NITROGEN OXIDE FORMATION IN LAMINAR
METHANE-AIR DIFFUSION FLAMES

by

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Abstract

The purpose of the investigation was to characterize diffusion flame structure and to determine the distribution and predominant mechanism of nitrogen oxide formation in such flames. To this end, a laminar methane-air diffusion flame has been extensively probed for its concentration and temperature profiles. The information obtained has been used to validate a theoretical model of diffusion flames capable of predicting flame characteristics and useful in analyzing pollutant formation and abatement strategies.

The theoretical model developed utilizes the Burke-Schumann flame sheet concept to locate the fuel-oxygen interface and hence, the points of heat release. The model eliminates the restrictions of the classical Burke-Schumann model in that allowances are made for natural convection effects and variable thermodynamic and transport properties. The experimentally determined and predicted thermal fields are in close agreement and evidence is provided which suggests that the predicted aerodynamic field is also valid. Analysis of the experimentally determined nitrogen oxide profiles indicate, however, that before the model can be used to adequately predict nitrogen oxide formation rates and aid in NOx abatement studies, allowance must be made for chemical reaction in the post flame region. Most of the oxides of nitrogen were found to be formed in the thin blue reaction zone just outside the luminous flame surface where free radical concentrations an order of magnitude higher than equilibrium exist. Without allowing for the reactions associated with the H2-O2 system and the carbon monoxide burnout reaction, the super-equilibrium radical concentrations can not be adequately predicted.

It was found that most of the NOx inside the luminous core was generated in the reaction zone and penetrated the flame surface principally by diffusion. Small amounts of NOx are generated inside the flame surface near the flame base and NOx is capable of being converted to nitrogen or other nitrogen containing species within the luminous core. The Zeldovich reactions were identified as constituting the predominant mechanism of NO formation in the post flame region.
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Professor of Chemical Engineering

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I cannot find the proper words to express how I really feel about the contributions of my wife, Kristin, who helped prepare some of the figures
and provided support throughout my years at MIT. The simple, but meaningful word "thanks" and the dedication of this entire work to her, must suffice.

Lovingly,

Reggie
To Kristin

...143...
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SUMMARY

INTRODUCTION

With current emphasis on environmental problems, some questions have been raised concerning the levels of nitrogen oxide emissions from both stationary and non-stationary combustion sources. Investigations have provided considerable insight into the dependency of nitrogen oxide emissions on such factors as furnace and burner design, equivalence ratio, firing intensity, and fuel and air preheat. The emphasis of these investigations has been confined largely to premixed systems. Conclusions drawn from fundamental premixed flames studies include the following:

(1) The Zeldovich mechanism, \( N_2 + O \rightarrow NO + N \), is the predominant mechanism of nitric oxide formation in the post-flame regime.

(2) In the early post-oxidation zone, oxygen radical concentrations which exceed their equilibrium concentrations by two-to-three orders of magnitude exist, but equilibrium values are approached as the distance from the flame front is increased.

(3) In the fuel-rich regime, it is possible to form fuel-nitrogen compounds via reactions such as \( CH + N_2 \rightarrow HCN + N \) which subsequently burn to produce nitrogen oxides.

Studies on diffusion flames, the flames characteristic of many practical combustion systems, are limited. Comparatively little is known about the mechanisms of nitrogen oxide formation in such flames. Investigators have speculated that since hydrocarbons coexist with nitrogen at high temperatures, \( NO_x \) formation via \( CN \) or \( HN \) intermediates may be important, and it has been suggested that in diffusion flames, sufficient time is available for radical
recombination reactions to equilibrate. From a modelling standpoint, whether or not superequilibrium radical concentrations exists must be determined, and establishing optimum control strategies requires that the predominant mechanism of NO formation be identified.

The objective of this study was therefore to investigate NO formation in laminar diffusion flames. Conclusions derived from studies of laminar diffusion flames are not only pertinent to combustion systems which exhibit such flames, but are also important in the characterization of processes occurring in turbulent flames which can be modelled by wrinkled laminar flame surfaces or burning eddies with laminar boundaries.

Previous studies of laminar flames have usually neglected the effects of buoyancy and temperature dependent transport coefficients. In addition, in view of the enormous number of primary reactions involved in the combustion process, uncertainty exists on what represents an adequate approximation of the combustion reactions. Complementary theoretical and experimental studies were used to determine the adequacy of simplified models in predicting flame heights, temperature distributions and concentrations of stable species. The experimental study identified the fundamental characteristics of diffusion flame structure and provided data to validate the theoretical model developed. The experimental procedure and results are briefly discussed in the following sections.

EXPERIMENTAL APPARATUS AND ANALYTICAL PROCEDURE

A vertical, cylindrical diffusion flame burner was designed to produce a steady, enclosed, atmospheric laminar diffusion flame. The burner consists of two concentric tubes of radii 0.635 and 2.54 cm connected to a perforated
solid brass disc 7.62 cm in diameter and 1.27 cm thick. This brass disc served as the burner plate. Fuel flows through the inner tube and air flows through the outer tube. This type of burner assembly resulted in parallel flow at the burner outlet and the high thermal conductivity of brass assured a flat outlet temperature. A pyrex glass cylinder rests on top of the burner plate. This cylinder served to shield the flame and to define the boundaries of the combustion system.

The burner was mounted on a x-y positioner so that discrete movement of the burner in the x-y plane was possible. Mounted above the burner on a x-z positioner was a quartz microprobe. Any portion of the flame or its surroundings bounded by the pyrex shield could be sampled by properly adjusting the positioners. The sample probe was designed so as to minimize the disturbance of the flame in the sampling process. The probe permitted sampling without any visual flame disturbance upstream of the probe location. Temperature measurements were made using three mil platinum vs. platinum – 13% – rhodium thermocouples. Radiation and conduction corrections were made to the thermocouple bead temperature to determine the unperturbed, local gas temperature at the bead location.

Methane and compressed air issued from their respective cylinders and were directed to the burner system. Critical orifices controlled the flow rates of these gases to the burner; reproducibility in flow was better than four percent. Upon ignition a cylindrical methane-air diffusion flame of definite shape resulted. After placing the pyrex shield into position, the quartz microprobe was moved to the desired sampling location. A vacuum pump was used to draw samples from the flame and pull them through the analytical equipment. The pressure inside the probe was maintained at one-half atmosphere. This assured critical flow across the 80μ probe tip (and hence,
a constant sampling rate), and aided in quenching reactions occurring in the
flame. The time the gases spent in the hot portion of the probe was calcu-
lated to be less than 0.2 msec.

Two Fisher-Hamilton gas partitioners were used to analyze for CO\textsubscript{2}, Ar
plus O\textsubscript{2}, N\textsubscript{2}, CH\textsubscript{4}, CO and H\textsubscript{2} content. Water analyses were made by deter-
mining the dew-point of the sample gas and nitrogen oxide analyses were made
using the modified Saltzman procedure (31)(67).

STABLE SPECIES CONCENTRATIONS AND TEMPERATURE

Figures 12, 13 and 14 show the concentration and temperature profiles
at three heights above the burner plate established in a methane-air diffusion
flame. The fuel was supplied at 5.7 cc/sec and the air at 187.7 cc/sec.
The luminous edge of the resultant flame closed at the burner axis 5.8 cm
above the burner plate. At each location three samples were taken. Where
one data point is shown the analysis of the three samples agreed to within
2% and the average value is shown.

Figure 12a shows the radial concentration profiles 1.2 cm above the burner
plate (about one-fifth the flame length). Methane is seen to diffuse to the
primary reaction zone, just outside the luminous flame edge, where it is
completely consumed. A stoichiometric amount of oxygen also diffuses to the
reaction zone; the oxygen concentration decreases from its inlet value as the
flame surface is approached, drops nearly to zero in the reaction zone, then
increases slightly as the symmetric axis is approached. The oxygen concen-
tration at the symmetric axis decreases as the height above the burner plate
is increased. This type of oxygen profile results because near the flame
base, the temperatures are low enough to allow some oxygen to penetrate the
Figure 12a Radial Concentration Profile, \( z = 1.2 \text{ cm} \)

Figure 12b Radial Temperature Profile, \( z = 1.2 \text{ cm} \)
flame surface. At greater distances above the burner plate, the temperatures in the reaction zone are high enough so that the oxygen is completely consumed before it can penetrate the flame surface. A concentration gradient in oxygen is thus established inside the luminous core.

Water and carbon dioxide concentration profiles maximize inside the thin blue reaction zone where the temperature profile also maximizes. In the lower regions of the flame the carbon monoxide and hydrogen profiles first increase with distance from the symmetric axis, maximize inside the luminous core, then decrease to zero in the reaction zone. Higher in the flame (Figure 13) the CO and H₂ profiles are essentially flat inside the luminous flame surface and fall to zero in the reaction zone. Near the tip of the flame (Figure 14), the methane is all consumed and the flame is supported by the burnout of H₂ and CO, and by the combustion of carbon particles and other pyrolysis products formed in the lower regions of the flame.

The temperature profiles indicate that the temperature in the reaction zone increases, as the height above the burner plate is increased, until the adiabatic flame temperature is approached, then slightly decreases until the flame tip is reached. This is due to the higher radiative and conductive heat losses to the burner plate in the lower regions of the flame and to the decrease in the burning velocity near the flame tip.

Analysis of the concentration profiles leads to the approximation that complete combustion of the methane takes place at two distinct surfaces which bound the reaction zone. The fuel-rich side of the reaction zone is bounded by the luminous flame surface. Here, methane is rapidly converted to CO, CO₂, H₂ and H₂O. The oxygen-rich side of the reaction zone is bounded by an imaginary surface through which an amount of oxygen, in stoichiometric
proportions to the methane fired, diffuses. The distance between these surfaces, $\delta$, is determined primarily by the burnout of CO to CO$_2$. Changes in gas composition outside these surfaces are principally due to the inter-diffusion of reactants and products. Thus, an adequate model of diffusion flames is one where diffusion is the predominant mechanism of material transport to and away from a narrow annular region of thickness $\delta$ where chemical reaction is rapid. The system considered by Burke and Schumann (15) represents such a system. Fuel and oxygen diffuse to an infinitely thin reaction zone ($\delta = 0$) in the proper proportions for reaction and products diffuse away. The model developed utilizes this flame sheet concept to locate either the luminous flame surface or the surface through which a stoichiometric amount of oxygen diffuses. It eliminates the restrictions of the classical Burke-Schumann model in that allowances are made for natural convection effects and variable thermodynamic and transport properties. The model is discussed in the following sections. The above temperature and concentration profiles serve to validate the model.

DESCRIPTION OF THE THEORETICAL MODEL

The model is concerned with an ideal mixture of fuel, air, and their combustion products. The combustion system closely parallels the experimental system in that fuel and air issue through two concentric tubes of radii $L$ and $R$. When the two gases make contact at the tube outlets, a diffusion flame of definite shape results. As in the experimental set-up, the combustion system is shielded. This allows appropriate conditions along the boundaries to be specified and defines the region of interest.

The steady-state forms of the conservation equations which describe the
axi-symmetric system under consideration are presented below:

Continuity equation:

\[ \nabla \cdot \bar{G} = 0 \quad (1) \]

Momentum equations:

radial-direction

\[ \nabla \cdot (\bar{G} \ n_r + \bar{\tau}_r) + \frac{\delta P}{\delta r} = 0 \quad (2) \]

axial-direction

\[ \nabla \cdot (\bar{G} \ n_z + \bar{\tau}_z) + \frac{\delta P}{\delta z} - \rho g = 0 \quad (3) \]

Energy equation:

\[ C_p (\bar{G} \cdot \nabla T) - \nabla \cdot (k \nabla T) - Q_{\text{gen}} + Q_{\text{loss}} = 0 \quad (4) \]

Species equation:

\[ \nabla \cdot (\bar{G} \ w_j - \rho D_{j,\text{mix}} \nabla w_j) - \dot{R}_j = 0 \quad j = 1, N \quad (5) \]

Allowance is made for variable thermodynamic and transport properties, for the generation and loss of energy due to chemical reaction and radiation, \( Q_{\text{gen}} \) and \( Q_{\text{loss}} \), and for the rate of appearance or disappearance of species \( j \) due to the chemical reaction \( \dot{R}_j \). The solution to the above set of non-linear, partial differential equations leads to the determination of composition, velocity, temperature and pressure everywhere in the system. The equations are solved subject to the following boundary conditions:

a. Specified inlet conditions

b. Symmetry about the centerline

c. Wall impervious to matter (and heat if adiabatic)
d. Constant wall temperature (if not adiabatic)

e. No slip at the wall

f. Zero axial gradients at the exit (if recirculation, the composition of the fluid entering the system at the exit boundary is that of air).

The vorticity and streamfunction are used to aid in finding the solution to the above system of equations. The vorticity, a measure of the amount of counter-clockwise rotation possessed by the fluid, is defined as:

$$\omega = \frac{\delta v_r}{\delta z} - \frac{\delta v_z}{\delta r}$$  \hspace{1cm} (6)

and the streamfunction is defined as:

$$rG_r = -\frac{\delta \psi}{\delta z}, \quad rG_z = \frac{\delta \psi}{\delta r}$$  \hspace{1cm} (7)

With the vorticity, the momentum equations can be combined to eliminate the pressure as a dependent variable and with the streamfunction, the radial and axial components of the mass flux vector can be replaced by a single function.

Integration over finite areas (42)(64) was used to obtain the finite difference representation of the above system of equations. The resulting non-linear algebraic equations were solved on the computer using an alternating-direction-implicit iterative scheme (48), (60), (81), (82).
APPLICATION OF THE BURKE-SCHUMANN FLAME SHEET CONCEPT

At the surfaces which bound the reaction zone, chemical reaction is assumed to be infinitely fast and reaction is considered to be frozen outside these surfaces. The only heat release is at these surfaces and the magnitude of the heat generation term depends upon the fluxes of fuel and oxygen to them. With this assumption, a single species conservation equation can be used to locate one or the other surface, for now, a single global reaction can be used in place of the array of possible reactions that can occur at either surface. The global reaction considered is of the form:

\[ [1 \text{ gm}] \text{ fuel} + [s \text{ gm}] \text{ O}_2 \rightarrow [(1 + s) \text{ gm}] \text{ products} \]  \hspace{1cm} (8)

Thus, at a surface, one gram of fuel combines with \( s \) grams of oxygen to give \((1 + s)\) grams of products. The reaction rates at the surface are related by:

\[
\dot{R}_{\text{fuel}} = \frac{1}{s} \dot{R}_{\text{O}_2} = -\frac{1}{1 + s} \dot{R}_{\text{products}} \hspace{1cm} (9)
\]

If it is assumed that the diffusion coefficients of the fuel and oxygen are the same, the oxygen conservation equation can be divided by \( s \) and subtracted from the fuel conservation equation to give

\[
\nabla \cdot \left[ \bar{G} \left( w_{\text{fuel}} - w_{\text{O}_2} / s \right) - \rho_{\text{fuel,mix}} \nabla (w_{\text{fuel}} - w_{\text{O}_2} / s) \right] = \frac{\dot{R}_{\text{fuel}} - \dot{R}_{\text{O}_2}}{s} = c \hspace{1cm} (10)
\]
Noting that the last term is zero and defining a new variable \( w^* \) as

\[
w^* = w_{\text{fuel}} - \frac{w_{O_2}}{s}
\]  

(11)

equation (10) can be rewritten as

\[
\nabla (G w^* - \rho_D w^*) = 0
\]  

(12)

With the flame sheet assumption, fuel and oxygen cannot exist at the same point in the flow field. Positive values of \( w^* \) represent fuel concentrations and negative values represent the oxygen concentration divided by \(-s\).

Depending on the value of \( s \) used, the locus of \( w^* = 0 \) represents either the surface where the fuel is consumed, or the stoichiometric oxygen surface. When \( s \) is related to the stoichiometric oxygen coefficient \( i \) of the global reaction,

\[
s = \frac{M_{O_2}}{M_{\text{fuel}}} \cdot i
\]  

(13)

where \( M_{O_2} \) and \( M_{\text{fuel}} \) denote the molecular weights of oxygen and the fuel, respectively, the locus of \( w^* = 0 \) represents the surface through which an amount of oxygen in stoichiometric proportions to the fuel fired diffuses. For an appropriate choice of \( s \) less than that given by equation (13), the luminous flame surface can be matched.

The model is not restricted to equal fuel and oxygen diffusion coefficients. When solving equation (12) for the distribution of \( w^* \), the diffusion coefficient of the fuel is used for \( w^* > 0 \) and that of oxygen is
used for $w^* < 0$.

**PREDICTED FLAME SHAPE AND PROFILES**

The model was used to predict the shape and height of various methane-air flames issuing from a burner having the same dimensions as those of the experimental burner (inner radius = 0.635 cm, outer radius = 2.54 cm, shield diameter = 5.08 cm). The overall course of reaction in methane combustion is

$$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad (14)$$

The oxygen stoichiometric coefficient, $i$, is two, therefore the fuel-oxygen mass fraction which determines the stoichiometric oxygen surface is

$$w^* = \frac{w_{\text{CH}_4} - w_{\text{O}_2}}{4}. \quad (15)$$

In Figure 19, a comparison is made between predicted and experimentally determined flame heights. Experimentally, flame height was taken as that distance above the burner surface at which the luminous zone of the diffusion flame closed at the burner axis. The data agrees with that of other investigators in that at low fuel flow rates, flame length is proportional to the volumetric fuel flow rate. As expected, when equation (15) is used as the fuel-oxygen mass fraction, the height at which $w^* = 0$ at the symmetric axis, lies above the height at which the luminous zone closes at the axis. The solid line in Figure 19 should represent the height at which the concentration of CO at the symmetric axis falls to zero. For the flame
experimentally probed (fuel Reynolds Number \( \approx 41 \)), the concentration of CO, 6.6 cm above the burner axis \( (z/D = 5.2) \) is 0.001 and is zero at 7.0 cm above the burner. This lends some support to the validity of the model.

It was found that when an oxygen stoichiometric coefficient of 1.76 was used, the experimentally determined flame heights could be matched (dashed line). A variable coefficient is probably needed since as the flame tip is approached, the primary fuel which determines the position of the luminous surface, and hence, the points of heat release, actually changes from CH\(_4\) to CO + H\(_2\). The coefficient would therefore decrease from 2.0 as the methane concentration decreased as the height about the burner port increased.

Averaged over the height of the flame, a value of 1.76 appears to adequately predict the height at which the luminous flame surface closes at the symmetric axis. A variable coefficient would show-up in the predicted flame shape and in the local radial concentrations. An oxygen stoichiometric coefficient less than two verifies the assumption of incomplete combustion of the fuel at the flame surface and indicates that the reactions at the flame surface result in an increase in the total number of moles.

Figure 20 shows how the predicted flame shape compares with that experimentally observed. Shown as circles is the profile of the luminous flame surface which closes at the symmetric axis 5.8 cm above the burner port. The square represent the profile of the visible edge of the blue reaction zone. The blue hue of the reaction zone is associated with the burnout of carbon monoxide, hence, the edge of the reaction zone roughly corresponds to the surface where combustion of the methane to CO\(_2\) and H\(_2\)O is complete. The predicted flame shape with \( i = 2.0 \) appears to coincide with this edge.

The dashed line in the figure represents the predicted flame shape when \( i = 1.76 \). It appears that the luminous edge of the flame can be matched by
the proper choice of the oxygen stoichiometric coefficient.

Figures 21, 22 and 23 show the comparison between predicted (with $i = 2.0$) and experimentally determined concentration and temperature profiles at three heights above the burner surface. The model is seen to overpredict the methane concentration and the temperature inside the flame surface, and the predicted temperature and oxygen concentration profiles appear to be slightly shifted away from the experimentally determined ones outside the flame surface. These discrepancies are attributed to the neglect of energy absorbing, endothermic reactions inside the flame core and to the finite rates of chemical reactions in the reaction zone.

Since the model does not allow for pyrolysis of the methane inside the flame core or for the production and subsequent consumption of CO or $H_2$, the predicted "fuel" profile lies above the experimentally determined methane profile. The dashed curve in each figure represents the combined mass fractions of $CH_4$, CO and $H_2$ experimentally determined. This curve, and the experimentally determined $CH_4$ profile, bracket the predicted "fuel" profile indicating that had allowances been made for incomplete combustion at the flame surface, concentration profiles inside the flame surface would be more adequately predicted.

Since the predicted temperature and nitrogen and oxygen concentration profiles are in moderate agreement, it is believed that the predicted aerodynamic field provides a good approximation of the actual flow field established during the combustive process. Figure 24 shows the velocity distribution predicted by the theoretical model. The methane and air streams enter the system at 4.5 and 9.88 cm/sec, respectively. Near the burner port a peak in the radial velocity profile is observed at the flame surface due
Figure 22a Comparison of Predicted and Experimentally Determined Radial Concentration Profiles: 
$z = 2.4$ cm.

Figure 22b Comparison of Predicted and Experimentally Determined Radial Temperature Profile: 
$z = 2.4$ cm.
Figure 23a Comparison of Predicted and Experimentally Determined Radial Concentration Profiles, $z = 5.0 \text{ cm}$.

Figure 23b Comparison of Predicted and Experimentally Determined Radial Temperature Profile, $z = 5.0 \text{ cm}$.
to the higher temperatures encountered. If increases in velocity were due to expansion alone, the peak in the velocity profile would coincide with the peak in the radial temperature profile. However, as the distance above the burner port is increased, the peak in the velocity profile approaches the symmetric axis faster than the flame surface does. The velocities encountered at the symmetric axis are also greater than the velocities expected due to natural convection effects. The reason for this is evident when the flow streamlines are considered. The streamlines, shown in Figure 25, point out that a large recirculation cell is established between the hot flame surface and the cooler shield wall. Air is entrained into the system at the shield outlet to balance the momentum of the inlet fuel and air streams and the frictional losses at the shield wall. The presence of this recirculation cell reduces the total area available for flow of the feed and combustion gases; hence, velocities are increased due to the combined effects of a reduced flow area and natural convection. Preliminary particle track studies verify the existence of the recirculation cell.

The model developed can be used to predict flame shape and height and can provide estimates of the temperature, velocity, and fuel, oxygen and nitrogen concentration profiles established during the combustion process. With this model, the effects of flow rate, fuel and air preheat, burner port size, shield temperature and equivalence ratio on diffusion flame structure can be evaluated without actual experimentation.

In order to determine if the present model is capable of predicting NO\textsubscript{x} emissions from such flames, and aid in emission abatement studies, the process of NO formation in laminar diffusion flames was investigated. The following section highlights the results of the investigation.
Figure 24: Radial Distribution of Axial Velocity

Figure 25: Stream Function Profile

- Ten equally spaced streamlines between $\psi_{\text{axis}}$ and $\psi_{\text{max}}$
- Four equally spaced streamlines between $\psi_{\text{axis}}$ and $\psi = 0.1$
NO\textsubscript{x} FORMATION IN LAMINAR DIFFUSION FLAMES

Radial nitrogen oxide concentration profiles at the three heights above the burner plate at which the stable species concentration profiles were obtained are presented in Figure 26. The NO\textsubscript{x} concentration profiles peak in the reaction zone where the radial temperature profiles also peak. The steep gradients away from the peaks indicate that nitrogen oxide formation is primarily confined to a narrow region just outside the flame surface where temperature and oxygen availability are suitable for NO formation.

The experimentally determined NO\textsubscript{x} concentration profiles were combined with the mass flux distribution predicted by the theoretical model to determine the total mass flow rate of NO\textsubscript{x} at various levels within the system and the total flow rate of NO\textsubscript{x} into the flame at various heights above the burner plate. The results are shown in the following table. The second column of the table shows that the total amount of nitrogen oxides formed increases as the height above the burner plate is increased. Comparison of the second and third columns indicates that at each level in the system, more NO\textsubscript{x} is outside the flame surface than inside, and that in general, the relative amount outside the surface increases as the height above the burner plate is increased.

Comparison of the third and fourth columns indicates that at 1.2 cm above the burner plate, more NO\textsubscript{x} is present inside the luminous core than penetrated the surface from the outside. This suggests that in the lower regions of the flame, NO\textsubscript{x} is generated inside the flame surface. The exact mechanism of core generated NO\textsubscript{x} is unknown but CN and HN intermediates are assumed to be involved.

When the total flow of NO\textsubscript{x} into the flame (2.43 × 10\textsuperscript{-6} gm/sec) was
Figure 26. Radial Distribution of NOx

- Methane-Air Diffusion Flame
- Port Diameter: 1.27 cm
- $Q_{\text{fuel}} = 5.7 \text{ cc/ sec}$
- $Q_{\text{air}} = 188 \text{ cc/ sec}$

- Height Above Burner Port:
  - $\circ Z = 1.2 \text{ cm}$
  - $\circ Z = 2.4 \text{ cm}$
  - $\triangle Z = 5.0 \text{ cm}$
### TABLE VII. Nitrogen Oxide Content of the Combustion Gases

<table>
<thead>
<tr>
<th>Height above burner, cm</th>
<th>Total mass flow of NO&lt;sub&gt;x&lt;/sub&gt;, $10^6$ gm/sec</th>
<th>Mass flow of NO&lt;sub&gt;x&lt;/sub&gt; inside the flame surface, $10^6$ gm/sec</th>
<th>Mass flow of NO&lt;sub&gt;x&lt;/sub&gt; into the flame, $10^6$ gm/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>2.068</td>
<td>0.615</td>
<td>0.295</td>
</tr>
<tr>
<td>1.5</td>
<td>2.852</td>
<td>0.637</td>
<td>0.558</td>
</tr>
<tr>
<td>1.8</td>
<td>3.017</td>
<td>0.983</td>
<td>1.122</td>
</tr>
<tr>
<td>2.1</td>
<td>3.559</td>
<td>0.484</td>
<td>1.759</td>
</tr>
<tr>
<td>2.4</td>
<td>4.301</td>
<td>1.043</td>
<td>1.838</td>
</tr>
<tr>
<td>5.0</td>
<td>6.453</td>
<td>0.659</td>
<td>2.142</td>
</tr>
<tr>
<td>5.8 (flame tip)</td>
<td>6.75 (extrapolated)</td>
<td>0.</td>
<td>1.953</td>
</tr>
</tbody>
</table>
compared to the total flow out of the flame \((0.478 \times 10^{-6} \text{ gm/sec})\), it was found that \(\text{NO}_x\) must be converted to \(\text{N}_2\) or other nitrogen containing species inside the flame surface. Less than 20% of the \(\text{NO}_x\) which penetrated the flame surface survived and less than 7% of the total mass flow of \(\text{NO}_x\) above the flame tip came from within the luminous core. Thus, only a negligible fraction of the \(\text{NO}_x\) above the flame tip was core generated. This indicates that any mechanism postulated to describe the formation of nitrogen oxide in the combustion system studied must be one which is effective in the post-flame region and sensitive to temperature. The Zeldovich (90) reactions constitute such a mechanism.

\[
\text{N}_2 + \text{O} \rightarrow \text{NO} + \text{N} 
\]

\[
\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O} 
\]

Since the NO concentrations observed in the flame are far from equilibrium, the NO formation rate via the Zeldovich mechanism is given by:

\[
\frac{d(\text{NO})}{dt} = 2k_{16}(\text{N}_2)(0) 
\]

In order to assess the Zeldovich reactions in describing the formation of NO in the combustion system studied, estimates of the oxygen free radical concentration must be obtained. Recent studies indicate the existence of superequilibrium radical concentrations in the post-flame region of hydrocarbon flames, therefore equilibrium oxygen radical concentrations cannot be assumed. Estimates of the oxygen radical concentration in the diffusion flame
studied were obtained from the stable species concentrations and temperature by assuming that the carbon monoxide burnout reaction and the bimolecular reactions associated with the $\text{H}_2 - \text{O}_2$ system were equilibrated.

\[
\text{CO} + \text{OH} = \text{CO}_2 + \text{H} \quad (19)
\]

\[
\text{H} + \text{O}_2 = \text{OH} + \text{O} \quad (20)
\]

\[
\text{O} + \text{H}_2 = \text{OH} + \text{H} \quad (21)
\]

\[
\text{H} + \text{H}_2\text{O} = \text{OH} + \text{H}_2 \quad (22)
\]

Evidence exists for the equilibration of these reactions subsequent to hydrocarbon depletion.

By appropriately combining the equilibrium relationships, the following expressions exists for the concentrations of the radicals in terms of the concentrations of the stable species:

\[
(\text{OH})^2 = \frac{K_{p19} K_{p20} K_{p21} K_{p22}}{K_{p20} K_{p21}} \frac{(\text{H}_2\text{O})(\text{CO})(\text{O}_2)}{(\text{CO}_2)} = K_{p20} K_{p21} (\text{H}_2)(\text{O}_2) \quad (23)
\]

\[
(\text{O}) = \frac{1}{K_{p21} K_{p22}} \frac{(\text{OH})^2}{(\text{H}_2\text{O})} \quad (24)
\]

\[
(\text{H}) = \frac{1}{K_{p20} K_{p21} K_{p22}} \frac{(\text{OH})^3}{(\text{O}_2)(\text{H}_2\text{O})} \quad (25)
\]

The CO and CO$_2$ concentrations, instead of the H$_2$ concentration, were used to determine the hydroxyl concentration because the H$_2$ concentration is
considered to be the concentration most affected by radical recombinations in the sampling probe and by departures from equilibrium in the flame. The hydroxyl concentrations determined by the two methods differed, in general, by less than a factor of 1.5 indicating that these effects were slight.

The hydrogen and oxygen radical concentrations so determined, were found to exceed their equilibrium values by one-to-two orders of magnitude. Figure 28 shows a comparison between the oxygen radical concentration in the flame and the equilibrium oxygen concentrations. Equilibrium concentrations are approached as the gases diffuse away from the reaction zone, but full equilibrium is not reached because the reactions are frozen by a rapid decrease in temperature outside the reaction zone.

The superequilibrium oxygen radical concentrations were combined with the nitrogen concentrations and rate constant expression of Baulch et al. (5) in equation 18 to determine the formation rate profile of NO predicted by the Zeldovich mechanism. The NO formation rate profiles obtained, Figure 30, exhibit a sharp peak in the reaction zone where temperature and oxygen availability favor the Zeldovich reactions. Integration of these profiles to obtain the total production of NO at the heights indicated, led to the conclusion that the Zeldovich mechanism was the predominant mechanism of NO formation in the post-flame region of the flame studied. This conclusion was based upon the agreement obtained when the total production rates of $\text{NO}_x$ determined from the radial $\text{NO}_x$ profiles of Figure 26 were compared with the results of this integration.

CONCLUSION

The Burke-Schumann flame sheet model has been modified to allow for
Figure 28. Comparison of Equilibrium Oxygen Atom Concentration and Oxygen Atom Concentration in the Flame Determined from the Stable Species
Figure 30. Nitric Oxide Formation Rate via Zeldovich Mechanism Determined From Measured Temperature and Species Concentrations.
natural convection effects and variable thermodynamic and transport properties. The model developed is adequate to provide estimates of the concentration, thermal and aerodynamic profiles established during the combustive process. The following conclusions have been derived from this fundamental study of diffusion flames:

(1) By use of an oxygen stoichiometric coefficient of 2.0 for the methane-oxygen flame, a good description of the outer surface of the blue reaction zone is obtained. A stoichiometric coefficient of 1.76 is found to accurately predict flame height and adequately describe the luminous flame surface.

(2) The predominate mechanism of NO formation is the Zeldovich mechanism. NO production from fuel-nitrogen intermediates represents only a small and almost negligible fraction of the total NO produced.

(3) Free radical concentrations in the reaction zone can exceed their equilibrium values by one-to-two orders of magnitude. Kinetic models of diffusion flames, adequate for the prediction of pollutant formation, must allow for the increase in the number of moles during the methane oxidation at the luminous flame surface, followed by the radical recombinations in the reaction zone.

(4) Partial equilibration of the fast $\text{H}_2 - \text{O}_2$ reactions and the carbon monoxide burnout reactions is a good assumption in the reaction zone.

(5) Approximately 80% of the NO which diffuses from the reaction zone and penetrates the luminous flame surface is destroyed.
Chapter I. INTRODUCTION

The brownish haze that nitrogen dioxide gives the atmosphere, the tendency of nitric oxide to promote formation of photochemical smog, and the possible toxic effects of these oxides are several reasons why the oxides of nitrogen are considered air contaminants. It is estimated that in this country alone, about fifty-three tons of nitrogen oxides are emitted to the atmosphere annually by man-made processes. The combustion of fuel in both stationary and non-stationary sources accounts for the major portion of these emissions; chemical and manufacturing processes are relatively small contributors.

Large amounts of nitrogen compounds are formed, reacted, and scavenged by natural processes in the environment. Biological processes are involved in the generation of NH3, NO, NO2 and N2O. Emissions from natural processes, on a global basis, are much greater than urban pollutant emissions. The results of data compiled by Robinson and Robbins (65) shown in Table I, indicate the magnitude of global NO2 pollution sources. From an air pollution standpoint, the natural scavenging processes are probably not rapid enough to affect the hour-to-hour NO2 concentrations in urban areas. It is, therefore, the responsibility of man to consider various methods for the control of nitrogen oxide concentrations in our atmosphere.

I.1 THE OXIDES OF NITROGEN

The important oxides of nitrogen are nitric oxide (NO), nitrogen dioxide (NO2), dinitrogen tetroxide (N2O4) and nitrous oxide (N2O).
Table I. Estimated Annual Global Emissions of Nitrogen Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Source</th>
<th>Estimated Emissions (tn/yr)</th>
<th>Emissions as Nitrogen (tn/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO\textsubscript{x}</td>
<td>Coal combustion</td>
<td>26.9 \times 10^6</td>
<td>8.2 \times 10^6</td>
</tr>
<tr>
<td></td>
<td>Petroleum refining</td>
<td>0.7 \times 10^6</td>
<td>0.2 \times 10^6</td>
</tr>
<tr>
<td></td>
<td>Gasoline combustion</td>
<td>7.5 \times 10^6</td>
<td>2.3 \times 10^6</td>
</tr>
<tr>
<td></td>
<td>Other oil combustion</td>
<td>14.1 \times 10^6</td>
<td>4.3 \times 10^6</td>
</tr>
<tr>
<td></td>
<td>Natural gas combustion</td>
<td>2.1 \times 10^6</td>
<td>0.6 \times 10^6</td>
</tr>
<tr>
<td></td>
<td>Other combustion</td>
<td>1.6 \times 10^6</td>
<td>0.5 \times 10^6</td>
</tr>
<tr>
<td>NO\textsubscript{x}</td>
<td>Total</td>
<td>52.9 \times 10^6</td>
<td>16.1 \times 10^6</td>
</tr>
<tr>
<td>NH\textsubscript{3}</td>
<td>Combustion</td>
<td>4.2 \times 10^6</td>
<td>3.5 \times 10^6</td>
</tr>
<tr>
<td>NO</td>
<td>Biological action</td>
<td>501 \times 10^6</td>
<td>234 \times 10^6</td>
</tr>
<tr>
<td>NH\textsubscript{3}</td>
<td>Biological action</td>
<td>1160 \times 10^6</td>
<td>957 \times 10^6</td>
</tr>
<tr>
<td>N\textsubscript{2}O</td>
<td>Biological action</td>
<td>592 \times 10^6</td>
<td>378 \times 10^6</td>
</tr>
</tbody>
</table>

*Assumes emissions of NO\textsubscript{x} to be NO\textsubscript{2}.
Of these N₂O₄ and N₂O can be eliminated from consideration as man-produced air contaminants. Emission sources are rare, and they have no measurable effect on man at low concentrations. At concentrations of 30% or so, N₂O is useful as an anesthetic. When N₂O₄ is diluted to any extent with air, it decomposes rapidly and is only present in trace quantities relative to NO and NO₂.

Nitrogen dioxide, a pungent, dark brown vapor has required emission source control for a number of years. Because of its toxic effects, current federal recommendations call for a maximum annual mean exposure level of 0.05 ppm. Levels of 2.8 ppm have been reported to cause chronic lung changes in animals, and levels of 25 ppm have been reported to cause significant plant damage. (44) The specific health hazards of NO₂ have not been unambiguously defined, but Mueller and Hitchcock (55) point out that in living species, NO₂ irritates sensory organs, inflames and oxidizes lung tissue and changes lung morphology. It is suspected that NO₂ tends to settle on the hemoglobin in the blood and also has a tendency to join with the moisture in the lungs to form dilute nitric acid. Sax (70) gives NO₂ a severe toxicity rating.

Nitric oxide is not ordinarily considered to have any toxic effects other than those caused by NO₂, to which it converts quite easily.

\[ 2\text{NO} + \text{O}_2 \not\rightarrow 2\text{NO}_2 \]

It is however, the precursor of two constituents of the eye-irritating smogs - ozone and peroxyacetyl nitrates (PAN). These compounds are products of photochemical reactions which take place in the presence of sunlight.
I.2 THESIS OBJECTIVE

Most of the oxides of nitrogen are produced during the combustion of fuel in which a part of the oxygen combines with atmospheric nitrogen in the flame rather than with the fuel. The process is referred to as nitrogen fixation and when fixation occurs, the predominant product is NO. Investigations into both stationary and non-stationary sources have provided considerable insight into the dependency of nitric oxide emissions on such factors as furnace and burner design, fuel to air ratio, firing intensity, and fuel and air preheat. The emphasis of most of these investigations has been on characterizing the emissions and in developing emission abatement technology for large scale units which account for the major fraction of the NO emitted into the atmosphere. The control techniques developed for large scale units such as two-stage combustion, flue gas recirculation, scrubbing and catalytic treatment of the exhaust gases are of limited or no value in application to smaller units such as the domestic gas range. Studies have shown that NO concentration exhaust is controlled primarily by the rate of NO formation during the high temperature part of the combustion process. Abatement technology for small units like the gas range therefore requires information on the process of nitric oxide formation in the flames exhibited by such units. This type of information can be gained only through a fundamental flame study: a study designed to characterize the combustion process itself, one that can identify the important flame species and determine how these species influence the formation rate of NO in the flame, a study that can determine the relation between flame fluid mechanics, temperature and NO formation. Such studies on premixed, idealized flat flames have been undertaken. (28, 57, 61, 72, 79) Such studies on diffusion
flames and partially premixed diffusion flames, the flames characteristic of many practical large and small combustion systems, are limited (80). This was, therefore, the objective of this study - to determine those factors which influence the formation rate and distribution of NO in laminar diffusion flames, and to propose emission abatement techniques for combustion systems exhibiting such flames.

In this fundamental flame study, a cylindrical, overventilated, laminar methane/air diffusion flame was extensively probed to determine its temperature distribution, and the distribution of the important stable flame species. A theoretical model of diffusion flames which can predict these profiles was also developed. Together, the experimental data and the theoretical model form a powerful unit which is useful in predicting the distributions of the unstable flame species, and velocity variations in the combustion system. The mass of information attainable directly leads to all factors which influence the formation rate and distribution of nitric oxide.

It is the purpose of this treatise to present the experimental and theoretical procedures and findings of this fundamental flame study in a clear and precise manner. The treatise begins with a general characterization of diffusion flames to familiarize the reader with the basic concepts of the combustion system under consideration. This section is followed by a discussion on the formation of nitric oxide by nitrogen fixation in combustion systems. The experimental apparatus and procedure are described in the third section. The results of the experimental program are presented and a critical discussion of the results follows. The theoretical model is developed in the fourth section. The fifth section combines the results of the theoretical model with the experimental data in a manner that attempts to define
the processes of NO formation and distribution in diffusion flames. This section is followed by conclusions, recommendations, and appendices made-up of supporting material.
Chapter II. DIFFUSION FLAMES

Diffusion flames have been known for generations. Candle or oil-wick flames which early man used as artificial light are relatively simple examples of diffusion flames. The luminous flames obtained when the air inlet hole of bunsen burners are blocked are other examples of diffusion flames. The most distinctive characteristic of such flames is that the burning rate is not controlled by chemical reactions as in premixed flames, but is controlled by the rate at which the fuel and oxidizer are brought together in the proper proportions for reaction. It is difficult to give a general treatment of diffusion flames largely because no simple, measurable parameter, analogous to the burning velocity of premixed flames, can be used to characterize the burning process.

The dominant physical process is that of mixing. Whenever mixing is slow enough compared to reaction rates that the mixing time controls the burning rate, a diffusion flame is said to exist. Fristrom and Westenberg (36) point out the existence of a continuum of intermediate stages between perfect premixed flames and perfect diffusion flames. They give a rather crude criterion which defines the degree of mixedness as the ratio of a diffusion time, $t$, and a residence time, $t_R$. When fuel and oxidizer depart from a separating wall at velocity $v$, they will diffuse together in a zone of thickness $\delta$. With a distance $\ell$ traveled before reaction starts, the ratio is given by:

$$\frac{t_D}{t_R} \propto \frac{\delta^2 v}{DL} \quad (1.1)$$
where $D$ is the diffusion coefficient. If $t_D/t_R$ is much less than one, the flame produced is premixed, whereas if the ratio is much greater than one a diffusion flame results. In slow burning diffusion flames typified by candle flames, the fuel rises slowly and laminar flow ensues. The mixing process occurs solely by molecular diffusion and the properties of the flame are determined only by molecular quantities. In industrial burners, and in gas turbines, where the fuel is usually introduced in the form of discrete droplets or fine solid particles, burning is rapid, flow speeds are high, and the mixing process is associated with the turbulence of the flow. The aerodynamics of the system will then dominate to a larger extent the molecular properties. This fundamental flame study concerns itself with gaseous, laminar diffusion flames where mixing is slow and the properties of the flame are determined by molecular quantities.

II.1 GENERAL CHARACTERISTICS

Gaseous diffusion flames occur upon the ignition of a jet of fuel entering either an atmosphere of quiescent oxidant or an oxidant stream. The resultant flame emits heat and light and has a discrete reaction zone. This reaction zone is referred to as the flame front and it has been hypothesized that fuel and oxidant reach this zone in stoichiometric proportions. Near the flame front, diffusion which is a relatively slow process, tends to change the composition of the gas, but chemical reaction quickly follows and does not allow any chemical potential to develop. The gases leaving this zone are thus in chemical equilibrium. The mass of hot burnt gas leaving the flame zone grows thicker and the concentration gradient away from this region becomes less steep. The overall velocity of combustion therefore slows
down until the final flame temperature is reached and the concentra-
tion of each of the constituents of the burnt gas is uniform.

Since actual reaction apparently takes place rapidly in a narrow
zone, the changes in gas composition are principally due to the inter-
diffusion of reactants and products. If a cross-section were taken
through the flame (see Figure I) it would be found that the fuel con-
centration has a maximum at the axis and falls away rapidly to the
flame front. Similarly, the oxidizer concentration decreases from its
free-stream concentration as the flame surface is approached and falls
approximately to zero at the boundary. The concentration of products
has a maximum in the flame zone where the major extent of reaction is
occurring and falls away in both directions, the direction outside the
flame surface being somewhat preferred. Similar to the product concen-
tration distribution, the temperature is maximum at the flame surface
and falls off rapidly as the distance from the surface is increased.

The flame surface is of extremely small, but finite, thickness
and it strictly defines the region in which complete combustion occurs.
Since reaction is normally very rapid, it represents the position at
which the fuel/oxidizer ratio becomes stoichiometric. As the fuel
concentration will decrease with height about the inlet port for over-
ventilated flames, the position of the flame surface moves toward the
axis and converges at the tip where all the fuel is consumed. For
underventilated flames, the flame surface moves away from the axis
until all the oxidant is consumed. In principle, for overventilated
systems, the flame should be conical in shape, reaction being confined
largely to a thin region forming the flame surface which corresponds
closely to the reaction zone in the premixed flame.
Figure 1. Concentration and Temperature Profiles Through a Laminar Diffusion Flame
II.2 FLAME APPEARANCE

Fuel and oxidizer flow rates are probably the most important factors of flame appearance and height. If the flow is laminar into and through the flame front, a narrow reaction zone is established which is determined by the coupling of reaction, convection, and molecular transport processes. Increasing the flow to the turbulent region increases the thickness of the reaction zone and the apparent propagation rate. As the flow is increased to the turbulent region, the height of overventilated laminar flames is increased, almost linearly, until turbulent mixing occurs. This appears first at the tip and moves down progressively with increase in velocity. The flame length also falls in this region as the reaction zone thickens. Eventually a stage is reached at which both the height of the flame and the position of the transition, known as the breakpoint, remain constant irrespective of any additional increase in fuel velocity. These various effects are shown in Figure II. The work of Hawthorne, Weddell and Hottel (45) suggests that this phenomenon is related to fluid flow rather than to combustion effects. They found the same break-point behavior with small liquid jets.

Changes in flow pattern due to thermal convection and differing densities of fuel and air cause varied flame configurations. Barr (3) observed some of these for a butane/air system. Figure III illustrates some of these configurations under certain limiting flow conditions. At low fuel flows, meniscus-shaped flames sometimes occur; flames which are capped-shaped but lift so that they hold to the burner port at only one point are also observed. With higher fuel flows, lifted flames and vortex-shaped flames occur. The reasons for lift are not fully understood, but Bradley (10) suggests that as
FIGURE 2
Progressive Change in Flame Type with Increase in Nozzle Velocity
fuel velocity is increased the entrainment of air at the burner rim produces some of the characteristics of premixed flames and combustion occurs only when the fuel/oxygen ratio has fallen sufficiently. A velocity is eventually reached at which only lifted flames occur and beyond this region a blow-out limit exists. The dashed line represents the smokepoint, smoke appearing as the fuel flow is increased. Below the line, normal overventilated diffusion flames exist; above the line, underventilated, fan-shaped flames. The areas of the convective flames, lifted, and vortex-shaped flames are essentially zones of unstable flames. Lambent flames which oscillate from side to side and rich tilted flames occur in the convective zone and lean, tilted flames in the vortex zone. The extinction regions are zones which will not support combustion.

For a given fuel flow, the shorter flame indicates a greater burning rate per unit volume than the taller flame. Because of this, flame height is sometimes used as a measure of burning rate. In the region of low fuel velocities the flame height is independent of the air velocity. At higher fuel velocities, the lower the air velocity, the higher the flame. Increasing the fuel/oxygen ratio causes increased flame height per unit air velocity. Figure II indicates that as the fuel flow is decreased the flame becomes smaller and smaller until quenching action of the nozzle is sufficient to prevent propagation.

Flame height is independent of pressure for very small flames only. For larger flames, height is only constant with pressure when diffusion is not the rate determining process. In the thin reaction zone, as the pressure is increased, the concentration gradients become
so steep that the chemical reaction rates become important and the flame height increases. The principle effect of pressure change on flame structure is thus to change the thickness of the reaction zone.

Changes in inlet temperature cause only minor changes in flame appearance and do not effect flame microstructure. Composition effects luminosity. In hydrocarbon flames color changes from pale blue, through intense blue, to sooty yellow as the flame becomes more fuel rich.

II.3 HYDROCARBON DIFFUSION FLAMES

In the complex flame structure of hydrocarbon diffusion flames two distinct zones are readily identifiable - the thin blue reaction zone and a luminous zone. The location of these zones is shown in Figure IV. In the main reaction zone, which extends vertically from the burner port, the gaseous reactions take place and diffusion is the rate determining factor. In the luminous part, the combustion of the carbon particles takes place. Gaydon and Wolfhard (39) state that carbon particles are formed whenever the carbon atom to oxygen atom ratio is greater than unity. In a hydrocarbon/air diffusion flame, the fuel is slowly heated as it diffuses towards the reaction zone. As the oxygen bearing constituents are in very low concentration in the region, the \( n_c/n_o \) ratio (carbon atom to oxygen atom ratio), is high; thus, carbon is formed as soon as the temperature is high enough to decompose the fuel. As the carbon particles rise vertically, radiating as they do so, they penetrate deeper into the wedge of hot burnt gases containing \( H_2O, CO \) and \( CO_2 \), and in this region will be in a gas of lower \( n_c/n_o \) ratio. There will therefore be a tendency, provided the temperature is above 1000°K, for the carbon particles to react with water vapor and carbon dioxide to give CO. Whether the
Figure 4. The Luminous and Reaction Zones of Hydrocarbon Diffusion Flames
particles are entirely consumed in this way or whether they cool to a temperature below that at which the equilibrium favors CO formation, so giving soot, depends on the geometry of the flame.

II.4 THE METHANE-AIR DIFFUSION FLAME

II.4.1 The Inner Mantle

Detailed studies on the chemistry in the luminous zone of cylindrical, laminar hydrocarbon diffusion flames are somewhat limited. Luminosity is related in a positive manner to the amount of carbon formation; so the primary fuel must in some way decompose. Wolfhard and Parker (87) examined the region spectroscopically on the basis of a deepening absorption as the flame was probed from the axis towards the flame surface. Although they could not evaluate the importance of the pyrolysis process, they concluded that it must play a role in the mechanism of burning. Smith and Gordon (74) followed the chemistry of the combustion of a cylindrical methane diffusion flame by mass spectrometric techniques and showed that pyrolysis was the only route for the disappearance of the methane. Gordon, Smith and Mc Nesby (41) coupled mass spectrometric techniques with gas chromatography and photochemical techniques to analyze samples drawn from the inner mantle of methane diffusion flames and determined that the rate determining reaction of the fuel molecules is their pyrolysis. Primary reactions involved in the pyrolysis of methane are difficult to identify. Back (2) states that since methane is the least reactive of the paraffins, secondary reactions of the products of the initial pyrolysis step became important at very early stages, making studies of the initial pyrolysis step very difficult. She gives the overall course of the reactions in the pyrolysis of methane as follows:
\[ 2\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2 \rightarrow \text{C} + \text{H}_2 \]

The series of elementary reactions by which the products form has not been established. The most commonly postulated sequence is discussed below.

The two most probable initiation steps are:

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{CH}_3 + \text{H} & \text{R2} \\
\text{CH}_4 & \rightarrow \text{CH}_2 + \text{H}_2 & \text{R3}
\end{align*}
\]

Studies on the pyrolysis of methane in shock tubes (53, 73) and in tubular flow reactors (52, 59) give supporting material. The second step can be achieved by either of the following bimolecular reactions.

\[
\begin{align*}
\text{CH}_2 + \text{CH}_4 & \rightarrow \text{C}_2\text{H}_6 & \text{R4} \\
\text{CH}_3 + \text{CH}_3 & \rightarrow \text{C}_2\text{H}_6 & \text{R5}
\end{align*}
\]

Dissociation of the ethane to ethylene can account for the third step.

\[
\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 & \text{R6}
\]

The ethylene formed can react with \( \text{CH}_2 \)

\[
\text{CH}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_6 & \text{R7}
\]

or it can pyrolyze.

\[
\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2 & \text{R8}
\]

The acetylene produced can then decompose to carbon and hydrogen thus completing the course of reaction in methane pyrolysis put forth by Back.

\[
\text{C}_2\text{H}_2 \rightarrow 2\text{C} + \text{H}_2 & \text{R9}
\]

In support of this final decomposition step, at temperatures greater than 1000°C where polymerization has become unimportant, the chief products of acetylene pyrolysis are carbon, hydrogen and methane. The methane is presumably formed by the reverse reactions R8, R6, R4, and R3.
All the above pyrolysis products have been observed in the luminous zone of methane/air diffusion flames. The methyl acetylene observed by Smith and Gordon (74) could be formed by the decomposition of the propylene produced via reaction R7. The pyrolysis products accounted for about one mole percent of the carbonaceous materials found in the inner mantle of the flame studied by Gordon, Smith and McNesby (41). They observed no oxygenated hydrocarbons having a concentration greater than one part in $10^5$. These reactions products were completely consumed as they diffused to the flame surface.

II.4.2 THE PRIMARY REACTION ZONE

The reactions occurring in the primary reaction zone of methane/air diffusion flames are probably the same as those occurring in fuel-rich and fuel-lean premixed methane/air systems. The small quantity of pyrolysis products produced probably have little effect on establishing the thickness of the reaction zone, so their mechanisms of combustion will not be considered in detail. It will be sufficient to say that the overall course of reaction in the burning of the pyrolysis products is as follows:

$$(C_2H_6, C_2H_4, C_2H_2, C) + (H, O, OH) \rightarrow (CO, CO_2, H_2, H_2O)$$

Detailed studies (22, 35, 61) on premixed methane/air and methane/oxygen systems lead to the following conclusions. As the methane diffuses to the flame surface, it is subject to attack by H, O and OH radicals to form the methyl radical.

$$CH_4 + H \rightarrow CH_3 + H_2 \quad \text{R10}$$

$$CH_4 + O \rightarrow CH_3 + OH \quad \text{R11}$$

$$CH_4 + OH \rightarrow CH_3 + H_2O \quad \text{R12}$$
The CH₃ can then be oxidized to a peroxide which can rapidly decompose to form formaldehyde.

\[ \text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{OH} \]  R13
\[ \text{CH}_3 + \text{O} \rightarrow \text{CH}_3\text{O} \rightarrow \text{CH}_2\text{O} + \text{H} \]  R14

The formaldehyde produced can further react to give HCO and H₂O.

\[ \text{CH}_2\text{O} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O} \]  R15

The formyl radical then leads to the formation of CO which is finally oxidized to CO₂.

\[ \text{HCO} + \text{OH} \rightarrow \text{CO} + \text{H}_2\text{O} \]  R16
\[ \text{HCO} + \text{M} \rightarrow \text{CO} + \text{H} + \text{M} \]  R17
\[ \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \]  R18

The following chain branching reactions, and linear combinations of these are necessary to propagate the reaction sequence,

\[ \text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O} \]  R19
\[ \text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H} \]  R20
\[ \text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH} \]  R21

and the following recombination reactions serve to terminate the sequence in the post-flame regions.

\[ \text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M} \]  R22
\[ \text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M} \]  R23
\[ \text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M} \]  R24
\[ \text{H} + \text{O} + \text{M} \rightarrow \text{OH} + \text{M} \]  R25

The above reaction sequence is important only in establishing the thickness of the primary reaction zone. As illustrated in Figure IV, this reaction zone completely encloses the luminous region of overventilated flames. The thickness is only about two millimeters at the maximum flame diameter and decreases as the flame tip is
approached. The blue radiation from this region is partially \( \text{O}_2 \) Schumann-Runge and partially \( \text{CO} + \text{O} \) radiation, both types being dependent on the existence of high temperatures.
Chapter III. NITRIC OXIDE FORMATION VIA NITROGEN FIXATION IN HYDROCARBON FLAMES

Studies have shown that the formation rate of nitric oxide in premixed, hydrocarbon flames are significantly higher in the flame zone than they are in the post-flame region. Tuteja and Newhall (80) (and this study) have shown that nitric oxide formation in diffusion flames is confined primarily to the fuel-lean side of the thin reaction zone. Both flame types thus indicate that NO concentration exhausted is controlled primarily by the rate of NO formation during the high temperature part of the combustion process. The reactions reported in the literature as being important in determining the formation rate of nitric oxide in the high temperature regions of hydrocarbon flames are listed below.

\[
\begin{align*}
N_2 + O &= NO + N & \text{R26} \\
N + O_2 &= NO + O & \text{R27} \\
N + OH &= NO + H & \text{R28} \\
N_2 + OH &= N_2O + H & \text{R29} \\
N_2 + O_2 &= N_2O + O & \text{R30} \\
N_2O + O &= NO + NO & \text{R31}
\end{align*}
\]

Reactions R26 and R27 constitute the Zeldovich (90) mechanism. Investigators (9, 56, 68, 79) have found that this chain mechanism can satisfactorily predict the formation rate of nitric oxide in the flame zone as well as in the post-flame region of lean, premixed, hydrocarbon flames if the local oxygen atom concentration is correctly assessed. The postulated 'correct' oxygen atom concentration is that oxygen concentration established when the flame gases are said to be
in partial equilibrium (56, 61, 68, 69). At partial equilibrium, the fast bimolecular reactions associated with carbon burnout and the hydrogen/oxygen system are assumed to be in equilibrium, (reactions R18, R19, R20 and R21), even though the combustion system as a whole is not.

\[
\begin{align*}
\text{CO} + \text{OH} &= \text{CO}_2 + \text{H} \quad \text{R18} \\
\text{H} + \text{O}_2 &= \text{OH} + \text{O} \quad \text{R19} \\
\text{O} + \text{H}_2 &= \text{OH} + \text{H} \quad \text{R20} \\
\text{H} + \text{H}_2\text{O} &= \text{H}_2 + \text{OH} \quad \text{R21}
\end{align*}
\]

Thus, in the primary flame zone it is possible for a state to exist where the oxygen atom concentration exceeds its equilibrium value, i.e., reaction R22 is not equilibrated.

\[
\text{O} + \text{O} + \text{M} + \text{O}_2 + \text{M} \quad \text{R22}
\]

The superequilibrium oxygen atom concentrations obtainable can therefore account for the 'prompt' NO observed first by Penimore (28) and later reported by other investigators (57, 72).

Bowman and Seery (9) found that reaction R28 becomes important in determining the formation rate of NO as fuel-rich conditions are approached. Theoretical calculations by Williams and Sarofim (85) indicate that this reaction also becomes important when equilibrium concentrations of NO are approached. Their calculations also indicate that the formation of NO via the N\textsubscript{2}O intermediate (reactions R29, R30, and R31) is negligible at flame temperatures, but increases in significance as the temperature is lowered. They found, however, that the overall rate of NO formation (reactions R25-R31) is unimportant below 1800°K, the rate at 1800°K being only a few parts per million per second.
The rate equation determined from reactions R26, R27 and R28 assuming steady-state for the nitrogen atom concentration is given below:

$$\frac{d(NO)}{dt} = \frac{\frac{k_{R26} k_{R27}(N_2)(O_2)(O) + k_{R26} k_{R28}(N_2)(O)(OH)}{k_{R26}^2(NO) + k_{R27}(O_2) + k_{R28}(OH)}} - \frac{k_{R26}^2 k_{R27}(NO)^2(O) + k_{R26}^2 k_{R28}(NO)^2(H)}{k_{R26}^2(NO) + k_{R27}(O_2) + k_{R28}(OH)}$$

In the above equation the prime indicates the rate constant of the reverse reaction. The rates of reactions R26 and R27 have been investigated by numerous researchers under a variety of conditions. Results of static systems, flow systems, and shock tube systems were critically evaluated by Bortner and Golden (8) and by a group at The University of Leeds (5, 6). Using the experimentally determined rate expressions over the temperature range covered in the different studies, a new expression which best fits all the data was developed. Over the temperature range of interest in flame studies, the forward rate constant expressions developed in the two review papers differed by about a factor of 1.8 for reaction R26 and by a factor of about 1.25 for reaction R27. These differences are generally considered small for high temperature rate constants. The rate constant expressions developed in the two review papers are given in Table II. The rate expression for reaction R28, based on the data of Campbell and Thrush, (16) is also given.

Examination of the rate constants indicates that reaction R26 is the rate limiting reaction. The high activation energy associated with this reaction makes the formation rate of NO very temperature sensitive.

The experimental results of Tuteja and Newhall (80) indicate that
in laminar diffusion flames nitric oxide formation is confined to an extremely narrow region exhibiting an appropriate combination of temperature and oxygen availability. The nitric oxide formed therein diffuses to both the fuel-rich and fuel-lean zones. This feature was also observed in the present study.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Bortner, et al.</th>
<th>Leeds Report</th>
<th>Campbell &amp; Thrush</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2 + \text{O} \rightarrow \text{NO} + \text{N} )</td>
<td>( 6.8 \times 10^{13} \exp(-75,000/\text{RT}) )</td>
<td>( 1.36 \times 10^{14} \exp(-75,400/\text{RT}) )</td>
<td>( 4.1 \times 10^{13} \exp(-800/\text{RT}) )</td>
</tr>
<tr>
<td>( \text{NO} + \text{N} \rightarrow \text{N}_2 + \text{O} )</td>
<td>( 13 \pm 4 \times 10^{12} )</td>
<td>( 3.1 \times 10^{13} \exp(-334/\text{RT}) )</td>
<td>( 1.64 \times 10^{14} \exp(-48,600/\text{RT}) )</td>
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<tr>
<td>( \text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O} )</td>
<td>( 1.5 \times 10^{13} \exp(-7900/\text{RT}) )</td>
<td>( 6.40 \times 10^{9} \exp(-3150/\text{RT}) )</td>
<td></td>
</tr>
<tr>
<td>( \text{NO} + \text{O} \rightarrow \text{N} + \text{O}_2 )</td>
<td>( 3.10 \times 10^{12} \exp(-39,900/\text{RT}) )</td>
<td>( 1.55 \times 10^{9} \exp(-38,640/\text{RT}) )</td>
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</table>
Chapter IV. PREVIOUS MODELS OF DIFFUSION FLAMES

Despite their practical importance, diffusion flames have received relatively little attention in theoretical flame studies. Part of this neglect has been due to the two-dimensional nature of most steady diffusion flames. Unlike premixed flames, they can not be made quasi-unidimensional - the solution of the appropriate conservation equations for one-dimensional systems being relatively simpler. The theoretical studies on the flame structure of cylindrical diffusion flames which do appear in the literature generally fall into one of two categories:

(a) studies which treat the flame surface as an infinitely thin surface, and

(b) studies which attempt to broaden the reaction zone by letting chemical reactions determine the thickness over which fuel and oxygen can coexist.

Figure 5 shows the system of interest. It consists of a laminar fuel jet discharging through a circular nozzle into either an infinite supply of stagnant air, or into a laminar air stream. The tubes through which the fuel and oxidizer flow are concentric and have radii of length L and R, respectively. The two gases make contact at the outlet of the inner tube; the resultant flame has a definite shape similar to that of a candle flame. The problem is to solve the appropriate conservation laws governing the transport of mass, energy and momentum in the combustion system. In discussing the previous models used to predict diffusion flame structure, attention will focus on the method used to describe the fuel concentration distribution.

The general elliptic differential equation which describes the species concentration distribution in the flow system is that obtained
Figure 5. Schematic of Theoretical Model of Confined Laminar Diffusion Flames
from the conservation law of chemical species. The steady-state form of this species balance for the axi-symmetric system under consideration is given below.

\[
\frac{\partial c_i}{\partial r} v_r + \frac{\partial c_i}{\partial z} v_z = \frac{1}{r} \frac{\partial}{\partial r} \left( D_{i,\text{mix}} r \frac{\partial c_i}{\partial r} \right) + \frac{\partial}{\partial z} \left( D_{i,\text{mix}} \frac{\partial c_i}{\partial z} \right) + R_i
\]

In this equation \( c_i \) is the concentration of chemical species \( i \) which can be consumed via chemical reaction at rate \( R_i \). The species can be transported by molecular diffusion and convection at rates proportional to its diffusivity, \( D_{i,\text{mix}} \), and the radial and axial velocities, \( v_r \) and \( v_z \). The axial and radial directions are denoted by \( r \) and \( z \) respectively. Some of the assumptions and approximations used by investigators to solve this species balance equation are discussed below.

IV.1 INFINITESIMALLY THIN FLAME SURFACE MODELS

The infinitesimally thin flame surface models, or global, one-step reaction models, have been under consideration for a number of years. Briefly, the model comprises an infinitesimally thin surface separating regimes of fuel plus products and oxygen plus products. Chemical reaction is confined to this thin sheet and a single, global, one-step infinitely fast reaction involving fuel, oxygen and reaction products is assumed to encompass the array of possible chemical reactions. At the flame boundary, reactant concentrations vanish, gradients of concentration are discontinuous and the rates of reactant diffusion into the sheet are in stoichiometric proportions. The flame sheet can thus be thought of as a source of reaction products and a sink for the reactants. In the present context, the global, one-step reaction occurring at the flame surface is

\[
CH_4 + 2O_2 \rightarrow 2H_2O + CO_2
\]

Since it is assumed that at the flame surface the above reaction is
the only reaction occurring, the rates of consumption of the fuel and oxygen are related by

\[ \dot{R}_{CH_4} = \frac{1}{2} \dot{R}_{O_2} \]  

4.2

The species conservation equations for methane and oxygen are shown below in vector form.

\[ \dot{v} \cdot \nabla C_{CH_4} = \dot{v} \cdot \left( D_{CH_4,mix} \nabla C_{CH_4} \right) + \dot{R}_{CH_4} \]  

4.3

\[ \dot{v} \cdot \nabla C_{O_2} = \dot{v} \cdot \left( D_{O_2,mix} \nabla C_{O_2} \right) + \dot{R}_{O_2} \]  

4.4

If the oxygen equation is divided by its stoichiometric coefficient and subtracted from the methane equation, the following differential equation results:

\[ \dot{v} \cdot \nabla (C_{CH_4} - C_{O_2}/2) = \dot{v} \cdot \left( D_{CH_4,mix} \nabla C_{CH_4} - D_{O_2,mix} \nabla C_{O_2} \right) \]

\[ + \dot{R}_{CH_4} - \dot{R}_{O_2}/2 \]  

4.5

If it is assumed that the fuel and oxygen have the same diffusivity, the above differential equation can be combined with equation 4.2 to give

\[ \dot{v} \cdot \nabla C_{fu} = \dot{v} \cdot \left( D_{fu,mix} \nabla C_{fu} \right) \]  

4.6

where

\[ C_{fu} = C_{CH_4} - C_{O_2}/2 \]  

4.7

Equation 4.6 is the differential equation considered by Burke and Schumann (15) to predict flame shape and height. They hypothesized that since the oxygen combined with the fuel in a fixed ratio to form a neutral product, for purposes of mathematical analysis the oxygen could be regarded as "negative fuel". Thus a concentration \( C_2 \) of oxygen is equivalent to a concentration \(-C_2/2\) of fuel. The
"fuel" concentration, \( C_{fu} \), is defined by equation 4.7. Positive fuel concentrations denote methane concentrations and negative fuel concentrations denote oxygen concentrations divided by the negative of the stoichiometric coefficient. The problem is thus reduced to the diffusion of a single gas having a certain initial distribution and subject to certain boundary conditions. The flame front is the surface where the concentration of the fuel is zero; flame height is the height at which the fuel concentration is zero at the symmetric axis.

In solving equation 4.6, Burke and Schumann made the following assumptions:

(a) radial convection and axial diffusion are negligible,

(b) the velocities of the gas and air in the tube are the same and constant in the region of the flame, and

(c) the coefficient of interdiffusion of the two gas streams is constant.

The first assumption is valid for fairly tall flames only. For short flames, axial diffusion could play an important part in determining flame shape. Large differences in velocity, at different points in the system are expected due to the high temperatures developed by the flame. The temperature variations also lead to variations in the gas diffusivity. It is possible however, that variations in the ratio \( D_{fu,mix}/v_z \) are small since any increase in velocity due to a rise in temperature could be counterbalanced by a corresponding increase in the diffusion coefficient. The last two assumptions, when considered together, are therefore heuristic and possibly legitimate. In the light of these assumptions, equation 4.6 can be expanded to give
\[
\frac{3C_{fu}}{3z} = \frac{D}{V_1} \left( \frac{3^2C_{fu}}{3r^2} + \frac{1}{r} \frac{3C_{fu}}{3r} \right)
\]

4.8

The initial condition is

\[C_{fu} = C^0_{CH_4} \quad \text{from } r = 0 \quad \text{to } r = L \quad \text{at } z = 0\]

\[C_{fu} = -\frac{C^0_{O_2}}{2} \quad \text{from } r = L \quad \text{to } r = R \quad \text{at } z = 0\]

and the boundary conditions are

\[\frac{3C_{fu}}{3r} = 0 \quad \text{when } r = 0 \quad \text{and } r = R\]

A solution of equation 4.8 which satisfies the given conditions is

\[C_{fu} = \frac{L^2}{R^2} C^0 - \frac{C^0_{O_2}}{2} + \frac{2LC^0_{O_2}}{R^2} \sum_{\lambda} \frac{J_1(\lambda L)J_1(\lambda R)e^{-\frac{DA^2}{VL}}}{[J_1(\lambda R)]^2}\]

4.9

In this equation \(C^0 = C^0_{CH_4} + C^0_{O_2}/2\) where the superscript denotes conditions at the inlet, and \(\lambda\) assumes the value of all the positive roots of the equation \(J_1(\lambda R) = 0\) where \(J_0\) and \(J_1\) are zero- and first-order Bessel functions. The shape of the flame is determined by finding those values of \(r\) and \(z\) which satisfy equation 4.9 when \(C_{fu} = 0\). The height of the flame is given by the value of \(z\) when \(r = 0\). Determining the concentration contours described by equation 4.9 is not an easy process. Burke and Schumann described a rather tedious graphical method which they used to obtain the profile of a cylindrical methane/air flame.

Savage (71) obtained the solution, however, in dimensionless form and presented the methane/air concentration distribution using dimensionless coordinates for a system whose diameter ratio \((R/L) = 10\). From his Figure 1, concentration profiles for a variety of methane/air systems can be conveniently determined. Flame shape and height can also be easily determined from his figure.
Before equation 4.9 can be used to predict flame shape and height, a value for the diffusivity of the fuel must be determined. Burke and Schumann found that the diffusivity of methane at ambient conditions gave inaccurate results. They then assumed a value for the coefficient which best agreed with a particular experiment. This value, 0.492 cm^2/sec, was found to be good for all methane/air flames they considered.

For carbon monoxide/air flames they determined a value for the diffusion coefficient of 0.671 cm^2/sec. They then experimentally probed a CO/air flame for its radial CO, CO_2 and N_2 concentration profiles. The agreement they obtained between theory and experiment afforded strong support for their theory of diffusion flames.

Barr (4) extended the work of Burke and Schumann and alleviated one of their restrictions but introduced another, perhaps more serious one. In Barr's study, the fuel and air could have different velocities. The velocity of the fuel is constant at V_1 over the inner core and the velocity of air is constant at V_2 over the annulus. Barr further postulated that no momentum transfer occurred during diffusion, i.e., the air and fuel maintained their respective velocities as they inter-penetrated. As noted by Barr, this is somewhat of a serious assumption, for without momentum transfer by diffusion the concept of viscosity would not exist for a perfect gas. The solution to equation 4.6 subject to the same initial and boundary conditions previously considered, but with v = V_1 for 0 < r < L and v = V_2 for L < r < R was determined by Barr. The shape of the flame is given by the values of r and z which satisfy

\[
\frac{R^2 - L^2}{2L} - \frac{r v_1 L}{2a v_2} = 4.10
\]
In this equation $i$ is the stoichiometric coefficient and $a$ is the oxygen index, $(a = 0.21$ for air$)$. The summation is again over the positive roots of $J_1(\lambda R) = 0$. It was found that equation 4.10 could adequately predict flame shape and height if the proper value of the diffusivity is used. In addition to representing a mean diffusivity over the range of temperatures from room temperature to the flame temperature, $D$ was also a correction factor which made up for any errors induced by the assumptions. Over inlet air velocities ranging from 4.45 to 13.05 cm/sec, and fuel velocities ranging from 0.85 to 2.61 cm/sec, Barr found that $D$ ranged only from 0.18 to 0.26 cm$^2$/sec. That $D$ should be so nearly constant is encouraging, but as reported by Barr, this may perhaps be fortuitous in view of the nature of the assumptions made.

If interest is solely in flame height, Hottel and Hawthorne (47) and Wohl, Gazley and Kapp (86) independently determined empirical equations which relate the volume flow-rate of nozzle gas to flame height. Each group applied the approach of Burke and Schumann to open diffusion flames; here, however, the neglect of the radial transport of momentum can not be accepted as a reasonable assumption. Nevertheless, by allowing two empirically determined constants to appear in their formulas, they obtained expressions which were in good agreement with the experimental data available. Hottel (46) compared the two expressions and found that the equation of Hottel and Hawthorne better fits the data over the middle range of flame lengths considered, (20 to 60 cm). The expressions of both groups stated that flame height varied approximately as the square root of the fuel flow. This non-linear behavior was attributed to the variation in the fuel diffusion coefficient. They concluded that the diffusivity determined the time necessary to completely combust the gas which emerged from the nozzle.
per second. Both groups considered the linear results obtained by Burke and Schumann as a special case of the open flame, since the flame heights reported by them fell in the region of short open flames where linear representation was a fair approximation.

The fact that the variation of the diffusion coefficient along the flame is not a completely satisfactory explanation for the non-linear behavior observed for open diffusion flames was put forth by Browne and Powell (62). They carried out an analytical investigation of mixing similarity and concluded that the assumption of a mean diffusivity by Burke and Schumann was justified, and might also be justified for the open diffusion flame. Browne and Powell (63) also found that gross departures in flame shape and height from the Burke and Schumann analytical predictions are primarily due to hydrodynamic effects which stem from density differences in the fuel and oxidant streams.

Fay (26) attempted to predict the distributions of concentration and temperature in open laminar jet diffusion flames. By assuming that (1) natural convection of the hot gases is negligible; (2) the diffusion coefficients of all the species are the same; and (3) Prandtl and Schmidt numbers are both unity, he showed that the concentration and temperature fields in the flame could be expressed as linear functions of the velocity. Concentration and temperature were thus expressed in the following form:

\[ c_i = a_i + b_i u \] \hspace{1cm} 4.11

and

\[ c_p T = e + f u \] \hspace{1cm} 4.12

where \( c_i \) represents the concentration of species \( i \); \( a_i, b_i, e \) and \( f \) are arbitrary constants determined by the boundary conditions; \( c_p \) is the
heat capacity, assumed constant; T, the temperature; and u, the velocity in the axial direction.

As did Burke and Schumann (15), Fay assumed that the region inside the flame surface consisted only of fuel, products, and inert gases while the region outside the surface consisted of oxidant, products, and inert gases. An infinitely thin boundary separated the two regimes, the concentrations of the fuel and oxidant at the boundary being zero. This boundary, conditions far from the flame, and mass and energy conservation laws serve to determine the constants in equations 4.11 and 4.12.

Once the solution of the equation of motion is determined, the temperature and concentration fields can be obtained from equations 4.11 and 4.12. The equation of motion is shown below:

\[ u \frac{\partial u}{\partial z} + v \frac{\partial u}{\partial r} = \frac{1}{\rho r} \frac{\partial}{\partial r} \left( \mu r \frac{\partial u}{\partial r} \right) \]  

4.13 

Fay obtained an approximate solution to the above equation for the case

\[ \mu = \mu_r \left( \frac{T}{T_r} \right) \]  

4.14

The reference temperature, \( T_r \), was chosen to be that at the point of maximum drag in a transverse plane at the flame tip. To use his approximate solution, the density on the symmetric axis must be assumed. Fay gives the following equation for flame length.

\[ L = \frac{3}{8\pi} \frac{1 + \varepsilon \alpha (1 + \beta)}{\varepsilon \alpha (1 + \beta)} \frac{M \rho_\infty}{\mu_r \rho_r} \left( \frac{\rho_\infty}{\rho_f} \right)^{-1} \]  

4.15

In this equation

\( \varepsilon \) = mass fraction of oxygen in the atmosphere

\( \alpha \) = mass ratio of fuel to oxygen in a stoichiometric mixture

\( \beta \) = mass ratio of diluent to fuel in the jet

\( M \) = total jet mass flow

\( \mu \) = viscosity
The subscript $r$, $f$, and $\infty$ represent conditions at the reference point, the flame surface, and ambient conditions, respectively. The function $I(\phi_\infty/P_f)$ is graphically given. Equation 4.15 shows that the predicted flame length increases linearly with the average flow velocity at the nozzle and with the square of the nozzle diameter.

Comparison of predicted flame lengths with experimental measurements indicated that Fay's model of open diffusion flames is not universally good. Agreement is adequate in the low fuel flow range ($Q < 8\text{cc/sec}$); the model tends to over-predict flame length as the fuel volumetric flow rate is increased. The neglect of axial velocities and convective forces in obtaining the theoretical solution were sighted as the major sources of error.

IV.2 REACTION ZONE BROADENING MODELS

Theoretical studies of diffusion flames which fall into this category attempt to more realistically describe the reaction zone of diffusion flames. Since reaction rates are finite, the zone of reaction must have finite thickness and possess a structure with respect to the concentration and its gradients.

Sternling and Wendt (76) developed a model of diffusion flames in which the thickness of the reaction zone was determined by the diffusion flux of oxygen into the flame front. The zone was treated as a well-stirred region. This allowed existing kinetic mechanisms developed for premixed systems to be used. Their approach followed that of Friedlander and Keller (32). These authors determined the concentration distribution for one-dimensional, quasi steady processes in which diffusion and reaction occur through two gas films. A schematic of the system of interest is shown in Figure 6. Five zones arranged parallel to the flame front were considered. The bulk of the
Figure 6. Reaction Zone Broadening Model of Sterning and Wendt (76) and Friedlander and Keller (32)
fuel and the oxidizer gas were assumed to be uniform in composition and temperature. Between these two layers the composition and temperature varied due to the diffusion of heat and mass up to and away from the flame front. In zone A, there was no oxygen, and hence, no reaction. In zone R, of small thickness relative to zones A and B, there was reaction since both fuel and oxygen existed. Friedlander and Keller employed similarity transformations and solved the differential equation describing the concentration distribution in the reaction zone for very fast, but not infinitely fast, reactions having second- and third-order kinetics on an analog computer. Sternling and Wendt used the results of Friedlander and Keller to determine the hypothetical reaction volume established during the combustion of $H_2$ and HCN mixtures. Their predicted NO concentrations were not in exact quantitative agreement with experimental data, but the predicted effects of combustion intensity and bound nitrogen conversion on NO emission showed the correct functional dependence.

Models of flat diffusion flames have been developed by several investigators. Clark (17) interpreted the original Burke-Schumann flame sheet model as a singular perturbation problem. Perturbation velocities, enthalpy, concentrations and temperature were superimposed on the free stream values of these quantities. The convective terms in the conservation equations were linearized in the manner of Oseen and the derived equations were split on the basis of velocity components which had irrotational and solenoidal forms. The uniqueness of the split had been established by previous investigators. Irrotational parts (or waves) were defined to take care of disturbances which were dominantly due to pressure changes and to temperature changes and solenoidal parts were defined which accounted for the
viscous effects of shear. The results of such manipulations have been given the names "longitudinal or pressure wave", "temperature wave", "transverse or viscous wave" and "composition wave". Similarity in the four wave equations made solution of a general form of the equations desirable. Clark applied this procedure to irreversible, Burke-Schumann-type problems, and to frozen flow problems where the time needed for a reaction-inducing collision to occur was so much longer than the time needed for an element of reactant to flow through the flame, that virtually no creation or destruction of a species occurred, and the chemical terms in the composition wave vanished. The same technique of Oseen linearization was later employed to investigate reaction-broadening diffusion flames (18, 20, 54) and equilibrium-broadening flames (19). Reaction-broadening is due to a finite reaction time for an irreversible reaction, and equilibrium-broadening is due to a finite equilibrium constant for an infinitely fast reaction. The method of matched asymptotic expansions was used to solve the system of equations. The method involves the construction of asymptotic series for the dependent variables which are valid for certain, overlapping regions in the independent variable field. The outer solution is analogous to the Burke-Schumann flame-sheet model of a fast irreversible reaction, and the inner solutions provide information on flame zone structure. Prediction of the structure of methane/oxygen diffusion flames by Melvin and Moss (54) was consistent with experiment for fuel-lean systems. Some ambiguity existed in the fuel-rich structure, however; the ambiguity could probably be traced to their choice of reaction rate constants.

Edelman (24, 25) et al. presented a mathematical model of a cylindrical, axisymmetric laminar-jet diffusion flame. Their analysis
included the effects of inertia, viscosity, diffusion, gravity and combustion on flame structure. These mechanisms were coupled in a boundary layer type formulation and solutions were obtained by an explicit finite difference technique. Edelman et al. assumed that the basic model formulation required an accurate definition of the thermal field rather than the details of the chemical species. Their selection of a chemical system in terms of the number and kinds of species was therefore somewhat arbitrary. The initial reactant temperature and the fuel/air ratio were considered to be the two principal parameters needed to characterize flame structure. The entire spectrum of equivalence ratios possible in the flame was modeled by three distinct regimes defined according to the fuel to oxygen ratio. These regimes are depicted in Figure 7 for a general hydrocarbon/air system. A 'local' equilibrium state is assumed to prevail at each point in the flow field and is referred to as "shifting" equilibrium.

In the lean regime complete oxidation of the fuel forming CO$_2$ and H$_2$O is assumed. The upper limit for this regime is the stoichiometric point where the atom balance is given by:

$$\frac{1}{2} C_H + 2C_C = C_O$$  \hspace{1cm} 4.16

where $C_i$ represents the molar concentration of species $i$. Accordingly, the lean regime is defined within the limits:

$$\frac{w_0}{M_0} > \frac{1}{2} \frac{w_H}{M_H} + \frac{2w_C}{M_C} > 0$$  \hspace{1cm} 4.17

where $w$ represents weight fraction and $M$, molecular weight. In the fuel rich side, CO appears in substantial quantities and pure fuel appears as the fuel equivalence ratio increases. In zone A, the molar concentration of water is nearly constant and carbon is oxidized
Figure 7. Schematic of Complete Combustion Chemistry Model Investigation by Edelman, et al.\(^{24}\)
to CO and CO₂. This domain is bounded by the limits:

\[
\frac{2w_C}{M_C} + \frac{1}{2} \frac{w_H}{M_H} > \frac{w_O}{M_O} > \frac{w_C}{M_C} + \frac{1}{2} \frac{w_H}{M_H}
\]

4.18

In zone B, pure fuel, CₙHₘ, appears and the mole fraction of CO decreases. The bounds are:

\[
\infty > \frac{w_C}{M_C} + \frac{1}{2} \frac{w_H}{M_H} > \frac{w_O}{M_O}
\]

4.19

Nitrogen is assumed not to react in any of the three regimes. The authors state that this model represents the thermal field quite well for the temperatures of interest. This statement was based on the excellent agreement obtained between theoretical and experimental measurements of flame height, shape and velocity. The maximum temperature contour was used to identify the flame surface.

Edelman et al. used the model to study the effects of gravity and environmental composition upon the structure of open, laminar, hydrocarbon diffusion flames. The accuracy of the predictions is excellent for normal gravity, high Reynolds number flames. The neglect of the axial diffusion of mass, energy and momentum caused their predictions for zero-gravity, low Reynolds number flames to be not as good.

Numerous investigators have used slightly modified versions of the aforementioned models to determine some of the finer aspects of heat, mass and momentum transfer in diffusion flames, as well as to determine the effects external forces have on flame structure. Goldberg and Cheng (40) used boundary layer similar solutions to investigate the fluid dynamic problems posed by laminar diffusion flames. Fendell (27) employed the method of matched asymptotic expansions considered above by Clark (17) to investigate the ignition and extinction limits in the
combustion of initially unmixed reactants. Jones et al. (49) used finite difference techniques to solve the one-dimensional conservation equations for the opposed-jet diffusion flame when a 21-reaction kinetic mechanism was employed. The effect of electric fields on such flames was their primary emphasis.

Perhaps the most used of the above models is the Burke and Schumann (15) flame sheet model. Its simplicity readily lends itself to a number of uses. Drivas (23) determined the corresponding temperature distribution assuming a unit Lewis number and predicted NO emission from the flame. The predicted effect of firing intensity and fuel and air preheat on NO emissions showed the correct functional dependency. Pun and Spalding (64) employed the Burke-Schumann model to predict flow and mixing patterns in an axisymmetric combustion chamber. Their procedure was later generalized by Gosman et al. (42). A finite-difference integration procedure was presented to solve the conservation laws with variable thermodynamic and transport properties in a variety of combustion systems in which gaseous fuel and air entered separately.

Except for the basic treatment by Pun and Spalding (64) and the 'shifting equilibrium' treatment by Edelman et al. (24,25), all of the previous models of axisymmetric diffusion flames fall into one of the following categories:

(a) Semi-empirical approaches based upon correlation of specific data, or
(b) Special treatment of the conservation equations which made it possible to obtain a closed form solution for flame structure.
The semi-empirical approaches were necessary, for they afforded good, ground-breaking works, instructional as to flame shape and height. The special treatments were limited to constant velocities, constant thermodynamic and transport properties, and a unit Lewis number. The approaches of Pun and Spalding and Edelman et al. eliminate these restrictions. Although the model of Edelman et al. predicts the thermal field quite well for axisymmetric, laminar jet diffusion flames, the concentration field is not adequately predicted, primarily because of their equilibrium restrictions. By imposing local equilibria, they predetermined the non-existence of excess radical concentrations. Superequilibrium radical concentrations may be important in determining the nitric oxide formation rate in diffusion flames.

The mathematical model of diffusion flames developed in this study follows the general approach of Pun and Spalding. Initially, the Burke-Schumann flame sheet model will be employed to determine the aerodynamic and thermal fields when allowance is made for natural convection and variable thermodynamic and transport properties. The model will then be modified to allow for partial equilibrium outside the flame surface. The theoretical model is developed and discussed in Chapter VI.
Chapter V. THE EXPERIMENTAL PROGRAM

In determining those factors which influence the formation rate of nitric oxide in flames, it is necessary to obtain the velocity, temperature, and concentration profiles established by the combustion process. The experimental program was designed to obtain the necessary information for a cylindrical, laminar, methane-air diffusion flame.

V.1 EXPERIMENTAL APPARATUS

A vertical, cylindrical diffusion flame burner was designed to produce an enclosed, steady, atmospheric laminar diffusion flame. The burner, shown schematically in Figure 8, consists of two concentric brass tubes of radii 0.635 and 2.54 cm, respectively. The tubes are packed with four, evenly-spaced, 40 mesh, stainless steel screens. These screens helped maintain a flat velocity profile inside the tubes and hence, a uniform distribution at the tube outlets. The burner plate is a solid brass disc, 7.62 cm in diameter and 1.27 cm thick, machined as shown in Figure 9. The disc was perforated with 0.159 cm diameter holes in the pattern indicated. This type of burner plate helped maintain parallel flow at the tube outlets, and the high thermal conductivity of brass assured a flat outlet temperature profile.

A pyrex glass cylinder, 5.1 cm in diameter, rests in the silicone oil liquid seal groove of the burner plate. This cylinder served to shield the flame and to define the boundaries of the combustion system.

The burner was mounted on a x-y positioner so that discrete move-
Figure 8 Schematic of Laboratory Burner
Figure 9  Schematic of the Burner Plate
ment of the burner in the x-y plane was possible. Mounted above the burner, on a x-z positioner was a quartz microprobe. Any portion of the flame or its surroundings bounded by the pyrex glass shield could be sampled by properly adjusting the positioners.

The probe was designed so as to minimize the disturbance of the flame in the sampling process. The probe permitted sampling without any visible flame disturbance upstream of the probe location. A schematic of the probe is shown in Figure 10. The portion of the probe in the flame had a maximum outside diameter of about 0.75 mm. The probe was tapered to about 0.15 mm at the tip. This type of probe was made by carefully drawing a 5 mm o.d., 2 mm i.d. quartz tube and fire polishing the tip to the desired inside diameter (about 50 μ) as described by Fristrom and Westenberg. (37)

Critical orifices were used to control the flow rates of the gases to the burner. The principal advantages of using critical orifices are:
(a). flow through the orifice depends only on the upstream pressure;
(b). a linear relation between flow and upstream pressure exist; and
(c). flow through the orifice has a low dependency on temperature.
Andersen and Friedman (1) give the following equation for flow through a critical orifice:

\[ \dot{m} = CAP_1 \left[ \frac{\delta M}{RT_1} \frac{2}{(\frac{\delta + 1}{\delta - 1})^{\frac{1}{2}}} \right] \]

where \( \dot{m} \) = mass flow rate, g/sec
\( A \) = orifice throat area, cm \(^2\)
\( P_1 \) = upstream pressure, dynes/cm \(^2\)
Figure 10  Schematic of Quartz Sampling Microprobe
\[ \delta = \text{specific heat ratio } \frac{c_p}{c_v} \]

\[ M = \text{molecular weight} \]

\[ T_u = \text{upstream temperature, } ^\circ \text{K} \]

\[ R = \text{gas constant } (8.31 \times 10^7 \text{ erg/mole-}^\circ\text{K}) \]

\[ C = \text{discharge coefficient} \]

The discharge coefficient is a constant factor which accounts for the effects of boundary layer in the orifice. This empirical constant is determined by calibration and for small orifices falls in the range 0.8 to 0.95. Calibration curves for the 0.008 cm diameter orifice used to control the methane flow rate and the 0.040 cm diameter orifice used to control the air flow rate are shown in Appendix I.

V.2 ANALYTICAL PROCEDURE

Technical grade methane (98.0% pure) and compressed air issued from their respective cylinders and were directed to the burner system. The methane was supplied by Matheson Gas Products and the air was supplied by the Middlesex Welding Company. Critical orifices controlled the flow rates of these gases to the burner; reproducibility in flow was better than four percent. Upon ignition a cylindrical methane-air diffusion flame of definite shape and height resulted. After placing the pyrex glass shield into position, the quartz microprobe was moved to the desired sampling location. A cathetometer was used to obtain the exact distance the probe was above the burner plate and a previously calibrated turn screw was used to determine the exact distance from the flame surface. The pressure inside the probe was maintained at one-half atmosphere.
This assured critical flow across the probe tip and hence, a constant sampling rate. The time inside the hot portion of the flame was calculated to be less than 0.2 msec. A discussion of the error incurred in probe sampling appears in Appendix II.

A vacuum pump was used to draw samples from the flame and pull them through a Drierite column to remove water and through two Fisher-Hamilton gas partitioners connected in series. The pressure in the partitioners was maintained at one-half atmosphere. Each partitioner was equipped with two columns and a thermal conductivity cell. The first column was packed with 30% di-2-ethylhexylsebacate on 60-80 mesh Chromosorb P. This is a liquid phase known as DEHS. The second column was packed with 42-60 mesh Molecular Sieve. The first column separated CO₂ from the sample gas; the second column separated the remaining constituents.

In the first partitioner helium was used as the carrier gas and analysis was made for CO₂, O₂ plus Ar, N₂, CH₄, and CO content. Argon and oxygen passed through the Molecular Sieve at the same rate and, therefore, reached the thermal conductivity cell at the same time. To determine the O₂ and Ar concentrations, it was assumed that argon diffused in the combustion system at the same rate as nitrogen. The argon to nitrogen ratio was thus assumed to be the same everywhere in the system – the ratio which exists in air.

The second partitioner used argon as the carrier gas and H₂ analysis was made. Similarity in thermal conductivity between hydrogen and helium made it impractical to determine hydrogen concentrations using helium as the carrier gas, and loss in sensitivity and linearity in response made it impractical to use argon as the carrier gas when determining the
concentrations of the other components in the sample.

Water analysis was made by bypassing the Drierite column and directing the sample to a General Electric Dew Point Indicator, (Cat. No. 989 4861 G). The sample gas was continuously pulled through the test chamber of the indicator which was maintained at a pressure less than 6.0 in Hg. The base of the chamber was a highly reflective surface. As the sample gas was pulled through the chamber, the temperature of the base was lowered. The temperature at which the first vapor condensed was the dew point of the sample gas at the pressure in the chamber. The mole fraction of water in the sample was determined by applying Dalton's law of partial pressures and Raoult's law, both laws being applicable at the low system pressure. From a combination of these laws the mole fraction of water in the sample is given by:

\[
y_{H_2O} = \frac{p^V_{H_2O}}{p}
\]  

where \( y \), \( p^V \) and \( p \) denote mole fraction, vapor pressure, and system total pressure, respectively.

Determination of the relative concentrations of the major flame species from the chromatograms of the gas partitioners is shown in Appendix III along with the method used to obtain the complete composition of the sample gas. Sample calculations are also given.

Nitrogen oxide analysis was made by the modified Saltzman method. The Saltzman method is a colorimetric procedure for NO\(_2\) which involves absorption of NO\(_2\) from a known volume of the gas to be analyzed in an azo-dye absorbent solution. Gas phase oxidation of NO to NO\(_2\) is necessary
if the concentration of the total oxides of nitrogen is desired. A sample from the flame was drawn through the probe into a previously purged and evacuated calibrated sample flask containing a known volume of absorbent, until the pressure in the flask was one-half atmosphere. The pressure in the flask was then brought up to one atmosphere with oxygen. A twenty-four hour period was allowed for complete oxidation of NO to NO$_2$ and for complete absorption of the NO$_2$ into the azo-dye. The intensity of the characteristic pink color of the diazosulfanilic acid formed during the liquid phase reaction between NO$_2$ and the absorbent, was read on a Baush and Lomb, Spectronic 20 spectrophotometer at 550 nm. The intensity of the pink color was proportional to the amount of NO$_2$ absorbed in the dye. A calibration curve served to determine the gas phase NO$_2$ concentration. A detailed discussion of the determination of the total oxides of nitrogen by the modified Saltzman method can be found in Appendix IV.

Three mil, platinum vs. platinum - 13% rhodium thermocouples were used to obtain the temperature profiles in the combustion system. The thermocouple assembly, shown in Figure 11, was made by flame welding three mil wires of the respective metals and coating them with silica to reduce catalytic errors. The three mil thermocouple lead wires were then welded to twenty mil platinum and platinum 13% rhodium supports wires which were connected to a Tektronix, 5103 N oscilloscope. Flame temperature profiles were obtained by carefully positioning the thermocouple bead, (4.5 mil diameter cylinder), in the combustion system and determining its exact location by means of a cathetometer and calibrated turn screw. The potential developed at the thermocouple bead was read on the oscilloscope and a thermocouple calibration table supplied by Omega.
Figure 11 Thermocouple Assembly
Engineering, Inc. served to determine the bead temperature. The gas temperature was determined from the bead temperature by applying an energy balance to the thermocouple bead and lead wires. The energy balance allowed for radiative and conductive energy exchange between the bead, lead wires and surrounding gas. The steady-state form of this energy balance is given below:

\[
\frac{d}{dx} \left( k \frac{dT}{dx} \right) + \frac{4h}{d} (T_g - T) - \frac{4\sigma}{d} \left( \epsilon_w T^4 - \alpha T_{shield}^4 \right) = 0
\]

where

\( \alpha = \) surrounding shield absorptivity

\( \sigma = \) Stefan - Boltzmann constant

\( d = \) wire diameter

\( \epsilon_w = \) wire emissivity

\( h = \) heat transfer coefficient

\( k = k(T) = \) wire thermal conductivity

\( T = T(x) = \) wire temperature

\( T_g = \) gas temperature

\( T_{\text{shield}} = \) surrounding shield temperature

\( x = \) distance along the lead wire measured from one of the support legs

The above equation assumes negligible energy exchange between the gas and the wire and that the surrounding shield is black to radiation from the wire. The absorption term, \( \alpha T_{shield}^4 \), is usually negligible.

The temperature distribution in the wire is a function of the
position of the thermocouple in the combustion system. An iterative procedure is, therefore, necessary to solve for the wire and gas temperature distributions which satisfy equation 5.3. Application of this energy balance to determine the gas temperature profiles in the system is outlined in Appendix V.

V.3 EXPERIMENTAL RESULTS AND DISCUSSION OF RESULTS

V.3.1 The Stable Species Concentrations and Temperature

Figures 12 to 15 show the resultant temperature profiles and concentration profiles of the major flame species at three heights above the burner plate, and along the symmetric axis, for the base case methane-air diffusion flame studied. The fuel was supplied at 5.7 cc/sec, and the air at 187.7 cc/sec. The luminous edge of the resultant flame closed at the burner axis 5.8 cm above the burner plate. At each location three samples were taken. Where one data point is shown, the analysis of the three samples agreed to within 2% and the average value is presented.

Figure 12a shows the radial concentration profiles 1.2 cm above the burner plate. Methane is seen to diffuse to the reaction zone where it is completely consumed. The oxygen concentration outside the flame region is near its inlet value, drops nearly to zero in the reaction zone, and increases slightly as the symmetric axis is approached. The oxygen concentration at the symmetric axis decreases as the height above the burner plate increases. This type of oxygen profiles results because near the flame base, the temperatures are low enough to allow some oxygen to penetrate the flame. At greater distances above the burner plate, the temperature in the reaction zone is high enough so that the oxygen is
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Figure 12a. Radial Concentration Profile, $z=1.2\text{cm}$
Figure 12b  Radial Temperature Profile, z=1.2 cm
completely consumed before it can penetrate the flame. A concentration
gradient in oxygen is, therefore, established inside the flame surface.
Water and carbon dioxide concentration profiles maximize inside the blue
reaction zone where the temperature profile also maximizes. In the lower
regions of the flame the carbon monoxide and hydrogen profiles first
increase with distance from the symmetric axis, go through a maximum,
then decrease to zero in the reaction zone. Higher in the flame, Figure
13a, the CO and $H_2$ profiles are essentially flat in the luminous zone
and fall to zero just outside the blue reaction zone. Near the tip of
the flame, Figure 14a, the methane is all consumed and the flame is
supported by the combustion of the carbon particles formed in the lower
regions of the flame, and by the burnout of CO and $H_2$.

Figures 12b, 13b, and 14b indicate that the temperature in the
reaction zone increases as the height above the burner is increased
until the adiabatic flame temperature is reached, then slightly decreases
until the flame tip is reached. This is due to the higher radiative
and conductive heat losses to the burner plate in the lower regions of
the flame, and to the decrease in the burning velocity near the flame
tip. From Figures 12 and 13, it is seen that the radial temperature
profile does not maximize at the edge of the luminous zone, but maximize
where the methane concentration falls to zero, about 1 1/2 millimeters
outside the luminous edge. At heights above the burner surface for
which no methane exists, the radial temperature profile appears to peak
at the edge of the luminous zone, (see Figure 13b).

The rapid disappearance of methane inside the flame surface and the
ease with which nitrogen can penetrate the flame is evident from the axial
Figure 13a Radial Concentration Profile,
$z = 24 \text{ cm}$
Figure 13b. Radial Temperature Profile, $z = 24$ cm
Figure 14a. Radial Concentration Profile

$z = 5.0 \text{ cm}$
Figure 14b. Radial Temperature Profile, $z = 5.0 \text{ cm}$
concentration profiles at the symmetric axis presented in Figure 15. The methane concentration at the centerline is less than 5% at about half the flame height, and falls to zero before the luminous zone closes at the axis. Only one centimeter above the burner port, nitrogen represents 40% of the gas at the centerline. The temperature at the symmetric axis increases from about 400°K, 0.5 cm above the port, peaks at about 1900°K at the tip of the flame, then gradually decreases as the distance away from the flame tip is increased. The temperatures at the axis from about 2.5 to 5.0 cm above the port were not obtained because of the tendency of carbon particles to collect on the thermocouple bead. These particles changed the radiative heat loss of the bead by changing its emissivity and diameter, making it impossible to make accurate radiational and conductive corrections to the bead temperature.

It can be seen from Figures 12a, 13a and 14a that the water vapor concentration profiles asymptote to a value of about one mole percent, 1.2 and 2.4 cm above the burner surface and to a value of about three mole percent, 5.0 cm above the surface. This is due to the fact that moist air was entrained into the system at the pyrex shield outlet. Primary particle track studies indicate that a recirculation cell is established between the hot flame surface and the cooler wall of the protective shield. Entrained air flows down the shield wall to about half the flame height, then curves up, towards the flame surface and flows out of the system. Flow streamlines predicted by the theoretical model confirm the existence of this recirculation cell. The model is developed and discussed in Chapter VI.

Unfortunately, the moisture content of the air in the area of the
Figure 15a. Concentration Profile Along The Symmetric Axis
Figure 15b. Temperature Profile Along the Symmetric Axis
burner was not measured. The combustion products were exhausted into the
laboratory, therefore, the water content of the air in the test area
was higher than that in other regions of the laboratory. The maximum
possible concentration of water vapor in the entrained air can be
determined from the temperature and pressure in the laboratory by assuming
that the entrained air is saturated. The average temperature and pressure
in the laboratory at the time water measurements were made at a height
of 5.0 cm above the burner surface were 26°C and 767 mm Hg, respectively.
The saturation humidity of air at 26°C is 0.0216 gm H₂O/gm dry air. This
leads to a maximum concentration of water in the entrained air of 3.36
mole percent. For heights above the burner surface equal to and greater
than five centimeters, the sampling probe was within the recirculation
cell for distances greater than 1.25 cm from the symmetric axis. The
2.8 mole percent asymptotic value of the water vapor concentration profile
is thus indicative of the moisture content of the entrained air.

V.3.2 Carbon Material Balance

The only carbon input into the system was the carbon content of the
methane fired. Therefore, the total carbon content of the gases at any
cross-section of the system must be equal to this quantity. Thus, if
\( v_z(r) \) and \( N(r) \) are the radial distributions of axial velocity and molar
density at a height \( z \) above the burner surface, and \( V_1(r) \) the axial
diffusional velocity of species 1 at the same height, then for the
cylindrical system under consideration

\[
0.75 \left( \frac{\dot{Q}_{CH_4}}{\rho_{CH_4}} \right) = 2\pi M_c \int_0^R N(r) \left[ \sum_{i=1}^k \left( v_i(r) + V_i(r) \right) \right] r \, dr
\]
In this equation \( n_i \) is the atoms of carbon in one mole of species \( i \), and the summation is over all carbon containing species. The quantities \( \dot{Q}_{CH_4} \) and \( \rho_{CH_4} \) are the volumetric flow rate and mass density of the methane fired and the factor 0.75 results from the molecular weight ratio of carbon to methane. The bracketed term under the integral sign represents the contribution each of the species makes to the total mass flux via diffusion as well as convection. In terms of the total mass flux distribution, (product of mass density and velocity), equation 5.4 can be rewritten as:

\[
0.75 \dot{Q}_{CH_4} \rho_{CH_4} = 2\pi \int_0^R \rho(r)v(r) \left[ \Sigma \frac{m_i M_i}{M} \right] rdr
\]

In this equation \( m_i \) and \( M_i \) represent the mass fraction and molecular weight of species \( i \), respectively. The summation is again over all carbon containing species. The bracketed term represents the fraction of the total mass flux, which is due to carbon and is given the symbol \( W_c \). Similarly, \( W_H \) and \( W_O \) represent the fraction of the total mass flux which is due to hydrogen and oxygen, respectively. The total grams of carbon, hydrogen and oxygen at any cross section of area available for flow is thus:

\[
G_{carbon} = 2\pi \int_0^R \rho(r)v(r) W_c(r) r dr
\]

\[
G_{hydrogen} = 2\pi \int_0^R \rho(r)v(r) W_H(r) r dr
\]

\[
G_{oxygen} = 2\pi \int_0^R \rho(r)v(r) W_O(r) r dr
\]
In these equations \( W_c(r) \), \( W_H(r) \) and \( W_O(r) \) represent the radial distributions of the carbon, hydrogen and oxygen weight fractions and \( G_i \) represents the total flow of species \( i \) in grams per second. At any point in the combustion system, these weight fractions are determined by:

\[
W_c = \frac{M_c}{M_{\text{gas}}} (y_{CH_4} + y_{CO} + y_{CO_2})
\]

5.9

\[
W_H = \frac{M_H}{M_{\text{gas}}} (4y_{CH_4} + 2y_{H_2O} + 2y_{H_2})
\]

5.10

\[
W_O = \frac{M_O}{M_{\text{gas}}} (2y_{O_2} + 2y_{CO_2} + y_{CO} + y_{H_2O})
\]

5.11

The average molecular weight of the gas is denoted by \( M_{\text{gas}} \); and \( M_c \), \( M_H \) and \( M_O \) denote the molecular weights of atomic carbon, hydrogen and oxygen, respectively.

The radial distributions of these quantities are shown in Figures 16a, b and c for the three heights above the burner surface at which the measurements of the stable species concentrations were made. At each height, the weight fraction of carbon is seen to fall to zero as the concentrations of the carbon bearing species fall to zero. The oxygen weight fraction increases from the symmetric axis and peaks outside the flame surface where the \( CO_2 \) and \( H_2O \) concentrations peak. As the \( CO_2 \) and \( H_2O \) concentrations decrease, the \( O_2 \) concentration increases; this results in a minimum in the \( O \)-profile before the oxygen asymptotic value is reached. Although a minimum is observed in the oxygen profile, due to natural convection in the radial direction, the net flux of oxygen atoms
Figure 16a Radial Distribution of Carbon, Hydrogen and Oxygen. \( Z = 1.2 \, \text{cm} \)
Figure 16b Radial Distribution of Carbon, Hydrogen and Oxygen $Z = 2.4$ cm.
Figure 16c Radial Distribution of Carbon, Hydrogen, and Oxygen \( Z = 5.0 \text{ cm} \)
is towards the flame surface, in all cases. The asymptotic value is
determined by the weight fraction of oxygen in the inlet air in the lower
regions of the system and is influenced by the weight fraction of oxygen
in the entrained air as the height above the burner surface is increased.
The hydrogen weight fraction decays from the symmetric axis as the
methane is consumed in the lower regions of the flame. The rate of decay
is slightly decreased outside the flame surface as H\textsubscript{2}O is produced. Near
the flame tip, in the region where no methane exists, the H concentration
is somewhat unchanged as H\textsubscript{2} is oxidized to H\textsubscript{2}O. The asymptotic value of
the hydrogen weight fraction profile is influenced by the moisture content
of the entrained air.

The total carbon content of the gases at heights of 1.2, 2.4, and
5.0 cm above the burner surface were obtained by numerically integrating
the right hand side of equation 5.6. Velocity and mass density distribu-
tions were obtained from the theoretical model of diffusion flames, (see
Chapter VI). The results of the numerical integration are shown in
Table III.

<table>
<thead>
<tr>
<th>Height above burner surface/cm</th>
<th>Carbon Content of Gas, gm/sec</th>
<th>Percent of carbon fired</th>
<th>W*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00280</td>
<td>100.0</td>
<td>--</td>
</tr>
<tr>
<td>1.2</td>
<td>0.00267</td>
<td>95.2</td>
<td>0.0088</td>
</tr>
<tr>
<td>2.4</td>
<td>0.00258</td>
<td>92.0</td>
<td>0.0134</td>
</tr>
<tr>
<td>5.0</td>
<td>0.00238</td>
<td>85.1</td>
<td>0.0715</td>
</tr>
</tbody>
</table>

* W = average weight fraction of unaccounted for carbon if all undetected
carbon bearing species were inside the flame surface.
Comparison of the calculated grams of carbon (second column), at heights of 1.2, 2.4 and 5.0 cm above the burner surface, with the grams of carbon fired \((z = 0)\), indicates that the carbon material balance is not closed. The third column of the table shows the percent of the grams carbon fired accounted for at each height. Three possible sources of error exist which could cause the carbon material balance not to be closed:

(i) errors in the measured \(\text{CH}_4\), \(\text{CO}_2\) and \(\text{CO}\) concentrations;
(ii) errors associated with the predicted mass flux distribution; and
(iii) errors caused by not considering the concentrations of other possible carbon bearing species.

At each sample location, three samples were drawn from the flame and analyzed; reproducibility was good. In general, the percent difference in the three samples was less than \(\pm 2.5\%\). At the luminous edge and at the flame tip, reproducibility was not as good. The maximum percent difference in the three samples was \(\pm 7.9\%\) in the \(\text{CO}_2\) concentration, 1.2 cm above the burner surface at the luminous edge of the flame. With this degree of reproducibility, it is believe that errors associated with the experimentally determined concentrations of \(\text{CH}_4\), \(\text{CO}\) and \(\text{CO}_2\) are small. As of this time, velocities in the combustion system have not been determined; therefore, no experimental data are available to validate the predicted mass flux distribution. In Chapter VI, support is given for the accuracy of the predicted mass flux based on the comparisons between the predicted and experimental temperature and nitrogen concentration profiles.

Methane pyrolysis products were present inside the flame surface and
could account for some of the undetected carbon containing species. Carbon particles were very much in evidence inside the flame surface. From thermodynamic consideration, if the temperature is high enough to decompose the fuel, carbon particles can be formed whenever the carbon to oxygen atom ratio is greater than unity. Figure 17 shows the axial and radial distributions of this ratio along the symmetric axis and at three heights above the burner surface. The carbon to oxygen atom ratio is seen to be greater than unity in the lower regions of the flame; the ratio decreases as the height above the burner surface is increased, and as the flame surface is approached — regions in which the CO, NO and H₂O concentrations are relatively higher. Pure methane is quite stable at temperatures up to about 1075°K (74), therefore, carbon formation would only be possible in those regions where \( \frac{n_c}{n_o} > 1.0 \), and the temperature is greater than 1075°K. In the flame studied, this region is roughly bounded by the volume of gas within

\[
0.18 < r < 0.28 \text{ cm} \\
1.7 < z < 1.9 \text{ cm}
\]

Visual observation of the flame led to the conclusion that carbon particles were being formed in a broader region than estimated above. Therefore, a mechanism other than thermal decomposition must also be important in the pyrolysis of methane. It is well known that small amounts of oxygen have very large effects on increasing the rate of pyrolysis of hydrocarbons. The small amounts of oxygen found inside the luminous core could thus promote methane decomposition in other regions of the flame.
Figure 17 Carbon to Oxygen Atom Ratio Distribution
Methane pyrolysis products could, therefore, account for some of the undetected carbon bearing species.

The last column of Table III shows the average mass fraction of the unaccounted for carbon if all the undetected carbon bearing species were inside the flame surface. In determining this average mass fraction, it was assumed that the predicted mass flux distribution was correct. From the mass spectrometric analysis of methane - air diffusion flames by Smith and Gordon (74), the methane pyrolysis products are present in small and relatively constant concentrations inside the luminous core. The combined concentrations of acetylene, ethylene, ethane and methyl acetylene, the major carbon bearing pyrolysis products, represented less than one-half mole percent of the combustion gases. The values in the last column of Table III are thus not indicative of the concentrations of the gaseous methane pyrolysis products. Gordon, Smith and McNesby (41) found that the only intermediate product of methane pyrolysis, in a methane - air diffusion flame, which appeared in a reasonably high concentration was hydrogen. They found no evidence of the fate of the carbon in the methane from their gas analyses and concluded that it appeared as carbonaceous particles.

A measure of the fraction of methane fired that could produce carbon particles is not readily available. Tesner, Rabinovitch and Rafalkes (77b), however, studied the formation of dispersed carbon in hydrocarbon diffusion flames. Their results showed that the dispersion of carbon black at different points of a laminar methane diffusion flame varied. The carbon black yield, reported as a percent of the carbon content of gas fired, increased with increasing height above the burner surface, peaked between 60-70% of the flame height, then gradually decreased. Measurements of
particle size made across and along the height of the flame indicated that in the lower and middle regions of the flame, particles of carbon black grew, whereas in the upper part of the flame, they were gasified and completely burned. The rate of particle formation was found to be different in different regions of the flame. A sharp increase in the formation rate was observed in the middle of the flame, resulting in the mean particle diameter in this region to be about 200 Å larger than that in the region about the flame edge (300 Å).

Tesner, et al. found that changes in nozzle diameter and in gas velocity effected the dispersion and yield of carbon black. A three-fold increase in gas velocity (0.5 to 1.5 liter/min) caused a 1.4-fold decrease in dispersion and a 1.6-fold increase in yield. A three-fold increase in nozzle diameter (1mm to 3mm) resulted in a four-fold increase in yield (0.5 to 2.0% of carbon fired).

A comparative study of the process of carbon formation in diffusion flames of methane mixed with ethane, ethylene, acetylene and propane showed that the addition of these hydrocarbons to methane always resulted in an increase in the yield of carbon black. An addition of only one percent of ethylene or acetylene to methane caused about a 18% increase in yield.

In all the cases investigated by Tesner, Rabinovitch and Rafalkes (77b), the reported yield of carbon black never exceeded two percent of the carbon content of the gas fired. Gaydon and Wolfhard (39b) report that the yield of carbon depends to some extent on the air supply and size of flame, but with natural gas, it is always low: from 1% to 5% of the possible carbon content of the fuel. At heights of 2.4 and 5.0 cm
above the burner surface, carbon particles tended to settle on the sampling probe, many times clogging the probe tip. When sampling just inside the luminous edge, carbon black was even noticed inside the probe walls. It is possible, that since the relationship between CO, CO$_2$ and solid carbon is governed by the so-called Boudouard reaction,

$$2 \text{ CO} = \text{ CO}_2 + \text{ C}^{\text{solid}}$$

the particles about the probe tip act as quenching surfaces and cause the carbon monoxide to dissociate to give CO$_2$ and solid carbon, thus increasing the percent of the carbon content of the gas fired that can appear as carbonaceous particles.

It is believed that within experimental error, the carbon material balance can be closed by considering all sources of carbon in the system: the carbon content of CH$_4$, CO$_2$ and CO; the carbon content of the gaseous methane pyrolysis products; the carbon content of the solid particles formed in the pyrolysis process; and, the solid carbon formed due to the possible dissociation of CO in the probe via the Boudouard reaction.

V.3.3 Hydrogen Material Balance

If the only hydrogen bearing species entering the combustion system were methane, at any cross section of the area available for flow, the following relation would be satisfied:

$$\frac{M_H \int_0^R W_c(r) v_z(r) \rho(r) r \, dr}{M_c \int_0^R W_H(r) v_z(r) \rho(r) r \, dr} = 0.25$$

5.12
This is a statement that the carbon to hydrogen atom ratio should be the same as that in methane, one to four. However, as explained above, the air entrained into the system at the pyrex shield outlet contained some water vapor, therefore, this ratio should be less than 0.25. The predicted mass flux distribution was used in the numerical determination of the integrals in equations 5.7 and 5.12 to obtain the total hydrogen content, and the carbon to hydrogen atom ratio at various heights in the combustion system. The results are shown in Table IV.

Comparison of the hydrogen content of the gas (column 2) at heights of 1.2, 2.4 and 5.0 centimeters above the burner surface, with the hydrogen content of the gas fired (z = 0), indicates the degree to which the water content of the entrained air influenced the hydrogen content of the gas at that particular level. The third column of Table IV shows to what extent the hydrogen material balance can be closed if the integral in equation 5.7 is evaluated only out to that radius at which the hydrogen mass fraction reached its asymptotic value. The fourth column shows to what extent the balance can be closed if the integral is evaluated out to the radius which includes all material that was fired to the burner. The values in this column are influenced by the hydrogen which diffused from the recirculation cell towards the flame surface. Columns three and four bracket the percent of the hydrogen fired accounted for. These values lend considerable support to the accuracy of the experimentally determined $H_2$ and $H_2O$ concentrations, and to the validity of the predicted mass flux distribution.

From the values in the fifth column of Table IV, it is seen that the ratio of carbon atoms to hydrogen atoms is slightly greater than 0.25
### TABLE IV. Hydrogen Content of Combustion Gas and Carbon to Hydrogen Atom Ratio

<table>
<thead>
<tr>
<th>Height above burner surface, cm</th>
<th>Hydrogen content of gas, gm/sec</th>
<th>Percent of H fired* accounted for out to $W_H$ asymptote</th>
<th>Percent of H fired** accounted for out to recirculation cell</th>
<th>$(C/H)^{+}$, $r = r_f$</th>
<th>$(C/H)^{+}$, $r = R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0009325</td>
<td>100.0</td>
<td>100.0</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>1.2</td>
<td>0.001072</td>
<td>97.5</td>
<td>111.7</td>
<td>0.26</td>
<td>0.21</td>
</tr>
<tr>
<td>2.4</td>
<td>0.001094</td>
<td>96.0</td>
<td>107.6</td>
<td>0.27</td>
<td>0.20</td>
</tr>
<tr>
<td>5.0</td>
<td>0.001407</td>
<td>101.9</td>
<td>101.9</td>
<td>0.31</td>
<td>0.15</td>
</tr>
</tbody>
</table>

* Integral in equation 5.7 evaluated out to radius at which $W_H$ profile reached its asymptotic value.

** Integral in equation 5.7 evaluated out to radius which included all material outside of recirculation cell.

\[
+C/H = \frac{M_H \int_0^R W_c(r)v_z(r) \rho(r) \, r \, dr}{M_c \int_0^R W_H(r)v_z(r) \rho(r) \, r \, dr}
\]
inside the luminous flame core. This suggests that hydrogen bearing species diffuse more rapidly than the carbon bearing species to the fuel-lean side of the flame surface. The effect appears to be more pronounced as the height above the burner surface is increased. Since the methane pyrolysis products are present in small and relatively constant concentrations inside the luminous core, about two moles of hydrogen are produced for each mole of methane which decomposes. The hydrogen, which diffuses relatively faster than the other molecules, is converted to water as it reaches the primary reaction zone. Based on gradients to and from the reaction zone, water preferentially diffuses to the lean side of the flame surface, causing the carbon to hydrogen atom ratio inside the flame surface to be greater than the carbon to hydrogen atom ratio of methane.

The last column of Table IV shows the combined effect of the moisture content of the entrained air and of the formation of carbon particles on the gas phase carbon to hydrogen atom ratio. Both effects lead to a decrease in this atom ratio. The moisture in the entrained air increases the hydrogen content of the gases fed to the system, and the formation of carbon particles decreases the carbon content of the gas phase.

The experimentally determined temperature and concentration profiles of Figures 12, 13, 14 and 15 have been discussed in some detail. The values are believed to be accurate to within ± 10% inside the flame surface and better than ± 5% outside the surface where the measurements were not influenced by the presence of carbon particles. Closure of the hydrogen material balance lends considerable support to the validity of the predicted mass flux distribution.
The primary fuel was shown to disappear inside the luminous core of the flame mainly by reactions at the flame surface, but also by pyrolysis. Where temperatures are high enough for reaction, methane and oxygen co-exist only in a small annular region which is nominally two millimeters thick. Reaction is most intense here, and product concentration and temperature both maximize in this region. In the lower regions of the flame, CO and H$_2$ are both intermediate combustion products whose concentrations maximize inside the luminous core and fall to zero in the reaction zone where they are oxidized to CO$_2$ and H$_2$O, respectively. High in the flame after the methane concentration has fallen considerably, CO and H$_2$ become the primary fuel and their concentrations are maximum at the symmetric axis and fall to zero as the luminous edge is approached.

The adiabatic flame temperature is reached in the reaction zone, and the temperature gradients away from this region are quite steep. In Chapter VI it will be shown that the measured temperatures inside the luminous core could possibly be influenced by the fact that carbon particles may have settled on the thermocouple bead affecting the bead emissivity. The reported temperatures are thought to be correct to within ten percent.

The experimentally determined concentration and temperature profiles will be used to validate the theoretical model of diffusion flames developed in Chapter VI. In Chapter VII, the theoretical model and experimental data are combined to investigate the factors which influence nitric oxide formation in diffusion flames.
Chapter VI. THE THEORETICAL MODEL

In the experimental program outlined in Chapter V, concentration and temperature profiles established by the methane-air diffusion flame under consideration were obtained and extensively evaluated. Since all possible flames cannot be investigated in quite this detail, it would be useful to have a tool which could predict the effects of various parameters on flame macrostructure and, at least qualitatively, on nitric oxide production. The development of such a tool has been undertaken in this study. A mathematical model of diffusion flames which makes allowances for natural convection, variable thermodynamic and transport properties, radiative heat losses and chemical reaction effects is being considered. Upon completion of the model, the effects of flow rate, fuel and air preheat, nozzle size and other factors which determine diffusion flame macrostructure and nitric oxide formation rate can be investigated without the costly and time consuming effects of actual experimentation. The temperature and concentration profiles presented in Chapter V serve to validate this theoretical model.

As stated in Chapter IV, the model is developed in two stages. In the first stage, the Burke-Schumann flame sheet concept is employed in determining the aerodynamic and thermal fields when allowance is made for natural convection and variable thermodynamic and transport properties. In the second stage of development, the model is modified to allow for reaction zone broadening. The concept of partial equilibrium will be employed in determining the rates of appearance and disappearance of the radicals and stable flame species. The first stage of development
has been completed and is discussed below in detail.

VI.1 DESCRIPTION OF THE MODEL

The model is concerned with an ideal mixture of methane, air and their combustion products. The combustion system, represented in Figure 18, closely parallels the experimental system of Chapter V. It essentially consists of two concentric tubes of radius L and R through which the fuel and air flow, respectively. When the two gases make contact at the tube outlets, a diffusion flame of definite shape results. As in the experimental set-up, the combustion system is shielded. This helps to define the region of interest and allows appropriate conditions along the boundaries to be specified.

VI.2 CONSERVATION LAWS

The complete set of equations which describe the system are those derived from the well-established, conservation laws of mass, momentum, and energy transfer. Derivations of the equations can be found in most text on transport phenomena and is omitted here. The steady-state forms of the conservation equations which describe the axisymmetric case under consideration are presented below.

Continuity Equation:

\[ \nabla \cdot \overrightarrow{G} = 0 \]  \quad (6.1)

Conservation of Momentum:

radial direction: \[ \nabla \cdot (\overrightarrow{G} v_r + \overrightarrow{r}) + \frac{\delta P}{\delta r} = 0 \]  \quad (6.2)
Figure 10 Schematic of Theoretical Model
axial direction: \[ \nabla \cdot (\bar{G} v_z + \tau_z) + \frac{\delta P}{\delta z} - \rho g = 0 \quad 6.3 \]

Conservation of Energy:
\[ C_p (\bar{G} \cdot \nabla T) - \nabla \cdot (k \nabla T) - Q_{\text{gen}} + Q_{\text{loss}} = 0 \quad 6.4 \]

Conservation of Chemical Species j:
\[ \nabla \cdot (\bar{G} w_j - \rho D_{j,\text{mix}} \nabla w_j) - \dot{R}_j = 0 \quad j = 1,N \quad 6.5 \]

The terms used in the above equations are identified in Table VI., located at the end of this chapter.

The equation of continuity is a statement of the fact that the rate of creation of matter is zero. The momentum equations represent a force balance on an arbitrary control volume in the system. It states that shear stresses and pressure and gravitational forces acting on the control volume are balanced by the net inflow of momentum into the control volume. In the conservation of energy equation allowance is made for the transport of energy by convection and conduction, and for the generation and loss of energy due to chemical reaction and radiation. Equation 6.4 neglects viscous dissipation terms, compression terms and diffusion-thermo or Dufour effect terms, all of which are negligible in comparison to the terms retained, for the system of interest. The chemical species equation makes allowances for the convection and the concentration driven diffusion of species j, and for the appearance or disappearance of species j due to chemical reaction. Pressure driven diffusion and thermal driven diffusion, the Soret effect, are assumed to be second order effects and are omitted from the chemical species conservation equation. The solution to the above set of non-linear partial
differential equations leads to the determination of composition, velocity, temperature and pressure everywhere in the system. Finding the solution is a rather involved and tedious process which requires rewriting the conservation equations in finite-difference form and using iterative techniques.

Two additional parameters can be defined which will aid in finding the solution to the above set of equations. The first of these is the vorticity $\omega$, a measure of the amount of counter-clockwise rotation possessed by the fluid. It is defined as:

$$\omega = \frac{\delta v}{\delta z} - \frac{\delta v}{\delta r}$$  \hspace{1cm} 6.6

The stream function $\psi$, is the second parameter and is simply a means of replacing the radial and axial components of the mass flux vector by a single function. It is defined as:

$$\frac{rG}{r} = -\frac{\delta \psi}{\delta z} \quad \frac{rG}{z} = \frac{\delta \psi}{\delta r}$$  \hspace{1cm} 6.7

Such a definition satisfies the continuity equation. The vorticity and stream function are related as follows:

Stream Function Equation:

$$\frac{\delta}{\delta z} \left( \frac{1}{r \rho} \frac{\delta \psi}{\delta z} \right) + \frac{\delta}{\delta r} \left( \frac{1}{r \rho} \frac{\delta \psi}{\delta r} \right) = -\omega$$  \hspace{1cm} 6.8

Formulation of the vorticity transport equation serves to eliminate the pressure as one of the dependent variables in the above set of
equations. By differentiating the r-direction contribution of the momentum equation with respect to z, and the z-direction contribution with respect to r, and subtracting the two, an equation independent of pressure results. The final equation is termed the vorticity transport equation and is presented below:

\[
\nabla \cdot \left( \frac{\vec{G}}{r} \right) + \frac{1}{r} \nabla \left( \frac{v_r^2 + v_z^2}{2} \right) \cdot \text{iso} = \frac{1}{r^2} \nabla \cdot \left[ r^2 \nabla (\mu \frac{\partial}{r}) \right] + \frac{1}{r} \frac{\partial}{\partial r} (\rho g) + S_{\omega} \quad 6.9
\]

The quantity \( S_{\omega} \) is identical to zero for incompressible flow. It involves gradients of the viscosity and density and is nearly zero for all fluid flow. It is assumed to be negligible in this mathematical description of diffusion flames.

The conservation equations of energy and mass, the stream function equation, and the vorticity transport equation, (equations 6.4, 6.5, 6.8 and 6.9) represent the set of equations which are used to describe the various distributions in this theoretical model of diffusion flames. This set of equations is made non-dimensional by considering the following dimensionless groups, which represent ratios of various forces or effects in the system.

Reynolds No.:

\[
\text{Re} = \frac{\text{inertial forces}}{\text{viscous forces}} = \frac{4 \psi_{\text{wall}}}{\mu_{\text{ref}} R}
\]

Grashof No.:

\[
\text{Gr} = \left( \frac{R}{e} \right)^2 \frac{\text{buoyancy forces}}{\text{inertial forces}} = \frac{2 \rho_{\text{ref}} g R^3 (T_{\text{ref}} - T)}{T_{\text{ref}}^2 \mu_{\text{ref}}} \]

Prandtl No.:

$$Pr = \frac{1}{Re} \frac{\text{heat transport by convection}}{\text{heat transport by conduction}} = \frac{\mu_{\text{ref}} C_{\text{p,ref}}}{k_{\text{ref}}}$$

Schmidt No.:

$$Sc = \frac{1}{Re} \frac{\text{mass transport by convection}}{\text{mass transport by diffusion}} = \frac{\mu_{\text{ref}}}{\rho_{\text{ref}} (D_{j,\text{mix}})_{\text{ref}}}$$

Normalized Dependent Variable:

Temperature: \( \Theta = \frac{T}{T_o - T_{\text{ref}}} \)

Stream function: \( \psi^* = \psi/\psi_{\text{wall}} \)

Vorticity: \( \omega^* = \frac{\omega}{(\psi_{\text{wall}}/R^3 \rho_{\text{ref}})} = \frac{\omega}{\omega_{\text{scale}}} \)

The physical properties are normalized by their values at some reference temperature, \( T_{\text{ref}} \), and the radial and axial coordinates are normalized by the radius of the outer tube, \( R \). In the above ratios, the subscript \( \text{ref} \) refers to the property evaluated at some temperature, \( T_{\text{ref}} \), and the system total pressure.

The mass, energy and vorticity transport equation can each be expanded and expressed in terms of the stream function and the above dimensionless quantities. After minor manipulation, each equation can be rewritten in the following general elliptic equation form:
\[ a_\phi \left[ \frac{\delta}{\delta \eta} \left( \frac{\delta \psi^*}{\delta \xi} \right) - \frac{\delta}{\delta \xi} \left( \frac{\delta \psi^*}{\delta \eta} \right) \right] - \frac{\delta}{\delta \eta} \left[ b_\phi \xi - \frac{\delta}{\delta \eta} (c_\phi \psi) \right] - \frac{\delta}{\delta \xi} \left[ b_\phi \xi - \frac{\delta}{\delta \xi} (c_\phi \psi) \right] + \xi d_\phi = 0 \quad 6.10 \]

In the above equation \( \phi \) denotes the main dependent variable and \( a_\phi \), \( b_\phi \), \( c_\phi \) and \( d_\phi \) denote various parameters associated with a particular \( \phi \). The first bracketed term represents the convective contributions to the net inflow of \( \phi \) into an arbitrary control volume in the flow field. The second two bracketed terms represent the net inflow of \( \phi \) into the control volume by molecular motion; and the final term represents the net rate of change in \( \phi \) per unit volume, due to any sources or sinks of \( \phi \). Table V gives the parameters \( a_\phi \), \( b_\phi \), \( c_\phi \), and \( d_\phi \) associated with each \( \phi \).

VI.3 BOUNDARY CONDITIONS

The above equations are solved subject to the following boundary conditions:

a. Specified inlet conditions  
b. Symmetry about the centerline  
c. Constant stream function along the wall and centerline  
d. Wall impervious to matter (and heat if adiabatic)  
e. Constant wall temperature (if not adiabatic)  
f. No slip at the wall  
g. Zero axial gradients at the exit if no recirculation. If recirculation, the composition of the fluid entering the system at the exit boundary is that of air.
Table V. Parameters $a_\phi$, $b_\phi$, $c_\phi$ and $d_\phi$ to be used in the General Elliptic Equation for a Specified $\phi$.

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>$a_\phi$</th>
<th>$b_\phi$</th>
<th>$c_\phi$</th>
<th>$d_\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi^*$</td>
<td>0</td>
<td>$\frac{1}{\xi^2 \rho^*}$</td>
<td>1</td>
<td>$-\omega^*/\xi$</td>
</tr>
<tr>
<td>$\theta$</td>
<td>$\frac{1}{4} \text{RePrCp}^*$</td>
<td>$k^*$</td>
<td>1</td>
<td>$\frac{R^2}{\Delta T_f \text{k ref}} (Q_{\text{gen}} - Q_{\text{loss}})$</td>
</tr>
<tr>
<td>$\omega_1$</td>
<td>$\frac{1}{4} \text{ReSc}$</td>
<td>$\rho^* D_{1,\text{mix}}^*$</td>
<td>1</td>
<td>$\frac{-R^2}{\rho_{\text{ref}} (D_{1,\text{mix}} \text{ref})}$</td>
</tr>
<tr>
<td>$\frac{w^*}{\xi}$</td>
<td>$\frac{1}{4} \xi^2 \text{Re}$</td>
<td>$\xi^2$</td>
<td>$\mu^*$</td>
<td>$\frac{T_f}{\Delta T_f} \frac{4 \text{Gr} \delta D^*}{\text{Re} \delta \xi}$</td>
</tr>
</tbody>
</table>
VI.4 FINITE-DIFFERENCE REPRESENTATION

The finite difference representation of the general elliptic equation is derived by a method due to Pun and Spalding\(^{64}\) and outlined in their text with Gosman et al.\(^{42}\). The method is called integration over finite areas and has the advantage over other difference schemes in that it ensures that the conservation laws are obeyed over arbitrarily large or small portions of the flow field. The method is best illustrated by considering the following diagram:

![Diagram of finite difference representation](image)

The general elliptic equation is to be applied at the node point \(P\), which is surrounded on the north, south, east and west by the node points \(N, S, E\) and \(W\). The node \(P\) is representative of the entire area enclosed by the dashed lines. Since an axisymmetric system is being considered, the node \(P\) is actually representative of the volume formed by the rotation of the rectangle through an angle of \(2\pi\) radians about the axis of symmetry. The elliptic equation is integrated about this volume. In doing so, when integrating with respect to \(\xi\) along \(SW\ SE\), the physical properties along this boundary are assumed constant at the arithmetic average of
the values computed at P and S. The value of the dependent variable along this side depends on the direction of flow. If flow is from S to P, the dependent variable takes the value at S; if flow is from P to S, it takes the value at P. Axial derivatives along this boundary are estimated from the values at P and S. This allows the necessary integration along this side to be performed. Integration along the other boundaries is in an analogous manner. The complete integration technique is described in Appendix VI.

The resultant finite difference equation is written in the form:

\[
\phi_P = C_W \phi_W + C_E \phi_E + C_N \phi_N + C_S \phi_S + D \tag{6.11}
\]

The coefficients, \( C_i \), are functions of the thermodynamic and physical properties, the stream function, and the radial and axial coordinates. The coefficients are all positive and sum to unity for the stream function, temperature and mass fraction. The above equation shows that the dependent variable at grid point P is just a weighted average of the variables about the point P, supplemented by a source term, D. There is one such equation for each variable at each grid point in the flow field. This set of non-linear algebraic equations is solved by an alternating-direction-implicit procedure commonly referred to as A.D.I. The procedure is due to Peaceman and Rachford \(^{(60)}\) and the merits of such a technique have been discussed by numerous investigators. \(^{(48)(81)(82)}\) For the class of problems to which equation 6.10 belongs, the A.D.I procedure was found to have a higher rate of convergence than the iterative methods
referred to as Jacobi, Gauss-Seidel, and successive over-relaxation. 
Application of the A.D.I. procedure to the set of equations represented 
by equation 6.11 is given in Appendix VI.

VI.5 APPLICATION OF THE BURKE-SCHUMANN FLAME SHEET CONCEPT

In the Burke-Schumann flame sheet model discussed in Chapter IV, 
the assumption is made that the chemical reactions which take place in the 
reaction zone are infinitely fast. Thus, the reaction zone has infinitesimal 
thickness. The fuel and oxygen diffuse to this infinitesimal flame surface 
in stoichiometric proportions and products diffuse away. The only heat 
release is, therefore, at the flame surface and changes in composition 
are due solely to the interdiffusion of reactants and products. This 
assumption reduces the number of species equations needed to determine 
flame shape, for now, a single global reaction can be used in place of the 
array of possible reactions which can occur in the reaction zone. The 
global reaction is of the form:

\[ 1 \text{ (fuel)} + i \text{ (O}_2\text{)} \rightarrow (1 + i) \text{ (Products)} \]

Thus, at the flame surface, one gram of fuel reacts with \( i \) grams of oxygen 
(the stoichiometric amount), to form one plus \( i \) grams of products. The 
relation between the rates of reaction are given below:

\[ \dot{R}_{\text{fuel}} = \frac{1}{i} \quad \dot{R}_{O_2} = \frac{1}{1+i} \quad \dot{R}_{\text{prod}} \]

6.12
From equation 6.5, the conservation equations for fuel and oxygen are:

\[ \nabla \cdot \left( \overline{G} w_{\text{fuel}} - \rho_{D_{\text{fuel, mix}}} \nabla w_{\text{fuel}} \right) - \frac{\dot{R}_{\text{fuel}}}{i} = 0 \quad 6.13 \]

\[ \nabla \cdot \left( \overline{G} w_{O_2} - \rho_{D_{O_2, mix}} \nabla w_{O_2} \right) - \frac{\dot{R}_{O_2}}{i} = 0 \quad 6.14 \]

If it is assumed that the diffusion coefficients of the fuel and oxygen are the same, then subtraction of the above equations, after dividing the oxygen equation by \(i\), results in:

\[ \nabla \cdot \left[ \overline{G}(w_{\text{fuel}} - w_{O_2}/i) - \rho_{D_{\text{fuel, mix}}} \nabla (w_{\text{fuel}} - w_{O_2}/i) \right] - \left[ \frac{\dot{R}_{\text{fuel}}}{i} - \frac{\dot{R}_{O_2}}{i} \right] = 0 \quad 6.15 \]

Noting that the last bracketed term on the left is zero and defining a new variable \(w^*\) such that

\[ w^* = w_{\text{fuel}} - w_{O_2}/i, \quad 6.16 \]

equation 6.15 can be rewritten:

\[ \nabla \cdot \left( \overline{G} w^* - \rho_{D_{\text{fu, mix}}} \nabla w^* \right) = 0 \quad 6.17 \]

With this flame sheet assumption, fuel and oxygen cannot exist at the same point in the flow field. Positive values of \(w^*\) denote fuel concentrations
and negative values represent oxygen concentrations divided by the negative of the stoichiometric coefficient, i.e. The locus of $w^* = 0$ represents the fuel-oxygen interface, or the flame surface.

In combining equations 6.13 and 6.14 to give equation 6.15, it was assumed that the diffusion coefficients of the fuel and oxygen were the same. However, the model is not restricted to this. When solving equation 6.17 for the distribution of $w^*$ in the combustion system, the diffusion coefficient of the fuel is used whenever $w^* > 0$, and that of oxygen is used for $w^* < 0$.

The amount of heat release at the flame surface can be determined from the diffusive and convective fluxes of the fuel to the flame surface. The heat generation term in equation 6.4 must have the units cal/cc-sec, thus,

\[
Q_{\text{gen}} = \left[ \text{Rate of consumption of the fuel at the flame surface} \right] \left[ \text{Heat of combustion of the fuel} \right]
\]

6.18

In obtaining the rate of consumption of the fuel at the flame surface assume that the flame surface passes through the control area represented by the node point P.
In the above diagram, the north-east corner of the rectangle is outside the flame surface. Pure fuel crosses the south and west sides of the rectangle. Let \( f_k \) be the fraction of the \( k^{th} \) side of the rectangle through which the fuel passes. Thus,

\[
\begin{align*}
    f_w &= f_s = 1.0 \\
    f_n &= \frac{w^{*}}{w^{*}_n - w^{*}_e} \\
    f_e &= \frac{w^{*}}{w^{*}_s - w^{*}_e}
\end{align*}
\]

In the above relations \( n, s, e \) and \( w \) denote the north, south, east and west sides of the rectangle which encloses the node point \( P \); and \( w^{*}_{1,m} \) represents the mass fraction of the "fictitious fuel" at the \( 1,m \) corner of the rectangle. The rate of consumption of the fuel within the rectangle can be determined from a mass balance on the fuel. If \( G_r \) and \( G_z \) represent components of the mass flux vector and if the sides of the rectangle are denoted by \( \Delta r \) and \( \Delta z \), then a mass balance on the fuel is given below:

\[
\begin{align*}
    \left[ G_r^{*} w - D\rho \frac{\Delta w^{*}}{\Delta r} \right] f_w \Delta z - \left[ G_r^{*} w - D\rho \frac{\Delta w^{*}}{\Delta r} \right] f_e \Delta z \\
    + \left[ G_z^{*} w - D\rho \frac{\Delta w^{*}}{\Delta z} \right] f_s r\Delta r - \left[ G_z^{*} w - D\rho \frac{\Delta w^{*}}{\Delta z} \right] f_n r\Delta r = - \cdot \cdot \cdot \\
\end{align*}
\]

6.19
The subscripts on the bracketed terms denote the boundaries at which the fluxes should be evaluated.

Equation 6.18 can be rewritten as follows:

\[
Q_{\text{gen}} = - \frac{\cdot}{R_{\text{fuel}}} \Delta H_{\text{fuel}}
\]

6.20

Thus, the heat generated at the flame surface can be determined from the convective and diffusive fluxes of the "fictitious fuel" and the heat of combustion of the fuel fired by combining equations 6.19 and 6.20.

The above model was used to predict the shape and height of various methane-air flames issuing from a burner having the same dimensions as those of the experimental burner (inner radius = 0.635 cm; outer radius = 2.54 cm; shield diameter = 5.08 cm). The global reaction considered was

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}
\]

R34

On a weight basis, the above reaction translates to

\[
[1 \text{ gm}] \text{CH}_4 + [4 \text{ gm}] \text{O}_2 \rightarrow [2.75 \text{ gm}] \text{CO}_2 + [2.25 \text{ gm}] \text{H}_2\text{O}
\]

The stoichiometric coefficient to use in equation 6.16 is thus 4.0, and the fuel-oxygen mass fraction, \(w^*\), is given by:

\[
w^* = w_{\text{CH}_4} - \frac{1}{4} w_{\text{O}_2}
\]

6.21
Flame height was taken as that distance above the burner port at which \( w^* = 0 \) at the symmetric axis. Transport and thermodynamic properties needed in the model were obtained from the literature and presented in Appendix VII.

In Figure 19, a comparison is made between predicted and experimentally determined flame heights. Experimentally, flame height was taken as that distance above the burner port at which the luminous zone of the diffusion flame closed at the burner axis. The data agrees with that of other investigators in that at low fuel flow rates, flame length is proportional to the volumetric fuel flow rate. The model over-predicts flame height by about 12% when reaction R34 is used as the global reaction. This is not surprising because not only does the locus of \( w^* = 0 \) represent the stoichiometric fuel-oxygen interface, it also represents the surface where complete reaction occurs, i.e., where one mole of carbon dioxide and two moles of water vapor are produced for each mole of methane consumed. Analysis of the concentration profiles presented in Chapter V shows that this does not occur at the luminous flame surface. Carbon monoxide and hydrogen are also present which subsequently burnout to \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) outside the luminous surface. The solid line in Figure 19 should therefore represent the height at which the concentrations of \( \text{CO} \) and \( \text{H}_2 \) at the symmetric axis fall to zero. From the experimental data (fuel Reynolds number of 41), the mole fraction of \( \text{CO} \) at the symmetric axis, 6.6 cm above the burner port (\( L/D = 5.2 \)) is 0.001, and that of \( \text{H}_2 \) is zero. This lends some support to the validity of the model.

The dashed line in Figure 19 represents the predicted flame height when a value of 1.76 is used as the stoichiometric oxygen coefficient. This
Figure 19 Comparison of Predicted and Experimentally Determined Flame Heights
value is seen to result in predicted flame heights which agree with the experimentally observed ones. An oxygen stoichiometric coefficient less than two indicates incomplete combustion at the flame surface and also indicates that the reactions at the flame surface result in an increase in the total number of moles.

Figure 20 shows how the predicted flame shape compares with that experimentally observed. The experimentally observed shape was obtained from a photograph of the actual flame. Shown as circles is the profile of the luminous flame surface which closes at the symmetric axis 5.8 cm above the burner port. The squares represent the profile of the visible edge of the blue reaction zone. The blue hue of the reaction zone is associated with the burnout of carbon monoxide; hence, the edge of the reaction zone roughly corresponds to the surface where the CO concentration falls to zero. The predicted flame shape, with $i = 2$, appears to adequately outline the locus of the edge of the reaction zone. The dashed line in the figure represents the predicted flame shape when $i = 1.76$. It appears that the luminous edge of the flame can be matched by the proper choice of the oxygen stoichiometric coefficient.

The purpose of the model is not so much as to be able to predict the shape of the luminous flame surface, but to be able to predict the temperature, concentration and velocity fields established during the combustion process. As of this time, measured velocity profiles are not available to validate the predicted velocity field, but good prediction of the temperature and concentration fields would yield considerable support for the validity of the velocity field. Figures 21, 22 and 23 show the comparison between predicted (with $i = 2$) and experimentally
Figure 20 Comparison of Predicted and Experimentally Determined Flame Shape
determined concentration and temperature profiles at three heights above the burner surface. From these figures the following observations are made:

(i) the model overpredicts the methane concentration;
(ii) the predicted oxygen concentration profiles appear to be shifted to the left of the experimentally determined ones at 1.2 and 2.4 cm above the burner port;
(iii) the predicted nitrogen concentrations are too high just outside the flame surface and too low near the symmetric axis;
(iv) the predicted temperatures inside the flame surface exceed the experimentally determined temperatures; and,
(v) the temperature profiles at 1.2 and 2.4 cm seem to be shifted 0.5 mm to the left and 0.25 mm to the right, respectively.

These observations are associated with the Burke-Schumann flame sheet concept; the fourth observation is also associated with radiational losses and energy absorbed by endothermic reactions inside the luminous core. Each of these characteristics are discussed below.

In the model, the only region for consumption of the methane is at the flame surface where complete combustion takes place instantaneously. No allowance is made for pyrolysis of the fuel inside the flame surface or for the production and subsequent consumption of CO or H₂. Thus, from the viewpoint of the CO₂ and H₂O products, the "fuel" which diffused to the flame surface consisted of methane, hydrogen, carbon
Figure 21a Comparison of Predicted and Experimentally Determined Radial Concentration Profiles, \( z = 1.2 \) cm.
Figure 21b Comparison of Predicted and Experimentally Determined Radial Temperature Profile, $z = 1.2$ cm.
Figure 22a Comparison of Predicted and Experimentally Determined Radial Concentration Profiles: $z = 2.4$ cm.
Figure 22b Comparison of Predicted and Experimentally Determined Radial Temperature Profile: $z = 2.4$ cm
Figure 23a Comparison of Predicted and Experimentally Determined Radial Concentration Profiles, $z = 5.0$ cm.
Figure 23b Comparison of Predicted and Experimentally Determined Radial Temperature Profile, $z = 5.0$ cm
monoxide and pyrolysis products. Therefore, the predicted "fuel" profile should lie above the experimentally determined methane profile. It was found that the predicted profile was bracketed by the experimentally determined \( \text{CH}_4 \)-profile and \( \text{(CH}_4 + \text{CO} + \text{H}_2) \)-profile. The dashed curve in each of the figures represents the combined mass fractions of \( \text{CH}_4 \), \( \text{CO} \) and \( \text{H}_2 \). The agreement between the dashed curve and the predicted "fuel" curve is quite good 5.0 cm above the burner surface. It was also found that if allowance is made for incomplete combustion at the flame surface \((i < 2.)\), the experimentally determined \( \text{CH}_4 \)-profile could be matched.

The discrepancy in the predicted oxygen concentration profile is attributed to the combined effect of using the Burke-Schumann flame sheet concept and in approximating the derivatives. Since oxygen is treated as "negative fuel," the radial "fuel" concentration profile has an inflection point at the flame surface. The second derivative of \( w^* \) with respect to \( r \) thus vanishes. When the methane and oxygen gradients at the flame surface are steep, the error associated with the approximations to the derivatives is relatively large near the inflection point. As the methane and oxygen gradients become less steep, the error diminishes. Hence, the predicted \( \text{O}_2 \) concentration profile is in greater error low in the flame because of the steeper gradients. The predicted profile at 5.0 cm is in close agreement with the experimental profile because of the finer grid near the symmetric axis and because of the decrease in the methane and oxygen gradients.

The overprediction of the nitrogen concentrations just outside the flame surface is a consequence of partial equilibrium conditions which exist in this region of the combustion system. Partial equilibrium is discussed in some detail in the following chapter and the reader is referred to section VII.2 for an explanation of the partial equilibrium concept. It will suffice to say at this time that mole increasing reactions are important near the flame surface, so the total number of
moles increases just outside the flame surface before the mole decreasing reactions gain in significance. The result is for the mole fraction of an inert species to decrease as the total number of moles increases. Since the average molecular weight of the gas also increases as the distance away from the flame surface is increased, the mass fraction of an inert must also decrease as the total number of moles increases. Thus, the Burke-Schumann flame sheet concept is also responsible for the third observation listed above. Since allowance is not made for these mole increasing reactions, the predicted nitrogen concentration profiles cannot exhibit the decrease just outside the flame surface. Nevertheless, the predicted and experimentally determined nitrogen concentration profiles agree to within 7%, even at the symmetric axis where the model tends to underpredict.

Inside the luminous flame core, the predicted and experimentally determined temperature profiles do not agree. Disagreement is partially associated with radiation corrections applied to the thermocouple bead temperature when determining the actual gas temperature. As stated in Chapter V and in Appendix V, carbon particles were very much in evidence inside the flame surface. When measuring temperatures, particles tended to settle on the portions of the thermocouple assembly which were just inside the luminous surface. From about three to five centimeters above the burner surface, particles collected on the thermocouple bead and lead wires so fast that it was impossible to get an accurate measure of the gas temperature. This was because energy losses due to radiation were changing as the bead emissivity changed and as the surface area available for radiation changed as more and more particles collected on
the bead and lead wires. At the locations in the system for which temperatures are reported, no change in bead or wire size was observed. When making radiation corrections to the thermocouple bead temperature to determine the actual gas temperature, allowance was not made for a change in emissivity. The value 0.22, recommended by Kaskén (51) for the emissivity of silica-coated platinum-rhodium wires, was used throughout. Thus, the shaded circles in the figures represent corrected temperatures when an emissivity of 0.22 was used both inside and outside the flame surface. The open triangles in the figures represent corrected temperatures when an emissivity of 0.5 was used inside the flame surface and 0.22 used outside the surface. The measured temperatures just inside the flame surface better agree with the predicted temperatures, however, those temperatures well inside the flame surface still do not agree. This disagreement is attributed to carbon particles radiating energy outside the flame surface and to a further shortcoming of the model.

Since the model does not allow for endothermic pyrolysis reactions to take place, the predicted distribution of energy inside the flame surface is different from the distribution of energy in the actual flame. The following endothermic reactions govern the consumption of carbon particles in hydrocarbon diffusion flames:

\[ \text{C} + \text{CO}_2 \rightarrow 2 \text{CO} \quad \text{R32} \]

\[ \text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \quad \text{R35} \]

The following global reaction encompasses the array of methane pyrolysis
reactions:

\[ \text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \]

Using these three reactions, it can be shown that in order to absorb enough energy to decrease the temperature inside the flame surface by 300°K, about 5% of the methane fired would have to be converted to carbon. As stated in Chapter V, the yield of carbon depends to some extent on the air supply and the size of the flame, but with natural gas, the yield is from 1% to 5% of the possible carbon content of the fuel.

In the actual flame, near the burner surface when fuel and oxygen make contact, reaction does not proceed until the ignition temperature is reached. In the model, no allowance is made for an induction period. As a matter of fact, the model predicts greatest reaction intensity near the burner surface because this is where the fuel and oxygen concentration gradients at the flame surface are steepest. Reaction intensity steadily decreases along the flame surface in the model whereas in the actual flame, reaction intensity first increases from the burner surface, passes through a maximum, then decreases as the fuel concentration gradients become less steep when the flame tip is approached. Thus, in the model, in the lower regions of the flame, more energy is capable of being conducted towards the symmetric axis than is possible in the actual flame. The result is for predicted temperatures to be too high in the lower regions of the flame. This same effect also contributes to the steeper concentration gradients at the flame surface near the burner port.
Outside the flame region, a rapid decrease in temperature is observed as energy is convected and conducted away from the hot flame surface to the cooler shield wall. The slight displacement of the predicted temperature profiles in the lower regions of the system are associated with the finite thickness of the reaction zone. At 1.2 cm above the burner port, the model predicts complete combustion 0.65 cm from the symmetric axis, and the predicted temperature profile peaks at this location. At this same location in the actual flame, the carbon monoxide concentration is about 2%, therefore a small, but significant amount of energy is released outside of 0.65 cm. The experimentally determined profile therefore lies to the right of the predicted profile at this level. At higher heights in the flame, the distance from the centerline at which the CO concentration falls to zero and the predicted flame surface are in closer agreement. The slight shift at 2.4 cm can easily be explained by a 0.25 mm displacement between the predicted and experimental peak temperatures or possibly by a 0.25 mm error in determining the exact location of the luminous edge of the flame at this particular level.

The discrepancies between the predicted and experimentally determined concentration and temperature profiles are primarily associated with the Burke-Schumann flame sheet concept. In addition, the overprediction of temperatures inside the flame surface is associated with radiational losses from the luminous core due to the presence of carbon particles, to the neglect of energy absorbing, endothermic reactions, and to the overprediction of reaction intensity near the flame base. Despite the
discrepancies, however, the predicted temperature and nitrogen and oxygen concentration profiles are not in gross error. The magnitude of the predicted temperatures near the flame surface are within seven percent of the experimental values and the predicted nitrogen concentrations are also within seven percent of the experimentally determined ones. Aside from the temperature discrepancies in the inner flame core, the Burke-Schumann flame sheet concept results in predicted temperature and oxygen concentration profiles slightly shifted (less than 0.5 mm) to either side of the experimentally determined ones outside the flame surface. The shift is a result of the actual finite thickness of the reaction zone which is not allowed for in the model.

Since the predicted temperature and nitrogen and oxygen concentration profiles are in moderate agreement, it is believed that the predicted aerodynamic field is sufficient to represent the actual flow field established during the combustive process. The mass flux distribution predicted by the model has already been used in Chapter V to analyze some of the experimental data, and closure of a hydrogen material balance was cited as lending considerable support to the validity of the predicted mass flux distribution.

Figure 24 shows the velocity distribution predicted by the theoretical model. The methane stream entered the system at 4.5 cm/sec and the air stream entered at 9.88 cm/sec. Near the burner surface a peak in the radial velocity profile is observed at the flame surface due to the higher temperatures encountered there. If increases in velocity were due to expansion alone, the peak in the velocity profile would coincide with the peak in the radial temperature profile. However, as
Figure 24 Radial Distribution of Axial Velocity
che distance above the burner port is increased, the peak in the
temperature profile approaches the symmetric axis faster than the flame surface
does. The velocities encountered at the symmetric axis are also found
to be greater than the velocities expected due to natural convection
effects. The reason for this is evident when the flow streamlines are
considered. The streamlines, shown in Figure 25, point out that a large
recirculation cell is established between the hot flame surface and the
cooler shield wall. Preliminary flow tracer experiments verify the
existence of this cell. Air is entrained into the system at the
shield outlet to balance the momentum of the inlet fuel and air streams
and the frictional losses at the shield wall. The presence of this re-
circulation cell reduces the total area available for flow of the feed
and combustion gases; hence, velocities are increased due to the
combined effects of a reduced flow area and natural convection.

The model, using the Burke-Schumann flame sheet concept, may be
useful to aid in analyzing experimental data, especially if the thermal
and aerodynamic fields are all the model need predict. But as a tool
useful in predicting nitrogen oxide formation rates and distribution in
the combustion system, the model needs modification. In Chapter VII,
it will be shown that the region just outside the flame surface is where
NO formation reactions are most important, and it is this region that the
present model fails to accurately predict. Therefore, the model is being
modified in an attempt to better predict the region just outside the
luminous flame surface. The model is referred to as a reaction zone
broadening model. It involves using a stoichiometric oxygen coefficient
less than two to locate the edge of the luminous flame surface. Outside
Figure 25: Stream Function Profile

... ten equally spaced streamlines between $\psi_{\text{_axis}}$ and $\psi_{\text{max}}$

+++ four equally spaced streamlines between $\psi_{\text{_axis}}$ and $\psi = 0.1$
the surface, allowance is made for finite reaction rates. The partial equilibrium concept of Schott (71a) is employed in determining the burnout rates of CO and H₂ and the concentrations of the radicals and stable species in the reaction zone. At the present time, the modified model has not been completed.

A theoretical model which can adequately predict the thermal and aerodynamic fields established during the combustion of fuel in a laminar diffusion flame system has been described. The model makes allowances for variable thermodynamic and transport properties, natural convection effects and radiative heat losses. In an attempt to better predict the concentration profiles of the major flame species and also to obtain the concentrations of radicals in the reaction zone, a modification has been proposed which will allow for chemical reaction outside the flame surface. With the modified model, it will be possible to predict nitrogen oxide formation rates in the combustion system and hence, the nitrogen oxide distribution. The effects of flow rate, fuel and air preheat, burner port size, and other factors which determine diffusion flame macrostructure and nitric oxide formation rates in such flames can be investigated. The thermal and aerodynamic fields which the model currently predicts can be used to aid in interpreting experimental data.
Table VI. Nomenclature used in Theoretical Model

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_p )</td>
<td>constant pressure heat capacity</td>
<td>cal/gm(^o)K</td>
</tr>
<tr>
<td>( D_{j, mix} )</td>
<td>trace diffusion coefficient of species ( j )</td>
<td>cm(^2)/sec</td>
</tr>
<tr>
<td>( g )</td>
<td>gravitational constant</td>
<td>cm/sec(^2)</td>
</tr>
<tr>
<td>( \bar{G} )</td>
<td>mass flux vector</td>
<td>gm/cm(^2)-sec</td>
</tr>
<tr>
<td>( i )</td>
<td>oxygen stoichiometric coefficient</td>
<td></td>
</tr>
<tr>
<td>( k )</td>
<td>gas thermal conductivity</td>
<td>cal/cm(^o)K-sec</td>
</tr>
<tr>
<td>( L )</td>
<td>inner tube radius for fuel flow</td>
<td>cm</td>
</tr>
<tr>
<td>( P )</td>
<td>system total pressure</td>
<td>gm/cm-sec(^2)</td>
</tr>
<tr>
<td>( Q_{gen} )</td>
<td>rate of energy generation by reaction</td>
<td>cal/cc-sec</td>
</tr>
<tr>
<td>( Q_{loss} )</td>
<td>rate of energy loss by radiation</td>
<td>cal/cc-sec</td>
</tr>
<tr>
<td>( r )</td>
<td>radial coordinate</td>
<td>cm</td>
</tr>
<tr>
<td>( R )</td>
<td>outer tube radius for air flow</td>
<td>cm</td>
</tr>
<tr>
<td>( R_j )</td>
<td>rate of creation of species ( j )</td>
<td>gm/cc-sec</td>
</tr>
<tr>
<td>( T )</td>
<td>temperature</td>
<td>°K</td>
</tr>
<tr>
<td>( \bar{v} )</td>
<td>velocity vector</td>
<td>cm/sec</td>
</tr>
<tr>
<td>( w_j )</td>
<td>mass fraction of species ( j )</td>
<td></td>
</tr>
<tr>
<td>( z )</td>
<td>axial coordinate</td>
<td>cm</td>
</tr>
</tbody>
</table>

Greek:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu )</td>
<td>gas viscosity</td>
<td>gm/cm-sec</td>
</tr>
<tr>
<td>( \rho )</td>
<td>mass density</td>
<td>gm/cc</td>
</tr>
<tr>
<td>( \tau )</td>
<td>shear stress tensor</td>
<td>gm/cm-sec(^2)</td>
</tr>
<tr>
<td>( \psi )</td>
<td>stream function</td>
<td>gm/sec</td>
</tr>
</tbody>
</table>
Table VI, continued

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega )</td>
<td>vorticity</td>
<td>( \text{sec}^{-1} )</td>
</tr>
</tbody>
</table>

Subscripts:

\( j \) refers to jth species

\( o \) denotes inlet condition

\( r \) radial component

\( \text{ref} \) reference condition

\( z \) axial component

Normalized Variables:

\( \eta = \frac{z}{r}, \text{normalized axial coordinate} \)

\( \theta = \frac{T}{T_0 - T_{\text{ref}}}, \text{normalized temperature} \)

\( \xi = \frac{r}{R}, \text{normalized radial coordinate} \)

\( \psi^* = \frac{\psi}{\psi_{\text{wall}}}, \text{normalized stream function} \)

\( \omega^* = \frac{\omega}{(\psi_{\text{wall}}/R^3 \rho_{\text{ref}})}, \text{normalized vorticity} \)

Dimensionless Physical Properties:

\( C_{P}^* = \frac{C_P}{C_{P_{\text{ref}}}}, \text{normalized heat capacity} \)

\( D_{j, \text{mix}}^* = \frac{D_{j, \text{mix}}}{(D_{j, \text{mix}})_{\text{ref}}}, \text{normalized diffusion coefficient} \)

\( k^* = \frac{k}{k_{\text{ref}}}, \text{normalized thermal conductivity} \)

\( \mu^* = \frac{\mu}{\mu_{\text{ref}}}, \text{normalized viscosity} \)

\( \rho^* = \frac{\rho}{\rho_{\text{ref}}}, \text{normalized mass density} \)
Table VI, continued

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dimensionless Ratios:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Gr</strong></td>
<td>Grashof number $= \frac{2 \rho_{\text{ref}} g R^3 (T_o - T_{\text{ref}})}{T_{\text{ref}} \mu_{\text{ref}}^2}$</td>
<td></td>
</tr>
<tr>
<td><strong>Pr</strong></td>
<td>Prandtl number $= \frac{\mu_{\text{ref}} C_{p_{\text{ref}}} / k_{\text{ref}}}{\mu_{\text{ref}}}$</td>
<td></td>
</tr>
<tr>
<td><strong>Re</strong></td>
<td>Reynolds number $= \frac{4 \psi_{\text{wall}}}{\mu_{\text{ref}} R}$</td>
<td></td>
</tr>
<tr>
<td><strong>Sc</strong></td>
<td>Schmidt number $= \frac{\mu_{\text{ref}} / \rho_{\text{ref}} / (D_{j,\text{mix}})<em>{\text{ref}}}{\mu</em>{\text{ref}}}$</td>
<td></td>
</tr>
</tbody>
</table>
Chapter VII. THE FORMATION OF NITRIC OXIDE
IN METHANE–AIR DIFFUSION FLAMES

The temperature and concentration profiles discussed in Chapter V, and the predicted mass flux distribution considered in Chapter VI together form a basis for establishing factors which influence the formation rate of nitric oxide in laminar, methane–air diffusion flames. From the standpoint of NO formation in such flames, the following questions would like to be answered:

(i) How is NO distributed in the vicinity of the flame?
(ii) What is the predominant mechanism of NO formation in diffusion flames?

The sections which follow are concerned with the answers to these questions. The answers provide considerable insight into the factors which influence nitric oxide formation in laminar, methane–air diffusion flames.

VII.1 NITRIC OXIDE DISTRIBUTION

As explained in Chapter V, nitrogen oxide analysis was made by the modified Saltzman method (31), (67). The method is a colorimetric procedure for the determination of the total oxides of nitrogen (N₂O excluded) and is discussed in some detail in Appendix IV. Radial nitrogen oxide concentration profiles were obtained at various levels in the combustion system. In Figure 26, the NOₓ profiles at the three heights above the burner surface at which the stable species concentration profiles were obtained are presented. The NOₓ concentration profiles are seen to peak just outside the luminous
Figure 26. Radial Distribution of NOX
edge of the flame where the radial temperature profile also peaks. The steep gradients away from the peaks suggest that nitrogen oxide formation is primarily confined to a narrow annular region just outside the flame surface where temperature and oxygen availability are suitable for NO\textsubscript{x} formation. This indicates that nitrogen oxide formation is due principally to nitrogen fixation, and since NO is the predominant nitrogen fixation product, the NO\textsubscript{x} concentration profiles are strongly influenced by the NO distribution in the combustion system.

The predicted mass flux distribution discussed in Chapter VI was used to determine the total mass flow rate of NO\textsubscript{x} at various levels within the system. If m\textsubscript{NO}(r) denotes the radial distribution of the NO\textsubscript{x} mass fraction at a height z in the system, and ρ(r) and v(r) the corresponding mass density and axial velocity distributions, then the total mass flow rate of NO\textsubscript{x} at that height in the system, G\textsubscript{NO}, is given by:

\[
G_{\text{NO}} = 2\pi \int_{0}^{R} m_{\text{NO}}(r) \rho (r) \ v(r) \ r \ dr
\]  

Similarly, the total mass flow of NO\textsubscript{x} inside the flame surface at a given level is

\[
G_{\text{NO}}^{f} = 2\pi \int_{0}^{r_{f}} m_{\text{NO}}(r) \rho (r) \ v(r) \ r \ dr
\]  

where r\textsubscript{f} is the radius of the flame surface at that particular level. The experimentally determined NO\textsubscript{x} concentration profiles were combined with the predicted mass flux distribution in the numerical integration of equations 7.1 and 7.2. The results are shown in Table VII. The second column of the
<table>
<thead>
<tr>
<th>Height above burner surface, cm</th>
<th>Total mass flow* NO&lt;sub&gt;x&lt;/sub&gt;, 10&lt;sup&gt;6&lt;/sup&gt; gm/sec</th>
<th>Mass flow NO&lt;sub&gt;x&lt;/sub&gt; ** inside the flame surface, 10&lt;sup&gt;6&lt;/sup&gt; gm/sec</th>
<th>Net flow of NO&lt;sub&gt;x&lt;/sub&gt; *** into the flame surface, 10&lt;sup&gt;6&lt;/sup&gt; gm/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>2.068</td>
<td>0.615</td>
<td>0.295</td>
</tr>
<tr>
<td>1.5</td>
<td>2.852</td>
<td>0.637</td>
<td>0.558</td>
</tr>
<tr>
<td>1.8</td>
<td>3.017</td>
<td>0.983</td>
<td>1.122</td>
</tr>
<tr>
<td>2.1</td>
<td>3.559</td>
<td>0.984</td>
<td>1.759</td>
</tr>
<tr>
<td>2.4</td>
<td>4.391</td>
<td>1.043</td>
<td>1.838</td>
</tr>
<tr>
<td>5.0</td>
<td>6.453</td>
<td>0.659</td>
<td>2.142</td>
</tr>
<tr>
<td>5.8 (flame tip)</td>
<td>6.75 (extrapolated)</td>
<td></td>
<td>1.953</td>
</tr>
</tbody>
</table>

* \[ G_z = 2\pi \int_0^R m_{NO} \rho v r \, dr \]

** \[ G_z^f = 2\pi \int_0^{R_f} m_{NO} \rho v r \, dr \]

*** \[ \text{Net inflow of NO at the flame surface} = -\int \int \nabla G_{NO} \cdot \vec{n} \, dS \]
table shows that the total amount of nitrogen oxides formed increases as the height above the burner port is increased. Comparison of the second and third columns indicates that at each level in the system, more NO$_x$ is outside the flame surface than inside, and that, in general, the relative amount outside the surface increases as the height above the burner port is increased. The concentration profiles presented in Figure 26 indicate that NO$_x$ gets inside the luminous flame core via diffusion and, depending upon the velocity vector, convection at the flame surface. To determine if this is indeed the case, the net inflow of NO$_x$ at the flame surface was calculated. If $\overrightarrow{G}_{NO}$ is the mass flux vector of NO$_x$ at a control element of the flame surface of area $dS$, and $\overrightarrow{\eta}$ is a unit vector normal to $dS$, then the net inflow of NO$_x$ into the control element is $-(\overrightarrow{G}_{NO} \cdot \overrightarrow{\eta})dS$. The net inflow of NO$_x$ into the flame is found by integrating over the entire flame surface. Thus

$$\left[\text{Net inflow of NO}_x \text{ into the flame} \right] = - \int_S (\overrightarrow{G}_{NO} \cdot \overrightarrow{\eta})_f dS$$

$$= 2\pi \int_0^Z (\overrightarrow{G}_{NO} \cdot \overrightarrow{\eta})_f r_f dz \quad 7.3$$

The radial and axial components of $\overrightarrow{G}_{NO}$, $(G_{NO})_r$ and $(G_{NO})_z$ are determined from the total radial and axial fluxes of NO$_x$ via diffusion and convection and are given by:

$$(G_{NO})_r = N M_{NO} y_{NO} [v_r + (V_{NO})_r] \quad 7.4$$

$$(G_{NO})_z = N M_{NO} y_{NO} [v_z + (V_{NO})_z] \quad 7.5$$
where

\[ M_{NO} = \text{molecular weight of NO} \]
\[ N = \text{molar density, gmole/cc} \]
\[ v_r = \text{radial convective velocity, cm/sec} \]
\[ v_z = \text{axial convective velocity, cm/sec} \]
\[ (v_{NO})_r = \text{radial diffusive velocity of NO, cm/sec} \]
\[ (v_{NO})_z = \text{axial diffusive velocity of NO, cm/sec} \]
\[ y_{NO} = \text{mole fraction of NO} \]

Equations 7.4 and 7.5 were used in equation 7.3 to determine the net inflow of \( NO_x \) into the flame up to various heights above the burner surface. Axial diffusion was assumed to be negligible in comparison to axial convection at the flame surface. The results are shown in the last column of Table VII. At 1.2 cm above the burner surface, it is seen that more \( NO_x \) was present inside the luminous flame core than penetrated the surface from the outside. This indicates that in the lower regions of the flame, \( NO_x \) is generated inside the flame surface. The exact mechanism of \( NO_x \) formation inside the flame core is not known, but it is believed to involve CH and HN intermediates. The reaction path is postulated to be as follows:

\[ CH_4 \rightarrow CH_3 \rightarrow CH_2 \rightarrow N_2 + 2 \text{CN, HN, } \rightarrow NO, NO_2 \]

Core generated \( NO_x \) accounts for about 52% of the total \( NO_x \) present inside the flame at 1.2 cm above the burner surface. However, this represents only 15.5% of the total \( NO_x \) generated up to this particular level in the combustion system.

The last entry in the fourth column of Table VII indicates that the net
flow of NO\textsubscript{x} along the entire flame surface was into the luminous core. The decrease in the cumulative flow is indicative of a net outward NO flux from the flame near the flame tip. In evaluating equation 7.3, it was observed that the flow of NO\textsubscript{x} at the flame surface was into the flame core up to a height of 4.3 cm and that above this height, the flow of NO\textsubscript{x} was out of the core. When the total flow of NO\textsubscript{x} into the flame (2.43 \times 10^{-6} \text{ gm/sec}) was compared to the total flow from the flame (0.478 \times 10^{-6} \text{ gm/sec}), it was found that NO\textsubscript{x} must be converted to N\textsubscript{2} or other nitrogen containing species inside the flame core. About 80\% of the NO\textsubscript{x} which penetrated the flame surface was converted. This finding is consistent with the findings of Sarofim et al. (69a). They observed that when methane-air diffusion flames were seeded with NO, as much as 90\% of the NO fed to the methane stream could be converted. The percent conversion of NO to N\textsubscript{2} was found to decrease as the feed gases became more fuel-lean. The amount of NO\textsubscript{x} converted up to any height can be found by taking the difference between the third and fourth columns. It was found that up to about 2.0 cm above the burner port, NO\textsubscript{x} was being converted at a rate of about 1.2 \times 10^{-6} \text{ gm/cm-sec} and that above this height, the conversion rate was about 2.8 \times 10^{-7} \text{ gm/cm-sec}.

Extrapolating the values in the second column to the flame tip reveals that less than 7.1\% of the total mass flow of NO\textsubscript{x} above the flame came from within the luminous core. Since more than 83\% of the NO\textsubscript{x} inside the flame was actually produced outside the flame, it is safe to say that less than 1.2\% of the NO\textsubscript{x} present above the flame tip was formed inside the flame surface. Thus, any mechanism postulated to describe the formation of nitrogen oxide in the combustion system studied must be one which is effective in the post flame region and, also sensitive to temperature. Recent studies (68) (69) have
shown that the Zeldovich reactions (90) constitute such a mechanism. The mechanism is represented by the following reactions:

\[ \text{N}_2 + \text{O} = \text{NO} + \text{N} \quad \text{R26} \]

\[ \text{N} + \text{O}_2 = \text{NO} + \text{O} \quad \text{R27} \]

The nitric oxide concentrations found in the flame are far from equilibrium, therefore, estimates of the NO formation rates can be determined from the forward Zeldovich reactions. From these reactions, the formation rate of NO in parts per million per second is given by:

\[ \frac{d(\text{NO})_{\text{ppm}}}{dt} = 2 \times 10^6 k_{\text{R26}} \text{N} y_{\text{N}_2} y_0 \quad \text{7.6} \]

In the above equation, \( k_{\text{R26}} \) represents the forward rate constant of reaction R26 in cc/mole/sec; \( (\text{NO})_{\text{ppm}} \), the NO concentration in parts per million; \( y_i \) the mole fraction of species i; \( \text{N} \), the molar density in mole/cc; and \( t \), the time in seconds. Before equation 7.6 can be used to obtain the formation rate of NO in the flame, however, estimates of the oxygen radical concentrations in the regions where NO formation rates are important must be made.

VII.2 RADICAL CONCENTRATIONS

One problem associated with microprobe sampling of flames in the manner employed in this study is that analysis of samples withdrawn from the flame are found to consist only of stable species. One question which needs answering is, what happened to the radicals? In the sampling process, the
radicals can be destroyed in either of two ways: by gas-phase radical recombination reactions, or, by radical interaction with the probe wall. The wall reactions involve chemisorption of radicals and molecules on the probe wall, followed by reactions between gas-phase species and chemisorbed species; and, between two chemisorbed species to form gas-phase stable species. If the radical concentrations were at, or near, their equilibrium values, the errors caused by recombination of radicals on the measured concentrations of H₂O, H₂ and O₂ would be only a few percent. If, however, the radicals were present in quantities which greatly exceeded their equilibrium values, the error could be considerable and the analysis of the sample gas would not represent the composition of the flame gas. The concentration of molecular hydrogen would be the most affected. This is because in the flame, the concentration of atomic hydrogen can be within an order of magnitude of the molecular hydrogen concentration. In the probe, when H recombines to H₂, the sample gas would be considerably richer in H₂ than was the flame gas. This is also true of molecular oxygen just outside the flame surface where O₂ concentrations are small. The concentrations of CO, CO₂ and H₂O are less affected by recombination basically because of their high concentrations relative to the concentrations of H, O and OH.

It would be possible to back-calculate the composition of the flame gas if the pressure-temperature distribution in the probe were also known. The uncertainty in the values of the rate constants and efficiencies of the possible reactions does not, however, warrant the difficulty associated with solving the coupled momentum, energy and species conservation equations needed to determine the pressure-temperature distribution in the probe and the composition of the gas fed to the probe.
Estimates of the radical concentrations can be obtained, however, from the composition of the sample gas if the following reactions are equilibrated in the flame:

\[
\begin{align*}
H + O_2 &= OH + O \quad \text{R19} \\
O + H_2 &= OH + H \quad \text{R20} \\
H + H_2O &= H_2 + OH \quad \text{R21} \\
H_2 + O_2 &= OH + OH \quad \text{R21a} \\
H_2 + O_2 &= H_2O + O \quad \text{R21b} \\
O + H_2O &= OH + OH \quad \text{R21c}
\end{align*}
\]

Several studies (56)(61)(68)(69) have been undertaken which support the equilibration of these reactions in the flame zone of methane-oxygen and methane-air premixed flames. The following expressions relate the concentration of the radicals to those of the stable species when the above reactions are equilibrated.

\[
\begin{align*}
y_{OH}^2 &= K_{P19}K_{P20}y_{H_2}y_{O_2} \quad \text{7.7} \\
y_o &= \frac{y_{OH}^2}{K_{P20}K_{P21}y_{H_2O}} \quad \text{7.8} \\
y_{H}^3 &= \frac{y_{OH}^3}{K_{P19}K_{P20}K_{P21}y_{O_2}y_{H_2O}} \quad \text{7.9}
\end{align*}
\]

In the above equations \(K_{Pj}\) is the equilibrium constant associated with reaction \(R_j\) and \(y_i\) denotes the mole fraction of species \(i\).

As stated above, the concentration of molecular hydrogen is thought to be the composition most affected by probe sampling. A method of estimating
the radical concentrations which does not involve the hydrogen concentration is, therefore, desirable. Such a method would exist if the carbon monoxide burnout reaction, R18, were also equilibrated:

$$\text{CO} + \text{OH} = \text{CO}_2 + \text{H} \quad \text{R18}$$

Flame studies by Fenimore and Jones (29)(30) and by Kaskan (50) indicate that this reaction is equilibrated in hydrogen and hydrogen plus carbon monoxide and carbon dioxide flames. Further analyses of the post flame region of lean hydrocarbon premixed flames by Pohl (61)(68) and Kaskan (50) indicate that this reaction becomes equilibrated as soon as the primary fuel has been consumed. Prior to the consumption of the primary fuel, hydrocarbon-radical reactions change the radical concentrations faster than the above exchange reaction can equilibrate. When reaction R18 is equilibrated, it can be combined with the aforementioned exchange reactions to yield the following expression for the hydroxyl concentration in terms of the concentrations of the stable species.

$$y_{\text{OH}}^2 = K_{\text{P18}} K_{\text{P19}} K_{\text{P20}} K_{\text{P21}} \frac{y_{\text{H}_2\text{O}} y_{\text{CO}} y_{\text{O}_2}}{y_{\text{CO}_2}}$$

7.10

This equation and equations 7.8 and 7.9 serve to estimate the concentrations of the radicals in the regions of the flame where reactions R18 through R21 are assumed equilibrated.

Following the hypothesis of Friedman and Burke (33), the complete combustion of methane in the diffusion flame under consideration is assumed to
take place in two stages. In the first stage, methane is converted to CO, 
CO₂, H₂ and H₂O and in the second stage, CO and H₂ are converted to CO₂ and 
H₂O, respectively. Since the luminosity of the diffusion flame is due to the 
emissions of C, and CH species associated with the pyrolysis of the methane, 
it is reasonable to postulate that the disappearance of luminosity and methane 
are correlated; and that, therefore, the luminous edge separates the regions 
in which the first and second stages of combustion predominate. Analysis 
of the radial concentration profiles of the stable species presented in 
Figures 12 and 13 of Chapter V supports this hypothesis. The methane con-
centration is less than one mole percent at the edge of the luminous zone 
and is zero about one millimeter into the blue reaction zone which surrounds 
the luminous core. The blue hue of the reaction zone is associated with 
carbon monoxide burnout. Thus, approximately one millimeter outside the 
luminous edge of the flame, the combustion system can be considered a 
hydrogen plus carbon monoxide and carbon dioxide flame, similar to the 
systems of Fenimore and Jones (28)(30) and Kaskan (50).

The experimental data can be used to determine if reactions R18 and 
R21 are indeed in equilibrium in the region outside the flame surface. Addition 
of these two exchange reactions results in the water-gas reaction:

\[
\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \quad \text{R33}
\]

The ratio of the forward to reverse rate constants of this reaction is 
given by:

\[
R = \frac{y_{\text{CO}_2}y_{\text{H}_2}}{y_{\text{CO}}y_{\text{H}_2\text{O}}} = 7.11
\]
At equilibrium, \( k \) is equal to the equilibrium constant of the water-gas reaction. The equilibrium constant of the water-gas reaction was determined from the equilibrium constants of reactions R18 and R21. Fristrom and Westenberg (37a) fitted the data from the JANAF tables (48a) in the following form:

\[
K_{P_{33}} = 3.907 \times 10^{-2} \exp \left(\frac{6951}{RT}\right)
\]

Values of temperature and the stable species concentrations were used to determine \( K_{P_{33}} \) and \( R \) in the region outside the flame surface. A comparison between these two quantities is shown in Table VIII. The agreement is seen to be quite good despite the effect that recombination had on the concentrations of the different species. This agreement lends support to the equilibration not only of reactions R18 and R21, but to the equilibration of the other bimolecular reactions as well. Equations 7.8, 7.9 and 7.10 can, therefore, be used to estimate the concentrations of the radicals in the regions where nitric oxide formation is important.

Figure 27 shows the calculated radical concentration profiles outside the luminous core at the three heights above the burner surface for which stable species concentration profiles were obtained. The hydroxyl concentration was calculated using the \( \text{H}_2 \) concentration in equation 7.7 (solid line) and using the \( \text{CO} \) and \( \text{CO}_2 \) concentrations in equation 7.10 (dashed line). The disagreement is indicative of the combined effects of quenching and recombination in the probe on the concentrations of the different stable species and on departures from partial equilibrium in the flame. The radical concentration profiles generally increase with increasing distance.
Table VIII. Water-Gas Equilibrium in the Reaction Zone

\[
\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2
\]

\[
R = \frac{y_{\text{CO}_2} y_{\text{H}_2}}{y_{\text{CO}} y_{\text{H}_2 \text{O}}}
\]

\[
K_p = 3.907 \times 10^{-2} \exp (6951/RT)
\]

\[\begin{array}{ccccccccc}
z = 1.2 \text{ cm; flame surface: } r = 0.535 \text{ cm} \\
\hline
r & 0.5 & 0.55 & 0.6 & 0.65 & 0.7 & 0.75 & 0.8 \\
K_p & 0.306 & 0.262 & 0.235 & 0.227 & 0.227 & 0.244 & 0.303 \\
R & 0.352 & 0.272 & 0.262 & 0.261 & 0.228 & 0.215 & 0.228 \\
\hline
z = 2.4 \text{ cm; flame surface: } r = 0.50 \text{ cm} \\
\hline
r & 0.5 & 0.55 & 0.6 & 0.65 & 0.7 & 0.75 \\
T,^\circ\text{K} & 2050. & 2080. & 1970. & 1805. & 1650. & 1450. \\
K_p & 0.215 & 0.210 & 0.231 & 0.271 & 0.326 & 0.436 \\
R & 0.223 & 0.257 & 0.283 & 0.285 & 0.272 & 0.167 \\
\hline
z = 5.0 \text{ cm; flame surface: } r = 0.267 \text{ cm} \\
\hline
r & 0.20 & 0.25 & 0.30 & 0.35 & 0.40 & 0.45 \\
K_p & 0.232 & 0.229 & 0.230 & 0.233 & 0.240 & 0.254 \\
R & 0.291 & 0.304 & 0.335 & 0.258 & 0.230 & 0.212
\end{array}\]

Figure 27 Radical Concentration Profiles Outside the Flame Surface
from the flame surface, pass through a maximum, and then decrease rapidly. The initial increase is due to the combined effect of an increase in temperature and an increase in the molecular oxygen concentration as the gases move away from the flame surface. The decrease is associated with the decrease in the water vapor concentration and with the increased significance of the following three-body recombination reactions as the rates of the bimolecular exchange reactions decrease, due to a decrease in temperature.

\[
\begin{align*}
O + O + M & \rightarrow O_2 + M \quad \text{R22} \\
H + H + M & \rightarrow H_2 + M \quad \text{R23} \\
H + HO + M & \rightarrow H_2O + M \quad \text{R24} \\
H + O + M & \rightarrow OH + M \quad \text{R25}
\end{align*}
\]

The oxygen radical concentrations presented graphically in Figure 27 can thus be used in equation 7.6 to determine the formation rates of NO in the regions of the flame where the Zeldovich mechanism dominates.

With the estimated radical concentrations the effect of recombination in the probe can be more critically evaluated. In the probe, radicals are destroyed by gas phase recombination reactions as well as by radical interaction with the probe wall. Insufficient data on the efficiencies of the wall reactions makes it impossible to evaluate their significance in a direct manner, but analysis of the gas phase reactions can lend some insight to their significance. From the direction of shift in their equilibrium constants with decreasing temperature, the carbon monoxide burnout reaction and the three-body recombination reactions will tend towards the right as written and the bimolecular reactions associated with the \( \text{H}_2-\text{O}_2 \) system will
tend to the left, except for reaction R21b. Based on steric grounds, however, reactions R21a and R21b are highly unlikely. Thus, the coupling of all the above reactions (reactions R21a and R21b excluded) will determine the increase or decrease of each species in the probe. In this evaluation, it will be useful to define the extent of each of the reactions as follows:

\[
\begin{align*}
\delta_{18} &= k_{18} (CO)(OH) - k'_{18} (CO_2)(H) \\
\delta_{19} &= k_{19} (H)(O_2) - k'_{19} (OH)(O) \\
\delta_{20} &= k_{20} (O)(H_2) - k'_{20} (OH)(H) \\
\delta_{21} &= k_{21} (H)(H_2O) - k'_{21} (H_2)(OH) \\
\delta_{21c} &= k_{21c} (O)(H_2O) - k'_{21c} (OH)^2 \\
\delta_{22} &= k_{22} (O)^2(M) - k'_{22} (O_2)(M) \\
\delta_{23} &= k_{23} (H)^2(M) - k'_{23} (H_2)(M) \\
\delta_{24} &= k_{24} (H)(OH)(M) - k'_{24} (H_2O)(M) \\
\delta_{25} &= k_{25} (H)(O)(M) - k'_{25} (OH)(M)
\end{align*}
\]

The rate of production of each of the species in the reaction zone via the above equations can be determined as follows:

\[
\begin{align*}
\dot{R}_{H_2} &= -\delta_{20} + \delta_{21} + \delta_{23} \\
\dot{R}_{H_2O} &= -\delta_{21} - \delta_{21c} + \delta_{24} \\
\dot{R}_{O_2} &= -\delta_{19} + \delta_{22} \\
\dot{R}_{CO_2} &= +\delta_{18} \\
\dot{R}_0 &= \delta_{19} - \delta_{20} - \delta_{21c} - 2\delta_{22} - \delta_{25} \\
\dot{R}_{CO} &= -\delta_{18}
\end{align*}
\]
\[
\dot{R}_H = \delta_{18} - \delta_{19} + \delta_{20} - \delta_{21} - 2\delta_{23} - \delta_{24} - \delta_{25}
\]

\[
\dot{R}_{OH} = -\delta_{18} + \delta_{19} + \delta_{20} + \delta_{21} + 2\delta_{21c} - \delta_{24} + \delta_{25}
\]

The forward and reverse rate constants needed to evaluate the above rates of production are shown in Table IX. To complete the discussion the composition of the following typical point in the reaction zone will be considered:

Height above burner surface = 1.2 cm
Distance from symmetric axis = 0.70 cm
Temperature = 1990°K

Mole Fractions:

\[y_{CO} = 0.0135\]
\[y_{CO_2} = 0.076\]
\[y_{H_2} = 0.0075\]
\[y_{H_2O} = 0.188\]
\[y_{O_2} = 0.0085\]
\[y_{OH} = 0.00453\]
\[y_{O} = 0.000762\]
\[y_{H} = 0.00174\]
\[y_{H_2} = 0.70\]

The pressure inside the sampling probe was one-half atmosphere. Assuming flow through the orifice tip was adiabatic and reversible, the cooling due to such an expansion results in a temperature just inside the probe tip of about 1500°K. Using the above gas composition and a temperature and pressure inside the probe of 1500°K and 1/2 atm, respectively, the extents of
Table IX. Reaction Rate Constants

\[ k = A T^B \exp (-C/RT) \]

Units are gmole/cc-sec; cal/gmole; °K

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A \times 10^x</th>
<th>B</th>
<th>C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO + OH → CO_2 + H</td>
<td>3.72 \times 10^{11}</td>
<td>0</td>
<td>700</td>
<td>13a</td>
</tr>
<tr>
<td>CO_2 + H → CO + OH</td>
<td>3.51 \times 10^{16}</td>
<td>-0.80</td>
<td>25,142</td>
<td>13a</td>
</tr>
<tr>
<td>H + O_2 → OH + O</td>
<td>2.24 \times 10^{14}</td>
<td>0</td>
<td>16,800</td>
<td>6</td>
</tr>
<tr>
<td>O + OH → H + O_2</td>
<td>1.71 \times 10^{13}</td>
<td>0</td>
<td>870</td>
<td>(a)</td>
</tr>
<tr>
<td>O + H_2 → OH + H</td>
<td>1.74 \times 10^{13}</td>
<td>0</td>
<td>9,450</td>
<td>6</td>
</tr>
<tr>
<td>H + OH → O + H_2</td>
<td>7.70 \times 10^{12}</td>
<td>0</td>
<td>7,580</td>
<td>(a)</td>
</tr>
<tr>
<td>H + H_2O → H_2 + OH</td>
<td>1.80 \times 10^{14}</td>
<td>0</td>
<td>20,660</td>
<td>(a)</td>
</tr>
<tr>
<td>H_2 + OH → H + H_2O</td>
<td>2.19 \times 10^{13}</td>
<td>0</td>
<td>5,150</td>
<td>6</td>
</tr>
<tr>
<td>O + H_2O + OH → O + OH</td>
<td>5.75 \times 10^{13}</td>
<td>0</td>
<td>18,100</td>
<td>6</td>
</tr>
<tr>
<td>OH + OH → O + H_2O</td>
<td>5.38 \times 10^{12}</td>
<td>0</td>
<td>1,050</td>
<td>(a)</td>
</tr>
<tr>
<td>O + O + M → O_2 + O_2 + M</td>
<td>8.9 \times 10^{14}</td>
<td>-0.44</td>
<td>0</td>
<td>13a</td>
</tr>
<tr>
<td>O_2 + M + O + O + M</td>
<td>2.5 \times 10^{16}</td>
<td>-0.5</td>
<td>117,945</td>
<td>13a</td>
</tr>
<tr>
<td>H + M + H + H + M</td>
<td>1.0 \times 10^{18}</td>
<td>-1.0</td>
<td>0</td>
<td>13a</td>
</tr>
<tr>
<td>H_2 + M → H + H + M</td>
<td>7.15 \times 10^{17}</td>
<td>-0.82</td>
<td>103,240</td>
<td>13a</td>
</tr>
<tr>
<td>H + OH + M → H_2O + M</td>
<td>1.5 \times 10^{17}</td>
<td>-0.5</td>
<td>0</td>
<td>13a</td>
</tr>
<tr>
<td>H_2O + M + H → OH + O + M</td>
<td>3.96 \times 10^{17}</td>
<td>-0.31</td>
<td>118,027</td>
<td>13a</td>
</tr>
<tr>
<td>H + O + M → OH + M</td>
<td>3.0 \times 10^{14}</td>
<td>0</td>
<td>0</td>
<td>13a</td>
</tr>
<tr>
<td>OH + M → H + O + N</td>
<td>6.96 \times 10^{13}</td>
<td>0.21</td>
<td>101,292</td>
<td>13a</td>
</tr>
</tbody>
</table>

(a) Computed from the equilibrium constant
reaction have the following values:

\[
\begin{align*}
\delta_{18} &= 2.489 \times 10^{-4} \text{ mole/cc-sec} \\
\delta_{19} &= -5.325 \times 10^{-4} \text{ mole/cc-sec} \\
\delta_{20} &= -9.849 \times 10^{-6} \text{ mole/cc-sec} \\
\delta_{21} &= -1.236 \times 10^{-3} \text{ mole/cc-sec} \\
\delta_{21c} &= -9.678 \times 10^{-4} \text{ mole/cc-sec} \\
\delta_{22} &= 1.387 \times 10^{-7} \text{ mole/cc-sec} \\
\delta_{23} &= 1.353 \times 10^{-7} \text{ mole/cc-sec} \\
\delta_{24} &= 2.046 \times 10^{-6} \text{ mole/cc-sec} \\
\delta_{25} &= 1.585 \times 10^{-7} \text{ mole/cc-sec}
\end{align*}
\]

From the above values it is seen that the rates of the three-body reactions are two-to-three orders of magnitude slower than the rates of the bimolecular reactions, therefore the combustion products will not follow a path towards full equilibrium in the probe. Further analysis shows that \( \text{H}_2 \) is destroyed by reaction R21 much faster than it can be formed by reactions R20 and R23. The result is for the \( \text{H}_2 \) concentration of the sample gas to be too low and that of \( \text{H}_2\text{O} \) to be too high relative to the \( \text{H}_2 \) and \( \text{H}_2\text{O} \) concentrations in the flame at the sample location. The \( \text{O}_2 \) concentration of the sample gas will also be higher than the \( \text{O}_2 \) concentration in the flame due primarily to reaction R19. Similarly, due to reaction R18, the \( \text{CO}_2 \) concentration will be too high resulting in a CO concentration too low.

The minimum percentage change in the concentrations of the stable species from their inlet values to the probe can be estimated from the rates of production of the species. Using the values of the extents of reaction in the rate expressions results in:
\[ R_{H_2} = -1.246 \times 10^{-3} \text{ mole/cc-sec} \]
\[ R_{H_2O} = 2.206 \times 10^{-3} \text{ mole/cc-sec} \]
\[ R_{O_2} = 5.326 \times 10^{-4} \text{ mole/cc-sec} \]
\[ R_{CO_2} = 2.489 \times 10^{-4} \text{ mole/cc-sec} \]
\[ R_{CO} = -2.489 \times 10^{-4} \text{ mole/cc-sec} \]
\[ R_{O} = 4.447 \times 10^{-4} \text{ mole/cc-sec} \]
\[ R_{H} = 2.005 \times 10^{-4} \text{ mole/cc-sec} \]
\[ R_{OH} = -3.965 \times 10^{-3} \text{ mole/cc-sec} \]

One thing which is immediately noticeable is that O and H radicals are still being produced just inside the probe tip. The importance of the wall reactions in increasing the quenching effectiveness becomes evident. Table X shows the percentage change in the concentrations of the stable species when the above rates are effective for various residence times.

<table>
<thead>
<tr>
<th>Species</th>
<th>Residence Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^{-6}$ sec</td>
</tr>
<tr>
<td>$H_2$</td>
<td>-2.71%</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>0.192%</td>
</tr>
<tr>
<td>$O_2$</td>
<td>1.023%</td>
</tr>
<tr>
<td>CO</td>
<td>-0.301%</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>0.053%</td>
</tr>
</tbody>
</table>
From Table X it is seen that if the gases were subjected to the above rates for $10^{-6}$ sec, the minimum change that can be expected in the $\text{H}_2$ concentration is 2.71%. The fact that $\text{H}_2$ was observed in the sample gas indicates that the above rates were not effective for $10^{-4}$ sec.

The linear velocity across the probe tip was calculated to be about 6500 cm/sec (assuming critical flow through a 80$\mu$m orifice). At this rate, in $10^{-5}$ sec the sample gases would have traveled about 0.65 mm into the probe and the rate of quenching would have been increased due to further expansion and to the diffusion of species to the probe wall. Thus, it is believed that the second column of Table X appropriates the error incurred in microprobe sampling of flame gases in the manner employed. A more detailed analysis of the effect of microprobe sampling on the composition of the sampled gas is impossible without actually solving the coupled continuity, momentum and species conservation equations.

Studies of the post flame region of flat, premixed hydrocarbon-air and hydrogen plus carbon monoxide and carbon dioxide flames indicated the existence of superequilibrium radical concentrations, (14)(50)(58)(68). Knowledge of whether or not superequilibrium oxygen radical concentrations exist in diffusion flames is important from a modelling standpoint. If equilibrium oxygen radical concentrations exist in the reaction zone, the need to predict the $\text{O}$ concentration by reaction zone broadening reactions will be unnecessary. Predicted temperatures and $\text{O}_2$ concentrations would be sufficient to determine the $\text{O}$ concentration. To determine if superequilibrium radical concentrations do exist in diffusion flames, the estimated hydrogen and oxygen radical concentrations were compared to the radical hydrogen and oxygen concentrations that would exist if reactions R22 and R23 were
equilibriated. Figures 28 and 29 show this comparison. As seen, hydrogen and oxygen concentrations which greatly exceed their equilibrium values are present in the reaction zone of methane-air diffusion flames.

The creation of radical concentrations which exceed their equilibrium values can be explained by considering the partial equilibrium postulation of Schott (71a). The bimolecular exchange reactions, R19, R20 and R21, and linear combinations of these reactions, are responsible for the generation of H, O and OH radicals at flame temperatures. The bimolecular reactions involve small activation energies, which while significant at low temperatures, are no real deterrents to fast reaction at high temperatures. Conversely, recombination rates are either temperature independent, or decrease slightly with increasing temperature. Thus, high temperatures favor the separation of the rates of equilibration of these two kinds of reactions. Hence, it is possible for a state to exist where the bimolecular reactions are equilibrated, even though the system as a whole is not. In the absence of surfaces, the only route for the consumption of the radicals formed is by way of the recombination reactions. But since the rates of these three-body reactions are relatively slower than the rates of the bimolecular reactions at high temperatures, radicals can be produced faster than they can be consumed. This leads to superequilibrium radical concentrations. As the temperature decreases, the rates of the bimolecular reactions decrease, and become comparable in magnitude to the rates of the recombination reactions. The bimolecular and recombination reactions become competitive, and further chemical reaction leads to full equilibrium, unless the reactions are frozen by a rapid decrease in temperature.

Since the approach to full equilibrium is by way of the three-body
Figure 28. Comparison of Equilibrium Oxygen Atom Concentration and Oxygen Atom Concentration in the Flame Determined from the Stable Species
Figure 29  Comparison of Equilibrium Hydrogen Atom Concentration with Hydrogen Atom Concentration in the Reaction Zone
recombination reactions, the total number of moles decreases as reaction proceeds. The bimolecular exchange reactions are mole conserving reactions, but since the overall stoichiometry in methane combustion does not involve a change in moles, at least one mole increasing reaction, prior to hydrocarbon depletion, must be important. The net effect of pyrolysis results in an increase in the total number of moles, but the degree of pyrolysis might not be sufficient to offset the decrease in moles associated with the recombination reactions. One likely mole increasing reaction to consider involves the formation of carbon monoxide from the formyl radical via reaction R17:

\[ \text{HCO} + \text{M} \rightarrow \text{CO} + \text{H} + \text{M} \]  

This reaction is fairly endothermic ($\Delta H^\circ = 28583$ cal/mole) and must compete with the following exothermic reaction ($\Delta H^\circ = -90747$ cal/mole) in consuming HCO:

\[ \text{HCO} + \text{OH} \rightarrow \text{CO} + \text{H}_2\text{O} \]  

Using the values of the forward rate constants reported by Browne et al. (13a)

\[ k_{16} = 3 \times 10^{13} \quad \text{cc/mole-sec} \]

\[ k_{17} = 7 \times 10^{13} \exp(-15000/RT) \]

it is possible to ascertain which reaction is the most effective in destroying the formyl radical. The ratio of the rate constants at various
temperatures is shown below:

<table>
<thead>
<tr>
<th>T, °K</th>
<th>( \frac{k_{17}}{k_{16}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500.</td>
<td>0.01522</td>
</tr>
<tr>
<td>1600.</td>
<td>0.02084</td>
</tr>
<tr>
<td>1700.</td>
<td>0.02750</td>
</tr>
<tr>
<td>1800.</td>
<td>0.03520</td>
</tr>
<tr>
<td>1900.</td>
<td>0.04390</td>
</tr>
<tr>
<td>2000.</td>
<td>0.05353</td>
</tr>
</tbody>
</table>

Since \((M)(OH)\) is within the range \(10^2\) to \(10^3\) at the flame surface, reaction R17 is about three- to fifty-times more effective in producing CO from HCO than is reaction R16. Thus, an increase in the total number of moles is expected as carbon monoxide is produced from the formyl radical.

From the radial concentration profiles presented in Chapter V., it is possible to identify the regions in which a mole increase and a mole decrease occur. If attention is focused on the nitrogen profiles, it is noticed that at 1.2 and 2.4 cm above the burner port, the \(N_2\) concentration decreases from its free-stream value to its value at the centerline; at 2.4 cm the decrease is almost linear. This type profile is expected as \(N_2\) diffuses towards the flame surface. However, at 5.0 cm when the nitrogen concentration at the centerline has reached 92% of its free-stream value, the \(N_2\) concentration decreases from the symmetric axis, levels off in the region just outside the flame surface, then gradually increases to its free-stream value. Since \(N_2\) undergoes no chemical reaction which would appreciably change its concentration in the manner indicated, the total moles of combustion gas must
influence the profiles. The initial decrease in the $N_2$ profile is due to an increase in the total number of moles as HCO is converted to CO on the fuel-rich side of the flame surface. The leveling-off is associated with the region in which the bimolecular, mole conserving reactions predominate; and the final increase in the profile is due to a decrease in the total number of moles as the three-body recombination reactions become more important. At heights of 1.2 and 2.4 cm above the burner surface, this effect of the change in the total number of moles on the $N_2$ profile is masked by the steeper gradients as $N_2$ diffuses towards the symmetric axis. The effect is somewhat difficult to see with species undergoing considerable change in concentration due to chemical reaction.

Thus, the partial equilibrium postulation of Schott (71a) appears to be sufficient to explain the superequilibrium radical concentrations encountered in the reaction zone of methane-air diffusion flames. With the oxygen radical concentrations so determined, it is possible to assess the Zeldovich mechanism in describing the formation of NO in the post-flame region of diffusion flames.

VII.3 NO-FORMATION VIA THE ZELDOVICH MECHANISM

Now that estimates of the oxygen radical concentrations in the region outside the flame surface are available, equation 7.6 can be used to calculate the formation rates of NO in the flame via the Zeldovich mechanism. The expression used for the rate constant of reaction R26 is that of Baulch et al. (6).

$$k_{26} = 1.36 \times 10^{14} \exp (-75400/RT)$$
As discussed in Chapter III, at the temperatures at which reaction R26 is important, this expression gives rate constants which are about 1.8 times larger than the rate constants of other investigators. However, several investigators (68)(69) have found that by using this expression the formation rate of NO so determined can account for the quantities of NO observed in the actual combustion system.

Combining equations 7.6 and 7.15 yields the following expression for the formation rate of NO via the Zeldovich mechanism in parts per million per second:

\[
\frac{d(\text{NO})_{\text{ppm}}}{dt} = 3.315 \times 10^{18} \frac{1}{\text{T}} \exp \left( -\frac{75400}{\text{RT}} \right) y_{N_2} y_0
\]

The \(1/\text{T}\) term results from using the gas law to express the molar density. Figure 30 shows the nitric oxide formation rate profiles, calculated from equation 7.16 at the three heights above the burner surface for which oxygen radical concentrations were obtained. The formation rate of NO is seen to peak in the blue reaction zone just subsequent to the completion of the hydrocarbon combustion, and then to rapidly fall off. At 2.4 cm above the burner surface, in less than three millimeters from the edge of the luminous zone, the nitric oxide formation rate increases from about 2500 ppm/sec to over 6000 ppm/sec, then decreases to less than 1 ppm/sec. The rapid decay in the rate is due to the combined effect of a decrease in the oxygen radical concentration and in the temperature. Equation 7.16 shows that the NO formation rate is proportional to the oxygen radical concentration. Further analysis of this equation shows that a 5% decrease in temperature from 2000\(^\circ\)K causes over a 250% decrease in the rate. Sensitivity of the NO formation rate
Figure 30. Nitric Oxide Formation Rate via Zeldovich Mechanism Determined From Measured Temperature And Species Concentrations
to temperature is thus evident.

To determine if the nitric oxide formation profiles presented in Figure 30 are sufficient to account for the amounts of NO\textsubscript{x} observed in the flame, the total production of NO per centimeter height, at each of the three levels at which the formation rate profiles are available, were compared with the total production per centimeter determined from the experimentally obtained NO\textsubscript{x} distributions. The total production per centimeter, at a height \( z \), determined from the formation rate profile is given by:

\[
\text{Total production of NO per centimeter at height } z = 2\pi \int_0^R \left( \frac{d(\text{NO})}{dt} \right) r \, dr
\]

7.17

The total production per centimeter height determined from the experimental NO\textsubscript{x} data is obtained from the slope of the curve of \( G^{\text{NO}}_x \) versus \( z \), where \( G^{\text{NO}}_x \) is the total mass flow of NO\textsubscript{x} at a height \( z \) above the burner surface.

Values of \( G^{\text{NO}}_x \) determined from equation 7.1 at various heights are given in the second column of Table VII. A comparison between the two methods is given in Table XI.

**Table XI. Comparison of the Total Production of NO per Centimeter Height Determined from the Experimental Data and from the Zeldovich Mechanism**

<table>
<thead>
<tr>
<th>Height above burner surface, cm</th>
<th>Total Production of NO per cm from the experimental data, gm/sec-cm</th>
<th>Total Production of NO per cm calculated from the Zeldovich Mechanism, gm/sec-cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>1.7 \times 10^{-6}</td>
<td>0.605 \times 10^{-6}</td>
</tr>
<tr>
<td>2.4</td>
<td>1.7 \times 10^{-6}</td>
<td>0.403 \times 10^{-6}</td>
</tr>
<tr>
<td>5.0</td>
<td>0.166 \times 10^{-6}</td>
<td>0.088 \times 10^{-6}</td>
</tr>
</tbody>
</table>
From Table XI it appears that the Zeldovich mechanism does not completely account for the quantities of NO observed in the flame. The values given in the third column are low by factors of 2.9, 4.2 and 1.9 respectively, at the three levels above the burner surface under consideration.

It is believed, however, that these factors are not all that bad, especially when the difficulty associated with obtaining the values in the table are considered. The values are subject to errors associated with

(i) the numerical integration of equations 7.1 and 7.17;
(ii) the determination of the oxygen radical concentration from the stable species concentrations using equations 7.8, 7.9 and 7.10;
(iii) the predicted mass flux distribution used in equation 7.1; and
(iv) the measured temperature profile.

Sensitivity of the NO formation rate via the Zeldovich mechanism to temperature and the oxygen radical concentration has already been mentioned. The measured temperatures are believed to be accurate to within 5%. A 5% increase in the temperatures in the reaction zone alone is more than sufficient to close the gap at 5.0 cm above the burner surface and brings the total production per centimeter calculated from the Zeldovich mechanism to within 80% of that determined from the experimental data at 1.2 cm. It is, therefore, concluded that the Zeldovich mechanism can sufficiently account for the quantities of nitric oxide generated in the reaction zone of the laminar methane-air diffusion flame studied.

The questions addressed at the beginning of this chapter concerning the distribution and formation mechanism of nitrogen oxides in the flame studied have been answered. The nitrogen oxide concentration profiles were shown to exhibit a sharp peak just outside the edge of the luminous flame surface.
This suggested that any mechanism postulated to describe the formation of NO in the system must be one which is effective outside the flame surface subsequent to hydrocarbon depletion. The high temperatures and super-equilibrium oxygen radical concentrations found in the reaction zone were sufficient to identify the Zeldovich reactions as being the predominant mechanism. The NO formation rate profiles determined from the Zeldovich reactions also exhibited a peak outside the flame surface and rapidly decreased as the temperature and oxygen radical concentrations decreased. The major portion of $\text{NO}_x$ inside the luminous flame core was found to be generated outside the flame surface. The $\text{NO}_x$ so formed penetrated the flame surface via convective and diffusive processes. Small amounts of nitrogen oxide were found to be generated inside the flame surface near the flame base presumably through CN and HN intermediates. The $\text{NO}_x$ inside the surface can be converted to $\text{N}_2$ or other nitrogen containing species. It was found that about 80% of the NO which penetrated the flame surface was converted.

The results presented in this chapter can be generalized and applied to other diffusion flames. The conclusions which follow in Chapter VIII are based on the results of the preceding three chapters.
Chapter VIII. CONCLUSIONS AND RECOMMENDATIONS

The theoretical model of laminar diffusion flames developed utilizes the Burke-Schumann flame sheet concept to locate the fuel-oxygen interface and hence, the points of heat release. The model eliminates the restrictions of the classical Burke-Schumann model in that allowances are made for natural convection effects, and variable thermodynamic and transport properties. The experimental concentration and temperature profiles obtained by extensively microprobing a confined, steady laminar methane-air diffusion flame served to validate the model. The experimentally determined and predicted concentration and thermal fields were in close agreement which suggested that the predicted aerodynamic field was also valid. The predicted aerodynamic field aided in analyzing the experimental NO\textsubscript{x} data.

Analysis of the nitrogen oxide experimental data indicates that before the theoretical model can be used to adequately predict nitrogen oxide formation rates and aid in NO\textsubscript{x} abatement studies, allowance must be made for chemical reaction in the post flame region. Without allowing for reactions associated with the H\textsubscript{2} - O\textsubscript{2} system and the carbon monoxide burnout reaction, the superequilibrium oxygen radical concentrations which are important in determining NO formation rates can not be adequately predicted.

Several conclusions can be drawn from the results of the foregoing investigation. These conclusions are outlined below.

On Laminar, Methane-Air Diffusion Flames:

(1) The changes in gas composition are principally due to the interdiffusion of reactants and products. Major chemical reaction takes place rapidly in a narrow annular region just outside the luminous flame surface.
(ii) Pyrolysis reactions occur inside the luminous flame surface resulting in a large number of carbon particles.

(iii) Near the flame tip the methane concentration is essentially zero and the flame is supported by the combustion of the carbon particles formed in the lower regions of the flame and by the burnout of CO and \( \text{H}_2 \) to \( \text{CO}_2 \) and \( \text{H}_2\text{O} \), respectively.

(iv) Oxygen can penetrate the flame surface near the flame base where temperatures are too low to allow adequate reaction. A concentration gradient in oxygen is thus set-up inside the flame surface. The small amounts of oxygen found inside the flame surface increase the rate of pyrolysis.

(v) Methane and oxygen diffuse to the reaction zone in stoichiometric proportions. Radial temperature and product concentration profiles maximize in the reaction zone.

(vi) Temperature in the reaction zone increases as the height above the burner surface is increased until the adiabatic flame temperature is reached, then slightly decreases as the flame tip is approached. This is due to the higher conductive heat losses to the burner surface in the lower regions of the flame and to the decrease in reaction intensity near the flame tip.

(vii) The water-gas shift reaction is equilibrated in the reaction zone which indicates equilibration of the bimolecular reactions associated with the \( \text{H}_2 - \text{O}_2 \) system as well.

(viii) Hydrogen and oxygen concentrations which exceed their equilibrium values are present in the reaction zone.

(xi) At least one mole increasing reaction must be important prior to
hydrocarbon depletion. The most likely mole increasing reaction aside from the methane pyrolysis reactions involves the formation of carbon monoxide from the formyl radical.

\[ \text{HCO} + \text{M} \rightarrow \text{H} + \text{CO} + \text{M} \quad \text{R17} \]

This reaction is five to fifty times more important in creating CO than is the following reaction:

\[ \text{HCO} + \text{OH} \rightarrow \text{CO} + \text{H}_2\text{O} \quad \text{R16} \]

On Probe Sampling:

(x) The procedure outlined in Appendix V to make radiation and conduction corrections to measured thermocouple bead temperatures is sufficient to determine the unperturbed local gas temperatures.

(xi) Quartz microprobe sampling of laminar methane-air diffusion flames is adequate to obtain concentration profiles of the major flame species. Molecular hydrogen is the concentration most affected.

(xii) Molecular hydrogen is destroyed in the probe via reaction R21

\[ \text{H} + \text{H}_2\text{O} = \text{H}_2 + \text{OH} \quad \text{R21} \]

faster than it can be produced by reactions R20 and R23

\[ \text{O} + \text{H}_2 = \text{OH} + \text{H} \quad \text{R20} \]
\[ H + H + M = H_2 + M \]

The result is for the \( H_2 \) concentration of the sample gas to be lower than the \( H_2 \) concentration in the flame at the sample location.

(xiii) Molecular oxygen is formed in the probe via reaction R19 and to a lesser extent, reaction R22.

\[ H + O_2 = OH + O \]

R19

\[ O + O + M = O_2 + M \]

R22

(xiv) Water vapor is formed in the probe primarily by reactions R21 and R21c. Reaction R24 freezes early in the probe and is not that effective in producing \( H_2O \).

\[ H + H_2O = H_2 + OH \]

R21

\[ 0 + H_2O = OH + OH \]

R21c

\[ H + OH + M = H_2O + M \]

R24

(xv) Carbon monoxide is converted to carbon dioxide in the probe via reaction R18.

\[ CO + OH \rightarrow CO_2 + H \]

R18
On Nitrogen Oxide Formation in Laminar Diffusion Flames:

(xvi) The NO\textsubscript{x} radial concentration profiles peak just outside the luminous flame surface suggesting that nitrogen oxide formation is primarily due to nitrogen fixation and that, therefore, the predominant oxide of nitrogen formed is NO.

(xvii) The NO\textsubscript{x} concentration gradients away from the peaks are quite steep which indicates that NO formation is confined to a narrow annular region where temperature and oxygen availability are suitable for NO formation.

(xviii) NO gets inside the luminous core principally by diffusion and depending upon the direction of the velocity vector, convection at the flame surface.

(xix) In the lower regions of the flame, NO\textsubscript{x} is generated inside the flame surface. The exact mechanism of NO\textsubscript{x} formation inside the surface is unknown, but is believed to involve CN and HN intermediates. A reaction path postulated is

\[ \text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2 \rightarrow \text{CH} + \overset{2}{\text{N}}_2, \text{HN} \rightarrow ^0\text{OH}, ^0\text{O}_2 \rightarrow \text{NO}, \text{NO}_2. \]

(xx) For the flame studied \(Q_{\text{CH}_4} = 5.7 \text{ cc/sec}, Q_{\text{AIR}} = 187.7 \text{ cc/sec}\), core generated NO\textsubscript{x} accounted for about 1.2% of the total NO\textsubscript{x} produced.

(xx) NO\textsubscript{x} is converted to \(N_2\) or other nitrogen containing species inside the flame surface. About 80% of the NO\textsubscript{x} which penetrated the flame surface was converted.
The Zeldovich mechanism is sufficient to account for the amount of $N_2O_x$ formed in the post flame region. The mechanism is given by the following reactions.

\[ N_2 + O \rightarrow NO + N \]  \hspace{1cm} R26

\[ N + O_2 \rightarrow NO + O \]  \hspace{1cm} R27

The rate limiting reaction is R26 and it is very temperature sensitive having an activation energy of 75400 cal/mole.

On the Theoretical Model of Diffusion Flames:

(xxiii) The Burke-Schumann (15) flame sheet concept can be applied to the general conservation laws to adequately predict thermal and aerodynamic fields established during the combustive process.

(xxiv) Before the model can be used to predict nitric oxide formation rates, allowance must be made for chemical reaction outside the luminous flame surface.

The following recommendations and improvements are also suggested:

On Laminar Methane-Air Diffusion Flames:

(i) The importance of pyrolysis reactions in destroying methane should be determined. The sum of the total amount of $CH_4$ at any level of the flame and the total amount of $CH_4$ which diffused to the flame surface up to that level can be subtracted from the total amount of $CH_4$ fired to determine the fraction of the methane fired that pyrolyzed. More radial $CH_4$ concentration profiles
are needed for better accuracy.

(ii) Transmissivity measurements can be used to determine the mass concentration of the carbon particles formed via pyrolysis reactions.

(iii) Mass spectrometric analysis of samples withdrawn from the flame can be used to identify the important pyrolysis products and give some idea of the important methane pyrolysis reactions.

(iv) Molecular beam sampling could be employed with the mass spectrometer to determine radical concentrations in the flame zone.

On Probe Sampling:

(v) A model should be developed which can show the effects of pressure and temperature on the composition of a gas sample as it flows through a probe. The model must make allowances for variable physical properties, chemical reaction and the destruction of radicals on the probe wall.

On Nitrogen Oxide Formation in Laminar Diffusion Flames:

(vi) The mechanism of NO formation inside the flame surface should be identified and factors which influence the formation of NO via this mechanism determined.

(vii) Nitrogen oxide conversion inside the flame surface should be more extensively evaluated.

(vii) The flame studied should be probed for its NO₂ concentration profiles. The small amounts of O₂ inside the flame surface can lead to the formation of HO₂ which is instrumental in NO₂ production.
NO + HO₂ + NO₂ + OH

On the Theoretical Model of Diffusion Flames:

(ix) The model should be modified to allow for chemical reaction outside the flame surface.

(x) Particle track studies should be initiated to verify the flow streamlines predicted by the model.
APPENDIX
Appendix I. Flow Through a Critical Orifice

The governing equation for flow through a critical orifice is given by:

\[
\dot{m} = \text{CAP}_1 \left[ \frac{\gamma M}{RT_1} \left( \frac{2}{\gamma + 1} \right)^{\frac{\gamma}{\gamma - 1}} \right]^{\frac{1}{2}} 
\]

I. 1

where

\( \dot{m} \) = mass flow rate, g/sec

\( A \) = orifice throat area, cm\(^2\)

\( P_1 \) = upstream pressure, dyne/cm\(^2\)

\( \gamma \) = specific heat ratio, \( C_p/C_v \)

\( M \) = molecular weight

\( T_1 \) = upstream temperature, \(^0\text{K}\)

\( R \) = gas constant (8.3138 x 10\(^7\) erg/mole - \(^0\text{K}\))

\( C \) = discharge coefficient

The discharge coefficient is a constant factor which accounts for the effects of boundary layer in the orifice. This empirical constant is determined by calibration and for small orifices falls in the range 0.8 to 0.95.

The volumetric flow rate through the orifice is given below:

\[
Q = \frac{\dot{m}}{\rho} 
\]

I. 2
where \( \rho \) is the density in g/cc. Equations I. 1 and I. 2 can be combined to give the volumetric flow rate in the form

\[
Q = C A K P_1
\]

I. 3

The following table gives the value of \( K \) for certain materials flowing through the orifice when the upstream and downstream temperatures are both 300 \( ^\circ \)K and the downstream pressure is 1 atm. To use the value of \( K \) in the table, \( A \) must be in square centimeters and \( P_1 \) in atmospheres.

<table>
<thead>
<tr>
<th>GAS</th>
<th>( M )</th>
<th>( \gamma )</th>
<th>( K, \text{ cm/atm-sec} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>28.95</td>
<td>1.40</td>
<td>( 2.0110 \times 10^4 )</td>
</tr>
<tr>
<td>Methane</td>
<td>16.04</td>
<td>1.31</td>
<td>( 2.6399 \times 10^4 )</td>
</tr>
<tr>
<td>Oxygen</td>
<td>32.00</td>
<td>1.40</td>
<td>( 1.9128 \times 10^4 )</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>28.02</td>
<td>1.40</td>
<td>( 2.0442 \times 10^4 )</td>
</tr>
</tbody>
</table>

TABLE A.1 Constant to use in Eq. I. 3 for determining volumetric flow rate through orifice.

Figures A.1 and A.2 show the calibration curves for a 0.008 cm orifice calibrated using methane and a 0.040 cm orifice calibrated using air. The linear relation between volumetric flow rate and upstream pressure predicted by equation I. 3 is thus shown to be true.
Orifice B1 (.008 cm diameter)
Calibration Gas: Methane
Least Squares Fit of the Data:
\[ Q = -0.14638 + 1.4116 \times P \]
\[ Q \text{, cc/sec} \quad P, \text{ atm} \]

Figure A.1 Orifice Calibration Curve
Orifice B5 (.040 cm diameter)

Calibration Gas: Air

Least Squares Fit of Data:

\[ Q = -1.46B + 21.950 \times P \]

[cc/sec, P, atm]

25°C

VOLUMETRIC FLOW RATE, cc/sec at 1 atm

Figure A.2 Orifice Calibration Curve
Appendix II. Sampling of Flame Gases using Quartz Microprobes

Since the introduction of any foreign material into the combustion system effects the system, at least locally, in some way, it is desirable to have a measure of the various perturbing effects. The degree to which the measured sample composition corresponds to the actual composition in the unperturbed flame at the position determined has been the topic of many investigations. A review of the material available led to the conclusion that the composition of the sample gas obtained using quartz microprobes corresponds adequately to the local composition of the unperturbed flame. The following effects were considered in reaching this conclusion:

a. aerodynamic effects
b. concentration gradient effects
c. thermal effects
d. catalytic effects
e. quenching effects
f. effect of radicals

AERODYNAMIC EFFECTS

Aerodynamic disturbances can arise both from sample withdrawal and from the bulk of the probe itself. The studies of Fristrom et. al \((38)\) on one-dimensional premixed flames indicated that a small tapered probe, introduced along the streamlines from the hot side of the flame, gave no
visual flame disturbance. Smith and Gordon\textsuperscript{(74)} reported that they observed no visual flame disturbance when using tapered quartz microprobes to sample diffusion flames. In the present study, with the quartz microprobe illustrated in Figure 10, no visual flame disturbance upstream of the sample location was observed. The composition of the gas was reproducible to within 5\% regardless of the bend angle.

The distortion introduced by sample withdrawal alone has been theoretically considered by Rosen.\textsuperscript{(66)} He calculated the velocity potential for a uniformly distributed sink disk. With this result the flow of an incompressible fluid into a sampling probe was estimated, and the distance from the probe at which the flow is distorted by a given amount was determined as a function of the sampling rate. The fractional flow distortion, \( f \), was given by:

\[
f = \frac{(\alpha-1)\sqrt{\alpha}}{2 \left( \left( \frac{z}{r} \right)^2 + \alpha \right)^{3/2}}
\]

\text{II. 1}

where

- \( \alpha = \) sampling rate ratio = \( Q/\pi \cdot r^2 \cdot v_\infty \)
- \( r = \) probe radius
- \( Q = \) volumetric flow rate into the probe
- \( v_\infty = \) unperturbed velocity
- \( z = \) distance from probe
Figure A.3 shows the distance away from the probe as a function of the sampling rate ratio for which flow would be distorted by 2., 5., 10. and 15 percent. From this figure it is seen that it is best to have a low sampling rate ratio. For the probe used in this study \( r \approx 40\mu \), the sampling rate ratio varies from about 30 to 150. A five percent distortion in flow would be estimated to occur 0.4 to 0.8 mm from the probe tip, not too serious an aerodynamic disturbance.

**CONCENTRATION GRADIENT EFFECT**

The flow perturbation set-up by the sample withdrawal would be expected to alter the original gradients established in the combustion process and thus the composition of the gas entering the probe. Westenberg et. al\(^{(84)}\) determined the importance of this alteration in composition in a non-reacting binary system containing a concentration gradient. Results of their experimental and theoretical studies indicated that the concentration at the entrance of the quartz microprobe used was negligibly different from that in the unperturbed gradient at the same position. They explained their findings by the "self-correcting" property of diffusion by which any new gradients set-up tend to be smoothed out; and by the fact that the tendency for the microprobe to "see" too high a concentration upstream is counteracted by too low a concentration downstream. The work of Yanagi et. al\(^{(88})(89)\) indicated that the composition of the gas sampled by a probe with finite inlet area (probe diameter greater than 0.5 mm) was different from the original composition at the sampling position, but that microprobe sampling gave
Figure A.3 Distance from probe at which flow is distorted by f percent

\[ \frac{Z_s}{\Delta Z} = \left( \frac{1}{f} \right)^{2/3} \left( \frac{\Delta Z}{\Delta Z} \right)^{1/3} \]
a substantially correct value for local composition. Their conclusion was reached after comparing the concentration profile predicted by the numerical solution of the diffusion equation with the profiles experimentally obtained using sample probes of different sizes. For the one-dimensional steady flow of a binary mixture of inert gases moving with constant velocity in the positive z-direction, the experimentally determined concentration profile using a microprobe (diameter = 0.2 mm) agreed adequately with the predicted concentration profiles.

**THERMAL EFFECTS**

Apart from flow disturbances which appear to be small, the probe represents a heat sink which can disturb the flame by reducing temperature and enthalpy in the region being sampled. Radiation is the primary mechanism for energy exchange between the hot flames gases and the probe for uncooled quartz probes. Using an emissivity of 0.02 for quartz and equating the energy gain of the probe via convection to the energy loss via radiation indicates that in a gas of temperature 2000 °K, the temperature at the surface of the probe used in this study is about 70 °K below the gas temperature. This indicates that less than four percent of the sample enthalpy had been extracted prior to sampling. Fristrom et. al. (38) used an optical pyrometer to measure the surface temperature of a quartz microprobe in the flame zone of a flat premixed flame. They found the probe surface temperature to be 50 °K below the 2000 °K temperature of the flame zone. This lends some support to the rough calculations made which indicate
that the thermal effects introduced by the insertion of the probe in
the flame zone are small. Since the effect varies as $T^4$, the
disturbance would decrease sharply as gas temperature decreases and
become negligible below 1000 °K.

**CATALYTIC EFFECTS**

Since the sample gas does not come into contact with the probe
walls to any important extent before entering the probe, any catalytic
effects would be confined to the region downstream of the probe tip.

Since the sample is taken ahead of the probe, catalytic effects
outside the probe are of little concern. However, investigations of
the catalytic effect of ceramic coated thermocouples indicate that
probe catalysis is not a serious factor. The importance of catalytic
effects inside the probe can be determined by varying the time the
gases spend in the probe. Gordon and Smith$^{(74)(75)}$ varied the residence
time in a quartz microprobe ten-fold and noted no appreciable effect
on composition. In this study, different quartz probes were used to
obtain samples from the same position; reproducibility of the results
tends to confirm that catalysis is not an important problem.

**QUENCHING EFFECTS**

If a probe is to provide a meaningful sample, it must be capable
of quenching any chemical reactions that may be occurring in the
unperturbed flow field. The combined drop in pressure and temperature
accompanying expansion of the gas as it flows through the probe serves
to quench reaction in critical flow probes. Because of the short
half-life of reaction, about 5 msec, an exceedingly rapid quench time
is required. Fristrom et. al\(^{(38)}\) hypothesized that if it takes a
fraction of a millisecond to get a sample to the cold part of the
probe, the sampling process would have a negligible effect on a reaction
whose half-life is 5 msec.

Friedman and Cyphers\(^{(34)}\) carried out a series of tests to determine
the quenching efficiency of fused quartz microprobes. Probes of
different degree of taper were used to withdraw samples from the post
flame region of premixed propane/air flat flames. The fact that the
gas samples contained at least some CO and \(\text{H}_2\) in the presence of a
large excess of \(\text{O}_2\) showed these probes to have a certain degree of
quenching effectiveness. Agreement in results between the quartz
probes tested when various inside pressures were used, as well as,
agreement in results between the quartz probes and a small water cooled
probe which exhibited excellent reaction quenching efficiency, made
them conclude that quartz microprobes have satisfactory quenching
effectiveness for reactions involving the species CO. They warned,
however, that extrapolation to conditions other than those considered
(lean propane/air flame at 46 mm Hg) may lead to erroneous conclusions.

Knowledge of the temperature – pressure history inside a probe
could be very useful in determining the quenching efficiency of a probe.
A reacting mixture can maintain itself nearly in chemical equilibrium with changing temperature and pressure only as long as the three-body recombination reactions follow fast enough. The two-body reactions may be individually in equilibrium merely exchanging radicals back and forth. This means that once the three-body reactions have frozen, large concentration changes can occur which may be opposite to that expected on the basis of full equilibrium. The expected behavior is for concentration to follow equilibrium conditions for a short way, then sharply deviate from equilibrium as freezing of the two-body reactions sets in. How fast the deviation from equilibrium sets in determines the extent to which the sample gas is different from its inlet composition. If the temperature - pressure history inside the probe were known, reaction mechanism could be combined with the best available rate constants to determine the change in inlet gas composition as the gas passed through the probe. Such a theoretical investigation was carried out by Westenberg and Favin.\(^{(83)}\) They considered the situation in which many elementary chemical reactions occurred simultaneously in a gas undergoing laminar, steady, one-dimensional, adiabatic flow through a supersonic expansion nozzle. The interaction between chemical and fluid dynamic variables was illustrated. The inlet gas composition was an equilibrium mixture of carbon, oxygen and hydrogen having elemental mass fractions in the ratio 0.25:0.1:0.65. The static pressure and temperature at the inlet of the divergent section of the nozzle were 40 atm and 3000 °K, respectively. Their results indicated the freezing of all composition changes in about
50μ sec, at which time the temperature had dropped to 1500 °K and the pressure twenty-fold. The concentrations of the major species were within a few percent of their input values. Their study emphasized the crucial importance of the input pressure level in determining the freezing point: the lower the pressure, the quicker the quenching.

The time it takes to reach a given area ratio (the quantity which determines the degree of quenching) would be considerably shorter for a microprobe than it would be for the large nozzle of Westenberg and Favin (1.0 cm). Therefore, it seems quite likely that microprobes should provide very efficient quenching action.

EFFECT OF RADICALS

A major problem associated with microprobe sampling of flames is that radicals recombine in the probe resulting in the sampled gas being different in composition than the actual flame gas at the sample location. The errors caused by recombination of radicals on the measured concentrations of CH₄, H₂O, H₂ and O₂ would be small if the concentrations of CH₃, H, O and OH did not greatly exceed their equilibrium values. However, H and O concentrations which exceed their equilibrium values by as high as three orders of magnitude have been found in the post flame region of some flames. It is necessary
to investigate each case separately to determine the extent to which recombination of radical affects the composition of the flame gas.

In Chapter VII, section VII.2 this problem is addressed. The reader is encouraged to refer to this chapter to see what affect recombination had on the composition of the flame gases in this study.
Appendix III. Determination of the Composition of the Sample Gas

WATER-FREE COMPOSITION

Samples from the flame were passed through a Drierite column to remove water and then analyzed on a Fisher-Hamilton gas partitioner equipped with a thermal conductivity cell and two columns. The first column was packed with 30% di-2-ethylhexylsebacate on 60-80 mesh Chromosorb P, a liquid phase referred to as DEHS. The second column was packed with 42-60 mesh Molecular Sieve. Helium was used to carry the sample gas through the partitioner, thus analysis for hydrogen was impractical due to their similarity in thermal conductivity.

All the components of the sample, except carbon dioxide are swept quickly through the first column and passed to a detector, which indicates their presence as an electrical signal which is recorded as a composite peak. As the CO$_2$ emerges, it too is recorded. The composite mixture and CO$_2$ then pass to the second column where CO$_2$ is permanently absorbed and the composite mixture separated. As the separate components emerge from the column, they pass to another detector. The resulting electrical signals produce a chromatogram showing an individual peak for each component.

A sample component is quantitatively determined by comparing its peak height with that of a standard. A comparison must be made for each component of the standard and sample gas. This is because peak
height is proportional not only to concentration, but also to thermal conductivity, which is different for each component. The relationship between the concentration of each component in the sample to that in the standard is

$$\frac{\frac{y_i}{h_i}}{h_i}_{s} = \frac{y_i}{h_i}_{std}$$

where $y_i$ denotes the mole fraction of species $i$; and $h_i$, the peak height of species $i$ in the chromatogram. The subscripts $s$ and std denote the sample and standard gas, respectively. Normalizing such that the hydrogen-free, water-free mole fractions sum to one results in

$$y_i_s = \frac{\left( \frac{y_i}{h_i} \right)_{std} h_i_s}{\sum_{i} \left( \frac{y_i}{h_i} \right)_{std} h_i_s}$$

The summation is over all components which exhibited peaks in the chromatogram.

Hydrogen analysis was made by passing the sample gas to another Fisher-Hamilton partitioner which used argon as the carrier gas. The resultant chromatogram gave a relative measure of hydrogen to nitrogen
in the sample. Again, a standard gas is needed to quantitatively determine this ratio in the sample. The relationship between the ratio in the sample to that in the standard is given below:

\[
\left(\frac{y_{H_2}}{y_{N_2}}\right)_s = \left(\frac{h_{H_2}}{h_{N_2}}\right)_{s \text{ std}} \left(\frac{y_{H_2}}{y_{N_2}}\right)_{\text{std}}
\]

III. 3

Knowing the hydrogen to nitrogen ratio in the sample gas allows the water-free mole fractions in the samples to be determined.

Argon and oxygen passed through the first partitioner at the same rate and reached the thermal conductivity cell at the same time. The resultant peak on the chromatogram thus represented oxygen plus argon content of the sample gas. To obtain a relative measure of the \(O_2\) and \(Ar\) concentrations, it was assumed that argon diffused in the combustion system at the same rate as nitrogen. The argon to nitrogen ratio was therefore the same everywhere in the system, the ratio which exists in air. Thus,

\[
\left(\frac{y_{Ar}}{y_{N_2}}\right)_s = \left(\frac{y_{Ar}}{y_{N_2}}\right)_{\text{AIR}} = 0.01196
\]

III. 4
**SAMPLE CALCULATION**

A standard gas mixture consisting of CO₂, O₂, N₂, H₂, CH₄, and CO was obtained from Matheson Gas Products. Their analysis was certified to be accurate to within 2% for each component. Comparison of different standard gas mixtures supported their claim. A sample calculation is presented below for a gas sample taken at the flame surface, 2.4 cm above the burner surface. The data obtained by passing the standard gas and sample gas through the first partitioner appears below.

<table>
<thead>
<tr>
<th>Component</th>
<th>Standard Gas</th>
<th>Sample Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mole Fraction</td>
<td>Peak Height</td>
</tr>
<tr>
<td>CO₂</td>
<td>.0820</td>
<td>8 x 52.77</td>
</tr>
<tr>
<td>O₂ + Ar</td>
<td>.0218</td>
<td>2 x 68.97</td>
</tr>
<tr>
<td>N₂</td>
<td>.8621</td>
<td>64 x 76.86</td>
</tr>
<tr>
<td>CH₄</td>
<td>.0060</td>
<td>1 x 22.156</td>
</tr>
<tr>
<td>CO</td>
<td>.0259</td>
<td>1 x 87.52</td>
</tr>
<tr>
<td>H₂</td>
<td>.0022</td>
<td>-</td>
</tr>
</tbody>
</table>

The peak heights given for the standard gas are the average of five runs. Reproducibility, allowing for changes in sample size, was less than 2%.

The hydrogen-free, water-free concentrations were determined by applying equation III. 2. Listed on the following page are the terms
needed for use in the equation, and the results of applying the equation.

<table>
<thead>
<tr>
<th>Component</th>
<th>$\left{ \frac{y_i}{h_i} \right}_{\text{std}}$</th>
<th>$\left{ \frac{y_i}{h_i} \right}_{\text{std}}$</th>
<th>$h_i$</th>
<th>$y_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>$1.942 \times 10^{-4}$</td>
<td>.09479</td>
<td>.09615</td>
<td></td>
</tr>
<tr>
<td>O$_2$ + Ar</td>
<td>$1.580 \times 10^{-4}$</td>
<td>.01254</td>
<td>.01272</td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td>$1.753 \times 10^{-4}$</td>
<td>.83002</td>
<td>.84191</td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>$2.708 \times 10^{-4}$</td>
<td>.001565</td>
<td>.001590</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>$2.959 \times 10^{-4}$</td>
<td>.04696</td>
<td>.04763</td>
<td></td>
</tr>
</tbody>
</table>

The last column gives the hydrogen-free, water-free concentration.

The data obtained by passing the sample through the second partitioner are shown below.

<table>
<thead>
<tr>
<th>Standard Gas</th>
<th>Sample Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{y_{H_2}}{y_{N_2}}$</td>
<td>peak height $H_2$</td>
</tr>
<tr>
<td>.002552</td>
<td>.04360</td>
</tr>
</tbody>
</table>

The ratio given for the standard gas is again the average of six runs, reproducibility being less than five percent.
From equation III. 3

\[
\begin{pmatrix}
\frac{y_{H_2}}{y_{N_2}} \\
\end{pmatrix}
\text{sample} = 0.4448 \times \left(\frac{0.002552}{0.04360}\right) = 0.02604
\]

therefore

\[
y_{H_2} = 0.02604 \quad y_{N_2} = 0.02192
\]

Normalizing so that fractions sum to unity results in the following water-free concentrations.

<table>
<thead>
<tr>
<th>Component</th>
<th>Water-free Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>0.09409</td>
</tr>
<tr>
<td>O₂ + Ar</td>
<td>0.01245</td>
</tr>
<tr>
<td>N₂</td>
<td>0.82385</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.00156</td>
</tr>
<tr>
<td>CO</td>
<td>0.04661</td>
</tr>
<tr>
<td>H₂</td>
<td>0.02145</td>
</tr>
</tbody>
</table>

To determine the oxygen and argon mole fractions, it is necessary to use equation III. 4

\[
\frac{y_{Ar}}{y_{N_2}} = 0.01196
\]
Therefore

\[ y_{\text{Ar}} = 0.01196(0.82385) = 0.00985 \]

From the above water-free concentrations:

\[ y_{\text{Ar}} + y_{O_2} = 0.01245 \]

therefore

\[ y_{O_2} = 0.01245 - y_{\text{Ar}} = 0.00260 \]

and the water-free mole fractions become

<table>
<thead>
<tr>
<th>Component</th>
<th>Water-free Mole Fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>0.09409</td>
</tr>
<tr>
<td>O₂</td>
<td>0.00260</td>
</tr>
<tr>
<td>N₂</td>
<td>0.82385</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.00156</td>
</tr>
<tr>
<td>CO</td>
<td>0.04661</td>
</tr>
<tr>
<td>H₂</td>
<td>0.02145</td>
</tr>
<tr>
<td>Ar</td>
<td>0.00985</td>
</tr>
</tbody>
</table>
WATER CONCENTRATION IN THE SAMPLE

Water concentration was determined from the dew point of the sample. The Drierite column was by-passed and samples from the flame were directed to the chamber of a General Electric Dew Point Indicator, (Cat. No. 9894861 G), which has a highly reflective surface as a base. The pressure in the chamber was less than 6.0 in Hg and held constant. The temperature at the base of the chamber was lowered until a spot of mist just appeared on the reflective surface. The pressure in the chamber, and temperature at which the first vapor condensed defined the dew-point of the sample. The dew point was checked by maintaining the temperature at the base at the value previously determined and lowering the pressure until any mist on the reflective surface disappeared. The pressure was then slowly increased until the mist spot just began to reappear. The temperature and pressure so determined again defined the dew point. The two methods generally agreed to within five percent.

To complete the sample calculation, the following results were obtained for the sample taken at the flame surface, 2.4 cm above the burner surface.

<table>
<thead>
<tr>
<th>Chamber Pressure</th>
<th>Dew-Point</th>
<th>Vapor Pressure Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.82 in Hg</td>
<td>57.5 °F</td>
<td>0.4772</td>
</tr>
</tbody>
</table>
The mole fraction of water in the sample was determined by applying Dalton's law of partial pressures and Raoult's law. From a combination of these laws, the following relation exist between the mole fraction of water, $y_{\text{H}_2\text{O}}$, the total pressure, $P$, and the vapor pressure of water, $P^v_{\text{H}_2\text{O}}$:

$$y_{\text{H}_2\text{O}} = \frac{P^v_{\text{H}_2\text{O}}}{P}$$

III. 5

Using the data in equation III. 5 results in

$$y_{\text{H}_2\text{O}} = \frac{0.4772}{2.82} = 0.16922$$

After renormalizing so that the concentrations sum to unity when the mole fraction of water is 0.16922, the following gas composition was obtained for the sample taken at the flame surface, 2.4 cm above the burner plate:
<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>.07817</td>
</tr>
<tr>
<td>O₂</td>
<td>.00216</td>
</tr>
<tr>
<td>N₂</td>
<td>.68444</td>
</tr>
<tr>
<td>CH₄</td>
<td>.00130</td>
</tr>
<tr>
<td>CO</td>
<td>.03872</td>
</tr>
<tr>
<td>H₂</td>
<td>.01782</td>
</tr>
<tr>
<td>Ar</td>
<td>.00818</td>
</tr>
<tr>
<td>H₂O</td>
<td>.01692</td>
</tr>
</tbody>
</table>

In the following tables are the compositions of the sample gas at various locations in the flame determined as outlined above.


TABLE A.2a

Concentrations of the Stable Flame Species

\[ z = 1.2 \text{ cm} \]

<table>
<thead>
<tr>
<th>Radius (cm)</th>
<th>CO$_2$</th>
<th>O$_2$</th>
<th>N$_2$</th>
<th>CH$_4$</th>
<th>CO</th>
<th>H$_2$</th>
<th>H$_2$O</th>
<th>Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0428</td>
<td>0.0069</td>
<td>0.489</td>
<td>0.296</td>
<td>0.0321</td>
<td>0.0308</td>
<td>0.0970</td>
<td>0.0058</td>
</tr>
<tr>
<td>0.133</td>
<td>0.0507</td>
<td>0.0066</td>
<td>0.510</td>
<td>0.263</td>
<td>0.0346</td>
<td>0.0313</td>
<td>0.0970</td>
<td>0.0061</td>
</tr>
<tr>
<td>0.267</td>
<td>0.0573</td>
<td>0.0047</td>
<td>0.567</td>
<td>0.181</td>
<td>0.0384</td>
<td>0.0327</td>
<td>0.112</td>
<td>0.0068</td>
</tr>
<tr>
<td>0.401</td>
<td>0.0659</td>
<td>0.0035</td>
<td>0.613</td>
<td>0.107</td>
<td>0.0427</td>
<td>0.0330</td>
<td>0.129</td>
<td>0.0073</td>
</tr>
<tr>
<td>Radius (cm)</td>
<td>CO₂</td>
<td>O₂</td>
<td>N₂</td>
<td>CH₄</td>
<td>CO</td>
<td>H₂</td>
<td>H₂O</td>
<td>Ar</td>
</tr>
<tr>
<td>------------</td>
<td>------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>0.401</td>
<td>0.0660</td>
<td>0.0032</td>
<td>0.617</td>
<td>0.102</td>
<td>0.0419</td>
<td>0.0332</td>
<td>0.129</td>
<td>0.0074</td>
</tr>
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<td>0.0667</td>
<td>0.0027</td>
<td>0.617</td>
<td>0.103</td>
<td>0.0422</td>
<td>0.0332</td>
<td>0.129</td>
<td>0.0074</td>
</tr>
<tr>
<td>0.534</td>
<td>0.0682</td>
<td>0.0073</td>
<td>0.660</td>
<td>0.0187</td>
<td>0.0404</td>
<td>0.0273</td>
<td>0.170</td>
<td>0.0079</td>
</tr>
<tr>
<td>0.534</td>
<td>0.0848</td>
<td>0.0031</td>
<td>0.647</td>
<td>0.0194</td>
<td>0.0410</td>
<td>0.0268</td>
<td>0.170</td>
<td>0.0078</td>
</tr>
<tr>
<td>0.534</td>
<td>0.0763</td>
<td>0.0021</td>
<td>0.654</td>
<td>0.0202</td>
<td>0.0419</td>
<td>0.0271</td>
<td>0.170</td>
<td>0.0077</td>
</tr>
<tr>
<td>0.668</td>
<td>0.0843</td>
<td>0.0028</td>
<td>0.688</td>
<td>0.0002</td>
<td>0.0199</td>
<td>0.0093</td>
<td>0.183</td>
<td>0.0082</td>
</tr>
<tr>
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<td>0.685</td>
<td>0.0002</td>
<td>0.0182</td>
<td>0.0093</td>
<td>0.188</td>
<td>0.0082</td>
</tr>
<tr>
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<td>0.0025</td>
<td>0.687</td>
<td>0.0002</td>
<td>0.0184</td>
<td>0.0093</td>
<td>0.188</td>
<td>0.0082</td>
</tr>
<tr>
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<td>0.0599</td>
<td>0.0537</td>
<td>0.718</td>
<td>0.0006</td>
<td>0.0008</td>
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<td>0.159</td>
<td>0.0086</td>
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<td>0.0008</td>
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<td>0.159</td>
<td>0.0086</td>
</tr>
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<td>0.0090</td>
</tr>
<tr>
<td>0.935</td>
<td>0.0263</td>
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<td>0.751</td>
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<td>0.0090</td>
</tr>
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<td>0.750</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0778</td>
<td>0.0090</td>
</tr>
<tr>
<td>Radius (cm)</td>
<td>CO$_2$</td>
<td>O$_2$</td>
<td>N$_2$</td>
<td>CH$_4$</td>
<td>CO</td>
<td>H$_2$</td>
<td>H$_2$O</td>
<td>Ar</td>
</tr>
<tr>
<td>------------</td>
<td>--------</td>
<td>-------</td>
<td>-------</td>
<td>--------</td>
<td>----</td>
<td>------</td>
<td>-------</td>
<td>----</td>
</tr>
<tr>
<td>1.069</td>
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<td>0.180</td>
<td>0.768</td>
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<td>0.0304</td>
<td>0.0092</td>
</tr>
<tr>
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<td>0.0122</td>
<td>0.177</td>
<td>0.771</td>
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<td>0.0</td>
<td>0.0304</td>
<td>0.0092</td>
</tr>
<tr>
<td>1.069</td>
<td>0.0122</td>
<td>0.178</td>
<td>0.770</td>
<td>0.0</td>
<td>0.0</td>
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<td>0.0092</td>
</tr>
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<td>0.0</td>
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<td>0.0091</td>
</tr>
<tr>
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<td>0.200</td>
<td>0.762</td>
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<td>0.0</td>
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<td>0.0091</td>
</tr>
<tr>
<td>1.203</td>
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<td>0.761</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0263</td>
<td>0.0091</td>
</tr>
<tr>
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<td>0.208</td>
<td>0.764</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0186</td>
<td>0.0091</td>
</tr>
<tr>
<td>1.336</td>
<td>0.0</td>
<td>0.208</td>
<td>0.765</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0186</td>
<td>0.0091</td>
</tr>
<tr>
<td>1.336</td>
<td>0.0</td>
<td>0.207</td>
<td>0.765</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0186</td>
<td>0.0091</td>
</tr>
<tr>
<td>Radius cm</td>
<td>CO₂</td>
<td>O₂</td>
<td>N₂</td>
<td>CH₄</td>
<td>CO</td>
<td>H₂</td>
<td>H₂O</td>
<td>Ar</td>
</tr>
<tr>
<td>----------</td>
<td>-----</td>
<td>----</td>
<td>----</td>
<td>-----</td>
<td>----</td>
<td>----</td>
<td>-----</td>
<td>----</td>
</tr>
<tr>
<td>0.10</td>
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<td>0.629</td>
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<td>0.0075</td>
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<td></td>
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<td>0.0037</td>
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<td>0.075</td>
<td>0.0075</td>
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</tr>
<tr>
<td>0.233</td>
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<td>0.0035</td>
<td>0.627</td>
<td>0.103</td>
<td>0.075</td>
<td>0.0075</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>0.0781</td>
<td>0.0022</td>
<td>0.082</td>
<td>0.0018</td>
<td>0.0075</td>
<td>0.0075</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE A.2b

Concentrations of the Stable Flame Species

z = 24 cm
<table>
<thead>
<tr>
<th>Radius</th>
<th>CO₂</th>
<th>O₂</th>
<th>N₂</th>
<th>CH₄</th>
<th>CO</th>
<th>H₂</th>
<th>H₂O</th>
<th>Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.634</td>
<td>0.0825</td>
<td>0.0102</td>
<td>0.688</td>
<td>0.0</td>
<td>0.0090</td>
<td>0.0067</td>
<td>0.196</td>
<td>0.0082</td>
</tr>
<tr>
<td>0.634</td>
<td>0.0798</td>
<td>0.0106</td>
<td>0.690</td>
<td>0.0</td>
<td>0.0088</td>
<td>0.0067</td>
<td>0.196</td>
<td>0.0083</td>
</tr>
<tr>
<td>0.634</td>
<td>0.0801</td>
<td>0.0102</td>
<td>0.690</td>
<td>0.0</td>
<td>0.0087</td>
<td>0.0067</td>
<td>0.196</td>
<td>0.0083</td>
</tr>
<tr>
<td>0.768</td>
<td>0.0640</td>
<td>0.0578</td>
<td>0.718</td>
<td>0.0</td>
<td>0.0014</td>
<td>0.0</td>
<td>0.150</td>
<td>0.0086</td>
</tr>
<tr>
<td>0.768</td>
<td>0.0622</td>
<td>0.0577</td>
<td>0.720</td>
<td>0.0</td>
<td>0.0014</td>
<td>0.0</td>
<td>0.150</td>
<td>0.0086</td>
</tr>
<tr>
<td>0.768</td>
<td>0.0616</td>
<td>0.0578</td>
<td>0.720</td>
<td>0.0</td>
<td>0.0014</td>
<td>0.0</td>
<td>0.150</td>
<td>0.0086</td>
</tr>
<tr>
<td>0.902</td>
<td>0.0293</td>
<td>0.131</td>
<td>0.745</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0863</td>
<td>0.0089</td>
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<tr>
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<td>0.0288</td>
<td>0.129</td>
<td>0.747</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0863</td>
<td>0.0089</td>
</tr>
<tr>
<td>0.902</td>
<td>0.0296</td>
<td>0.130</td>
<td>0.746</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0863</td>
<td>0.0089</td>
</tr>
<tr>
<td>1.035</td>
<td>0.0165</td>
<td>0.161</td>
<td>0.744</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0688</td>
<td>0.0089</td>
</tr>
<tr>
<td>1.035</td>
<td>0.0160</td>
<td>0.161</td>
<td>0.745</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0688</td>
<td>0.0089</td>
</tr>
<tr>
<td>1.035</td>
<td>0.0165</td>
<td>0.160</td>
<td>0.745</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0688</td>
<td>0.0089</td>
</tr>
<tr>
<td>Radius (cm)</td>
<td>CO₂</td>
<td>O₂</td>
<td>N₂</td>
<td>CH₄</td>
<td>CO</td>
<td>H₂</td>
<td>H₂O</td>
<td>Ar</td>
</tr>
<tr>
<td>------------</td>
<td>-----</td>
<td>----</td>
<td>----</td>
<td>-----</td>
<td>----</td>
<td>----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>1.169</td>
<td>0.00211</td>
<td>0.199</td>
<td>0.752</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0373</td>
<td>0.0090</td>
</tr>
<tr>
<td>1.169</td>
<td>0.00210</td>
<td>0.190</td>
<td>0.762</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0373</td>
<td>0.0091</td>
</tr>
<tr>
<td>1.169</td>
<td>0.00205</td>
<td>0.200</td>
<td>0.752</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0373</td>
<td>0.0091</td>
</tr>
<tr>
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<td>0.766</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0212</td>
<td>0.0092</td>
</tr>
</tbody>
</table>
TABLE A.2c
Concentrations of the Stable Flame Species

\[ z = 5.0 \text{ cm} \]

<table>
<thead>
<tr>
<th>Radius cm</th>
<th>( \text{CO}_2 )</th>
<th>( \text{O}_2 )</th>
<th>( \text{N}_2 )</th>
<th>( \text{CH}_4 )</th>
<th>( \text{CO} )</th>
<th>( \text{H}_2 )</th>
<th>( \text{H}_2\text{O} )</th>
<th>( \text{Ar} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0957</td>
<td>0.0014</td>
<td>0.707</td>
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<td>0.0250</td>
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TABLE A.2d

Concentrations of the Stable Flame Species

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Appendix IV. Determination of the Total Oxides of Nitrogen by the Modified Saltzman Method

The Saltzman method is a colorimetric procedure for the determination of the concentration of nitrogen dioxide in combustion gases. It involves the absorption of NO$_2$ from a known volume of the gas to be analyzed in an azo-dye absorbent solution. At the gas-liquid interface, absorbed NO$_2$ reacts with the absorbent to form diazosulfanilic acid. The intensity of the characteristic pink color of this acid is proportional to the NO$_2$ absorbed.

The apparatus, reagents, and procedures for determining NO$_2$ levels 1 ppm and below, and for levels above 1 ppm, are outlined in a paper by Saltzman (67) and can also be found in ASTM, Designation D1607-69. An absorption period of fifteen minutes with occasional shaking is recommended. The stable pink color is read on a spectrophotometer at 550 nm. A calibration curve relating moles NO$_2$ to intensity is used to determine the concentration of NO$_2$ in the sample. For convenience, in determining the calibration curve, sodium nitrite produces the same color as 1.0 mole of nitrogen dioxide (67). Thus, graduated amounts of NaNO$_2$ can successively be added to known volumes of the absorbent. After full color development, the intensity can be read on a spectrophotometer at 550 nm. A plot of absorbance versus milligrams of NaNO$_2$ per milliliter absorbent, expressed as
equivalent moles NO₂ per milliliter of absorbent can serve as the calibration curve. The plot follows Beer's law.

If the gas to be analyzed for total nitrogen oxide content contains NO, an oxidation step is necessary. Oxygen must be added to oxidize NO to NO₂ in the gas phase. An adequate period of time must be allowed for the complete oxidation of NO to NO₂ and the subsequent absorption of NO₂ into the absorbent before the color can be read. Fine(31) and Greig and Hall(43) have studied the oxidation of nitric oxide to nitrogen dioxide. The homogeneous oxidation reaction is given by:

\[ 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \]

The rate of production of NO₂ is given by:

\[ \frac{d(\text{NO}_2)}{dt} = k(\text{NO})^2 \left(\text{O}_2\right) \]

IV. 1

where the rate constant \( k = 2.4 \times 10^9 \exp(1040/RT) \text{ (cc/mole)}^2/\text{sec} \). If the oxygen concentration is large compared to that needed to completely oxidize the NO to NO₂, then the above rate equation can be integrated to give

\[ \frac{y_{\text{NO}_2}}{y_{\text{NO}}^o} = \frac{k\tau^2 y_{\text{O}_2} (y_{\text{NO}}^o)}{1 + k\tau^2 y_{\text{O}_2} (y_{\text{NO}}^o)} \]

IV. 2
In this equation \( y_{NO_o} \) denotes the nitric oxide mole fraction at time zero; \( y_{O_2} \), the oxygen mole fraction (assumed constant); and \( \rho \), the molar density. When oxygen is added to the sample gas, the mole fraction of oxygen in the gas to be analyzed is \( y_{O_2} \), and the relationship between the NO mole fraction prior to oxygen addition, \( y_{NO_s} \), and the NO mole fraction after the addition, \( y_{NO_{eff}} \), is:

\[
(y_{NO_{eff}}) = (1 - y_{O_2})(y_{NO_s})
\]

IV. 3

Using this relationship in equation IV. 2, realizing that

\[
(y_{NO_{eff}}) = (y_{NO_o}) \quad \text{results in}
\]

\[
\frac{(y_{NO_2})}{(y_{NO_s})} = (1 - y_{O_2}) \frac{k\rho^2 y_{O_2} (1-y_{O_2})(y_{NO_s})}{1 + k\rho^2 y_{O_2} (1-y_{O_2})(y_{NO_s})}
\]

IV. 4

It can be shown that for any given reaction time, \( t \), the value of \( y_{O_2} \) which maximizes \( (y_{NO_2})/(y_{NO_s}) \) is about 0.5. This maximum arises because the added oxygen dilutes the sample gas causing the effective NO mole fraction, \( y_{NO_{eff}} \), to decrease. Fine (31) followed the conversion of NO to \( NO_2 \) as a function of the oxygen concentration utilizing the Saltzman method. The experimental data points, Figure A.4, fall close to the theoretical curve, as predicted by equation IV. 4, confirming the value of the rate constant of the homogeneous gas phase oxidation reaction. The figure shows that by diluting to
FIGURE A4  RATE OF CONVERSION OF NO TO NO₂
AT DIFFERENT O₂ CONCENTRATIONS

- Theoretical Curve
- Experimental Points

50 % O₂, 64 ppm
60 % O₂, 52 ppm
1 % O₂, 50 ppm

NOₓ ppm

TIME, HOURS
50% oxygen, the conversion is 95% complete within 24-hours for samples containing initially 52 ppm NO. Figure A.5 shows the percentage conversion of NO to NO\textsubscript{2} for various initial NO concentrations when 50% dilution with oxygen and 24-hour oxidation-absorption period are allowed. Also shown is the absolute error in ppm NO. For NO concentrations in the flame from 10 to 100 ppm, the absolute error in the modified Saltzman method allowing a 24-hour oxidation-absorption period and diluting with 50% oxygen is about 2 ppm.

Determination of NO\textsubscript{x} concentration in the sample gas

Calibration curve

A standard solution of sodium nitrite was prepared having a concentration 0.0203 g/liter. One milliliter of this working solution produced a color equivalent to that of 4.0862 \times 10^{-7} mole NO\textsubscript{2}. Graduated amounts of this working solution were added to a series of 50-ml volumetric flasks and diluted to the marks with absorbing reagent. After fifteen minutes, the colors were read on a Baush and Lomb, Spectronic 20 spectrophotometer at 550 nm. Figure A.6 shows the resultant calibration curve. The curve was periodically checked during the time span of the experiments.

Procedure

A known volume of absorbing reagent, \( V_a \), was charged to a sampling flask of volume \( V_f \). The flask was evacuated \( \approx \) the incipient boiling point of the absorbent; the pressure in the flask was recorded, \( P_1 \).
Figure A.5 Percentage Conversion of NO to NO$_2$ and Absolute Error When Using Modified Saltzman Method (24-hr Reaction Time, 50% O$_2$ Dilution)
Figure A.6 Calibration Curve for Saltzman Method
Sample gas was then added to the flask until the pressure in the flask was about one-half atmosphere, $P_s$. The pressure in the flask was then brought up to one-atmosphere with oxygen, $P_f$. A twenty-four hour, oxidation-absorption period was allowed with occasional shaking.

The color was read on the spectrophotometer at 550 nm and the moles $NO_2/ml$ absorbent, $(N_{NO_2})$ was determined from the calibration curve. The concentration of $NO_x$ in parts per million, $(NO_x)_{ppm}$, corrected to 1 atm and 25°C, was calculated using the following expression:

$$\frac{(NO_x)}{\text{ppm}} = \frac{N_{NO_2} \cdot V_a}{(V_f - V_a)} \left( \frac{29.92}{(P_f - P_1)} \right) \left( \frac{T_R}{298} \right) \frac{1}{f} (2.4466 \times 10^{10}) \quad \text{IV. 5}$$

where

- $V_a$ = volume of absorbent used, cc
- $V_f$ = volume of collection vessel, cc
- $P_1$ = pressure in vessel after evacuation, in Hg
- $P_f$ = pressure in vessel after dilution with $O_2$, in Hg
- $P_s$ = pressure in vessel after sample added, in Hg
- $T_R$ = room temperature, °K
- $2.4466 \times 10^4$ = volume 1 mole gas occupies at 1 atm and 25°C, cc
- $f$ = oxygen dilution factor

$$f = \frac{P_s - P_1}{P_f - P_1} \quad \text{IV. 6}$$
SAMPLE CALCULATION

The following data were obtained for a sample taken at the flame surface, 2.4 cm above the burner plate.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Volume of flask, cc</th>
<th>Volume of used, cc</th>
<th>TR °C</th>
<th>Pi in Hg</th>
<th>Ps in Hg</th>
<th>Pf in Hg</th>
<th>absorb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>75</td>
<td>10</td>
<td>29.0</td>
<td>0.565</td>
<td>12.64</td>
<td>29.79</td>
<td>.285</td>
</tr>
<tr>
<td>2</td>
<td>75</td>
<td>10</td>
<td>29.0</td>
<td>0.69</td>
<td>11.69</td>
<td>30.29</td>
<td>.275</td>
</tr>
<tr>
<td>3</td>
<td>75</td>
<td>10</td>
<td>29.0</td>
<td>0.69</td>
<td>10.59</td>
<td>29.79</td>
<td>.245</td>
</tr>
</tbody>
</table>

The mole NO₂/ml absorbent was read from the calibration curve; the dilution factor calculated, and the concentration in parts per million determined from equation IV. 5. The results are shown below.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>moles NO₂</th>
<th>moles NO₂</th>
<th>f</th>
<th>(NOₓ) ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.83 x 10⁻⁸</td>
<td>0.83 x 10⁻⁷</td>
<td>.4132</td>
<td>78.4</td>
</tr>
<tr>
<td>2</td>
<td>0.80 x 10⁻⁸</td>
<td>0.80 x 10⁻⁷</td>
<td>.3716</td>
<td>82.9</td>
</tr>
<tr>
<td>3</td>
<td>0.71 x 10⁻⁸</td>
<td>0.71 x 10⁻⁷</td>
<td>.3402</td>
<td>82.1</td>
</tr>
</tbody>
</table>

The last column shows the NOₓ concentration at the luminous edge of the flame, 2.4 cm above the burner plate. In the following tables are NOₓ concentrations at various locations in the flame determined as outlined above.
<table>
<thead>
<tr>
<th>Height above Burner, cm</th>
<th>Radius, cm</th>
<th>NO$_x$ Concentration, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sample #1</td>
</tr>
<tr>
<td>0.25</td>
<td>0.0</td>
<td>6.7</td>
</tr>
<tr>
<td>0.50</td>
<td>0.0</td>
<td>8.1</td>
</tr>
<tr>
<td>1.2</td>
<td>0.0</td>
<td>21.2</td>
</tr>
<tr>
<td>1.2</td>
<td>0.267</td>
<td>35.0</td>
</tr>
<tr>
<td>1.2</td>
<td>0.535</td>
<td>55.7</td>
</tr>
<tr>
<td>1.2</td>
<td>0.602</td>
<td>75.7</td>
</tr>
<tr>
<td>1.2</td>
<td>0.668</td>
<td>76.2</td>
</tr>
<tr>
<td>1.2</td>
<td>0.735</td>
<td>35.2</td>
</tr>
<tr>
<td>1.2</td>
<td>0.802</td>
<td>28.6</td>
</tr>
<tr>
<td>1.2</td>
<td>0.936</td>
<td>13.0</td>
</tr>
<tr>
<td>1.5</td>
<td>0.0</td>
<td>23.9</td>
</tr>
<tr>
<td>1.5</td>
<td>0.25</td>
<td>29.3</td>
</tr>
<tr>
<td>1.5</td>
<td>0.50</td>
<td>66.3</td>
</tr>
<tr>
<td>1.5</td>
<td>0.57</td>
<td>97.9</td>
</tr>
<tr>
<td>1.5</td>
<td>0.635</td>
<td>75.3</td>
</tr>
<tr>
<td>1.5</td>
<td>0.70</td>
<td>60.0</td>
</tr>
<tr>
<td>1.5</td>
<td>0.77</td>
<td>48.3</td>
</tr>
<tr>
<td>1.5</td>
<td>0.90</td>
<td>26.9</td>
</tr>
<tr>
<td>1.5</td>
<td>1.035</td>
<td>9.8</td>
</tr>
<tr>
<td>1.5</td>
<td>1.17</td>
<td>4.1</td>
</tr>
<tr>
<td>Height above Burner, cm</td>
<td>Radius, cm</td>
<td>NO\textsubscript{x}\ Concentration, ppm</td>
</tr>
<tr>
<td>------------------------</td>
<td>------------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>1.8</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>1.8</td>
<td>0.235</td>
<td></td>
</tr>
<tr>
<td>1.8</td>
<td>0.470</td>
<td></td>
</tr>
<tr>
<td>1.8</td>
<td>0.535</td>
<td></td>
</tr>
<tr>
<td>1.8</td>
<td>0.61</td>
<td></td>
</tr>
<tr>
<td>1.8</td>
<td>0.67</td>
<td></td>
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<td>0.87</td>
<td></td>
</tr>
<tr>
<td>1.8</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>1.8</td>
<td>1.14</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>0.71</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>0.87</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Height above Burner, cm</td>
<td>Radius, cm</td>
<td>NO(_x) Concentration, ppm</td>
</tr>
<tr>
<td>------------------------</td>
<td>------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sample #1</td>
</tr>
<tr>
<td>2.1</td>
<td>1.14</td>
<td>4.2</td>
</tr>
<tr>
<td>2.1</td>
<td>1.24</td>
<td>4.4</td>
</tr>
<tr>
<td>2.4</td>
<td>0.1</td>
<td>43.5</td>
</tr>
<tr>
<td>2.4</td>
<td>0.235</td>
<td>46.2</td>
</tr>
<tr>
<td>2.4</td>
<td>0.50</td>
<td>63.7</td>
</tr>
<tr>
<td>2.4</td>
<td>0.57</td>
<td>94.1</td>
</tr>
<tr>
<td>2.4</td>
<td>0.64</td>
<td>91.3</td>
</tr>
<tr>
<td>2.4</td>
<td>0.77</td>
<td>54.2</td>
</tr>
<tr>
<td>2.4</td>
<td>0.90</td>
<td>29.7</td>
</tr>
<tr>
<td>2.4</td>
<td>1.17</td>
<td>10.6</td>
</tr>
<tr>
<td>3.0</td>
<td>0.0</td>
<td>34.9</td>
</tr>
<tr>
<td>4.0</td>
<td>0.0</td>
<td>69.8</td>
</tr>
<tr>
<td>5.0</td>
<td>0.0</td>
<td>69.9</td>
</tr>
<tr>
<td>5.0</td>
<td>0.267</td>
<td>95.6</td>
</tr>
<tr>
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<td>0.535</td>
<td>74.6</td>
</tr>
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<td>0.67</td>
<td>47.5</td>
</tr>
<tr>
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<td>0.80</td>
<td>31.1</td>
</tr>
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<td>0.935</td>
<td>22.6</td>
</tr>
<tr>
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<td>0.0</td>
<td>104.4</td>
</tr>
<tr>
<td>6.0</td>
<td>0.0</td>
<td>91.9</td>
</tr>
<tr>
<td>7.0</td>
<td>0.0</td>
<td>65.1</td>
</tr>
</tbody>
</table>
Appendix V. Gas Temperature Determination

A platinum vs. platinum 13% rhodium thermocouple assembly was used to obtain temperature profiles in the combustion system. The thermocouple, shown in Figure 11, was made by flame welding 3-mil wires of the respective metals and coating them with silica to reduce catalytic errors. The 3-mil thermocouple lead wires were then welded to 20-mil platinum and platinum 13% rhodium support wires which were connected to a Tektronix 5103N oscilloscope. This type of probe minimized the disturbance of the flame during the sampling process; only the 3-mil wires were ever in the flame. The thermocouple bead, 4.5 mil diameter cylinder, was carefully positioned in the flame; its exact location was determined by the use of a cathetometer and a calibrated turn screw. The potential developed at the head was read on the oscilloscope and a thermocouple calibration table supplied by Omega Engineering, Inc. served to determine the bead temperature. The gas temperature was calculated from the bead temperature by the application of an energy balance on the thermocouple bead and lead wires.

In general, the thermocouple bead does not attain the same temperature as the hot gas. Radiative energy exchange exists between the thermocouple and its surroundings and the thermocouple bead can gain or lose heat by conduction to the lead wires. The amount and direction of this conductive energy exchange between the bead and
lead wires depends upon the length of wire between the junction and the supports, and the gas temperature distribution the lead wires experience. In order to get an accurate measure of the gas temperature, radiation and conduction corrections must therefore be made to the thermocouple bead temperature.

The steady state energy equation for the thermocouple can be written as follows:

\[
\frac{d}{dx} \left( k \frac{dT}{dx} \right) + \frac{4h}{d} (T_g - T) - \frac{4\sigma}{d} (\varepsilon_w T^b - \alpha T^b_{\text{wall}}) = 0 \quad \text{V. 1}
\]

The above equation assumes negligible energy exchange between the gas and the wire and that the surrounding walls are black to radiation from the wire. The absorption term, \( \alpha T^b_{\text{wall}} \), is usually negligible. In equation V. 1, both the gas temperature, \( T_g \) and the wire temperature, \( T \), are function of \( x \), the distance along the wire measured from the platinum support leg. The wire thermal conductivity \( k \), emissivity \( \varepsilon_w \), and heat transfer coefficient \( h \), are functions of the wire temperature. The lead wire diameter is denoted by \( d \) and \( \sigma \) represents the Stefan-Boltzmann constant.

An iterative procedure is necessary to solve for the wire and gas temperature distributions which satisfy equation V. 1. The temperature distribution in the wire is a function of the position of the thermocouple in the hot gas. The thermocouple is situated in a plane
which passes through the symmetric axis. By traversing the thermocouple bead along a radius perpendicular to this plane, it is possible to obtain a first approximation to the gas temperature over the lead wires. Equation V. 1 can be solved to determine the temperature distribution. To determine the actual gas temperature and the actual temperature distribution in the lead wire, an iterative procedure is required.

As shown in the diagram below, the thermocouple lead of length \( XL \) is subdivided into \( M-1 \) segments. The bead is designated by segment \( L \) which has length equal to the bead diameter.

Distances along the lead wire are measured from the left support. Each segment has associated with it a wire temperature \( T_{y,x} \) and a gas temperature above it \( T_{g_{y,x}} \). The first subscript denotes the distance the lead wire is from the symmetric axis. The \( x \) and \( y \) coordinates of each segment determine the distance the segment is from the symmetric axis.
Equation V. 1 is applied to each segment of the thermocouple lead. The finite difference form of this equation applied to the $i^{th}$ segment is shown below

$$\frac{k_{i-\frac{1}{2}}}{x_i-x_{i-1}} \frac{T_{y,i-1} - T_{y,i}}{A_{w}^c} + \frac{k_{i+\frac{1}{2}}}{x_{i+1}-x_i} \frac{T_{y,i} - T_{y,i+1}}{A_{w}^c} + \left[ h \left( g_{xy} - T_{y,i} \right) + \varepsilon \sigma T_{y,i}^4 \right] A_{s}^s = 0 \quad \text{V. 2}$$

where $A_{w}^c = \text{cross-sectional area of wire} = \frac{1}{4} \pi d^2$,
$A_{s}^s = \text{surface area of } i^{th} \text{ segment} = \begin{cases} \pi d \Delta x_i \text{ for wire} \\ \pi d_b^2 \text{ for spherical bead} \\ \pi d_b \Delta x_b \text{ for cylindrical bead} \end{cases}$

Rewriting equation V. 2 in tridiagonal form results in

$$- \frac{k_{i-\frac{1}{2}}}{x_i-x_{i-1}} T_{y,i-1} + \frac{k_{i-\frac{1}{2}}}{x_i-x_{i-1}} - \frac{k_{i+\frac{1}{2}}}{x_{i+1}-x_i} + \left( h + \varepsilon \sigma T_{y,i}^3 \right) \frac{A_{s}^s}{A_{w}^c} T_{y,i}$$

$$- \frac{k_{i+\frac{1}{2}}}{x_{i+1}-x_i} T_{y,i+1} = h \frac{A_{s}^s}{A_{w}^c} T_{g,y,i} \quad \text{V. 3}$$
When \( i = L \), the wire temperature at this position is known, (the bead temperature) and equation V. 3 is rewritten so that the gas temperature is an unknown.

\[
\frac{-k_{L-1}}{x_L - x_{L-1}} T_{y,L-1} + \frac{h}{A^c} \frac{A^s}{A_{w}} T_{g_{y,L}} + \frac{-k_{L+1}}{x_{L+1} - x_L} T_{y,L+1} =
\]

\[
\frac{-k_{L-1}}{x_L - x_{L-1}} + \frac{k_{L+1}}{x_{L+1} - x_L} + \left( h + \varepsilon_0 T_{y,L}^3 \right) \frac{A^s}{A_{w}} T_{y,L}^V.
\]

At \( i = 1 \) and \( i = M \), the temperature of the wire is assumed to be the same as that of the bead when the bead was at the same distance from the symmetric axis as the ends of the lead. Equations V. 3 and V. 4 can therefore be applied to the various segments of the lead to determine \( T_{y,i} \) and \( T_{g_{y,L}} \) which corresponds to any gas temperature distribution.

To illustrate the iterative procedure employed to determine \( T_{g_{y,L}} \) at all \( y \), let \( j \) denote the \( y^{\text{th}} \) distance the bead was from the symmetric axis. When \( j = 1 \), the bead was at the axis. The procedure is as follows.

(1) Assume gas temperatures over the bead for all \( j \), i.e., assume \( T_{g_{j,L}} \), \( j = 1, \text{MAX} \).
(ii) \( j = 1 \) \((y = 0)\)

(iii) Determine the gas temperature over each segment of the wire by interpolating the assumed gas temperature distribution.

(iv) Solve equations V. 3 and V. 4 to determine the corresponding temperature distribution in the wire and the new estimate for the gas temperature over the bead, \( T_{g_j,L} \).

(v) Repeat (iii) and (iv) for \( j = 2 \) until \( j = j_{\text{MAX}} \).

(vi) Compare the new estimates of the gas temperatures over the bead with the previous estimates. If they agree convergence is achieved. If they do not agree, with these new estimates, repeat from (ii).

Upon convergence, gas temperature and wire temperature distributions which satisfy equation V. 1 will result. Radiation and conduction corrections will have been made to the thermocouple bead temperature to obtain the actual gas temperature about the bead.

The wire emissivity, \( \varepsilon_w \), and the heat transfer coefficient, \( h \), must be determined to make the above method possible. For coated wires the emittance depends on the diameter of the wire and the thickness
of the coating. Bradley and Entwistle\textsuperscript{(11)} give theoretical and experimental values of total hemispherical emittance for silica coated platinum 10\% rhodium wires of different coat thicknesses. Their data indicate that the effect of the silica coating is to decrease the emissivity; for thick coatings the value of the emissivity may even be less than that of the uncoated wire. For a core diameter of 0.5 mil and overall diameter ranging from 0.7 mil to 2.1 mil the emittance of platinum 10\% rhodium wires was shown to decrease from about 0.25 at 1000 °C to about 0.15 at 1500 °C, the curves flattening-out at the higher temperature. For uncoated platinum 10\% rhodium wires Bradley and Entwistle\textsuperscript{(12)} report that the emittance increases from about 0.18 at 1000 °C to about 0.23 at 1500 °C. The emittance of pure platinum increases from about 0.16 at 1000 °C to about 0.22 at 1500 °C. Kaskan\textsuperscript{(51)} recommends a constant value of 0.22 for the emissivity of coated platinum-rhodium wires in the determination of gas temperatures during combustion.

The heat transfer coefficient can be determined from the Nusselt number.

\[
Nu = \frac{hd}{k}
\]
The following expressions are generally used for the Nusselt number:

for the wire
\[ \text{Nu} = 0.42 \ Pr^{0.2} + 0.57 \ Pr^{0.33} \ Re^{0.5} \]  \hspace{1cm} V. 3

for the cylindrical bead
\[ \text{Nu} = 0.43 \ Pr^{0.38} + 0.5 \ Re^{0.5} \ Pr^{0.38} \]  \hspace{1cm} V. 4

for the spherical bead
\[ \text{Nu} = 2.0 + 0.236 \ Re^{0.606} \ Pr^{0.33} \]  \hspace{1cm} V. 5

Equation V. 3 is frequently used in anemometry for cross flow to a wire. Eckert and Drake\(^{23a}\) recommend equations V. 4 and V. 5 for the Nusselt number for cylinders and spheres in gas streams for Reynolds numbers between 1 and 1000.

Assuming a Prandtl number of 0.7 and velocities in the combustion system ranging from 5.0 cm/sec at the fuel nozzle to about 150 cm/sec along the flame surface, the Nusselt numbers for the wire and the thermocouple bead are bounded as follows:

for the wire:
\[ 0.91 < \text{Nu} < 1.05 \]

for the cylindrical bead:
\[ 0.93 < \text{Nu} < 1.07 \]

for a spherical bead:
\[ 2.28 < \text{Nu} < 2.37 \]

For the temperature correction, the gas thermal conductivity was assumed to be that of nitrogen at the respective gas temperature. The thermal conductivity data of the platinum 13% rhodium wire
were estimated from the data presented by Bradley and Matthews\textsuperscript{(13)} on the thermal conductivity of platinum and platinum 10% rhodium wires. Thermal conductivity data for pure platinum were taken from the literature.\textsuperscript{(78)}

Figures A. 7a, b and c show the uncorrected and corrected temperature profiles for heights of 1.2, 2.4, and 5.0 centimeters above the burner port for the base case flame studied, \((Q_{\text{fuel}} = 5.8 \text{ cc/sec}, Q_{\text{air}} = 187.7 \text{ cc/sec})\). The open circles represent the uncorrected gas temperature, i.e., the bead temperature at that position in the flame. The shaded circles represent the corrected temperatures, the result of applying equation V. 1 to successive segments of the thermocouple lead wire. For the corrected values, the Nusselt number of the wire was assumed to be 0.985, and that for the bead, 1.0; the wire emissivity was held at 0.23. The dashed lines indicate the confidence range, \((\pm 5\% \text{ on the measured bead temperature; } \pm 10\% \text{ change in the wire Nusselt number; the bead Nusselt number range from 0.93 to 2.3; and the wire emissivity range from 0.15 to 0.3})\). The range of the bead Nusselt number accounted for only a 5 \(^{\circ}\text{K}\) change in the corrected gas temperature. The range of the wire emissivity accounted for about a 80 \(^{\circ}\text{K}\) change in the highest corrected temperature.

It is noted that near the centerline, at heights of 1.2 and 2.4 centimeters above the burner port, the corrected gas temperatures are below the measured bead temperatures. This indicates that the bead gained more energy by conduction from the lead wires than it lost
Figure A.7a Radial Temperature Distribution \( Z = 1.2 \text{ cm} \)
Figure A.7b Radial Temperature Distribution
Z = 2.4 cm
Figure A.7c Radial Temperature Distribution

Z = 5.0 cm
by radiation. If only a radiation correction had been made, which is the usual procedure, the "correction" would have been in a direction away from the true gas temperature.

The fact that the adiabatic flame temperature is attained in the reaction zone, 2.4 cm above the burner port lends some validity to this method of allowing for conductive and radiative heat exchanges between the thermocouple and the gas and to the values of the Nusselt numbers and emissivity used.
Appendix VI. Mathematical Description of Laminar Diffusion Flames

A mathematical model of diffusion flames has been developed which makes allowances for natural convection, variable thermodynamic and transport properties and radiative heat losses from the flame zone. The purpose of this appendix is to outline in some detail the equations and boundary conditions employed.

The model is concerned with an ideal mixture of methane, air and their combustion products. The combustion system consists of two concentric tubes of radii \(L\) and \(R\) through which the fuel and air enter, respectively. The system is shielded by a cylinder of radius \(R\). The system is pictorially described in Figure 18 in Chapter VI. The steady-state forms of the conservation equations which describe the axisymmetric system are presented below:

**CONTINUITY EQUATION:**

\[
\nabla \cdot \vec{G} = 0
\]

**MOMENTUM EQUATIONS:**

- radial direction:
  \[
  \nabla \cdot (\vec{G}_r + \vec{\tau}_r) + \frac{\partial p}{\partial r} = 0
  \]

- axial direction:
  \[
  \nabla \cdot (\vec{G}_z + \vec{\tau}_z) + \frac{\partial p}{\partial z} - \rho g = 0
  \]

**ENERGY EQUATION:**

\[
C_p (\vec{G} \cdot \nabla T) - \nabla \cdot (k \nabla T) - Q_{\text{gen}} + Q_{\text{loss}} = 0
\]
SPECIES EQUATION:

\[ \nabla \cdot (\bar{G}_j - \rho D_{j,\text{mix}} \nabla w_j) - \dot{R}_j = 0 \quad j=1,N \quad \text{VI. 5} \]

A table of nomenclature is located at the end of Chapter VI.

The momentum equations make allowances for gravitational, pressure and shear stress forces which balance momentum forces caused by flow within the system. Axial and radial convection and conduction of energy are balanced by the generation and loss of energy due to chemical reaction and radiation in the energy conservation equation. The rate of appearance or disappearance of species \( j \) is balanced by the net fluxes of species \( j \) due to axial and radial convection and diffusion in the species conservation equation. When combined with the appropriate boundary and inlet conditions, the solutions of the above non-linear partial differential equations are the aerodynamic, thermal and concentration fields established during the combustive process.

The vorticity and stream function are two quantities which can aid in solving the previous equations. The vorticity \( \omega \), is defined as:

\[ \omega = \frac{\partial v_r}{\partial z} - \frac{\partial v_z}{\partial r} \quad \text{VI. 6} \]
and the stream function is defined as:

\[
\frac{d}{dz} \left( \frac{1}{r \rho} \frac{\partial \psi}{\partial z} \right) + \frac{d}{dr} \left( \frac{1}{r \rho} \frac{\partial \psi}{\partial r} \right) = -\omega
\]

VI. 7

The vorticity is a measure of the amount of counter-clockwise rotation possessed by the fluid and the integrals of the stream function results in streamlines, curves which particles of fluid entering the system follow. The vorticity and stream function are related as follows:

STREAM FUNCTION EQUATION:

\[
\frac{d}{dz} \left( \frac{1}{r \rho} \frac{\partial \psi}{\partial z} \right) + \frac{d}{dr} \left( \frac{1}{r \rho} \frac{\partial \psi}{\partial r} \right) = -\omega
\]

VI. 8

Formulation of the vorticity transport equation serves to eliminate the pressure as one of the dependent variables. By differentiating the r-direction of the momentum equations with respect to z and the z-direction with respect to r, an equation independent of pressure results when the two differentiated momentum equations are subtracted. The resultant equation is termed the vorticity transport equation and is presented below:

VORTICITY TRANSPORT EQUATION:

\[
\nabla \cdot \left( \mathbf{G} \, \frac{\omega}{r} \right) + \frac{1}{r} \nabla \left( \frac{\nabla^2 + \nabla^2}{2} \right) \cdot 180 \rho = \frac{1}{r^2} \nabla \cdot \left[ \frac{1}{r^2} \nabla \left( \mu \, \frac{\omega}{r} \right) \right] \\
+ \frac{1}{r} \frac{d}{dr} (\rho g) + \sum_{\omega}
\]

VI. 9
The quantity $S\omega$ involves gradients of the viscosity and density and is nearly zero for all fluid flow. It is assumed to be negligible in this mathematical description of diffusion flames.

The stream function equation, vorticity transport equation, and energy and chemical species conservation equations serve to describe the system of interest. These equations are made non-dimensional by normalizing the variables, physical properties and coordinates by reference quantities. The Reynolds, Grashof, Prandtl and Schmidt numbers serve to simplify the normalized equations. These quantities are identified in Chapter VI. After minor manipulation each equation can be rewritten in the following general elliptic equation form:

$$a_\phi \left\{ \frac{\partial}{\partial \eta} \left( \phi \frac{\partial \psi}{\partial \xi} \right) - \frac{\partial}{\partial \xi} \left( \phi \frac{\partial \psi}{\partial \eta} \right) \right\} - \frac{\partial}{\partial \eta} \left\{ b_\phi \xi \frac{\partial}{\partial \eta} (c_\phi \phi) \right\}$$

$$- \frac{\partial}{\partial \xi} \left\{ b_\phi \xi \frac{\partial}{\partial \xi} (c_\phi \phi) \right\} + \xi d_\phi = 0$$  \hspace{1cm} \text{VI. 10}

In this equation $\phi$ is the main dependent variable and $a_\phi$, $b_\phi$, $c_\phi$ and $d_\phi$ denote various parameters associated with a particular $\phi$. These parameters are identified in Table V in Chapter VI.
BOUNDARY CONDITIONS:

Inlet Conditions:

The model makes allowances for the inlet conditions to be specified. The inlet fuel and air velocities can be any function. Generally, the velocity profiles in the inlet tubes are either specified to be flat or parabolic. For a flat profile

\[ v_z(r) = \left[ v_{\text{fuel}} \right]_{\text{Ave}}, \quad v_r(r) = 0 \quad r < L \quad \text{VI. 11} \]

\[ v_z(r) = \left[ v_{\text{oxy}} \right]_{\text{Ave}}, \quad v_r(r) = 0 \quad r > L \quad \text{VI. 12} \]

and for a parabolic profile with \( v_z = 0 \) at \( r = L \) and \( r = R \)

\[ v_z(r) = 2 \left[ v_{\text{fuel}} \right]_{\text{Ave}} \frac{1 - \left( \frac{r}{L} \right)^2}{1} \quad r < L \quad \text{VI. 13} \]

\[ v_z(r) = 2 \left[ v_{\text{oxy}} \right]_{\text{Ave}} \frac{1 - \left( \frac{r}{R} \right)^2 + \frac{1 - k^2}{\ln(1/k)} \ln \left( \frac{r}{R} \right)}{1 - k^4 \frac{1 - k^2}{\ln(1/k)}} \quad r > L \quad \text{VI. 14} \]

\[ v_r(r) = 0 \quad \text{VI. 15} \]
In the above expressions for the velocity, \( \langle v_{\text{fuel}} \rangle_{\text{Ave}} \) and \( \langle v_{\text{oxy}} \rangle_{\text{Ave}} \) are the average linear velocities of the inlet fuel and oxygen streams, respectively; and \( k = \frac{L}{R} \).

From the velocity profiles at the inlet, the stream function and vorticity profiles along the inlet boundary can be determined from equations VI. 6 and VI. 7. Temperature and fuel, oxygen and nitrogen concentrations in the inlet tubes are generally specified such that

\[
\begin{align*}
\text{For } r < L & : \quad w_{\text{fuel}} = 1.0, \quad w_{O_2} = w_{N_2} = 0, \quad T = T_{\text{fuel}} \\
\text{For } r > L & : \quad w_{\text{fuel}} = 0.0, \quad \left( w_{O_2} \right)_{\text{AIR}} = \left( w_{N_2} \right)_{\text{AIR}}, \quad T = T_{\text{AIR}}
\end{align*}
\]

The fuel in the inner tube can be diluted with nitrogen and the composition of the gas in the outer tube can differ from the composition of air.

**Symmetric Axis Conditions:**

The stream function is constant along the symmetric axis and is given the value zero. Thus,

\[
\psi_{\text{Axis}} = 0.0 \quad \text{VI. 18}
\]
The vorticity is zero at the symmetric axis, however, the dependent variable in equation VI. 10 is \((\omega/r)\) when solving for the vorticity distribution, and this quantity is not zero at the centerline. To obtain an expression for \(\omega/r\) at the axis, it is assumed that the vorticity is parabolic near the axis, thus

\[
\omega = ar + br^3
\]
\[
\omega/r = a + b r^2
\]

The constants \(a\) and \(b\) are obtained from solving the equation when \(\omega\) is once and twice removed from the axis. The result is

\[
(\omega/r)_{\text{Axis}} = (\omega/r)_1 = \frac{(\omega/r)_2 r_3^2 - (\omega/r)_3 r_2^2}{r_3^2 - r_2^2}
\]

VI. 19

The subscripts 1, 2 and 3 denote quantities on the axis, and once and twice removed from the axis, respectively.

Symmetry about the centerline implies that

\[
\left(\frac{\partial \omega}{\partial r}\right)_{\text{Axis}} = \left(\frac{\partial \omega_{\text{fuel}}}{\partial r}\right)_{\text{Axis}} = \left(\frac{\partial \omega_{O_2}}{\partial r}\right)_{\text{Axis}} = \left(\frac{\partial \omega_{N_2}}{\partial r}\right)_{\text{Axis}} = 0
\]

VI. 20
Wall Conditions:

The stream function expression can be integrated to show that

$$\psi_{\text{WALL}} - \psi_{\text{Axis}} = \int_{\psi_{\text{Axis}}}^{\psi_{\text{WALL}}} d\psi = \int_{0}^{R} r \rho v_z(r) \, dr$$  \hspace{1cm} \text{VI. 21}$$

Since the stream function is constant along the wall, the density and velocity distributions at the inlet can be used in the above equation to determine the $\psi_{\text{WALL}}$.

The boundary condition for the vorticity at the wall must be derived from the vorticity transport equation by assuming that there should be no slipping between the wall and the fluid adjacent to it. This condition is satisfied by assuming that near the wall

(i) gradients in the direction parallel to the wall are negligible in comparison to those normal to it; and

(ii) gravitational, viscosity and density variations are negligible.

Applying these assumptions to the vorticity transport equation results in

$$\frac{\partial}{\partial r} \left( \omega \frac{\partial \psi}{\partial z} \right) - \mu r \frac{\partial^2 \omega}{\partial r^2} = 0$$  \hspace{1cm} \text{VI. 22}$$
Integrating with respect to \( r \) over a small region adjacent to the wall results in

\[
\left( \omega \frac{\partial \psi}{\partial z} \right)_R - \omega \frac{\partial \psi}{\partial z} - \mu R \left[ \frac{\partial \omega}{\partial r} \right]_R - \frac{\partial \omega}{\partial r} = 0 \quad \text{VI. 23}
\]

In carrying out the integration \( r \) in the second term was held constant at \( R \). Since the stream function is constant at the wall \((\partial \psi/\partial z)_R = 0\) and the above equation simplifies to

\[
\omega \frac{\partial \psi}{\partial z} - \mu R \frac{\partial \omega}{\partial r} = -\mu R \left[ \frac{\partial \omega}{\partial r} \right]_R \quad \text{VI. 24}
\]

This equation can be integrated again with respect to \( r \) to yield

\[
\omega_r - p \omega = \int_r^R \left\{ \left[ \frac{\partial \omega}{\partial r} \right]_R \exp \int_r^R \left[ \frac{1}{\mu R} \frac{\partial \psi}{\partial z} \right] \, dr \right\} \, dr \quad \text{VI. 25}
\]

The integration factor \( p \) is given by

\[
p = \exp \int_r^R - \frac{1}{\mu R} \frac{\partial \psi}{\partial z} \, dr \quad \text{VI. 26}
\]
Due to the assumptions made for the region near the wall, the stream function equation reduces to

\[
\omega = - \frac{\partial}{\partial r} \left( \frac{1}{\rho} \frac{\partial \psi}{\partial r} \right) = - \frac{1}{R\rho} \frac{\partial}{\partial r} \frac{\partial \psi}{\partial r} \tag{VI. 27}
\]

Integrating this equation twice and applying the conditions that \(v_z \bigg|_R = 0\) and \((\partial \psi / \partial r) \bigg|_R = 0\) results in

\[
\int_r^R \int_r^R \omega \, dr \, dr = \frac{1}{R\rho} (\psi_R - \psi) \tag{VI. 28}
\]

When \(\partial \psi / \partial z = 0\), the integration factor, \(P\) equals one and equation VI. 25 can be rearranged to yield

\[
\omega = \omega_R - \left( \frac{\partial \omega}{\partial r} \right)_R (R - r) \tag{VI. 29}
\]

Integrating this equation twice results in

\[
\int_r^R \int_r^R \omega \, dr \, dr = \frac{\omega_R}{2} (R - r)^2 - \frac{1}{6} \left( \frac{\partial \omega}{\partial r} \right)_R (R - r)^3 \tag{VI. 30}
\]
Combining equations VI. 28 and VI. 30 results in

\[
\frac{\omega_R}{2} (R - r)^2 - \frac{1}{6} \left( \frac{\partial \omega}{\partial r} \right)_R (R - r)^3 = \frac{1}{R \rho} (\psi_R - \psi) \tag{VI. 31}
\]

The region near the wall in which the above equation is assumed to apply is bounded by \( r_{NP} \) and \( R \). Applying the equation at \( r_{NP} \) and solving for \( \omega_R \) yields

\[
\omega_R = \frac{1}{3} (R - r_{NP}) \left( \frac{\partial \omega}{\partial r} \right)_R + \frac{2}{R \rho} \frac{\psi_R - \psi_{NP}}{(R - r_{NP})^2} \tag{VI. 32}
\]

Approximating the derivative of the vorticity at the wall by

\[
\left( \frac{\partial \omega}{\partial r} \right)_R \approx \frac{\omega_R - \omega_{NP}}{R - r_{NP}}
\]

and using this in equation VI. 32 results in

\[
\omega_R = \frac{3}{R \rho} \frac{\psi_R - \psi_{NP}}{(R - r_{NP})^2} - \frac{\omega_{NP}}{2} \tag{VI. 33}
\]

The above equation expresses the vorticity at the wall in terms of the stream function and the vorticity at a point adjacent to the wall and thus constitutes an adequate boundary condition for the vorticity at the wall.
The wall is impervious to matter, therefore at the wall

\[ \frac{dw_j}{dr} = 0 \quad j = 1, N \]  \hspace{1cm} \text{VI. 34}

If the system is assumed to be adiabatic

\[ \frac{\partial T}{\partial r} = 0 \]  \hspace{1cm} \text{VI. 35}

and if the wall is assumed to be at a constant temperature

\[ T = T_{\text{wall}} \quad \text{at} \quad r = R \]  \hspace{1cm} \text{VI. 36}

Outlet Conditions:

At the shield outlet little is known about the distributions of velocity, temperature or concentrations. The condition applied at the exit is that axial gradients of all variables are zero. When recirculation is predicted, the composition of any fluid entering the system at the outlet is assumed to be the same as that of air. Thus, at the outlet

\[ \frac{\partial \phi}{\partial z} = 0 \quad \phi = \text{any dependent variable} \]  \hspace{1cm} \text{VI. 37}
FINITE DIFFERENCE EQUATIONS

The finite difference representation of the general elliptic equation is derived by a method due to Pun and Spalding (64) and further outlined in a text by Gosman et. al. (42). The method is called integration over finite areas and has the advantage over other difference schemes in that it ensures that the conservation laws are obeyed over arbitrarily large or small portions of the flow field. The method is illustrated by considering the following grid system:

The general elliptic equation is to be applied at the node point P, which is surrounded on the north, south, east and west by the nodes N, S, E and W. The node P is representative of the entire area enclosed by the dashed lines. Since an axisymmetric system is being considered the node P is actually representative of the volume formed by rotation of this area element through an angle of 2\pi radians about the axis of symmetry. The sides of the dashed rectangle lie midway between the neighboring grid lines. The general elliptic
equation is integrated about this rectangle. The limits of integration are therefore the coordinates of the sides of the rectangle. The integrated elliptic equation is shown below:

\[ \int_{\eta_s}^{\eta_n} \int_{\xi_w}^{\xi_e} a_\phi \left\{ \frac{\partial}{\partial \eta} \left( \phi \frac{\partial \psi^*}{\partial \xi} \right) - \frac{\partial}{\partial \xi} \left( \phi \frac{\partial \psi^*}{\partial \eta} \right) \right\} d\xi d\eta \]

\[ - \int_{\eta_s}^{\eta_n} \int_{\xi_w}^{\xi_e} \left\{ \frac{\partial}{\partial \eta} \left( b_\phi \xi \frac{\partial}{\partial \eta} (c_\phi \phi) \right) + \frac{\partial}{\partial \xi} \left( b_\phi \xi \frac{\partial}{\partial \xi} (c_\phi \phi) \right) \right\} d\xi d\eta \]

\[ + \int_{\eta_s}^{\eta_n} \int_{\xi_w}^{\xi_e} \xi \phi \, d\xi d\eta = 0 \quad \text{VI. 38} \]

Inspection of the above equation reveals that all the terms but the last could be formally integrated once if \( a_\phi \) were a constant; and as shown in Table V, \( a_\phi \) is indeed constant for all variables except \( \omega^*/\xi \), for which it takes on the value \( \xi^2 \). Making the assumption that a suitable value for \( \xi \) is the value at the center of the rectangle, \( \xi_p^2 \) becomes the value of \( a_\phi \) when \( \phi = \omega^*/\xi \). Proceeding with the formal integration therefore results in.
\[
\int_{\xi_w}^{\xi_e} a_\phi \left[ \left( \phi \frac{\partial \psi^*}{\partial \xi} \right)_e - \left( \phi \frac{\partial \psi^*}{\partial \xi} \right)_s \right] d\xi - \int_{\eta_s}^{\eta_n} a_\phi \left[ \left( \phi \frac{\partial \psi^*}{\partial \eta} \right)_e - \left( \phi \frac{\partial \psi^*}{\partial \eta} \right)_w \right] d\eta \\
- \int_{\xi_w}^{\xi_e} \left\{ \left[ b_\phi \xi \frac{\partial}{\partial \eta} (c_\phi \Phi) \right]_e - \left[ b_\phi \xi \frac{\partial}{\partial \eta} (c_\phi \Phi) \right]_w \right\} d\xi \\
- \int_{\eta_s}^{\eta_n} \left\{ \left[ b_\phi \xi \frac{\partial}{\partial \xi} (c_\phi \Phi) \right]_e - \left[ b_\phi \xi \frac{\partial}{\partial \xi} (c_\phi \Phi) \right]_w \right\} d\eta \\
+ \int_{\eta_s}^{\eta_n} \int_{\xi_w}^{\xi_e} \xi d\phi d\xi d\eta = 0
\]

VI. 39

Those quantities which appear with the subscripts \(n, s, e, w\) are to be evaluated along the side of the rectangle denoted by the subscript.

The first two integrals represent convective terms, the second two, diffusive terms; and the fifth, the source term. Each of these integrals will be evaluated separately.

**CONVECTIVE TERM:**

\[
I_1 = \int_{\xi_w}^{\xi_e} a_\phi \left( \phi \frac{\partial \psi^*}{\partial \xi} \right)_e d\xi = a_\phi \int_{\xi_w}^{\xi_e} \frac{\partial \psi^*}{\partial \xi} d\xi
\]

VI. 40
An average value of $\Phi_n$ is denoted by $\overline{\Phi}_n$ and is defined as follows:

$$\overline{\Phi}_n = \frac{\int_{\xi_w}^{\xi_e} \left( \frac{\partial \psi^*}{\partial \xi} \right)_n \, d\xi}{\int_{\xi_w}^{\xi_e} \left( \frac{\partial \psi^*}{\partial \xi} \right)_n \, d\xi} = \frac{I_1}{a_p} \int_{\xi_w}^{\xi_e} \left( \frac{\partial \psi^*}{\partial \xi} \right)_n \, d\xi$$

Solving for $I_1$

$$I_1 = a_p \overline{\Phi}_n \int_{\xi_w}^{\xi_e} \left( \frac{\partial \psi^*}{\partial \xi} \right)_n \, d\xi = a_p \overline{\Phi}_n \left( \psi^*_{ne} - \psi^*_{nw} \right)$$

The variable $\Phi$ is uniform within each rectangle and has a value which prevails at the particular node which the rectangle encloses.

The value of $\overline{\Phi}_n$ therefore depends on the direction of flow. If flow is from P to N, then $\overline{\Phi}_n = \overline{\Phi}_p$ and if flow is from N to P, $\overline{\Phi}_p = \overline{\Phi}_n$. From the definition of the stream function the following is true:

- flow from P to N, \[ \psi^*_{ne} - \psi^*_{nw} > 0 \]
- flow from N to P, \[ \psi^*_{ne} - \psi^*_{nw} < 0 \]

Thus

$$I_1 = \frac{1}{2} a_p \overline{\Phi}_n \left[ \psi^*_{ne} - \psi^*_{nw} - \psi^*_{ne} - \psi^*_{nw} \right] + a_p \left[ \left( \psi^*_{ne} - \psi^*_{nw} \right) + \psi^*_{ne} - \psi^*_{nw} \right]$$
Similar treatment of the other convective terms yields

\[ I_{2} = \frac{1}{2} a_{p} \phi_{p} \left( \psi_{se}^{*} - \psi_{sw}^{*} \right) - \psi_{se}^{*} - \psi_{sw}^{*} + \phi_{S}^{\prime} \left( \psi_{se}^{*} - \psi_{sw}^{*} \right) + \psi_{se}^{*} - \psi_{sw}^{*} \]

\[ I_{3} = \frac{1}{2} a_{p} \phi_{p} \left( \psi_{ne}^{*} - \psi_{se}^{*} \right) - \psi_{ne}^{*} - \psi_{se}^{*} + \phi_{E} \left( \psi_{ne}^{*} - \psi_{se}^{*} \right) + \psi_{ne}^{*} - \psi_{se}^{*} \]

\[ I_{4} = \frac{1}{2} a_{p} \phi_{W} \left( \psi_{nw}^{*} - \psi_{sw}^{*} \right) - \psi_{nw}^{*} - \psi_{sw}^{*} + \phi_{p} \left( \psi_{nw}^{*} - \psi_{sw}^{*} \right) + \psi_{nw}^{*} - \psi_{sw}^{*} \]

The convective terms in equation VI. 39 thus become

\[ I_{\text{conv}} = I_{1} - I_{2} - I_{3} + I_{4} \]
\[ I_{\text{conv}} = \frac{1}{2} a_{p} \left\{ \left( \phi_{p} - \phi_{E} \right) \left[ \psi_{ne}^{*} - \psi_{se}^{*} \right] + \left[ \psi_{ne}^{*} - \psi_{se}^{*} \right] \right\} \]

\[ + \left( \phi_{p} - \phi_{W} \right) \left[ \psi_{sw}^{*} - \psi_{nw}^{*} \right] + \left[ \psi_{sw}^{*} - \psi_{nw}^{*} \right] \]

\[ + \left( \phi_{p} - \phi_{N} \right) \left[ \psi_{nw}^{*} - \psi_{ne}^{*} \right] + \left[ \psi_{nw}^{*} - \psi_{ne}^{*} \right] \]

\[ + \left( \phi_{p} - \phi_{S} \right) \left[ \psi_{se}^{*} - \psi_{sw}^{*} \right] + \left[ \psi_{se}^{*} - \psi_{sw}^{*} \right] \right\} \]

or

\[ I_{\text{conv}} = A_{E} \left( \phi_{p} - \phi_{E} \right) + A_{W} \left( \phi_{p} - \phi_{W} \right) + A_{N} \left( \phi_{p} - \phi_{N} \right) + A_{S} \left( \phi_{p} - \phi_{S} \right) \quad \text{VI. 41} \]

The value of the stream function at a corner of the rectangle is assumed to be equal to the average of the values on the four neighboring nodes. Hence,

\[ \psi_{ne}^{*} = \frac{1}{4} \left( \psi_{N}^{*} + \psi_{NE}^{*} + \psi_{p}^{*} + \psi_{E}^{*} \right) \]
\[ \psi_{nw} = \frac{1}{4}(\psi^*_{nw} + \psi^*_{w} + \psi^*_{n} + \psi^*_{p}) \]

\[ \psi^*_{sw} = \frac{1}{4}(\psi^*_{sw} + \psi^*_{w} + \psi^*_{s} + \psi^*_{p}) \]

\[ \psi^*_{se} = \frac{1}{4}(\psi^*_{se} + \psi^*_{e} + \psi^*_{s} + \psi^*_{p}) \]

and therefore,

\[ A_E = \frac{1}{8} a_p \left[ \left( \psi^*_{ne} + \psi^*_{n} - \psi^*_{se} - \psi^*_{s} \right) + \left| \psi^*_{ne} + \psi^*_{n} - \psi^*_{se} - \psi^*_{s} \right| \right] \quad \text{VI. 42} \]

\[ A_w = \frac{1}{8} a_p \left[ \left( \psi^*_{sw} + \psi^*_{s} - \psi^*_{nw} - \psi^*_{n} \right) + \left| \psi^*_{sw} + \psi^*_{s} - \psi^*_{nw} - \psi^*_{n} \right| \right] \quad \text{VI. 43} \]

\[ A_n = \frac{1}{8} a_p \left[ \left( \psi^*_{nw} + \psi^*_{w} - \psi^*_{ne} - \psi^*_{e} \right) + \left| \psi^*_{nw} + \psi^*_{w} - \psi^*_{ne} - \psi^*_{e} \right| \right] \quad \text{VI. 44} \]

\[ A_s = \frac{1}{8} a_p \left[ \left( \psi^*_{se} + \psi^*_{e} - \psi^*_{sw} - \psi^*_{w} \right) + \left| \psi^*_{se} + \psi^*_{e} - \psi^*_{sw} - \psi^*_{w} \right| \right] \quad \text{VI. 45} \]

Thus, the convective terms in equation VI. 39 are given by equation VI. 41 with the coefficients determined by equations VI. 42 through VI. 45.
DIFFUSIVE TERM

\[ I_5 = \int_{\xi_n}^{\xi_e} \left[ b_\phi \xi \frac{\partial}{\partial \eta} \left( c_\phi \phi \right) \right]_n d\xi \]

In evaluating the above integral, the following assumptions are made:

\[ \xi_e = \frac{1}{2}(\xi_E + \xi_p) \]

\[ \xi_w = \frac{1}{2}(\xi_p + \xi_w) \]

\[ b_\phi_n = \frac{1}{2}\left( b_\phi + b_\phi \right) \]

\[ \left[ \frac{\partial}{\partial \eta} \left( c_\phi \phi \right) \right]_n = \frac{c_\phi \phi_N - c_\phi \phi_p}{\eta_N - \eta_p} \]

Using these assumptions in \( I_5 \) results in

\[ I_5 = \frac{1}{2} \left( b_\phi N + b_\phi p \right) \frac{c_\phi \phi_N - c_\phi \phi p}{\eta_N - \eta_p} \left[ \xi_e \right]_{\xi_w} d\eta \]
\[ I_5 = \frac{1}{16} \left[ b_{\phi_N} + b_{\phi_P} \right] \left[ c_{\phi_N} \phi_N - c_{\phi_P} \phi_P \right] \left( \xi_E - \xi_W \right) \left( \xi_E + \xi_W + 2\xi_P \right) / \left( \eta_N - \eta_P \right) \]

Similar treatment of the other diffusive terms yields

\[ I_6 = \frac{1}{16} \left[ b_{\phi_S} + b_{\phi_P} \right] \left[ c_{\phi_P} \phi_P - c_{\phi_S} \phi_S \right] \left( \xi_E - \xi_W \right) \left( \xi_E + \xi_W + 2\xi_P \right) / \left( \eta_N - \eta_P \right) \]

\[ I_7 = \frac{1}{8} \left[ b_{\phi_E} + b_{\phi_P} \right] \left[ c_{\phi_P} \phi_P - c_{\phi_E} \phi_E \right] \left( \xi_E + \xi_P \right) / \left( \eta_N - \eta_S \right) \left( \xi_E - \xi_P \right) \]

\[ I_8 = \frac{1}{8} \left[ b_{\phi_W} + b_{\phi_P} \right] \left[ c_{\phi_P} \phi_P - c_{\phi_W} \phi_W \right] \left( \xi_W + \xi_P \right) / \left( \eta_N - \eta_S \right) \left( \xi_P - \xi_W \right) \]

The diffusive terms in equation VI. 39 become

\[ I_{\text{diff}} = -I_5 + I_6 - I_7 + I_8 \]

or

\[ I_{\text{diff}} = -B_E \left( C_{\phi_E} \phi_E - C_{\phi_P} \phi_P \right) - B_W \left( C_{\phi_W} \phi_W - C_{\phi_P} \phi_P \right) - B_N \left( C_{\phi_N} \phi_N - C_{\phi_P} \phi_P \right) - B_S \left( C_{\phi_S} \phi_S - C_{\phi_P} \phi_P \right) \]

VI. 46
where

\[ B_E = \frac{1}{8} \left( b_{\phi_E} + b_{\phi_p} \right) \left( \xi_p + \xi_E \right) \left( \eta_N - \eta_S \right) / \left( \xi_E - \xi_p \right) \]  

VI. 47

\[ B_W = \frac{1}{8} \left( b_{\phi_W} + b_{\phi_p} \right) \left( \xi_W + \xi_p \right) \left( \xi_N - \xi_S \right) / \left( \xi_p - \xi_W \right) \]  

VI. 48

\[ B_N = \frac{1}{16} \left( b_{\phi_N} + b_{\phi_p} \right) \left( \xi_E - \xi_W \right) \left( \xi_E + \xi_W + 2\xi_p \right) / \left( \eta_N - \eta_p \right) \]  

VI. 49

\[ B_S = \frac{1}{16} \left( b_{\phi_S} + b_{\phi_p} \right) \left( \xi_E - \xi_W \right) \left( \xi_E + \xi_W + 2\xi_p \right) / \left( \eta_p - \eta_S \right) \]  

VI. 50

The diffusive terms in equation VI. 39 are given by equation VI. 46 with the coefficients defined in equations VI. 47 through VI. 50.

**SOURCE TERM**

\[ I_{\text{SOR}} = \int_{\eta_N}^{\eta_S} \int_{\xi_W}^{\xi_E} \xi d_{\phi} d\xi d\eta \]

Assume \( d_{\phi} \) is uniform over the area of integration and takes on the value at \( \phi \). Thus,
\[ I_{SOR} = \frac{d}{p_{p}} \left( \eta_N - \eta_S \right) \left( \xi_E - \xi_W \right) \left( \xi_E + \xi_W + 2\xi_p \right) / 16 \]  

VI. 51

\[ I_{SOR} = V \frac{d}{p_{p}} \]  

VI. 52

The complete finite difference representation of the general elliptic equation is shown below

\[
A_E \left( \phi_p - \phi_E \right) + A_W \left( \phi_p - \phi_W \right) + A_N \left( \phi_p - \phi_N \right) + A_S \left( \phi_p - \phi_S \right) - B_E \left( C_{\phi_E} \phi_E - C_{\phi_p} \phi_p \right) \\
- B_W \left( C_{\phi_W} \phi_W - C_{\phi_p} \phi_p \right) - B_N \left( C_{\phi_N} \phi_N - C_{\phi_p} \phi_p \right) - B_S \left( C_{\phi_S} \phi_S - C_{\phi_p} \phi_p \right) + V \frac{d}{p_{p}} \phi_p = 0
\]  

VI. 53

Solving for \( \phi \) results in

\[
\phi_p = C_E \phi_E + C_W \phi_W + C_N \phi_N + C_S \phi_S + D
\]  

VI. 54

where

\[
C_E = \left( A_E + B_E \phi_E \right) / AB
\]  

VI. 55
\[ C_W = \left( A_w + B_w C_{\phi_W} \right) / AB \]

\[ C_N = \left( A_N + B_N C_{\phi_N} \right) / AB \]

\[ C_S = \left( A_S + B S C_{\phi_S} \right) / AB \]

\[ D = -d_{\phi} V_p / AB \]

\[ AB = A_E + A_w + A_N + A_S + C_{\phi_p} \left( B_E + B_w + B_N + B_S \right) \]

Equation VI. 54 is the equation used to solve for any dependent variable at node \( p \) in terms of the values of that variable at the nodes about \( p \). The coefficients, \( C \), are functions of the thermodynamic and transport properties, the stream function and the coordinates. They are all positive and except for when \( \Phi = \Omega^* / \xi \), they sum to unity. Equation VI. 54 shows that the value of the dependent variable at grid point \( p \) is just a weighted average of the variable at points about \( p \), supplemented by a source term, \( D \). There is one such equation for each variable at each interior grid point in the system. Analogous equations for the boundary nodes are obtained from the boundary conditions.
A.D.I. Iteration Scheme

The set of non-linear algebraic equations represented by equation VI. 54 is solved by an alternating-direction-implicit procedure commonly referred to as A.D.I. The procedure is due to Peaceman and Rachford (60) and the merits of such a technique have been discussed by numerous investigators (48)(81)(82). Application of the procedure to equation VI. 54 is discussed below.

Subscripts $i$ and $j$ denote radial and axial grid locations, respectively. The equations to be solved are of the form

$$\Phi_{i,j} = A_{i,j} \Phi_{i-1,j} + B_{i,j} \Phi_{i+1,j} + C_{i,j} \Phi_{i,j-1} + D_{i,j} \Phi_{i,j+1} + F_{i,j} \quad \text{VI. 61}$$

Comparison of VI. 54 and VI. 61 shows that $A_{i,j} = C_W$, $B_{i,j} = C_E$, $C_{i,j} = C_S$, $D_{i,j} = C_N$, and $F_{i,j} = D$ for a grid point $p$ at $i,j$. Since $A_{i,j} + B_{i,j} + C_{i,j} + D_{i,j} = 1.0$, the above equation can be rewritten in the following form:

$$-(A_{i,j} + B_{i,j} + C_{i,j} + D_{i,j})\Phi_{i,j} + A_{i,j} \Phi_{i-1,j} + B_{i,j} \Phi_{i+1,j} + C_{i,j} \Phi_{i,j-1} + D_{i,j} \Phi_{i,j+1} + F_{i,j} = 0 \quad \text{VI. 62}$$
The A.D.I. iteration parameter, $\alpha$, is defined as follows:

$$\frac{d\phi_{ij}}{dt} = \alpha \left( \phi_{ij}^{m+1} - \phi_{ij}^m \right)$$  \hspace{1cm} \text{VI. 63}$$

The superscripts denote the iteration time, i.e., $\phi_{ij}^m$ is the value of $\phi_{ij}$ at iteration $m$. At convergence

$$\alpha \left( \phi_{ij}^{m+1} - \phi_{ij}^m \right) = 0$$  \hspace{1cm} \text{VI. 64}$$

The A.D.I. procedure involves combining equations VI. 62 and VI. 64 and splitting the resultant equation in the following two parts.

\textbf{I.}

$$\alpha \left( \phi_{ij}^{m+\frac{1}{2}} - \phi_{ij}^m \right) = A_{ij} \phi_{i-1,j}^{m+\frac{1}{2}} - (A_{ij} + B_{ij}) \phi_{ij}^{m+\frac{1}{2}} + B_{ij} \phi_{i+1,j}^{m+\frac{1}{2}} + C_{ij} \phi_{i+1,j-1}^m$$

$$- (C_{ij} + D_{ij}) \phi_{i,j+1}^m + D_{ij} \phi_{i,j+1}^m = 0$$  \hspace{1cm} \text{VI. 65}$$

\textbf{II.}

$$\alpha \left( \phi_{ij}^{m+\frac{1}{2}} - \phi_{ij}^m \right) = A_{ij} \phi_{i-1,j}^{m+\frac{1}{2}} - (A_{ij} + B_{ij}) \phi_{ij}^{m+\frac{1}{2}} + B_{ij} \phi_{i+1,j}^{m+\frac{1}{2}} + C_{ij} \phi_{i+1,j-1}^m$$

$$- (C_{ij} + D_{ij}) \phi_{i,j+1}^m + D_{ij} \phi_{i,j+1}^m = 0$$  \hspace{1cm} \text{VI. 66}$$

Upon convergence, $\phi_{i,j}^{m+1} = \phi_{i,j}^{m+\frac{1}{2}} = \phi_{i,j}^m$, and the above equations when combined, will represent equation VI. 62
Using the notation

\[ \mathcal{L}_i \phi_{i,j} = A_{i,j} \phi_{i-1,j} - (A_{i,j} + B_{i,j}) \phi_{i,j} + B_{i,j} \phi_{i+1,j} \]  

VI. 67

and

\[ \mathcal{L}_j \phi_{i,j} = C_{i,j} \phi_{i,j-1} - (C_{i,j} + D_{i,j}) \phi_{i,j} + D_{i,j} \phi_{i,j+1} \]  

VI. 68

equations VI. 65 and VI. 66 can be written

I. \[ \alpha \left( \phi_{i,j}^{m+\frac{1}{2}} - \phi_{i,j}^m \right) = \mathcal{L}_i \phi_{i,j}^{m+\frac{1}{2}} + \mathcal{L}_j \phi_{i,j}^m + F_{i,j}^m = 0 \]  

VI. 69

II. \[ \alpha \left( \phi_{i,j}^{m+1} - \phi_{i,j}^{m+\frac{1}{2}} \right) = \mathcal{L}_i \phi_{i,j}^{m+\frac{1}{2}} + \mathcal{L}_j \phi_{i,j}^{m+1} + F_{i,j}^m = 0 \]  

VI. 70

Combining like terms

I. \[ (\alpha - \mathcal{L}_i) \phi_{i,j}^{m+\frac{1}{2}} = (\alpha + \mathcal{L}_i) \phi_{i,j}^m + F_{i,j}^m \]  

VI. 71

II. \[ (\alpha - \mathcal{L}_j) \phi_{i,j}^{m+1} = (\alpha + \mathcal{L}_i) \phi_{i,j}^{m+\frac{1}{2}} + F_{i,j}^m \]  

VI. 72
If \( \psi_{1j} \) is defined as follows

\[
\psi_{1j} = (\alpha - L^{-1}) \phi_{1j}^{m+\frac{1}{2}} = (\alpha + L^{-1}) \phi_{1j}^m + F_{1j}
\]

VI. 73

then the second step can be rewritten as

\[
(\alpha - L^{-1}) \phi_{1j}^{m+\frac{1}{2}} = 2\alpha \phi_{1j}^{m+\frac{1}{2}} - \psi_{1j} + F_{1j}^m
\]

VI. 74

The two-step A.D.I. procedure is represented by equations VI. 71 and VI. 74. Each step involves solving a tridiagonal system of equations, first in the radial direction, step I, then in the axial direction, step II. The two steps combined constitute one complete iteration. Fourier stability analysis can be applied to this two-step scheme to show that for large \( \alpha \), the method always converges. When the source term is small in comparison to the convective and diffusive terms, the scheme is stable for all \( \alpha \).

**ITERATION PROCEDURE**

An algorithm was written to solve equation VI. 54 using the A.D.I. iterative procedure. This algorithm is employed after calculating the various coefficients associated with each of the dependent variables. The following overall iterative procedure was used.

(a) Assume starting fields for all the dependent variables.

(b) Based on the assumed fields, determine all the transport and
thermodynamic properties.

(c) Up-date each of the fields, separately, in the following order: vorticity, stream function, temperature, concentrations.

(i) determine the parameters $a_\phi$, $b_\phi$, $c_\phi$ and $d_\phi$ associated with a particular $\phi$, (Table V);
(ii) determine the coefficients $A_{ij}$, $B_{ij}$, $C_{ij}$, $D_{ij}$ and $F_{ij}$ at each point in the flow field;
(iii) apply the A.D.I. algorithm.

(d) Test to see how well equation VI. 62 is satisfied. If the right hand side is sufficiently close to zero for all $\phi$, convergence is achieved. If not, the up-dated fields become the assumed fields and the procedure is repeated from (b).

In determining the starting fields, the Burke-Schumann (15) model (see Chapter IV) was used to generate temperature and concentration fields of the fuel, oxygen, water and carbon dioxide; the flow streamlines were assumed to be parallel and the vorticity zero.
Appendix VII. Transport and Thermodynamic Properties

Transport and thermodynamic properties of the different flame species were obtained from the compilations of Pohl (61) and are presented in Tables A.4 through A.7. Heat capacities are for ideal gases at atmospheric pressure and are presented as polynomial functions of temperature. Data were obtained from the JANAF (48a) tables. Viscosity and thermal conductivity data were taken from Svehla (77a) and the molecular parameters given by Svehla and the values of collision integrals given by Hirschfelder et. al (45a) were used in the Chapman-Enskog equations to determine the trace diffusion coefficients.
TABLE A.4 Heat Capacity

\[ C_p = a + bT + cT^2 + dT^3 + eT^4 \]

\( C_p \) in cal/gmole \(-^0K\)

\( 298 \, ^0K < T < 2500 \, ^0K \)

<table>
<thead>
<tr>
<th>Species</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>3.710</td>
<td>1.589 \times 10^{-2}</td>
<td>-6.577 \times 10^{-7}</td>
<td>-2.441 \times 10^{-9}</td>
<td>5.762 \times 10^{-13}</td>
</tr>
<tr>
<td>CO</td>
<td>6.277</td>
<td>2.044 \times 10^{-3}</td>
<td>-4.188 \times 10^{-7}</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>6.020</td>
<td>1.176 \times 10^{-2}</td>
<td>-5.771 \times 10^{-6}</td>
<td>9.884 \times 10^{-10}</td>
<td>0</td>
</tr>
<tr>
<td>H(_2)</td>
<td>6.856</td>
<td>2.952 \times 10^{-5}</td>
<td>2.612 \times 10^{-7}</td>
<td>1.540 \times 10^{-10}</td>
<td>-6.176 \times 10^{-14}</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>7.250</td>
<td>2.071 \times 10^{-3}</td>
<td>8.409 \times 10^{-7}</td>
<td>-3.128 \times 10^{-10}</td>
<td>0</td>
</tr>
<tr>
<td>N(_2)</td>
<td>6.922</td>
<td>-7.565 \times 10^{-4}</td>
<td>3.020 \times 10^{-6}</td>
<td>-1.686 \times 10^{-9}</td>
<td>2.872 \times 10^{-13}</td>
</tr>
<tr>
<td>NO</td>
<td>6.768</td>
<td>5.606 \times 10^{-4}</td>
<td>1.763 \times 10^{-6}</td>
<td>-1.237 \times 10^{-9}</td>
<td>2.314 \times 10^{-13}</td>
</tr>
<tr>
<td>O(_2)</td>
<td>6.018</td>
<td>3.675 \times 10^{-3}</td>
<td>-1.670 \times 10^{-6}</td>
<td>2.913 \times 10^{-10}</td>
<td>0</td>
</tr>
</tbody>
</table>
TABLE A.5  Viscosity

\[ \mu = \frac{a T^{3/2}}{b + T} \]

\( \mu \) in Cp
\( T \) in °K

<table>
<thead>
<tr>
<th>Species</th>
<th>a ( \times 10^{-3} )</th>
<th>b</th>
<th>temperature range</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>1.182</td>
<td>366.5</td>
<td>1000 - 3700 °K</td>
</tr>
<tr>
<td>CO</td>
<td>1.832</td>
<td>549.5</td>
<td>1000 - 3700 °K</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>1.697</td>
<td>339.4</td>
<td>1000 - 3700 °K</td>
</tr>
<tr>
<td>H(_2)</td>
<td>8.525 ( \times 10^{-4} )</td>
<td>557.0</td>
<td>1000 - 3700 °K</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>2.202</td>
<td>903.0</td>
<td>500 - 3700 °K</td>
</tr>
<tr>
<td>N(_2)</td>
<td>1.697</td>
<td>339.4</td>
<td>1000 - 3700 °K</td>
</tr>
<tr>
<td>O(_2)</td>
<td>2.102</td>
<td>420.4</td>
<td>1000 - 3700 °K</td>
</tr>
</tbody>
</table>
TABLE A.6 Thermal Conductivity

\[ k = \exp[a + b \ln (T/300)] \]

\[ k \text{ in } 10^{-5} \text{ cal/cm-sec}^{-\circ\text{K}} \]

\[ T \text{ in } \circ\text{K} \]

<table>
<thead>
<tr>
<th>Species</th>
<th>a</th>
<th>b</th>
<th>temperature range</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>2.48</td>
<td>1.010</td>
<td>900 - 2400 (\circ\text{K})</td>
</tr>
<tr>
<td>CO</td>
<td>1.856</td>
<td>0.776</td>
<td>900 - 2700 (\circ\text{K})</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>1.856</td>
<td>0.776</td>
<td>900 - 2700 (\circ\text{K})</td>
</tr>
<tr>
<td>H(_2)</td>
<td>3.742</td>
<td>0.764</td>
<td>600 - 3000 (\circ\text{K})</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>2.00</td>
<td>1.116</td>
<td>900 - 2700 (\circ\text{K})</td>
</tr>
<tr>
<td>N(_2)</td>
<td>1.856</td>
<td>0.752</td>
<td>300 - 3000 (\circ\text{K})</td>
</tr>
<tr>
<td>O(_2)</td>
<td>1.890</td>
<td>0.797</td>
<td>300 - 3000 (\circ\text{K})</td>
</tr>
</tbody>
</table>
TABLE A.7  Trace Diffusion Coefficients

\[ D_{1,N_2} = \exp[a \ln T - b] \]

\[ D_{1,N_2} \text{ in } \text{cm}^2/\text{sec} \]

\[ T \text{ in } ^\circ\text{K} \]

\[ 500 < T < 5000 \text{ } ^\circ\text{K} \]

<table>
<thead>
<tr>
<th>Species</th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>1.658</td>
<td>10.907</td>
</tr>
<tr>
<td>CO</td>
<td>1.657</td>
<td>11.0001</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>1.657</td>
<td>11.229</td>
</tr>
<tr>
<td>H(_2)</td>
<td>1.657</td>
<td>9.717</td>
</tr>
<tr>
<td>H(_2)(_O)</td>
<td>1.657</td>
<td>10.745</td>
</tr>
<tr>
<td>N(_2)</td>
<td>1.657</td>
<td>11.003</td>
</tr>
<tr>
<td>NO</td>
<td>1.657</td>
<td>11.001</td>
</tr>
<tr>
<td>O(_2)</td>
<td>1.657</td>
<td>11.001</td>
</tr>
</tbody>
</table>
Appendix VIII. Literature Citations


37. Ibid., p. 197.

37a. Ibid., p. 355.


39a Ibid., p. 209.


63. Ibid., p. 127.


84. Westenberg, A.A., Raezer, S.D. and Fristrom, R.M., Combustion and Flame, 1, 467 (1957).


Appendix IX. Computer Program

The computer program developed to carry out the operations needed in the theoretical model was written in Fortran. The program was divided into a number of subroutines so that the internal workings of the program are easily discernible. The program is designed so that when it is supplied with the necessary input parameters, it solves, by a sequence of operations, the set of simultaneous algebraic equations which result from differencing the conservation laws. This complete set consists of NV equations, the first three being respectively, the vorticity transport equation, the stream function equation and the energy equation. The remaining NV-3 equations represent species conservation equations for the NV-3 species.

The program is terminated after ITMAX iterations. After ITMAX iterations, the residual (how well the algebraic equation is satisfied) is calculated at each point in the flow field for each variable. Analysis of the residuals is required to determine if more iterations are needed. The progressive change in the variables at one grid point (ITEST, JTEST) with iteration is provided to aid in determining the number of additional iterations needed. From experience, about 100 iterations is necessary to determine the flow and thermal fields established by a diffusion flame.
The functions of the various subroutines are described below:

**MAIN.** This subroutine is the coordinating one. Its main function is to start the computations and to control the sequence of operations.

**GRID.** The radial and axial grid locations are determined. The radial grid is read in; the axial grid is determined by dividing the maximum height, $Z_{MAX}$, parabolically into $J_{MAX}$ divisions.

**INIT.** This subroutine determines the initial vorticity, stream function, temperature and species concentration fields.

**FLAME.** The coordinates of the flame surface are determined in this subroutine.

**PROPTY.** Transport and thermodynamic properties are calculated from the species concentrations and temperature.

**PARAM.** The parameters $a_{\phi}$, $b_{\phi}$, $c_{\phi}$ and $d_{\phi}$, in the general elliptic equation are determined in this subroutine.

**ADI.** The alternating direction implicit procedure is used to update the fields and to calculate the residuals at the last iteration.

**PRINT.** The dependent variables are printed out at each grid point every $NPRIN$ iterations in this subroutine.

**PARRAY.** An $M \times N$ array can be printed out using this subroutine.

**NOFORM.** The nitric oxide formation rates and distribution are determined in this subroutine. If $NNO=2$, equilibrium oxygen radical concentrations are used in the Zeldovich mechanism for NO formation rates.
SPEED.  The radial and axial convective velocities are determined from the stream function in this subroutine.

PLOT.  An M x N array can be plotted to show contour lines.

COEFF.  The coefficients associated with the algebraic representation of each differential equation are determined, (i.e. C_N, C_S, C_E, C_W, and D).

FLUX.  Total mass convective and diffusive fluxes about any central element can be determined in this subroutine.

BSFLAM.  The Burke and Schumann diffusion flame model is used to establish starting concentration and temperature fields in this subroutine.

INPUT.  The input data is printed out in this subroutine.

THALG.  The Thomas algorithm is represented by this subroutine.

RATES  The rates of reaction of the various species are determined in this subroutine. Presently the model does not use this subroutine. It is being modified to use existing partial equilibrium programs to determine the rates of reaction.
The necessary input parameters are as follows:

**ALPH (NC)**
A.D.I. iteration parameter for each of the species equation, set at 50.0

**ALPHAO**
A.D.I. iteration parameter, set at 2.0

**AVMWL, AVMWR**
Average molecular weight of the gases in the inner and outer tubes, respectively

**DEHLH**
Heat of combustion of the fuel, cal/gm

**DENSO**
Average molecular weight of the gas at some reference temperature, gm/cc

**DIFFUO (NC)**
Diffusion coefficient of the species evaluated at some reference temperature, cm$^2$/sec

**HCO**
Average heat capacity of the gas evaluated at the reference temperature, cal/gm-cøK

**IADI**
Control variable: if 1, adiabatic system; if 2, wall held constant at $T_{WALL}$

**IMAX**
Maximum number of radial grid points

**ITMAX1, ITMAX2, ITMAX3**
Maximum iterations when determining the flow fields, species concentrations, and NO concentration, respectively.

**IPROP**
Control variable: If 1, variable property case; if 2, properties held constant at reference values.

**ITEST**
Radial grid of test node

**JMAX**
Maximum number of axial grids
JTEST  Axial grid of node
L     Radial grid of inner tube wall
LL    Radius of inner tube, cm
NNO   Control variable: If 1, stable species
centeration used to determine oxygen
radical concentration in NO formation
rate; if 2, equilibrium oxygen radical
centration used.

NPRIN  Complete fields printed out every NPRIN
       iterations

NREAD  Control variable: Determines starting
       fields. If 1, no starting fields read
       in; if 2, fields of first fine
       variables read in; if 3, all fields
       read in

NYMAX  Maximum number of dependent variables
PI     System total pressure, atm
RR     Radius of outer tube, cm
STOICF Stoichiometric oxygen coefficient
TCO    Thermal conductivity of gas evaluated
       at reference temperature, cal/cm-sec- K
TF     Fuel adiabatic flame temperature, K; 
       usually the physical properties are
       evaluated at TF
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFUEL, TOXI</td>
<td>Temperature of inlet fuel and air, respectively; (^0)K</td>
</tr>
<tr>
<td>TWALL</td>
<td>Wall temperature, (^0)K</td>
</tr>
<tr>
<td>VFUEL, VOXI</td>
<td>Inlet velocities of the fuel and oxidizer gas, respectively, cm/sec</td>
</tr>
<tr>
<td>VISCO</td>
<td>Average viscosity of the gas evaluated at the reference temperature</td>
</tr>
<tr>
<td>XCO(_2)L, XCO(_2)R</td>
<td>Mass fraction CO(_2) in the inlet gas in the inner and outer tubes, respectively</td>
</tr>
<tr>
<td>XFUEL, XFUER</td>
<td>Mass fraction of the fuel in the inner and outer tubes</td>
</tr>
<tr>
<td>XH(_2)O(_2)L, XH(_2)O(_2)R</td>
<td>Mass fraction of water vapor in the inner and outer tubes</td>
</tr>
<tr>
<td>XN(_2)L, XN(_2)R</td>
<td>Mass fraction of nitrogen in the inlet tubes</td>
</tr>
<tr>
<td>XNOL, XNOR</td>
<td>Mass fraction of nitric oxide in the inner and outer tubes</td>
</tr>
<tr>
<td>XO(_2)L, XO(_2)R</td>
<td>Mass fraction of oxygen in the inner and outer tubes</td>
</tr>
<tr>
<td>ZMAX</td>
<td>Maximum axial height, cm</td>
</tr>
</tbody>
</table>
C THIS MAIN PROGRAM IS THE CALLING PROGRAM FOR SOLVING THE LAMINAR
C JET DIFFUSION FLAME PROBLEM
REAL LL
DIMENSION P(26*26),TVALUE(12*100),ALPH(10)
COMMON NVMAX,IMAX,JMAX,L,LL,RR,DENS(26*26),X(11*26*26)
COMMON/RGRID/R(26),Z(26),VP(26*26),DEL(26),DELZ(26)
COMMON/PROP/SC(8),PR,GR,TC(26*26),VISC(26*26),MC(26*26)
COMMON/PROP/DIFFU(8*26*26),TDF,DTF,TCO,VISCO,HCO,DIFFUO(8),DENSO
COMMON/PROP/WSC,DELH,STOICF,PSI(26)
COMMON/ADIV/AADI(26*26),BADI(26*26),CADI(26*26),DADI(26*26)
COMMON/ADIV/FADI(26*26),RES(26*26)
COMMON/FLAM/IFLAM(26),JFLAM,RFLAM(26),ZFLAM,IPFLAM(26)
COMMON/RATES/RX(11*26*26)
COMMON/VELOC/VZ(26*26),VR(26*26)
MR = 5
MW = 6
ITER = 0
IITER = 0
NPRT = 0
C READ BURNER DIMENSIONS AND RELATED INFORMATION
READ(MR*100),IMAX,JMAX,L,LL,RR,ZMAX
C READ PRINTING, ITERATION, VARIABLE AND CONVERGENCE INFORMATION
READ(MR*101),NVMAX,NPRINT,ITEST,JTEST,ITNO
READ(MR*102),ITMAX1,ITMAX2,ITMAX3,ALPHA0,ALPH(M),M=1,5
CALL GRID(MR,ZMAX)
C INITIALIZATION OF ALL DEPENDENT VARIABLES TO ZERO
DO 8 NV = 1,11
DO 8 J = 1,JMAX
DO 8 I = 1,IMAX
X(INV*I+J) = 1.0E-10
RX(INV*I+J) = 0.0
8 CONTINUE
CALL INIT(MR,MW,PI,TWALL,AADI,IPRONTREAD)
C IF NHALF = 1 THE FLAME SURFACE AND INNER PROFILES ARE DETERMINED
C IF NHALF = 2 PROFILES OUTSIDE THE FLAME ARE DETERMINED
NHALF = 1
ITMAX = ITMAX1
ALPHA = ALPHA0
2 IITER = IITER + 1
C SAVE VALUES OF THE VARIABLES AT NODE ITEST, JTEST
TVALUE(IITER) = IITER
DO 20 NV = 1,NVMAX
NVP1 = NV + 1
20 TVALUE(NVP1,IITER) = X(NV*ITEST,JTEST)
ITER = IITER + 1
NPRT = NPRT + 1
IF(NHALF .EQ. 2) GO TO 22
IF(NVMAX .LT. 9) GO TO 10
CALL FLAME
C IF IPR == 2 ALL PHYSICAL PROPERTIES ARE HELD CONSTANT
IF(IPR == 2) GO TO 10
CALL PROPTYP(PI)
10 DO 9 NV = 1,5
CALL PARAM(NV,PI)
CALL ADI(ALPHA,NV,TWALL,AADI,ITER,ITMAX,STOICF)

IF(ITER .EQ. ITMAX) GO TO 11
IF(NPRIN .NE. 0 .AND. NPRT) GO TO 9
11 CALL PRINT(MW*ITER*NV)
IF(NV .EQ. 5) NPRT = 0
IF(ITER .NE. ITMAX) GO TO 12
WRITE(MW*114)
CALL PARRAY(IMAX,JMAX,RES)
12 IF(NV .NE. 5) GO TO 9
WRITE(MW*110) ITEST,JTEST
WRITE(MW*111)
NSTOP = NPRIN
IF(NPRIN .GT. ITER) NSTOP = ITER
DO 21 IITER = 1NSTOP
21 WRITE(MW*112) (TVALUE(NVD*IITER) ,NVD = 16)
IITER = 0
9 CONTINUE
IF(ITMAX-ITER) 1,1,2
1 ITMAX = ITMAX+1
NHALF = 2
ITER = 0
C
INITIALIZATION OF THE SPECIE FIELDS IF STARTING FIELDS NOT READ IN
IF(NREAD .EQ. 5) GO TO 2
DO 24 J = 2,JMAX
DO 24 I = 1,JMAX
X(6+I*J) = -STOICF*X(4+I*J)
IF(X(6+I*J) .LE. 0.0) X(6+I*J) = 0.0
TERM = 1.0-X(4+I*J)*X(5+I*J)*1.0171
IF(X(4+I*J) .LE. 0.0) TERM = 1.0-X(6+I*J)-X(5+I*J)*1.0171
X(7+I*J) = 0.55*TERM+0.099
X(8+I*J) = 0.45*TERM+0.001
X(9+I*J) = 0.55*TERM+0.001
X(10+I*J) = 0.45*TERM+0.001
24 CONTINUE
IF(NNO .EQ. 1) GO TO 2
CALL PRINT(MW*ITMAX1*S6)
GO TO 28
22 CALL RATE(PI)
DO 5 NV = 6,9
ALPHA = ALPH(NV-5)
CALL PARAM(NV,PI)
CALL ADI(ALPHA,NV,STWALL,IADE,ITER,ITMAX,STOICF)
IF(ITER .EQ. ITMAX) GO TO 13
IF(NPRIN .NE. NPRT) GO TO 5
13 CALL PRINT(MW*ITER*NV)
IF(ITER .NE. ITMAX) GO TO 5
WRITE(MW*114)
CALL PARRAY(IMAX,JMAX,RES)
5 CONTINUE
C
DETERMINATION OF THE HYDROGEN CONCENTRATION BY DIFFERENCE
NV = 10
DO 4 J = 2,JMAX
DO 4 I = 1,IMAX
SUM = X(4+I*J)
DO 4 M = 5,9
4 SUM = SUM + X(M+I*J)
\( X(10s1sJ) = 1.0 - X(5s1sJ) \times 0.0171 - \sum \)
\( !F(X(10s1sJ) \lt 0) X(10s1sJ) = 0 \)

9 CONTINUE

IF(ITER = EQ. ITMAX) GO TO 14
IF(NPRINT = NE. NPRT) GO TO 26

14 CALL PRINT(MW,ITER,NV)
NVRT = 0
IF(ITER = NE. ITMAX) GO TO 26
WRITE(MW,110) ITEST, JTEST
WRITE(MW,111)
DO 19 IITER = 1, NPRINT

19 WRITE(MW,112) (TVALUE(NVD, IITER) * NVD = 1.12)
IITER = 0

26 CONTINUE

IF(ITMAX = ITER) 6, 6, 2

6 CONTINUE

C MAXIMUM NUMBER OF ITERATIONS EXCEEDED
C DETERMINATION OF THE NO DISTRIBUTION AND RATE

28 NV = 11
ITMAX = ITMAX3
ALPHA = ALPHAO
CALL NOFORM(ALPHAO, PI, ITMAX, NNO)

C PUNCH RESULTS OUT ON DATA CARDS
IF(NNO = EQ. 2) NVMAX = 5
DO 16 NV = 1, NVMAX
DO 16 J = 1, JMAX
WRITE(7,106) (X(NV, I, J) + 1 = 1, IMAX)

16 CONTINUE

C DETERMINATION OF NO CONCENTRATIONS AND RATES IN PPM OF VOLUME
DO 25 I = 1, IMAX
DO 25 J = 1, JMAX
RT = 82.1 * X(2, I, J) * DTF
X(11, I, J) = X(11, I, J) * DENS0 * DENS(I, J) / 30. * RT / PI * 1.0E06
P(I, J) = RX(11, I, J) * 1.0E06 / 30. * RT / PI

25 CONTINUE

CALL PRINT(MW, ITMAX3, 11)
WRITE(MW, 114)
CALL PARRAY(IMAX, JMAX, RES)
WRITE(MW, 113)
CALL PARRAY(IMAX, JMAX, P)

C DETERMINATION OF AXIAL AND RADIAL VELOCITIES
CALL SPEED
WRITE(MW, 115)
CALL PARRAY(IMAX, JMAX, VZ)
WRITE(MW, 116)
CALL PARRAY(IMAX, JMAX, VR)
IF(NVMAX = LE. 3) GO TO 17

C WRITE OUT THE POSITION OF THE FLAME FRONT
ZFLAM = 2FLAM * RR
JFLA = JFLAM - 1
DO 7 J = 1, JMAX
Z(J) = Z(J) * RR
IF(J = GT. JFLA) GO TO 7
RFLAM(J) = RFLAM(J) * RR

7 CONTINUE
WRITE(MW*103)
WRITE(MW*105) ZFLAM
WRITE(MW*104) (Z(J)+IFLAM(J)+RFLAM(J)*J = 1*JFLAM)

17 CONTINUE

PLOT THE STREAM FUNCTION, TEMPERATURE, AND LOCUS OF THE FLAME ZONE

NV = 2

19 DO 18 I = 1*IMAX
DO 18 J = 1*JMAX

18 P(I,J) = X(NV*1+J)
IF(NV .GE. 4) P(IMAX+1) = -1*9.*
IF(NV .GE. 2) WRITE(MW*107)
IF(NV .GE. 3) WRITE(MW*108)
IF(NV .GE. 4) WRITE(MW*109)
CALL PLOT(IMAX*JMAX*RZ*P)
NV = NV + 1
IF(NV .LE. 4) GO TO 19

100 FORMAT(215*10*5)
101 FORMAT(S15*6F10*5)
102 FORMAT(1)
103 FORMAT('POSITION OF THE FLAME FRONT'///)
104 FORMAT('HEIGH = 'F8.3* ' CM NODE TO THE RIGHT OF'
105 FORMAT('FLAME = 'I14* ' DISTANCE FROM THE CENTERLINE = 'F8.3* ' CM'///)
106 FORMAT('///'' FLAME HEIGHT = 'F8.3* ' CM'///)
107 FORMAT(IP8E10*3)
108 FORMAT(1H1+T50*s 'STREAM FUNCTION PLOT'///)
109 FORMAT(1H1+T50*s 'TEMPERATURE'///)
110 FORMAT(1H1+T50*s 'LOCUS OF THE FLAME FRONT'///)
111 FORMAT(1H1+T50*s 'CONVERGENCE OF THE VARIABLES AT NODE' s213///)
112 FORMA(T2*s 'ITER' s77 'VORTICITY' sT17*s 'STR' s0 F10 'T31's 'TEMPS' sT40*'
113 FORMAT(T12*s 'FRAC' s10 'CO FRAC' s6 'T16' s3 'H2 FRAC' s117 'NO FRAC' s17)
114 FORMAT(F4*0*1P11E11*3)
115 FORMAT(1H1+T50*s 'NO PRODUCTION RATE PPM/SEC'///)
116 FORMAT(1H1+T30*s 'AXIAL VELOCITY CM/SEC AT NODE BOUNDARIES'///)
117 FORMAT(1H1+T30*s 'RADIAL VELOCITY CM/SEC AT NODE BOUNDARIES'///)
STOP
END
SUBROUTINE GRID(MR, ZMAX)
C THIS SUBROUTINE DETERMINES THE GRID USED
REAL LL
COMMON NVMAX, IMAX, JMAX, L, LL, RR, DENS(26, 26) * X(11, 26, 26)
COMMON/RZGRID/R(26) * Z(26) * VP(26, 26) * DELR(26) * DELZ(26)
C DETERMINATION OF RADIAL GRIDS
READ(MR, 100) L, R(I), I = 1, IMAX
100 FORMAT(110, (7F10.5))
C DETERMINATION OF VERTICAL GRIDS
W = 0.
DELW = 1e/(JMAX - 1)
Z(1) = 0.
DO 1 J = 2, JMAX
   W = W + DELW
   Z(J) = ZMAX * W * 2 / RR
1 CONTINUE
IMAXM1 = IMAX - 1
JMAXM1 = JMAX - 1
IMAXM2 = IMAX - 2
JMAXM2 = JMAX - 2
C DETERMINATION OF DELR(I)
DELR(1) = 0.
DELR(2) = (R(2) + R(3)) / 2.
DELR(IMAX) = 0.
DELR(IMAXM1) = R(IMAX) - (R(IMAXM1) + R(IMAXM2)) / 2.
DO 5 I = 3, IMAXM2
   DELR(I) = (R(I + 1) - R(I - 1)) / 2.
5 CONTINUE
C DETERMINATION OF DELZ(J)
DELZ(1) = 0.
DELZ(JMAX) = 0.
DELZ(2) = (Z(3) + Z(2)) / 2.
DELZ(JMAXM1) = Z(JMAX) - (Z(JMAXM1) + Z(JMAXM2)) / 2.
DO 6 J = 3, JMAXM2
   DELZ(J) = (Z(J + 1) - Z(J - 1)) / 2.
6 CONTINUE
C DETERMINATION OF THE VOLUMES WHICH EACH NODE REPRESENTS
DO 4 J = 1, JMAX
   VP(I, J) = 0.
4 CONTINUE
DO 2 I = 1, IMAX
   VP(I, 1) = 0.
2 CONTINUE
DO 3 J = 1, JMAXM1
   VP(I, J) = 0.
3 CONTINUE
RETURN
END
SUBROUTINE INIT(MR*1, IP*1, T WALL*1, IADI*1, IPROP*1, NREAD*1)

C THIS SUBROUTINE DETERMINES THE VALUES AT THE INLET AND ALSO
C DETERMINES INITIALLY ASSUMED VALUES AT THE OTHER NODES

REAL LL
COMMON NVMAX, IMAX, JMAX, L, LL, RR, DENS(26, 26), X(11, 26, 26)
COMMON/RGRID/R(26, 26), VP(26, 26), DELR(26), DELZ(26)
COMMON/DATA/TFUEL, XFUEL, XO2L, XO2R, XH2OL, XH2OR, XNOL, XNOR, VOXI
COMMON/DATA/DENSL, DENSR, VO
COMMON/PROP/RE, SC(8), PR, GR, TC(26, 26), VISC(26, 26), HC(26, 26)
COMMON/PROP/DIFFU(8, 26, 26), TDF, TCO, VISCO, HCO, DIFFUO(8), DENSO
COMMON/PROP/WSC, DELH, STOICF, PSI(26)
COMMON/FLAM/IFLAM(26), JFLAM, IFLAM(26), ZFLAM, IPFLA(26)

C CONDITIONS AT THE BURNER PORT
READ(MR*100), TFUEL, XFUEL, XO2L, XO2R, XH2OL, XH2OR, XNOL, XNOR, AVMWL
READ(MR*100), TOXI, XFUEA, XO2R, XCO2R, XH2OR, XN2R, XNOR, AVMWL

100 FORMAT(18F10.5)
C IF IADI = 1 ADIABATIC SYSTEM, IF ADI = 2 CONSTANT WALL TEMPERATURE
C NREAD IS INFORMATION ABOUT DATA READ IN ON CARDS
READ(MR*114), NREAD, IADI, TWALL, PI, VFUEL, VOXI

114 FORMAT(1110, 4F10.5)
C PROPERTIES AT THE REFERENCE CONDITIONS
READ(MR*133), IPROP, TCO, VISCO, HCO, DENSO, DELH, STOICF

103 FORMAT(110, 7F10.5)
READ(MR*100), (DIFFUO(I) * I = 1, 8)
IF(NREAD * EQ. 1) GO TO 21
NSTOP = NVMAX
IF(NREAD * EQ. 2) NSTOP = 5
DO 23 NV = 1, NSTOP
DO 23 J = 1, JMAX
READ(MR*115), (X(NV, J, I) * I = 1, IMAX)

21 CONTINUE
23 CONTINUE
C DENSITIES IN THE TWO ENTERING STREAMS
DENSL = PI * AVMWL / 26, 1 / TFUEL
DENSR = PI * AVMWL / 27, 1 / TOXI
C DETERMINATION OF THE NORMALIZED STREAM FUNCTION AT THE INNER WALL
X(2, IMAX) = (DENSL * VFUEL * LL / 2 + DENSR * VOXI * (RR**2 - LL**2)) / 2
C DETERMINATION OF THE REYNOLDS NUMBER AND THE VORTICITY SCALE
RE = 4 * PI * (2, IMAX) / VISCO / RR
WSC = X(2, IMAX) / DENSO / RR**3
C DETERMINATION OF THE STREAM FUNCTION AT THE INNER TUBE WALL
PSILL = DENSL * VFUEL * LL / 2, 1 / X(2, IMAX)
C DETERMINATION OF THE AVERAGE MASS FLUX FIRED AND THE AVERAGE
C VELOCITY FIRED
DENSV = 2 * PI * (2, IMAX) / RR**2
V = (VOXI * (RR**2 - LL**2) + VFUEL * LL**2) / RR**2
C DETERMINATION OF THE AVERAGE INLET TEMPERATURE
TIN = (TOXI * (RR**2 - LL**2) + TFUEL * LL**2) / RR**2
DTF = TF - TIN
C DETERMINATION OF THE PRANDTL NUMBER
PR = VISCO * HCO / TCO
C DETERMINATION OF THE GRASHOF NUMBER
GR = DENSO**2 * RR**3 * DTF * 980.7 / TF / VISCO**2
DETERMINATION OF THE SCHMIDT NUMBERS
DO 7 M = 1*8
7 SC(M) = VISCO/DENSO/DIFFUSO(M)
CALL INPUT(IW,PI,TWALL,IAIDI,IPROP)
NORMALIZE THE WALL TEMPERATURE
TWALL = TWALL/DTF
ASSUMED VALUES AT THE INLET
DO 101 NV = 1*NVMAX
DO 101 I = 1*IMAX
101 IF (I .GT. L) GO TO 102
IF (NV .GE. 6) GO TO 6
GO TO (1*2*3*4*5) *NV
1 X(NV*I-1) = 0.
GO TO 101
2 X(NV*I-1) = DENSL*VFUEL*R(I) **2.0/2.0/X(2*IMAX*1)*RR**2
GO TO 101
3 X(NV*I-1) = TFUEL/DTF
GO TO 101
4 X(NV*I-1) = XFUEL - XO2L/STOICF
GO TO 101
5 X(NV*I-1) = XN2L
GO TO 101
6 X(NV*I-1) = 0.
IF (NV .EQ. 6) X(NV*I-1) = XO2L
GO TO 101
102 IF (NV .GE. 6) GO TO 16
GO TO (11*12*13*14*15) * NV
11 X(NV*I-1) = 0.
GO TO 101
12 X(NV*I-1) = PSILL + RR*RR*DENSR*VOXI*(R(I) *R(I) -(LL/RR)**2)/2.0/
1 X(2*IMAX*1)
GO TO 101
13 X(NV*I-1) = TOXI/DTF
GO TO 101
14 X(NV*I-1) = XFUEL - XO2R/STOICF
GO TO 101
15 X(NV*I-1) = XN2R
GO TO 101
16 X(NV*I-1) = 0.
IF (NV .EQ. 6) X(NV*I-1) = XO2R
CONTINUE
X(1*1+1) = (X(1*2+1) *R(3) **2 - X(1*3+1) *R(2) **2) / (R(3) **2 - R(2) **2)
X(1*IMAX+1) = 3.0*(X(2*IMAX+1) - X(2*IMAX-1+1))/R(IMAX) **2.0/DENSR
1 *DENSO/(R(IMAX) = R(IMAX-1) **2 - X(NV*IMAX+1) *R(IMAX-1)/R(IMAX))/2
X(3*IMAX+1) = TWALL
Initially assumed values at the other nodes when NREAD is not equal to 3.

IF NREAD = 1 NO FIELDS ARE READ IN ON DATA CARDS AND THE BURKE-
SCHEMMAN SYSTEM IS USED TO GENERATE STARTING VALUES
IF NREAD = 2 STARTING FIELDS FOR THE FIRST 5 VARIABLES ARE READ IN
IF NREAD = 3 ALL FIELDS ARE READ IN ON DATA CARDS.
GO TO (19*22*22) * NREAD
19 DO 17 I = 1*IMAX
DO 17 J = 1:JMAX 
X(IoJ) = X(1o1oJ) + (4s\#V/RR/WS - X(1o2o1))/Z(J)/Z(JMAX) 
IF(I EQ IMAX AND J GT 1) X(IoJ) = 4s\#V/RR/WS 
X(2o1oJ) = X(2o2o1) 
17 CONTINUE 
25 IF(NVMAX LT 3) GO TO 22 
CALL BSFLAM(IADIoTWALLoDTFoDELHoTFoSTOICF) 
GO TO 22 
C 
INITIALLY ASSUMED NORMALIZED PROPERTIES AT THE OTHER NODES 
22 DO 24 J = 1:JMAX 
DO 24 I = 1:IMAX 
DENS(IoJ) = 1s 
TC(IoJ) = 1s 
MC(IoJ) = 1s 
VISC(IoJ) = 1s 
DO 27 NC = 1:8 
27 DIFFU(NCoJoJ) = 1s 
24 CONTINUE 
C VALUES OF THE STREAM FUNCTION ALONG THE INLET BOUNDARY AT THE 
C HALF NODE 
IEND = IMAX - 1 
RLL = LL/RR 
PSI(I) = 0s 
PSI(IMAX) = X(2sIMAX+1) 
DO 28 J = 2sL 
28 PSI(I) = X(2sI+1)*((R(I+1)+R(I))/R(I))**2/4s 
LP1 = L + 1 
DO 29 I = LP1:IEND 
PSI(I) = PSILL + (X(2sI+1)-PSILL)*((R(I+1)+R(I))**2/4s-RLL**2) 
1/(R(I)**2-RLL**2) 
29 CONTINUE 
PSI(IEND) = 1s0 
RETURN 
END
SUBROUTINE FLAME
 THIS SUBROUTINE DETERMINES THE FLAME HEIGHT AND THE POSITION OF
 THE FLAME FRONT AT EACH HEIGHT
 IFLAM IS THE NODE IMMEDIATELY TO THE RIGHT OF THE FLAME FRONT
 IPFLA IS THE NODE IN WHICH THE FLAME FRONT IS LOCATED
 JFLAM IS THE NODE IMMEDIATELY ABOVE THE TIP OF THE FLAME
 REAL LL
 COMMON NVMAX*I1MAX*J1MAX*L1MAX*LL*RR*DEN(S*26*26)*X(11*26*26)
 COMMON/RGRID/R(26)*Z(26)*VP(26*26)*DZR(26)*DZL(26)
 COMMON/FLAM/IFLAM(26)*JFLAM*RFLAM(26)*ZFLAM*IPFLA(26)
 DO 1 J = 1*J1MAX
 IF(X(1*J) .LE.* 0.) GO TO 3
 DO 2 I = 1*I1MAX
 IF(X(I*J) .GT.* 0.0) GO TO 2
 IFLAM(J) = I
 GO TO 1
 2 CONTINUE
 1 CONTINUE
 3 JFLAM = J
 JFLA = JFLAM - 1
 IF(JFLAM .EQ.* J1MAX) JFLA = J1MAX
 DO 4 J = 1*JFLA
 IFLA = IFLAM(J)
 RFLAM(J) = (X(4*IFLA*J) - X(4*IFLA-1*J)) / (X(4*IFLA - 1*J) - X(4*IFLA-1))
 IF(RFLAM(J) .GT.* (R(1*IFLA) + R(1*IFLA-1)) / 2.) IPFLA(J) = IFLAM(J)
 4 CONTINUE
 RFLAM(1) = LL/RR
 IF(JFLAM .EQ.* J1MAX) GO TO 5
 ZFLAM = (X(4*1*JFLAM) - X(4*1*JFLAM-1)) / (X(4*1*JFLAM) - X(4*1*JFLAM-1))
 1 JFLAM = X(4*1*JFLAM-1)
 GO TO 6
 5 ZFLAM = Z(J1MAX)
 6 DO 7 J = JFLAM*J1MAX
 IPFLA(J) = 2
 7 IFLAM(J) = 2
 RETURN
 END
SUBROUTINE PROPTY(IP)

C THIS SUBROUTINE DETERMINES THE PHYSICAL PROPERTIES ASSUMING
C ONLY CH4, N2, O2, CO2, AND H2O ARE PRESENT IN THE SYSTEM.
C SUBSCRIPTS ON MASS AND MOLE FRACTIONS ARE AS FOLLOWS:
C   1 = CH4, 2 = N2, 3 = O2, 4 = CO2, 5 = H2O, 6 = CO, 7 = H2, 8 = NO.
C REAL MU(5), K(5), LNTN3, LNTM(5), SLL
C DIMENSION XMOL(5), CCP(5), XF(5)
C COMMON NVMAX, IMAX, JMAX, LLL, RRR, DENS(26,26), X(11,26,26)
C COMMON/RZGRID/R(26,26), Z(26,26), V(26,26), DELR(26), DELZ(26)
C COMMON/PROP/RE(8,26,26), PR(26,26), TC(26,26), VISC(26,26), H(26,26)
C COMMON/PROP/DIFFU(8,26,26), TF, DTF, TCO, VISCO, HC, DFFU(8,26,26), DENO
C COMMON/PROP/WSC, DELH, STOICF, PSI(26)
C COMMON/FLAM/IFLAM(26), JFLAM, RFLAM(26), ZFLAM, IPFLA(26)
C DATA MW/16.028, 28.0, 32.0, 44.0, 18.0/
C DO 100 I = 1, IMAX
C DO 100 J = 1, JMAX
C
C DETERMINATION OF MASS FRACTIONS
C IF(X(I,J) = 0.0) 999, 10
C
9 XF(1) = 0.0
   XF(3) = X(4+I,J) * STOICF
   GO TO 11
10 XF(1) = X(4+I,J)
   XF(3) = 0.0
11 XF(2) = X(5+I,J)
   XF(4) = (1.0 - XF(1) - XF(3) - XF(2)) * MW(4) / (MW(4) + 2.0 * MW(5))
   XF(5) = XF(4) * MW(5) / MW(4)
C
C DETERMINATION OF THE MOLE FRACTIONS, XMOL
C SUM = 0.0
C DO 3 NNV = 1, 5
C SUM = SUM + XF(NNV) * MW(NNV)
C DO 7 NNV = 1, 5
C XMOL(NNV) = XF(NNV) * MW(NNV) / SUM
C DETERMINATION OF THE AVERAGE MOLECULAR WEIGHT
C SUM = 0.0
C DO 8 NNV = 1, 5
C SUM = SUM + MW(NNV) * XMOL(NNV)
C AVMW = SUM
C
C DETERMINATION OF THE DENSITY
C DENS(I,J) = PI * AVMW / 82.1 / X(3+I,J) / DENS0 / DTF
C DETERMINATION OF THE HEAT CAPACITY AT CONSTANT PRESSURE AND TEMPERATURE
C T = X(3+I,J) * DTF
C IF(T <= 2900.0) GO TO 5
C T2 = T / 2.0
C T3 = T2 / 2.0
C T4 = T3 / 2.0
C CCP(1) = 37.71 + 1.589E-02 * T - 6.577E-07 * T2 - 2.441E-09 * T3 + 5.762E-13
C T4
C CCP(2) = 6.822 - 7.656E-04 * T + 3.020E-06 * T2 - 1.686E-09 * T3
C T4 + 2.672E-13 * T4
C CCP(3) = 6.010 + 3.675E-03 * T - 1.670E-06 * T2 + 2.913E-10 * T3
C CCP(4) = 6.02 + 1.716E-02 * T - 5.771E-06 * T2 + 9.884E-10 * T3
C CCP(5) = 7.25 + 2.071E-03 * T + 8.409E-07 * T2 - 3.128E-10 * T3
C SUM = 0.0
C DO 4 NNV = 1, 5
C SUM = SUM + XMOL(NNV) * CCP(NNV)
4 CONTINUE
   HC(I,J) = SUM/HCO/AVMW
   GO TO 6
5 HC(I,J) = 1.
6 T15 = T**1.5
   MU(1) = 0.001182*T15/(366.5 + T)
   MU(2) = 0.001697*T15/(339.4 + T)
   MU(3) = 0.002102*T15/(420.4 + T)
   MU(4) = 0.001697*T15/(339.4 + T)
   MU(5) = 0.002202*T15/(903.5 + T)
   SUM = 0.
   DO 1 NNV = 1,5
   1 SUM = SUM + XMOLE(NNV)*MU(NNV)
   VISC(I,J) = SUM*0.001/VISCO
C DETERMINATION OF THE THERMAL CONDUCTIVITY, TC, IN CAL/CM/K/SEC
   LNT03 = ALOG(T/300.)
   K(1) = EXP(2.48 + 1.01*LNT03)
   K(2) = EXP(1.856 + 0.752*LNT03)
   K(3) = EXP(1.89 + 0.797*LNT03)
   K(4) = EXP(1.856 + 0.776*LNT03)
   K(5) = EXP(2.00 + 1.116*LNT03)
   SUM = 0.
   DO 2 NNV = 1,5
   2 SUM = SUM + XMOLE(NNV)*K(NNV)
   TC(I,J) = SUM*0.00001/TC0
C DETERMINATION OF THE DIFFUSION COEFFICIENT, DIFFU, IN SQ CM/SEC
   LNT = ALOG(T)
   DIFFU(1:I:J) = EXP(1.657*LNT-10.907)/DIFFUO(1)
   IF(I .GE. JFLAM(J)) DIFFU(1:I:J) = EXP(1.657*LNT-11.001)/DIFFUO(1)
   IF(J .GE. JFLAM) DIFFU(1:I:J) = EXP(1.657*LNT-11.001)/DIFFUO(1)
   DIFFU(2:I:J) = EXP(1.657*LNT-11.001)/DIFFUO(2)
   DIFFU(3:I:J) = EXP(1.657*LNT-11.001)/DIFFUO(3)
   DIFFU(4:I:J) = EXP(1.657*LNT-11.229)/DIFFUO(4)
   DIFFU(5:I:J) = EXP(1.657*LNT-10.745)/DIFFUO(5)
   DIFFU(6:I:J) = EXP(1.657*LNT-11.001)/DIFFUO(6)
   DIFFU(7:I:J) = EXP(1.657*LNT-9.717)/DIFFUO(7)
   DIFFU(8:I:J) = EXP(1.657*LNT-11.001)/DIFFUO(8)
100 CONTINUE
   RETURN
END
SUBROUTINE PARAM(NV, PI)
C THIS SUBROUTINE CALCULATES THE PARAMETERS AP, BP, CP, DP IN THE
C GENERAL ELLIPTIC EQUATION
REAL LL
DIMENSION XMOL(S10), XF(10), EP(10,26), Z(10,26), VP(10,26), DELR(26), DELZ(26)
COMMON/NVMAX, IMAX, JL, LL, RR, DENS(10,26), X(1,11,26,26)
COMMON/RZGRID/R(26), Z(26), VP(26,26), DELR(26), DELZ(26)
COMMON/PROP/RESC(18), PRGR, TC(26,26), VISC(26,26), HC(26,26)
COMMON/PROP/DIFFU(8,26,26), TF, DTF, TCO, VISO, HC0, DIFFU(8), DENSO
COMMON/PROP/NSC0, DELH, STOICF, PSI(26)
COMMON/FLAM, RFLAM(26), SFLAM, ZFLAM, IPFLA(26)
COMMON/FLAM/AP(26), BP(26,26), CP(26,26), DP(26,26)
COMMON/RATES/RX(11,26,26)
JMAXM1 = JMAX = 1
IMAXM1 = IMAX = 1
TFO = TF/DTF
IF(NV .GE. 4) GO TO 4
GO TO (1,2,3), NV
1 DO 100 J = 1, JMAXM1
   DO 100 I = 1, IMAXM1
      API(I) = R(I)*R(I)*RE/4a
      CP(I,J) = VISO(I,J)
      DP(I,J) = 0
   CONTINUE
100 CONTINUE
C DETERMINATION OF THE VORTICITY SOURCE TERM
   DO 5 J = 2, JMAXM1
      DO 5 I = 2, IMAXM1
         DRDRE = (DENS(I+1,J)-DENS(I,J))/(R(I+1)-R(I))
         DRDRW = (DENS(I,J)-DENS(I-1,J))/(R(I)-R(I-1))
         DRD = (DRDRE*(R(I)-R(I-1))+DRDRW*(R(I+1)-R(I)))/(R(I+1)-R(I-1))
         DP(I,J) = -4a*TFO*GR/RE*R(I)*DRD
      CONTINUE
   GO TO 200
2 DO 101 J = 1, JMAX
   DO 101 I = 1, IMAX
      API(I) = 0a
      CP(I,J) = 1a
      DP(I,J) = -X(1,1,1)
   CONTINUE
101 CONTINUE
   GO TO 200
3 DO 20 I = 1, IMAX
   DO 20 J = 1, JMAX
      20 EP(I,J) = DENS(I,J)*DIFFU(I,J)
   DO 102 J = 1, JMAXM1
      DO 102 I = 1, IMAXM1
         BP(I,J) = TCO(I,J)
      CP(I,J) = 1a
      DP(I,J) = 0a
   CONTINUE
102 CONTINUE
C DETERMINATION OF THE HEAT GENERATED IN THE AREA IN WHICH THE
C FLAME CROSSES
   DO 8 J = 1, JFLAM
      IFLA = IFLAM(J) + 3
      DO 8 I = 1, IFLA
         HGEN = 0a.
Determination of the fuel concentrations at the corners of the areas inside the flame surface

\[ \begin{align*}
X_{NE} & = (X(4i+1,4j+1) + X(4i+1,4j+1)) + X(4i+1,4j+1) + X(4i+1,4j+1) + X(4i+1,4j+1))/4 \\
X_{NW} & = (X(4i-1,4j+1) + X(4i-1,4j+1) + X(4i-1,4j+1) + X(4i-1,4j+1))/4 \\
X_{SW} & = (X(4i-1,4j-1) + X(4i-1,4j-1) + X(4i-1,4j-1) + X(4i-1,4j-1))/4 \\
X_{SE} & = (X(4i+1,4j-1) + X(4i+1,4j-1) + X(4i+1,4j-1) + X(4i+1,4j-1))/4 \\
\end{align*} \]

IF (I NE 2) GO TO 9

\[ \begin{align*}
X_{NW} & = (X(4i+1,4j) + X(4i+1,4j+1))/2 \\
X_{SW} & = (X(4i-1,4j) + X(4i-1,4j-1))/2 \\
\end{align*} \]

9 IF (J NE 2) GO TO 11

\[ \begin{align*}
X_{SE} & = X(4i,4j+1) \\
X_{SW} & = X(4i,4j+1) \\
\end{align*} \]

11 CONTINUE

Test to see if the flame crosses the boundaries

IF (X_{NE} GE 0.0 AND X_{SE} LT 0.0) GO TO 13

IF (X_{NW} GE 0.0 AND X_{XW} GE 0.0) GO TO 13

IF (X_{XW} GE 0.0 AND X_{SE} LT 0.0) GO TO 13

Determination of the area on each boundary thru which CH4 flows

13 FRACN = XNW/(XNW+XNE)

IF (XNW < GT 0.0 AND XNE < GT 0.0) FRACN = 1.0

IF (XNW LT 0.0 AND XNE LT 0.0) FRACN = 0.0

IF (I EQ 2) GO TO 14

FRACS = XSW/(XSW+XSE)

14 IF (XSW < GT 0.0 AND XSE < GT 0.0) FRAC = 1.0

IF (XSW LT 0.0 AND XSE LT 0.0) FRAC = 0.0

Determination of the flux of fuel in and out of the control area

\[ \begin{align*}
XPSIN & = X(2i+1,j+1) + X(2i+1,j+1) - X(2i-1,j+1) - X(2i+1,j+1) \\
XPSIS & = X(2i+1,j+1) + X(2i+1,j+1) - X(2i-1,j+1) - X(2i+1,j+1) \\
XPSIE & = X(2i+1,j+1) + X(2i+1,j+1) - X(2i-1,j+1) - X(2i+1,j+1) \\
XPSIW & = X(2i+1,j+1) + X(2i+1,j+1) - X(2i+1,j+1) - X(2i+1,j+1) \\
\end{align*} \]


TERM = (AN+BN) * FRAC*(X(4i+1,j+1) - X(4i+1,j-1)) + (AS+BS) * FRAC*(X(4i+1,j-1) - X(4i+1,j)) + (AW+BW) * FRAC
2 *(X(4i+1,j-1) - X(4i+1,j)) + (BS+BN) * FRAC
3 XPSIW * XPSIE * XPSI = XPSI
4 XPSIW * XPSIE + XPSI
5 HGEN = DENS + DENS*DIFFUO(VI/VF) + (HGEN-HLOSS)

Determination of the heat loss due to radiation

7 HLOSS = 0.0

\[ \begin{align*}
DPI(1,j) & = -RR*RR/DF/TCO*(HGEN-HLOSS) \\
\end{align*} \]
8 CONTINUE
   GO TO 200
4  DO 6 J = 1, JMAX
   DO 6 I = 1, IMAX
      AP(I) = RESC(NV-3)/4.
      BP(I,J) = DENS(I,J)*DIFFU(NV-3,I,J)
      CP(I,J) = 1.
      DP(I,J) = -RR*RES/RSO/DIFFUO(NV-3)*RX(NV-3,I,J)
6  CONTINUE
200 RETURN
END
SUBROUTINE ADI(ALPHA,NV,TWALL,IAIDI,ITER,ITMAX,STOICF)
C THIS SUBROUTINE CARRIES OUT THE ADI PROCEDURE
REAL LL
DIMENSION ATHOM(26),BTHOM(26),CHTHOM(26),FTHOM(26),XX(26),
1 YSAVE(26,26),PSI(26,26),XAIR(12),XPSI(26)
COMMON NVMAX,IMAX,JMAX,LLL,RR,DENS(26,26),X(11,26,26)
COMMON/RGRID/R(26),Z(26),VP(26,26),DEL(26),DELZ(26)
COMMON/ADIV/AADI(26,26),BADI(26,26),CADI(26,26),DADI(26,26)
COMMON/ADIV/FADI(26,26),RES(26,26)
COMMON/PARA/PM(26,26),CP(26,26),DP(26,26)
COMMON/FLAM/IFLAM(26),JFLAM,RFLAM(26),ZFLAM,IPFLA(26)
DATA XAIR/0.292,0.795,0.292,0.0,0.0,0.0,0.0,0.0,0.0/ 
S = 0,2
DO 7 NN = 1,NVMAX
DO 7 I = 1,IMAX
J = JMAX + 1
X(NN+I,J) = X(NN+I,JMAX)
7 CONTINUE
C VALUES OF THE STREAM FUNCTION ALONG THE OUTLET BOUNDARY AT THE
C HALF NODE
IM1 = IMAX + 1
XPSI(I) = 0
XPSI(IMAX) = 1.0
J = JMAX
DO 15 I = 2,IM1
XPSI(I) = (X(2*I+1,J) + X(2*I,J))/2
CALL COEFF(NV,I,IAIDI)
15 CONTINUE
C DETERMINATION OF THE ITERATION PARAMETER
ALPHA = ALPHA
DO 100 J = 2,ITMAX
I = 2
M = I-1
IF(NV .GE. 3) GO TO 3
GO TO (11,12),NV
1 ATHOM(M) = 0
BTHOM(M) = AADI(2,J) + BADI(2,J) = AADI(2,J) + R(3)*(R(3)**2/(R(3)**2
1 - R(2)**2))
CHTHOM(M) = -BADI(2,J) + AADI(2,J)*R(3)**2/(R(3)**2 - R(2)**2)
FTHOM(M) = CADI(2,J)*X(NV*2,J-1) + ALPHA*CADI(2,J) = DADI(2,J)*
1*X(NV*2,J) + DADI(2,J)*X(NV*2,J+1) + FADI(2,J)
PSI(2,J) = FTHOM(M)
GO TO 4
2 ATHOM(M) = 0
BTHOM(M) = AADI(2,J) + BADI(2,J)
CHTHOM(M) = -BADI(2,J)
FTHOM(M) = CADI(2,J)*X(NV*2,J-1) + ALPHA*CADI(2,J) = DADI(2,J)*
1*X(NV*2,J) + DADI(2,J)*X(NV*2,J+1) + FADI(2,J)
PSI(2,J) = FTHOM(M)
GO TO 4
3 ATHOM(M) = 0
BTHOM(M) = AADI(2,J) + BADI(2,J)
CHTHOM(M) = -BADI(2,J)
FTHOM(M) = CADI(2,J)*X(NV*2,J-1) + ALPHA*CADI(2,J) = DADI(2,J)*
1*X(NV*2,J) + DADI(2,J)*X(NV*2,J+1) + FADI(2,J)
PSI(2,J) = FTHOM(M)
4 IEND = IMAX - 2
DO 101 I = 3, IEND
  M = I - 1
  ATOM(M) = -AADI(IoJ)
  BTHOM(M) = ALPHA + AADI(IoJ) + BADI(IoJ)
  CTHOM(M) = -BADI(IoJ)
  FTHOM(M) = CADI(IoJ) * X(NVioJ - 1) + (ALPHA - CADI(IoJ) - DADI(IoJ)) * 
  X(NVioJ) + DADI(IoJ) * X(NVioJ + 1) + FADI(IoJ)
  PSI(IoJ) = FTHOM(M)
101 CONTINUE
  I = IMAX - 1
  M = I - 1
  IF(NV GE 3) GO TO 14
  GO TO 11, 12, NV
11 ATOM(M) = -AADI(IoJ)
  A = 3 * R(IMAX) - 2 * DENS(IMAXoJ) / (R(IMAX) - R(I)) ** 2 * X(2oIMAXoJ) - 
  1 * (2oJ))
  B = -R(I) / R(IMAX) / 2
  BTHOM(M) = ALPHA + AADI(IoJ) + BADI(IoJ) * (1 - B * S)
  CTHOM(M) = 0
  IF(I > EQ 1) WSTAR = X(1oIMAXoJ)
  WSTAR = S * (A + B * X(1oJ)) + (1 - S) * WSTAR
  TERM = BADI(IoJ) * (A * S + (1 - S) * WSTAR)
  FTHOM(M) = CADI(IoJ) * X(NVioJ - 1) + (ALPHA - CADI(IoJ) - DADI(IoJ)) * 
  X(NVioJ) + DADI(IoJ) * X(NVioJ + 1) + FADI(IoJ) + TERM
  PSI(IoJ) = FTHOM(M) - TERM
  GO TO 5
12 ATOM(M) = -AADI(IoJ)
  BTHOM(M) = ALPHA + AADI(IoJ) + BADI(IoJ)
  CTHOM(M) = 0
  FTHOM(M) = CADI(IoJ) * X(NVioJ - 1) + (ALPHA - CADI(IoJ) - DADI(IoJ)) * 
  X(NVioJ) + DADI(IoJ) * X(NVioJ + 1) + FADI(IoJ) + BADI(IoJ) * X(NVioJ)
  2IMAXoJ)
  PSI(IoJ) = FTHOM(M) - BADI(IoJ) * X(NVioIMAXoJ)
  GO TO 5
13 ATOM(M) = -AADI(IoJ)
  BTHOM(M) = ALPHA + AADI(IoJ) + BADI(IoJ)
  CTHOM(M) = 0
  FTHOM(M) = CADI(IoJ) * X(NVioJ - 1) + (ALPHA - CADI(IoJ) - DADI(IoJ)) * 
  X(NVioJ) + DADI(IoJ) * X(NVioJ + 1) + FADI(IoJ) + BADI(IoJ) * TWALL
  PSI(IoJ) = FTHOM(M) - BADI(IoJ) * TWALL
  GO TO 5
14 IF(IADI EQ 2 .AND. NV EQ 3) GO TO 13
  ATOM(M) = -AADI(IoJ)
  BTHOM(M) = ALPHA + AADI(IoJ) + BADI(IoJ)
  CTHOM(M) = 0
  FTHOM(M) = CADI(IoJ) * X(NVioJ - 1) + (ALPHA - CADI(IoJ) - DADI(IoJ)) * 
  X(NVioJ) + DADI(IoJ) * X(NVioJ + 1) + FADI(IoJ)
  PSI(IoJ) = FTHOM(M)
5 NEG = IMAX - 2
  CALL THALG(XXoNEQoATHOMoBTHOMoCTHOMoFTHOM)
  DO 102 I = 1, NEG
    M = I + 1
    YSAVE(MoJ) = XX(I)
  102 CONTINUE
100 CONTINUE
  IEND = IMAX - 1
  DO 103 I = 2*IEND
    J = 2
    M = 1
    ATHOM(M) = 0
    BTHOM(M) = ALPHA + CADI(IoJ) + DADI(IoJ)
    CTHOM(M) = -DADI(IoJ)
    FTHOM(M) = 2*ALPHA*YSAVE(IoJ) + FADI(IoJ) - PSI(IoJ) + CADI(IoJ)
    1*X(NV*ISO2)
    IF(NV .GT. 0) GO TO 107
    ATHOM(M) = 0
    BTHOM(M) = 1
    CTHOM(M) = 0
    FTHOM(M) = X(12*ISO2)
  107 CONTINUE
    DO 104 J = 3*JMAX
      M = J - 1
      ATHOM(M) = -CADI(IoJ)
      BTHOM(M) = ALPHA + CADI(IoJ) + DADI(IoJ)
      CTHOM(M) = -DADI(IoJ)
      FTHOM(M) = 2*ALPHA*YSAVE(IoJ) + FADI(IoJ) - PSI(IoJ)
      IF(J .GT. JMAX) GO TO 104
      BTHOM(M) = BTHOM(M) + CTHOM(M)
      IF(NV .LT. 4) GO TO 104
      IF((XPSI(I) - XPSI(I - 1)) .GT. 0) GO TO 104
      ATHOM(M) = 0
      BTHOM(M) = 1
      CTHOM(M) = 0
      FTHOM(M) = XAIR(NV = 3)
      IF(NV .EQ. 4) FTHOM(M) = -FTHOM(M)/STOICF
  104 CONTINUE
    NEQ = JMAX - 1
    CALL THALG(X*X, NEQ, ATHOM, BTHOM, CTHOM, FTHOM)
    IF(NV .GE. 5) GO TO 18
    DO 19 M = 1, NEQ
      J = M + 1
      X(NV*ISO2) = XX(M)
    19 CONTINUE
    GO TO 103
  18 DO 20 M = 1, NEQ
      J = M + 1
      X(NV*ISO2) = (XX(M) + ABS(XX(M)))/2 + 1.0E-20
  20 CONTINUE
  103 CONTINUE
C DETERMINATION OF VALUES AT THE BOUNDARIES
  DO 106 J = 2*JMAX
    IF(NV .GE. 3) GO TO 23
    GO TO (21, 22), NV
  21 X(NV*ISO2) = X(NV*ISO2)*R(2)**2 - X(NV*ISO2)*R(3)**2)/(R(2)**2 - R(3)**2)
    X(NV*ISO2) = 3.0*DENS(IMAX, J)/R(IMAX)**2*(R(IMAX) - R(IMAX - 1))**2
    1*X(NV*ISO2) = X(NV*ISO2) - X(NV*ISO2)*R(IMAX - 1)
    GO TO 106
  22 X(NV*ISO2) = 0.0
    X(NV*ISO2) = X(NV*ISO2)
GO TO 106

23 X(NV+10J) = (R(3)*R(2))/R(3) - R(2))*X(NV+30J)/(R(3)-R(2))/R(3)
1 (R(2) = R(3)
IF(NV = GE = 5) X(NV+10J) = ABS(X(NV+10J))
H1 = R(IMAX-1)-R(IMAX-2)
H2 = R(IMAX)-R(IMAX-1)
X(NV+IMAX+J) = (((H1+H2)*X(NV+IMAX+10J)-H2)*X(NV+IMAX+20J))/
1 /H1/(H1+20H2)
IF(NV = EQ = 2) X(NV+IMAX+J) = TWALL
106 CONTINUE
IF(ITER = NE = ITMAX) GO TO 8

C DETERMINATION OF RESIDUALS AT THE LAST ITERATION
IM1 = IMAX - 1
JMO1 = JMAX - 1
DO 9 J = 20JMI
DO 9 I = 20I1
RES(I+J) = -X(NV+I+J) + AADI(I+J)*X(NV+I+10J) + BADI(I+J)*X(NV+I+10J+1)
+ FADI(I+J)
9 CONTINUE
DO 6 J = 10JMAX
RES(10J) = RES(20J)
6 RES(IMAX+J) = RES(IM1+J)
DO 10 I = 10I1
RES(I+1) = 0
10 RES(I+JMAX) = RES(I+IM1)
8 RETURN
END
SUBROUTINE PRINT(IW*ITER*NV)
C
THIS SUBROUTINE IS THE CALLING PROGRAM TO PRINT THE RESULTS
AFTER ITER ITERATIONS
REAL LL
DIMENSION XX(26*26)
COMMON NVMAX*IMAX*JMAX*L*LL*RR*DENSI(26*26)*X(11*26*26)
COMMON/RZGRID/R(26)*Z(26)*VP(26*26)*DELR(26)*DELZ(26)
WRITE(IW*100) ITER
DO 1 J = 1*IMAX
   DO 1 I = 1*IMAX
      XX(I*J) = X(NV*I*J)
   1 CONTINUE
GO TO (11*12*13*14*15*16*17*18*19*20*21)*NV
11 WRITE(IW*101)
   DO 116 J = 1*JMAX
      DO 116 I = 1*IMAX
         XX(I*J) = XX(I*J)*R(I)
      116 CONTINUE
   CALL PARRAY(IMAX*JMAX*XX)
   GO TO 4
12 WRITE(IW*102)
   CALL PARRAY(IMAX*JMAX*XX)
   GO TO 4
13 WRITE(IW*103)
   CALL PARRAY(IMAX*JMAX*XX)
   GO TO 4
14 WRITE(IW*104)
   DO 14 J = 1*JMAX
      DO 14 I = 1*IMAX
         IFXX = XX(I*J) *LE* 0* A
         XX(I*J) = 0* A
      2 CONTINUE
   CALL PARRAY(IMAX*JMAX*XX)
   GO TO 4
15 WRITE(IW*105)
   CALL PARRAY(IMAX*JMAX*XX)
   GO TO 4
16 WRITE(IW*106)
   CALL PARRAY(IMAX*JMAX*XX)
   GO TO 4
17 WRITE(IW*107)
   CALL PARRAY(IMAX*JMAX*XX)
   GO TO 4
18 WRITE(IW*108)
   CALL PARRAY(IMAX*JMAX*XX)
   GO TO 4
19 WRITE(IW*109)
   CALL PARRAY(IMAX*JMAX*XX)
   GO TO 4
20 WRITE(IW*110)
   CALL PARRAY(IMAX*JMAX*XX)
   GO TO 4
21 WRITE(IW*111)
   CALL PARRAY(IMAX*JMAX*XX)
   CONTINUE
100 FORMAT('1 ITERATION',I4,') VALUES OF THE DEPENDENT VARIABLE AT THE
111S ITERATION ARE AS FOLLOWS:

101 FORMAT( /// ) VORTICITY
102 FORMAT( /// ) NORMALIZED STREAM FUNCTION
103 FORMAT( /// ) TEMPERATURE, DEGREES K
104 FORMAT( /// ) METHANE Mass FRACTION
105 FORMAT( /// ) NITROGEN Mass FRACTION
106 FORMAT( /// ) OXYGEN Mass FRACTION
107 FORMAT( /// ) CO2 Mass FRACTION
108 FORMAT( /// ) H2O Mass FRACTION
109 FORMAT( /// ) CO Mass FRACTION
110 FORMAT( /// ) H2 Mass FRACTION
111 FORMAT( /// ) NITRIC OXIDE CONCENTRATION,PPM

RETURN
END
SUBROUTINE PARRAY(NN,MM,X)
C FORTRAN SUBROUTINE TO PRINT AN M BY N ARRAY IN SECTIONS OF TEN COLUMNS
C
DIMENSION X(26,26)
NTEN = (NN-1)/10 + 1
DO 95 K = 1, NTEN
JSTART = (K - 1)*10 + 1
IF(10*K - NN) 20, 25, 25
20 JEND = 10*K
GO TO 30
25 JEND = NN
30 WRITE(*,100)
   DO 99 I = 1, MM
      WRITE(*,101) (X(J,I), J = JSTART, JEND)
99 CONTINUE
100 FORMAT(1M )
101 FORMAT(10E13.5)
RETURN
END
SUBROUTINE NOFORM(ALPHA, PI, ITMAX, NNO)

DETERMINATION OF THE RATE OF FORMATION OF NO IN GM/CC/SEC


COMMON NVMAX,JMAX,L*LL*RR*DENS(26*26)*X(11*26*26)

COMMON/RGRID/R(26)*Z(26)*VP(26*26)*DELZ(26)

COMMON/PROP/RE*SC(8)*PR*GR*TC(26*26)*VISC(26*26)*HC(26*26)

COMMON/PROP/DIFFU(8*26*26)*TF*DTF*TCO*VISCO*HCO*DIFFUO(8)*DENO

COMMON/PROP/WS/C*DELH*STOICF*PSI(26)

COMMON/FLAM/IFLAM(26)*JFLAM*RFLAM(26)*ZFLAM*IPFLA(26)

COMMON/PARA/AP(26)*BP(26*26)*CP(26*26)*DP(26*26)

COMMON/RATES/R(11*26*26)

NV = 11

JMAXM1 = JMAX = 1

IMAXM1 = IMAX = 1

REATIONS CONSIDERED IN THE ORDER IN WHICH THE SUBSCRIPTS REFER

TO THEM ARE AS FOLLOWS

*************** N2 + O = NO + N (12) ***************

*************** N + O2 = NO + O (13) ***************

*************** N + OH = NO + H (14) ***************

PARAMETERS IN THE NO SPECIES EQUATION

DO 1 J = 1*JMAX
DO 1 I = 1*IMAX

AP(I,J) = RE*SC(8)/4.

BP(I,J) = DENS(I,J)*DIFFU(8*I,J)

CP(I,J) = 1.

DP(I,J) = 0.

1 CONTINUE

GO TO (4*5)*NNO

4 DO 2 ITER = 1*ITMAX

DO 3 J = 2*JMAXM1

DO 3 I = 2*IMAXM1

T = DTF*X(3*I,J)

IF(T LE 500) GO TO 3

RT = 19870*T

KF12 = 1.36E14*EXP(-75400/RT)

KR12 = 3.1E13*EXP(-334/RT)

KF13 = 6.43E09*T*EXP(-6250/RT)

KR13 = 1.55E09*T*EXP(-38640/RT)

KF14 = 4.1E13*EXP(-800/RT)

KR14 = 16.4E15*EXP(-48600/RT)

KEQ1 = 13.1*EXP(-19931/RT)

KEQ2 = 2.26*EXP(-1874/RT)

KEQ3 = 4.73*EXP(-15175/RT)

RHOI = DENS(I,J)*DENSO

RHO1SQ = RHOI*RHOI

TERM1 = 9*KEQ1*RHO1SQ/KEQ3/16*X((10*I,J)*X(6*I,J)/X(8*I,J)

TERM2 = KF12*KF13/896*X((5*I,J)*X(6*I,J)

TERM3 = KF12*KF14*X((5*I,J)/224*SQRT(KEQ1*KEQ2*X(6*I,J)*X((10*I,J)


TERM6 = KR12*X(11*I,J)/32*KF13*X(6*I,J)/32*KF14/8*SQRT(KEQ1

1*KEQ2*X((10*I,J)*X(6*I,J)

RTNO = TERM1*TERM2 + TERM3 - TERM4 - TERM5)/TERM6

RX(11*I,J) = RTNO*30.
DPI(I,J) = -RX(11*I+J)*RR*RR/DENSO/DIFFUO(8)
3 CONTINUE
CALL ADI(ALPHA*NV*TWALL*IADI*ITER*ITMAX*STOICF)
2 CONTINUE
GO TO 6
C NO FORMATION RATE CALCULATED ASSUMING O/O2 EQUILIBRIUM
5 DO 7 J = 2*JMAXM1
   IFLAMJ = IFLAM(J)
   DO 7 I = IFLAMJ+1*JMAXM1
      T = DTF*X(3*I+J)
      IF(T LE 500) GO TO 7
      RT = 1.0987*RT
      DELG = -119.882 + 0.02958*T + 6.261E-07*T*T
      XKAP = EXP(-1000.0*DELG/RT)
      KF12 = 1.36614*EXP(-79400/RT)
      RTNO = 1.394603*KF12*DENSO*(5*I+J)*SQRT(X(6*I+J)*
      1 DENSO(I,J)*DENSO/T/XKAP)
      RX(11*I+J) = RTNO*30*
      DPI(I,J) = -RX(11*I+J)*RR*RR/DENSO/DIFFUO(8)
7 CONTINUE
   DO 8 ITER = 1*ITMAX
      CALL ADI(ALPHA*NV*TWALL*IADI*ITER*ITMAX*STOICF)
8 CONTINUE
6 RETURN
END
SUBROUTINE SPEED
THIS SUBROUTINE DETERMINES RADIAL AND AXIAL VELOCITIES AT EACH
GRID POINT IN CM/SEC.
COMMON NVMAX=IMAX=JMAX=LL=RL=RR=DENS(26*26)*X(11*26*26)
COMMON/ZGRID/R(26)*Z(26)*V.P(26*26)*DELR(26)*DELZ(26)
COMMON/PROP/RESC(8)*PR=GR=TC(26*26)*VISC(26*26)*HC(26*26)
COMMON/PROP/DIFU(8*26*26)*TF=DTF=TC=VISO=HC=F=DIFU0(8)*DENSO
COMMON/PROP/WS*C=DELH=STOICF=PSI(26)
COMMON/VELOC/VZ(26*26)*VR(26*26)
JMAX = JMAX -1
IMAX = IMAX = 1
J = 1
DO 1 I = 2*IMAX
VR(I,J) = 0.
1 VZ(I,J) = RR*WSC*(PSI(I)-PSI(I-1))/DENS(I+J)/R(I)/DELR(I)
VR(I+1) = 0.
VR(IMAX+1) = 0.
VZ(I+J) = VZ(2*J)
VZ(IMAX+1) = 0.
DO 3 J = 2*JMAX
DO 3 I = 2*IMAX
DYDRE = (X(I+1*J)-X(I*J))/R(I+1)/R(I)
DYDZN = (X(I+1*J)-X(I*J))/(Z(J+1)-Z(J))
VR(I,J) = -2*RR*WSC/R(I)/DENS(I+J+1)/DENS(I+J)*DYDZN
VZ(I,J) = 4*RR*WSC*DYDRE/(R(I+1)/R(I))/*DENS(I+1*J)/DENS(I+J)
3 CONTINUE
DO 2 J = 2*JMAX
I = 1
VR(I,J) = 0.
VZ(I,J) = 2*RR*WSC*X(2*2*J)/DENS(I+J)/R(2)**2
I = IMAX
VR(I,J) = 0.
VZ(I,J) = 0.
VZ(IMAX,J) = 0.
2 CONTINUE
DO 7 I = 2*IMAX
J = JMAX
VR(I,J) = VR(I,J-1)
VZ(I,J) = VZ(I,J-1)
7 CONTINUE
RETURN
END
SUBROUTINE PLOT(IMAX,JMAX,R,Z,P)

THIS SUBROUTINE PLOWS OUT THE TEMPERATURE AND STREAM FUNCTION
FIELDS ON A LINE PRINTER
THE Z-DIRECTION IS PRINTED ON THE HORIZONTAL AND THE R-DIRECTION
IS PRINTED ON THE VERTICAL

DIMENSION R(26),Z(26),P(26,26),XVAL(30),YVAL(120)
DIMENSION NNUM(120),NPL0T(7),X(30),Y(30),DELX(30),DELY(30)
COMMON/FLAM/IPLAM(26),JFLAM,RFLAM(26),ZFLAM,IPFLA(26)
DATA NPL0T/1,4,1,6,8,10,12/;

CALCULATE X AND Y POSITION VECTORS. ARATIO IS FIXED AT 4.

MP2 = IMAX
NP2 = JFLAM + 1
IF(JFLAM.EQ.JMAX) NP2 = JFLAM
DO 1 I = 1,MP2
1 X(I) = R(I)
DO 2 J = 1,NP2
2 Y(J) = Z(J)*4/Z(NP2)

SCALE THE TEMPERATURE AND STREAM FUNCTION

PMAX = P(1,1)
PMIN = P(1,1)
DO 3 I = 1,MP2
3 DO 3 J = 1,NP2
IF (P(I,J) .LE. PMIN) PMIN = P(I,J)
IF (P(I,J) .GE. PMAX) PMAX = P(I,J)
DO 4 I = 1,MP2
4 DO 4 J = 1,NP2
P(I,J) = 10.05*(P(I,J)-PMIN)/(PMAX-PMIN)
WRITE(6,27) PMAX,PMIN
WRITE(6,28) Z(NP2)

CALCULATE X AND Y POSITION VECTORS ON LINE PRINTER

10 DO 30 J = 1,120
30 NNUM(J) = NPL0T(J)
WRITE(6,26) NPL0T(J),NNUM(J),J = 1,120
NPL0T(J) = 1
IIM1 = I - 1
XVAL(I) = IIM1/29
IF (I.EQ.1) I = 1
6 IF (X(I) .GE. XVAL(I)) GO TO 7
IF (I.EQ.1) MP2 = 2
7 IP1 = I
I = I - 1
AIX = (XVAL(I) - X(I))/(X(IP1) - X(I))
DO 5 JJ = 1,120
5 JJ = JJ - 1
YVAL(JJ) = 4*(JJM1/119)
IF (JJ .EQ. 1) J = 1
8 IF (Y(J) .GT. YVAL(JJ)) GO TO 9
   IF (J .EQ. NP2) GO TO 9
   J = J + 1
   GO TO 8
9 JP1 = J
   J = J - 1
   A1Y = (YVAL(JJ) - Y(J))/(Y(JP1) - Y(J))
   JP = NDUM(JJ)
   IF(JP .EQ. 0 .OR. JP .EQ. 10) GO TO 15
   JPO2 = JP/2
   KP = JPO2+2
   IF(JP .NE. KP) GO TO 14
   NDUM(JJ) = NPLLOT(JPO2)
   GO TO 5
14 NDUM(JJ) = NPLLOT(6)
   GO TO 5
15 NDUM(JJ) = NPLLOT(5)
5 CONTINUE
   WRITE(6,26) NPLLOT(7) *(NDUM(J)) * J = 1* 120) * NPLLOT(7)
10 CONTINUE
   DO 31 J = 1* 120
31 NDUM(J) = NPLLOT(7)
   WRITE(6,26) NPLLOT(7) *(NDUM(J)) * J = 1* 120) * NPLLOT(7)
26 FORMAT(1H9, 5X, 122A1)
27 FORMAT(1H0, 39X, 'PMAX = ', E15.8, 'PHIN = ', E15.8, ' //')
28 FORMAT(1H, 'MAXIMUM NORMALIZED HEIGHT PLOTTED IS ', F7.4, ' //')
RETURN
END
SUBROUTINE COEFF(NV*ADI)

THIS SUBROUTINE DETERMINES THE COEFFICIENTS IN THE ADI ROUTINE

REAL LL
COMMON NVMAX*LMAX*JMAX*LL*RR*DENS(26*26)*X(11*26*26)
COMMON/RGRID/R(26)*Z(26)*VP(26*26)*DEL(26)*DEL(26)
COMMON/PROP/RES(8)*PR*GR*TC(26*26)*VISC(26*26)*HC(26*26)
COMMON/PROP/DIFFU(8*26*26)*TF*TD*TCO*VISC*HCO*DIFFUO(8)*DENS0
COMMON/PROP/WSC*DELH*STOICF*PSI(26)
COMMON/ADI/ADI(26*26)*BADI(26*26)*CADI(26*26)*DADI(26*26)
COMMON/ADI/FADI(26*26)*RES(26*26)
COMMON/Para/AP(26)*BP(26*26)*CP(26*26)*DP(26*26)
COMMON/FLAM*IFLAM(26)*JFLAM*RFLAM(26)*ZFLAM*IPFLA(26)
REPR = RE * PR / 4s

DETERMINATION OF PARAMETERS JUST ABOVE THE FLOW FIELD

J = JMAX + 1
IEND = IMAX + 1
DO 6 I = 1*IEND
BP(I,J) = BP(I,JMAX)
CP(I,J) = CP(I,JMAX)
DP(I,J) = DP(I,JMAX)
DENS(I,J) = DENS(I,JMAX)
Z(J) = Z(JMAX) + Z(JMAX-1)
X(2*I,J) = X(2*I,JMAX)
DELZ(J) = DELZ(JMAX)
6 CONTINUE

COEFFICIENTS AT THE INTERIOR AND EXIT NODES
DO 10 I = 1*IEND
DO 10 J = 2*JMAX
PSIE = X(2*I+1,J+1) + X(2*I+1,J-1) - X(2*I+1,J-1) - X(2*I+1,J-1)
IF(I.EQ.0)continued
PSIW = X(2*I+1,J+1) + X(2*I+1,J-1) - X(2*I+1,J-1) - X(2*I+1,J-1)
IF(I.EQ.0)continued
PSIN = X(2*I+1,J+1) + X(2*I+1,J-1) - X(2*I+1,J-1) - X(2*I+1,J-1)
IF(I.EQ.0)continued
PSIEND = X(2*I+1,J+1) + X(2*I+1,J-1) - X(2*I+1,J-1) - X(2*I+1,J-1)
1 = X(2*I+1,J+1) + X(2*I+1,J-1) - X(2*I+1,J-1) - X(2*I+1,J-1)
IF(I.EQ.1)continued
PSIW = X(2*I+1,J+1) + X(2*I+1,J-1) + X(2*I+1,J-1) + X(2*I+1,J-1) = 4*PSI(I)
PSIW = 4*PSI(I-1) - X(2*I+1,J-1) - X(2*I+1,J-1) - X(2*I+1,J-1) - X(2*I+1,J-1)
PSIW = 4*PSI(I-1) - PSI(I-1)
5 AE = AP(I) * (PSIE + ABS(PSIE))/8
AW = AP(I) * (PSIW + ABS(PSIW))/8
AN = AP(I) * (PSIN + ABS(PSIN))/8
AS = AP(I) * (PSIEND + ABS(PSIEND))/8
IF(NV .NE. 3) GO TO 7
AE = REPR*HC(10,0) * (PSIE + ABS(PSIE))/8
AW = REPR*HC(10,0) * (PSIW + ABS(PSIW))/8
AN = REPR*HC(10,0) * (PSIN + ABS(PSIN))/8
AS = REPR*HC(10,0) * (PSIEND + ABS(PSIEND))/8
7 IF(NV .GE. 3) GO TO 3
GO TO (1*2) * NV
1 BE = (R(I+1)+R(I))*3*DELZ(J)/(R(I+1)-R(I))/8.
BW = (R(I-1)+R(I))*3*DELZ(J)/(R(I)-R(I-1))/8.
BN = R(I)*3*DELR(I)/(Z(J+1)-Z(J)).
BS = R(I)*3*DELR(I)/(Z(J)-Z(J-1)).
IF(I *EQ* 2) BW = 0.
GO TO 4.
2 BE = DELZ(J)/(DENS(I+1)+DENS(I+1))/(R(I+1)+R(I))/(R(I+1)-R(I)).
BW = DELZ(J)/(DENS(I-1)+DENS(I-1))/(R(I-1)+R(I))/(R(I)-R(I-1)).
BN = DELR(I)/(Z(J+1)-Z(J)).
BS = DELR(I)/(Z(J)-Z(J-1)).
IF(J *EQ* 2) BS = 0.
GO TO 4.
3 BE = (BP(I+1)+BP(I+1))/4*(R(I)+R(I))
IF(I *EQ* 1) BE = 0.
IF(I *EQ* 3) BE = 0.
BW = (BP(I-1)+BP(I-1))/4*(R(I-1)+R(I))
BN = (BP(I+1)+BP(I+1))/2*(R(I)+R(I))
BS = (BP(I-1)+BP(I-1))/2*(R(I)+R(I)).
IF(NV *GE* 4) BS = 0.
IF(I *EQ* 2) BW = 0.
4 CONTINUE
SUMAB = AE + AW + AS + AN + CP(I) * (BE + BW + BS + BN).
CE = (AE + BE*CP(I+1))/(SUMAB).
CW = (AW + BW*CP(I-1))/(SUMAB).
CN = (AN + BN*CP(I+1))/(SUMAB).
CS = (AS + BS*CP(I-1))/(SUMAB).
D = -DP(I)*VP(I)/SUMAB.
AAD(I) = CW.
BAD(I) = CE.
CAD(I) = CS.
DAD(I) = CN.
FAD(I) = D.
10 CONTINUE
RETURN.
END.
SUBROUTINE FLUX(NV*J*EP*AE*AW*AN*AS*BE*BW*BN*BS)
THIS SUBROUTINE DETERMINES THE FLOW ACROSS BOUNDARIES DUE TO
CONVECTION AND DIFFUSION
REAL LL
DIMENSION KVMAX*IMAX*JMAX*L*L*L*LL*RR*DENS(26*26)*X(1*26*26)
COMMON/RZGRID/R(26*26)*Z(26*26)*VP(26*26)*DELR(26)*DELZ(26)
COMMON/PROP/RE*SC(8)*PR*GR*TC(26*26)*VISC(26*26)*HC(26*26)
COMMON/PROP/DIFFU(8*26*26)*TF*DTF*TCOS*VISC*HCO*DIFFU(8)*DENSO
COMMON/PROP/WSC*DELH*STOICF*PSI(26)
IEND = IMAX + 1
PSIE = X(2*I+1,J+1) + X(2*I,J+1) - X(2*I+1,J-1) - X(2*I,J-1)
IF(I .EQ. IEND) PSIE = 0.
PSIW = X(2*I+1,J-1) + X(2*I,J-1) - X(2*I-1,J+1) - X(2*I-1,J-1)
IF(I .EQ. 2) PSIW = 0.
PSIN = X(2*I-1,J+1) + X(2*I-1,J) - X(2*I+1,J+1) - X(2*I+1,J)
IF(I .EQ. 2) PSIN = -X(2*I,J+1) - X(2*I,J) - X(2*I+1,J+1) - X(2*I+1,J)
IF(I .EQ. IEND) PSIN = X(2*I+1,J+1) + X(2*I-1,J+1) + X(2*I+1,J) + X(2*I-1,J)
1 = 4*X(2*IMAX+J)
PSIS = X(2*I+1,J-1) + X(2*I+1,J) - X(2*I-1,J-1) - X(2*I-1,J)
IF(I .EQ. 2) PSIS = X(2*I+1,J) + X(2*I,J) + X(2*I+1,J) - 4*PSI(I)
IF(I .EQ. IEND) PSIS = 4*PSI(I-1) - X(2*I-1,J+1) - X(2*I-1,J) - X(2*I+1,J) - X(2*I+1,J)
PSIS = 4*(PSI(I) - PSI(I-1))
2 CONTINUE
BE = (EP(I+1,J)+EP(I,J))/4*(R(I+1)+R(I))*DELZ(J)/(R(I+1)-R(I))
IF(I .EQ. IEND) BE = 0.
IF(I .EQ. 2) BW = 0.
BN = (EP(I,J+1)+EP(I,J))/2*R(I)*DELR(1)/(Z(J+1)-Z(J))
BS = (EP(I,J-1)+EP(I,J))/2*R(I)*DELR(1)/(Z(J)-Z(J-1))
IF(J .EQ. 2) BS = 0.
KV = NV
IF(NV .EQ. 3) KV = 4
AE = (PSIE + ABS(PSIE)) / 8 * RE*SC(KV-3) / 4
AW = (PSIW + ABS(PSIW)) / 8 * RE*SC(KV-3) / 4
AN = (PSIN + ABS(PSIN)) / 8 * RE*SC(KV-3) / 4
AS = (PSIS + ABS(PSIS)) / 8 * RE*SC(KV-3) / 4
1 RETURN
SUBROUTINE BSFLAM(IADI,TWALL,DTF,DELH,TF,STOICF)
THIS PROGRAM DETERMINES STARTING CONCENTRATIONS AND TEMPERATURE
PROFILES BY ASSUMING A BURKE-SCHUMANN TYPE SYSTEM
REAL LL
DIMENSION A(26),B(26),C(26),F(26),XGAS(26),TEMP(26),XN2(26),XX(26)
DIMENSION RFLA(201),IFLA(201),W(201)
COMMON NMAX,I MAX,JMAX,L,LL,RR,DENS(26),X(11,26)
COMMON/RZGRID/R(26),Z(26),VP(26,26),DELR(26),DELZ(26)
COMMON/PLAM/RFLAM(26),JFLAM/RFLA(26),ZFLAM,IFLA(26)
COMMON/DATA/TFUEL,XFUEL,XO2L,XCO2L,XH2OL,XN2L,XNOL,XVFUEL
COMMON/DATA/TOXI,XFUERXO2R,XCO2R,XH2OR,XN2R,XNOR,VOXI
COMMON/DATA/DENSL,DENSR,V
D = 0.62
HC = DELM/(TF=TOXI)/(1 + STOICF + XN2R*STOICF/XO2R)
A1 = D/VFUEL
NOPUL = 1
DO 29 I = 1,L
XGAS(I) = XFUEL
TEMP(I) = TFUEL
XN2(I) = XN2L
29 CONTINUE
IST = L + 1
DO 26 I = IST,I MAX
XGAS(I) = -XO2R/STOICF*DENSR/DENSL
TEMP(I) = TOXI
XN2(I) = XN2R
26 CONTINUE
JDIV = 4
JJ = 1
W(1) = Z(1)
DO 22 J = 2,JMAX
DELZJ = (Z(J) - Z(J-1))/JDIV
DO 22 JJJ = 1,JDIV
JJ = JJJ + 1
W(JJJ) = W(JJ-1) + DELZJ
22 CONTINUE
JMAX = JJ
JJJ = JMAX + 1
W(JJJ) = W(JMAX) + DELZJ
J = 2
DO 100 JJ = 2,JMAX
Determination of gas concentrations
NV = 1
DO 1 I = 1,I MAX
XX(I) = XGAS(I)
1 CONTINUE
2 A(I) = 0
B(I) = 1 + R(2)**2/A1/(W(JJ+1)-W(JJ-1))
C(I) = -1
F(I) = R(2)**2/A1/(W(JJ+1)-W(JJ-1))*XX(I)
IEND = I MAX + 1
DO 3 I = 2,I END
A(I) = (R(I-1)+R(I))/((R(I-1)-R(I))
B(I) = (R(I+1)-R(I-1))/((R(I+1)+R(I-1)+2*R(I))/2/A1/(W(JJ+1)-W(JJ
1-1))+(R(I+1)+R(I))/((R(I+1)-R(I))+(R(I)+R(I-1))/(R(I)-R(I-1))
})
}
C(I) = (R(I+1)-R(I))/R(I-R(I+1))
F(I) = (R(I+1)-R(I-1))*R(I+1)+R(I-1)/2e/A1/(W(JJ+1)-W(JJ-1))
XX(I) = XX(I)
3 CONTINUE
I = IMAX
A(I) = -1e
B(I) = 1e + (R(I)-R(I-1))*2e/A1/(W(JJ+1)-W(JJ-1))
C(I) = 0e
F(I) = (R(I)-R(I-1))*2e/A1/(W(JJ+1)-W(JJ-1))
GO TO (4,5,6) NV
4 CONTINUE
CALL THALG(NX=NX,MAX=MAX,A=A,B=B,C=C,F)
DO 7 I = 1,IMAX
XGAS(I) = XX(I)
7 CONTINUE
Determination of the temperatures
NV = 2
DO 8 I = 1,IMAX
XX(I) = TEMP(I)
8 CONTINUE
GO TO 2
5 CONTINUE
GO TO (19,15)* NOFUL
9 I = 0
11 I = I+1
IF (XGAS(I)) 12,12,11
12 IF (I = 1) 13,13,14
13 NOFUL = 2
   RFLA(JJ) = 0e
   IFLA(JJ) = 1
   ZFLAM = W(JJ)
   GO TO 19
14 IFL2 = 1
   IFL1 = I-1
   IFLA(JJ) = IFL2
   FRAC = XGAS(IFL1)/(XGAS(IFL1)-XGAS(IFL2))
   RFLA(JJ) = R(IFL1) + FRAC*R(IFL2)-R(IFL1)
   I = IFL1
   SOURC = 2e* RFLA(JJ)*A1*DEHL/HC/(R(IFL2)**2e-R(IFL1)**2e)*XGAS(IFL1)
   / RFLA(JJ)*R(IFL1) *DENS/DENSR
   F(IFL1) = F(IFL1) + (1-FRAC)*SOURC*(R(IFL2)-R(IFL1-1))*(R(IFL2)+
            R(IFL1-1) +2e*R(IFL1))/A1/4e
   F(IFL2) = F(IFL2) + FRAC*SOURC*(R(IFL2+1)-R(IFL1))*R(IFL2+1)+R(IFL
   1 L1) +2e*R(IFL2))/A1/4e
   GO TO 10
15 RFLA(JJ) = 0e
   IFLA(JJ) = 1
   GO TO (16,17)* IADI
10 IF IADI = 1 THE WALLS ARE IMPERVIOUS TO HEAT
   IF IADI = 2 THE WALLS ARE HELD AT A CONSTANT TEMPERATURE
16 I = IMAX
   A(I) = -1e
   B(I) = 1e + (R(I)-R(I-1))*2e/A1/(W(JJ+1)-W(JJ-1))
   C(I) = 0e
   F(I) = (R(I)-R(I-1))*2e/A1/(W(JJ+1)-W(JJ-1))**XX(I)
GO TO 18
17 A(IMAX) = 0
   B(IMAX) = 1
   C(IMAX) = 0
   F(IMAX) = TWALL*DTF
18 CALL THALG(XX,IMAX,A,B,C,F)
   DO 19 I = 1,IMAX
         TEMP(I) = XX(I)
   19 CONTINUE

C DETERMINATION OF NITROGEN CONCENTRATIONS
   NV = 3
   DO 20 I = 1,IMAX
         XX(I) = XN2(I)
   20 CONTINUE
GO TO 2

6 CALL THALG(XX,IMAX,A,B,C,F)
   DO 21 I = 1,IMAX
         XN2(I) = XX(I)
   21 CONTINUE

JN = J*JDIV - JDIV + 1
   IF(JJ - JN) 100,23,100

23 CONTINUE
   IFLAM(J) = IFLA(JJ)
   RFLAM(J) = RFLA(JJ)
   DO 24 I = 1,IMAX
         X(3*I+J) = TEMP(I)/DTF
         X(4*I+J) = XGAS(I)
         IF(XGAS(I) .LT. 0.0) X(4*I+J) = XGAS(I)*DENS/DENS
         X(5*I+J) = XN2(I)
   24 CONTINUE

J = J + 1

100 CONTINUE
RETURN
END
SUBROUTINE INPUT(IW*,PI*,T WALL*,I ADI*,I PROP*)
THIS SUBROUTINE PRINTS OUT THE INPUT DATA
REAL LL
COMMON NVMAX*,IMAX*,JMAX*,L*,LL*,RR*,DENS(26*26)*X(11*26*26)
COMMON/RZGRID/R(26)*Z(26)*VP(26*26)*DELRR(26)*DELZ(26)
COMMON/DATA/T FUEL*,XFUEL*,XO2L*,XCO2L*,XH2OL*,XN2L*,XNOL*,VFUEL
COMMON/DATA/TOXI*,XFUER*,XO2R*,XCO2R*,XH2OR*,XN2R*,XNOR*,VXLI
COMMON/DATA/DENSL*,DENSH*,SV
COMMON/PROP/RE*,SC(8)*PR*,GR*,TC(26*26)*VISC(26*26)*HC(26*26)
COMMON/PROP/DIFFU(8*26*26)*TF*,DTF*,TCO*,VISCO*,HCO*,DIFFUO(8)*DENSO
COMMON/PROP/MSC*,DELH*,STOIC*,PSI(26)
WRITE(IW*,100)
WRITE(IW*,101) LL*,RR
WRITE(IW*,102) TFUEL*,TOXI
WRITE(IW*,103) VFUEL*,VXLI
WRITE(IW*,104) XFUEL*,XFUER
WRITE(IW*,105) XO2L*,XO2R
WRITE(IW*,106) XCO2L*,XCO2R
WRITE(IW*,107) XH2OL*,XH2OR
WRITE(IW*,108) XN2L*,XN2R
WRITE(IW*,109) XNOL*,XNOR
GO TO (1*2)*I ADI*
1 WRITE(IW*,110) PI
GO TO 3
2 WRITE(IW*,111) PI*,T WALL
9 WRITE(IW*,112)
WRITE(IW*,113) DENSH*,DIFFUO(1)
WRITE(IW*,114) HCO*,DIFFUO(2)
WRITE(IW*,115) VISCO*,DIFFUO(3)
WRITE(IW*,116) TCO*,DIFFUO(4)
WRITE(IW*,117) TF*,DIFFUO(5)
WRITE(IW*,118) DTF*,DIFFUO(6)
WRITE(IW*,119) DIFFUO(7)*DIFFUO(8)
WRITE(IW*,117)
WRITE(IW*,118) RE*,SC(1)
WRITE(IW*,119) PR
WRITE(IW*,120) GR
IF (PROP*EQ*2) WRITE(IW*,125)
WRITE(IW*,121)
WRITE(IW*,122) (R(I)*I = 1*IMAX)
WRITE(IW*,123)
WRITE(IW*,122) (Z(J)*J = 1*JMAX)
100 FORMAT(T5*,"INPUT PARAMETERS'/*)
101 FORMAT(T2*,"CONDITIONS IN THE INNER TUBE OF RADIUS'*,F8.3*, CM'*,T65*,
1*CONDITIONS IN THE OUTER TUBE OF RADIUS'*,F8.3*, CM'/*)
102 FORMAT(T5*,"TEMPERATURE = '*,F8.2*, DEG K'*,T70*, TEMPERATURE = '*,F8.2*,
1* DEG K'*)
103 FORMAT(T5*,"VELOCITY = '*,F8.3*, CM/SEC'*,T70*, VELOCITY = '*,F8.3*, CM/S*
1*EC'*)
104 FORMAT(T5*,"MASS FRACTION FUEL = '*,F7.3*,T70*, MASS FRACTION FUEL = '*,
1*F7.3*)
105 FORMAT(T5*,"MASS FRACTION OXYGEN = '*,F7.3*,T70*, MASS FRACTION OXYGEN
1* = '*,F7.3*)
106 FORMAT(T5*, "MASS FRACTION CO2 = '*,F7.3*,T70*, MASS FRACTION CO2 = '*,
1*F7.3*)
107 FORMAT(T5&'MASS FRACTION H2O = ',F7.3,T70&'MASS FRACTION H2O = ',
          F7.3)
108 FORMAT(T5&'MASS FRACTION N2 = ',F7.3,T70&'MASS FRACTION N2 = ',F7.3)
109 FORMAT(T5&'MASS FRACTION NO = ',F7.3,T70&'MASS FRACTION NO = ',F7.3
1/)
110 FORMAT('THE SYSTEM IS AT A TOTAL PRESSURE OF ',F6.2,' ATM AND THE
1E SYSTEM IS ADIABATIC')
111 FORMAT('THE SYSTEM IS AT A TOTAL PRESSURE OF ',F6.2,' ATM AND THE
1E WALLS ARE AT ',F7.2,' DEG K')
112 FORMAT(T2&'THE PHYSICAL PROPERTIES ARE NORMALIZED BY THE FOLLOWING
1 REFERENCE VALUES')
113 FORMAT(T10&'DENSITY = ',F10.7,' GRAM/CC',T70&'FUEL DIFFUSION COEFF
1ICIENT = ',F7.3,' SQ CM/SEC')
114 FORMAT(T10&'HEAT CAPACITY = ',F7.3,' CAL/GRAM K',T70&'NITROGEN DIFF
1USION COEFFICIENT = ',F7.3,' SQ CM/SEC')
115 FORMAT(T10&'VISCOSETY = ',F9.6,' GRAM/CM/SEC',T70&'OXYGEN DIFFUSION
1ICENT = ',F7.3,' SQ CM/SEC')
116 FORMAT(T10&'THERMAL CONDUCTIVITY = ',F9.5,' CAL/SEC/CM/K',T70&' 1 CO2 DIFFUSION COEFFICIENT = ',F7.3,' SQ CM/SEC')
117 FORMAT(T2&'THE VALUES OF THE FOLLOWING DIMENSIONLESS GROUPS ARE US
1ED')
118 FORMAT(T10&'REYNOLDS NUMBER = ',F9.3,T50&'FUEL SCHMIDT NUMBER = ',
1F9.3)
119 FORMAT(T10&'PRANDTL NUMBER = ',F9.3)
120 FORMAT(T10&'GRASHOP NUMBER = ',F9.3)
121 FORMAT(T2&'NORMALIZED RADIAL GRIDS ARE AS FOLLOWS: (R1/R)')
122 FORMAT(T10&'NORMALIZED VERTICAL GRIDS ARE AS FOLLOWS: (Z/J/RR)')
123 FORMAT(T10&'ADIABATIC FLAME TEMPERATURE = ',F7.2,' DEG K',T70&'H2O D
1IFFUSION COEFFICIENT = ',F7.3,' SQ CM/SEC')
124 FORMAT(T2&'THIS IS A CONSTANT PROPERTY CASE')
125 FORMAT(T10&'DTF = TF - TIN = ',F7.2,' DEG K',T70&'CO DIFFUSION COEFF
1ICIENT = ',F7.3,' SQ CM/SEC')
126 FORMAT(T10&'HYDROGEN DIFFUSION COEFFICIENT = ',F7.3,' SQ CM/SEC')
170&'NO DIFFUSION COEFFICIENT = ',F7.3,' SQ CM/SEC')
RETURN
END
SUBROUTINE THALG(X, NEQ, A, B, C, F)

THOMAS ALGORITHM

DIMENSION A(26), B(26), C(26), F(26), P(26), Q(26), X(26)

P(1) = C(1)/B(1)
Q(1) = F(1)/B(1)

DO 1 I = 2*NEQ
  P(I) = C(I)/((B(I) - A(I)*P(I-1))
  Q(I) = (F(I) - A(I)*Q(I-1)) / (B(I) - A(I)*P(I-1))

1 CONTINUE

X(NEQ) = Q(NEQ)

DO 2 I = 2*NEQ
  J = NEQ-I+1
  X(J) = Q(J) - P(J)*X(J+1)

2 CONTINUE

RETURN
END
SUBROUTINE RATE(P1)

THIS SUBROUTINE DETERMINES THE RATES OF PRODUCTION OF THE STABLE SPECIES IN GRAMS/CC/SEC EVERYWHERE IN THE FLOW FIELD.

SPECIE REPRESENTATION ON VARIABLE X*** 6 = O2, 7 = CO2, 8 = H2O
9 = CO, 10 = H2, 11 = NO

RATE REPRESENTATION 1 = CH4, 2 = N2, 3 = O2, 4 = CO2
5 = H2O, 6 = CO, 7 = H2, 8 = O, 9 = H, 10 = OH, 11 = NO

REAL MW(10), LL, KEQ1, KEQ2, KEQ3, KF7, KR7, KF8, KR8, KEQ8, KF9, KR9, KEQ9
REAL KF10, KR10, KEQ10, KF11, KR11, KEQ11, KEQ7, LNT

DIMENSION EP(26,26)

COMMON VNMAX, I MAX, J MAX, LL, RR, DENS(26,26), X(11,26,26)
COMMON/RZGRID/R(26,26), Z(26,26), VP(26,26), DELR(26,26), DELZ(26,26)
COMMON/PR/RES/SC(8), PR/GR/TC(26,26), VISC(26,26), HC(26,26)
COMMON/PROP/DIFFU18(26,26), DTF, TCO, VISCO, HCO, DIFFUO18, DENSO
COMMON/PROP/WSC, DELH, STO1CF, PSI(26,26)
COMMON/FLAM/IFLAM(26), ZFLAM, IFLAM(26)
COMMON/RATES/RX(11,26,26)

DATA MW/(16,28,32,44,18,28,2,16,1,17,1)

NNV = 6

IMAX = IMAX + 1
JMAX = JMAX + 1

DO 1 NC = 1, 11
DO 1 J = 1, JMAX
DO 1 I = 1, IMAX

1 RX(NC, I, J) = 0.

RATE OF PRODUCTION OF O

DO 4 J = 1, JMAX

LNT = ALOG(DTF*X(3, I, J))

4 EP(I, J) = DENS(I, J) * EXP(1, 2, 26, 26) * LNT + (2, 26, 26) / DIFFUO(3)

XMWO = MW(5) * MW(8) / MW(3) / MW(7)

DO 5 I = 2, IMAX
DO 5 J = 2, JMAX

IF(I = LT, IFLAM(J), OR, DTF*X(3, I, J) = LT 1000) GO TO 5

IP1 = I + 1
IM1 = I - 1
JP1 = J + 1
J MJ = J - 1

RT = DTF*X(3, IP1, J) * 1207
KEQ1 = 13 * EXP(-15931/RT)
KEQ2 = 2 * EXP(-1874/RT)
KEQ3 = 4 * EXP(-15179/RT)

XOE = XMWO * KEQ1 * KEQ3 * X(16, IP1, J) * X(10, IP1, J) / X(8, IP1, J)

RT = DTF*X(3, IM1, J) * 1207
KEQ1 = 13 * EXP(-15931/RT)
KEQ2 = 2 * EXP(-1874/RT)
KEQ3 = 4 * EXP(-15179/RT)

XO = XMWO * KEQ1 * KEQ3 * X(16, IM1, J) * X(10, IM1, J) / X(8, IM1, J)

RT = DTF*X(3, JP1, J) * 1207
KEQ1 = 13 * EXP(-15931/RT)
KEQ2 = 2 * EXP(-1874/RT)
KEQ3 = 4 * EXP(-15179/RT)

XON = XMWO = KEQ1/KEQ3*X(16, JP1, J) * X(10, JP1, J) / X(8, JP1, J)

IF(J = EQ, 2) GO TO 10

RT = DTF*X(3, JM1, J) * 1207
KEQ1 = 13.1*EXP(-15931/RT)
KEQ2 = 2.26*EXP(-1874/RT)
KEQ3 = 4.73*EXP(-15175/RT)
XOS = XMWO * KEQ1/KEQ3*X(6*I+JM1)*X(10*I+JM1)/X(8*I+JM1)

GO TO 11

10 XOS = 0.0

11 RT = DTF*X(3*I+J) + 1.987
KEQ1 = 13.1*EXP(-15931/RT)
KEQ2 = 2.26*EXP(-1874/RT)
KEQ3 = 4.73*EXP(-15175/RT)
XOP = XMWO * KEQ1/KEQ3*X(6*I+J)*X(10*I+J)/X(8*I+J)
CALL FLUX(NV,N1,N2,J,EP,AE,AW,AN,AS,BW,BN,BS)
RO = (BE+AE)*(RO-1)+XOP-XOW + (BS + AS)*
1 (XOP-XOS) + (BN + AN)*(XOP-XON)
RX(I,J) = RO /VP(I,J)*DENS0*DIFFUO(3)/RR*RR

5 CONTINUE

C

RATE OF PRODUCTION OF H
DO 6 I = 1*IMAX
DO 6 J = 1*JMAX
LNT = ALOG(DTF*X(3*I+J))

6 EP(I,J) = DENS(I,J)*EXP((1.658*LNT-9312)/DIFFUO(7)
 XMWH = MW(5)/SQRT(MW(7)*MW(5))/MW(7)
 DO 7 I = 2*IMAXM1
 DO 7 J = 2*JMAXM1
 IF(I + LT*IFLAM(J) OR DTF*X(3*I+J) + LT*1000) GO TO 7
 IP1 = I + 1
 IM1 = I - 1
 JP1 = J + 1
 JM1 = J - 1
 RT = DTF*X(3*IP1+J) + 1.987
 KEQ1 = 13.1*EXP(-15931/RT)
 KEQ2 = 2.26*EXP(-1874/RT)
 KEQ3 = 4.73*EXP(-15175/RT)
 XHE = XMWH*SQRT(KEQ1*KEQ2*X(6*IP1+J)*X(10*IP1+J)/KEQ3*X(10*IP1+J)
 1/X(8*IP1+J)
 RT = DTF*X(3*IM1+J) + 1.987
 KEQ1 = 13.1*EXP(-15931/RT)
 KEQ2 = 2.26*EXP(-1874/RT)
 KEQ3 = 4.73*EXP(-15175/RT)
 XHW = XMWH*SQRT(KEQ1*KEQ2*X(6*IM1+J)*X(10*IM1+J)/KEQ3*X(10*IM1+J)
 1/X(8*IM1+J)
 RT = DTF * X(3*JP1)+1.987
 KEQ1 = 13.1*EXP(-15931/RT)
 KEQ2 = 2.26*EXP(-1874/RT)
 KEQ3 = 4.73*EXP(-15175/RT)
 XHN = XMWH*SQRT(KEQ1*KEQ2*X(6*JP1)*X(10*JP1)/KEQ3*X(10*JP1)
 1/X(8*JP1)
 IF(J = EQ 2) GO TO 12
 RT = DTF*X(3*I+JM1) + 1.987
 KEQ1 = 13.1*EXP(-15931/RT)
 KEQ2 = 2.26*EXP(-1874/RT)
 KEQ3 = 4.73*EXP(-15175/RT)
 XHS = XMWH*SQRT(KEQ1*KEQ2*X(6*JM1)*X(10*JM1)/KEQ3*X(10*JM1)
 1/X(8*JM1)
 GO TO 13
12 XHS = 0
13 RT = DTF\*X(3\*I\*J)\*1.987
    KEQ1 = 13.1\*EXP\(-15931/RT\)
    KEQ2 = 2.26\*EXP\(-1874/RT\)
    KEQ3 = 4.73\*EXP\(-15175/RT\)
    XHP = XMWH/SQRT(KEQ1\*KEQ2\*X(6\*I\*J)\*X(10\*I\*J))/KEQ3\*X(10\*I\*J)
    1/\(X(8\*I\*J)\)
    CALL FLUX(INV\*J\*J,EP\*AE,AW\*AN,AS\*BE,BW\*BN,BS)
    RH = (BE + AE)*(XHP-XHE) + (BW + AW)*(XHP-XHW) + (BS + AS)*
    1 (XHP=XHS) + (BN + AN)*(XHP=XHN)
    RX(9\*I\*J) = RH /VP(I\*J)*DENS\*DIFFUG(7)/RR*RR
    7 CONTINUE

C RATE OF PRODUCTION OF OH
    DO 8 I = 1*IMAX
    DO 8 J = 1*JMAX
    LNT = ALOG(DTF\*X(3\*I\*J))
    8 EP(I\*J) = DENS(I\*J)*EXP(1.658*LNT-10.701)/DIFFUG(5)
    XMWH = MW(10)/SQRT(MW(7)*MW(3))
    DO 9 I = 2*IIMAX1
    DO 9 J = 2*JIMAX1
    IF(I.LT.IPLAM(J)) OR. DTF\*X(3\*I\*J) LT. 1000 GO TO 9
    IP1 = I + 1
    IM1 = I - 1
    JP1 = J + 1
    JM1 = J - 1
    RT = DTF\*X(3\*IP1\*J) * 1.987
    KEQ1 = 13.1\*EXP\(-15931/RT\)
    KEQ2 = 2.26\*EXP\(-1874/RT\)
    KEQ3 = 4.73\*EXP\(-15175/RT\)
    XOH = XMWH/SQRT(KEQ1\*KEQ2\*X(10\*IP1\*J)*X(6\*IP1\*J))
    RT = DTF \(X(3\*IM1\*J)\) \*1.987
    KEQ1 = 13.1\*EXP\(-15931/RT\)
    KEQ2 = 2.26\*EXP\(-1874/RT\)
    KEQ3 = 4.73\*EXP\(-15175/RT\)
    XOHW = XMWH/SQRT(KEQ1\*KEQ2\*X(10\*IM1\*J)*X(6\*IM1\*J))
    RT = DTF \(X(3\*JP1\*J)\) \*1.987
    KEQ1 = 13.1\*EXP\(-15931/RT\)
    KEQ2 = 2.26\*EXP\(-1874/RT\)
    KEQ3 = 4.73\*EXP\(-15175/RT\)
    XOH = XMWH/SQRT(KEQ1\*KEQ2\*X(10\*JP1\*J)*X(6\*JP1\*J))
    IF(EQ E2) GO TO 14
    RT = DTF\*X(3\*JM1\*J) * 1.987
    KEQ1 = 13.1\*EXP\(-15931/RT\)
    KEQ2 = 2.26\*EXP\(-1874/RT\)
    KEQ3 = 4.73\*EXP\(-15175/RT\)
    XOH = XMWH/SQRT(KEQ1\*KEQ2\*X(10\*JM1\*J)*X(6\*JM1\*J))
    GO TO 15
14 XOH = 0.0
15 RT = DTF\*X(3\*I\*J) * 1.987
    KEQ1 = 13.1\*EXP\(-15931/RT\)
    KEQ2 = 2.26\*EXP\(-1874/RT\)
    KEQ3 = 4.73\*EXP\(-15175/RT\)
    XOH = XMWH/SQRT(KEQ1\*KEQ2\*X(10\*I\*J)*X(6\*I\*J))
    CALL FLUX(INV\*J\*J,EP\*AE,AW\*AN,AS\*BE,BW\*BN,BS)
    RH = (BE + AE)*(XOH-XOH)* (BW+AW)*(XOH-XOHW) + (BS+AS)
1 *(XOHP-XOHS) + (BN + AN)*(XOHP-XOHN)
RX10*I*J = ROH /VP(I,J)*DENSO*DIFFUG(5)/RR*RR
9 CONTINUE

C REACTIONS CONSIDERED IN THE ORDER IN WHICH THE SUBSCRIPTS REFER
C TO THEM ARE AS FOLLOWS:
C
********** H + O2 = OH + O 
********** O + H2 = H + OH 
********** H + H20 = OH + H2 
********** CO + OH = CO2 + H 
********** H + H + M = H2 + M 
********** H + OH + M = H20 + M 
********** O + O + M = O2 + M 
********** H + O + M = OH + M

DO 16 J = 2,IMAXM1
IFLAMJ = IFLAM(J)
DO 17 I = IFLAMJ,IMAXM1
T = DTF*X(3,I,J)
IF(T LT 1000.E0) GO TO 17
RT = 1.E987*T
T2 = T*T
T3 = T2*T
T4 = T3*T
KEQ1 = 13.8*EXP(-15931/RT)
KEQ2 = 2.26*EXP(-1874/RT)
KEQ3 = 4.73*EXP(-15175/RT)
DELG7 = -24.5799 + 1.2704E0*RT - 9.480E0*RT*T2
KEQ7 = EXP(-DELG7*10000/RT)
KF7 = 7.5E12*EXP(-7700/RT)
KR7 = KF7/KEQ7
DELG8 = -10.53924 + 2.491E0*RT + 9.872E0*RT*T2
KEQ8 = EXP(-DELG8*10000/RT)
KF8 = 0.65E15
KR8 = KF8/821/T/KEQ8
DELG9 = -11.93842 + 2.69815E0*RT + 20.4456E0*RT*T2 - 34.6502E0
1 * T3 + 2.0474E0*RT*T
KEQ9 = EXP(-DELG9*10000/RT)
KF9 = 9.40E15
KR9 = KF9/821/T/KEQ9
DELG10 = -11.93842 + 2.958E0*RT + 6.261E0*RT*T2
KEQ10 = EXP(-DELG10*10000/RT)
KF10 = 4.3*14
KR10 = KF10/821/T/KEQ10
DELG11 = -103.0097 + 2.3138E0*RT + 11.3734E0*RT*T2 - 4.3302E11*RT
KEQ11 = EXP(-DELG11*10000/RT)
KF11 = 5.0E15
KR11 = KF11/821/T/KEQ11
RHO = PI/821/T
RHO1 = DENSI*J)*DENSO

C COMMONLY USED EXPRESSIONS IN THE RATES OF PRODUCTION
RHO1SQ = RHO1*RHO1
RHCUB = RHO1SQ*RHO
XM02 = X16*I*J)/MW(3)
XMCO2 = X7*I*J)/MW(4)
XMH2O = X6*I*J)/MW(5)
XMCO = X9*I*J)/MW(6)
XMH2 = X(10*I+J)/MW(7)
H2O2 = XMH2*XM2
H2H2O = XMH2/XMH2
SORTHO = SORT(H2O2)
XX1K2 = KEQ2*KEQ2
SQRK12 = SORT(XX1K2)

C
REACTION RATE EXPRESSIONS

DEL7 = KF7*SQRK12*RHO1SQ*SORTH0*XMCO = KR7*SQRK12*RHO1SQ/KEQ3*
1 SORTH0*XMCO2*H2H20
DEL8 = KF8*XX1K2/KEQ3/KEQ3*RHOCUB*H2O2*H2H20*H2H20 = KR8*RHO1*RHO*
1 XMH20
DEL11 = KF11*SQRK12*KEQ1/KEQ3/KEQ3*RHOCUB*SORTH0*XM2*H2H20*H2H20
1 = KR11*SQRK12*RHO*RHO1*SORTH0

C
RATES OF PRODUCTION OF THE STABLE SPECIES

RX(3*I+J) = -(RX(8*I+J)/MW(8) -RX(9*I+J)/MW(9)/2a -RX(10*I+J)/(1 1 MW(10)/2a -DEL8 -DEL9 -DEL10 -DEL11)*MW(3)
RX(4*I+J) = DEL7*Mw(4)
RX(5*I+J) = (RX(8*I+J)/MW(8) +RX(9*I+J)/MW(9) -DEL7 + 2a*(DEL8
1 +DEL9 + DEL10 + DEL11))*MW(5)
RX(6*I+J) = -DEL7*Mw(6)
RX(7*I+J) = -(RX(8*I+J)/MW(8) -RX(10*I+J)/MW(10)/2a -3a*RX(9*I+J)
1/MW(9)/2a + DEL7 -2a*(DEL8 + DEL9 + DEL10 + DEL11))*MW(7)

17 CONTINUE
16 CONTINUE
RETURN
END
Appendix X. Biographical Note

The author, Reginald Eugene Mitchell, was born on May 16, 1947 in Houston, Texas. Elementary and secondary schools were attended in the Houston Independent School District. Upon graduation in 1964, he received a Worthing Scholarship for use at the college of his choice. He attended the University of Denver and graduated in June, 1968 with a B.S.Ch.E. The author obtained a M.S.Ch.E. from Newark College of Engineering in January, 1970 before entering the Massachusetts Institute of Technology in February, 1970.

In June, 1969 the author married the former Kristen Eriksson whom he met while attending the University of Denver. During the summer of 1968 the author worked as a "summer engineer" at the Procter and Gamble Company in Cincinnati, Ohio and during the winter of 1969 he worked as a quality control technician at Hunt Wesson Foods in Houston, Texas while he finished his master's dissertation.

At M.I.T. the author was a part-time research assistant under the supervision of Professor Adel F. Sarofim until he passed the doctoral examinations in January, 1971. He then began his doctoral thesis work and has been a full-time research assistant since then. Upon graduation from M.I.T. in August with the degree of Doctor of
Science, the author and his wife will move to Livermore, California where he will work as a chemical engineer at Sandia Laboratories. There, his research in the field of combustion will continue.

Reginald Mitchell is a member of the honorary society of the Sigma Xi and the American Institute of Chemical Engineers.