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ARPA Order No. 22-59
TASK 5

TG 331-8
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TASK R

Quarterly Progress Report No. 8

for the period

1 January - 31 March 1961

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TASK R IS A PROGRAM OF RESEARCH IN BASIC PHENOMENA ASSOCIATED WITH THE BEHAVIOR OF MATERIALS IN HIGH TEMPERATURE GAS ENVIRONMENTS. IT IS SUPPORTED BY THE ADVANCED RESEARCH PROJECTS AGENCY THROUGH CONTRACT NORD7386 WITH THE BUREAU OF NAVAL WEAPONS, DEPARTMENT OF THE NAVY.

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THE JOHNS HOPKINS UNIVERSITY
APPLIED PHYSICS LABORATORY
8621 GEORGIA AVENUE SILVER SPRING, MARYLAND

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GENERAL OBJECTIVES OF TASK R

Many of the wide variety of problems associated with the use of materials at high temperatures occur in connection with advanced propulsion systems, and of these, some of the most critical and complex are encountered in high performance rocket motors. Present trends in rocket design and propellant formulation resulting in gas flows of increased temperature, pressure, and corrosiveness may be expected to aggravate the materials situation. It seems self-evident that future, long-range solutions to these problems must rely on more sophisticated approaches and broader knowledge of the behavior of materials in high temperature gas environments than is characteristic of the usual "quick-fix", or expensive cut-and-try test procedures. It also seems likely that improvement in structural materials themselves (i.e., higher strength at high temperature, higher melting point, etc.) has reached the point of diminishing returns, so that various other subterfuges must be tried.

Research performed under Task R at the Applied Physics Laboratory or its subcontracting agencies is intended to provide some of the fundamental knowledge necessary for a rational understanding of the behavior of materials at high temperatures. This is a very broad and very complex field involving many different scientific disciplines. While no attempt is made to rigidly limit the scope of Task R, the general emphasis is on appropriate research in the flow and physical chemistry of high temperature gases such as are characteristic of advanced solid propellant rocket motors, and the phenomena basic to heat transfer and cooling techniques in such environments, rather than in the properties of materials themselves.

A. A. Westenberg
Program Coordinator

SUMMARY

Page

I. High Temperature Chemical Kinetics in Laminar Flames 1

The approach taken in this project is to obtain high temperature chemical kinetic information by means of the detailed analysis of laminar flame structure. Work has continued during this quarter on developing a scavenger probe technique for H-atoms. A preliminary profile of H-atom concentration in a spherical $\text{CH}_4\text{-O}_2$ flame was obtained, as were several results on H-atoms generated in an electrodeless discharge.

II. Thermal Conductivity of Gases 5

High temperature gas thermal conductivity measurements by means of a line source in a laminar flow are being carried out. The technique has now been proven to be reliable, and data on $\text{CO}_2\text{-N}_2$ mixtures are now being obtained. Results on this binary system at room temperature are presented.

III. Rocket Nozzle Fluid Dynamics 9

This project aims at careful experimental measurement of the flow properties in a rocket nozzle employing a typical solid propellant. Some previously noted differences between the experimental and theoretical pressure distribution in the standard 25° nozzle have been studied further and are discussed. Some infrared spectroscopic results have been obtained in the nozzle, both in situ and in gases sampled from the flow.

I. HIGH TEMPERATURE CHEMICAL KINETICS IN LAMINAR FLAMES

(R. M. Fristrom, C. Grunfelder, A. A. Westenberg)

Objective

The effect of chemical reactions is one of the important problems in the dynamics of high temperature, high speed gas flow. Chemistry and aerodynamics (and sometimes molecular transport processes) are strongly coupled in various nozzle flow and boundary layer phenomena. Advances in understanding in these areas cannot be made without a great deal more knowledge of high temperature chemical kinetics than is present available. The important reactions are extremely rapid and lie in temperature regions where materials present problems. Therefore, conventional experimental techniques are not generally applicable, and the extrapolation of information from lower temperature reaction rate studies is not satisfactory. Several experimental techniques have been devised to surmount these difficulties. Shock tube studies are useful for very simple reaction systems. Molecular beam studies of chemical kinetics (inelastic scattering) are in their infancy, but offer interesting and exciting possibilities. The approach taken in this project is to study high temperature kinetics by a detailed quantitative analysis of laminar flame structure. From this analysis it is hoped that eventually the kinetics of elementary combustion reactions can be obtained. The present work allows the determination of the rates of appearance or disappearance of all of the stable species in a flame as a function of position (or time), temperature, and chemical composition. This is the same type of data obtained in conventional kinetic studies, and a much wider temperature range is accessible. Techniques for determining atom and radical concentrations are being developed.

Determination of the Local Concentrations of Atoms and Radicals in Flames

The main problem in the derivation of chemical kinetic constants from flame structure data is the lack of information on the concentrations of radical and atom species. This problem is not unique to flame studies, but in conventional chemical kinetic studies the steady-state approximation is used to circumvent the difficulty. The situation with flames is too complex for this solution and there is considerable doubt as to the validity of the approximations in flame systems. Therefore, we consider this to be an experimental problem. Several techniques have been developed to study radicals in flames (Refs. 1-3), but none of these seemed to offer both analytical reliability and high spatial resolution, so that we have undertaken development of a technique to provide this information. The so-called scavenger probe method combines the techniques of probe sampling with those of chemical scavenging. The principle is straightforward: A sample of the radical-containing gas is withdrawn rapidly so that the composition of the gas is effectively frozen. This can be accomplished by using a properly designed nozzle (Ref. 4) and a fast pump. These radical-containing gases are then mixed with an excess of a scavenger species which reacts quantitatively with the radical to give a characteristic product.

The advantages of this technique are: (1) The analysis is an absolute one (provided sampling and scavenging have been quantitative), (2) there is no interference with other radicals, (3) high spatial resolution may be attained (limited by orifice diameter), (4) high sensitivity

(as high as $1:10^5$), and (5) wide range of temperature and pressure (up to 2000°K and 10^{-3} - 10 cm of Hg). The disadvantages are: (1) Slow response time ($t_{\frac{1}{2}} = 30$ sec) due to adsorption in the flow system at the low pressures and sampling rates employed, and (2) requirement of a separate scavenger for each radical species.

An apparatus has been developed and tested which allows the study of H-atom concentration in flames and electric discharges using this technique. It consists of a tapered quartz probe attached to a modified oil diffusion pump (see Fig. I-1) whose oil (Convachlor 12) also serves as the scavenger. The reaction of H-atom with this chlorinated hydrocarbon yields HCl which may be detected by the mass spectrometer (CEC 21-620).

Sampling should be quantitative because of "frozen flow" in the probe nozzle and short residence time prior to mixing (3 milliseconds). Wall recombination reactions were inhibited by cleaning the glass surfaces with chromic and phosphoric acids (Ref. 5). The scavenging reaction ($\text{H} + \text{C}_n \text{Cl}_{2n+2} \rightarrow \text{HCl} + \text{C}_n \text{Cl}_{2n+1}$) was favored by dilution of the sample in the gas phase ($1:10^4$) and the oil film on the walls. Estimates of the rates of competitive reactions (three-body gas phase recombination and wall recombination) indicate that the scavenging should be quantitative, although proof of this awaits further work.

To test the apparatus a study was made of H-atom concentration in a flame (CH_4 - 9%, O_2 - 19%, A - 72%; P = 3 cm of Hg). The results are given in Fig. I-2. The curve giving H-atom concentration as a function of distance through the flame front appears to be reproducible and reasonable. No comparison has been made between these results and the calculations of

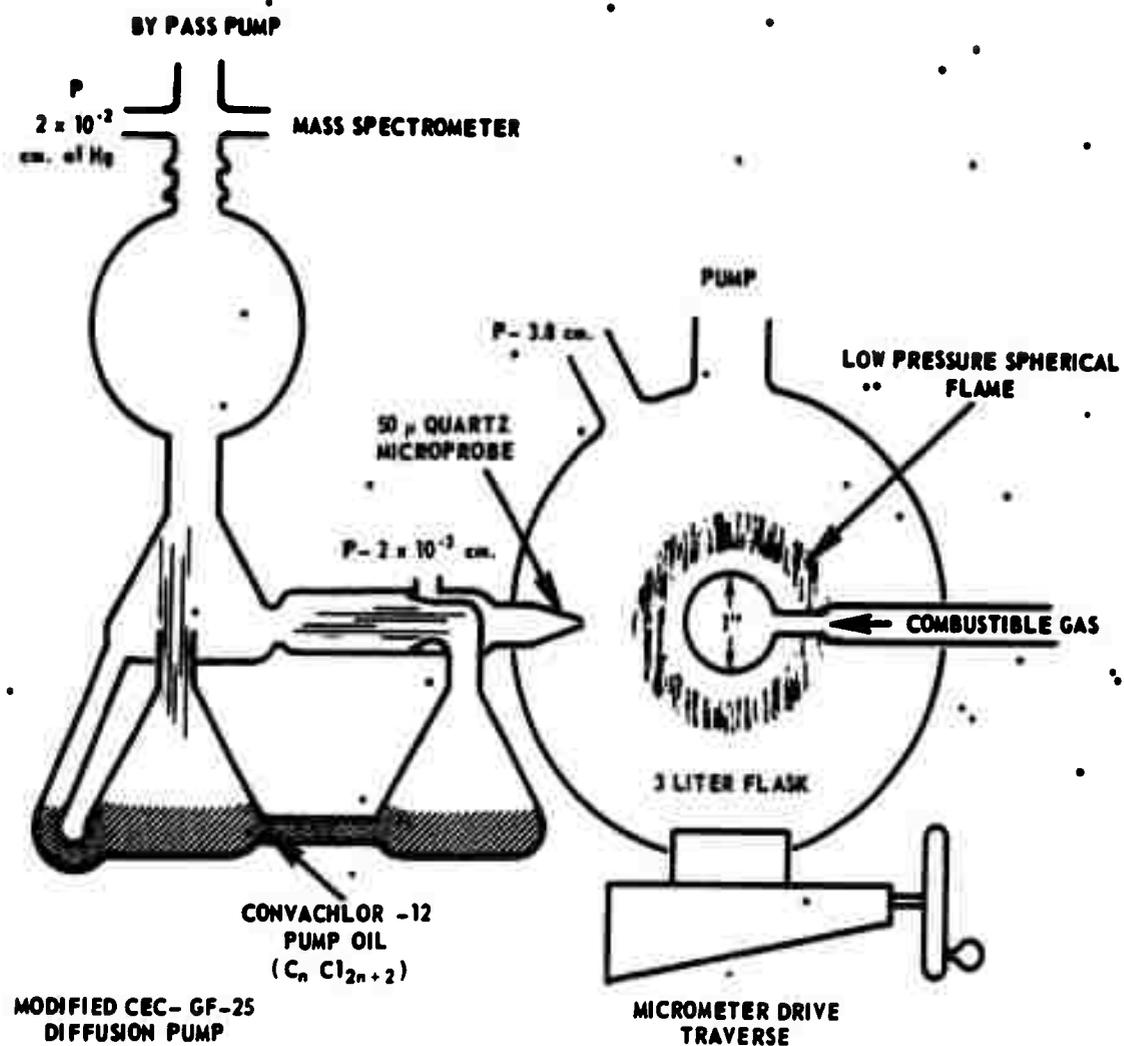


Fig. I-1. SCHEMATIC DIAGRAM OF SCAVENGER PROBE AND SPHERICAL FLAME APPARATUS

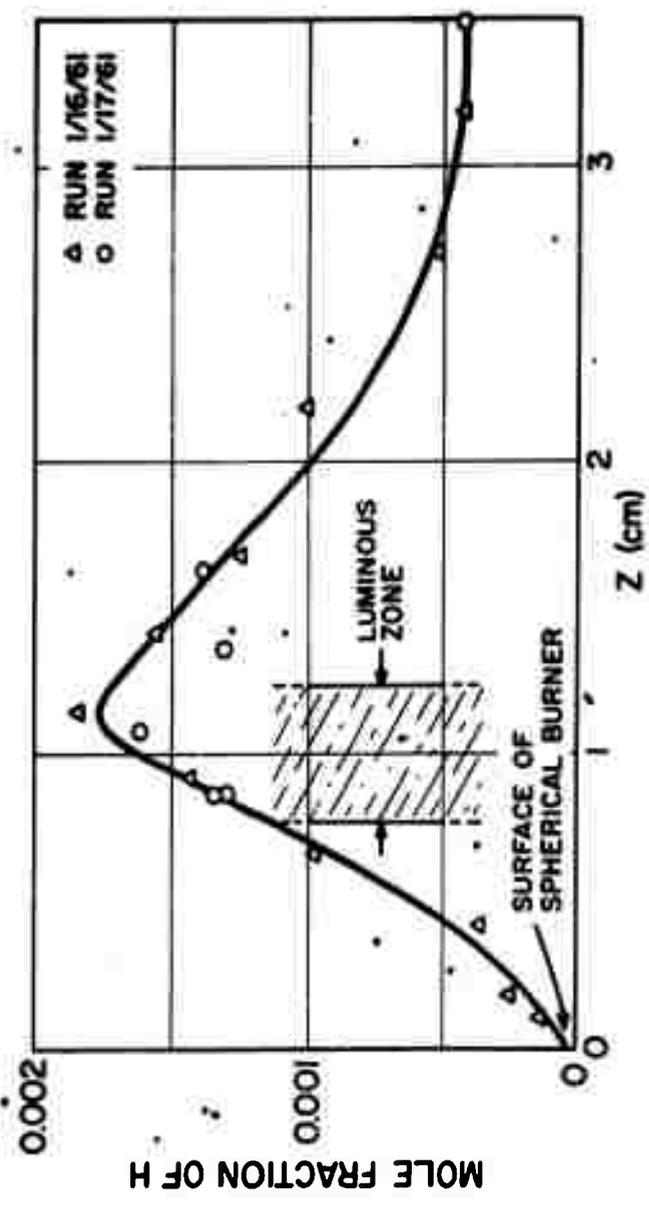


FIG. 1-2: H-ATOM PROFILE IN CH₄ - O₂ - AT SPHERICAL FLAME OBTAINED WITH SCAVENGER PROBE. (PRESS = 3 CM Hg)

concentration of H-atom in the equilibrium flame gases, except as to order of magnitude, because of uncertainty in the initial enthalpy of the flame used (both composition and heat losses were uncertain). To remedy this, a new spherical flame system has been constructed which should allow particularly accurate evaluation of inlet conditions. Quantitative estimates can then be made of radical concentration in the burned gases and the reliability of the scavenger probe system assessed.

A study also was made of H-atom concentration at the exit of a microwave discharge (2 KMc, 100 watts max). The concentration of H-atom was directly proportional to apparent power of the discharge and the mole fraction increased with decreasing pressure. (The maximum partial pressure was obtained at 2 mm.) A traverse downstream of the discharge tube showed the expected exponential decrease in H-atom with distance. The same discharge in pure water vapor evolved large amounts of H_2 and showed similar amounts of H. Adding an excess of methane to the water vapor discharge made the H-atoms (but not the H_2) disappear, presumably the reaction $CH_4 + H \rightarrow H_2 + CH_3$.

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II. THERMAL CONDUCTIVITY OF GASES

(N. deHaas and A. A. Wesenberg)

Objective

The analysis of the problem of convective heat transfer both in the laminar and turbulent flow regimes requires that the properties of the gases involved be quantitatively understood. The coefficient of thermal conductivity is one such property. Measurement of thermal conductivity of gases has not been a forsaken field of research, and several common gases have been investigated up to temperatures approaching reaction motor temperatures. The primary shortcomings of past and present research in the study of thermal conductivity of gases for application to such heat transfer problems are: a) Inability to apply present experimental methods to temperatures above about 1000°K (most measurements are made at substantially lower temperatures than this), b) the complexity and difficulty in using the usual apparatus for this measurement (thermal-conductivity cells), and 3) the lack of measurements of species (and mixtures) prevalent in reaction motors. Other shortcomings could be listed.

Recent measurements of molecular diffusion coefficients - a closely related transport property - of common flame gases at temperatures in excess of 1000°K applied a simple concept (Ref. 1) that could, in principle, be used for measuring other gas transport properties (conductivity and viscosity). In this method, a point source of a trace gas is located in the center of a uniform, heated laminar jet of a second gas. A series of gas samples removed immediately downstream of the source and quantitatively analyzed is used to determine the molecular diffusion coefficient. The technique has good precision (+1-2%) and is quite adaptable to high temperatures and various gas types.

Adaptation of this method to the measurement of thermal conductivity of gases is an obvious extension. The source of trace gas is replaced with a line source of heat and the temperature rise downstream of the heat source is measured with an appropriate technique. The method is simple, should have good precision, and can be used with a variety of gases at high ambient temperature (approaching flame temperatures). Thus, the objective of this research is to develop the line-source technique for the measurement of gas thermal conductivity, and to use the method of obtaining data over a wide range of temperature on pure gases and mixtures of propulsive interest.

Apparatus

A problem noted in previous quarterly reports, viz. a low frequency noise in the differential thermocouple used to measure wake width downstream of the line source, was largely overcome during this period. The noise had been previously attributed to instability in the jet. However, it was finally shown that the D.C. breaker amplifier used to amplify the thermocouple output was contributing a major portion of the apparent instability. This was due to faulty operation of the breaker contacts in the amplifier and was remedied at the factory. The instrument is much improved as a result, and most of the annoying noise has been eliminated.

Various other refinements and improvements in the apparatus have been made. The system of mounting the 0.5 mil platinum wire used for the line source was changed several times. A difficulty noted with the original system was that, although the wire was mounted taut when first installed (i.e., cold), when the necessary heating current was passed

through it tended to loosen, and sometimes was even set into vibration. An alternative mount for the wire was devised which has a slight spring tension (adjustable) incorporated in it, so that the wire is kept taut at all times. Minor changes were also made in the probe mounts for the thermocouples and the hot wire anemometer.

Results

Using the line source technique in its present form (see p. 4, Ref. 2), several check points were obtained on N_2 and CO_2 over a temperature range of several hundred degrees, as shown in Table 1. Values from other investigators are given for comparison. The NBS tabulations are probably the best standard for N_2 . Agreement is seen to be very good.

With this indication that the technique was reliable, measurements of these two gases and their binary mixtures were begun. It is intended to cover as wide a range in temperature as is possible with the present apparatus. So far N_2 - CO_2 mixtures at room temperature have been completed and the data are shown in Fig. II-1. After more data are obtained at high temperatures, the theoretical implications of the results will be examined.

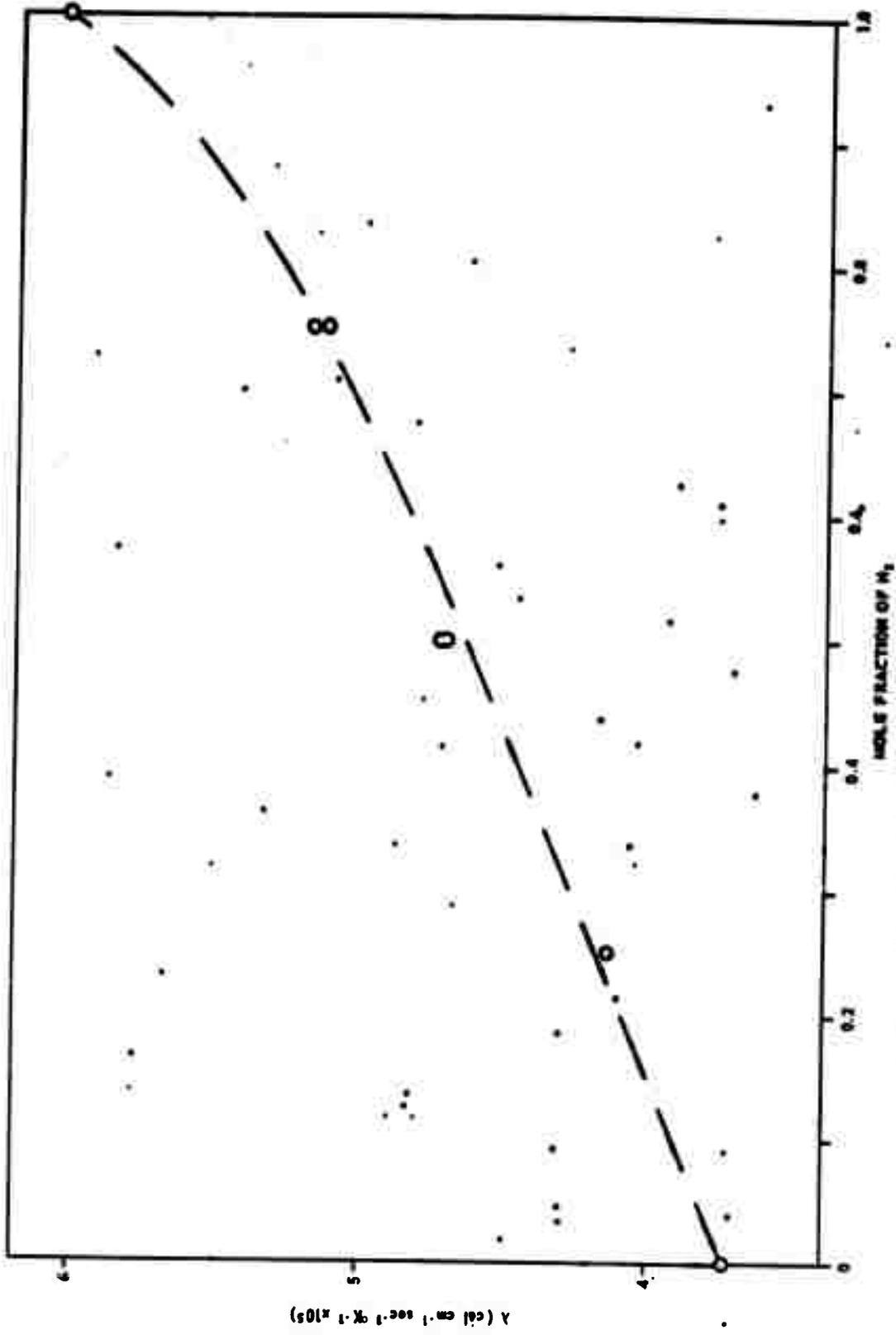


FIG. 11-1. THERMAL CONDUCTIVITY OF CO₂ - H₂ MIXTURES AT 285°K

Table 1. Comparison of measured thermal conductivity for N₂ and CO₂ with results of other investigators.

<u>Gas</u>	<u>T(°K)</u>	<u>λ (cal cm⁻¹ sec⁻¹ °K⁻¹ x 10⁵)</u>
N ₂	295	6.10 This work
		6.14 NBS (Ref. 3)
	502	9.40 This work
		9.50 NBS (Ref. 3)
		9.40 Nuttall & Ginnings (Ref. 4)
		9.20 Johannin & Vodar (Ref. 5)
	773	13.2 This work
		13.1 NBS (Ref. 3)
		13.1 Vines (Ref. 6)
		12.7 Rothman & Bromley (Ref. 7)
CO ₂	295	3.73 This work
		3.83 NBS (Ref. 3)
		3.97 Rothman & Bromley (Ref. 7)
	715	11.7 This work
		12.0 Vines (Ref. 6)
		11.6 Rothman & Bromley (Ref. 7)

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III. ROCKET NOZZLE FLUID DYNAMICS

(F. K. Hill, H. J. Unger, & E. A. Wallskog)

Objective

The dynamics of high-speed gas flows in rocket nozzles has become increasingly important to the efficient utilization of high-energy solid propellants. The flow characteristics of the gas mixture are dependent on the thermodynamic properties of the components and certain time-dependent phenomena such as chemical reaction rates, recombination and condensation. Acquisition of the experimental data required for an accurate description of the gas flow from a relatively simple propellant and rocket nozzle combination has been the first objective.

In order to provide realistic and representative testing conditions for the experiment, a double-base solid propellant (ARP)* has been chosen which provides the basic constituents common to most high-impulse propellants. These are hydrogen, nitrogen, carbon monoxide, carbon dioxide and water vapor. Impurities of the order of 2 to 3% are present as is the case in all propellants and it is possible to add in well controlled amounts and sizes solid particles for future extensions of the experimental studies. To begin with, it is believed advisable to keep the problems as uncomplicated as possible while still retaining the fundamental aspects of the phenomena under investigation. Combustion pressure and temperature of the grain are 1100 psi, nominal, and 2500°K, respectively; end burning is employed for either 10-second or 30-second operation. These conditions are sufficient

* The propellant is manufactured and proof-tested at Allegany Ballistics Laboratory.

to introduce measurable effects due to the variable gas properties as the gas expands through the nozzle, gas non-equilibrium conditions in the expanded flow and heat transfer and nozzle divergence angle effects. Associated phenomena, such as erosion and deposition of solid particles, are also present for observation providing additional data.

It is anticipated that as the work progresses higher specific impulse propellants will be utilized providing temperature in the 3000°K to 4000°K range, and that investigations will be undertaken of the effects of metal additives to the grain and some properties of materials as they are affected by the rocket gases.

Static Pressure Distribution

The previous Quarterly Progress Report (Ref. 1) contained the preliminary results of a test in which the objective was to observe the behavior of the static pressure distribution in the standard 25° nozzle in the region between the throat and a point approximately one inch downstream. This test was undertaken as a result of the analysis and discussion contained in Ref. 2 which considered earlier static and pitot pressure measurements. It was suggested that the disturbances causing the observed departures from predicted behavior may have been the shock waves associated with the reattachment point of a small region of separated flow in the neighborhood of the throat. If the source of trouble was indeed separated flow, it should then be possible to affect its existence or extent by

lengthening the transition section at the throat of the nozzle. With this idea of reducing the flow acceleration in mind, a nozzle was constructed which had a throat profile defined by arcs of larger radius.

The nozzle fabricated for the current tests is similar to the normal 25° nozzle, except for the region around the throat, that is, the transition section between the inlet and exit conical surfaces. The geometry of the modified nozzle is shown in Fig. III-1 wherein it is noted that the throat profile arc radius was increased to two times normal (the standard nozzle has a single arc of 0.770 inches radius) on the upstream side of the throat and three times normal on the downstream side. This nozzle is approximately one-half inch longer than the normal one due to the lengthened transition region. Seven static pressure taps are located at one-quarter inch intervals downstream of the throat.

In the present quarterly period, two tests were conducted using the modified nozzle; the second was simply a repeat of the first to substantiate the data before the nozzle was modified for pitot pressure measurements. The results of these tests are shown in Fig. III-2 along with data from the normal 25° nozzle.

As an over-all comment, it is concluded that the general agreement between theory and experiment is somewhat better for the modified nozzle than for the normal nozzle. There is a striking similarity, however, in that the pressure recorded at the point where the throat profile arc is tangent to the exit cone is substantially lower in both cases. The

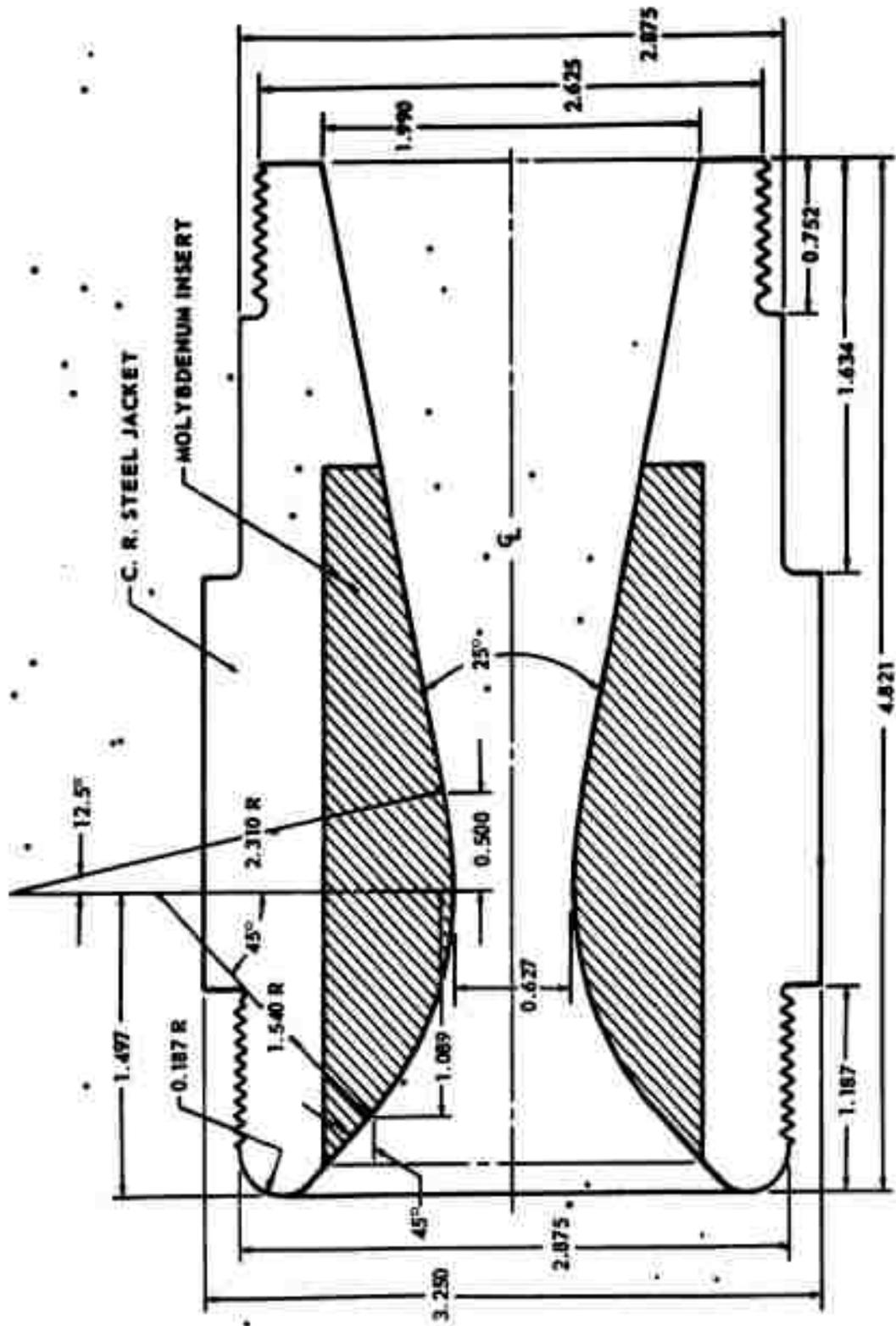


FIG. III-1. GEOMETRY OF THE MODIFIED 25° NOZZLE (UNCOOLED)

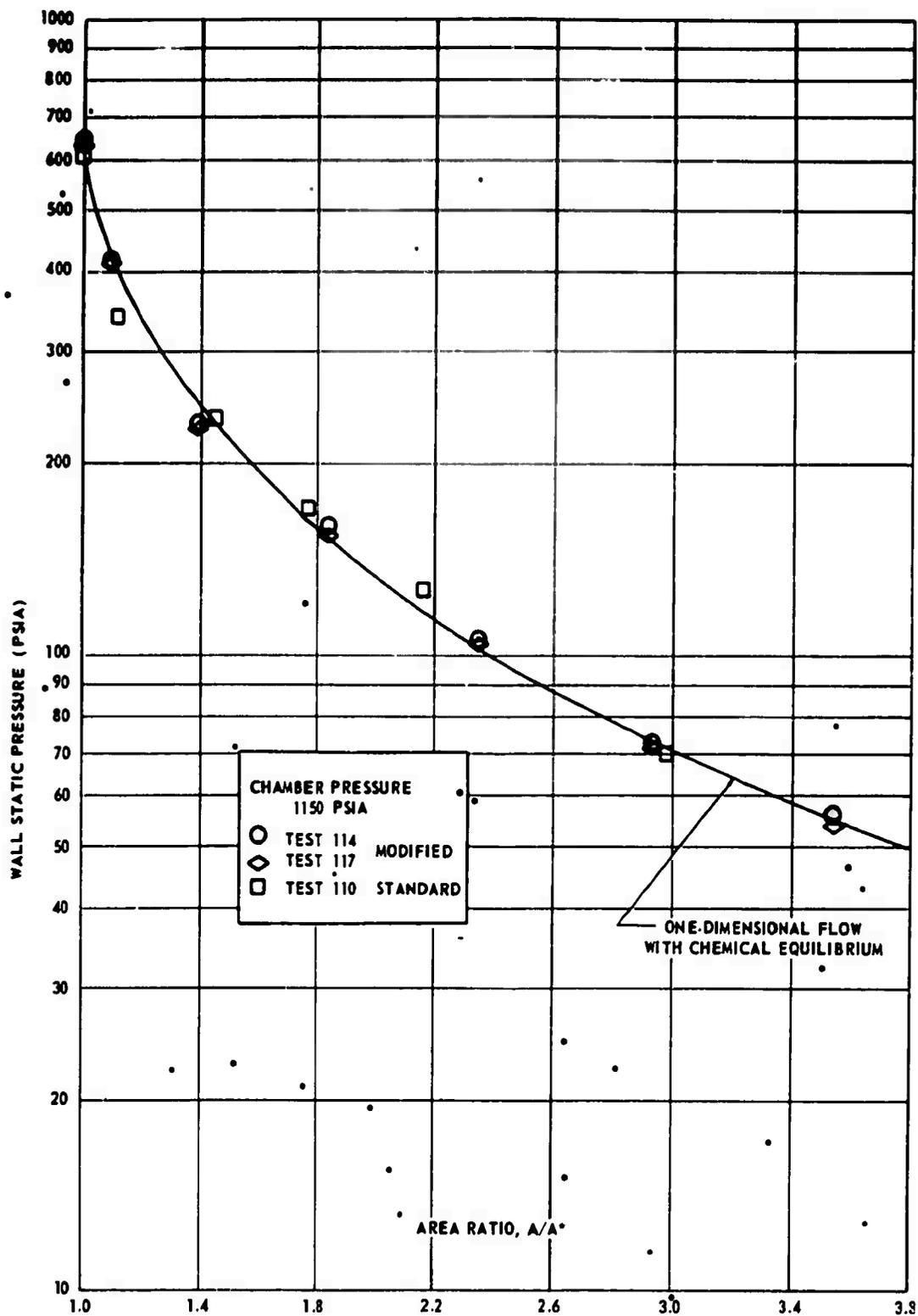


Fig. III-2. STATIC PRESSURE DISTRIBUTION IN THE STANDARD AND MODIFIED 25° TOTAL EXPANSION ANGLE NOZZLES

experimental point is 12% lower than theory in the case of Test No. 110 (unmodified nozzle) and 7% and 10% lower for the modified nozzle. In each case this low pressure region is followed by a region of somewhat higher than anticipated pressures. Assuming that instrument peculiarities did not contribute significantly to the unusual traces obtained, it is concluded that the lengthening of the throat transition region served to eliminate or at least to reduce the region of separated flow. The remaining disparity may be due to a smaller region of separated flow or may be a consequence of transition to turbulent flow in the boundary layer. This latter possibility is considered in the light of visual observation of the nozzle after the run. Inspection of each nozzle showed that a ring of longitudinal striations exist in the region near and downstream of the throat. After the run these striations are quite noticeable to the touch and are made more apparent visually by light polishing. These markings appear to exist farther downstream in the case of the modified nozzle. A normal unmodified nozzle used a single time in an earlier test contained severe longitudinal striations which began abruptly on the upstream side of the throat near the juncture between the inlet cone and the throat profile arc. Wall static pressures measured 3 and 4 inches downstream of the exit of this nozzle were 11% and 29%, respectively, lower than the calculated values using estimated boundary layer thicknesses and the assumption of mixed flow (chemical equilibrium to 1500°K and frozen thereafter). An additional item of interest from this test was that of the measured pressures decreased steadily during the run 10% and 17%, respectively, of the mean values.

The net result of the consideration of these several items leads to the following conclusions: In the region near the throat of the normal nozzle there is separated flow. This separated flow region is either reduced in extent or eliminated by increasing the length of the transition region between the inlet and exit cones (modified nozzle). Assuming that the separation is eliminated in the modified nozzle, the remaining disparity may be the consequence of transition of the boundary layer to turbulent flow.

While turbulent boundary layers might not be expected in these circumstances, the possibility is admitted because of the discontinuity in the second derivative of the nozzle profile. Transition to turbulent flow of the boundary layer in the neighborhood of the downstream discontinuity in the second derivative would produce a weak shock wave much in the same manner as the reattachment of a separated flow region and, thus, could also "explain" the irregular pitot pressure profile measured at the one-inch-diameter station. This possibility will be investigated by using in the modified nozzle two pitot probes for measuring pressure; one of the probes will be on the centerline and one midway toward the wall.

In the case of the normal nozzle, it is felt that the separated flow picture is accurate for two reasons: First, the existence of separation at the throat produces a smaller critical area $(A)^*$ which in turn produces area ratios larger than would be calculated on nozzle geometry considerations alone. Thus, the measured static pressures can

be substantially lower than calculated, which is in accord with observation. Second, the increasing wall temperature at the throat causes a reduction in the heat transfer which results in the separation region increasing with time. Records of wall static and pitot pressures nearly always show decreasing values with time; indicating that the effective area ratio (A/A^*) is increasing with time.

One question which remains unanswered at present is why the pressure at the downstream tangent point is substantially lower than predicted, while the pressure immediately upstream is in agreement and immediately downstream is somewhat higher than predicted. This single fact might suggest that a small region of separated flow still exists in the throat area of the modified nozzle. The lowering of downstream static pressures due to the reduction in effective throat area (A^*) is compensated by the pressure rise due to shock waves and thus the individual effects are not obvious. The magnitude of the pitot pressures to be measured at the one-inch-diameter station should shed some light on the subject.

Auxiliary Settling Chamber

In view of the occasionally severe erosion experienced by probe tips, it appeared desirable to interpose an auxiliary chamber between the combustion chamber and the nozzle-test section. This auxiliary settling chamber would serve the dual purpose of providing a large volume so as to reduce the turbulence level which is probably quite high under normal circumstances, and of providing a means of trapping at least the larger particles which normally flow downstream. These considerations led to the

arrangement shown in Fig. III-3. Since two combustion chambers were available, it was convenient to utilize the second one as part of the auxiliary chamber. The downstream two-thirds of the auxiliary unit is a normal combustion chamber and therefore provides the same inlet conditions to the nozzle. Earlier tests using the two-color radiation pyrometer to observe throat temperatures indicated that perhaps the output was being influenced by extraneous light reflections from the propellant flame. An incidental advantage of the present arrangement is that it provides an effective light shield between the burning propellant and the nozzle throat region.

A recent test of the auxiliary chamber indicated that significant quantities of solid particles were trapped on the central portion of the molybdenum cup which faces the jet issuing directly from the combustion chamber. This deposition is shown in the photograph of the molybdenum cup (see Fig. III-4). In addition to this hard, granular deposit, it appears that a metallic element was collected on the cylindrical part of the cup near the lip. This is most likely a condensate since the cup would undoubtedly remain quite cold relative to the gas. The interior of the upstream end of the auxiliary chamber is shown in Fig. III-5 as it appeared after the run with the cup removed. A small blunt-nosed centerbody had been used in earlier tests involving the 4-inch test section and was observed to suffer severe erosion in the neighborhood of the stagnation point. For this test this same centerbody was repolished and installed in the usual position in the test section. The end of the probe was blackened, but showed practically no signs of the sand blasting type erosion previously found.

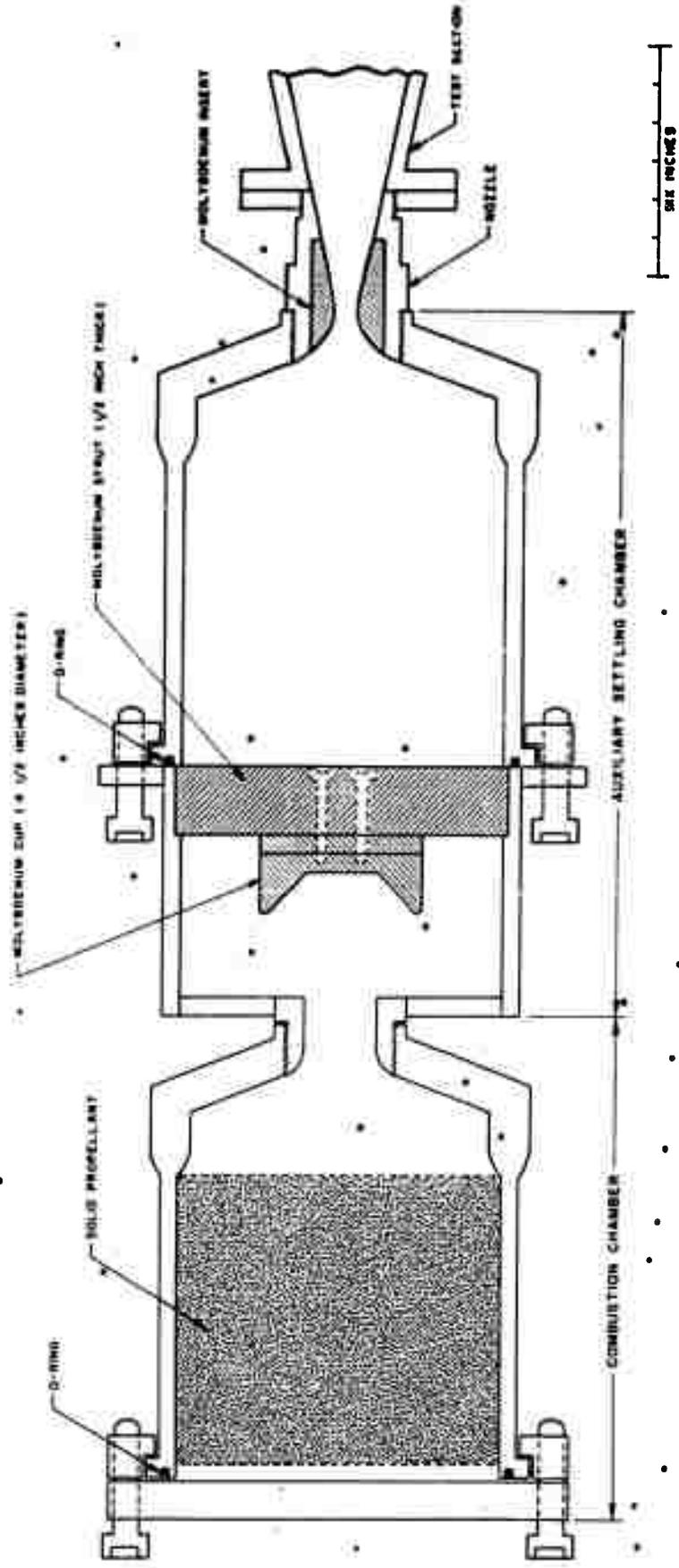


FIG. III-3. ARRANGEMENT OF THE ROCKET WIND TUNNEL,
 INCLUDING THE AUXILIARY SETTLING CHAMBER



Fig. III-4. POST-RUN VIEW OF THE MOLYBDENUM CUP FROM
THE AUXILIARY SETTLING CHAMBER

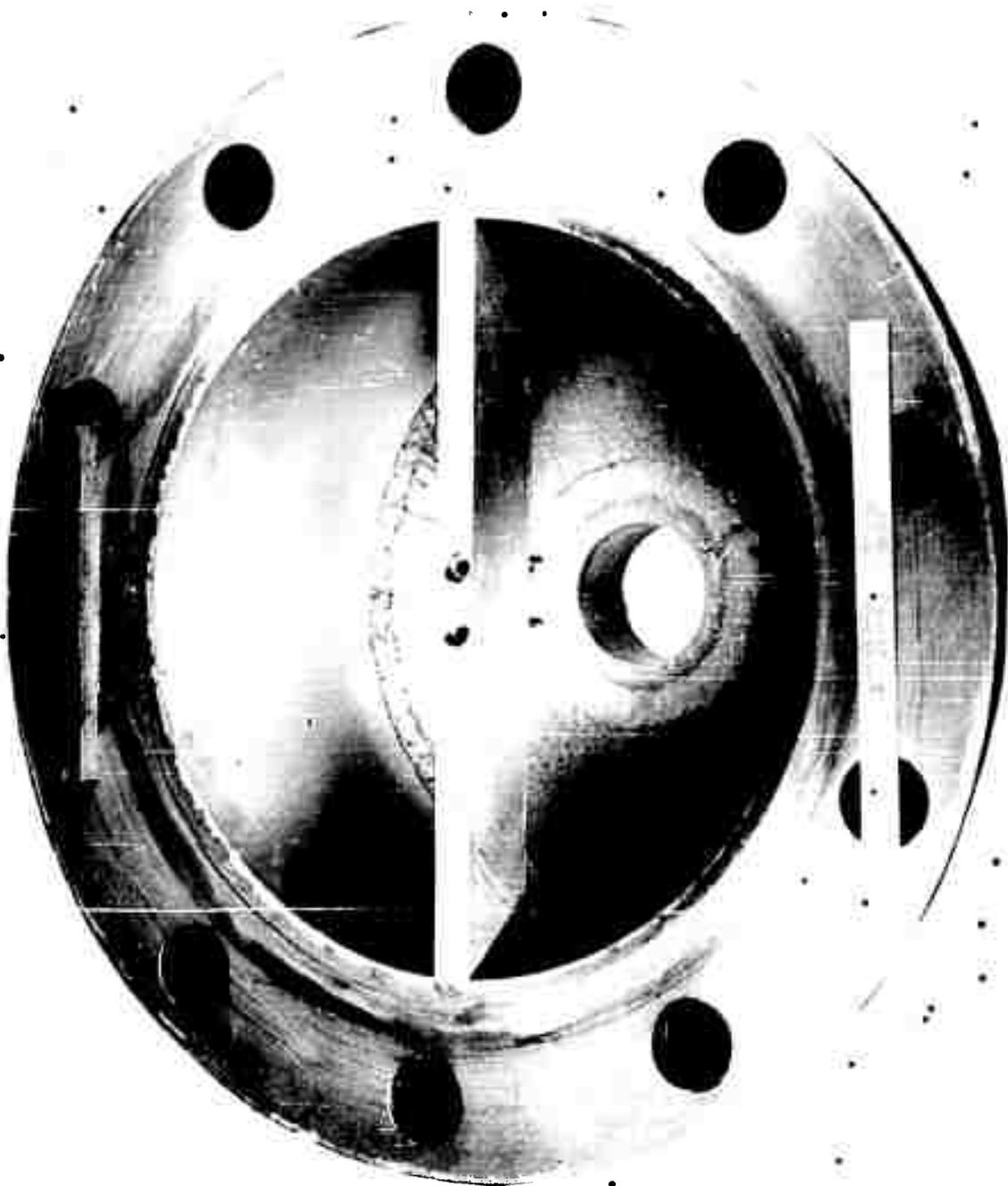


FIG. III-5. POST-RUN VIEW OF THE INTERIOR OF THE UPSTREAM END OF THE AUXILIARY SETTLING CHAMBER (MOLYBDENUM CUP REMOVED)

Spectrographic Development

The preliminary tests made with the new infrared absorption spectrometer and described in the previous report (Ref. 1) showed that several changes were desirable before giving it a shakd-down test on the high-temperature, rocket-powered wind tunnel. The Perkin-Elmer Model 83 monochromator which has been modified to scan a limited spectral range of 4-7 μ at 5 cps was found to perform very satisfactorily, but the electrical resolution was lower than the spectral resolution. Over-all resolution was poor as shown by the pictures of the 2.7 μ H₂O vapor and CO₂ bands in Ref. 1. In order to correct this difficulty, a number of changes could have been made such as increasing the chopper rate, widening the video amplifier pass-band and decreasing the sweep rate of the Littrow mirror. To change the chopping frequency would have been a major problem since it had already been raised from 990 to 1980 cps by installing a 3600 rpm synchronous motor. Further increase would have involved increased chopper size and/or gearing changes.

The resolution problem was solved finally by doing two things: slowing down the spectral sweep rate and broadening the video band-pass. The sweep rate was changed in two ways: by increasing the cam rotation time from 0.17 sec to 0.83 sec and using a sawtooth instead of a sinusoidal sweep for the mirror. The mirror cam was cut to give a nearly linear wavelength sweep during 300° of a revolution and a smooth inflection curve return in 60° to prevent shocking the mirror. The video amplifier band-pass was made 600 cps and Fig. III-6 shows the air absorption in the total light path, 100", of the spectrometer. The 4.2 μ CO₂ band and the 6.2 μ water vapor band are shown with good resolution for this monochromator. This spectrogram was taken with a Polaroid camera on a

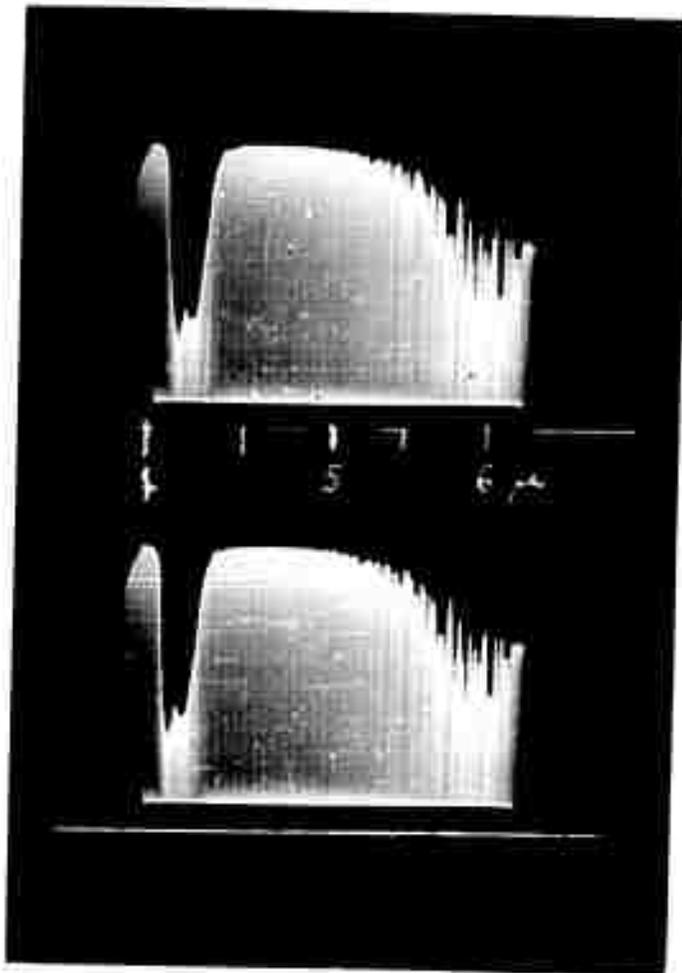


Fig. III-6. .ATMOSPHERIC ABSORPTION FOR A PATH LENGTH OF 100 INCHES
Spectral region, 4.0 to 6.5 μ ; P-2, 5" C.R.O. screen;
Fixed camera sweep time, 0.83 seconds

5-inch oscilloscope with a P-7 screen. The video signal has not been blanked as shown in Ref. 1, because the solid background seems more realistic for portraying absorption spectra. For visual observation, the contrast seems better with this type of presentation.

When continuous monitoring is desired, as in an actual test run, it has been found advantageous to use an oscilloscope with a P-11 (short persistence) screen and not to sweep the beam horizontally. The horizontal presentation as shown in Fig. III-7 was obtained with a Dumont Model 321 continuous feed camera using 35 mm movie film at a speed of 200 in/min. Inadvertently, the oscilloscope has a built-in timer in the form of a 60 cps modulation on the beam intensity. This modulation is shown clearly in Figures III-7 thru III-12 and numerous counts have shown the sweep time to be $50/60 \text{ sec} = 0.83 \text{ sec}$. The return sweep time is $6/60 \text{ sec} = 0.10 \text{ sec}$ which gives an effective scanning time of 0.73 sec. Since the nominal running time for the wind tunnel is 10 seconds, this gives twelve spectra on 33 inches of film, which makes processing of the data film easy as well as economical.

For visual observations and display purposes, a 21-inch I.T. and T. oscilloscope has been used with a P-7 screen. The spectra obtained are very impressive and this spectrometer would be useful in observing and monitoring certain chemical reactions. It would also be a valuable teaching aid.

The programmed slit feature of this spectrometer has not been used to date because fixed slits have been adequate with the AuGe detector in the 4-6.5 μ region. Figure III-8 shows the spectrogram obtained when the entire system has been flushed for a few minutes with dry air from a "Lectro" activated alumina drier. It was intended to use the dry air for a preliminary flushing and then use super-dry nitrogen during a test. Fortunately, the air

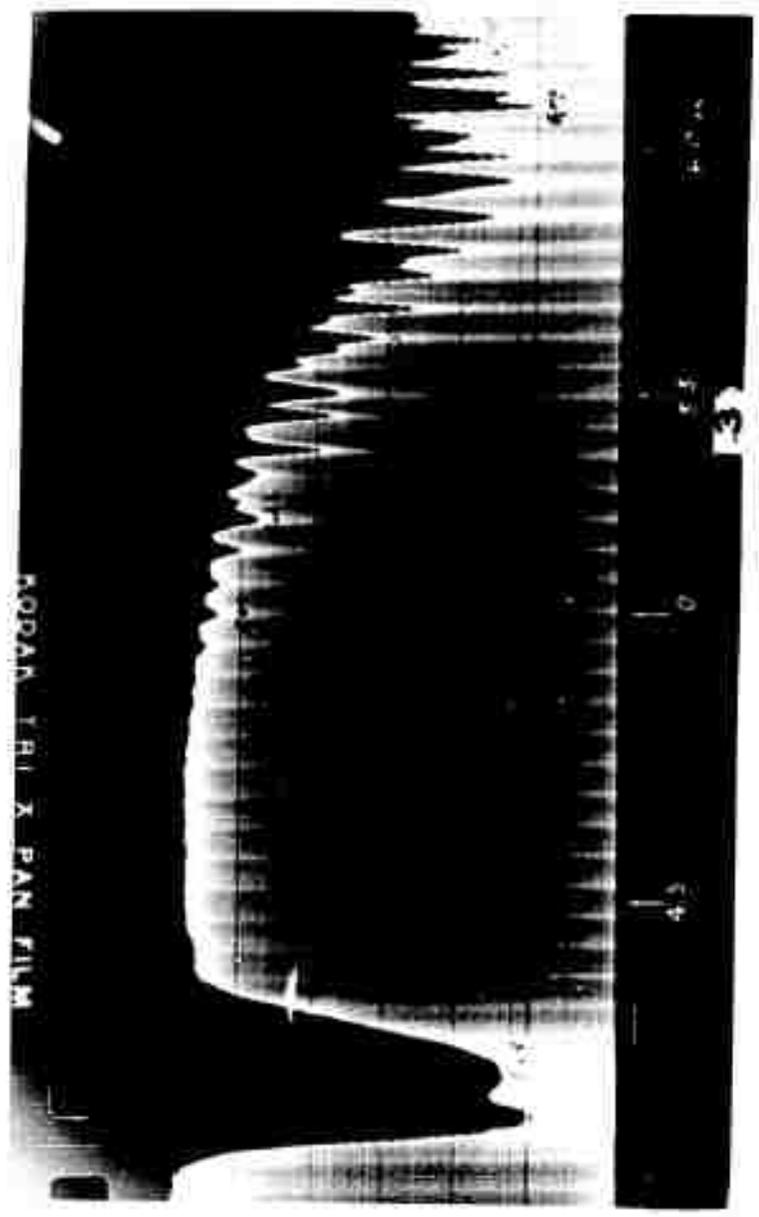


FIG. III-7. ATMOSPHERIC ABSORPTION FOR A PATH LENGTH OF 100 INCHES
Spectral region, 4.0 to 6.5 μ ; P-11, 5" C.R.O. screen;
Moving film camera at 200 inches per second; f/1.5

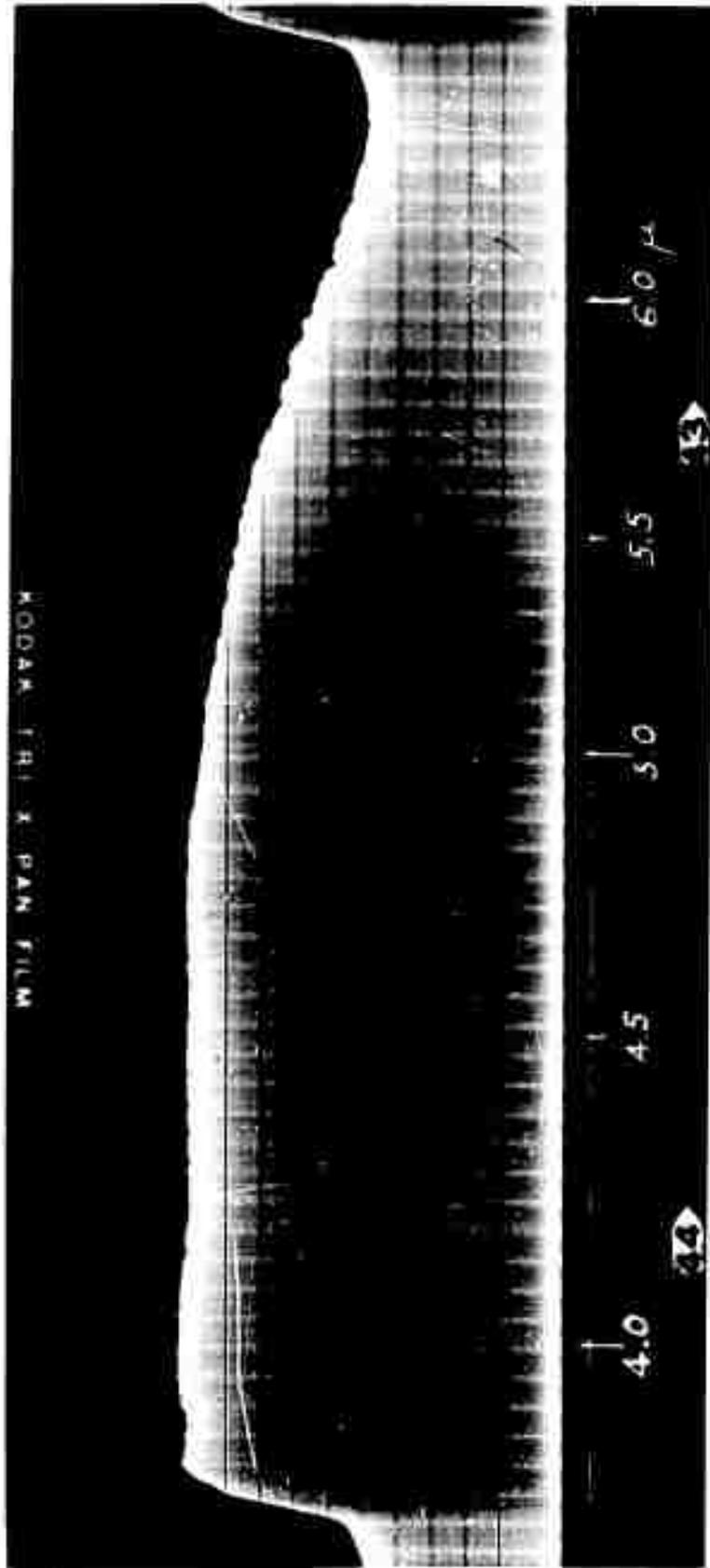


Fig. III-8. SPECTRAL REGION WITH DRY AIR PATH FOR 4.0 to 6.5 μ
(Note that there is no CO₂ absorption at 4.2 μ and only a small residual of the H₂O bands at 6 μ)

flushing did a better job removing the water vapor, as well as the CO_2 , than the super-dry nitrogen. An overnight purging of the drier was sufficient for eight hours continuous operation of the spectrometer. It is not understood why the alumina removes the CO_2 as well as the water vapor, but others (Ref. 3) have observed selective absorption of certain gases with activated alumina.

Three tests have been run with this spectrometer in the wind tunnel test cell. Test No. 115 was made with the tunnel as an absorption cell, using CaF_2 windows flushed in the usual manner to prevent sooting as previously described. Figure III-9 shows one of the spectrograms of this test just after the burning started (the absorption due to the primer gases is shown) and it is obvious that noise was generated in the system. The CO_2 , CO and H_2O bands are visible, but only the CO_2 band is intense enough for good quantitative analysis. Sooting of the windows caused a 25% reduction in amplitude half way through the test and 50% by the end of the run. The percentage of absorption by the soot appears to be a constant percentage over the band width so correction should not be difficult. Figure III-10 is a spectrogram taken 5 seconds after ignition which is about half-time for the run. Figure III-11 is a spectrogram taken just after burn-out when the pressure in the tunnel had returned to normal atmospheric value. The 4.2μ CO_2 band has become very intense and other bands have appeared that were absent during burning. The strong band at 5.3μ was attributed to NO and the one at 4.4μ to N_2O . The 6μ water vapor band has also become very strong and absorption at 5.8μ and 6.3μ is attributed to nitrogen dioxide, NO_2 . From

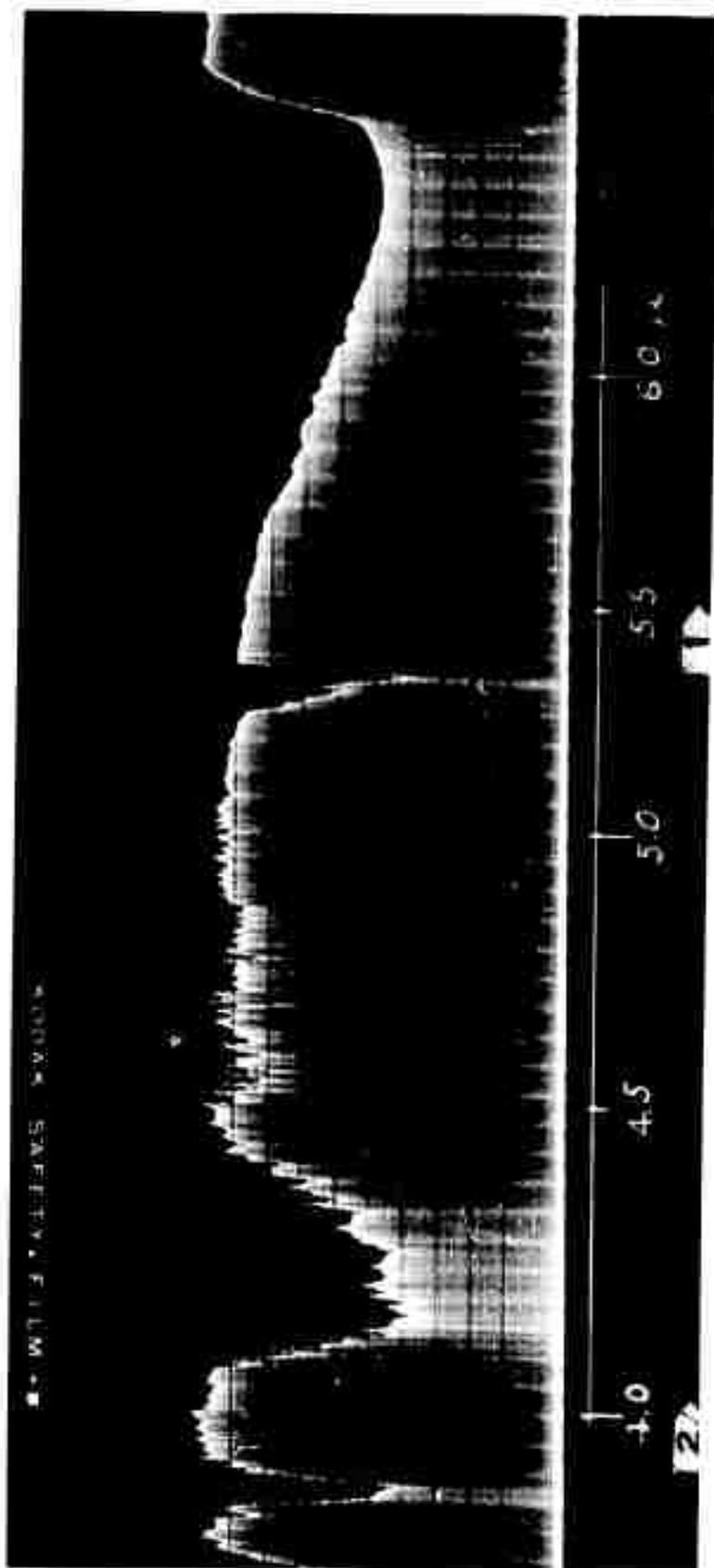


FIG. III-9. SPECTROGRAM OF THE ABSORPTION OF THE ROCKET TUNNEL EXHAUST GAS DURING THE FIRST HALF OF A SECOND AFTER IGNITION IN TEST NO. 113 (Note the sharp absorption cut at about 5.0 due to the primer ignition and the immediate appearance of the CO₂ and CO bands.) The ragged signal was due to vibration of the Nernst glower and the collimating mirrors.

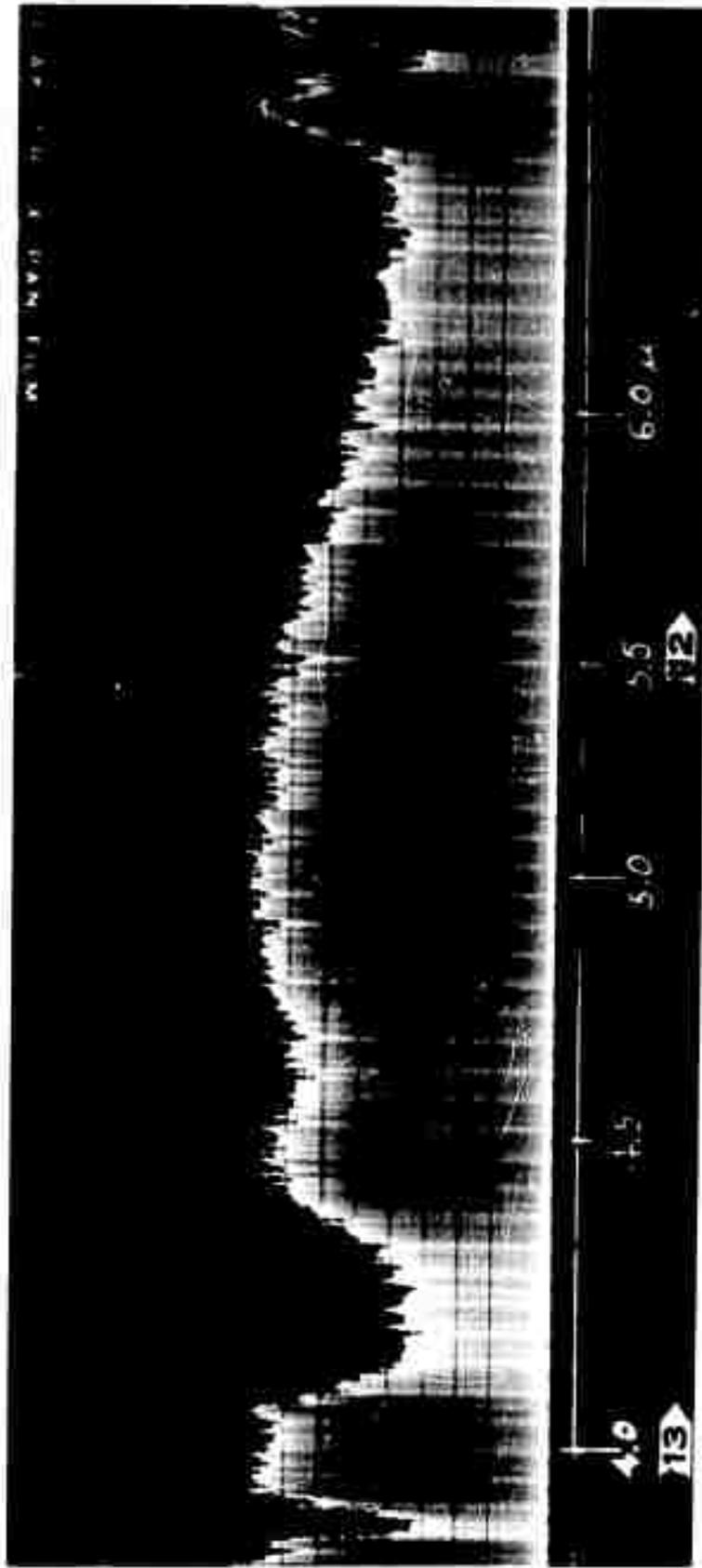


Fig. III-10. ABSORPTION SPECTRUM IN TEST NO. 115, 5 SECONDS AFTER IGNITION
Absorption of 4.2 μ CO₂ band - 50 per cent
Absorption of 4.6 μ CO band - 11 per cent

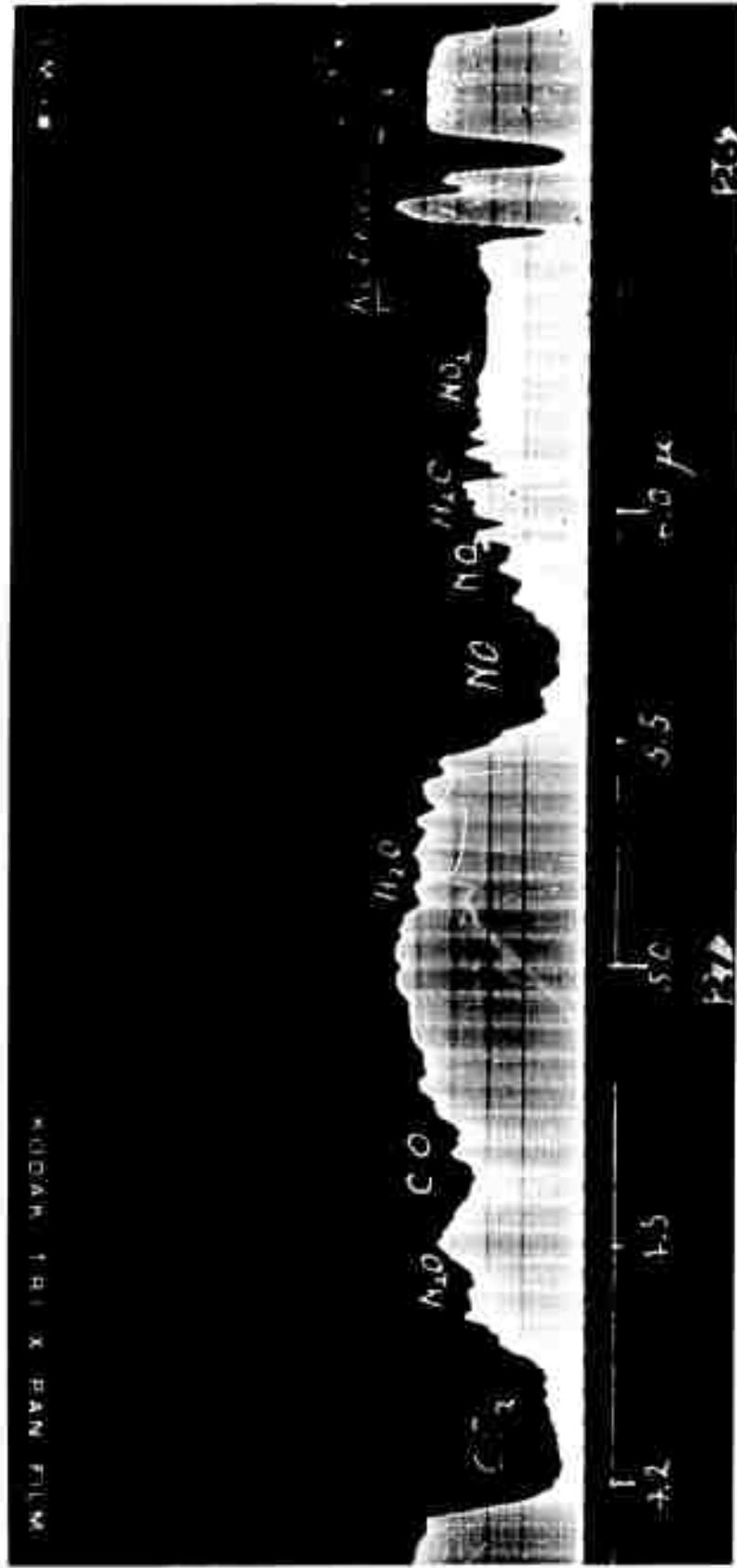


Fig. III-11. ABSORPTION SPECTRUM IN TEST NO. 115, 7 SECONDS AFTER IGNITION AND JUST AFTER BURN-OUT

The increased absorption over that shown in Figures 4 and 5 was due to the rise in pressure to normal atmospheric. Bands of N_2O , NO and NO_2 appear momentarily.

Fig. III-10 measurements of the absorption have been made and are compared in Table 1 with those from a sample of gas at ambient temperature as shown in Fig. III-12.

Table 1. Comparison of spectroscopic measurements taken in the nozzle and in a gas sample withdrawn from the same station.

	Apparent Cell Length	Pressure	Temperature	% Absorption	
				CO ₂	CO
Test No. 115 (Fig. 10)	4.0"	75 mm	700°K	50%	11%
Fig. 12 (Sample of gas mixture taken from Test No. 116)	4.0"	75 mm	Ambient	39.4%	10%
	4.0"	150 mm	Ambient	64%	16.4%
Ratio Abs. 150 mm/Abs. at 75 mm =				1.62	1.64
Test No. 116	4.0"	75 mm	700°K	44%	5.5%

Chemical analysis of gas samples taken from Test 116 were made, and the results (without water vapor) are given in Table 2.

Table 2. Orsat gas analysis of sample taken in Test No. 116. (The water vapor has not been included in this analysis.)

Run	Sample	% CO ₂	% O ₂	% CO	% H ₂	% N ₂
1	100.0 ml	15.5	---	46.5	18.9	19.1
2	79.4 ml	15.5	---	46.9	18.4	19.1

Although the data taken from test Nos. 115 and 116 are slightly indeterminate because of the noise, it appears that the absorption of CO₂ and CO is relatively insensitive to the temperature. However, absorption tests made with the 4.2μ CO₂ band with the gas diluted with dry nitrogen showed that the light absorption

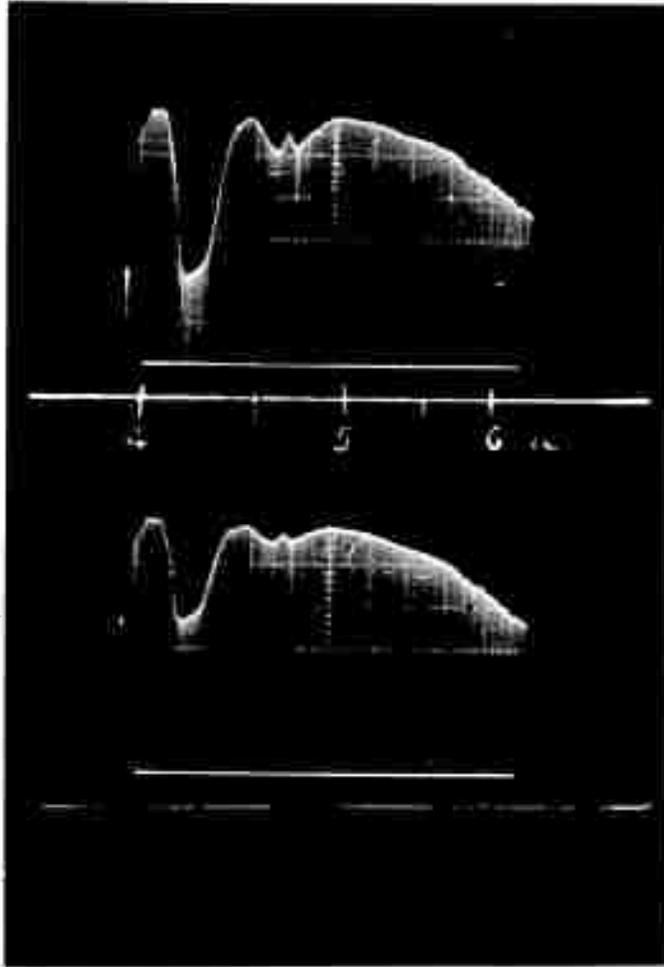


Fig. III-12. ABSORPTION SPECTROGRAMS TAKEN OF THE GAS COLLECTED DURING TEST NO. 116, 4-INCH ABSORPTION CELL AT 150 AND 75 MM TOTAL PRESSURE

Gas	Absorption at 75 mm Pressure	150 mm Pressure	Ratio = $\frac{\text{Abs. (150}\mu\text{)}}{\text{Abs. (75}\mu\text{)}}$
4.2 μ CO ₂ band	0.394	0.64	1.62
4.6 μ CO band	0.10	0.164	1.64

was very sensitive to the change in total pressure. Fortunately, the amount of nitrogen present in the rocket tunnel gas is constant at about 12% so that the pressure effect of this gas on the absorption bands will not vary. Calibration of the absorption system will involve variation in the relative amounts of the other constituent gases to see if Beer's law is applicable. If it is, then the calibration will be relatively easy to perform.

Test No. 117 was made to determine whether the apparent noise shown in Test No. 115 and No. 116 was caused by rapid variations in the transmission of the absorption cell due to, say, turbulence of the soot particles or to vibration of the light source and collimating mirror system. The results of this test indicated that the noise was all due to mechanical instability and the Nernst glower assembly was the most likely offender. Consideration is being given to replacing the fragile Nernst glower with a 1/4-inch-diameter glowbar. The output of this spectral region is equally as good as the Nernst glower and its size and massiveness should eliminate the vibration problem.

References

1. Task R Quarterly Progress Report No. 7, for the period 1 October - 31 December 1960, Applied Physics Laboratory, Johns Hopkins University Report No. TG-331-7 (January 1961).
2. Task R Quarterly Progress Report No. 6, for the period 1 July - 30 September 1960, Applied Physics Laboratory, Johns Hopkins University Report No. TG-331-6 (October 1960).
3. ASTIA AD No. 162-225.

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