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A STUDY OF
BORON PARTICLE IGNITION

DISSERTATION
Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of the Ohio State University

by
Harold Francis Chambers, Jr., As.E., M.Sc.

The Ohio State University

Approved by

[Signature]
Adviser

Department of Aeronautical and
Astronautical Engineering
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Preface

This dissertation was conducted in the ramjet Technology Branch, ramjet Engine Division of the AF Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio.

The author wishes to express appreciation to Professor Rudolph Edse for serving as adviser for this work. His interest and advice were very instrumental in the successful completion of the effort.

A special acknowledgement is made to the many individuals in the Laboratory whose help and encouragement were invaluable. Also included are the Laboratory technicians, Messrs. P. Schelenz and D. Cincerelli, for their assistance and suggestions during the testing phase.
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January 1966.

"Analytical Study of Shock Tunnel Simulation of Combustor
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<thead>
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<th>Definition</th>
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<tr>
<td>A</td>
<td>Area (cm²)</td>
</tr>
<tr>
<td>C_D</td>
<td>Drag coefficient</td>
</tr>
<tr>
<td>C_OX</td>
<td>Oxidizer concentration (mole/cm³)</td>
</tr>
<tr>
<td>C_S</td>
<td>Specific heat of particle (cal/gm-°K)</td>
</tr>
<tr>
<td>d</td>
<td>Diameter (cm)</td>
</tr>
<tr>
<td>E_A</td>
<td>Activation energy (cal/mole)</td>
</tr>
<tr>
<td>H_R</td>
<td>Heat of reaction (cal/mole)</td>
</tr>
<tr>
<td>H_V</td>
<td>Heat of vaporization (cal/mole)</td>
</tr>
<tr>
<td>k</td>
<td>Thermal conductivity (cal/cm-sec-°K)</td>
</tr>
<tr>
<td>M_W</td>
<td>Molecular weight (gm/mole)</td>
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<tr>
<td>Nu</td>
<td>Nusselt number</td>
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<tr>
<td>P_R</td>
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<td>Vapor pressure (atm)</td>
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<tr>
<td>q</td>
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<td>Q_CH</td>
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</tr>
<tr>
<td>Q_CON</td>
<td>Convective Heat Flux (cal/cm²-sec)</td>
</tr>
<tr>
<td>Q_R</td>
<td>Radiative Heat Flux (cal/cm²-sec)</td>
</tr>
<tr>
<td>Q_V</td>
<td>Evaporative Heat Flux (cal/cm²-sec)</td>
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<tr>
<td>R</td>
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<td>REY</td>
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</tr>
<tr>
<td>T</td>
<td>Temperature (°K)</td>
</tr>
<tr>
<td>t</td>
<td>Time (sec)</td>
</tr>
<tr>
<td>T_V</td>
<td>Vibrational relaxation time (sec)</td>
</tr>
<tr>
<td>V</td>
<td>Velocity (cm/sec)</td>
</tr>
</tbody>
</table>
$x$ - Displacement (cm)

$z$ - Pre-exponential factor (cm/sec)

$\varepsilon$ - Emissivity

$\mu$ - Viscosity (gm/cm·sec)

$\rho$ - Density (gm/cm$^3$)

$\sigma$ - Stefan-Boltzmann constant ($13.54 \times 10^{-13}$ cal/cm$^2$·°C·sec)

**Subscripts**

$g$ - Gas

$p$ - Particle

In many metal combustion studies boron has been referred to as a metal, although it is not a metal.
I

INTRODUCTION

The use of light metals as fuel additives in chemical propulsion systems has become important due to increasingly stringent systems requirements. These metals offer both high heat release per unit mass and high density, making them attractive on the basis of volume utilization. On the basis of these properties, boron is a particularly attractive candidate as shown in table 1.

TABLE 1.

FUEL COMPARISON

<table>
<thead>
<tr>
<th>FUEL</th>
<th>DENSITY (gm/cc)</th>
<th>HEATING VALUE (Kcal/gm)</th>
<th>HEATING VALUE (Kcal/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beryllium</td>
<td>1.85</td>
<td>16.132</td>
<td>29.844</td>
</tr>
<tr>
<td>Boron</td>
<td>2.34</td>
<td>13.90</td>
<td>32.55</td>
</tr>
<tr>
<td>Magnesium</td>
<td>1.74</td>
<td>5.91</td>
<td>10.29</td>
</tr>
<tr>
<td>Aluminum</td>
<td>2.70</td>
<td>7.02</td>
<td>20.05</td>
</tr>
<tr>
<td>JP-7</td>
<td>.775</td>
<td>10.52</td>
<td>8.16</td>
</tr>
</tbody>
</table>

Unfortunately, inability to attain theoretical performance has been encountered in the use of particulate boron.
additives. Three reasons are offered for this inefficiency: first, it is difficult to ignite the metal particle because of its high ignition temperature; second, inefficient combustion due to slow surface-burning process rather than rapid vapor-phase combustion; and third, two phase flow losses in the nozzle due to solid metal oxide particles: The first of these, the ignition process, is the subject of this dissertation.

**METAL PARTICLE IGNITION**

In reference [5], Classman has made three observations on metal ignition and combustion based on physical reasoning:

(1) Boiling point temperature of metal oxides limit flame temperatures of metals.

(2) If the boiling point temperature of the metal oxide is above that of the metal, "steady state" combustion will take place in the vapor phase.

(3) If the boiling point temperature of the oxide is below that of the metal, a surface combustion process will occur.

The melting and boiling temperatures of boron and boron oxide are shown in table 2, from reference [8].
<table>
<thead>
<tr>
<th>Species</th>
<th>Melting Temperature (°K)</th>
<th>Boiling Temperature (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>2450</td>
<td>3931</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>723</td>
<td>2338</td>
</tr>
</tbody>
</table>

Therefore according to the model by Glassman, boron would be expected to ignite and burn on the surface.

A consequence of the presence of condensed phase reactants is the predominance of heterogeneous reactions in metal combustion. Unless the metal is vaporized artificially, ignition is always preceded by reaction on the metal surface involving a protective oxide coating. This surface coating is the unique property of the metal ignition problem. As indicated by low-temperature oxidation rate laws the oxide film is initially protective but at high temperature the film becomes non-protective.

A model for the ignition process of a metal particle with an oxide coating has been presented in reference [5], based upon the works of several investigators at Princeton. A particle was assumed to be spherical and heated in a static oxidizing atmosphere by the net effects of several heat sources and losses. A heat balance is established
by examining the rate of heat input and loss through a thin control volume enclosing the reacting surface of the particle.

The following sketch illustrates the heat source and loss effects as a function of particle temperature.

Figure 1. Particle Heat Source and Loss
Four temperatures are indicated in the sketch:

1. \( T_{OX} \) - The low temperature, slow surface oxidation of a metal.

2. \( T_{CR} \) - The critical temperature, lowest temperature from which the particle may self-heat to steady state combustion.

3. \( T_{IG} \) - Normal ignition temperature at which flame appears.

4. \( T_{F} \) - Flame temperature of steady state, self-sustained combustion.

The first and last of these temperatures represent stable states but the second is unstable. At temperatures slightly higher or lower than \( T_{CR} \), the system will pass to the value of \( T_{F} \) or \( T_{OX} \), respectively. The distinction between a critical temperature and ignition temperature allows for the definition of an ignition delay time and a long self-heating period prior to ignition, after attainment of the critical temperature, would be detrimental to ignition efficiency.

The preceding discussion may be slightly modified to allow the inclusion of a solid metal oxide coating on the surface of a particle. At low temperature a metal oxide film leads to a protective oxidation rate law of the general form,

\[
\frac{dx}{dt} = K x^{m-1} \quad (1)
\]
The variable X may be the mass of metal transformed to oxide or the oxide layer thickness but generally is the mass of oxygen consumed per unit area at a given time. Integration of the rate expression leads to various forms dependent upon the value of the index n, three examples of which are:

(1) $n = 2$, parabolic law $x^2 = 2k_2t + C_2$

(2) $n = 3$, cubic law $x^3 = 3k_3t + C_3$

(3) $n = 1$, linear law $x = k_7t + C_7$

The first two forms are termed protective while the third is non-protective. At low temperature the oxidation rate follows a protective law, while at high temperature a non-protective law appears. The temperature which distinguishes these two regimes is defined as the transition temperature. Two points concerning the transition temperature are important:

(1) The transition may be due to a physical change, i.e. melting or cracking of the oxide film.

(2) It must be lower than the ignition temperature and represents the lowest possible ignition temperature.
Figure 2 shows the modification of figure 1 when the transition temperature is included.

As shown in figure 2, the transition temperature may be less than or greater than the critical temperature. The ignition process is said to be either transition or critical temperature controlled depending on which is the lower temperature. In either case, the ignition temperature is greater than the controlling temperature.
Thus the history of a particle may be divided into three segments whether it is either critical or transition temperature controlled:

1. Heat-up time - Time for a particle to heat from the initial temperature to the controlling temperature.

2. Ignition delay time - Time for a particle to heat from the controlling temperature to ignition.

3. Combustion time - Time from particle ignition until it is consumed.

As particle size decreases, the ratio of surface area to volume \((S/V)\) increases. Three points are of importance concerning the relationship of \((S/V)\) ratio and the previously discussed temperatures:

1. Transition temperature, being a function of physical properties, would be independent of \((S/V)\) ratio.

2. Critical temperature, being a function of heat source and loss relationships, would decrease with increased \((S/V)\) ratio.

3. Ignition temperature will be independent of size for a transition controlled metal, while it will decrease with decreasing particle diameter for a critical controlled temperature.
Results of previous boron studies have not been examined to determine the validity of these surface ignition and combustion models. Determination of the controlling temperature, critical or transition, will aid in both understanding and improving the ignition of boron.

Results From Previous Boron Studies

A number of previous experimental approaches have been used to study the ignition and combustion of boron. A summary of results is presented here to describe the state-of-the-art in boron ignition and aid in presenting the necessity for the present study. Details of the previous research are included in Appendix I.

The ignition and combustion of boron particles has been studied in sizes ranging from 35 to 1000 microns diameter. In these experiments, the heat-up time was not separated from the ignition delay time. Experiments have shown the time from exposure of a particle to a heat source, until appearance of a flame, to vary inversely with gas temperature, oxygen concentration, and water vapor concentration. The time varied directly with particle diameter. No conclusive effect of pressure may be drawn from previous results.

Typically the time to ignite a particle was very long, 1000's of microseconds, which may be attributed to the large particle diameter and test gas environment. As shown in Table III for a 34.5 micron diameter particle, from the
results of reference [14], the time to ignite and burn a particle is too long for airbreathing propulsion requirements. A representative velocity of 500 ft/sec was selected. Therefore, it is necessary to pursue the study of ignition and combustion at increased gas pressure and gas temperature and decreased particle diameter.

TABLE 3.
Boron Particle Ignition and Combustion Time and Distance, $d_p = 34.5$ Microns

<table>
<thead>
<tr>
<th>$P_{O_2}$ (ATM)</th>
<th>$T_g$ (°K)</th>
<th>$t_{ignite}$ (seconds $\times 10^{-3}$)</th>
<th>$t_{burn}$</th>
<th>$t_{total}$</th>
<th>$x (\leq 500$ft/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>.23</td>
<td>2280</td>
<td>9.8</td>
<td>21</td>
<td>30.8</td>
<td>15.4</td>
</tr>
<tr>
<td>.20</td>
<td>2430</td>
<td>8.4</td>
<td>20.5</td>
<td>28.9</td>
<td>14.45</td>
</tr>
<tr>
<td>.23</td>
<td>2870</td>
<td>4.3</td>
<td>11.2</td>
<td>15.5</td>
<td>7.75</td>
</tr>
<tr>
<td>.28</td>
<td>2490</td>
<td>7.9</td>
<td>13.9</td>
<td>21.8</td>
<td>10.9</td>
</tr>
<tr>
<td>.37</td>
<td>2450</td>
<td>7.3</td>
<td>9.8</td>
<td>17.1</td>
<td>8.55</td>
</tr>
</tbody>
</table>

The delay time under these conditions was on the order of $2 \times 10^{-3}$ seconds, nominally 10% of the total time. Under similar conditions the heat-up time and burning time for a one-micron particle would be on the order of $2 \times 10^{-6}$ and $10 \times 10^{-6}$ seconds, respectively. The heat-up time assumed to be that necessary for a particle to reach 1900°K, starting from 300°K and burning time estimated using the "d-squared" law which assumes a particle's diameter to vary as $d^2 \alpha t$. This burning rate law is actually faster than
one would expect for a particle but gave an order of magnitude agreement with the experimental data shown in Table 3. The heat-up and burning time for the one-micron particle are on the order of $10^3$ shorter than those for the 35 micron particle. If the delay time would be reduced by a similar factor, the total time required to consume a particle would be well within the limits for airbreathing application. However, if the delay time is not reduced similarly, and continued to be on the order of $10^{-3}$ rather than $10^{-6}$ seconds, it would become the controlling factor in the particle's combustion history.

Present Study

The subject of this dissertation is thus the study of ignition delay time of particulate boron described in the previously discussed model of metal particle ignition. Specific tasks involved are:

(1) To develop a technique for separation of heat-up from ignition delay time for a metal particle.

(2) Obtain ignition delay data on nominal one-micron diameter boron particles.

(3) Determine the effects of pressure, temperature, oxidizer concentration, and particle diameter upon boron ignition delay.
(4) Examine the results of boron ignition experiments on the basis of metal ignition theory to determine the type of controlling temperature.

(5) Establish the influence of ignition delay upon air-breathing combustor operating requirements.

Both the separation of heat-up from ignition delay time and the experimental shock tube technique for study of ignition delay time of a metal particle are new. This study of boron particle ignition also differs from previous works in the diameter of particles studied and values of test gas variables. No previous studies have been found involving measurement of ignition delay time for a particle. Particle ignition studies using a shock tube have been limited to ignition limit measurements on boron, references [10] and [24], and cellulose, reference [2].

Two major differences exist between this study and previous analytical models used to describe particle motion and heating. In this study, particle motion analysis is improved through use of a drag law which is valid over a wider range of Reynolds numbers than previously employed. Chemical heating of a particle prior to ignition is included as part of the particle heating model presented in this study. This is consistent with the metal ignition
theory previously discussed. Details of the analytical particle model developed in this dissertation are described in Section II and those of previous investigators in Appendix I.

Since the theory of shock tube operation has been described extensively in the literature, only two figures are presented here to explain terms used in the present shock tube experiments.

Figure 3 shows an ideal wave diagram for a shock tube. In this figure the notation used in the text for various regions of the shock tube is shown. The conditions in region two will be referred to as incident shock conditions and region five, reflected shock conditions.

Figure 4 depicts the sequence of events experienced by a powder sample in the test section of the shock tube. It depicts formation of the particle cloud by the incident shock and ignition behind the reflected shock. The test conditions are subscripted so as to relate to the wave diagram in Figure 3. Details of the experimental technique are presented in Section III.
Region | Conditions
--- | ---
1 | Driven tube initial conditions $T_1, P_1$
2* | Conditions behind incident shock $T_2, P_2$
3 | Conditions in expanding driven gas
4 | Driver tube initial conditions $T_4, P_4$
5* | Reflected region, conditions behind reflected shock $T_5, P_5$

Contact surface - Gas separating driver and driven gases

* Conditions in regions 2 and 5 are pertinent to particle heating and ignition, referred to as incident and reflected conditions.

Figure 3. Shock Tube Wave Diagram
(1) Initial conditions in test section $T_1, P_1$

(2) Powder went off knife edge by incident shock wave, $T_2, P_2$

(3) Reflected shock passes through powder cloud

(4) Powder ignites behind reflected shock
The following is a summary of temperature and ignition delay definitions used in the text. It is included to clarify the discussion in the following sections.

(1) Ignition temperature - Particle temperature at which flame appears.

(2) Ignition limit temperature - Gas temperature, for a given pressure, above which ignition will occur and below which it will not occur.

(3) Critical temperature - The lowest particle temperature from which it may self heat to ignition.

(4) Transition temperature - Particle temperature below which an oxide coating on the particle is protective and above which it is non-protective.

(5) Ignition delay (theory) - The time interval from when the particle attains the critical temperature and ignition when flame appears.

(6) Ignition delay (experimental) - The time a particle resided in the reflected region of the shock tube prior to ignition.
II
THEORETICAL STUDIES

In both the shock tube and combustor of an engine, a metal particle that is to be burned must be surrounded by the oxidizer and heated to an ignition temperature. Thus any analytical model describing a particle's motion and temperature change must include chemical reaction and momentum and energy transfer.

Ignition delay time for gas phase reactants has been defined as the interval between the time a homogeneous combustible mixture attains a temperature sufficient to ignite and the time spontaneous ignition occurs. This definition contains two implicit assumptions. First, the term "homogeneous" assumes that intimate mixing of fuel and oxidizer has already occurred and no physical mixing time is included in the ignition delay. Secondly, it is assumed the ignition temperature is attained very rapidly in a time interval much shorter than the delay time. Thus no appreciable chemical reaction occurs as the temperature is raised. In the heterogeneous case of metal ignition, ignition delay was defined as the interval between the time
a particle attains its critical temperature and the time at which a flame appears. The difference between critical and ignition temperature has been described in Section I and illustrated in Figure 1.

By proper selection of test conditions, the shock tube is capable of meeting the requirements specified for measurement of the ignition delay time for a particle. Previous shock tube experimental studies, references [10] and [24], have determined the ignition limit temperature for one micron boron particle as a function of pressure. These results are shown in Figure 5. Ignition limit temperature is the gas temperature, for a given gas pressure, above which ignition will occur and below which it will not occur. Thus the definition of ignition limit temperature closely resembles the critical temperature of a particle defined in Section I. The critical and ignition limit temperatures are similar in that they both separate conditions under which ignition is possible from those under which it is not. The difference between the two temperatures is that the former refers to the particle temperature while the latter refers to gas temperature. Using the experimentally determined ignition limit temperatures, shock tube conditions were selected which kept the gas below the ignition limit behind the incident shock and above the ignition limit behind the
reflected shock. Consequently, the ignition delay time was equal to the residence time of a particle behind the reflected shock prior to ignition. Discussion of the particle mixing and rate of temperature change requirements for measurement of ignition delay time will be included in Section IV.

The purpose of the analysis presented here was to describe the motion and temperature change of a single particle in the shock tube as a function of time until ignition. The model consists of three simultaneous non-linear differential equations. The derivation of each of these three equations will be discussed separately. In formulating the equations, four basic assumptions were made:

(1) The particles are considered to be spheres of constant diameter since no significant mass is consumed prior to ignition.

(2) The particles are sufficiently large in comparison to the mean free path of the surrounding gas molecules that continuum transport properties are valid.

(3) The particle cloud density is low enough that interparticle radiant heat transfer is negligible.

(4) The mass of the particle sample is sufficiently small so as not to decrease the surrounding gas temperature.
Shock Tube Method of Ignition
By Uda (24) and Jones (10)
$d_x = 1$ (micron)

![Graph of Oxygen Partial Pressure vs. Gas Temperature](image)

**Figure 5.** Boron Particle Ignition Limit Curve
The consequences of these assumptions and the application of the theory for a single particle to a multi-particle situation will be discussed in Section IV following the experimental results.

Particle Position and Velocity

To determine the ignition delay time for a particle in the shock tube, it was necessary to derive expressions for the particle's position and velocity as a function of time.

The particle position was expressed as:

\[ V_p = \frac{dX_p}{dt} \]  

To evaluate the particle's velocity in the horizontal direction, Newton's second law of motion was employed. Motion in the horizontal direction resulted from the drag force exerted on the circular cross-sectional area of the particle. Vertical motion due to gravity was negligible for the particle size and test time of the experiment. A calculation for a one micron particle shows its path to deviate less than one tenth of a degree from the horizontal during the time of a test. The same calculation for a 100 micron particle shows a deviation of about five and one-half degrees from the horizontal.

The velocity was thus expressed:

\[ F = \mathcal{m}_p \frac{dv_p}{dt} \]

\[ F = \rho \pi d_p^3 \frac{dv_p}{dt} \]
The drag force acting on the particle was expressed as:

\[ F = C_D \pi \rho A \frac{1}{2} \left( \frac{V_0 - V_p}{\rho} \right)^2 \frac{a^2}{4} \]  

(4)

Equating these expressions yielded the general form for particle velocity:

\[ \frac{dV_p}{dt} = \frac{3}{4} \frac{\rho g}{\rho} \left( V_0 - V_p \right)^2 C_D \]  

(5)

This form of the velocity expression has been used previously in single boron particle analysis, references (4), (13), and (20). However, drag coefficient relationships previously used were found not adequate, when compared to experimental data on spheres, reference (21), for the wide range of Reynolds number covered in the shock tube experiments. A survey yielded several forms of drag coefficient for spheres as a function of Reynolds number. Values of the drag coefficient calculated with these relationships are shown on Figure 6, together with the experimental values from reference (21).

Evaluation of the drag coefficient relationship by Langmuir and Blodgett:

\[ \frac{C_D}{24} R_{\text{Re}} = 1.0 + 0.197 R_{\text{Re}}^{0.63} + 2.6 \times 10^{-4} R_{\text{Re}}^{1.32} \]  

(6)
showed it to agree well with experimental data over the range of Reynolds number from 1. to 1000. This equation was used in the velocity calculation with the Reynolds number written as:

\[ R_{E_y} = \frac{d \rho f^2 (V_g - V_p)}{\mu g} \]  

(7)

The expression for the drag coefficient of spheres used in this study is different from that used by other authors. By extending the range of application of the particle motion theory to higher Reynolds number it represents an improvement. At the same time the drag coefficient expression reduces to values very close to Stokes law for small Reynolds number.
\[ C_D = \frac{24}{\text{Rey}} \]
\[ C_D = \left(\frac{100}{\text{Rey}}\right)^{2/3} \]
\[ C_D = \frac{18}{\text{Rey}^{1.6}} \]
\[ C_D = \frac{27}{\text{Rey}^{0.8}} \]
\[ C_D = \frac{6000}{\text{Rey}^{1.7}} \]
\[ C_D \text{ REY} = 1 + 1.197 \text{REY}^{0.63} + 2.6 \times 10^{-4} \text{REY}^{1.38} \]

**Figure 6. Sphere Drag Coefficient**

**Reynolds Number**
Particle Heating

The temperature change of a particle in the shock tube may be established from the properties of several heating and cooling processes which may occur simultaneously. An original model for particle heating prior to ignition was formulated by this author to include four processes considered to be of primary importance.

(1) Heating processes
   (a) Convection to the particle
   (b) Chemical reaction

(2) Cooling processes
   (a) Radiation by the particle
   (b) Evaporation from the particle's surface

This heating model of the ignition period differs from those of previous authors, as discussed in Section I, by the addition of surface evaporation and chemical reaction.

Convective heating of the particle results from a difference of both temperature and velocity between the particle and the gas in the shock tube. The form of the convection term is:

\[ Q_{\text{CON}} = \frac{N_u k_0}{\rho} (T_g - T_f) \text{ (cal/cm}^2\text{sec)} \]  

The Nusselt number used is of the empirical form,

\[ N_u = 2.0 + 0.276 R^\frac{1}{3} R_y^{\frac{1}{2}} \]  

reference (4), however, it does not account for ablation into
the boundary layer. The Nusselt number will be largest as the particle is initially swept off the knife edge by the incident shock. It will decrease as the particle accelerates. As the particle reaches the gas velocity, the temperature difference will be responsible for the remaining heating. The velocity used to calculate the Reynolds number is the relative velocity between the particle and gas. The thermal conductivity and viscosity were calculated by the methods of Wilke for individual species and Mason and Saxena for mixtures as described in reference (3). The thermodynamic variables, i.e. specific heats, were taken from the JANAF tables, reference (8).

Detailed steps in the surface problem of boron particle ignition are complex and have not been resolved. Thus the objective of the model presented here was to give a macroscopic picture of the process.

The problem must involve both a surface and chemical reaction process. Two surface processes possible are first, evaporation of vapor phase boron or second, production of a gaseous oxide by a process similar to chemical adsorption.

First, the evaporation process may be represented as:

\[ B(s) \rightarrow B(g) \] (10)

where monatomic rather than diatomic boron was selected on the basis of values of equilibrium constants presented in the JANAF tables, reference (8).
The second process is a chemical adsorption. Chemical adsorption processes produce a chemical reaction at a surface between the adsorbate and the adsorbant. The product which is later desorbed may have changed chemically, i.e. oxygen adsorbed on charcoal produces carbon monoxide as the desorbed species. Steps in this process may be summarized as:

1. Diffusion of gaseous reactant to the surface
2. Adsorption on the surface
3. Reaction within the adsorbed film
4. Desorption of the product
5. Diffusion of products away from the surface

A possible series of steps in this process for the oxidation of boron would be:

1. \( O_2(g) \rightarrow O_2 \) (adsorbed)
2. \( O_2 \) (adsorbed) \( \rightarrow \) \( 2O \) (adsorbed)
3. \( O \) (adsorbed) + \( B(s) \rightarrow BO \) (adsorbed)
4. \( BO \) (adsorbed) \( \rightarrow \) \( BO(g) \)

There is also a possibility that this process may occur on or within a liquid \( B_2O_3 \) coating on the particle's surface.

Neither rate constants nor energy values for the steps of the adsorption process are presently available. Therefore, a two-step process was selected for the surface reaction consisting of evaporation of gaseous boron followed by gas phase partial oxidation of the boron gas at the particle's
surface. The gas phase product would then complete oxidation after diffusing away from the surface. The two-step process was selected as representative of the surface process since it was possible to estimate its effect upon the particle.

The vaporization rate was expressed as:

\[ P_v \left( \frac{M_w}{2 \pi R T_p} \right)^{1/2} \text{ (gm/cm}^2\text{-sec)} \]  

with a vapor pressure of boron, reference (1), given by:

\[ P_v = \exp \left( 18.4 - \frac{71500}{T_p} \right) \text{ (ATM)} \]  

and a heat of vaporization of:

\[ H_v = 132.8 \text{ Kcal/mole} \]

The vapor pressure expression is an empirical equation derived to fit experimental data obtained over a range of 2100°-2400°K.

If the particle temperature exceeds the melting point of boron, 2450°K, the previous surface reaction, vapor pressure, and heat of vaporization were replaced by:

\[ B(l) \rightarrow B(g) \]  

\[ P_v = \exp \left( 15.6 - \frac{61330}{T_p} \right) \text{ (ATM)} \]  

\[ H_v = 121.8 \text{ (Kcal/mole)} \]
The vapor pressure of the liquid was assumed to be given by the Clasius-Clapeyron equation.

A cooling rate for the particle due to evaporation was expressed as:

\[ Q_v = P_v \left( \frac{M_w \rho}{2 \pi R T_0} \right)^{1/2} H_v \text{ (cal/cm}^2\text{sec)} \] (15)

The effect of particle melting would be an increase in both vaporization and cooling rates as compared to the solid particle.

The overall reaction selected as representative of heterogeneous oxidation of elemental boron at the particle's surface was:

\[ B(g) + O_2 \rightarrow BO_2(g) \] (16)

It is recognized that the postulated overall reaction represents a large number of elementary reactions in the oxidation process. Table 4 contains several possible elementary reactions in the gas phase oxidation of the metal.
TABLE 4.

Vapor Phase Reaction Summary

1. \( \text{B} + \text{O} + \text{M} \rightarrow \text{BO} + \text{M} \)
2. \( \text{O}_2 + \text{M} \rightarrow \text{O} + \text{O} + \text{M} \)
3. \( \text{BO} + \text{O} + \text{M} \rightarrow \text{BO}_2 + \text{M} \)
4. \( \text{B} + \text{B} + \text{M} \rightarrow \text{B}_2 + \text{M} \)
5. \( \text{B} + \text{BO} \rightarrow \text{B}_2 + \text{O} \)
6. \( \text{BO} + \text{BO} \rightarrow \text{O} + \text{BO}_2 \)
7. \( \text{BO} + \text{O} \rightarrow \text{BO}_2 + \text{O} \)
8. \( \text{BO} + \text{BO} \rightarrow \text{B}_2 + \text{O} \)
9. \( \text{BO} + \text{O} \rightarrow \text{B} + \text{O}_2 \)

TABLE 5.

Boron-Oxygen Gas Phase Species

<table>
<thead>
<tr>
<th>Species</th>
<th>Molecular Weight (GM/GM-MOLE)</th>
<th>Standard Heat of Formation (KCAL/MOLE)</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>10.82</td>
<td>132.8±4.4</td>
<td>Monatomic</td>
</tr>
<tr>
<td>B(_2)</td>
<td>21.64</td>
<td>195.0±6.4</td>
<td>Diatomic</td>
</tr>
<tr>
<td>BO</td>
<td>26.8104</td>
<td>0.±2</td>
<td>Diatomic</td>
</tr>
<tr>
<td>*B(_2)O</td>
<td>37.622</td>
<td>23. ±25</td>
<td>(\text{v}),</td>
</tr>
<tr>
<td>BO(_2)</td>
<td>42.810</td>
<td>-68. ±2</td>
<td>Linear, O-B-0</td>
</tr>
<tr>
<td>B(_2)O(_2)</td>
<td>53.64</td>
<td>-109.0±2</td>
<td>Linear, O-B-B-0</td>
</tr>
<tr>
<td>B(_2)O(_3)</td>
<td>69.6202</td>
<td>-199.8±1.</td>
<td>(\text{v}),</td>
</tr>
</tbody>
</table>

*Postulated Species, No Referenc. To Spectroscopic Evidence*
### Table 6.

**Boron Flame Spectra**  
**Visible Region**

<table>
<thead>
<tr>
<th>CRC FLAME Spectrum, Band Peak¹</th>
<th>Scheller &amp; Morrison Flame Spectrum, Band Peak²</th>
<th>Johns BO₂ Visible Spectrum Band Peak³</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Å)</td>
<td>(Å)</td>
<td>(Å)</td>
</tr>
<tr>
<td>4530</td>
<td>4550</td>
<td>4500</td>
</tr>
<tr>
<td>4713</td>
<td>4750</td>
<td>4930</td>
</tr>
<tr>
<td>4940</td>
<td>5000</td>
<td>5180</td>
</tr>
<tr>
<td>5180</td>
<td>5200</td>
<td>5450</td>
</tr>
<tr>
<td>5470</td>
<td>5500</td>
<td>5800</td>
</tr>
<tr>
<td>5790</td>
<td>5800</td>
<td>6200</td>
</tr>
<tr>
<td>6030</td>
<td></td>
<td>6380</td>
</tr>
<tr>
<td>6200</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹ All lines identified as due to BO₂ emission, reference [6].

² Most visible emission from boron flames results from very strong BO₂ bands near 5500Å, reference [19].

³ Visible emission responsible for green color of boron flames, results from two electronic transitions. Very high intensity lines at 5470.89Å, reference [9].
Table 5 shows the possible gas phase species in the boron-oxygen system with data from reference [8] and Table 6, the results of three studies of the emission from boron flames in the visible region, 4000-7000Å. The selection of \( \text{BO}_2 \) as the product of gas phase oxidation of the metal was thus based upon the spectroscopic observations presented in Table 6 showing the dominance of \( \text{BO}_2 \) in the boron flame. Its selection was also felt to be appropriate since ignition was to be studied rather than the subsequent phases in the combustion process in which \( \text{B}_2\text{O}_3 \) is formed.

It is generally assumed, [2] and [4], that the rate of particle heating due to a surface chemical reaction may be expressed:

\[
Q_{CH} = H_R \cot \, Z \exp \left(-\frac{E_A}{RT_P}\right) \text{ (cal/cm}^2\text{-sec)} \tag{17}
\]

Values of both the pre-exponential factor and activation energy were obtained from references [4] and [18], based upon burning time data of reference [13]. These were given as:

\[
Z = 5000 \text{ (cm/sec)} \quad E_A = 3.972 \text{ (kcal/mole)}
\]

The heat of reaction, \( H_R \) in equation (17), was calculated using the global reaction shown in equation (16). Both the \( \text{B}(g) \) and \( \text{BO}_2 \) species were assumed to be at a temperature equal to the particle surface temperature, while the \( \text{O}_2 \) was assumed to be at the ambient test gas temperature.
A second mechanism of cooling for the particle was due to radiation. Only emission of radiation from the particle was considered. Gas radiation was felt to be negligible at the temperatures involved. Effects of neglecting inter-particle radiation will be discussed later. The expression for radiative cooling of the particle was:

\[ Q_R = \varepsilon \sigma T_0^4 \text{ (cal/cm}^2\text{-sec)} \]  \hspace{1cm} (18)

with a value of 0.5 selected for the particle's emissivity, \( \varepsilon \).

Particle temperature change was considered to be only a time dependent function. Space dependence of particle temperature, temperature gradient within the particle, was neglected as a result of the study in reference [18] showing space dependence to be negligible for particles of nominal 50 microns diameter or less.

The sum of the four energy sources and sinks resulted in the following differential equation describing the temperature change of a particle with time.

\[
m_p c_s \frac{d(T_p)}{dt} = Q A_p d(t) - \rho_p \pi \frac{d^3}{6} c_s d(T_p) = \left\{ \frac{N_u k_g}{d_p} (T_g - T_p) - \varepsilon \sigma T_0^4 \rho_H \left( \frac{M_{av}}{2 \pi R_{av}} \right)^{1/2} \right. \\
\left. + H_n \rho_c z \exp \left( -\frac{E_n}{R_{av}} \right) \right\} \pi d_p^2 \, dt \\
\frac{dT_p}{dt} = \frac{c}{\varepsilon \rho_c c_s} \left[ \frac{N_u k_g}{d_p} (T_g - T_p) - \varepsilon \sigma T_0^4 \\
- \rho_H \left( \frac{M_{av}}{2 \pi R_{av}} \right)^{1/2} + H_n \rho_c z \exp \left( -\frac{E_n}{R_{av}} \right) \right] \right\} \hspace{1cm} (19)
Discussion of the method of solution of the differential equations describing the particle's position, velocity, and temperature as a function of time, as well as an example of the results of the analytical model, is contained in the following section.

Solution of Equations and Results of Model

The differential equations (2), (5), and (19) describing the particle position, velocity, and temperature change as a function of time are non-linear and required a numerical solution. A Runge-Kutta method, reference [11], was selected for solving the equations. The initial conditions used in the calculation were:

\[ \begin{align*}
  t &= 0, \\
  x_p &= 0, \\
  v_p &= 0, \\
  T_p &= 300.0^\circ K
\end{align*} \]

A solution also required values of the test gas conditions behind the incident and reflected shock, incident and reflected shock speeds, particle diameter, time increment between calculations, and total time for which calculations were to be performed. The calculations proceeded until either the total time interval was completed or the particle traveled the complete length of the test section. Output from the computer program consisted of the values of distance traveled, velocity, temperature attained, and the Reynolds number, drag coefficient, and Nusselt number for a single particle as a function of time. An option in the program would provide computer-generated graphs of distance, velocity, and temperature as functions of time.
Details of the computer program are presented in Appendix II. Figures 7, 8, and 9 show results of the theoretical model as applied to several particle diameters from one to fifty microns. These show the effect of diameter upon particle motion and temperature. The primary differences due to diameter may be observed by examining the curves for one and fifty micron particles in detail.

Curves for the one micron diameter particle show it is accelerated and heated very rapidly to essentially constant velocity and temperature values behind the incident shock. Upon encountering the reflected shock wave the particle rapidly decelerates to rest and experiences a further rise in temperature. The graph of distance which the particle travels shows that it comes to rest prior to traveling the complete twenty-seven centimeter length of the test section. Results of the calculation performed for a fifty micron diameter particle are quite different. The large particle still experiences heating and acceleration due to the incident shock but as expected at a more gradual rate than for the small particle. No steady values are achieved for either variable and the process continues through the reflected wave. The large particle travels the full length of the test section. Further discussion concerning use of the particle analysis program is contained in Section IV.
Test Section Length = 27. CM.

Figure 7. Particle Distance Prediction
Gas Velocity Behind Incident Shock = 95.176 (CM/SEC)

**Figure 0. Particle Velocity Prediction**
Figure 9. Particle Temperature Prediction
Shock Tube Performance Analysis

Analytical predictions of the test conditions produced by the shock tube were necessary for both test data reduction and particle analysis.

A computer program written for this purpose allowed calculation of the gas velocity, temperature, pressure, composition, and transport properties behind the incident and reflected shock. The program required initial values of gas pressure, temperature, and composition in the driven tube, and the shock wave velocity, which was obtained by measuring the time required by the wave to traverse a fixed distance between two pressure transducers. All calculations were based on the assumption of equilibrium flow. The computation involved the technique of iterative solution of the Rankine-Hugoniot equation by finding the proper pressure and temperature values.

In the calculation of changes across the incident shock, first a set of pressure and temperature values were determined which satisfied the Hugoniot. These were then used to calculate an incident shock speed. The calculated speed was compared with the measured one and the process repeated until agreement between the values was obtained.

A similar procedure was followed in the calculation of changes across the reflected shock. After a set of pressure and temperature values were obtained which satisfied
the Hugoniot, these were used for calculation of the gas speed behind the incident shock. The speed value was compared with that from the incident shock calculation. The process was repeated if necessary until agreement was obtained.

All of the iterative calculations were repeated until the change between two consecutive values or the agreement between two values was within 0.1%. All thermodynamic values were taken from the JANAF tables, reference [8], with linear interpolation used between tabulated values. Details of the computer program used in the shock tube analysis are presented in Appendix II.

Figures 10 and 11 show both theoretical and experimental values of pressure ratio across the incident and reflected shock respectively as a function of shock Mach number. The figures are constructed from data of the experiments using a 20% oxygen-80% argon test gas mixture. The data covers a range of $P_1$ values but only one $T_1$ value, 300°C/K. The pressure measurement technique is presented in Section III.

Two theoretical results are presented: first, the results of the previously described computer program using shock relations for gas only; second, results of a study to include the effects of the powder sample cooling of the test gas.
Figure 10. Pressure Ratio Across Incident Shock

(20% O₂ - 80% Argon)
Figure 11. Pressure Ratio Across Reflected Shock

(20% O₂ - 80% Argon)
The effect of the sample cooling was analyzed by assuming a one-dimensional heat removal from a supersonic gas stream in a constant area duct. This effect produces a slight increase in the gas velocity and decrease in pressure. In order to determine the heat sink of the powder sample, the length of the particle cloud was first estimated at the time of the pressure reading behind the incident shock. Assuming the particle cloud extended from the position a one micron particle would reach at this time, back to the knife edge on which the sample originally rested, the ratio of the mass of test gas to particle sample was calculated by:

\[
\frac{M_g}{M_p} = \frac{\pi d^2 \rho_c L_c}{4 M_p} \tag{20}
\]

\(d\) = Shock tube diameter

\(L_c\) = Length of particle cloud

\(M_g\) = Mass of gas

\(M_p\) = Mass of powder sample

\(\rho_c\) = Gas density

Using this mass ratio a mixture temperature was then calculated by:

\[
T_{mix} = \left( \frac{M_g \rho_c}{M_p \rho_g} \right) T_2 + 300 \tag{21}
\]

This temperature represents the equilibrium temperature which would be attained by mixing a hot gas at \(T_2\) with a powder sample initially at 300°K. The resulting specific
heat of the mixture was then calculated by:

\[ C_{p_{\text{mix}}} = \left( \frac{M_g/M_p}{1 + M_g/M_p} \right) C_{p_g} + \left( \frac{1}{1 + M_g/M_p} \right) C_{p_g} \]  \hspace{1cm} (22)

Two basic assumptions are inherent in these three equations:

(1) A uniform gas-particle mixture is established in the cloud.

(2) The entire sample mass enters into the cooling process.

Using these values for the specific heat and temperature of the gas-particle mixture, the pressure of the mixture was determined through use of the following set of equations:

\[ \beta \gamma_2 = \rho_{\text{mix}} V_{\text{mix}} = \text{constant} \]  \hspace{1cm} (23)

\[ \beta + \beta \gamma_2^2 = \rho_{\text{mix}} \gamma V_{\text{mix}}^2 = \text{constant} \]  \hspace{1cm} (24)

\[ C_{p_2} T_2 + \frac{V_2^2}{2} = C_{p_{\text{mix}}} T_{\text{mix}} + \frac{V_{\text{mix}}^2}{2} = \text{constant} \]  \hspace{1cm} (25)

All conditions subscripted 2 are gas properties resulting from the shock tube calculations previously discussed. This analysis gave gas-particle mixture temperatures typically 3% lower than the gas temperature for a 10 milligram sample and 26% lower for a 100 milligram sample. In all cases the mixture velocity was within 10% of the corresponding gas velocity. The resulting theoretical pressure ratio across the incident shock is shown in Figure 10.

It may be seen in Figure 10 that this calculation technique yields theoretical pressure ratios across the incident
shock within 10%, compared to 20% for the gas only calculation, of the experimental values except in the case of the 100 milligram samples. Two reasons are offered for the existing deviation between theoretical and experimental pressure ratios. First, in the experiments using 10 milligram samples the length of particle-gas mixing may be smaller than assumed. This would result in a high particle to gas ratio within the cloud and slightly lower mixture temperatures. Second, in the case of the 100 milligram samples the mass of the powder entering into the gas cooling process may be smaller than the actual sample mass. Particle heating calculations previously discussed show that particles whose diameter is in excess of 10 microns will not heat appreciably in the test time of the experiments. Later experiments, described in Section III, show that approximately 20% of a sample's mass is contained in particles exceeding 10 microns. Thus a reduction in the sample mass involved in cooling the test gas will produce higher mixture temperatures and pressure ratios than previously calculated. This effect would be present in the smaller sample masses but to a lesser degree due to the small total mass involved.

The final item shown in Figure 10 is the vertical bars indicating the maximum error in the pressure measurement. This was a constant ± 2.6 psia rather than a percentage
of the absolute pressure value. Thus the error is larger for some points than others.

Figure 11 shows the experimental and theoretical pressure ratios across the reflected shock. Theoretical results from both the gas and gas-particle mixture analyses using the previously discussed techniques are presented. Again the agreement between theory and experiment is improved by accounting for powder sample cooling of the test gas. Generally, the pressure measurements from the side wall transducer are lower than those taken at the end wall of the shock tube. (This includes the ten and fifty percent oxygen in argon mixtures not shown on Figure 11). This indicates the gas cooling by the powder sample is a localized process and does not effect regions outside of the cloud. It also supports the particle motion analysis which predicted the small particles would stop prior to reaching the end wall of the tube after passing through the reflected shock. No range of error in the experimental pressure measurement is shown on Figure 11 since the possible error range was very small in companion to the magnitude of the reflected shock pressure.
III

EXPERIMENTAL PROGRAM

The main objective of the experimental program was to investigate the effects of both gas and particle properties upon the ignition delay time for boron powder. A secondary objective was the measurement of particle cloud position to verify the theoretical model for particle motion. All experiments were conducted in a shock tube. Pressure and light emission were measured to determine shock tube performance and ignition delay. The particle cloud position was determined from pictures taken by means of a laser holographic technique. An analysis of the size and geometry of the particles in the test samples was obtained from scanning electron microscope pictures and floatation tests.

Apparatus

The shock tube used in these experiments is described in detail in references (10), (20), and (24). Briefly, it consists of three stainless steel sections of constant two inch internal diameter with driver tube, driven tube, and test section of 300, 240, and 22 inches in length, respectively. The test section contains two rectangular quartz windows of approximately eight inches by one-fourth inch,
three pressure transducers, and a particle support. The particle support consists of a thin knife edge brazed to a stainless steel sleeve with the sleeve arranged so that its inside diameter is flush with that of the shock tube. The knife edge is fixed in a horizontal position on the centerline and extends across the width of the shock tube. Boron powder samples were placed on the knife edge, swept off by the gas flow behind the incident shock and ignited behind the reflected shock as shown schematically in Figure 4. Details of the test section are shown in Figure 12 and instrumentation locations.

**Instrumentation**

Instrumentation and support equipment used to monitor the shock tube performance and obtain the experimental data are shown in Figure 13.

Shock tube performance was obtained as a result of the shock velocity and pressure measurements. The transducers in the side and end walls of the test section were used for this purpose. A transducer upstream of the test section triggered the sweep of the oscilloscope displaying the transducers' output which was then photographically recorded.

The transducer mounted in the side wall measured the pressure behind both the incident and reflected shock. It also starts a microsecond time counter. The end wall transducer measures pressure behind the reflected shock and stops the microsecond counter.
**Figure 12. Test Section Schematic**

**TRANSUCERS**

$X_{D1}$ - Trigger Transducer, Kistler 603A

$X_{D2}$ - Side Wall Transducer, Kistler 601L

$X_{D3}$ - End Wall Transducer, Kistler 603A
In both the ignition delay and particle cloud position experiments, light emission was used to indicate particle ignition. During the ignition delay experiments both total light and monochromatic emission were monitored. The total light emission was monitored by recording the output from a light sensitive diode. For the second method, the light from the test section was passed through a monochromator set at 5470 Å. Selection of this wavelength of emission from the NO species was based upon the work of references (9) and (19) as discussed in Section I. The output from a photomultiplier tube connected to the monochromator was then recorded. Display and recording procedures for these signals were the same as that of the pressure traces but on a second oscilloscope. Both of these oscilloscopes were triggered at the same time by the transducer upstream of the test section.

The technique to determine the pressure and speed of the shock wave was unchanged in the cloud position experiments. The light emission from both the laser and the particle combustion was monitored by the photodiode. The oscilloscope used to record the light emission was triggered by a delayed output signal from the oscilloscope recording the pressures.
Figure 13. Shock Tube Instrumentation and Support Equipment

Ignition Delay Tests
Summary of Experiments for Determination of Ignition Delay

The objective of the experiments was to determine the effects of particle diameter, particle concentration, gas temperature, gas pressure, and oxidizer concentration on the ignition delay. In order to determine the effect of these parameters, a set of basic test conditions were selected and each parameter individually varied to observe any effect.

Base values for the test variables were:

1. Gas temperature - 3000°K
2. Gas pressure - 150 psia
3. Gas composition - 10% O₂, 90% A by volume
4. Sifted particle diameter range - 74-88 micron
5. Sample mass - 10 mg

The sifted particle diameter range was obtained by using powder which passed through an 88 micron but would not pass through a 74 micron sieve. These large particles were later shown to be agglomerates of smaller particles of nominally one micron diameter. Helium was used as the driver gas in all tests. Values of the test variables, ignition delay times, and calculated particle ignition temperatures are summarized in Table 7. The P₅ value was that measured by the end wall pressure transducer and T₅ from the calculated shocked gas temperature rather than the cooler particle-gas mixture temperature. Pressure and time measurement reading accuracy of oscilloscope traces were ±2.6 psia and ±5.5 microseconds. Powder sample mass...
<table>
<thead>
<tr>
<th>Test No.</th>
<th>Oxygen % by Volume in O2/A Mixture</th>
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<th>Sifted Diameter Range of Boron Particles (micron)</th>
<th>P5 (psia)</th>
<th>T5 (°K)</th>
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<th>Sifted Diameter Range of Boron Particles (micron)</th>
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<th>T₅ (°K)</th>
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<th>Ignition Temperature d = 1 micron P (°K)</th>
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<td>44</td>
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*Powder not sifted*
Figure 14. Typical Data Traces of Ignition Delay Experiments
measurement accuracy was ±0.1 milligram. Typical data recordings from the ignition delay experiments are shown in Figure 1.4.

Cloud Position Measurements

An accurate prediction of the position of a particle within the shock tube as a function of time was necessary in determining the ignition delay. Analysis of data from a previous experiment, reference (20), has shown that under non-burning conditions the cloud leading edge motion agrees well with the single particle prediction using the theory presented in Section II. This is shown in Figure 15. The object of the present study was to determine if similar agreement of experiment and theory would be attained under test conditions sufficient for combustion.

The data recording technique of the non-burning experiments using a Polaroid camera was not suitable for tests involving combustion. An attempt was made to obtain high speed motion pictures of the cloud motion with a Beckman-Whitley Dynafax camera. However, a successful combination of the light source, film type and framing rate was not achieved. A laser holographic system, designed and operated by personnel of TRW Systems Division, Los Angeles, appeared to meet the objective of recording the location of the particle cloud without overexposure by the combustion flash. Reconstruction and photography of the holograms was done by this author.
A method used for recording cloud position by a light scattering holographic technique is described in reference (16). The light source was a ruby laser with a pulse duration of approximately 50 nanoseconds. Figure 16 is a schematic of the experimental system. Holograms were reconstructed with a helium-neon laser and photographed. Next, the cloud position was determined from these photographs. The position of the head of the cloud of powder was considered to be that point where the laser light was completely obscured.

Figure 17 is an example of a photograph prepared from a reconstructed hologram. It shows the end of the test section viewing window, a rectangular reference target, and one tooth of a reference rake which extended the length of the window. Light is cut off at the left side of the photograph by the powder cloud.

Table 8 lists values of the measured cloud leading edge position and predicted single particle location at the time the hologram was made. Theoretical values are listed for both a one micron and 2.5 micron diameter particle using the previously discussed position, velocity, and drag relationships. In all but one case the experimental position was less than the theoretical value. The good agreement shown may only exist because small particles are accelerated rapidly to the gas velocity \( U_2 \) but the comparison does not allow one to verify the accuracy of the theory.
Figure 15. Particle Path in Shock Tube
Figure 16. Shock Tube Instrumentation and Laser System
<table>
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<tr>
<th>Laser Test Number</th>
<th>Shock Mach Number</th>
<th>$p_5$ (psia)</th>
<th>$T_5$ ($^\circ$K)</th>
<th>Mass of Boron Powder Sample (mg)</th>
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<th>Test Number</th>
<th>Theoretical Particle Location (cm)</th>
<th>Cloud Leading Edge Measurement (cm)</th>
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<td>6</td>
<td>$24.2$</td>
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Figure 17. Photograph of Reconstructed Hologram
In test number one of Table 8, the particle cloud was moving behind the incident shock wave at the time the hologram was taken. All remaining holograms were taken after the particle cloud has passed through the reflected shock and decelerated to rest. Distances shown in Table 8 were measured from the knife edge upon which the boron powder sample was initially placed. All distance measurements are estimated to be accurate to within ±0.5 centimeter.

Electron Microscope Particle Measurements

In formulating the theoretical model of particle motion and heating, discussed in Section II, this author had assumed particles to be spherical. It was thus desired to determine the validity of this assumption. The second objective of the electron microscope pictures was to determine the sizes of the particles used in the experiments. Although the manufacturer of the boron powder reported the primary size to be one micron, particle diameters smaller than thirty microns had not been successfully separated. Thus it was necessary to determine which of two possible geometric situations existed:

(1) the large particles were agglomerates of small particles, or

(2) the sample consisted of single large particles whose surface was covered with small particles.
To answer these questions, pictures of powder samples were taken through a scanning electron microscope (SEM) by personnel of the Air Force Materials Laboratory. Two powder samples were taken for analysis, one sifted in the 74-88 micron diameter range and one unsifted. In preparing the sample of unsifted powder, very large particles were removed to obtain a more uniform sample. Pictures were taken at magnifications of 51, 204, 2040, and 10,200.

Photographs show the majority of particles in both samples to be spherical in nature and have a rough surface. Particles in the sifted sample were less regular in shape than those of the unsifted sample. At highest magnification, the surface of the large particles was shown to consist of small spherical particles nominally of one micron diameter. Photographs of a sample at two magnifications are shown in Figure 18. Table 9 contains particle size data obtained from the photographs.

<table>
<thead>
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<td>PARTICLE SIZE MEASUREMENTS</td>
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<table>
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<th>Sample</th>
<th>Average Large Particle Diameter (microns)</th>
<th>Small Particle Diameter (microns)</th>
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<td>Unsifted</td>
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<td>.76 → 1.5</td>
</tr>
<tr>
<td>Sifted</td>
<td>35</td>
<td>.53 → 2.3</td>
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Figure 18. Scanning Electron Microscope Photographs of Powder Samples
Particle Floatation Tests

To aid in more fully understanding the size and mass distribution of particles within a sample, floatation tests were conducted by personnel of the Aerospace Research Laboratories which gave both size and mass distribution. Figure 19 shows results of this test. It shows the percent of a sample's mass which is contained in particles less than or equal to the diameters shown. For example, 80% of the sample's mass is contained in particles of less than 10 microns diameter. The median diameter was 1.7 microns with one-half the mass in particles less than and one-half in those greater than this diameter. Further tests show the most frequently occurring diameter to be one micron. This test gave equivalent spherical diameters where the SEM photographs gave more quantitative information on the particle shapes.

Results of this test show the reason that assuming all the 100 milligram mass sample to enter into gas cooling, produced too low a mixture temperature. A better assumption in the cooling calculation would appear to be 75-80% of the total sample mass. The resulting mass distribution also supports the assumption of the data to be representative of nominally one micron diameter particles.
Figure 19, Mass Distribution in Test Sample

Median Diameter = 1.7 microns

75% Mass in particles less than 4.3 microns
IV
DISCUSSION

Results of Present Experiments

Results of the scanning electron microscope photographs and floatation experiments have shown a typical powder sample's mass to be carried in particles of less than 55 microns with the dominant diameter being one micron. Position measurements of the cloud's leading edge have been in good agreement with the single particle predictions, using the theory presented in Section II, for the one micron diameter over a wide range of test condition.

The largest particle diameter evident in the floatation tests was smaller than those possible to separate by sifting. Therefore the particles in a powder sample were assumed to be agglomerated prior to a test and separated into the smaller sizes during cloud formation. It is not known if the agglomeration of the smaller particles is a mechanical or electrostatic process. Separation of the smaller particles may occur through a combination of inter-particle collisions and shearing by the high velocity test gas and during acceleration. A size distribution of particles would be expected within the cloud with the leading edge containing the smallest, nominally one micron diameter.
particles. Some discrepancy has existed between the cloud leading edge position measurements and single particle position predictions. These may be attributed to:

1. A time requirement for breakup of large particles into the smaller ones.
2. Deviation from the assumed spherical shape, i.e. angularity of the particle affecting the particle's drag coefficient.
3. A possible slip velocity existing between the gas and a one micron diameter particle.

The first two reasons are based upon the results of the scanning electron microscope and floatation experiments, the last requires further discussion.

The Knudsen number is defined as the ratio of the mean free path of the gas to a characteristic body dimension. In reference (23), the region of gas flow with Knudsen number less than 0.01 is defined as continuum and from 0.01 to 1.0 as slip flow. The theoretical development for particle motion presented in Section II was based on continuum assumptions. However, the Knudsen number for a one micron particle using the actual test conditions in the incident shock region were the order of 0.1 and reflected region 0.01. These values of Knudsen number would place the tests at the beginning of slip flow. The effect of slip at the particle's surface is to reduce both drag and heat transfer coefficients below their continuum values.
By reducing the particle's drag coefficient the experimentally measured locations for a particle would be less than the theoretical values at the same time. However, the effect of particle surface roughness would be to increase its drag and the experimentally measured positions would be greater than the theoretical values. It does not appear possible to determine theoretically the quantitative effects of slip and roughness upon the particle's drag. The net effect of these two was a decrease in the value of the drag resulting in the cloud leading edge lagging the theoretical single particle position in the incident shock region and leading it in the reflected region.

Theoretical position description for a one micron particle was within 10% of the cloud leading edge measurement. Differences in theoretical position due to the primary particle diameter range were about 3.5%. Therefore the analysis using the one micron particle prediction was used for describing the cloud leading edge position.

The ignition delay time data were obtained by subtracting the single particle residence time in the incident shock region from the total time in both the incident and reflected shock regions prior to ignition as determined from the light emission recordings.

Ignition delay data obtained from the shock tube experiments are presented in Figure 20 as functions of both
gas temperature and oxidizer partial pressure. Values of temperature and pressure shown are all for the reflected region of the shock tube. The ignition delay time was found to vary inversely with both the gas temperature and oxidizer partial pressure. Curves shown represent a best fit through a band of data covering each range of partial pressure. This variation was approximately:

\[ \Delta t \propto T_g^{-3.77} P_2^{-0.28} \]  

There were neither any noticeable effects upon ignition delay of particle concentration, due to sample mass variations, nor any correlation of total pressure alone.

The lack of any effects due to sample mass variation may be attributed to the cloud structure and ignition process. As previously discussed, the acceleration of the particles from the knife edge leads to the formation of a cloud in which the particles will be separated by size. The leading edge of the cloud consists of the smallest, nominally one micron diameter particles. It is this leading edge which will first encounter the reflected shock and the conditions behind it which are sufficient to ignite the particles. Besides encountering the reflected shock first, the small particles will heat to ignition faster than the larger ones found farther back in the cloud. It is thus the particles at the leading edge of the cloud which ignite first and whose ignition is indicated by the light emission recordings. The ignition
Figure 20. Boron Particle Ignition Delay Time, Shock Tube Measurements

\[ (\text{Gas Temperature})^{-1} (\text{oK} \times 10^{-4})^{-1} \]
process would then continue through the cloud as the larger particles are heated to ignition. However in the experiments using the larger, 100 milligram, samples not all the powder was ignited and burned. Post test inspection of the residue within the test section of the shock tube showed some of the original black powder mixed with the white oxide powder. The temperature of the shock heated gas was used for correlation of the ignition delay time rather than the mixed gas-particle temperature discussed in Section II. This was selected since ignition proceeded from the cloud's leading edge where any cooling of the test gas by the powder sample would be slight.

The lack of a mass effect also suggests single particle ignition rather than a cloud effect upon particle heating. It appears reasonable to assume that the leading edge particle density will vary with the total sample mass. The primary effect of the cloud upon the particle heating would be to suppress the particle's cooling by radiation. In the single particle analysis presented in Section II, it was assumed that a particle was free to radiate to a cold wall, 300°K. A particle within a cloud would be radiating to others of the same temperature and would receive as much energy as it would lose. This assumes the surrounding particles to be all approximately the same size.
To investigate this effect, two calculations were performed for a one and a five micron diameter particle. In the first calculation the particle was free to cool by radiation and the second no radiation was included. Both radiation calculations used an emissivity of 0.5. In the calculations for both diameters, the final particle temperatures with radiation were within 0.5% of those without radiation. The effect of radiation was slightly greater for the larger diameter particle. Thus in this diameter size it may be assumed that the particles ignite singly and inter-particle radiation will have little effect upon the particle's temperature history.

The trends in the shock tube ignition delay data due to gas temperature and oxidizer pressure variations were as expected for the surface process ignition theory of metals discussed in Section I. Increases in gas temperature and oxidizer pressure would contribute to increased particle heating by convection and chemical reaction respectively. Also the ignition model presented in reference (5) predicts a slight decrease in ignition temperature with increasing oxidizer pressure.

Particle Ignition Process

The effect of particle diameter upon ignition delay may be determined by correlation of the shock tube data from a previous investigation, reference (13). A diameter effect
may be explained by the ignition theory of metals described in Section I and will be useful in understanding the ignition process. Figure 21 shows the ignition delay time determined from the data of reference (13) for particles averaging 34.5 and 44.2 microns diameter. Ignition delay time was defined to be the interval from the time a particle attained a temperature equal to the ignition limit temperature (dependent upon the oxygen partial pressure) to the time ignition was observed. This assumes the critical temperature for the particle to be very close to the ignition limit temperature of the gas. The relationship between gas and particle temperature will be more fully discussed later.

Ignition limit temperatures in reference (13) were found to be approximately 50°K higher than those shown in Figure 5 for the one micron diameter particle. Data from the two average particle diameters produced separate delay time curves. Pressure effects in the data were not apparent, however tests were only conducted over a narrow range of oxidizer partial pressures. A curve is included in Figure 21 from the shock tube data at the lowest oxygen partial pressure. Approximately an order of magnitude decrease in ignition delay time was evident with the reduction in average particle diameter shown. This variation was approximately:

\[ \Delta t \propto d_p^{60} \]  

(27)
Figure 21. Boron Particle Ignition Delay Time, Diameter Effect
A variation of ignition delay time with particle diameter may be explained by the theory of metal ignition presented in Section I. In the model, particle ignition may be controlled by either the critical or transition temperature. The distinction between these is discussed in detail in Section I. A critical temperature controlled metal would show a decrease in both critical and ignition temperature with a decrease in particle diameter. A transition temperature controlled metal would show no changes with diameter. Also as particle diameter decreases the ratio of surface area to volume will increase. This area to volume increase will result in an increased heating rate to the particle and produce a decrease in ignition delay time. Therefore, boron particle ignition is identified as being critical temperature rather than transition temperature controlled. Further reductions in diameter may be expected to produce proportional reduction in ignition delay time.

Particle Temperature Study

An analytical study of a particle's temperature history in the shock tube experiments was conducted using the theory discussed in Section II. The calculations were
for a one micron diameter particle. There were three objectives of the study:

(1) To verify that the shock tube properly produces conditions for the study of ignition delay.

(2) To verify that the proposed heating model for a particle was consistent with experimental observations.

(3) To determine the particle temperature at ignition and compare with the theoretical prediction of 2350°K, reference (5).

(4) To determine the effect of primary particle diameter range upon ignition temperature.

The conditions which must be produced for measurement of ignition delay are rapid attainment of the ignition temperature with little chemical reaction occurring as the temperature is increased. In order to evaluate these conditions, Figure 22 was prepared from the computer program results for particle temperature. Test conditions from experiment twelve were used. The resulting curve is typical in shape for all three gas compositions and range of experimental temperatures at the lower gas pressures. The relative magnitude of the shock and chemical heating rates in the incident and reflected shock regions are shown in Table 10.
TABLE 10.

SHOCK AND CHEMICAL HEATING RATES

<table>
<thead>
<tr>
<th></th>
<th>Incident Region (°K/Microsecond)</th>
<th>Reflected Region (°K/Microsecond)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shock</td>
<td>63.</td>
<td>117.5</td>
</tr>
<tr>
<td>Chemical</td>
<td>0.68</td>
<td>2.46</td>
</tr>
</tbody>
</table>

The heating rate values were calculated from the slope of portions of the temperature history curve for experiment twelve in Figure 22. Shock heating rates represent the slope of the temperature curve where the particle was accelerating or decelerating behind the incident and reflected shocks respectively. After the particle speed has stopped changing, the slope of the temperature curve changes significantly. These portions were used to calculate the chemical heating rates. The shock and chemical heating periods refer to the primary heat sources during each one. In the case of shock heating, the large velocity and temperature differences between the gas and particle result in high convective heating rates. The chemical heating period that follows the rapid acceleration or deceleration and heating is a result of chemical reaction at the particle's surface.

To meet the ignition delay criteria for the particle, very little chemical reaction may occur behind the incident
shock and the temperature rise must be rapid behind the reflected shock. From Figure 22 and Table 10 it may be seen that shock heating rates are much greater than chemical heating rates and shock heating time very short in comparison to residence time. Very little chemical heating occurs behind the incident shock. Heating of the particle to ignition behind the reflected shock occurs in approximately 7.5 microseconds. This is an order of magnitude shorter time than the resulting ignition delay. Particle temperature was also less than ignition limit temperature in the incident shock region. This is consistent with experimental observation in that no emission from the particle-gas mixture was detected prior to contact with the reflected shock. Thus it was concluded that under this type of test condition, the shock tube properly produces particle heating conditions for study of ignition delay. Also, the analytical model was consistent with experimental observation, although particle ignition temperature was higher than anticipated.

The second curve on Figure 22 shows the results of particle heating analysis for experiment number twenty, a high pressure operating condition. Chemical heating behind the incident shock predicted by the analytical model was of a magnitude which would violate the conditions for ignition delay measurement. In the incident shock region the
particle temperature was also predicted to significantly exceed the ignition limit, leading to ignition behind the incident shock. These results of particle temperature prediction were not consistent with experimental observation.

Based upon these observations, it appeared that the activation energy of 3.972 kcal/mole may be too low. A value of 20.3 kcal/mole was then calculated from the slope of the ignition delay time curves in Figure 20. The large difference in this and the previous value may result from the two representing different processes. Data from particle burning time experiments rather than ignition delay data was used to calculate the previous value of 3.972 kcal/mole. The effect of using this activation energy in the particle temperature calculation is shown in Figure 23.

In Figure 23 curve number one is the result of the calculation using the original activation energy and number two the result with the increased activation energy. The latter curve shows a reduction of chemical heating in the incident shock region to a level similar to the result for lower pressure conditions. Particle temperature in the incident region also remains below the ignition limit temperature in the incident region. Results of the particle temperature calculation with the higher activation are thus consistent with requirements for ignition delay measurement and experimental observations.
Figure 22. Particle Temperature History

\( d_0 = 1.0 \text{ (micron)} \)
Particle Temperature History

- Particle Hit by Reflected Shock
- Particle Peaches Gas Speed

<table>
<thead>
<tr>
<th></th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_2(\text{K})$</td>
<td>1568</td>
<td>1568</td>
<td>1410</td>
</tr>
<tr>
<td>$T_5(\text{K})$</td>
<td>2888</td>
<td>2888</td>
<td>2600</td>
</tr>
<tr>
<td>$E_A (\text{kcal/mole})$</td>
<td>3.972</td>
<td>20.344</td>
<td>20.344</td>
</tr>
</tbody>
</table>

Figure 23. Particle Temperature History
Test Number 22.
A second possible method of altering the particle heating calculation such that the temperature history corresponds to experimental observation would result from a variation in surface process. A surface process was assumed to be represented by the global reaction:

$$B(s) + O_2 \rightarrow BO_2$$  \hspace{1cm} (28)

The heat of reaction for this process was reduced from the value of the previous reaction, shown in equation (16), by the heat of vaporization of boron. The expression used to account for cooling of the particle due to vaporization, equation (15), was dropped from the particle heating calculation. Results of the calculation are shown in Table 11.

The resulting shape of the particle temperature history curve in all cases was similar to that of experiment 12 in Figure 22. Thus the chemical heating portion of the temperature history curve of experiment 20 was reduced in the same manner as using a higher activation energy.

Particle ignition temperature was reduced in the first four cases, consisting of ten and twenty percent oxygen mixtures, to values close to those obtained using the high activation energy. However, in the case of fifty percent oxygen mixture the results were different. In experiment 22, the ignition temperature was reduced by only half the amount as for the high activation energy. A higher ignition temperature was calculated in experiment 20 than for the original conditions.
The high ignition temperature calculated in the fifty percent oxygen cases leads to the conclusion that the high activation energy is a better modification to the original analysis than the reduced heat of reaction.

The last curve on Figure 23 is the result of the calculation in which an attempt was made to evaluate the effect of slip on particle temperature. The effect of slip would be to reduce the heat transfer coefficient between the gas and particle. Previously particle motion analysis gave an estimate of 5-10% reduction in drag part of which may be attributed to slip. To estimate the slip effect on particle temperature, the gas temperature was reduced by 10% in both the incident and reflected regions. As shown in Figure 23 the result of gas temperature reduction was an approximate 10% reduction in particle temperature due to shock heating. No significant effect upon the shape of the portion of the particle temperature curve due to chemical heating was evident. The following table presents a summary of results from the particle ignition temperature study for the three types of analysis. Test numbers correspond to those shown in Table 7 of Section II in which the details of the tests are shown.
### TABLE 11.

PARTICLE IGNITION TEMPERATURE

<table>
<thead>
<tr>
<th>Test Number</th>
<th>Original Conditions (°K)</th>
<th>High Activation Energy (°K)</th>
<th>Reduced Heat of Reaction (°K)</th>
<th>Reduced Gas Temperature (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>3393</td>
<td>2882</td>
<td>2734</td>
<td>2499</td>
</tr>
<tr>
<td>7</td>
<td>3180</td>
<td>2915</td>
<td>2759</td>
<td>2657</td>
</tr>
<tr>
<td>11</td>
<td>3451</td>
<td>2716</td>
<td>2781</td>
<td>2526</td>
</tr>
<tr>
<td>12</td>
<td>3354</td>
<td>2582</td>
<td>2618</td>
<td>2416</td>
</tr>
<tr>
<td>20</td>
<td>3829</td>
<td>2657</td>
<td>4336</td>
<td>2493</td>
</tr>
<tr>
<td>22</td>
<td>3635</td>
<td>2637</td>
<td>3144</td>
<td>2450</td>
</tr>
</tbody>
</table>

All four methods of calculating particle temperature gave ignition temperatures higher than predicted by the theory of Glassman, reference (5). Ignition temperature was predicted to be the oxide boiling temperature, 2350°K, by this theory. One reason for the higher temperatures was probably the high environmental gas temperature. However, the ignition temperatures given in the last two columns of Table 11, which are felt to be more realistic than in the first column, are closer to the oxide boiling point than the metal boiling point as predicted in reference (18).
The final portion of the particle temperature study was to determine the effect of primary particle diameter upon the calculated particle ignition temperature. Particle temperature histories were calculated for diameters of 0.5 and 2.5 microns, corresponding to the range determined from the SEM photographs. These were conducted for the same experiments as shown in Table 11, using both the original and higher values of activation energy. Results of the study are shown in Table 12. An average ignition temperature range due to the particle diameter of approximately 160°K was calculated for the original conditions and 240°K using the higher activation energy value.

### TABLE 12.

DIAMETER EFFECT UPON PARTICLE IGNITION TEMPERATURE

<table>
<thead>
<tr>
<th>Test Number</th>
<th>Original Conditions (°K)</th>
<th></th>
<th>Higher Activation Energy (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d_p = 0.5</td>
<td>2.5</td>
<td>0.5</td>
<td>2.5</td>
</tr>
<tr>
<td>6</td>
<td>3244</td>
<td>3362</td>
<td>2895</td>
</tr>
<tr>
<td>7</td>
<td>2916</td>
<td>3021</td>
<td>2739</td>
</tr>
<tr>
<td>11</td>
<td>3251</td>
<td>3526</td>
<td>3680</td>
</tr>
<tr>
<td>12</td>
<td>3051</td>
<td>3487</td>
<td>2465</td>
</tr>
<tr>
<td>20</td>
<td>3791</td>
<td>3882</td>
<td>2641</td>
</tr>
<tr>
<td>22</td>
<td>3513</td>
<td>3710</td>
<td>2524</td>
</tr>
</tbody>
</table>
Results of the particle temperature study lead to the conclusion that the calculated particle ignition temperatures are only accurate within ± 20%.

Representative shock tube experiments, 50% oxygen - 50% argon mixtures, were examined to determine if any significant vibrational relaxation time existed during the ignition delay period. The vibrational relaxation time was calculated by:

$$\frac{1}{T_v} = 1.2 \times 10^{-7} n_{AR} T_g^{4/5} \left[ 1 - \exp \left( \frac{-2.278}{T_g} \right) \exp \left( \frac{-1.04 \times 10^7}{T_g} \right) \right] \text{ (sec)}^{-1} \quad (29)$$

taken from reference (25). The results are shown in Table 13. In all cases the vibrational relaxation time was significantly less than the ignition delay time. Vibrational non-equilibrium was concluded to be of no problem in the experiments.

**TABLE 13.**

<table>
<thead>
<tr>
<th>Test No.</th>
<th>P_0 (psia)</th>
<th>T_0 (°F)</th>
<th>T_V (Microsec)</th>
<th>t (Microsec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>324</td>
<td>2888</td>
<td>0.71</td>
<td>50</td>
</tr>
<tr>
<td>22</td>
<td>153</td>
<td>2785</td>
<td>1.76</td>
<td>65</td>
</tr>
<tr>
<td>26</td>
<td>305</td>
<td>3146</td>
<td>0.52</td>
<td>32</td>
</tr>
</tbody>
</table>
Application to Combustor Design

In Section I, the heat-up and burning times for a one micron diameter boron particle were estimated to be on the order of twenty and ten microseconds respectively. The calculated particle heating rates for the shock tube test conditions were typically 100°C/microsecond. This rate results in heat-up times on the order of fourteen to nineteen microseconds, consistent with the magnitude of the original estimate. No burning rate data for small boron particles are available at high oxygen pressures. However, the original estimate of ten microseconds is felt to be a reasonable upper value for the burning time with burning times being in the one to ten microsecond range.

Results of the present study show that a trade-off between particle diameter, gas pressure, and gas temperature is possible to produce a range in ignition delay time. However, attainment of ignition delay time for a one micron particle on the same order of magnitude as the heat-up and burning time would require severe combustor operating requirements. At conditions other than high oxygen pressure and gas temperature, ignition delay time would be the longest part of the particle history in the combustion process of the one micron particle. Ignition delay would be an order of magnitude longer than either the heat-up or burning time. The very high oxygen pressure conditions
are not consistent with airbreathing combustor operation. Therefore, the combustion of particulate boron may be accomplished within reasonable lengths, less than one foot, under low pressures if gas temperature and particle diameter are kept at the proper limits.
CONCLUSIONS AND RECOMMENDATIONS

The results of this study have led to several conclusions regarding both the shock tube technique for the measurement of metal particle ignition delay and ignition of particulate boron.

It is possible to separate the heat-up from ignition delay time for a particle by use of the shock tube technique. However the technique properly meets the criteria for ignition delay study only for particles of nominally one micron diameter or less. The results apply only when the gas density is high since it has been assumed that continuum theory may be used. The shock tube technique produces data which apply to individual particles and not only to the whole cloud of particles.

Ignition of boron was found to occur at the surface, rather than in the gas phase. The observed characteristics of the ignition may be qualitatively explained by a heterogeneous process ignition theory. The ignition process was shown to be controlled by the particle's critical temperature. Thus both the temperature from which a particle may self-heat to ignition (the definition of critical temperature) and particle ignition temperature are directly proportional
to particle diameter. Although particle temperature at ignition was not quantitatively measured, it appears from analysis to be closer to the oxide boiling point than the metal boiling point. It was also concluded that oxidizer pressure rather than gas total pressure affects particle ignition. Thus past data showing anomalies of pressure effects upon ignition should be re-examined.

As a result of this study it is now possible to make quantitative prediction of ignition delay time for boron particles as a function of diameter, gas temperature, and oxygen partial pressure. Ignition delay time varied as:

$$\Delta t \propto \frac{d_0^{10}}{T_g^{3.77} P_o^{2.28}} \quad (30)$$

Under all but very high temperature and oxidizer pressure conditions, the ignition delay time will be the longest portion of the combustion process for a one micron particle. The activation energy previously given for boron ignition is too small. The value based on the shock tube ignition delay data is 20.34 kcal/mole which is much greater than the previous reported value of 3.972 kcal/mole.

Two conclusions were drawn concerning the use of particulate boron in airbreathing combustors. First, it is possible to ignite and burn boron particles within a short length, less than one foot, under low pressure conditions
If the particle diameter is the order of one micron and gas temperature above 2000°K. Second, it is not possible under practical combustor design limitations to reduce the ignition delay of a one micron particle to the same order of magnitude as heat-up and burning time.

There are several extensions of this work to areas of possible future research concerning both airbreathing propulsion and industrial applications. The shock tube research may be extended to include the study of effects of water vapor upon ignition of small particles. Water vapor effects upon ignition and combustion of one micron boron particles have been investigated theoretically in reference (1). It was proposed that water vapor will both lower the ignition temperature and increase the burning rate of boron. Next, shock tube experiments may be conducted in which particle temperature may be measured during the pre-ignition period and ignition temperature determined. It would be best to conduct these at gas temperatures slightly, i.e. 100°K, above the ignition limit temperature to more easily separate convective and chemical self-heating. A particle temperature measurement technique similar to that described in reference (2) may be used for this purpose.

A third possible extension of the shock tube technique is in the study of gas-particle mixtures found in industrial applications, i.e. pulverized coal gasifiers, large furnaces, and industrial stack effluents.
APPENDIX I.
SURVEY OF PREVIOUS BORON ANALYTICAL AND EXPERIMENTAL STUDIES

A number of different approaches has been used to study the ignition and combustion of boron. These may be divided into five general techniques used to heat the metal to ignition:

1. Electrical resistive heating
2. Gas burners
3. Flash tubes
4. Lasers
5. Shock tube

The experimental approach and results will be summarized for each of these techniques.
During the late 1950's, Talley, reference (22), studied the steady state oxidation of one millimeter diameter boron rods which were heated resistively. The oxidation rates were measured as a function of oxygen pressure and rod temperature (1400-2300°K). The principal observations made were:

(1) A layer of liquid oxide formed on the surface of the rod as it was heated. The thickness of this liquid layer varied inversely with temperature and directly with pressure and ranged from ten microns at 1400°K to one micron at 1900°K. The liquid phase disappeared at 2300°K.

(2) The rate of oxidation was measured by the rate of oxygen uptake and determined to depend upon temperature by an Arrhenius law with an activation energy of 77 kcal/mole.

(3) When the combustion becomes self-sustained at rod temperatures of about 2500°K, the oxidation rate is independent of pressure. At lower temperatures it is inversely proportional to the pressure.

(4) The oxidation rate increased significantly with the addition of water vapor but the activation energy decreased to 56 kcal/mole. The inverse pressure effect continued.
(5) Oxidation rates increased with increasing oxygen flow rate past the rods.

Experiments on boron particle ignition and combustion in flames of gas burners were conducted by Macek, reference (13), and Edelman, reference (4). Gas compositions were varied to give a range of temperature and free oxygen content at a pressure of one atmosphere. In Macek's experiments particles averaging 34.5 and 44.2 microns diameter were ignited in atmospheres with and without water vapor. The particle diameters in Edelman's experiments ranged from 50 to 1000 microns and all oxidizing atmospheres contained water vapor. In both experiments ignition delay was computed from the measured distance of particle travel from injection to the first appearance of luminosity. These studies lead to the following observations:

(1) Ignition delay is inversely proportional to gas temperature and oxygen and water vapor concentration.

(2) Ignition delay is directly proportional to particle diameter in the diameter range studied.

(3) The minimum gas temperature necessary for ignition is approximately 1900°K.

The use of a flash tube in the study of boron particle ignition and combustion is reported by Miller, reference (18).
In this experiment the particles are dropped through a helical discharge tube and ignited by the incident radiation from the light pulse of a capacitor discharge lamp. Xenon gas was used in the flash tube. The experimental system was designed to allow particle heating in an inert atmosphere, after which the particle fell into a secondary chamber containing a cold oxidizing atmosphere. The ignition delay was considered to be the time interval from initial exposure to the thermal source to the appearance of luminosity. Four observations were made in relation to the particle ignition:

1. Ignition time was not dependent upon particle diameter. This was a result of the radiative rather than convective particle heating.
2. The ignition time decreased with increased oxygen percentage.
3. Particle ignition temperature was determined to be about 1850°K.

Another type of radiative heating technique used in boron particle study has been the laser. Two separate experiments of this type have been conducted. The first, conducted by Macek, reference (14), involved laser heating of seventy-five micron diameter particles followed by ignition and combustion in cold oxidizing atmospheres at pressures up to thirty-five
atmospheres. These were dropped through a focused laser beam which rapidly heated the particle to approximately 2000°K. At this condition the particle would exhibit a dull glow. The ignition point was evident by transition from the dull glow to a bright flame. The principal observation in this experiment was that the ignition delay period was independent of pressure up to ten atmospheres and thereafter became longer with increased pressure. The calculated particle ignition temperature was found to decrease with increasing pressure.

The second laser heating experiment was conducted by McLain and Cotugno as reported in reference (17). The experiment consisted of igniting three different forms of sixty micron diameter particles and measuring burning times.

The three types of particles consisted of uncoated particles, those doped with lithium fluoride to remove or modify the surface coating, and particles exposed to gamma radiation from a cobalt-60 source.

In these experiments no quantitative ignition delay data were reported due to scatter. Qualitatively, the ignition delay was reduced in the case of both the lithium fluoride doped and gamma-irradiated particles in comparison to those uncoated. This may result from a partial destruction of the surface oxide coating to allow an increase transport of interior boron atoms to the surface where reaction may occur.
The shock tube has been used for study of particle cloud motion, reference (20), under non-burning conditions and to determine ignition limits (required temperature for a given pressure) of boron particles in air, references (10) and (24). The incident shock wave swept a sample of particles off a knife edge and the resulting cloud ignited in the reflected shock zone. The ignition temperature was found to decrease from 1900°C at one atmosphere, to 1400°C at twenty atmospheres and remain constant to 120 atmospheres.

An interesting observation has been reported in several experiments concerning an apparent two-stage combustion process in air and oxygen/argon mixtures. The first stage after ignition was a period of low brightness tending to decrease in intensity. This period is followed by a brighter, more intense period during which the particle is consumed.

Three analytical descriptions of varying complexity have been developed for the motion and heating of boron particles. All analyses have assumed particles to be spherical and of uniform temperature, no temperature gradient within the particles.

First, the analysis by Macek, reference (13), described a particle's position, velocity, and temperature from the time it was exposed to the hot gas source until ignition.
occurred. Drag coefficients for the spherical particles were expressed as,

1. \[ C_D = 24/R_{EY}, \text{Reynolds number } \leq 1. \]
2. \[ C_D = (100/R_{EY})^{2/3}, \text{Reynolds number } > 1. \]

Particle temperature change was assumed due to convective heating and radiative cooling but no chemical heating was included.

The second analysis, by Miller, reference (18), segmented the particle history into three periods: heat-up, ignition, and combustion. Heat-up period was defined as the interval for a particle to heat from ambient to 1850°C by convection alone. Next, the ignition period was the time interval for a particle to heat from 1850°C to 3930°C. During the ignition period heating by both convection and chemical reaction were considered. Finally, the combustion period lasted until the particle was consumed. The 3930°C temperature is the boiling point of boron and considered in reference (18) to be the particle temperature under self-sustained combustion.

Last, the third and most complex analysis of particle history was presented by Edelman, reference (4). In his analysis an attempt was made to treat the entire particle history in a unified manner by including all relevant physical processes in a differential equation describing particle temperature change.
Particle drag was assumed to be given by Stokes drag law. The particle temperature change calculation included convection and chemical heating and radiative and evaporative cooling. The analysis also included both reactant and product diffusion and a rate of particle diameter change, \( \frac{d^2 \rho}{d t} \). Finite chemical reaction rates were used. A differential equation was derived which was both unwieldy and of questionable utility due to the required estimates of diffusion rates, chemical reaction rates, and diameter change proportionately constant.
APPENDIX II.

COMPUTER PROGRAM DETAILS

Shock Tube Analysis Program

The shock tube analysis program calculates conditions in the incident and reflected regions of the shock tube, regions 2 and 5 of Figure 3, using one-dimensional form of the equations for conservation of mass, momentum and energy across the shock in a wave fixed coordinate system. The program input values are gas temperature, gas pressure, oxygen percentage and time reading from a microsecond counter. The time value is used to determine an incident shock Mach number. Calculations for changes across the shock wave are started by using ideal, constant specific heat values of pressure and temperature ratios. The ideal value are substituted in the Hugoniot and iterated upon to correct for chemical reaction, and variation in specific heats. The following flow diagram shows the procedure and accuracy agreements held in the program.
Shock Tube Program Flow Diagram

Start

READ IN: RUN NO., T₁, P₁, n₀₂, t

SET I, J, K, L = 1

WRITE RUN NUMBER

CALCULATE CONDITIONS IN REGION 1 BASED ON T₁, P₂, n₀₂ AND Mₛ BASED ON t

CALCULATE IDEAL T₂, P₂ BASED ON 1 AND Mₛ

CALCULATE COMPOSITION IN REGION 2 BASED ON T₂, P₂;

IS HUGONIOT EQUATION SATISFIED BY CONDITIONS AND COMPOSITION IN REGIONS 1 AND 2

No

I = I + 1

I > 100

Go To End

No

I ≤ 100

CALCULATE NEW P₂

CALCULATE U₂, W₁, Mₛ₁

GO TO Mₛ₁ CHECK

FROM T₂ CALCULATION
From $M_{S1}$ Calculation

\[ |M_{S1} - M_S| / M_S > 0.005 \]

\[ L = L + 1 \]

\[ L > 100 \]

Calculate new $T_2$

Calculate conditions and transport properties in region 2

Calculate ideal $P_5, T_5$

Calculate composition in region 5 based on $P_5, T_5$

Is Hugoniot equation satisfied by conditions and composition in regions 2 and 5

\[ J = J + 1 \]

\[ J > 100 \]

Go to Region 2 Composition Calculation

Go to End

Calculate new $P_5$
SYMBOLS IN FLOW DIAGRAM

$M_S$ - Shock Mach Number

$P$ - Pressure

$T$ - Temperature

$t$ - time

$U$ - Gas speed

$W$ - Wave speed

$\gamma$ - Ratio of specific heats

$\eta_{O_2}$ - Oxygen mole fraction

Subscripts

1 - Initial conditions in test section

2 - Conditions behind incident shock

2,5 - Conditions behind incident shock into which reflected shock moves

5 - Conditions behind reflected shock

51 - Ratio of conditions behind reflected shock to initial condition in test section
Particle Motion and Heating Computer Program

The computer program calculates the position, velocity and temperature, as a function of time, for a single particle in the shock tube by the analysis presented in Section II. Procedures for conducting the calculations are shown in the following flow diagram. The program accounts for particle acceleration and deceleration within the incident and reflected regions, numbered 2 and 5 in Figure 3, respectively. Velocity changes in the program are limited to 3000 cm/sec, nominally 5% or less, between consecutive time increments. A provision is included to change particle properties, i.e. specific heat, after the particle reaches the melting temperature. Upon reaching the melting temperature, the particle is held constant temperature until the particle melts. After melting the particle temperature is again allowed to increase. Two distance limits are included in the program. The first being the location of particle and reflected shock encounter and second, the particle traversing the complete length of the test section. Both distance limits must be met within ±.1 cm or the time increment for calculation decreased until the agreement is reached.
Start

READ IN: RUN NO., SHOCK TUBE CONDITIONS, TIME INCREASEMENTS, PARTICLE DIAMETER, MAXIMUM TOTAL TIME, THERMOCHEMISTRY DATA, PLOT CODES

CALCULATE TOTAL HEAT NECESSARY TO MELT PARTICLE, QTm

SET INITIAL CONDITIONS: \( t = 0, v_p = 0, v_r = u_2 \)
\( T_P = 298.16^\circ \)

CALCULATE TIME FOR SHOCK TO TRAVEL LENGTH OF TEST SECTION, \( t_A \)

From \( t < t_A \)

CALCULATE (2): \( Re_y, C_D, Nu, v_r \)

If \( \Delta v_r \leq 3000 \) CM/SEC

If \( \Delta v_r > 3000 \)

DECREASE TIME INCREMENT

\( \leq 3000 \)

SET TIME INCREMENT EQUAL TO ORIGINAL INPUT VALUE

\( v_r = v_r + \Delta v_r \)

If \( v_r \leq 1.0 \) CM/SEC

\( > 1. \)

\( \leq 1. \)
From $V_R \leq 1$.

WRITE: PARTICLE REACHES GAS VELOCITY

$V_p = U_2 - l$. CONSTANT

CALCULATE THE TIME A CONSTANT VELOCITY PARTICLE STAYS IN REGION 2 PRIOR TO ENCOUNTERING REFLECTED SHOCK, $t_2$

DIVIDE $t_2$ INTO $N$ EVEN TIME INCREMENTS, $N = \frac{t_2}{\Delta t}$, AND CALCULATE TEMPERATURE AND DISTANCE FOR THE $N$ TIME INCREMENTS

WRITE: $t, x_p, V_p, T_p, \text{REY, CD, Nu}$

GO TO REFLECTED SHOCK CALCULATION

From $V_R > 1$.

$V_p = U_2 - V_R$

If $T_p < 2450$, $T_p \equiv 2450$.

IS HEAT ACCUMULATED IN PARTICLE

IF $T_p \leq 2450$, USE SOLID PROPERTIES

IF $T_p \geq 2450$, USE LIQUID PROPERTIES

To $\Delta T_p$
From Solid/Liquid Property Selection

From OSI < QTM

Calculate heat to particle in this time increment, OSI

Add increment to accumulated heat to particle, OSI

Tp = 2450. (constant)

Calculate \( \Delta Tp \)

\[ Tp = Tp + \Delta Tp \]

Calculate \( \Delta Xp \)

\[ Xp = Xp + \Delta Xp, \quad t = t + \Delta t \]

Write: \( t, Xp, Vp, Tp, P_fy, C_p, N_{\text{U}} \)

Go to Calculate (2)

Is \( t \leq t_A \)

Go to Calculate (2)

Is \( t > t_A \)

Calculate distance reflected shock has moved

\(< 27.\) Go to Calculate (2)

\( > 27.\) Check absolute value

\( > 27.\) Go to reflected shock calculation

Is the distance the particle moved plus reflected shock moved \( > 27.0 \text{cm} \)
From Distance Calculation > 27.

\[ |L| \text{ IS THE ABSOLUTE VALUE IN EXCESS OF 27. } \frac{\text{.1 CM}}{\text{.1}} \]

\[ \text{REPEAT THE CALCULATION FOR } X_p, V_p, T_p \text{ USING REDUCED TIME INCREMENT UNTIL DISTANCE AGREEMENT REACHED} \]

\[ \text{WRITE: } t, X_p, V_p, T_p, R_{EV}, C_D, N_u \]

\[ \text{WRITE: PARTICLE HIT BY REFLECTED SHOCK} \]

\[ \text{SET INITIAL CONDITIONS } t = t_2, X_p = X_{p2} \]

\[ \text{FOR REFLECTED SHOCK CALCULATION: } V_{PR} = U_2 - V_R \]

\[ T_p = T_{p2} \]

\[ \text{CALCULATE (5): } R_{EV}, C_D, \Delta V_{PR} \]

\[ \text{IS } \Delta V_{PR} \gg 3000. \text{ CM/SEC} \]

\[ \gg 3000 \]

\[ \text{DECREASE TIME INCREMENT} \]

\[ \text{SET TIME INCREMENT EQUAL TO ORIGINAL VALUE} \]

\[ V_{PR} = V_{PR} + \Delta V_{PR} \]

\[ \text{TO } V_{PR} \text{ CHECK} \]
IS \( V_p \) \( \geq 1 \) CM/SEC

WRITE: PARTICLE STOPS

Go to \( t_{\text{max}} \) To Plot

IS (TIME IN REGION 2, \( t_2 \) + TIME IN REGION 5, \( t_5 \)) \( \geq t_{\text{max}} \)

CALCULATE DIFFERENCE BETWEEN \( t_{\text{max}} \) AND SUM OF \( t_2 \) AND \( t_5 \), AND DIVIDE INTO \( M \) EVEN INCREMENTS.

WRITE: \( t, \theta_p, V_p, T_p, \text{REY}, \text{CD}, \text{Nu} \)

\( \leq 2450 \)

Go to Plot

IS \( T_p \) \( \leq 2450 \)

IS HEAT ACCUMULATED IN PARTICLE \( \geq \) HEAT NECESSARY TO MELT

CALCULATE HEAT TO PARTICLE IN THIS TIME INCREMENT, \( \Theta_{\text{SI}} \)

IF \( T_p \leq 2450 \), USE SOLID PROPERTIES

IF \( T_p \geq 2450 \), USE LIQUID PROPERTIES

To \( \Delta T_p \)
From Solid/Liquid Property Selection

1. Calculate \( \Delta T_p \)

\[ T_p = T_p + \Delta T_p \]

2. Calculate \( \Delta X_p \)

\[ X_p = X_p + \Delta X_p \quad t = t + \Delta t \]

3. Write: \( t, X_p, V_p, T_p, R_e, C_D, N_u \)

Go To \#27

Calculate

\[ \text{IS THE TOTAL DISTANCE PARTICLE HAS TRAVELED} \]

\[ \approx 27 \text{ CM} \]

\[ > 27. \]

\[ \text{IS THE ABSOLUTE VALUE OF EXCESS} \]

\[ > 0.1 \]

\[ > 0.1 \]

\[ \text{REPEAT THE CALCULATION FOR} \quad X_p, V_p, T_p \text{ USING} \]

\[ \text{REDUCED TIME INCREMENT UNTIL DISTANCE AGREEMENT} \]

\[ \text{REACHED} \]

Write: \( t, X_p, V_p, T_p, R_e, C_D, N_u \)

Plot: \( X_p, V_p, T_p \text{ vs.} \ t \text{ IF CALLED BY PLOT CODES} \)

End
SYMBOLES IN FLOW DIAGRAM

\[ C_D \]  - Drag coefficient
\[ Nu \]  - Nusselt number
\[ Q_{SI} \]  - Heat transfer to particle in one time increment (cal)
\[ Q_{TM} \]  - Total heat necessary to melt a particle (cal)
\[ R_{EY} \]  - Reynolds number
\[ T \]  - Temperature (°K)
\[ t \]  - time (sec)
\[ t_{MAX} \]  - Maximum total time for conducting calculation (sec) in incident region
\[ U_2 \]  - Gas velocity (cm/sec)
\[ V \]  - Velocity (cm/sec)
\[ X \]  - Distance (cm)
\[ \text{Incremental amount} \]

Subscripts

\[ P \]  - Particle
\[ P_R \]  - Particle in reflected region
\[ P_2 \]  - Particle in incident region
\[ R \]  - Relative (i.e., relative velocity between gas and particle)


