AFOSR Scientific Report
AFOSR 67-0933

BEHAVIOR OF ULTRA-SMALL COLLOID PARTICLES

AFOSR Scientific Report

AF 49(638)-1675

June 1967

Department of the Air Force
Air Force Office of Scientific Research (OAR)
Arlington, Virginia 22209

Thiokol
CHEMICAL CORPORATION
REACTION MOTORS DIVISION
DENVILLE, NEW JERSEY

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RMD Project 5522

June 1967

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FOREWORD

This is an annual report on work sponsored by the Air Force Office of Scientific Research under Contract AF49(638)-1675 with Dr. B. T. Wolfson as the AFOSR project monitor.

The research effort was conducted during the period from January 1, 1966 to December 31, 1966 at Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey.

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THIOKOL CHEMICAL CORPORATION
Reaction Motors Division

I. SUMMARY

This program is an investigation of the growth and agglomeration behavior of ultra-small metal oxide particles such as Al_2O_3 or BeO particles which are 10 to 10,000 Å in diameter. The behavior of such particles is of considerable interest in a variety of processes, including particle lag in a rocket nozzle or wind tunnel, air-augmented propulsion using advanced propellants, radiative and impingement heat transfer and ablation giving condensed products. However, even the qualitative behavior of such particles is largely unknown, partly because of theoretical problems but mainly because of experimental difficulties. Results from this program will, for example, provide improved design criteria for rocket nozzles and for the secondary combustion chamber in air-augmented propulsion and also will provide additional insight into radiative heat transfer from particle systems.

Initial work on this program has been oriented toward Al_2O_3 particles. A premixed flat flame at low sub-atmospheric pressures (2-16 torr) was examined as a technique for generating a cloud of Al_2O_3 particles. $Al(CH_3)_3$ and O_2 or air were used. Electron microscopy indicated the formation of 50 and 100 Å diameter particles in the O_2 and air systems, respectively. Extinction and scattering techniques for measuring size and

concentration in situ in the particle cloud were unsuccessful because the cloud was optically very thin at such low pressures. Particle and gas temperatures were measured by radiation and reversal techniques and were both about 2300°K in the second reaction zone, indicating no hot particle - cool vapor problem.

Absolute intensity measurements of the continuum radiation being emitted from the hot particles in the burned-gas zone indicated that no growth of the particles was occurring in the burned-gas zone. The measured absorption coefficient of the molten aluminum oxide, 30 mm^{-1} at 1.5μ, is comparable to that observed for molten sapphire.

II. INTRODUCTION

The behavior of colloid particles which are 10 to 10,000 Å (0.001 to 1 micron) or so in diameter is of interest from a wide variety of viewpoints, including:

a) kinetics of particle formation (nucleation, growth, and agglomeration),

b) thermal and mechanical lag between the particles and a gas stream,

c) heat transfer,

d) emissivity,

e) light scattering and radar attenuation,

f) electron attachment and emission,

g) surface energy,

h) agglomeration between a particle and a wall (i.e., wall plastering).

A list of practical applications would include particle lag in a rocket nozzle, cloud formation and hurricanes, condensation of liquid N_2 drops in a supersonic wind tunnel, and the plastering of B_2O_3 drops onto turbine blades. A particularly intriguing example is colloid propulsion, where a vapor-free beam of charged colloid particles about 30 Å in diameter is required.

The present program was concerned with the growth and agglomeration behavior and the radiative properties of metal oxide particles. The objective

was to obtain information necessary for the formulation of an accurate analytical model for particle behavior leading to improved design criteria for rocket nozzles and wind tunnels and also to provide additional insight into radiative heat transfer from particle systems. The result will be a generalized analytical model for particle behavior, and these results will be applied to tracing particle behavior through a rocket combustion chamber and expansion nozzle.

Results would be particularly applicable to the particle-lag problem in a rocket nozzle. For example, current high-energy rocket propellants often contain metalized fuels, either metals such as Al, B, or Be or compounds such as borohydrides. Such fuels usually give oxide particles in the combustion products. These particles must be passed through the expansion nozzle in order to convert heat to momentum, and an efficient conversion requires negligible thermal lag of the particles in the expanding gas stream. However, with practical systems, particles larger than about 0.5 microns in diameter exhibit significant lag in the nozzle.

The nozzle-lag problem thus can be rephrased in terms of adjusting the upstream conditions in order to avoid the formation of the undesired large particles. Crudely, the particle-formation process can be divided into:

a) nucleation and growth of particles in a flame zone in the combustion chamber,

b) agglomeration of these particles in the aft end of the combustion chamber,

c) growth and agglomeration in the expansion nozzle (the gas is being cooled and thus can condense additional material onto the particles).

In principle, if the nucleation, growth, and agglomeration phenomena and also the flow patterns in the chamber and nozzle were understood, the particle size in the nozzle could be controlled - that is, many small non-lagging particles would be present in the nozzle instead of a few large lagging particles.

In practice, of course, such phenomena are only very poorly understood. Indeed, even a qualitative understanding is usually lacking. For example, in our opinion, heterogeneous combustion often gives particles which are 50 Å or so in diameter. However, with an aluminized solid propellant, Al_2O_3 particles which are 1 to 10 microns or so in diameter have been reported to be present in the products existing from the nozzle.

It can readily be shown that the individual 50 Å-diameter particles could not merely grow to 1-micron particles. *

* Adiabatic flame calculations of typical metalized propellant usually indicate that at least 50% or so of the metal component should condense in the combustion chamber to form particles, and 50% or so thus remains uncondensed. If this remaining 50% deposited onto 50 Å-diameter particles during the expansion cooling in the nozzle, the new particle radius would be 62.5 Å.

Therefore, the mechanism whereby the 1-micron particles are formed would seem to be either (a) agglomeration of many 50 Å particles to form a few 1-micron particles or (b) the direct formation of 1-micron particles in the flame zone. The lag problem thus would be eliminated if agglomeration were inhibited or if the formation process were interfered with and small particles formed.

However, the behavior of ultra-small particles is one of the major current problem areas in chemical physics, partly because the problem is difficult to examine from a theoretical viewpoint but mainly because of experimental problems.

III. PRESENT WORK

This experimental investigation was undertaken for the purpose of studying the behavior of small metal oxide particles, giving particular attention to the growth and agglomeration behavior and the radiative properties of such particles.

A system in which condensation occurred from a gas phase reaction is more suitable than one involving a solid reactant (e.g. the burning of metallic particles), for the complications associated with heterogeneous gas-solid kinetics are avoided.

A low-pressure flat flame was chosen as the particle source. The advantages of such flames are that the flat flame gives one-dimensional temperature and concentration profiles, and the low pressure spreads out the reaction zone.

From these considerations, a low-pressure trimethyl-aluminum-oxygen flat flame producing aluminum oxide particles was selected as the system for study. Previous experimental work with this flame had been done at Thiokol.[1,2] It was found that the flame contains two distinct reaction zones. The emission from the first zone is almost completely that of a continuum with two maxima, one in the visible and the other in the infrared. The emission from the second zone consists of the continuum and

band spectra characteristic of a hydrocarbon flame. It is believed that the formation of aluminum oxides occurs in the first zone and the combustion of the hydrocarbon components occurs in the second zone. Most experimental measurements were conducted with a 2 torr TMA/O_2 flame, for this flame was the most stable and could be run for about 15 minutes without plugging of the burner holes. In addition, some measurements were taken with a 4 torr TMA/O_2 flame and a 16 torr TMA/Air flame. Several of the flame characteristics are given in Table I.

Table I

Characteristics of Investigated Flames

System	2 torr TMA/O_2	4 torr TMA/O_2	16 torr TMA/Air
Fuel/Oxygen Ratio, by volume	0.167 (Stoich)	0.167 (Stoich)	0.167 (Stoich)
Burner Diameter, cm	5.08	5.08	5.08
Cold Gas Velocity, m/sec	14.30	7.15	1.76
Adiabatic Flame Temp, ^{o}K	2520	2617	2240
First Reaction Zone Thickness, mm	3.5	1.75	Not Measured
Second Reaction Zone Thickness, mm	10	5	Not Measured

Growth and agglomeration kinetics of the aluminum oxide particles were to be investigated with emphasis given to extinction-scattering techniques.

Mie theory indicates that the particle concentration and size can be determined if the wavelength of the incident light is of the order of the particle size and if the complex index of refraction of the particles is known. Further verification of the particle size can be obtained by determining the angular dependence of the intensity of scattered light at one or more wavelengths.

The complex index of refraction of aluminum oxide (in the form of sapphire) has been determined from room temperature to the melting point. Although the complex index of refraction of molten aluminum oxide has not been measured, at or near the melting point the imaginary part of the refractive index appears to increase by several orders of magnitude.[3, 4] From a measurement of the concentration and particle size at increasing distances from the burner and a determination of the gas velocity, it would be possible to determine the time dependence of growth and agglomeration. While particle growth is occurring the products of concentration and particle volume would be increasing with distance, and when only agglomeration is occurring it would remain a constant.

The radiative properties of the aluminum oxide particles can be determined from absolute measurements of the infrared emission. From these measurements with appropriate corrections for optical thickness and a knowledge of size and number density, the imaginary part of the complex index of refraction for flame produced aluminum oxide can be determined and compared to the literature values for sapphire.

Due to the lack of knowledge about the imaginary part of the index of refraction for liquid alumina, the wavelength span of the light extinction and scattering measurements were restricted to the visible and ultraviolet, since in this region the imaginary part of the index of refraction is negligible (i.e., the particles behave as scatterers except at a very small particle diameter). Also the real part of index of refraction of solid alumina has a small wavelength and temperature dependency and it is unlikely that it would change with melting. Theoretical extinction curves and scattering curves calculated from Mie theory then could be used for comparison with experimental results.

In order to assist in the understanding of the condensation of aluminum oxide it is also necessary to determine the gas and particle temperatures. It is conceivable that under some conditions the particles would be hotter than the gas as a result of condensation reactions at the particle surface.

Since the absorption coefficient of aluminum oxide remains nearly constant from 1 to 2 microns one should be able to determine the particle temperature from a color temperature measurement.

Gas temperature measurements were to be determined by sodium line reversal and reversal of the aluminum resonance doublet at 3093 and 3082 Å and the OH(0, 0) band head at 3075 Å.

The electron concentration was to be investigated by microwave attenuation measurements.

IV. RESULTS AND DISCUSSION

Extinction and scattering in both the 4 torr TMA/O_2 flame and the 16 torr TMA/air flame were immeasurable, i.e., the flames were better than 99% transparent to visible and ultraviolet light in the reaction and burned-gas zones. This result suggested that the particles are extremely small. In order to confirm this result, particle samples from the burned-gas region were collected on screens and examined under an electron microscope at Stevens Institute of Technology. It was found that particles from the oxygen flame ranged in size from 50 - 100 Å in diameter and those from the air flame were slightly higher, about 100 - 200 Å in diameter (Figure 1).*

Particle size could also be investigated by using a rotating disc mass spectrometer constructed by the Physics and Combustion Laboratory of Thiokol-RMD. However, we feared that obtaining unequivocal experimental data by this technique would require considerable time and money, and mass spectrometry was postponed.

A calculation of the extinction for particles of this size is straightforward since the formulae of Rayleigh are applicable. The extinction is given by

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* Some agglomeration occurred on the sample screen while it was being viewed in the electron microscope.

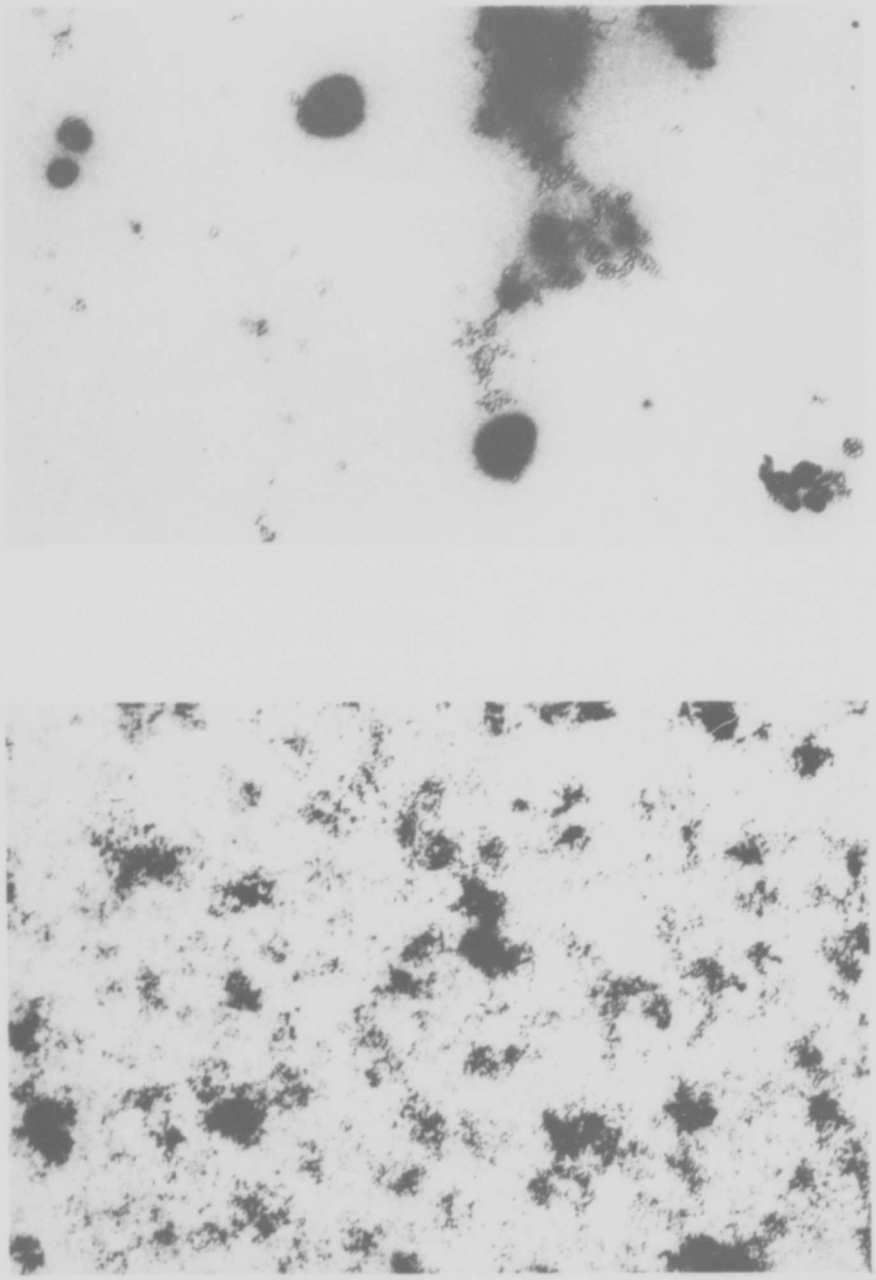

Figure 1. Al_2O_3 Particles from 4 torr TMA/O_2 Flame (bottom) and 16 torr TMA/Air Flame (top) 60,000 x Magnification

$$(1) \qquad \tau = N\pi r^2 (Q_{sca} + Q_{abs})l$$

where τ is the measured extinction, N is the number density of particles, l is the path length, r is the particle radius and Q_{abs} and Q_{sca} are the efficiency factors for absorption and scattering. From the formulae of Rayleigh, we obtain

$$(2) \qquad Q_{sca} = \frac{128\pi^4 r^4}{3\lambda^4} \left| \frac{(n-in')^2 - 1}{(n-in')^2 + 2} \right|^2$$

$$(3) \qquad Q_{abs} = \frac{8\pi r}{\lambda} \; \mathrm{Im} \left\{ \frac{(n-in')^2 - 1}{(n-in')^2 + 2} \right\}$$

where n and n′ are the real and imaginary parts of the complex index of refraction and λ is the wavelength of the incident light.

Assuming complete condensation of the aluminum oxide and literature values for the index of refraction, a calculation of the extinction was made and it was found that the extinction should not be measurable. Moreover, since the scattering is Rayleigh in nature in the present low pressure flames it is not possible to determine concentration and particle size from extinction or scattering measurements, and thus growth and agglomeration kinetics could not be investigated by these techniques.

Attempts were made to increase the pressure of the TMA/O_2 flame and thereby obtain both larger particles and a higher number density. Since

trimethyl aluminum is pyrophoric it was decided to substitute the flat burner with an open end concentric glass tube burner (14 mm in diameter with a mixing length of 10 cm) to explore the behavior of a TMA/O_2 flame at higher pressure. It was found that the higher-pressure flames were unstable, and at 20 torr spontaneous reaction of the TMA and oxygen occurs in the burner tube. The same behavior was observed in the flat flame burner although the pressure for spontaneous reaction was lower (about 10 torr).

Absolute infrared emission measurements were taken in the 2 torr TMA/O_2 flame from the second reaction zone to a height of 50 mm above the burner. The spectral shape of the continuum emission from the second reaction zone is given in Figure 2. The intensity of the emission in the burned-gas region was too low to permit a determination of the spectral shape in this region. However, a plot of the spectral radiance at 1.58 microns versus distance is given in Figure 3. A similar plot for the 4 torr flame is given in Figure 4.

The spectral radiance measurements can be related to the optical properties of the flame produced aluminum oxide in the following manner.

Secondary scattering is certainly small in the flames studied. From Kirchoff's law we obtain

$$(4) \qquad E\lambda = \frac{N_f\lambda}{N_{bb}}\lambda = \left(1-e^{-\tau}\right)\left(\frac{Q_{abs}}{Q_{abs}+Q_{sca}}\right) = \left(1-e^{-N\pi r^2\left[Q_{abs}+Q_{sca}\right]}\right)\left(\frac{Q_{abs}}{Q_{abs}+Q_{sca}}\right)$$

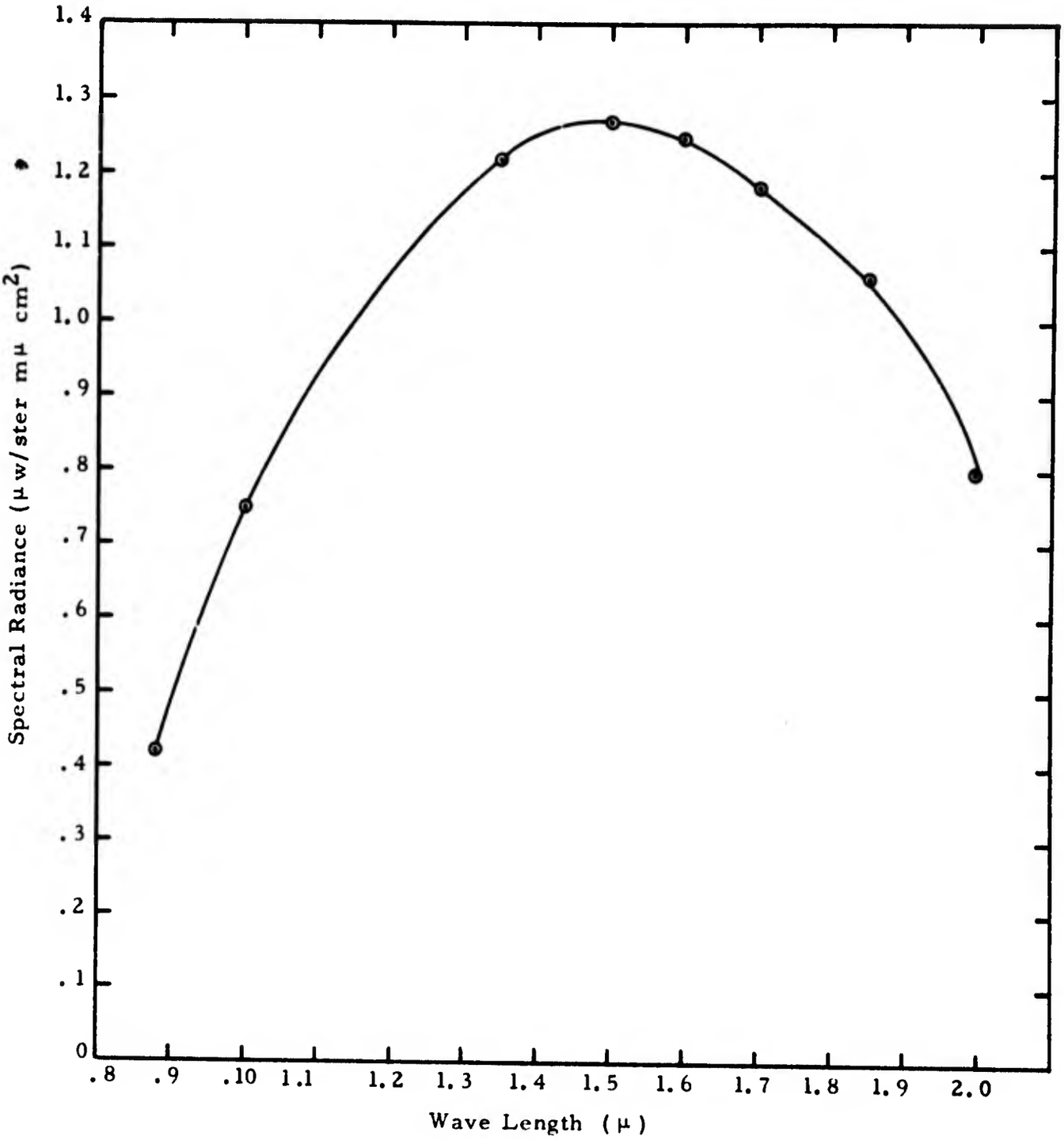

Figure 2. Spectral Shape of the Continuum in the Second Reaction Zone for a Stoichiometric 2 torr TMA/O_2 Flame (6.4 mm from Burner Rim)

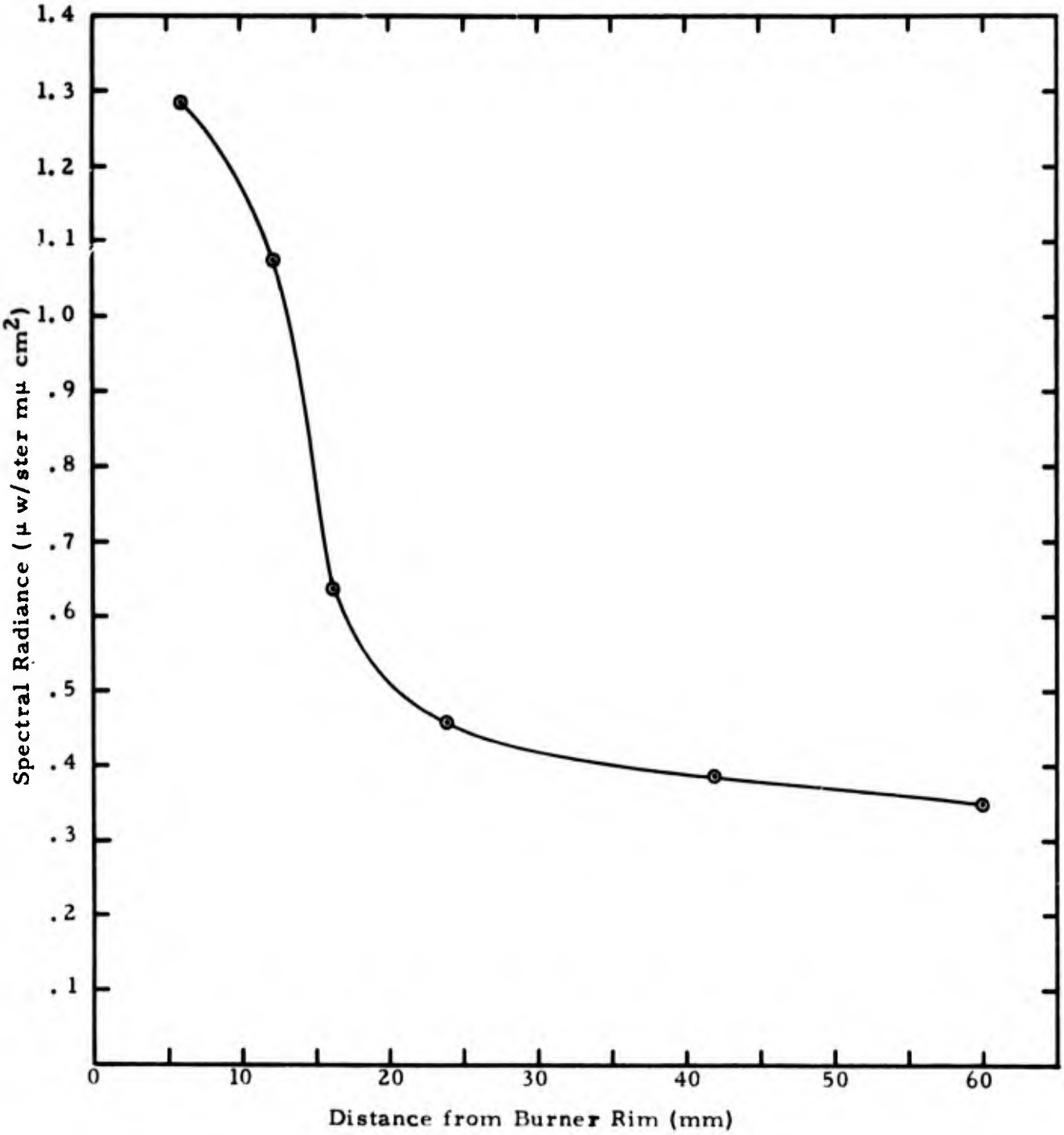

Figure 3. Spectral Radiance Profile of the Continuum at 1.58 Micron in a Stoichiometric 2 torr TMA/O_2 Flame

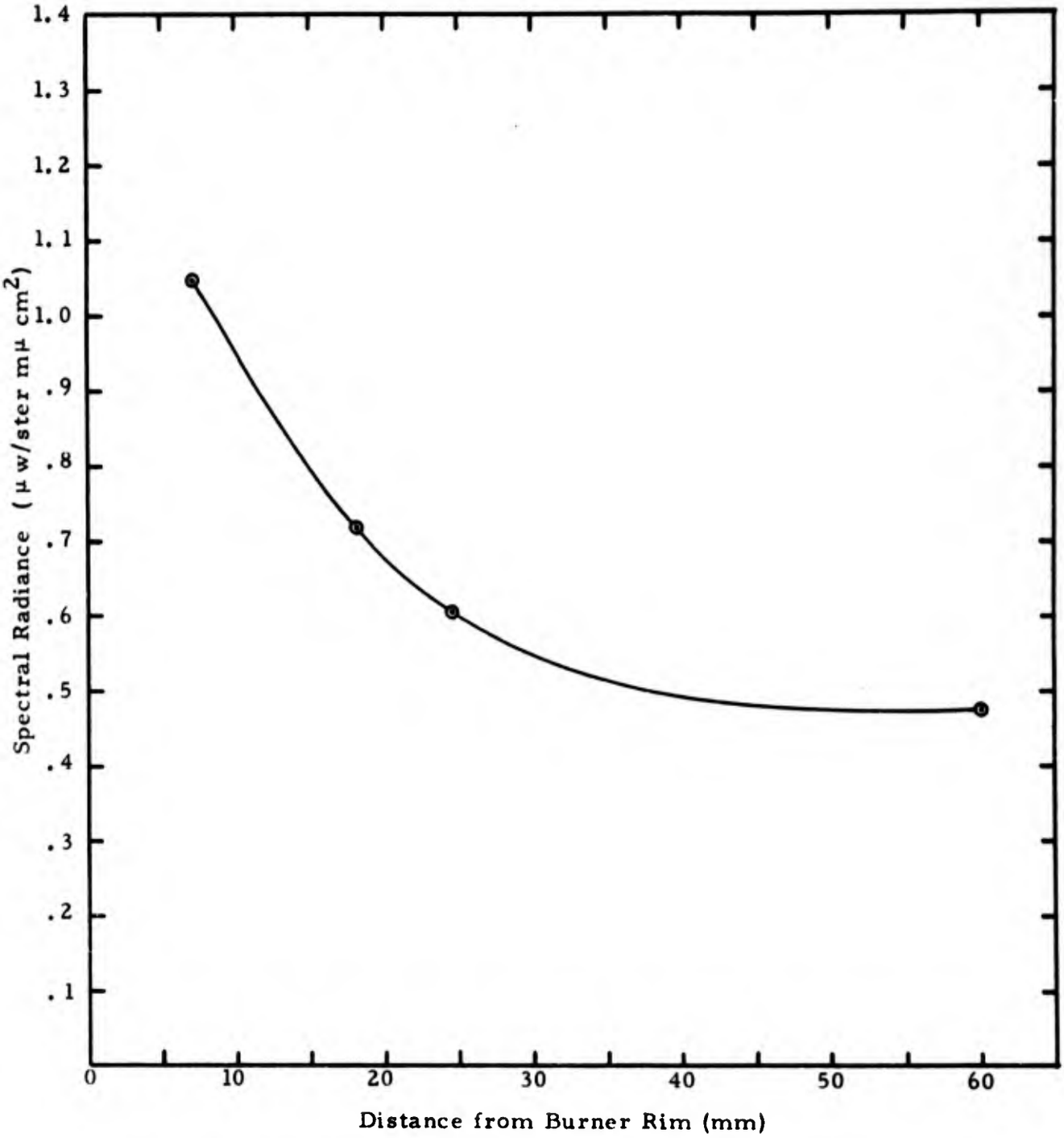

Figure 4. Spectral Radiance Profile of the Continuum at 1.58 Micron in a Stoichiometric 4 torr TMA/O_2 Flame

where $E\lambda$ is the spectral emissivity of the flame, N_f and N_{bb} are the spectral radiances of the flame and a black body, τ is the extinction, l is the optical path length, Q_{abs} and Q_{sca} are the efficiency factors for absorption and scattering, N is the particle concentration and r is the particle radius.

Moreover, the extinction is extremely small and equation (4) can be expanded to obtain

$$(5) \qquad E\lambda = N\pi r^2 Q_{abs} l$$

The particles are smaller than the wavelength and again using the Rayleigh formula for the absorption coefficient we obtain from equation (5)

$$(6) \qquad E\lambda = \frac{9Vn\gamma l}{(n^2 - n'^2 + 2)^2 + 4n^2n'^2} = \frac{N_f}{N_{bb}}$$

where V is the volume fraction of condensed oxide, and γ is the absorption coefficient of the aluminum oxide (equal to $4\pi n'/\lambda$).

From the data of Gryvnak and Burch it can be seen that the absorption coefficient of aluminum oxide is nearly constant and small in the wavelength region from 1.7 to 2.4 micron.[3] In addition the real part of the index of refraction remains nearly constant in this region.[4] Since this wavelength region is a minimum in the absorption curve of the oxide it is very likely that the emissivity will also remain nearly constant in the liquid phase. Consequently, we would expect that the particle cloud will behave as a grey body in this wavelength region and that a two-color temperature determination will give the actual temperature of the particles.

From a series of two-color temperature calculations using wavelength pairs in the region from 1.6 to 2 microns we obtain a particle temperature of 2300°K ± 100°K in the second reaction zone.

Gas temperature measurements in a 2 torr TMA/O_2 flame based on the sodium line reversal technique are presented in Figure 5. Attempts to obtain temperature measurements by reversal of the aluminum resonance doublet and the OH band were not successful. Reversal could not be obtained with the ultraviolet-tungsten lamp operating at a temperature of 2600°K, indicating that these species are abnormally excited and not in equilibrium with the translational temperature of the gas. This result places some uncertainty on the gas temperature as determined by sodium line reversal. However, other investigators have observed that the temperature obtained by sodium line reversal is equal to the translational gas temperature in the burned gas region of a flame but usually higher in the reaction zone.[5,6]

An estimation of the temperature drop resulting from radiative heat loss indicates that the temperature drop in going from the second reaction zone to a distance of six centimeters into the burned gas zone would be about 20°K (Appendix B). Thus, it is very likely that the temperature changes are controlled by conductive and convective heat loss to the nitrogen shroud.

Taking the extrapolated portion of the gas temperature curve as a better measure of the temperature in the reaction zone than the sodium line

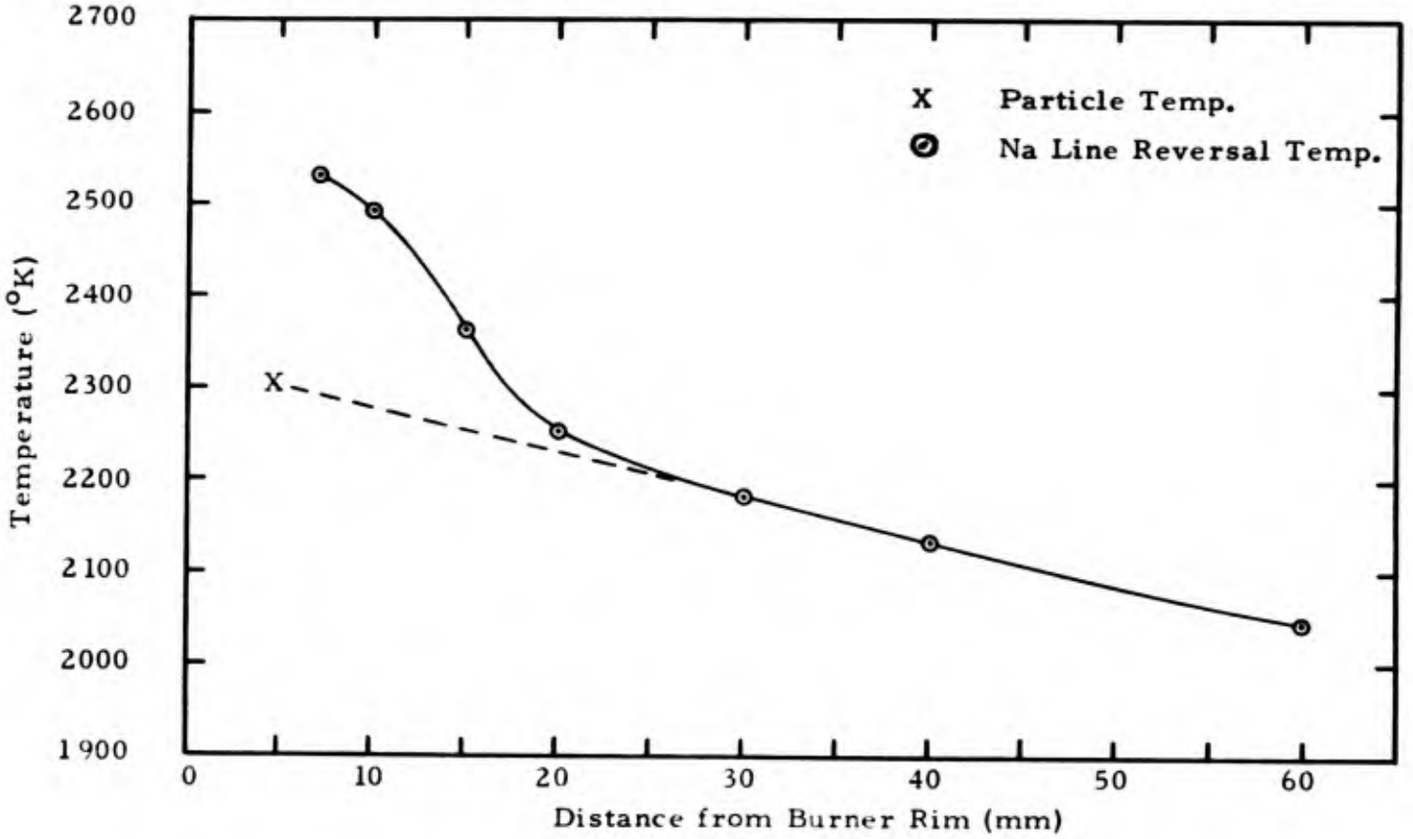

Figure 5. Gas Temperature Profile of Stoichiometric TMA/O_2 Flame at 2 torr Based on Na Reversal Measurement

reversal points, we obtain a gas temperature of about 2300°K in the region where the particle temperature was measured to be about 2300°K. Therefore it appears that there is no great disparity between the particle and gas temperature.

From equation (6) it can be seen that the flame emissivity will be directly proportional to the volume fraction of condensed oxide. Since there is no increase in spectral radiance over the flame regions examined (Figures 3 and 4), it is very likely that the volume fraction of condensed oxide does not increase in going from the second reaction zone to the burned gas zone, i.e., particle growth is completed in the first reaction zone.

Theoretical performance calculations indicated that at the adiabatic flame temperature essentially all the aluminum will exist as the condensed oxide, and therefore the completion of particle growth in the first reaction zone is thermodynamically favorable.

A calculation of the absorption coefficient of the flame produced oxide, assuming negligible loss of alumina by its depcsition on the burner face gives a value of 30 mm^{-1} at a wavelength of 1.5 micron and a temperature of 2300°K. This value is of the order to be expected for aluminum oxide in the molten state and 3 orders of magnitude higher than that for solid aluminum oxide. Therefore, it appears that in the second reaction zone the particles exist as liquid droplets. Moreover, since the radiance does not decrease

drastically over the flame region examined, it must be assumed that complete freezing of the droplets does not occur in the burned gas zone.

The overall reaction time for condensation can be taken as approximately equal to the gas residence time in the first reaction zone, about 70 microseconds.

The attenuation of 1-cm-wavelength microwaves in the first and second reaction zones of a 4 torr TMA/O_2 flame was not measurable. A calculation of the equilibrium concentration of electrons, based on the equilibrium aluminum atom concentration and the Saha equation, indicates that the electron concentration was too low to be detected by the microwave attenuation experiments (Appendix B).

In summary, the experimental results indicate: (1) that complete condensation to liquid aluminum oxide droplets with diameters of about 50 - 200 Å occurs in the first reaction zone of a TMA/O_2 flame, and that complete freezing of the droplets does not occur in the burned gas zone; (2) that the absorption coefficient of flame produced molten aluminum oxide is comparable to that of molten sapphire; and (3) that the temperatures of the gas and particles do not differ appreciably.

V. FUTURE WORK

Due to the recent interest in air augmented combustion our future efforts will be directed towards studying the combustion behavior of metal particles and the mixing kinetics in the secondary combustor of an air-augmented propulsion system.

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VII. APPENDIX

A. EXPERIMENTAL

B. RADIATION HEAT LOSS CALCULATIONS

C. MICROWAVE ATTENUATION CALCULATIONS

A. EXPERIMENTAL

1. Burner

The flat flame burner is made up of a single piece of aluminum as shown in Figure 6. The fuel and oxidizer are premixed through a column of glass beads. The mixture emerges through the burner plate (5 cm in diameter) which is perforated with channels of 1/8 inch diameter at 1/4 inch distance in a square pattern. In order to prevent condensation of the TMA vapor, the burner is heated to a constant temperature of 90°C by means of a water jacket. Ignition was accomplished with plate electrodes fed by a 2 kw transformer. A nitrogen shroud around the burner swept all products from the vacuum vessel and prevented secondary reactions with the environment.

Trimethylaluminum was obtained from the Ethyl Corporation and was used as received. The vendor's analysis indicated 36.7% aluminum and 0.09% chloride. Air, nitrogen and oxygen were obtained in commercial cylinders at 99.8% purity.

The gases were flow rated using conventional rotometers except for the TMA vapor which required a special technique. The TMA was heated to 90°C in the lecture bottle in which it was received. A metal throttle-valve regulated the vapor flow through a calibrated orifice. The orifice and its associated manometers were placed in a 90°C oil bath. All TMA lines were pyrex tubing and had heating wires spiralled around them to provide a

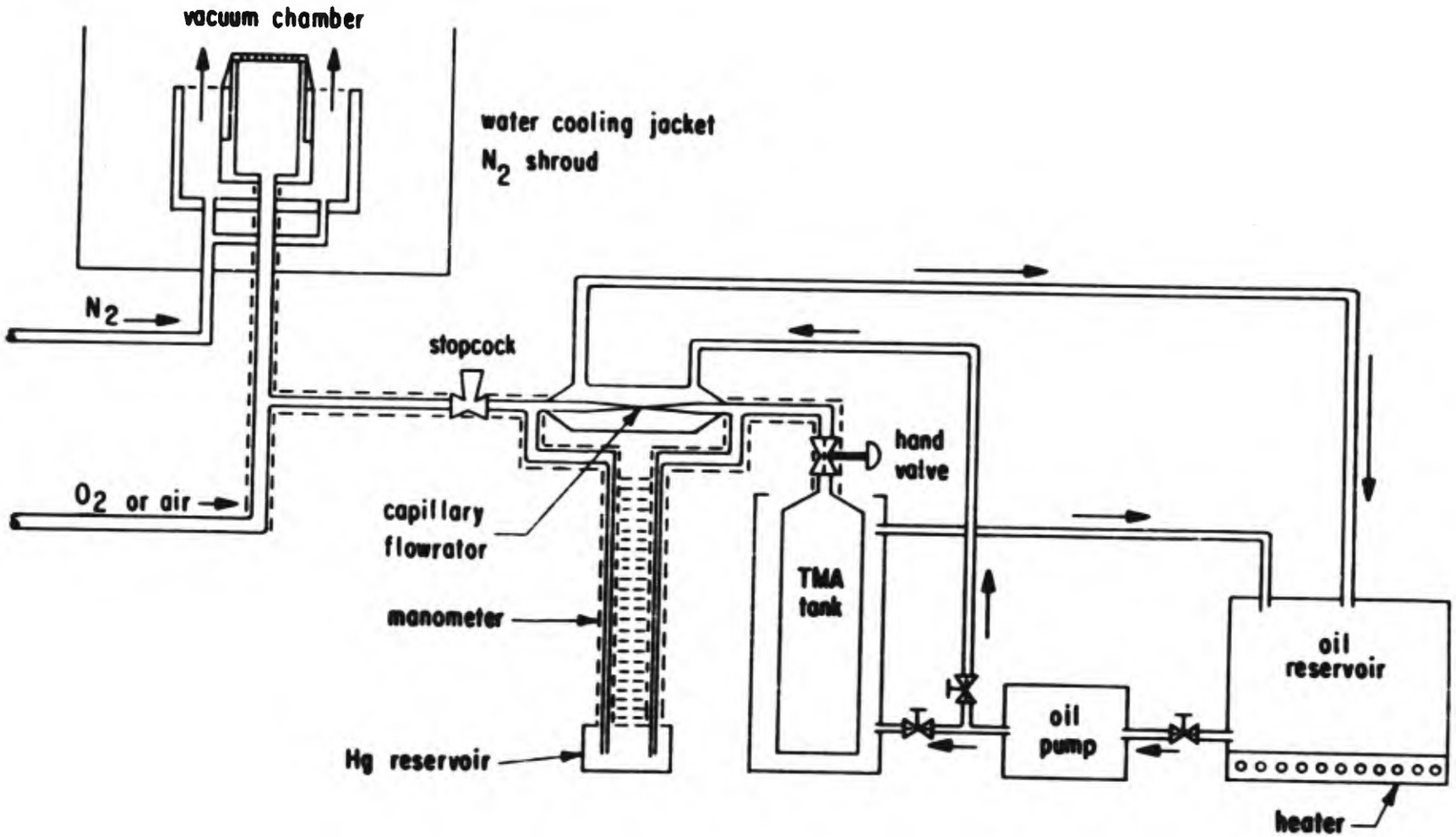

Figure 6. Schematic Diagram of Apparatus for Premixed TMA/O_2 Flame

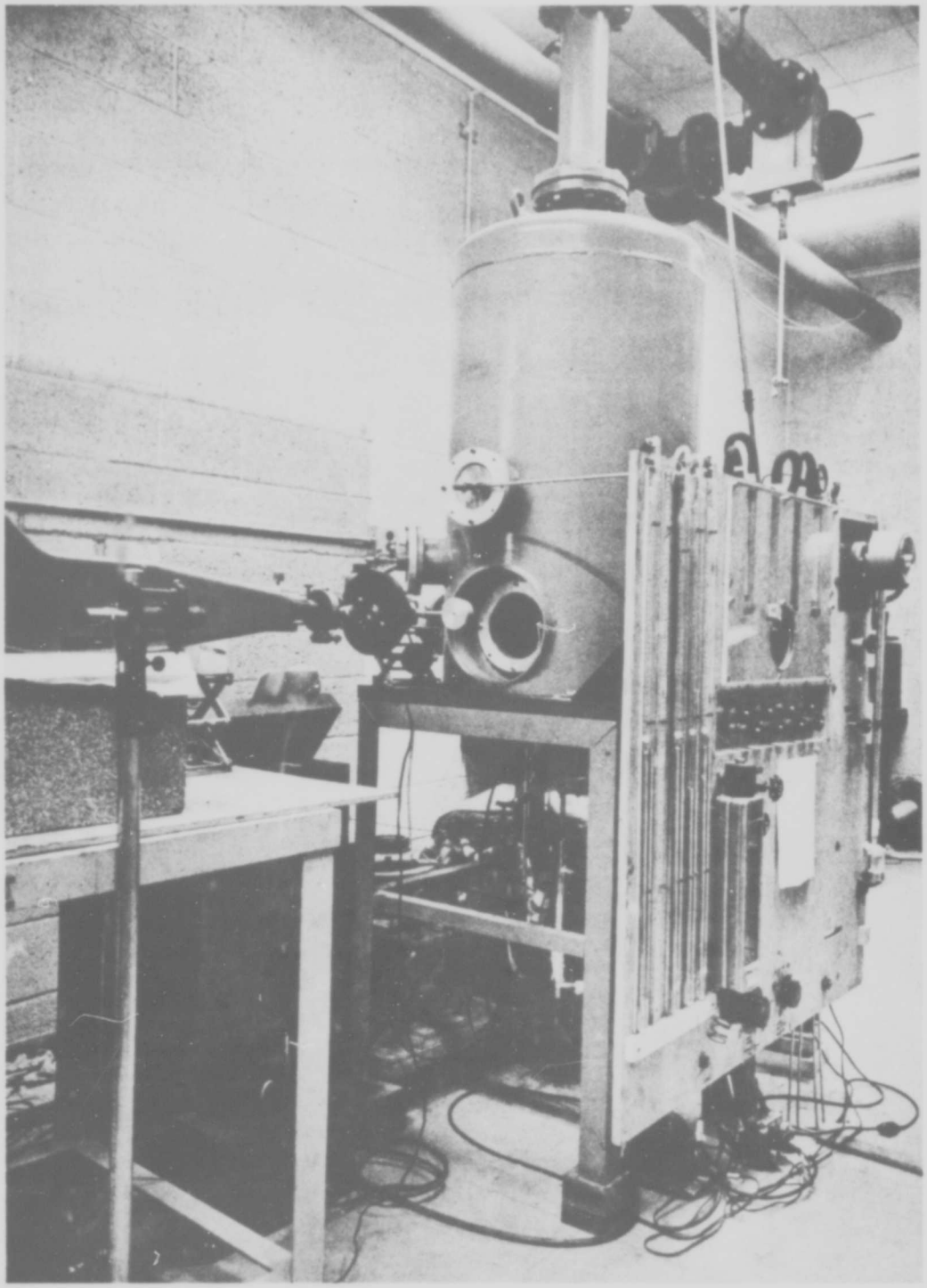

Figure 7. Photograph of Apparatus for Low-Pressure Premixed TMA/O_2 Flame

temperature of at least 90°C throughout the system. The TMA was introduced with the oxygen at the bottom of a 30-cm long aluminum tube leading to the mixing chamber. The vacuum chamber containing the burner is 2 feet in diameter and 4 feet high. The flame was observed through quartz windows. A schematic diagram and photograph of the burner system are given in Figures 6 and 7.

A calibrated vertical driving mechanism attached to the burner shaft permitted easy adjustment and measurement of the distance of the burner edge from the optical axis.

It was found that a trimethylaluminum-oxygen flame could be run at 2 torr for a period of about ten minutes without appreciable plugging of the burner holes. The 4 torr oxygen and 16 torr air flames could only be run for periods of about three minutes. The buildup of aluminum oxide on the burner face interfered with optical measurements of the emission from the first reaction zone. Consequently all axial traverses of the flame begin in the second reaction zone and extend to about six centimeters into the burned gas zone.

2. Extinction and Scattering Measurements

For the extinction and scattering measurements a Hanovia 1000 watt high pressure mercury-xenon arc lamp was used as the light source. The optical system consisted of two quartz achromat lenses with adjustable

diaphragms aligned to give a one to one image to source ratio at the center of the burner and the entrance slit of the spectrometer. The beam diameter at the center of the burner was about 4 mm. A Perkin-Elmer Model 12C Special Spectrophotometer with a fluorite prism, RCA IP28 phototube and Brown recorder was used for detection.

The beam chopper was placed between the light source and the flame in order to eliminate the steady signal due to flame emission.

The extinction measurements consisted of comparing the signal with the flame on and the flame off while the vacuum vessel was maintained at the operating pressure and the nitrogen shroud flow was on. Scattering measurements at 90°C were conducted in the same manner.

3. Infrared Emission Measurements

The optical system and detection system was the same as above except that a lead sulphide cell was used in place of the phototube and the beam chopper was placed between the flame and the spectrometer.

The recorder deflections were reduced to spectral radiance measurements by comparing them to the deflection obtained when a calibrated radiance standard tungsten lamp was viewed through the same optical system. This was accomplished by mounting the spectrometer together with the optical system on a turntable and focusing the image from a lamp placed at the spectrometer exit slit first at the center of the burner and then on the center of the tungsten strip filament. A calibrated neutral density filter was used

to reduce the intensity of the lamp to the level that was obtained from the flame.

A slit height of 2.5 mm and a slit width of 0.12 mm were chosen for the emission measurements. From previous measurements of water and carbon dioxide infrared band emission to ethylene and hydrogen/oxygen flames it was found that with this slit width the spectral windows at 2.2, 1.6 and 1.0 microns are present, i.e., in the vicinity of these wavelengths there was no signal. Thus the infrared particle continuum could be constructed by drawing a smooth curve through these points of the emission spectrum.

4. Line Reversal Measurements

A tungsten strip filament lamp with a quartz window was used as the background source. Spectrophotographs of the light source viewed through the flame were taken with a Wadsworth Jarrell-Ash 1.5 m grating spectrograph. The optical system was the same as for the other measurements. A spectrograph slit height of 2 mm and slit width of 80 μ was used. Alignment was accomplished by focusing the image of a lamp placed at the spectrograph plate holder first on the center of the burner and then at the center of the lamp strip filament. The spectrograph reception cones of light from the lamp and from the flame were the same.

For the aluminum and OH reversal measurements a Corning 7-54 filter was placed in front of the spectrograph entrance slit in order to

eliminate all visible radiation. For the sodium reversal measurements a Corning 3-74 filter was used to eliminate ultraviolet radiation. The sodium was introduced into the flame from a borax bead at the center of the burner.

5. Particle Sampling Techniques

Particles were collected on 1/8" copper screens upon which is deposited a carbon film. The screens were mounted at the bottom of a cylindrical metal container which had a small opening at the top. This container was attached to an aluminum rod and could be pushed into the center of the flame in the burned gas region and quickly withdrawn. The screen was held vertical except during the sampling. An electron micrograph of a screen that was inside the vacuum vessel during a run but not placed in the flame was taken. There was no evidence of aluminum oxide particles in the photograph, and it was concluded that the method could be somewhat useful to sample the flame produced aluminum oxide particles. However, particle sampling probably only gives an indication of the maximum particle size as agglomeration was observed to occur on the screen.

6. Microwave Measurements

Radio frequency (1 cm wavelength) attenuation measurements were made in the reaction zone of a 4 torr flame using a focused beam system. Maximum sensitivity of the system was such that a signal level change in the order of 0.05 db could be detected. The system was calibrated under vacuum

conditions with a calibrated, variable precision RF attenuation. The 6-inch diameter dielectric lens system produced a beam diameter, over the center of the burner, of one inch. Previous lens calibrations have shown that 95% of the RF energy is contained within the 1-inch diameter beam.

B. RADIATIVE HEAT LOSS CALCULATIONS

An estimation of the temperature change due to radiative heat loss can be obtained in the following manner.

From integration of the infrared spectral radiance curve (Figure 2) we obtain a particle radiance of about 2.2×10^{-4} cal/sec ster cm^2 in the second reaction zone of the 2 torr TMA/O_2 flame.

Since the field of view is narrow and the flame is optically thin we can determine the particle emission per unit volume from the following equation.

$$E_i = \frac{4\pi N_p}{l} = 5 \times 10^{-4} \text{ cal/cm}^3$$

where E_i is the particle emission per unit volume of gas in the second reaction zone, N_p is the particle radiance, and l is the optical path length (equal to the burner diameter). From the Stefan Boltzmann law we can write

$$E_i = k(T_i)T_i^4$$

where T_i is the particle temperature in the second reaction zone and k is proportional to the gas emissivity which in turn is a function of temperature but is here assumed to be constant. We can then write for the time rate of particle temperature change

$$\frac{dT}{dt} = \frac{E_i T_i^4}{T_i^4 N_{Al_2O_3} C_{Al_2O_3}} = \frac{15 E_i R T^5}{P C_{Al_2O_3} T_i^4}$$

where $N_{Al_2O_3}$ is the molar concentration of Al_2O_3, R is the gas constant and $C_{Al_2O_3}$ is the molar heat capacity of Al_2O_3, T is the temperature in ^oK, and P is the pressure. The rate of temperature change with distance is given by

$$\frac{dT}{dt} \cdot \frac{dt}{dd} = \frac{dT}{dt} \cdot \frac{1}{V(T)} = \frac{14E_i T_c R T^4}{P_c Al_2O_3 V_c T_i^4}$$

where V_c and T_c are the velocity and temperature of the cold gas and d is the distance. It is assumed that the divergence of the gas flow in the burned gas region is negligible and that the pressure is equal to the chamber pressure.

For the 2 torr TMA/O_2 flame we obtain the following equation

$$\frac{dT}{dd} = \frac{-3.3T^4}{T_i^4}$$

and by integration of the above

$$T = \left(\frac{T_i^4}{1.1\Delta d + T_i} \right)^{1/3}$$

where Δd is the distance from the point where the temperature is T_i. From the above with T_i equal to 2300^oK it can be seen that in a distance of 6 cm the particle temperature drop will be about 20^oK.

A similar equation can be developed for the radiative heat loss from the gas.

Since the intensity of the water bands near the continuum maximum are about equal to that from the continuum the emission from the gases is taken to be roughly equal to that from the particles.

We then obtain the following approximate equation for the rate of gas temperature change with distance (assuming an average molar heat capacity of 9 cal/mole for the gas).

$$T = \left(\frac{T_i^4}{.166\Delta d + T_i} \right)^{1/3}$$

Again we see that the temperature drop due to radiative heat loss over a distance of six centimeters would be negligible.

Thus, it is very likely that the particles and gas are in equilibrium and that the temperature drop is mainly due to conductive and convective heat loss to the nitrogen shroud.

C. MICROWAVE ATTENUATION CALCULATIONS

An estimate of the equilibrium concentration of electrons in a TMA/O_2 flame at 4 torr can be obtained from the Saha equation

$$\log K = \log \frac{X^2}{1-X^2} \quad P = \frac{-U}{4.573T} + \frac{5}{2} \log T - 6.49 + \log \frac{gAlge}{g_{Al}}$$

where K is the equilibrium constant, X is the fraction of initial amount of Al which ionized, P is the sum of the partial pressure of Al, Al+, and e, U is the first ionization potential of Al, T is the temperature in ^{o}K, g_{Al^+}, g_e and g_{Al} are the statistical weights of Al+, e, and Al (1, 2 and 6 respectively).

Using an initial aluminum partial pressure of 7×10^{-7} atm, and a temperature of $2617^{o}K$ (obtained from theoretical performance calculations on the TMA/O_2 system at 4 torr) and a first ionization potential for aluminum of 5.96ev [7], the electron concentration was calculated to be 2.5×10^{10} electrons/cm^3.

The microwave attenuation coefficient is given by the following formula

$$X = \frac{2\pi e^2 n}{mc} \left(\frac{\omega_1}{\omega^2 + \omega_1^2} \right) \sqrt{\mu}$$

where e is the electronic change, c is the velocity of light, n is the electron number density, m is the mass of the electron, μ is the magnetic permeability of the flame gas (approx = 1), ω is the angular frequency of the microwave, and ω_1 is the collision frequency of an electron with the gas molecules.

The collision frequency at 4 torr is about 3.23×10^8 and thus from the above equation we obtain a transmission for 1 cm microwaves of about 99.7%. Consequently, if the electron density is close to the theoretical value the attenuation of 1 cm microwave by the 4 torr flame would be below that which could be measured with our microwave system.

Unclassified

Security Classification

DOCUMENT CONTROL DATA - R & D

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

1 ORIGINATING ACTIVITY (Corporate author) Thiokol Chemical Corporation Reaction Motors Division Denville, New Jersey	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3 REPORT TITLE

BEHAVIOR OF ULTRA-SMALL COLLOID PARTICLES

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)

Scientific Interim

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

Welby G Courtney and Ronald Caruso

6. REPORT DATE December 1966	7a. TOTAL NO. OF PAGES 38	7b. NO. OF REFS 7
8a. CONTRACT OR GRANT NO. AF 49(638)-1675 b. PROJECT NO. 9711-01 c. 61445014 d. 681308	9a. ORIGINATOR'S REPORT NUMBER(S) RMD Project 5522 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) AFOSR 67-0933	

10. DISTRIBUTION STATEMENT

Distribution of this document is unlimited

11. SUPPLEMENTARY NOTES TECH, OTHER	12. SPONSORING MILITARY ACTIVITY AF Office of Scientific Research (SREP) 1400 Wilson Boulevard Arlington, Virginia 22209

13. ABSTRACT

This program is an investigation of the growth and agglomeration behavior of ultra-small metal oxide particles such as Al_2O_3 or BeO particles which are 10 to 10,000 Å in diameter.

Initial work on this program has been oriented toward Al_2O_3 particles. A premixed flat flame at low sub-atmospheric pressures (2-16 torr) was examined as a technique for generating a cloud of Al_2O_3 particles. $Al(CH_3)_3$ and O_2 or air were used. Electron microscopy indicated the formation of 50 and 100 Å diameter particles in the O_2 and air systems, respectively. Extinction and scattering techniques for measuring size and concentration in situ in the particle cloud were unsuccessful because the cloud was optically very thin at such low pressures. Particle and gas temperatures were measured by radiation and reversal techniques and were both about 2300°K in the second reaction zone, indicating no hot particle-cool vapor problem.

Absolute intensity measurements of the continuum radiation being emitted from the hot particles in the burned-gas zone indicated that no growth of the particles was occurring in the burned-gas zone. The measured absorption coefficient of the molten aluminum oxide, 30 mm^{-1} at 1.5μ, is comparable to that observed for molten sapphire.

DD FORM 1 NOV 68 1473

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Aluminum oxide particles						
Absorption coefficient of molten aluminum oxide						
Emission from molten aluminum oxide particles						
Condensation						
Particle growth						
Trimethyl aluminum-oxygen flame						
Extinction of aluminum oxide particles						
Scattering of aluminum oxide particles						