

AD-A172 892

FUEL-SOLID PROPELLANT BORON COMBUSTION(U) ATLANTIC
RESEARCH CORP ALEXANDRIA VA W K KING ET AL. 15 AUG 86
41-51687 AFOSR-TR-86-0882 F49620-85-C-0020

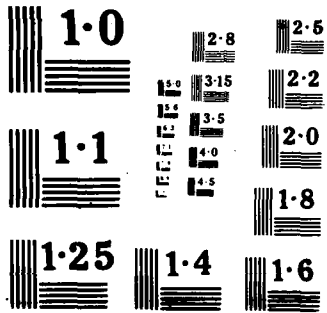
1/1

UNCLASSIFIED

F/G 21/2

NL

END
11/85



AD-A172 892

2

AFOSR-TR- 86 - 0882

REPORT 41-5160 F
FUEL-SOLID PROPELLANT BORON COMBUSTION

M.K. King
J. Komar

Atlantic Research Corporation
5390 Cherokee Avenue
Alexandria, VA 22312

DTIC
SELECTE
OCT 10 1986
B

FINAL REPORT

Air Force Office of Scientific Research/NA
Building 410
Bolling AFB, D.C. 20332

August 15, 1986

Contract F49620-85-C-0020

Approved for public release;
distribution unlimited.

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
NOTICE OF TRANSMITTAL TO DTIC
This technical report has been reviewed and is
approved for public release IAW AFR 19Q-12.
Distribution is unlimited.
MATTHEW J. KERPER
Chief, Technical Information Division

DTIC FILE COPY

86 10 8 094

UNCLASSIFIED

A172892

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1d. RESTRICTIVE MARKINGS			
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for Public Release; Distribution Unlimited			
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE						
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 41-5160F			5. MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TR- 86-0882			
6a. NAME OF PERFORMING ORGANIZATION Atlantic Research Corporation		6b. OFFICE SYMBOL (If applicable) N/A	7a. NAME OF MONITORING ORGANIZATION Air Force Office of Scientific Research/NA			
6c. ADDRESS (City, State and ZIP Code) 5390 Cherokee Avenue Alexandria, VA 22312			7b. ADDRESS (City, State and ZIP Code) Building 410 Bolling AFB, 20332-6448			
8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR		8b. OFFICE SYMBOL (If applicable) NA	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F4962085-C-0020			
8c. ADDRESS (City, State and ZIP Code) Building 410 Bolling AFB, DC 20332-6447			10. SOURCE OF FUNDING NOS.			
			PROGRAM ELEMENT NO. 61102F	PROJECT NO. 2308	TASK NO. A1	WORK UNIT NO.
11. TITLE (Include Security Classification)						
12. PERSONAL AUTHOR(S) King, Merrill K.; Komar, J.						
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM 11/15/84 TO 2/28/86		14. DATE OF REPORT (Yr., Mo., Day) 86-8-15		15. PAGE COUNT 29
16. SUPPLEMENTARY NOTATION						
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)			
FIELD	GROUP	SUB. GR.	Boron	Condensation	Oxide Condensation	
21	01		Boron Oxides	Permeability	Boron Combustion	
21	02		Boron Hydroxides	Boron Ignition	Ramjet Fuels	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) An apparatus for measurement of the permeability of oxygen gas through liquid boric oxide as a function of temperature was designed and built. Numerous difficulties were encountered in the course of this study, the most intractable being the uptake of oxygen by vessel wall materials at rates which swamped the rate of transport across the liquid boric oxide film separating vessels with differing initial oxygen levels, resulting in data with an unusably low signal-to-noise ratio. A burner and two-dimensional nozzle device were designed (and the burner constructed) for study of condensation of boron oxides and hydroxides (all to boric oxide, with elimination of hydrogen and excess oxygen as required by stoichimetry considerations in the latter case) from dry and wet combustion atmospheres, with and without seeding with submicron refractory solid particles as heterogeneous nuclei. In addition, diagnostic procedures for use in this condensation study (to be actually performed under a subsequent AFWAL/PORT contract) were selected from a wide array of potential candidates. A condensation model treating the flow of						
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS <input type="checkbox"/>				21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL <i>Julian M. Tishkoff</i>			22b. TELEPHONE NUMBER (Include Area Code) 202 767-4935		22c. OFFICE SYMBOL NA	

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

boron-loaded combustion product streams through a C-E nozzle with simultaneous treatment of finite-rate kinetics for gas-phase reactions and finite-rate nucleation and particle growth processes was developed. Several plausible modeling options as regards nucleation and particle growth processes were included in this analysis. Equation development, computer coding, and model check out were completed, and parametric studies with the model were initiated during the course of this program.

Accession	
NIEP	✓
DTIC	
Unavail	
Justif	
By	
Dist	
Avail	
Dist	A-1



UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

I. RESEARCH OBJECTIVES

- (1) Conduct an experiment to determine the rate of transport of oxygen gas across a liquid boron oxide film of controlled thickness and temperature.
- (2) Design and construct an apparatus for study of homogeneous and heterogeneous condensation of boron oxides and hydroxides from a hot-gas stream in a controlled-cooling-rate expansion process.
- (3) Determine the most appropriate diagnostics for measurement of condensation on-set, condensation rates, and species identification in the expansion process.
- (4) Develop a mechanistically realistic model of boron oxide and HBO_2 condensation in cooling flow (C-E nozzle) systems.

II ACOMPLISHMENTS AND PROGRESS

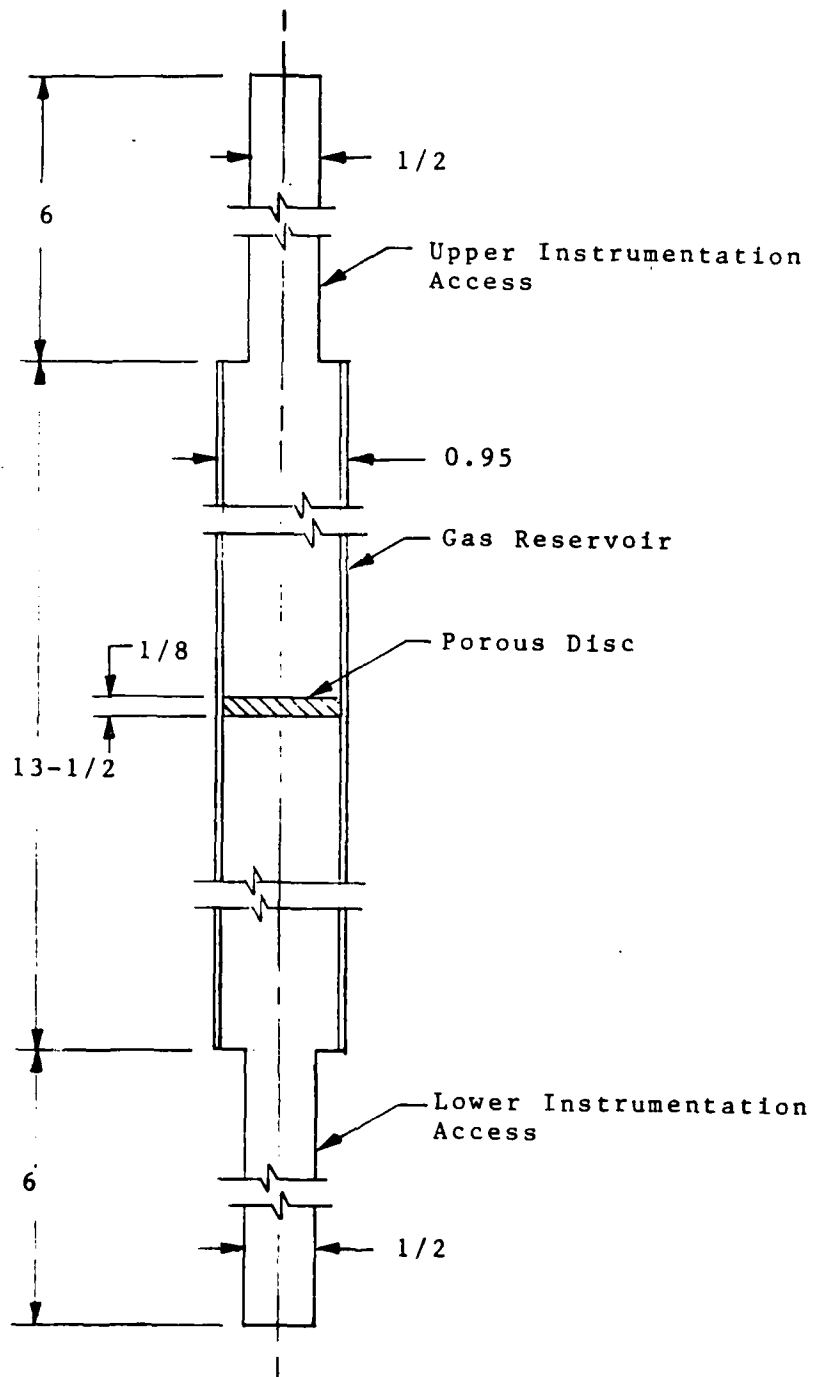
The objective of the first phase of the program, as outlined in the original proposal, was to identify and quantitate the mechanism by which oxygen and unreacted boron make contact in the presence of an oxide layer on a boron particle. Two hypotheses have been advanced: under the first, oxygen permeates through the liquid oxide layer to the boron/boric oxide interface where it reacts with the boron substrate; under the second, boron is transported across the liquid oxide layer to react with the oxygen at the liquid oxide-ambient gas interface. (Arguments and evidence for and against each hypothesis were presented and discussed in the proposal.)

A significant effort has been devoted to design of a unique apparatus to test the first hypothesis (and to quantitate the rate of such a process). The conceptual design of the apparatus proved to be reasonably straightforward, but reduction to practice was considerably more difficult due to unforeseen practical complications. The basic concept of the experiment is measurement of rate of transfer of oxygen from a vessel containing an argon/oxygen mixture into a second vessel containing (initially) pure argon gas, the two vessels being separated by a porous frit of known surface area, supporting a known thickness of liquid boric oxide at a controlled temperature. In all, six separate apparatus configurations have evolved in the course of this study, each building on information developed during testing of the previous configurations. A brief summary of the evolution of the permeability apparatus design follows:

The first design centered around a ceramic tube vessel supplied by an outside vendor. In this design, the vessel was surrounded with a split-tube resistance-heated furnace (to

supply the desired test temperature conditions) with instrumentation ports located above and below the heated region. (A schematic diagram is shown as Figure 1). The material selected for the vessel was high purity alumina, chosen for its non-reactivity at the temperatures envisioned for this experiment (700 to 1300°K). The support mechanism was a ceramic sintered porous disc, which would support the liquid B_2O_3 film without passing the material into the lower gas reservoir. The nominal operation mode called for a mixture of argon and oxygen (75%/25%) at approximately 17-20 psia in the upper chamber, and a 100% argon gas charge in the lower chamber. The pressure differential across the liquid film was maintained at levels of less than one millimeter Hg by use of an MKS Baratron differential pressure transducer. This approach insured a concentration gradient, but no pressure gradient across the liquid film. Early work with various support matrix materials showed that pressure gradients had a significant impact upon the amount of material (liquid B_2O_3) driven into the interstices of the film carrier. Under ideal conditions the liquid layer will be supported without significant wetting of the underlying material, resulting in complete mechanical support of the film, but permitting unimpeded (except by the liquid film itself) gas diffusion into the lower reservoir.

The initial attempts to have a suitable vessel (tube) assembly fabricated by an outside vendor failed for a number of reasons, not the least of which was the inability to effect a gas-tight seal at the joint where the support matrix and vessel tubes met. These problems were further aggravated when taking the vessel assembly to high temperature, in that failure to account for differences in the thermal expansion coefficients of the cement, ceramic and support matrix materials resulted in significant leakage. After several long turn-around times and additional evidence that our needs were not understood, we opted for outside fabrication of various pieces of the vessel, and assembly in-house, where crucial elements of quality-control



All Dimensions in Inches

Figure 1. Original Permeability Apparatus

could be monitored by the principal investigators.

A reworked ceramic vessel was assembled and checked leak-tight at room temperature conditions. However, when operated at the design temperature, several ceramic seal joints failed, resulting in significant deterioration of the cemented portion of the assembly. A total of six different cements were utilized to attempt a solution of the seal problem, but all were unsuccessful, even after extensive consultations with the manufacturer. Accordingly, a redesign utilizing an oxidation-resistant metal vessel was carried out.

This redesign of the vessel to incorporate Inconel fittings throughout the heated zone resulted in improved performance as well as permitting the use of sintered porous discs in a union fitting. However, the metal-to-metal seal at the union fitting proved to be unreliable when subjected to the hot-zone of the furnace, and it was finally concluded that joints and seals in the furnace zone were not going to work unless they could be permanently sealed in some manner. Since access to the support matrix was required from run-to-run, it was concluded that a design utilizing no seals or joints in the furnace must be accomplished.

This next design evolution incorporated a support mechanism for the liquid film which could be sealed outside the furnace zone, but incorporated an extensive portion of the support plumbing from the previous design. This proved to be the un-doing of this approach, in that we were never able to effect a completely leak-tight system with the multiple "swage-lok" type metal to metal fittings. Part of the difficulty stemmed from a shipment of stainless fittings which were all defective.

This design approach did show enough promise that the next approach incorporated many of its features, but with modification of the support system for the main permeability

vessel to include all hardened connections, thus eliminating multitudinous potential leak sources. In addition, optical ports were incorporated to permit access of laser scattering beams for detection of oxygen concentration increases in the lower (initially pure argon) chamber. This design, shown in Figure 2, proved to be leaktight under operational conditions (700-1300°K), providing positive indications that permeability measurements could finally be made.

A total of four data runs and two calibration tests were performed over an eight week period. Typical durations for a given run were from 140 to 160 hours of continuous operation. The indicated permeability rates were extremely slow and considerable effort was devoted to establishing a satisfactory measurement technique for low concentration values of oxygen. The method finally settled upon was a combination mass spectrometer/gas chromatograph (Hewlett-Packard Model 5992A/GC-MS) instrument.

The apparent low permeability rates were at least an order of magnitude slower than predicted, and it was conjectured that the oxygen was being consumed by the Inconel walls. Inconel is known to be highly oxidation resistant at high temperature. Moreover, it was surmised that if an oxide layer did form it would inhibit further oxidation. However, the Inconel used in the vessels contained up to seven percent iron in its composition, and this amount was sufficient to convert ferric-oxide on a continuous basis (over the duration of a data run). To test this hypothesis, two calibration tests were performed to establish the uptake rate of oxygen by the vessel walls, and the results confirmed a continuous conversion of oxygen by the iron in the Inconel. Other mechanisms could also be at work, but these tests showed conclusively that the results obtain during the four previous data runs were probably statistically insignificant in determining a B_2O_3 permeability

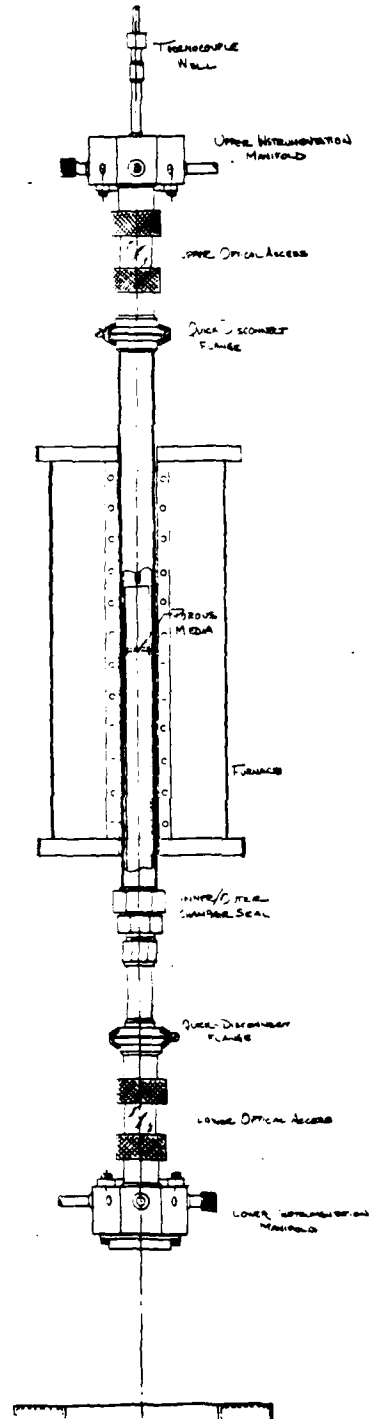


Figure 2. Permeability Apparatus Diagram

rate. It is likely that the uptake rate of oxygen by the vessel walls was greater than or equal to the diffusion rate through the B_2O_3 liquid film.

The approach developed during the foregoing effort has shown that a non-reacting, vacuum-tight vessel must be developed before any hope of generating meaningful data can be had. The essential elements of that design have now been worked out, and an effective method for preventing oxygen up-take has been devised. Since Atlantic Research considers resolution of the community debate over the mechanism(s) controlling reaction of oxygen with boron in the presence of an oxide film to be quite important as regards development of means of improving the ignitability of boron particles in airbreathing combustors, this effort will be pursued further under a 1986 IRAD program.

Boron, due to its extremely high potential volumetric heating value, offers significant advantages as a fuel ingredient for many air-breathing missile applications. Extensive review of the literature in the area of condensation of various boron oxides and hydroxides during expansion cooling in a nozzle or even during cooling resulting from the mixing of combustion products with dilution air has been carried out and questions as to whether such condensation will occur during the limited residence times raised.

The practical application of boron-containing fuels to missions defined for liquid ramjets, solid fuel ramjets, and ducted rockets has been hampered by a lack of understanding of how well condensation of boron oxides and hydroxides will track thermodynamic predictions during rapid cooling nozzle expansion processes. The reaction pathways from boron hydroxide (HBO_2), which is a principal product of boron combustion in hydrogen-containing systems, to liquid boron-oxide (B_2O_3) plus water gas (H_2O) have not yet been quantitated. Failure of $2HBO_2(g)$ to convert to $B_2O_3(l)$ plus $H_2O(g)$ results in loss of

approximately 23 percent of the potential heating value of the boron, a rather significant loss.

There are two major factors of importance as regards condensation of boron oxide and hydroxide gases to B_2O_3 (liquid) in a combustor during mixout with excess air or during nozzle expansion processes (in which the temperature of the expanding stream is reduced by conversion of PV energy to kinetic energy). The first factor is thermodynamics - thermodynamic principles determine the best that can be achieved as regards capture of the condensation heat of the gaseous oxides and hydroxides. If the combustion chamber temperature is too high to allow for the vapor pressures of the gaseous species to drop below the partial pressures of these species during the expansion process, no condensation can occur, regardless of reaction kinetics. Thus, kinetic effects need only be considered in cases where thermodynamic principles dictate possible condensation. In this case, kinetic limitations can cause inefficiencies relative to thermodynamic predictions. It is important to note that such inefficiencies are relative to thermodynamic limitations, not relative to one hundred percent condensation.

Generally, attainment of high combustion efficiency of boron particles in airbreathing propulsion systems requires that the particles be ignited and at least partly (preferably totally) burned in relatively high temperature ($2400^{\circ}K$ or higher) regions of the combustor. At any reasonable operating pressure (less than 200-300 psi) all of the product boron oxides and hydroxides will under these temperature conditions be gaseous (no condensation). Thus, for condensation to be possible, these initial products must be mixed with excess air and/or expanded thru a supersonic nozzle sufficiently that the temperature drops to a point where the partial pressures exceed vapor pressures - in general, such conditions will exist only for a small fraction of the overall combustor residence time, typically on the order of 1 millisecond or less. It is here

that kinetics considerations come into play.

As part of this effort, design of a test apparatus for experimentally studying the condensation of boron oxides and hydroxides under carefully defined rates of cooling of streams containing various gaseous boron combustion products, and selection of diagnostic procedures for obtaining the required data from these experiments have been carried out. In addition, preliminary development of a model of condensation of boron oxides and hydroxides, which will be calibrated and modified as dictated by results of experiments to be conducted in another (follower) program being funded by AFWAL/PORT, has been accomplished. A summary of these efforts is given in the following paragraphs.

In an attempt to understand the processes which will lead towards maximization of condensation of boron oxides, and therefore more fully utilize the high heating value potential of boron, we have designed an apparatus for the study of homogeneous and heterogeneous condensation of boron oxides and hydroxides in a hot-gas stream, using a controlled-cooling-rate expansion process. A long-residence-time, well-stirred combustor (with a long downstream burnout zone) burning carefully monitored amounts of hydrogen, oxygen, possible hydrocarbon fuels and either boron oxide or possibly a borane compound, along with nitrogen, is to be used to generate various product streams of well-defined total temperature and composition (particularly B_2O_3 gas and HBO_2 gas levels). A two-dimensional hot-wall nozzle throat at the end of the combustor will control operating pressure and serve as the entrance to a two-dimensional expansion section designed to control the transit time. It is important that the rate of temperature decrease (as well as absolute temperature level) be controlled for proper study of super-cooling effects. Approaches to the adjustment of the Damkohler similarity parameter (ratio of residence time to chemical reaction time) include varying

stagnation conditions in the plenum chamber, appropriate contouring of the expansion nozzle to ensure uniform regions of flow parameters, and the use of different expansion angles (for control of rate of temperature decrease in the expanding streams) with replaceable nozzle walls. This last approach (varying expansion angle) has the advantage of permitting the nozzles to be truncated during a test series, permitting measurements at various stages of the condensation process, and is the technique adopted for the condensation experiments to be performed. As discussed below, the plenum conditions will also be adjusted in order that a reasonable range of test conditions may be achieved.

The hot-gas generator to be used as a source of combustion products simulating ramjet combustion systems is shown in Figure 3. The reactor is capable of handling all-gas flows or a mixture of gas and slurry flows. Mixtures of hydrogen, oxygen, and nitrogen can be employed, while for water vapor-free tests, the feed streams can consist of carbon monoxide, oxygen, and nitrogen, for example. Feed rates of the various constituents may be chosen to produce product streams with total temperatures ranging from 1600°K to 3200°K at various pressures and compositions. Upper limits on reactor pressure are placed at 750 psia. The gas generator was designed, fabricated and tested in the latter months of this research investigation, and has now been operated over a moderate range of test conditions for purposes of establishing the nominal operations envelope.

This combustion reservoir chamber has been designed and constructed so as to provide a minimum heat loss from the reservoir walls, thereby maximizing the energy available for expansion of the combustion products. A silicon-carbide liner

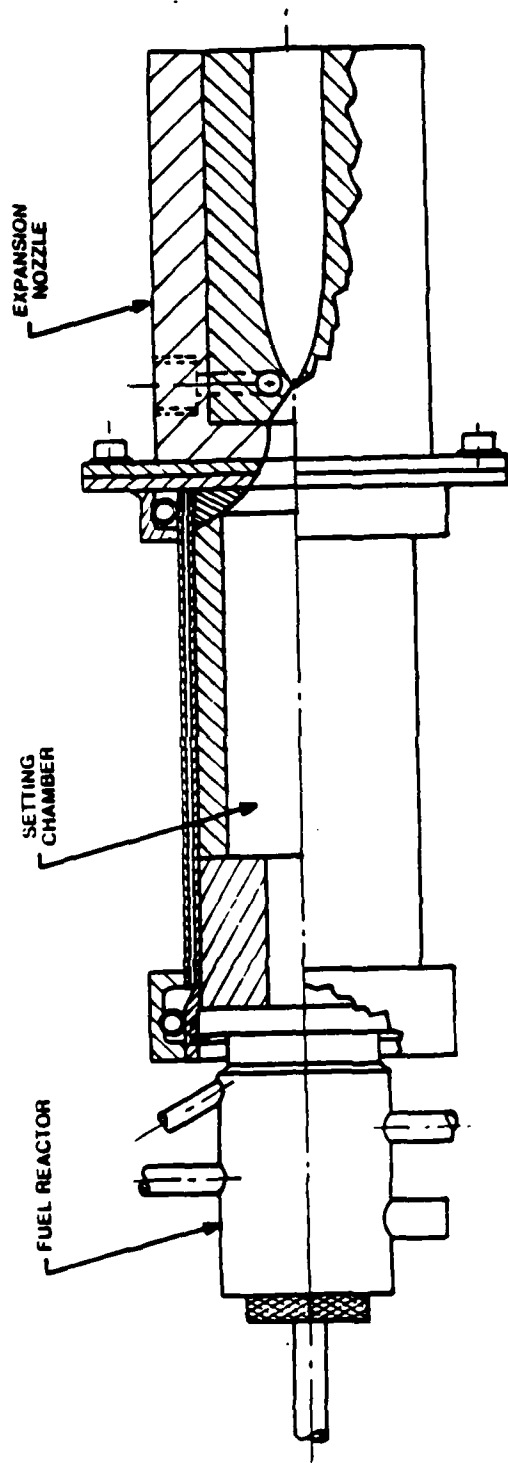


Figure 3. Conceptual Design of the Burner/Combustor/Nozzle Assembly.

is supported by a Nextel braided composite fiber wrapping, which is in turn surrounded by Fiberfrax insulating block. This assembly is installed inside a water-cooled pressure vessel and forms the support mechanisms upon which the nozzle assembly is mounted.

The nozzle assembly is composed of tungsten/rhenium walls, supported by an assembly of Nextel, Fiberfrax, silicon phenolic and boron nitride insulators, encased in a water-cooled steel pressure vessel. Our original conception of this nozzle was to build a gently sloping two dimensional nozzle with access ports for laser diagnostics. Considerable design effort was expended probing this approach, but in the final analysis, while glass technology has advanced significantly, there still does not appear to be a material available to operate at hot wall temperatures of 2000°K and still be able to withstand abrasion and crazing attendant with particle loaded flows. For this reason, the approach of variable expansion angles and different axial length nozzles (truncation approach) has been adopted as the means by which local conditions and their rate of change are varied.

The overall condensation facility is composed of the burner/plenum/nozzle assembly developed during this investigation, and a test section, diffuser, heat-exchanger, particle scrubber and exhaust system. A schematic diagram of the facility is shown in Figure 4. This facility is currently being prepared for installation in a new Combustion Research Laboratory at our Gainesville, Va location.

The measurements to be accomplished in support of the research objectives for the condensation experiment include static pressure, gas stream temperature, particulate concentration, flow velocity and condensate particle size and

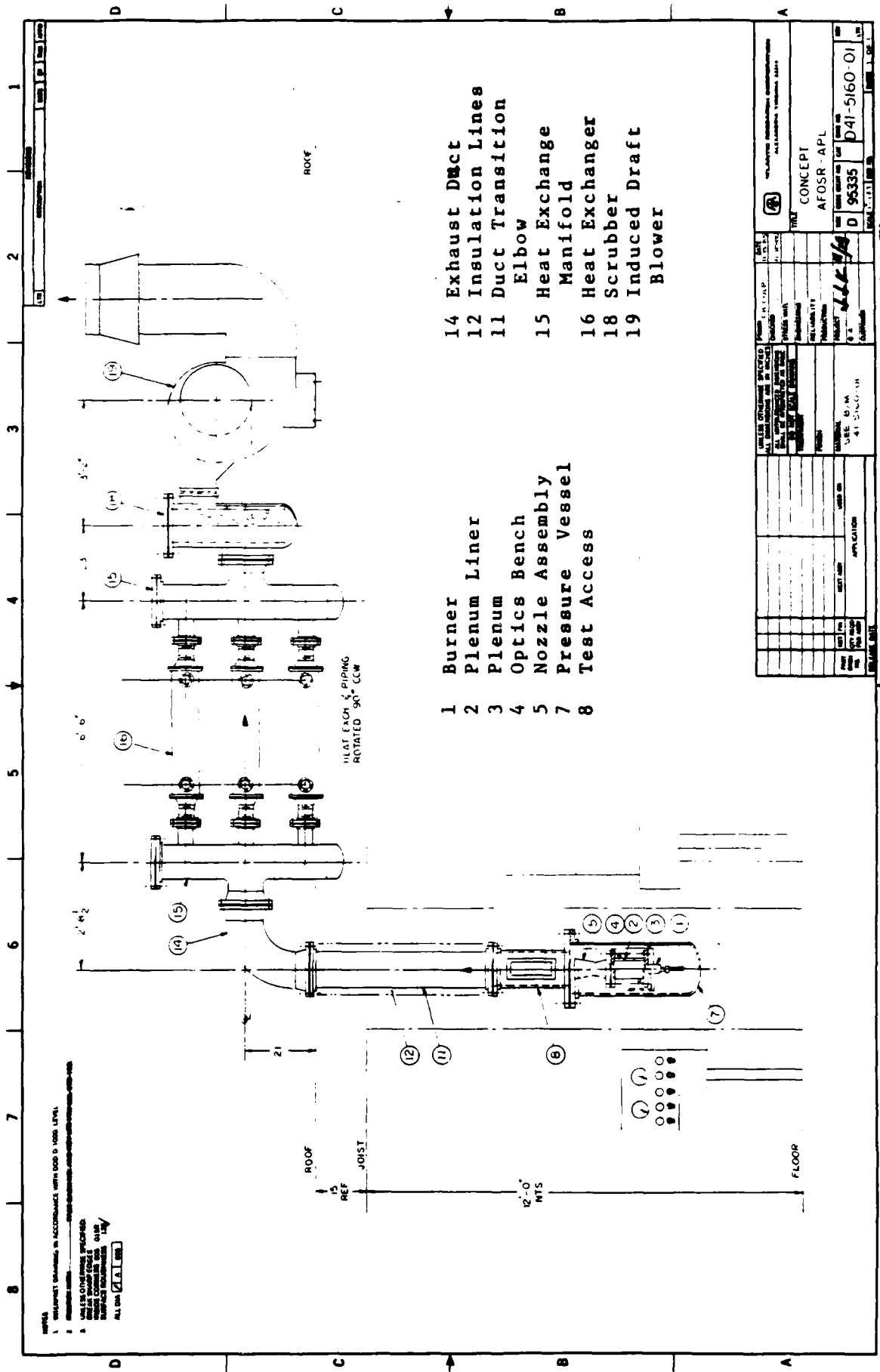


Figure 4. Overall Facility Schematic Diagram

number density as a function of nozzle length (axial location). The measurement of condensate particle temperature is considered beyond the current state-of-the-art in combustion diagnostics. Development of such capability is, in fact, feasible, but beyond the scope of the program reported herein. Calculations of combustion temperature, theoretical heating value and residence time for various feed combinations have been made and tabulated: measured degrees of condensation will be used for calculation of delivered heating values for comparison to the theoretical values. A majority of the foregoing measurements will be accomplished at the exit of incremental length truncated nozzle blocks.

The three basic measurements groups considered during this investigation include droplet characterization techniques, temperature measurement, and species concentration measurements. A brief summary of our investigations into each area is given in the material that follows.

Analytical modeling efforts directed towards condensation characterization emphasize the need for empirical data regarding droplet sizes versus axial distance along the nozzle. The measurement techniques to be used to characterize the droplets are discussed briefly below. Each of the techniques discussed has been implemented at Atlantic Research, through either contract funding or IR&D support. The preferred techniques for in-situ measurements of droplet size and distribution are laser-based, and include the Fraunhofer diffraction scattering technique embodied in the Malvern sizing instrument and the visibility/intensity measurement technique utilized by the Spectron Development Laboratories droplet sizing interferometer. Velocity measurements are to be accomplished with a 2-component Laser Doppler Velocimeter.

The Malvern Model 22200 Particle Sizer is based on principles of forward-light scattering or Fraunhofer

diffraction. When illuminated by a beam of monochromatic, coherent, collimated light from a HeNe laser, the smaller drops diffract light at larger angles to the optical axis than the larger drops and a unique diffraction pattern is formed. Detection is accomplished with an annular ring set of 30 solid state detectors. Detector outputs are multiplexed and the data signal averaged with a microprocessor. A computer routine proprietary to Malvern is used to interpret the light scattering pattern of the polydisperse drop systems. The drop-size data are available as either a set of two parameters, defining a Rosin-Rammler, log-normal, or normal distribution, or as a histogram of 15 size classes of drops without assumptions regarding the shape of the distribution (model independent).

The Malvern instrument is based upon first principles and therefore calibration should not be necessary. While in principle this may be true, considerable effort has been devoted to the assessment of instrument functions, detector variability, and maximum acceptable concentration levels. Laser beam-steering problems at elevated air temperatures can be caused by refractive index gradients resulting from temperature gradients and exhaust gas concentration gradients. The result is that the unscattered portion of the laser beam of the drop sizer, which normally is focused on the central detector, may wander onto other nearby detectors which are used to measure light scattered by the drops in the flow. Since large drops scatter light at the smallest angle and their scattered light is focused onto the inner detectors, the extra signal intensity due to the beam steering is interpreted by the instrument as more large drops than actually exist. Fortunately, the additional signals due to beam steering are typically limited to the inner six or eight of the thirty detectors, and are associated with large droplets. The detector radii increase rapidly in going away from the center spot, so that the beam steering perturbations, which effect the first few detectors at elevated temperature, must become much larger in magnitude to progress outward through the

larger radii detectors. Since our investigations are directed towards the onset of condensation (very small condensed droplets), "beam-wander" should not be significant.

Single particle counters provide the greatest potential for obtaining size and velocity distributions directly. The distributions are based on the measurements of individual drops and do not require the use of distribution functions. Single particle counters based on laser light scatter detection also have the potential of performing the measurements nonintrusively with high spatial resolution at realistic working distances. Recently developed methods also provide good resolution over a large size range.

Perhaps the most obvious approach to determining the condensation drop size is to use the measurement of the scattering cross-section or absolute scattering intensity of the droplet based on the light collected in the near forward direction. Off-axis light scatter detection has been suggested as a means to obtain improved resolution on drops greater than 50 microns. The first difficulty encountered with light scattering intensity measurements is related to the Gaussian intensity distribution of the laser beam. Random droplet trajectories through the beam result in an uncertainty of the incident light intensity on the droplet. Several methods have been devised to overcome this difficulty. A deconvolution approach was suggested by Holve and Yule, et. al. The inversion routine inevitably introduces errors and a second inversion required to obtain droplet size-velocity correlations compounds the errors. The method suggested by Bachalo utilizes a pointer beam of a different wavelength or polarization to indicate the essentially uniform intensity at the center of the beam. This method has been developed by Hess and Espinosa, with the pointer beam combined with signal visibility measurements as a method of continuous calibration of the system. The added complication to the optics and signal processing notwithstanding, the relative

sizes of the beams precludes the application of this method in flows with high number densities. While this limitation is not significant for our investigation, efforts are being devoted to reduction of the limitation by Bachalo, et. al. At present, the most promising spatially defined measurement technique in moderately dense flows is the visibility/intensity ratio observation obtained from the droplet sizing interferometer.

The advantages of this approach are the increased accuracy of the absolute intensity values, which uniquely define the particle size, and a significant expansion of dynamic size range. Factors of three to five-fold increases are possible in the measurement ranges and the ability to measure size and velocity simultaneously permit correlations not normally available. To implement this measurement technique, we will modify the transmitting optics of our existing particle size interferometer and add a second detector for the measurement of the absolute intensity. The software modifications to existing data acquisition and reduction routines will include the coincidence gating algorithm, a peak intensity sample and hold read-out routine, and additional look-up tables for the relative size data from the absolute intensity values.

The multiple objectives of the research program described herein have necessitated consideration of non-intrusive diagnostics for measurements of temperature, in that high free-stream temperatures (as high as 1600°K , with a total temperature of greater than 2000°K) and particle loading densities are greater than conventional temperature probing techniques are capable of handling for reliable data. Laser scattering methods have been considered, and a brief investigation of continuous wave (CW) Raman Scattering technique was attempted early in this investigation. While many Raman studies have been accomplished in clean laboratory flames, it may be quickly shown that CW lasers are unacceptable for practical combustion diagnostics. The primary drawback is the

signal to noise ratio comparison, when considering the extremely weak Raman scattering signal relative to the high background luminosity from the combusting flow-field. Background luminosity levels of several orders of magnitude greater than the scattered Raman signal are typical at temperature levels of 2000°K. Utilization of a high peak-power pulsed laser with a typical peak power level of 10^8 watts can improve the signal to noise level by as much as seven orders of magnitude. This capability suggests that major species constituents can be probed, even in highly luminous environments with such pulsed lasers.

As our laboratory efforts expanded, it became clear that the existing equipment might not provide the clear chance of success demanded by the complex research objectives to be accomplished during the condensation experimental program. A significant effort was devoted to the selection of an appropriate pulsed laser source, and purchase of a neodymium-YAG laser was made with Atlantic Research capital funds. Additional company investment in the appropriate signal processing equipment (e.g. gated boxcar amplifiers) and sensitive detection heads (gated silicon intensified target sensor) was also made and considerable effort has been devoted under IRAD funding towards bringing this measurement capability on-line. This work has been accomplished in parallel with the species concentration measurement development discussed in the next two paragraphs.

Important species in combustion processes include C, H, CH, NH, OH and certain polyatomic radicals, depending upon the fuel utilized. The respective concentrations of these and other species may be measured using laser-induced fluorescence. This technique is non-perturbing, temporally and spatially precise, and is a reasonable extension of other measurements being made with a tunable-dye laser. The measurement technique may be described as the population of an excited state of a molecule via resonant absorption of laser radiation, detection of the

subsequent fluorescent emission from the excited state and subsequent deduction, via calculation, of the concentration of the ground state molecule under consideration. In order that such measurements may be made, several criteria must be satisfied. There must be a known emission spectrum from the species measured, the excitation wavelength must be within the range of the turnable dye laser, the decay rates of the excited state must be known and collisional quenching rates must be well established. If fluorescence saturation occurs, the collisional quenching rate is no longer important, and some simplification of the analysis is obtained. However, the approach to equilibration between the excited and ground state populations (saturation) only occurs with intense pump radiation from the excitation source, and thus may represent a physical limitation in terms of available equipment.

One of the principal draw-backs to this measurement technique is its susceptibility to background luminosity and particle incandescence. Careful selection of the pump laser wavelength can offer some relief in this regard, but consideration of the available equipment will exert the strongest influence on the selected atomic or molecular specie. The simple expedient of increasing laser power can lead to increased particle incandescence, and thus becomes self-defeating. Some research into short-pulse, rapid coincidence detection has shown promise, but this is considered to be too immature a technology to be applied to this investigation. Species concentration measurements are also possible via Rayleigh, Raman, Absorption, and Coherent Anti-Stokes Raman Spectroscopy (CARS) measurement techniques. The choice of method is primarily determined by the atomic or molecular specie to be analyzed and the state of development of the various measurement technique within a given diagnostic laboratory. At this juncture, we favor the LIF approach, with CARS as a primary backup for the condensation experiment.

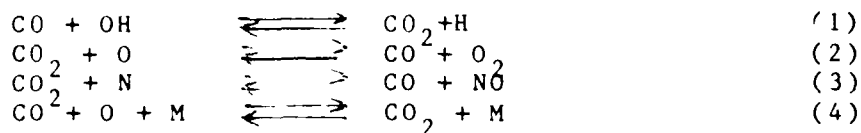
In the analysis of possible kinetic limitations leading to less than thermodynamically predicted condensation and their dependence on such parameters as residence time, cooling rate, absolute temperature level, pressure, and initial composition, a number of processes must be considered. These include:

- (1) Homogeneous nucleation (development of nuclei of minimum critical size)
- (2) Presence of heterogeneous nuclei (nuclei of other material such as refractory metal oxides or carbon)
- (3) Deposition of B_2O_3 gas molecules on either homogeneous or heterogeneous nuclei (particle growth)
- (4) Reactive deposition on either type of site with the condensing gas being B_xO_y or $H_zB_xO_y$ where in the former case y/x is not $3/2$. This is a complex deposition accompanied by elimination of H or stoichiometrically excess B or O. (e.g. $2HBO_2(g) \longrightarrow H_2O(g) + B_2O_3(l)$).
- (5) Gas phase reactions to replace B_2O_3 (gas) or other relatively easily condensed species as they are condensed at higher rates than the other HBO species, tending to lead to gas-phase non-equilibria. (e.g. $2HBO_2(g) \longrightarrow H_2O(g) + B_2O_3(g) \longrightarrow B_2O_3(l)$)

A condensation model addressing the above processes, coupled with analysis of expansion of combustion products through a combustor nozzle has been developed as part of this effort. This analysis is initiated with equilibrium chamber calculations for definition of species concentrations in the chamber to be used as initial conditions for differential equations describing the change of various species concentrations with incremental progress through the nozzle. The model has been developed for a B-H-O-C-N system

with the gas species tracked during the nozzle expansion process being O, O₂, H, H₂, OH, H₂O, N₂, NO, N, CO, CO₂, BO, BO₂, B₂O, B₂O₂, B₂O₃, HBO, HOBO, (HOBO)₂, and (HOBO)₃.

Approximately 100 possible gas-phase reactions which might be important in the overall process of oxide condensation were initially identified - these were reduced to 58 reactions in the computer code through careful weeding out of the slower reactions. Accurate experimental kinetic data were available for many of the reactions, but estimates based on methods of Benson and others had to be used for some of them. The resulting rate expressions were used in development of equations for the rate of change of the concentrations of each specie listed above with respect to axial distance. As an example, the gas reactions involving CO are:



leading to the following differential equation for CO concentration change with axial distance:

$$\begin{aligned}
 \frac{d[\text{CO}]}{dx} &= \frac{1}{u} \frac{d[\text{CO}]}{dt} = \frac{1}{u} \left\{ -k_1 [\text{CO}][\text{OH}] + \right. \\
 &k_{-1} [\text{CO}_2][\text{H}] + k_2 [\text{CO}_2][\text{O}] - k_{-2} [\text{CO}][\text{O}_2] + \\
 &k_3 [\text{CO}_2][\text{N}] - k_{-3} [\text{CO}][\text{NO}] - k_4 [\text{CO}][\text{O}][\text{M}] + \\
 &\left. k_{-4} [\text{CO}_2][\text{M}] \right\} \quad (5)
 \end{aligned}$$

where M represents a third body. Similar differential equations were developed for the other gaseous species, with inclusion of

additional terms associated with condensation of liquid B_2O_3 in the cases of any gaseous species involved in these condensation reactions. In addition, differential equations for temperature, velocity, and density versus axial distance were derived from equations for conservation of mass, momentum, and energy and used in combination with an equation of state for a gas-particle mixture (to determine pressure), enthalpy-temperature relationships for the various species, and the input nozzle contour. (Actually, for avoidance of the throat singularity problem, pressure versus axial distance distributions, based on equilibrium calculations, were specified up to and just past the choke point with cross-sectional area versus axial distance being specified downstream.

Finally, equations for the rate of homogeneous nucleation of B_2O_3 (along with inputs for heterogeneous nuclei concentrations) and for the rate of growth of particles subsequent to nucleation were developed for closure of the analysis. As will be discussed in the paper, several options as regards particle growth were examined, with the possibility of direct condensation of HBO_2 and its dimer and trimer on nuclei (with elimination of H_2O) being included among the options. Several possible equations for rate of homogeneous nucleation (in droplets per unit volume per unit time) were examined and one used by Griffin and Sherman selected for use in this analysis:

$$J = \left(\frac{P}{kT}\right)^2 \frac{1}{\rho_2} \left(\frac{2\sigma\mu}{\pi N_A}\right)^{1/2} \exp\left[-\frac{4\pi\sigma r^{*2}}{3kT}\right] \quad (6)$$

where:

$$r^* = \text{Critical Radius} = \frac{2\sigma\mu}{\rho_2 RT \ln S}$$

J = Condensation rate, droplets per unit volume per unit time

P= Partial pressure of condensing specie
 ρ_L = Liquid density
k= Boltzman gas constant
T= Temperature
 σ = Surface tension
 \mathcal{M} = Molecular weight
 N_A = Avagadro's number
R= Universal gas constant
S= Effective supersaturation $\approx P/P_{\infty}$
 P_{∞} = Saturation vapor pressure

As indicated above, several options as regards calculation of subsequent growth on nuclei were built into the model. These included a simple collision theory model, similar to that used by Edelman, with and without consideration of the effects of particle radius on saturation vapor pressure, for condensation of B_2O_3 gas and/or HOBO, dimer, and trimer on the nuclei, and a model in which the rate of heat transfer away from the nuclei to the surrounding gas is balanced against the rate of heat deposition into the nuclei accompanying condensation of gaseous molecules on them (a much more realistic model in the opinion of the author).

As implicit differential equation set solver based on the GEAR method for solution of stiff sets of differential equations was used to step along the nozzle solving for pressure (in the expansion section of the nozzle) or area (in the contraction section), temperature, velocity, mole fractions of various gas species, number of nuclei, diameter of particles initiated in each upstream step, and fraction of boron appearing as condensed phase oxide versus distance, for comparison with shifting equilibrium and frozen calculations run using a standard thermochemical equilibrium code.

In the course of this program, the analysis described above was developed and coded for the computer, with very preliminary test runs indicating that the code is operating properly - during the

course of the subsequent AFWAL/PORT program, the various options will be tested against experimental results for definition of the most accurate hypotheses among the options included in the analysis. In addition, extensions of the program to treat condensation in the combustion chamber (for cases where thermodynamic considerations permit such condensation) and to treat the presence of heterogeneous nuclei will be added. Finally parametric mapping will be carried out to define operating regimes favorable and unfavorable to condensation and to define the effects of addition of refractory seed material to fuel formulations on condensation.

III PUBLICATIONS

- (1) King, M.K., "A Finite-Rate-Kinetics Model for Formation of Liquid Boron Oxide in a Nozzle Expansion Process", To be presented at 23rd JANNAF Combustion Meeting, Oct. 1986. Will appear in CPIA Publication.
- (2) King, M.K., and Komar, J., "Measurement of Permeability of Oxygen in Boron Oxide Liquid". To be submitted to Combustion Science and Technology and/or Journal of Physical Chemistry.
- (3) King, M.K., "A Model of Boron Ignition Incorporating New Permeability and Kinetic Data", To be submitted to Combustion Science and Technology and/or Combustion and Flame.

IV PROFESSIONAL PERSONNEL

Dr. Merrill K. King

Dr. James J. Komar

V INTERACTIONS (COUPLING ACTIVITIES)

- (1) Atlantic Research has several advanced development contracts involving use of boron as a fuel. These include ducted rocket, slurry ramjet, and boron solid-fueled ramjet (BSFRJ) programs, funded by AFRPL, AFWAL, DARPA, and NWC. Drs. King and Komar are both active in these programs, providing modeling and diagnostic support in the areas of boron particle ignition and combustion and oxide condensation. As specific examples, Dr. King's ignition analyses are being incorporated in analyses used in design of a boron slurry ramjet combustor and in tailoring of boron solid fuel ramjet formulations.

- (2) Atlantic Research is currently under contract to AFWAL/PORT to do additional analytical and experimental studies, building on work done under this AFOSR contract, in the area of boron oxide/hydroxide condensation.

VI ADDITIONAL INFORMATION

As indicated earlier, we were not successful in obtaining good permeability measurements for the transport of oxygen through a liquid basic oxide film within the resources of this program. Since we feel strongly that attainment of such data and resolution of the debate as to how oxygen and boron meet and react in the presence of an intervening oxide film are vital to understanding of boron particle ignition and to development of strategies for minimizing ignition delay times, Atlantic Research is continuing this effort under an Independent Research and Development (IRAD) Program. It is currently anticipated that this work will be successfully completed by the end of 1986.

ATE
LMED
= 8