform injection over a 24 inch streamwise length of the boundary layer flow. The plates are of woven stainless steel plates sintered together. They were supplied by Aircraft Porous Media Inc., Long Island, N.Y. The surface of the boundary layer wall porous plate has a roughness height of less than 6μ. This smoothness was selected to keep the roughness height appreciably smaller than the thickness of the

* I am grateful to Professor Eugene Covert for suggesting this change.
sublayer (when it exists) on the wall.

An important time constant in the system operation is the equilibrium heat up time of the porous plate. To keep this time a minimum, it was necessary to select for the wall, as thin a plate as practicable. The thinness is limited by structural rigidity of the plate itself. However, to ensure uniform distribution of the injectant, and to eliminate pressure "feed back" effects due to possible fluctuations in the tunnel, a high pressure drop through the porous plate injector is desirable. High pressure drop means a thick plate. In order to meet the conflicting requirements of heat transfer and pressure drop, the plate was ordered as two laminae, together giving across them the total desired pressure drop. Spaced apart for thermal insulation, the plates are mounted such that the thinner plate with the smaller heat up time forms the boundary layer wall. The plates are assembled in two symmetrical stiffeners, each consisting of three separate pieces of metal strips held together with screws. Here, a reference to figure (A1.1) may be helpful in visualizing the set up.

The front end of the bottom porous plate has silver-soldered to it a bracket, figure (5.10), to prevent leak of fuel gas through this end and to provide structural support. At the rear end, leak is prevented through the mounting arrangement as shown in figure (5.10). When mounted in the tunnel, the porous plate assembly is sealed in with silicone rubber, to take care of the possible small leaks around the stiffeners, front and rear end.

Plate heat up times are calculated below. Boundary layer flow is established on the porous plate. At time \( t = 0 \), the flow of gases through the porous plate is started from the system at ambient temperature \( T_{\text{amb}} \). The combustion zone is established under the plate in a time short compared
to heat up time. Heat transfer from the reaction zone to the plate and to the incoming injectant, raises their temperature. Equilibrium is finally established. We are interested in knowing how long it would take to reach this equilibrium at various injection and mass flow rates.

While it would seem probable that a solution to this problem is available in the literature, I felt it would be quicker if I solved the problem here, instead of embarking on an exploration of possible books and journals.

The following assumptions are made in the analysis:

(i) Radiation is negligible (a conservative assumption);

(ii) Every point in the plate is at the same temperature at any instant of time (thin plate);

(iii) Reaction zone temperature, ambient temperature, wall injection rate, free stream flow rate are constant during the nonsteady heat up;

(iv) Changes in Stanton number during heat up are negligible.

Energy conservation:

Heat transfer rate towards the wall from the main flow = Heat input rate to the injectant + Heat input rate to the plate

\[ C_H c_{p_{ox}} G(T_b - T_w(t)) = \dot{m}'' c_w T_w(t) - T_a + c_{p} \rho_s s_l L_s \frac{dT_w}{dt} \]

(AI.4.1)

(AI.4.2)

In the above equation,

- \( C_H \) stands for Stanton number
- \( ox \) - oxidizer
- \( b \) - flame zone
- \( w \) - wall
\( f \) - fuel

\( ss \) - stainless steel plate

\( L \) - thickness of the plate

Defining, \( \Theta \equiv \frac{T_w - T_{w,ini}}{T_{eqb} - T_{w,ini}} \)  

we get

\[
\frac{C_H p_{ox} G T_b + \hat{m}_w' c_p T_a - T_{w,ini} \{C_H p_{ox} G + \hat{m}_w' c_p \}}{(T_{w,eqb} - T_{w,ini}) c_p \rho \ L \ ss \ ss} = \frac{C_H p_{ox} G + \hat{m}_w' c_p \ p_f}{c_p \rho \ L \ ss \ ss} \ \Theta + \frac{d\Theta}{dt}
\]  

(AI.4.4)

or  \[ A = B\Theta + \dot{\Theta} \]  

(AI.4.5)

The constants \( A \) and \( B \) represent quantities that are evident on comparing equations (AI4.4) and (AI4.5). Equation (AI4.5) has the solution,

\[ \Theta = \frac{A}{B} (1 - e^{-Bt}) \]  

(AI.4.6)

The time to reach 0.95 of the equilibrium wall temperature difference (i.e., \( \Theta = 0.95 \)) can be computed through equation (AI.4.6).

Figure (AI.2) was prepared using the following values for the constants,

\[ c_p^{ss} = 0.1 \ \text{BTU/lbm}^\circ\text{F} \]

\[ \rho^{ss} = 6 \times 62.4 \ \text{lbm}/\text{ft}^3 \]
L_{ss} = 0.00275 \text{ ft}

\begin{align*}
\frac{c_{p_{\text{ox}}}}{c_{p_{\text{fuel}}}} &= 0.25 \text{ BTU/lbm}^\circ\text{F} \\
C_{H_0} (\text{Stanton number with no blowing}) &= 0.03 R_x^{-0.2}
\end{align*}

$$
\frac{C_H}{C_{H_0}} = \frac{\ln(1 + B)}{B} \quad \text{for } B < 5
$$

$$
1.2 B^{-0.77} \quad \text{for } 5 < B < 95
$$

$$
\mu = 3 \times 10^{-5} \text{ lbm/ft sec}
$$
AII.1 Introduction

Consistent with the present philosophy of minimizing the total run duration of each test, all the individual components were designed/selected to have the minimum response time practicable. Within this limitation, the requirements of pressure and flow rate imposed on the fuel supply valve (whose function it is to interchange between purge and fuel, the gas fed through the porous plates into the tunnel) were too severe to be met by valves commercially available readily. The valve was specially invented, designed and built and is described below.

AII.2 Construction and Operation

As shown in figure (AII.1) the valve consists essentially of a housing (A), a moving element (B) capable of spinning inside the housing (A), a link (C) actuating the spin of (B), and the top cover (D) which receives the fuel and purge feed lines. The moving element (B), which is a circular cylinder, has a circular hole drilled in it, oblique with its axis, in such a way that the axis of the hole intersects the axis of the cylinder at the bottom face. The axis of the hole passes through the top surface of the cylinder at a radius of 1/2 in, which is also the radius of the circle on the circumference of which the fuel and purge lines (spaced 120° apart) feed through the top cover (D). Depending on the angular position of (B), the oblique hole in it can thus,

a) connect the purge feed to the outlet hole in the bottom of housing (A),
b) connect the fuel feed to the outlet hole in the bottom of housing (A), or

c) block both the purge and the fuel feed simultaneously.

There is little possibility of both fuel and purge gas being simultaneously fed through the valve assembly.

The actuation of the spin of cylinder (B) is, at present, through a two way pneumatic cylinder/piston arrangement [A in figure (5.2)]. The linear motion of the piston is transmitted as rotation to the link (C), through a conventional connecting rod, crank mechanism. With its present actuator, the valve is able to operate in only two stationary position, which are arranged to be purge gas flow and fuel flow positions.

The actuator and valve assembly (with one half of a tap!) are mounted on a base plate, with the transition piece (E) serving as the structural support. The plate is rigidly attached to the top of the tunnel through four of the twenty-six bolts that assemble the tunnel with top lids.

An operational problem that arose frequently during initial stages was that the "O" rings got sheared off easily and the broken bits obstructed the fuel flow orifice. Change of the "O" ring material from silicone rubber to neoprene seems to have solved this problem effectively. It also helped to chamfer the edge of the oblique hole in cylinder (B) to prevent the edge acting like a knife on the "O" rings.
APPENDIX III

PILOT IGNITOR

A dependable ignition source is needed to ensure satisfactory operation of the combustion tunnel. A hot gas pilot ignitor was designed and built to meet the requirements. It operates on the "stirred reactor" principle and runs on commercial grade methane and 40 percent oxygen enriched air.

As shown in figure (AIII.1) it consists of the copper combustion chamber (A), the stainless steel injector head (B) and the graphite exit nozzle (C). Two equal-momentum jets of oxidizer (D1 and D2), fed through sonic metering orifices in the injector head, impinge at an included angle of 120° inside the combustion chamber (A). The fuel jet, issuing from another metering orifice (E) in the injection head intersects the oxidizer impingement point symmetrically. A commercial, Champion sparkplug (F) ensures ignition of this mixture. The hot combustion gases are injected through a side wall, into the main tunnel in such a way that the axis of the jet of hot pilot gases lying in a plane perpendicular to the main flow direction in the tunnel, intersects the top surface of the tunnel on the centerline, [see figure (AIII.2)].

Even after numerous firing cycles, no problems have been found with the pilot operation.
Appendix IV

Traverse Mechanism

Probing of the boundary layer for various quantities of interest, within a short duration of time, requires a rapid traverse mechanism. An existing, hand-operated screw—"nut" mechanism was modified to meet requirements [figure (AIV.1)].

A 9000 rpm, 28 V.D.C., reversible AIRESearch motor (A) is mounted on an extension bracket and drives a 7 tooth pinion which meshes with and drives an 80 tooth gear (B) keyed to the main screw shaft (C) of the traverse mechanism. A 1000 Ω, ten turn Borg (lin.tol. 0.1 percent) potentiometer (D) mounted on another extension is driven by a rubber band through a 1:5 reduction ratio, direct pulley (E) arrangement from the screw shaft. The entire assembly is rigidly screwed to the movable bottom wall of the tunnel with a one inch aluminum spacer (F) between them. The potentiometer is used for probe position determination. The carriage (G) that rides on the screw carries a nylon bushing clamp holding the probe stem (H). The probe stem passes into the tunnel through a special nylon fitting attached to the bottom wall [see figure AIV.2)]. The motor receives its power through a SPDT relay energized by six 6V batteries in series. The relay contacts are so wired that when the probe tip touches the top wall, the power input to the motor driving the probe upward, is disconnected. From this position, the motor can drive the probe only downward. (Essentially a "limit switch" arrangement.)

Because of the mounting arrangement of the traverse mechanism, the probe stem is perpendicular to the bottom wall and depending on the bottom
wall setting for pressure gradient adjustments, makes with the vertical to the top wall, an angle equal to the angle of the bottom wall with the horizontal. The worst case streamwise shift thus introduced in the probe tip position as it travels from the top wall to the edge of the boundary layer is, however, 0.042 in which is considered negligible in view of the mild streamwise variations in turbulent boundary layer properties.
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Details above this plane not considered in section (a)

Vapor
Solid
FSV
Wall

Kinetic bond breaking of polymer

Conduction Heat Transfer into the solid

Bulk movement of the solid at a steady rate, i (the eigenvalue) to keep the wall stationary

Temperature
Mean fragment size

Fig. 1.1
Laminar situation, before transport

Laminar situation, after transport

Turbulent situation, before transport

Turbulent situation, after transport

Fig. 1.2
Fig. 2.3. Temperature profile in the solid polymer with phase changes.

Fig. 2.4. p profile versus nondimensional T.
Fig. 2.5. NONDIMENSIONAL REGRESSION RATE FOR ANY POLYMER WITH A CONSTANT ACTIVATION ENERGY
Fig. 2.6. NUMERICAL INTEGRATION OF EQUATIONS (PMMA)
FIG. 3.1. HYBRID BOUNDARY-LAYER MODEL
Fig. 4.2. PMMA THERMAL DEGRADATION
MOLECULAR WEIGHT

Fig. 4.3. VAPOR PRESSURE OF HYDROCARBONS
Fig. 4.4. PMMA REGRESSION RATE IN NONINERT ENVIRONMENTS
Figure 4.4A. REGENERATION RATE VERSUS MASS-FLOW RATE OF OXIDIZER, AND PMMA REGENERATION RATES IN NON-INERT ENVIRONMENTS.
Fig. 4.5. A POSSIBLE EXPLANATION OF THE LIQUID LAYER.
Fig. 4.5a MELTING POINT OF HYDROCARBONS
Fig. 4.6. LIQUID LAYER COMPUTATIONS
Fig. 4.7 THICKNESS OF THE LIQUID LAYER

PMMA

THICKNESS OF LIQUID LAYER, cm.

WALL TEMPERATURE, °K

i = 0.04 cm/sec.
Fig. 5.1 SCHEMATIC VIEW OF TUNNEL
Fig. 5.3 EXPERIMENTAL MEASUREMENTS
Fig. 5.4. PROBES USED FOR BOUNDARY-LAYER TRAVERSE: 1. Pitot-Static probe, 2. Impact tube
3. Convergent-Divergent sampling probe

(continued on next page)
Fig. 5.4. PROBES USED FOR BOUNDARY-LAYER TRAVERSE:
(continued)

2, IMPACT TUBE; 3, CONVERGENT-DIVERGENT SAMPLING
PROBE (not used in the experiments reported)
4, MULTIHEADED PROBE, a. Impact tube, b. static tube,
c. thermocouple, d. supersonic expansion sampling tube.
Fig. 5.5. Output of Traversing Probe showing tubing details of tubing; T-Pressure Transducer S-Sampling Bottle
Fig. 5.9. Gas Sampling Probe.
Fig. 5.11 INITIAL COLD RUNS; DYNAMIC HEAD.
Fig. 5.12. DYNAMIC HEAD PROFILES IN COLD RUNS
\[ \frac{U}{U_e} \]

- Cold Boundary-Layer Profiles

Fig. 5.13

- Run 23/N; \( R_x = 7.15 \times 10^5 \); No injection

- Run 24/N; \( R_x = 6.88 \times 10^5 \); Cold \( N_2 \) inj. \( B = 3.5 \)
\[ S = \frac{2u_\tau}{U} \left[ \left( 1 - \frac{u_w}{u_\tau} \right)^{1/2} + \frac{u_w}{u_\tau} \right]^{1/2} \]

Fig. 5.14

\[ R_x = 7.15 \times 10^5; \text{No injection} \]

\[ R_x = 6.88 \times 10^5; \text{Cold N}_2 \text{ inj.} \]

\[ B = 3.5 \]
Oxidizer concentration at 0.014" from wall

10.25 mole percent

Nominal $G = 0.06 \text{ lbm/sq.in.sec.}$

Nominal $p = 60 \text{ psia}$

Nominal $E = 6.0$

$U/U_e$

Fig. 5.15 MEASURED DYNAMIC HEAD AND PROCESSED VELOCITY RATIO
Measured oxidizer concentration at 0.014" from wall: 12.5 mole percent

Nominal P = 40 psia
Nominal B = 6
Nominal C = 0.04 lbm/sq.in. sec.

FIG 5.18 MEASURED DYNAMIC HEAD AND PROCESSED VELOCITY RATIO
Fig. 5.19 TEMPERATURE RATIO

Nominal $G = 0.04$ lbm/sq.in.sec.
Nominal $p = 40$ psia.
Nominal $B = 5$
Measured oxidizer concentration at 0.014" from wall: 10.19 mole percent

Nominal $G = 0.06 \text{ lb/m}^2\text{in.}\text{sec.}$
Nominal $p = 60 \text{ psia}$
Nominal $B = 5$

Fig 5.20 MEASURED DYNAMIC HEAD AND PROCESSED VELOCITY RATIO
Measured oxidizer concentration at 0.014" from wall: 8.52 mole percent

Nominal $G = 0.06 \text{ lbm/sq in. sec.}$
Nominal $p = 50 \text{ psia}$
Nominal $B = 3.5$

Fig. 5.22 Measured Dynamic Head and Processed Velocity Ratio
Temperature, °K/k00

Nominal \( G = 0.06 \) lbm/sq.in.sec.
Nominal \( p = 50 \) psia
Nominal \( B = 3.5 \)

Fig. 5.23 TEMPERATURE RATIO
Measured oxidizer concentration at 0.014" from wall: 9.7 mole percent

Nominal $G = 0.06 \text{ lbm/sq.in.sec.}$
Nominal $p = 40 \text{ psia}$
Nominal $B = 3.5$

Fig. 5.24 MEASURED DYNAMIC HEAD AND PROCESSED VELOCITY RATIO PROFILE
Fig. 5.25 TEMPERATURE PROFILE

Temperature, °K/100

Nominal Q = 0.06 lbm/sq.in./sec.
Nominal p = 40 psia
Nominal k = 3.5
Fig. 5.26. PRESSURE TRANSUDER (EDCLIFF) CALIBRATION
Nominal $G = 0.06 \text{ lbm/sq.in.sec.}$

Nominal $p = 50 \text{ psia}$

Nominal $E = 3.5$

(Before equilibration of wall temperature)

Fig. 5.27 TEMPERATURE PROFILE (Auxiliary data)
Nominal $G = 0.06$ lbm/sq.in.sec
Nominal $p = 40$ psia
Nominal $B = 3.5$

(Before equilibration of plate temperature)

Fig.5.28 TEMPERATURE RATIO (Auxiliary data)
Fig.5.29. TYPICAL GAS CHROMATOGRAPH READOUT OF PROBE SAMPLE.
Fig. 5.30. TYPICAL RECORD OF A COMBUSTION RUN (Chart readout)
Fig. AI.1 TUNNEL TEST SECTION (1:1)
Fig. A1.2 EQUILIBRIUM WALL TEMPERATURES IN THE SIMULATED HYBRID BOUNDARY-LAYER. ($c_p$ of injectant gas, 0.23 CHU/lbm.$^\circ$C)

(fig. cont. on next page)
Fig.AI.2 continued from previous page
also continued on next page
Fig. AI.2 Continued from previous two pages. Concluded here.
Fig.A.2.1 THE FUEL VALVE
Fig. A.2.2. THE FUEL VALVE DISASSEMBLED.
Fig.A.3.2. THE PILOT IGNITOR IN OPERATION IN THE TUNNEL
(Not during a regular run!)
Table I

Comparison of analytical solutions with numerical solutions (General polymer with a constant activation energy, \( E_{TD} = 32 \) kcal/mole, \( D = 280 \) cal/gm, \( c = 0.35 \) cal/gm°K)

<table>
<thead>
<tr>
<th>FSV</th>
<th>( T_w (°K) )</th>
<th>( \chi = \frac{\lambda}{\text{eq.2.24}} / \varepsilon )</th>
<th>( \chi_{\text{numerical}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>600</td>
<td>1.014</td>
<td>1.015</td>
</tr>
<tr>
<td>15</td>
<td>800</td>
<td>0.949</td>
<td>0.945</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
<td>16.25</td>
<td>16.598</td>
</tr>
<tr>
<td>2</td>
<td>800</td>
<td>12.65</td>
<td>13.075</td>
</tr>
<tr>
<td>Figure Number</td>
<td>Description of Figure</td>
<td>Nominal Oxidizer Mass Flow Rate, G (lbm/in²/sec)</td>
<td>Nominal Tunnel Static Pressure (psia)</td>
</tr>
<tr>
<td>---------------</td>
<td>--------------------------------------------------------------------------------------</td>
<td>-----------------------------------------------</td>
<td>-------------------------------------</td>
</tr>
<tr>
<td>5.15</td>
<td>Dynamic head output recorded and velocity ratio profile</td>
<td>0.06</td>
<td>60</td>
</tr>
<tr>
<td>5.16</td>
<td>Thermocouple output recorded and temperature profile</td>
<td>0.06</td>
<td>60</td>
</tr>
<tr>
<td>5.17</td>
<td>Dynamic head output recorded</td>
<td>0.06</td>
<td>30</td>
</tr>
<tr>
<td>5.18</td>
<td>Dynamic head output recorded and velocity ratio profile</td>
<td>0.04</td>
<td>40</td>
</tr>
<tr>
<td>5.19</td>
<td>Thermocouple output recorded and temperature profile</td>
<td>0.04</td>
<td>40</td>
</tr>
<tr>
<td>5.20</td>
<td>Dynamic head output recorded and velocity ratio profile</td>
<td>0.06</td>
<td>60</td>
</tr>
<tr>
<td>5.21</td>
<td>Thermocouple output recorded and temperature profile</td>
<td>0.06</td>
<td>60</td>
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<td>5.22</td>
<td>Dynamic head output recorded and velocity ratio profile</td>
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<td>50</td>
</tr>
<tr>
<td>5.23</td>
<td>Thermocouple output recorded and temperature profile</td>
<td>0.06</td>
<td>50</td>
</tr>
<tr>
<td>5.24</td>
<td>Dynamic head output recorded and velocity ratio profile</td>
<td>0.06</td>
<td>40</td>
</tr>
<tr>
<td>5.25</td>
<td>Thermocouple output recorded and temperature profile</td>
<td>0.06</td>
<td>40</td>
</tr>
</tbody>
</table>

**TABLE II**

...
### TABLE A.1
DETONATION CALCULATIONS

<table>
<thead>
<tr>
<th>Final Quantities (after a detonation)</th>
<th>Specific Heat Ratio $\gamma$ of Gases</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td>$p = 1 + a (\gamma - 1) [1 + \left(1 + \frac{2\gamma}{a(\gamma^2 - 1)}\right)^{1/2}]$</td>
<td>6.6</td>
</tr>
<tr>
<td>(Pressure = 1650 psi)</td>
<td>(2306.25 psi)</td>
</tr>
<tr>
<td>$\frac{1}{\rho} = 1 + a \left(\frac{\gamma - 1}{\gamma}\right) [1 + \left(1 + \frac{2\gamma}{a(\gamma^2 - 1)}\right)^{1/2}]$</td>
<td>0.5869</td>
</tr>
<tr>
<td>(Density = 0.5111 lbm/ft$^3$)</td>
<td>(0.5045 lbm/ft$^3$)</td>
</tr>
<tr>
<td>$M_o^+ = \left[1 + \frac{a(\gamma^2 - 1)}{2\gamma}\right]^{1/2} + \left[\frac{a(\gamma^2 - 1)}{2\gamma}\right]^{1/2}$</td>
<td>3.1564</td>
</tr>
<tr>
<td>$T_o = \frac{p}{\rho R}$</td>
<td></td>
</tr>
<tr>
<td>$V_{detonation} = M_o^+ \left[\sqrt{\gamma RT_o}\right]$</td>
<td>13337.4 fps</td>
</tr>
</tbody>
</table>
The author was born on the twelfth day of November, 1945 in Bangalore, India. After Higher Secondary and Pre-University education at the National Educational Society, he entered in 1961, the five-year Bachelor's programme at the University College of Engineering, then a part of The University of Mysore (now with the newly formed Bangalore University). He received the Bachelor of Engineering degree in Mechanical Engineering at the graduation exercises held in January 1967, where he was awarded Dr. Sir M. Visvesvaraya Centenary Commemoration Celebration Prize for securing the first place in his graduating class. In August 1966, he entered the two-year Master's programme at the Aeronautical Engineering Department, Indian Institute of Science. During the academic year 1967-68 the National Aeronautical Laboratory awarded him a Council of Scientific and Industrial Research fellowship. He received the Master of Engineering degree in the branch of Aerodynamics. In the fall of 1968, he entered M.I.T. department of Aeronautics and Astronautics on a DuPont memorial fellowship.

His principal research interests are in the fields of classical fluid mechanics, combustion and propulsion.

He is a member of The Combustion Institute.