NASA-CR-54833
SRI Proj~~ect~~ ~~No.~~ 5075

FINAL REPORT

EVALUATION OF OZONE DIFLUORIDE AS A LIQUID PROPELLANT ADDITIVE

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Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

December 1, 1966

CONTRACT NAS3-4187

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ABSTRACT

The hypergolicity of O_3F_2 at the saturation point in liquid oxygen with liquid and gaseous hydrogen is critically dependent upon the temperature of the combustion chamber. When this temperature is above $150^\circ K$, pressure, total injected weight ratio of oxidizer to fuel and injector type were the primary variables of importance.

The preparation, mixing, and use of solutions of O_3F_2 in liquid oxygen is reviewed. The storage life of these solutions at $90^\circ K$ is not expected to exceed one month.

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SYMBOLS

V = Velocity - ft/sec
P = Pressure - psi
ρ = Density - lbs/ft^3
g = Gravity - ft/sec^2
Z = Height - ft
S = Area - ft^2
$\overline{P}_i(eff)$ = Effective injector pressure - psi
t = Time - sec
P_i = Instantaneous injector pressure - psi
$\dot{w}$ = Flow rate, steady state - lbs/sec
$\mathring{w}$ = Equivalent flow rate during unsteady time interval - lbs/sec
Δt_i = Ignition delay - milliseconds
$\mathring{O}$ = Total integrated flow of oxidizer up to ignition time - lbs
$\mathring{F}$ = Total integrated flow of fuel up to ignition time - lbs
T = Absolute temperature - Degrees K
L^* = Chamber volume/nozzle throat area - ft

Subscripts:

1 = Station 1
2 = Station 2
3 = Station 3
O = Oxidizer
i = Injector
f = Fuel
L = Flow line
T = Tank
c = Engine chamber
a = Ambient

I SUMMARY

The over-all results of our investigation indicate that hypergolicity of O_3F_2 is associated with its thermal decomposition, which results in the formation of reactive radicals. Rapid ignition is associated with relatively warm combustion chambers (above 150°K); it also depends on the ambient pressure. A significant dependence of ignition delay on the time-averaged weight ratio of oxidant to fuel was found for all injector types; however, at comparable $\overset{\circ}{O}/\overset{\circ}{F}$ ratios, delay was dependent also on the injector type.

A number of problems associated with instrumentation and O_3F_2 handling were encountered; some of these remain unresolved such as quantitative calibration for transient, multi-phase flow through orifices, and analytical problems associated with the use of a highly reactive and thermally unstable additive. Significant advances were made experimentally in determining critical ignition parameters such as transient propellant mass flow rate and the time and place of ignition. It is believed that the experimental results provide the engineering background necessary for any future consideration of scale-up to larger rocket engines. While some progress was made in the field analysis of LOX/O_3F_2 solutions, a good method for characterizing LOX/O_3F_2 suspensions was not developed. This study has shown that rather critical requirements must be met if satisfactory ignition is to be achieved; hence O_3F_2 is not a simple panacea for eliminating ignition or combustion problems in rocket systems that use liquid oxygen.

While the practicality of using O_3F_2 in space propulsion cannot be unequivocally stated without a detailed engineering systems study, some critical conditions exist. These may be summarized as follows:

1. Liquid oxygen/O_3F_2 solution must be delivered to the injector face if the O_3F_2 is to be effective as an ignition parameter.
2. The combustion chamber should be at a temperature above 150°K.

3. The storage life of prepared LOX/O_3F_2 solution at 90°K is not expected to exceed one month; the storage life of solutions at temperatures above 90°K has not been determined.
4. The relatively long ignition delays of 5 to 50 milliseconds observed may preclude the use of LOX/O_3F_2 in small impulse bit devices.

It has been suggested that O_3F_2, by modifying the combustion mechanism, might promote combustion stability in small combustors where combustion may be chemically kinetic-limited. Our studies showed that, in the combustor investigated, the presence or absence of instability appeared to be more a feature of the injector design since severe combustion instability was observed using certain injectors.

II INTRODUCTION

The studies described in this report were carried out under NASA Contract No. NAS3-4187, and they have sought to clearly define the operational limits and critical parameters for the use of trioxygen difluoride (O_3F_2) as an additive in liquid oxygen to promote hypergolic ignition between hydrogen and oxygen. A prime goal of the experimental program was to obtain information at known environmental conditions in order to eliminate uncertainties in defining the transient flow characteristics of the system at and prior to ignition.

It is pertinent to note that the use of O_3F_2 as an ignition additive to liquid oxygen was first proposed by Kirshenbaum et al[1]. In later work[2] at Stanford Research Institute in a double-wall quartz engine chamber, the hypergolic ignition event was photographed.

Experimental studies were performed with liquid and gaseous hydrogen using a small cryogenic liquid propellant flow facility and a nominal 300-lb thrust chamber. The combustor was 3 inches in diameter and 10 inches long; it was used with a number of injector types. This combustor is representative of attitude control devices which might be considered adjuncts to a main stage based on current liquid hydrogen and liquid oxygen technology. The combustor was fitted with multi-station ion probes so that the precise location of the onset of ignition could be determined; thus, external blowback ignitions could be readily detected.

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[1] U.S. Patent 3,170,282.

[2] Investigation of O_3F_2 and the Hypergolic Bipropellant $LH_2/LO_2:O_3F_2$, NASA CR-54072, Contract NASr-49(00) [LeRC(01)], June 1964.

III EXPERIMENTAL APPROACH

A. General Description

The small rocket combustor used for most experiments could be maintained in a temperature-controlled environment at selected temperatures down to 77°K. To avoid problems arising from propellant accumulation in the chamber, the combustor was mounted vertically and the exhaust was fired through a deflector tube into a horizontal vacuum chamber, 2 feet in diameter and 12 feet long, equipped with a quick-acting blow-out port. The complete test assembly was mounted in an open-end concrete firing bay with 2-foot-thick walls and was connected by cryogenically insulated lines to the two propellant tanks located below ground level on the external pad. The hydrogen line was 3/4-inch, super-insulated pipe manufactured by the Linde Company, and the liquid oxygen line was a double-wall stainless steel pipe. A jacket of coolant LOX in the outside annulus maintained the oxidant line at the desired temperature of 90°K.

For expulsion of propellants, both propellant tanks could be pressurized with the appropriate gas to any desired pressure between 200 and 400 psig. A diagram of the facility flow system is given in Fig. 1. The test installation was fitted with auxiliary nitrogen gas and liquid nitrogen purge systems.

In studies of the ignition phenomena it was considered of the utmost importance to determine the physical state of the propellants prior to their entry into the combustor at the onset of ignition. Therefore, significant improvements in methods for measuring transient values of pressure, temperature, and propellant flow were required. Transient time resolution of less than 50 microseconds was considered necessary.

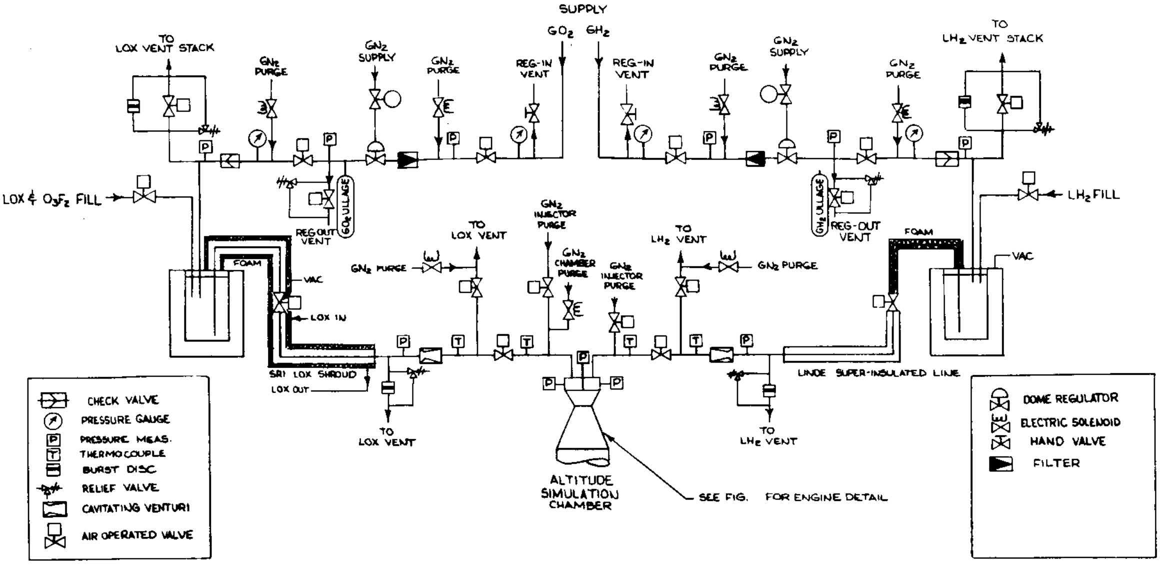

FIG. 1 FLOW SYSTEM

B. Instrumentation

Early in our investigation it was concluded that rather advanced instrumentation approaches were needed to obtain the required degree of accuracy in measuring the operational parameters of a small scale combustor using cryogenic propellants. These problems arose because:

1. Adverse thermal leakage is characteristic of a small flow facility.
2. Transducers are corroded by the O_3F_2/LOX solution (passivation by flourine did not completely eliminate this even though moisture was rigorously excluded).
3. Commercially available pressure and temperature transducers require large mountings with high heat leakages.

The problems of thermal leakage at transducer mounts were overcome in two ways. First, the entire injector and instrumentation assembly was continuously immersed in a liquid nitrogen bath (LN_2) so that the driving potential was never in excess of 53°K (the difference between liquid nitrogen and liquid hydrogen boiling points at 1 atmosphere). Second, in those parts of the system where cryogenic baths or super-insulation could not be employed, transducer assemblies of low total mass were designed and these were insulated with low density polyurethane foam. To further improve reproducibility, the propellant flow lines were vented prior to each test run at the upstream end of the main flow valves. The venting cycle was terminated when the line thermocouples upstream of the flow valves registered a uniform temperature characteristic of the cold liquid propellants.

Propellant flow was regulated by a control console which was connected to quick-response pneumatic and solenoid-controlled valves in the firing bay. All operations after the initial setting of tank pressures were controlled automatically through an electronic sequencer. Cool-down cycles, valve-opening sequences, purging time of the engine bay, inert gas bleed, and engine operating times were all variable and were controlled by dialing in the desired times on the sequencer.

Recording of data was done on a 36-channel oscillograph and two seven-channel tape recorders. The oscillograph provided quick-look data and sequencing information, while all data concerned with ignition delay measurements were recorded on tape for subsequent playback on either the oscillograph or an oscilloscope.

The engine was instrumented as shown in Fig. 2. High response Kistler (Type 601-A) gages (immersed in liquid nitrogen) were used to measure the injector and engine pressures. Ion gages located in the side of the engine and in the entrance elbow to the vacuum chamber just outside the engine nozzle were used to detect initiation and location of ignition. (in particular, precise information on whether ignition was interior or exterior was obtainable.) The cryogenic line temperatures were determined using locally prepared fast-response gold-cobalt vs copper thermocouples.

General information on transducer design and on the instrumentation and control interfaces is given in Appendix C.

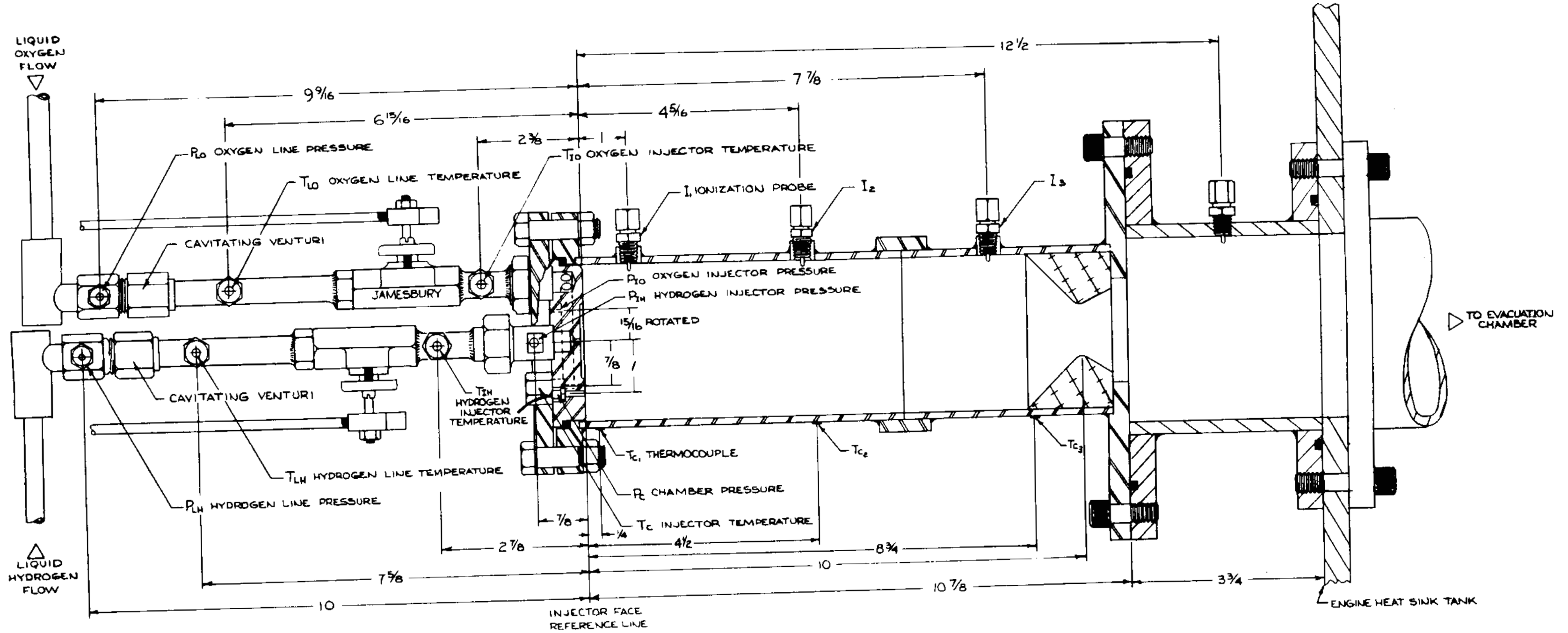

FIG. 2 INSTRUMENTED ENGINE ASSEMBLY

C. Rocket Combustor Design Factors

The basic combustor (Fig. 2) was 3 inches in diameter by 10 inches long. The engine L* could be changed from 52 to 26 by insertion of a liner which reduced the I.D. from 3 to 2 inches. The normally used 1.25-inch nozzle maintained the engine operating pressure in the range from 100-150 psig with total propellant flow about 1 lb/sec. Four injectors are shown in Figs. 3-5; 100- and 300- lb thrust single element triplets, 300-lb thrust 20-element coaxial, and 300-lb thrust 8-element vortex injector.

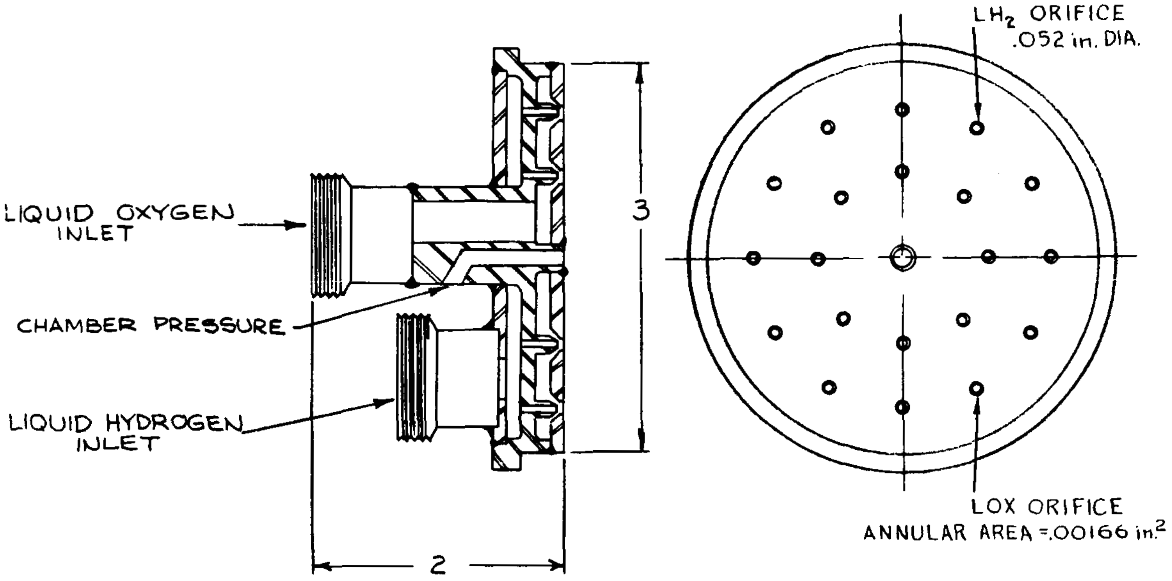

FIG. 3 MULTI-COAXIAL INJECTOR ASSEMBLY

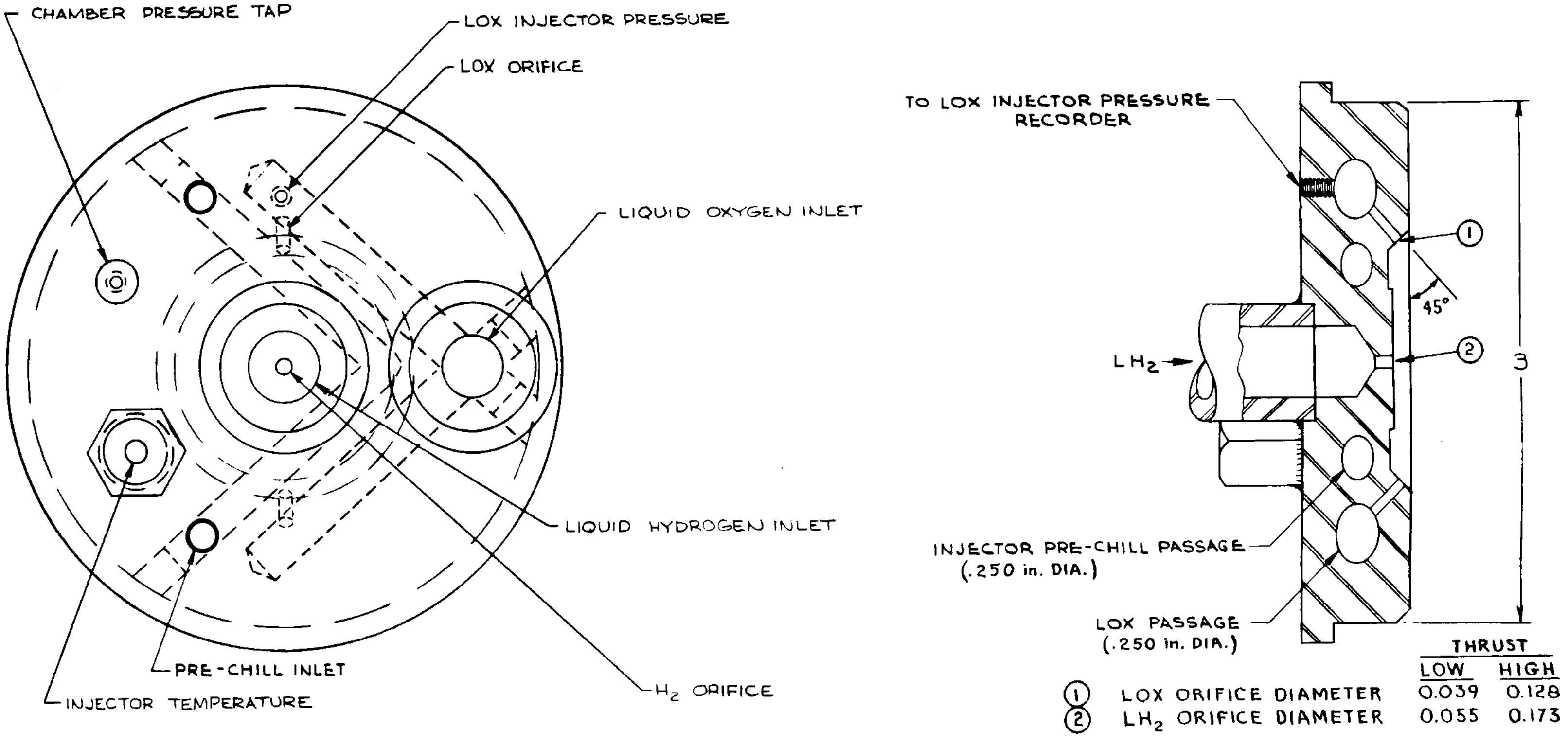

FIG. 4 TRIPLET INJECTOR ASSEMBLY

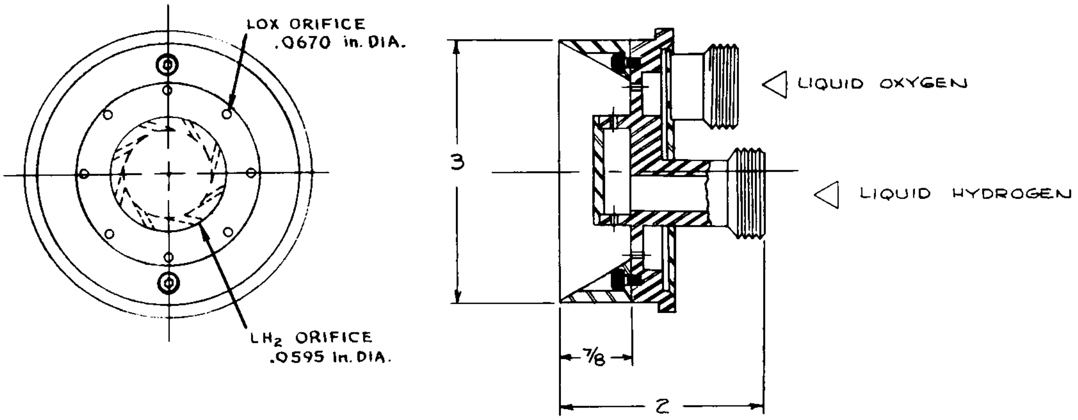

FIG. 5 IMPINGING-VORTEX INJECTOR ASSEMBLY

IV PREPARATION OF O_3F_2 AND SOLUTIONS WITH LIQUID OXYGEN

A. Preparation of O_3F_2

O_3F_2 for the rocket motor ignition tests was prepared by the method described previously[2].

B. Preparation of LOX/O_3F_2 Solutions

Neat O_3F_2, after preparation, was stored in the frozen state in a liquid nitrogen bath. The single 25-cc glass flasks contained from 10 to 20 cc O_3F_2. On run days the estimated number of flasks required that day were transferred to small dewars containing liquid oxygen and the O_3F_2 slowly melted. During the melting the flasks were frequently checked for fluidity and color. At 90°K the acceptance criteria for "good" O_3F_2 are that it melts in less than one hour and that its color changes from orange to deep red. If the contamination level (postulated to be O_2F_2) was too high in a sample, it would not melt in the range 77 to 90°K and was discarded.

When the required amount of O_3F_2 was melted from two or more flasks (about twice as much as necessary to saturate the 37 liters of LOX preloaded into the mix tank (Fig. 6) the liquid O_3F_2 was transferred through a LOX-jacketed transfer funnel attached to the mix tank. For safety reasons the funnel was equipped with a remote, magnetically operated ball valve and was firmly connected to the mix tank. This tank of stainless steel was 15-3/8 in. in dia. and 18 in. deep, and was insulated with 4 in. of low density polyurethane foam. It was fitted with a 12-in.-dia. turbine disc agitator which could be rotated at 100 rpm with an air motor. All foamed organic material was jacketed with copper or stainless steel sheet to prevent accidental fires from inadvertent contact with O_3F_2.

As soon as the transfer of the O_3F_2 was completed, the LOX was agitated for 30 minutes at 1 atmosphere to ensure thorough mixing and solution. After a 15-minute period to allow bulk undissolved O_3F_2 to settle, the solution was transferred into the LOX run tank through a vacuum insulated line. A one-inch stand pipe in the bottom of the mix tank ensured that the undissolved O_3F_2 remained in the mix tank. On subsequent warming of the tank the undissolved O_3F_2 decomposed.

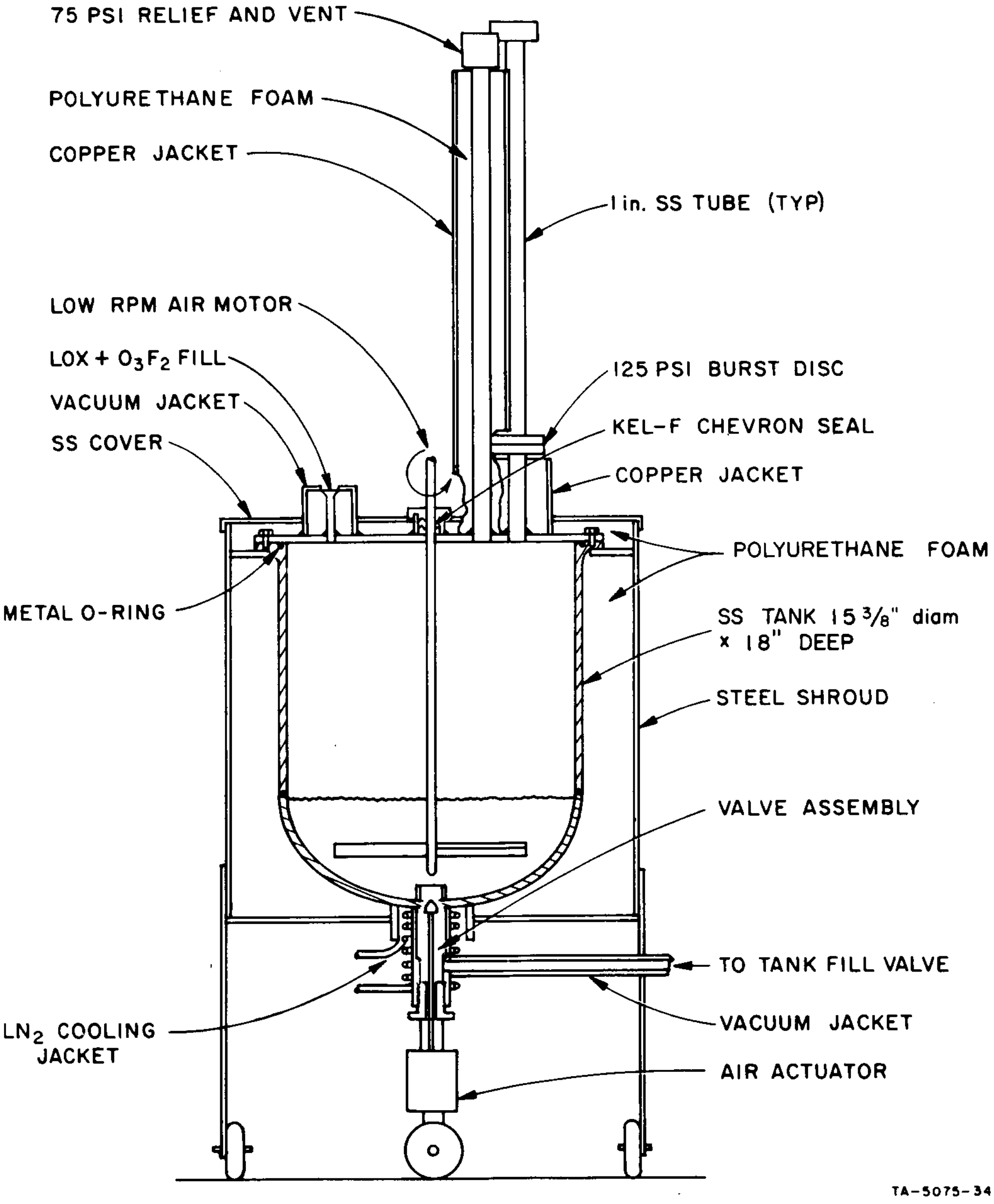

FIG. 6 MIX TANK FOR O_3F_2

V EXPERIMENTAL PROGRAM

A. Hypergolicity Between 20 to 77°K

Early in the test program it was necessary to ascertain if O_3F_2/LOX is hypergolic with hydrogen in the region from 20 to 77°K, since our test plan included working with the engine in liquid nitrogen with liquid hydrogen feed. Our test procedure was to saturate LOX with O_3F_2 at 90°K (approximately 0.1% by weight). A 10-cc sample was then sealed in a flask and frozen in liquid nitrogen. This vial was transferred by air-operated piston into an unsilvered dewar containing liquid hydrogen and the vial broken by mechanically forcing it against a backstop of steel spikes. The time required for the vial to become submerged and to be broken was less than one second.

High speed movies were taken of the experiment, which was carried out in duplicate. In both tests no ignitions occurred when the vial was broken. In one test the hydrogen evaporated in 10 minutes until LOX/O_3F_2 was exposed to relatively warm ambient atmosphere, and then ignition occurred. In the other similar test, decomposition occurred after the hydrogen had evaporated; in this case no explosive ignition was observed.

One of the more obvious results of this test is that there was no ignition as long as the LOX/O_3F_2 remained at 20°K. In order to interpret the results during the transition period between 20 and 77°K, the temperature of the vial as it was withdrawn from its equilibrium bath of liquid nitrogen, it is necessary to estimate the temperature distribution within the spherical mass of LOX/O_3F_2. The vial containing LOX/O_3F_2 was made as shown in Fig. 7. In order to calculate the temperature distribution in the sphere after it is plunged into liquid hydrogen, it is assumed that the thermal properties are continuous and are those of liquid oxygen at 77°K. The estimated temperature distribution is calculated for unsteady-state heat conduction by the method of Corslaw and Jaeger[3] and

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[3] H. S. Corslaw and J. C. Jaeger, Conduction of Heat in Solids, Oxford University Press (1959), p. 234.

plotted in Fig. 8. For immersion times of 3 and 171 seconds, it appears to be a conservative estimate from these data that the sphere was very close to 77°K when the glass was broken by the spikes at the bottom of the dewar and when the liquid oxygen with O_3F_2 contacted the hydrogen. Under these conditions it was concluded that the LOX mixture was non-hypergolic between 20 and 77°K.

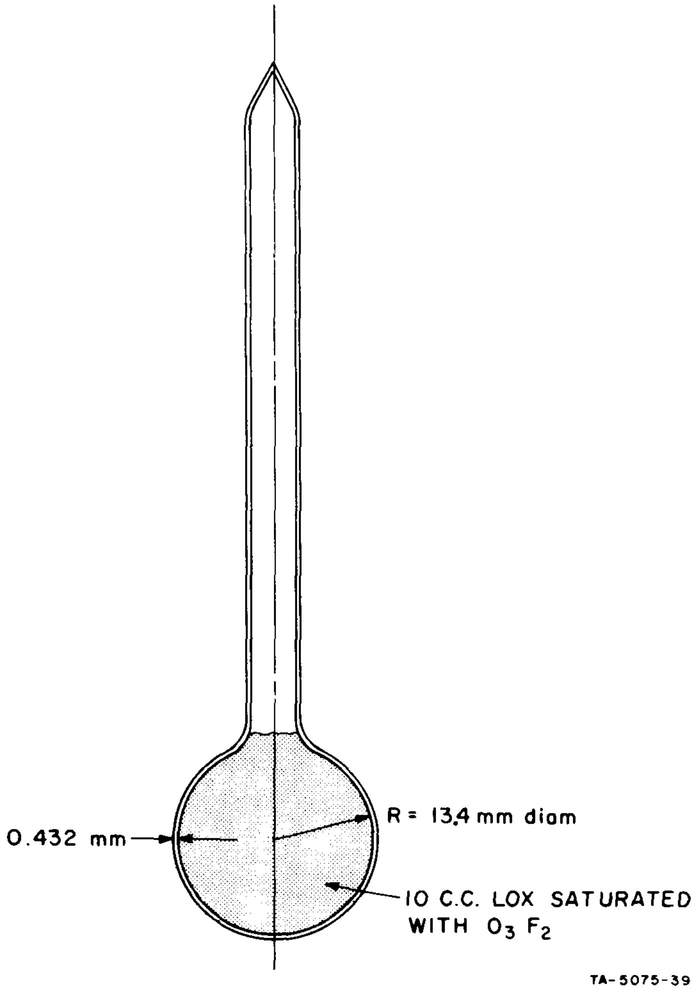

FIG. 7 VIAL DESIGN FOR HYPERGOLICITY TEST WITH LIQUID HYDROGEN

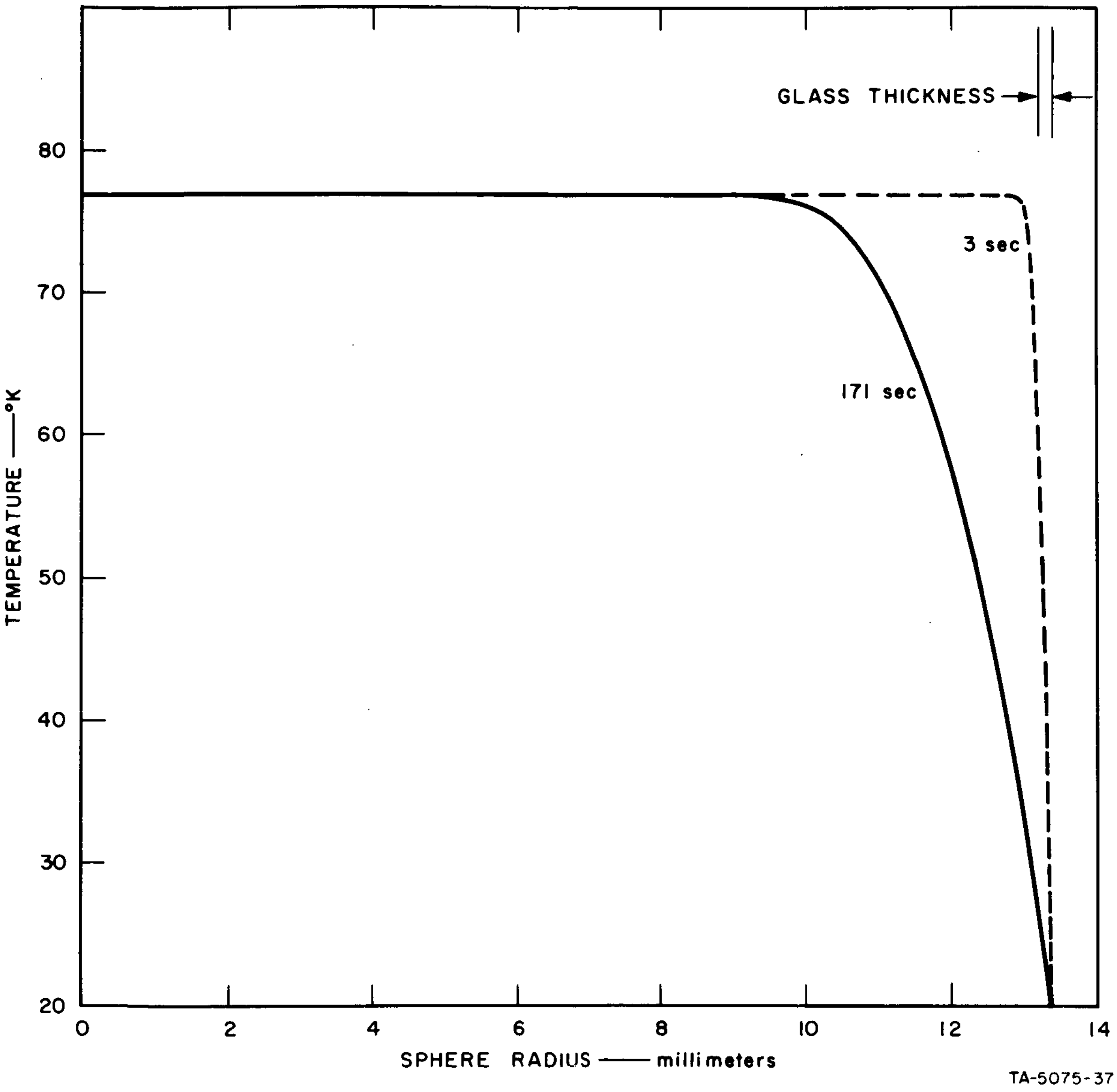

FIG. 8 TEMPERATURE DISTRIBUTION IN LOX/O_3F_2 SPHERE AT 77°K WHEN PLUNGED SUDDENLY INTO LIQUID H_2 AT 20°K

B. Ignition Tests Using Combustor

1. Experimental Procedure

The test runs in the combustor were limited to 250 milliseconds to conserve material and prevent burn-out of any part of the engine. As stated earlier, the propellant feed lines leading to the engine, main flow valves, cavitating venturi meters, and pressure and temperature measuring devices were submerged in a jacket of liquid nitrogen (Fig. 9). The combustion chamber environmental temperature could be varied in stages from ambient temperature to the boiling point of liquid nitrogen by means of a second bath around the exhaust nozzle and the combustion chamber body. Fluids used and corresponding temperatures were: nitrogen, 77°K; argon, 87°K; Freon 12, 130°K; dry ice and trichlorethylene, 190°K; ambient bath of trichloroethylene, 290°K. After the atmospheric pressure tests through test Series 3, the transition piece (Fig. 9 extending from the nozzle to the elbow leading to the vacuum tank) was added to the experimental set-up.. Then the engine exhausted through a 3-inch-dia. pipe into the vacuum tank equipped with a 6-inch blow-off port, which was simply an aluminum plate pressed against an O-ring held in a 6-inch flange.

A normal run sequence started with liquid oxygen venting through the oxidant line until the line temperature just ahead of the vent tee came to equilibrium at 90°K. This was monitored by comparing the galvanometer response on the oscillograph against a calibration mark. The liquid oxygen side of the flow system was then locked and the sequence repeated on the hydrogen side. Each side usually required up to 30 seconds to cool down. Within 10 seconds after lock-up on the hydrogen side the firing cycle was started on the automatic sequencer. This opened the main flow valves and closed them after the selected operating time was completed, a maximum of 250 milliseconds. Immediately after shutdown the engine was automatically purged with nitrogen through the injector to prepare the system for the next run. A summary of the test condition encompassed by the 10 test series, comprising some 138 test runs is shown in Table I. (The run test data for all the tests are given in Table II through Table X.)

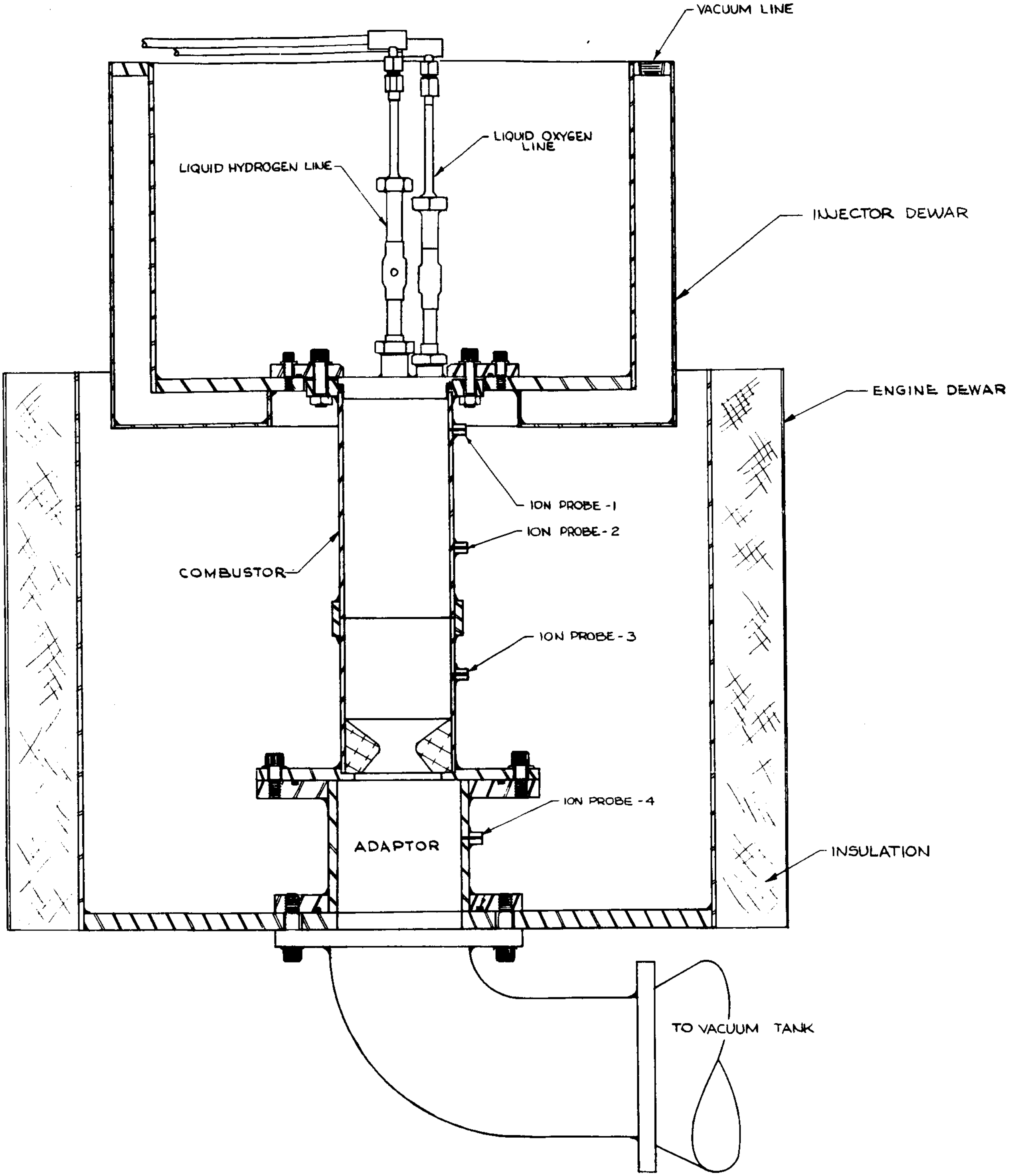

FIG. 9 DOUBLE DEWAR ASSEMBLY FOR CONTROLLING ENGINE START TEMPERATURE

TABLE I

SUMMARY OF TEST CONDITIONS

Test Series	Test No.	Injector Type	Engine L*	Nominal Thrust (lbs)	Engine Environment	Remarks
1	52	Small Triplet	58.7	100	LN_2	Glass engine failed
2	53→63	Small Triplet	58.7	100	LN_2	
3	66→74	Triplet	58.7	100	LN_2	
	75→77	Triplet	58.7	100	LAr	
4	78→82	Triplet	58.7	300	LN_2	
	83→86	Triplet	58.7	300	LAr	
	87→90	Coaxial	58.7	300	LN_2	
	91→92	Coaxial	58.7	300	LAr	
5	97→100	Triplet	58.7	300	Ambient	} LH_2 Lead
	102→103	Triplet	58.7	300	CO_2	
	104→112	Triplet	58.7	300	Ambient	110→112 H_2 (g)
6	113→119	Vortex	58.7	300	Ambient	
	120→122	Vortex	58.7	300	Freon	
	123	Vortex	58.7	300	CO_2	
7	124→127	Triplet	26	300	Ambient	Small L*
	128→130	Triplet	26	300	Freon	Small L*
	131→133	Triplet	26	300	CO_2	Small L*
8	134→142	Triplet	58.7	300	Ambient	Repeat of Series 5
9	145→167	Vortex	58.7	300	Ambient CO_2	Altitude & Ambient Press.
10	173→190	Vortex	58.7	300	Ambient CO_2	Gaseous H_2

Test Series 1 was originally designed to evaluate the feasibility of using a glass combustion chamber for studying the ignition process. The one run resulted in an extremely hard start. The resulting damage precluded the rapid repetition of a test. It was decided consequently to concentrate for Test Series 2 through 10 on experiments with the metal combustor in combination with multi-station ion probes for spatial resolution of the ignition center.

2. Data Reduction

Two types of data reduction were required to obtain the comparative ignition data from the test records. First, it was necessary to establish the location, in or out of the chamber, where ignition occurred. This was done by playing back the ion gages and Kistler chamber pressure gage responses during the ignition phase. Tape data were replayed through a Type M plug-in on a 535 or 555 Tektronix scope and recorded on Polaroid film so that all responses could be compared on the same time basis. A typical playback is shown in Fig. 10. Our time discrimination for this reduction was 20 microseconds. Since the travel time at detonation velocity ($\simeq$ 3000 meters/second) down the chamber to the ion gage outside the nozzle was of the order of 80 μsec, it was possible to precisely locate the ignition location. A second playback of chamber pressure, P_c, vs the lagging injector pressure gage response from the tape record was also used to establish the ignition delay.

The data analysis correlation required a mass flow integration of both fuel and oxidant during the transient and multi-phase flow conditions prior to ignition.

Establishing the total amounts of hydrogen and oxygen which flowed to the engine up to the time of ignition required several approximations. Examination of the problem early established that no satisfactory theoretical basis existed for using standard flow constriction since venturi meters and orifices are based upon the Bernoulli equation derived from Eulers' equations of motion for one-dimensional flow. The energy equation for transient flow phenomena[4] retains the expression for the time variation of flow in this manner:

$$\frac{V_1^2}{2} + \frac{P_1}{\rho_1} + gZ_1 = \frac{V_2^2}{2} + \frac{P_2}{\rho_2} + gZ_2 + \int_{S_1}^{S_2} \frac{\delta v}{\delta t} \, dS$$

Evaluation of the last term leads to difficulty in computing flow during the period of the ignition transient.

As a result of the above consideration, the following approximations were used. In calculations of liquid flow, the line temperature downstream from the cavitating venturi and the upstream line pressure allow an estimate to be made of the liquid density. This, together with the venturi calibration curves (against water) gave steady state flow $\dot{w}_o$ and $\dot{w}_h$. During steady flow time the line pressure was matched by a corresponding injector pressure and

$$\bar{P}_i \,(\text{eff}) = \int_0^{t\,=\,\text{ign}} \frac{P_i \, dt}{\Delta t_i}$$

The steady state flow was calculated in the case of the oxidant in the following manner:

$$\overset{\circ}{w}_o = \dot{w}_o \sqrt{\frac{\bar{P}_i(\text{eff})}{P_i(\text{steady})}}$$

$$\text{and } \overset{\circ}{o} = \overset{\circ}{w}_o \Delta t_i$$

where $\overset{\circ}{o}$ = total flow (lb), $\overset{\circ}{w}_o$ = average flow rate, (lb/sec) and

Δt_i = time from injector pressure rise to ignition.

A similar procedure was followed for the fuel.

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[4] Walther, Kaufman, Fluid Mechanics, McGraw Hill Book Co., N.Y. (1963) p. 55.

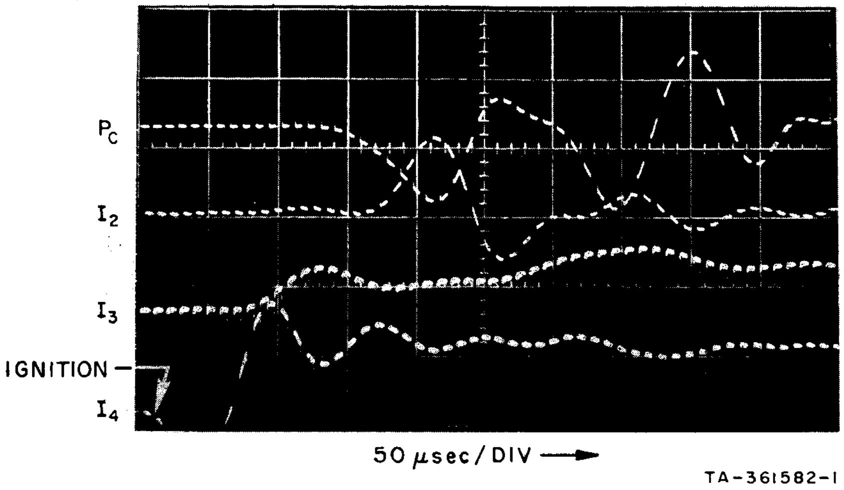

FIG. 10 KISTLER AND ION GAGES OSCILLOSCOPE TRACES SHOWING IGNITION OUTSIDE ENGINE

In the majority of tests, particularly in the case of hydrogen, it was found that initially the liquid flashed as gas, and transient choked gaseous flow occurred ahead of liquid flow through the injector orifices. Any significant gas phase flow through the injector orifices was assumed to have occurred up to the period defined by the first indication of a given injector pressure to its transient peak.

The test data for all the test firings are listed in tabular form at the conclusion of the discussion section of this report. The parameters listed include propellant flow data, engine test data, mixture ratio data, and ignition delay.

The legitimacy of correlating ignition delay with the time-averaged mixture ratio $\mathring{O}/\mathring{F}$ might be questioned, but it appears justifiable on the grounds that at the L* and flow rates used the propellant was largely contained in the combustor during the measured ignition interval. In those cases where ignition was external to the combustor ignition, the delay measured is identical to that for internal ignition. High propellant flow velocity through the chamber would increase the probability of external ignition. Injector design and the resulting mixing of fuel and oxidant (both from the standpoint of thermal equilibrium and homogeneous mixing) are of equal importance.

3. Experimental Results

a. Engine Environmental Temperature Variations

In Test Series 2 and 3 the engine ambient temperature was maintained by liquid nitrogen and liquid argon baths at 77°K and 87°K. Nominal thrust of this engine with a small triplet injector was 100 lb; the engine was started at atmospheric pressure. In Fig. 11 the ignition delays are plotted against $\overset{\circ}{O}/\overset{\circ}{F}$, the mass ratio of the total amount of liquid oxygen to the total liquid hydrogen which flowed to the engine up to the time of ignition. Ignition delay is defined as the time from lagging injector pressure to start of chamber pressure. At this thrust level and temperature all ignitions occurred inside the engine as indicated by ion gages.

The total propellant flow rate was then increased from about 0.3 lb/sec to 1.0 lb/sec. Both the coaxial and a triplet injector were designed to achieve this in Test Series 4. The engine was again started at ambient pressure with temperatures of 77 and 87°K. The correlation between ignition delay and $\overset{\circ}{O}/\overset{\circ}{F}$ is shown in Fig. 12. There is no apparent difference in delays between the triplet and coaxial injectors. However, all ignitions at these higher flow rates and low temperatures occurred outside the engine. This was determined with ion gage instrumentation and, significantly, the flashback into the engine traveled at the detonation velocity of premixed LOX/hydrogen flames. It appears that light-off occurred outside where the propellants encountered a hot environment (ambient compared with 77 and 87°K). It was therefore postulated that from 77 to 87°K during the higher thrust operation either of two factors might predominate: diffusion of O_3F_2 from LOX occurred too slowly to provide material for reaction in the engine; or kinetically it was not hot enough to break down to yield an active oxygen atom, which is conjectured to be the reactive ignition species. In view of the experimental evidence indicating no reaction between liquid hydrogen and LOX/O_3F_2 obtained from the sudden submersion tests described previously, it appears that the ignitions achieved with low flow rates in Test Series 2 and 3 were contradictory to the hypothesis that the reaction was kinetically limited up to 77°K. However, it appears that in Test Series 4 the data support this hypothesis and extend the temperature to 87° K. This anomaly could be attributed to a number of causes. Among the more likely reasons which are consistent with the experimental conditions existing in these tests are:

1. Higher heat leakage conditions would exist at low flow rates, thereby giving rise to higher reaction temperatures since both the delivered hydrogen and LOX should be hotter.
2. Valve leakage might be more critical at low flow rates. At high rates the over-all enthalpy of the entering material would be lower and thereby cool off any leakage material in the chamber. This would be less a factor at low flow rates.
3. The delivered O_3F_2 concentration might be different even though the mixing and delivery processes to the feed tank were unchanged. Up until the last test series no fast field test method existed to analyze the O_3F_2 concentration at the rocket engine.
4. Under the higher flow conditions, appreciably more LOX/O_3F_2 reached the high temperature environment outside the engine through the nozzle faster than under low flow conditions.

The latter cause for the apparent discrepancy is more consistent with the experimental observation that the ignition times are for the most part shorter in Test Series 4 than for Series 2 and 3.

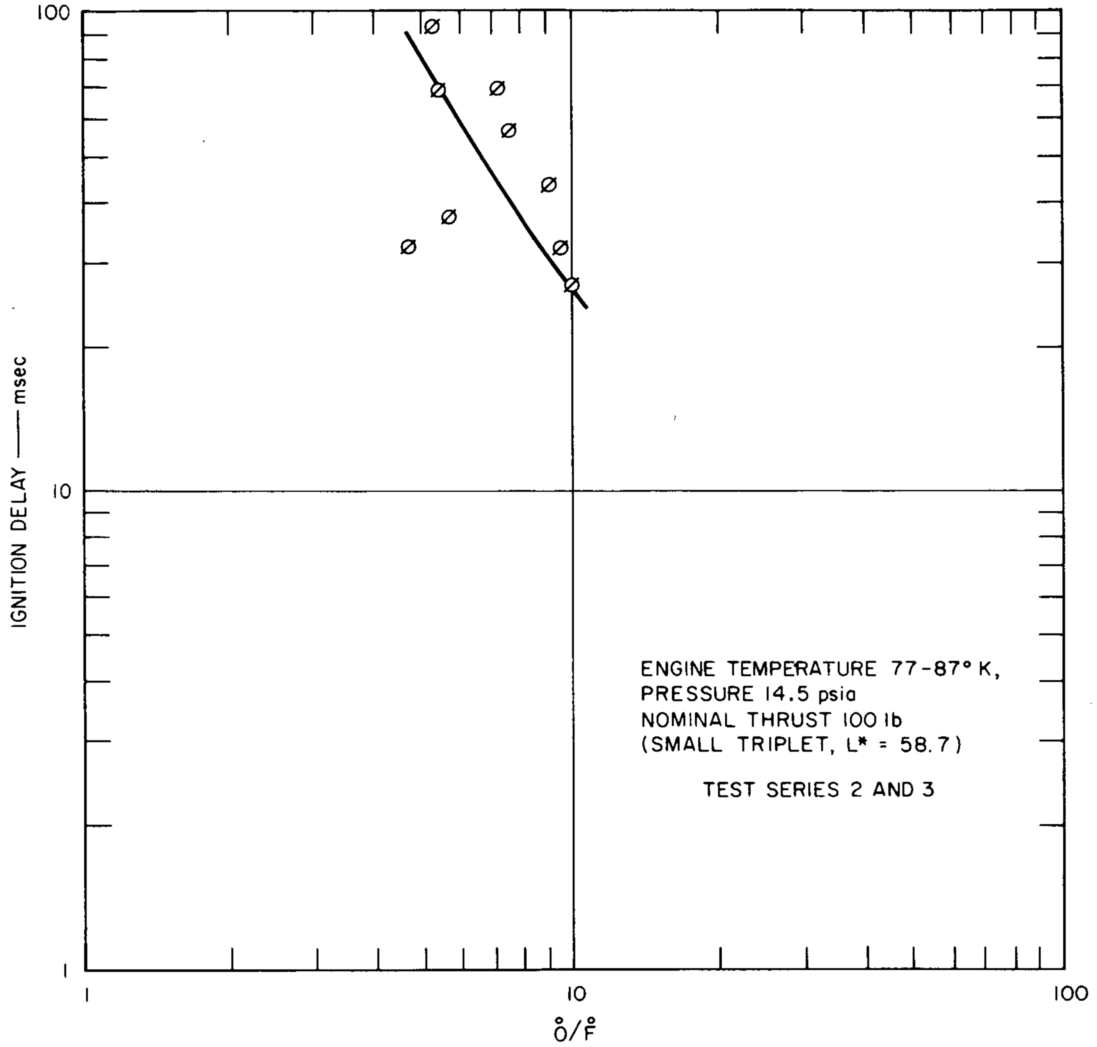

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FIG. 11 IGNITION DELAYS INSIDE ENGINE AT LOW TEMPERATURE AND LOW FLOW RATES

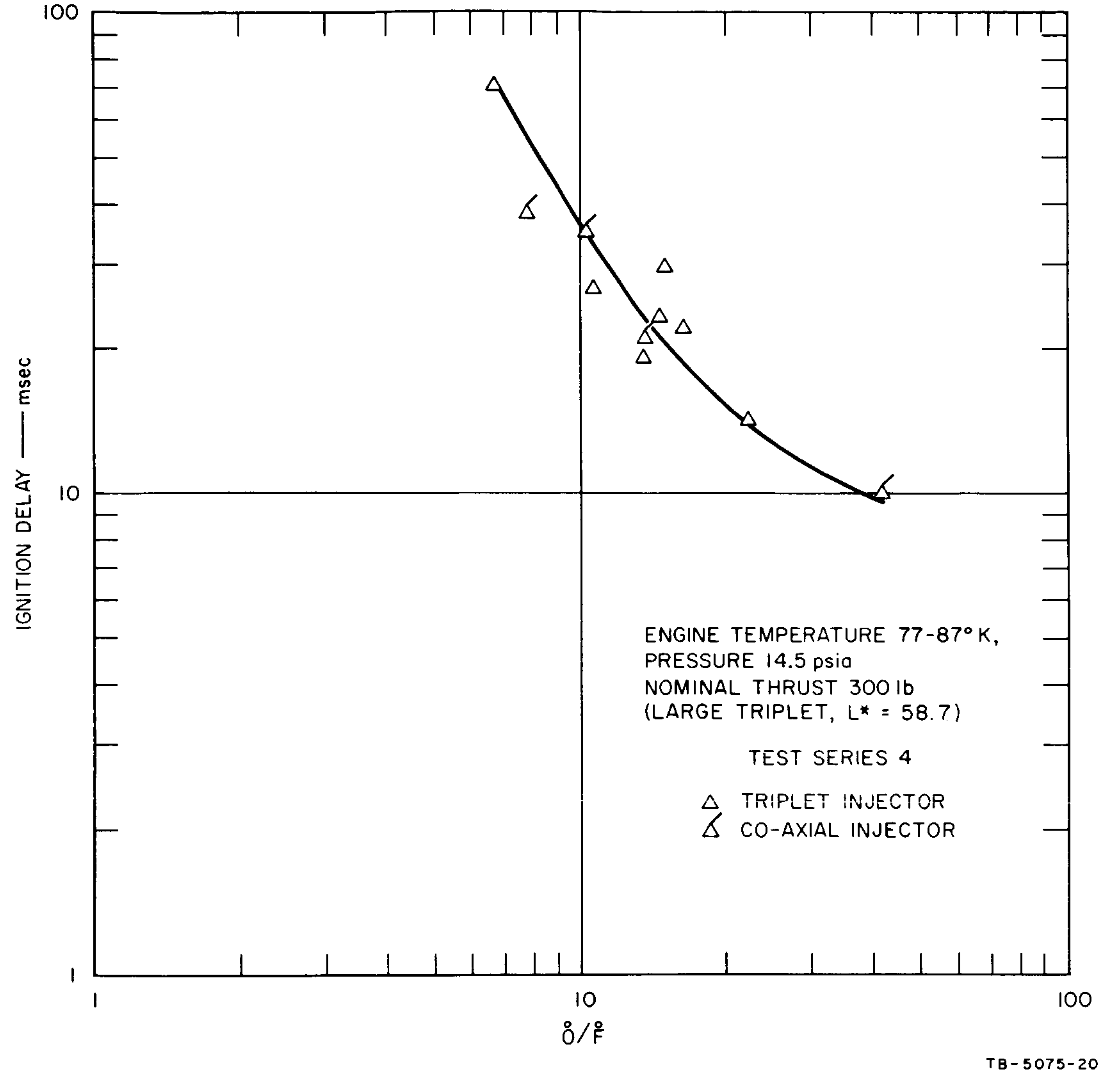


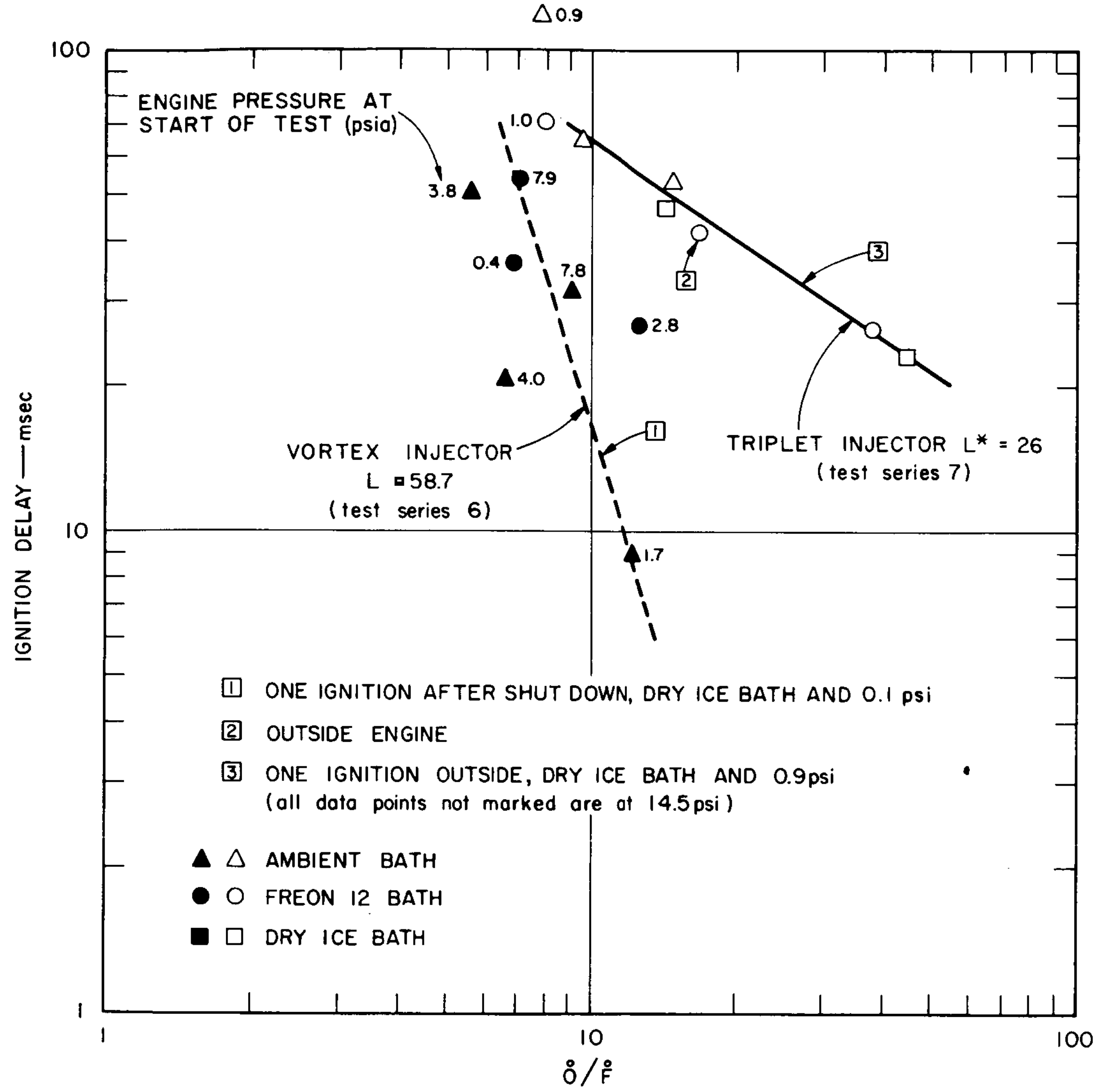
FIG. 12 IGNITION OUTSIDE ENGINE AT LOW TEMPERATURE AND HIGH FLOW RATES

In Test Series 6 and 7 (Fig. 13) the engine environmental temperature was decreased in discrete steps from 290°K (ambient bath) to 245°K (Freon 12 bath), to 190°K (dry ice in trichloroethylene). The single triplet injector was used in Test Series 7 and the vortex injector was used in Test Series 6. The engine starting pressure was also varied in these tests from 14.5 psia down to 0.1 psia. The role that chamber temperature and ambient pressure play in determining whether ignition is satisfactory is not capable of qualitative assessment. Statistically it can be seen that all ignitions were inside the engine at ambient temperature. As the engine temperature was decreased, more external light-offs occurred at both atmospheric and reduced pressures. It is believed that this behavior indicates a kinetically limited system below 200°K for this experimental setup; however, the influence of temperature and mixing on eddy diffusion might produce a similar effect, so this cannot be positively eliminated as the main factor which influenced the delays reported.

b. Injector Influence

Injector design was suspected of playing a role in ignition delay through its contribution to mixing energy. The single triplet injector gives a rather coarse spray which does not become fully developed until it passes a point three inches from the injector. The vortex injector produces a fine spray which comes off the splash plate at the injector (see Fig. 5).

Both injectors were fired with an engine L* of 58.7. Comparative data are shown in Figs. 14 and 15. For starts at high altitudes there appears to be no difference between the vortex and triplet injectors. With the LOX/LH_2 cryogenic system this appears logical, since the differences in droplet size produced by each and the differences in mixing action might be repressed by the high rate of vaporization occurring as the liquids flash into the engine. At atmospheric pressure, however, it would appear that the smaller droplet size and higher mixing energy of the vortex injector give smaller ignition delays when compared to those given by the triplet injector. The triplet injector data are composed of ignition delays measured in chambers with different L*, for reasons discussed later, but this variable apparently is not significant.



TB-5075-31

FIG. 13 IGNITION DELAYS FOR ENGINE ENVIRONMENTAL TEMPERATURES FROM 190°K TO 290°K

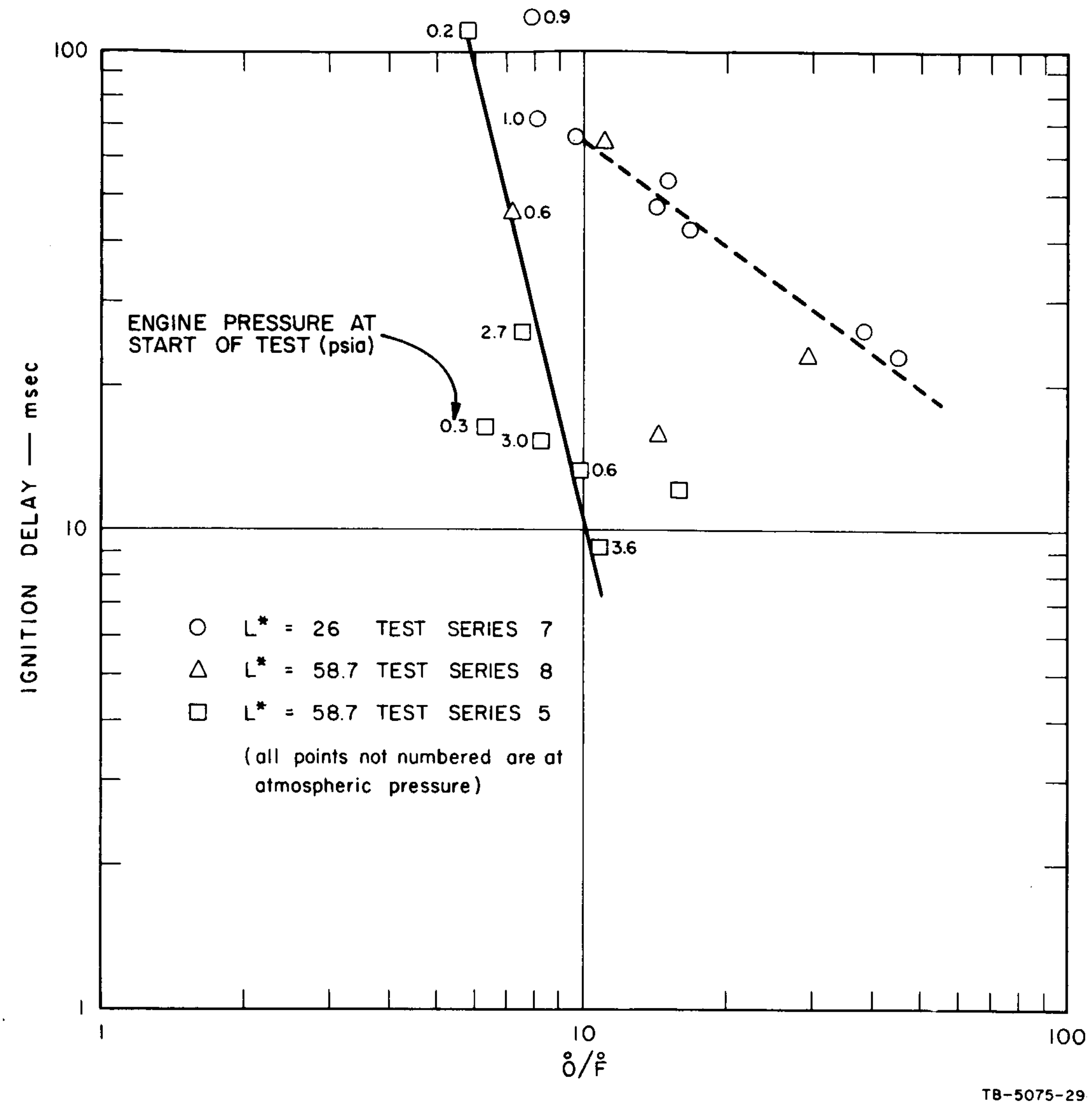


FIG. 14 L* VARIATIONS WITH THE TRIPLET INJECTOR

c. Thrust Level Changes

The changeover from the 100-lb to 300-lb single triplet injectors between Series 3 and 4 resulted in moving the point of ignition from inside to outside the engine. It is unknown whether this effect could have been detected at temperatures higher than the 77-to-87°K engine bath temperature of these series.

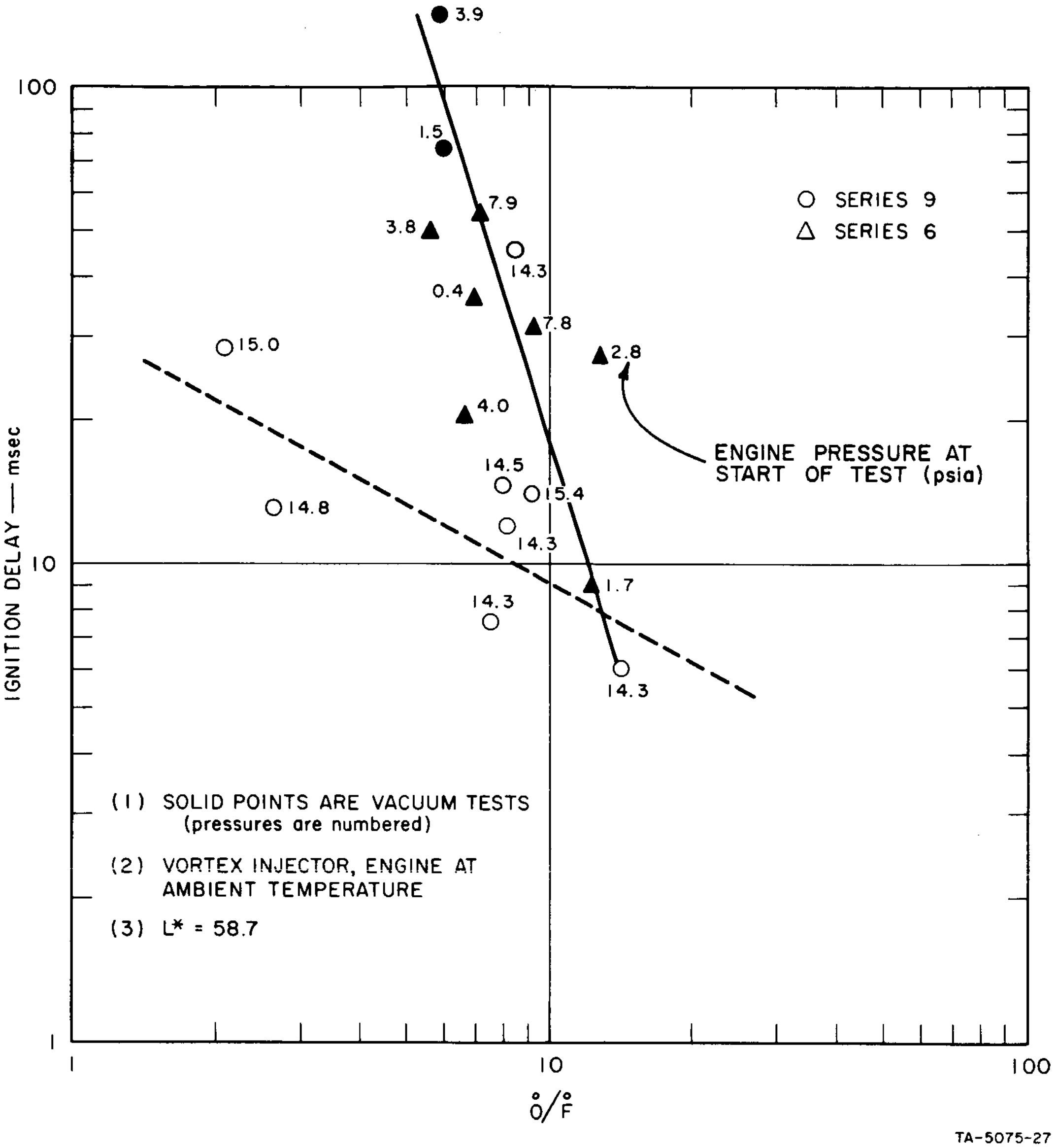


FIG. 15 EFFECT OF ALTITUDE USING VORTEX INJECTOR

d. Influence of L*

In Series 7 the triplet injector was used with an engine L* of 26. The ignition data from these tests are compared in Fig. 13 to Series 5 and 8 where the engine L* was increased to 58.7. All of the plotted points are for LOX leads. The hydrogen lead data were not correlated because on hydrogen lead the injector port coincides axially with the nozzle and all lead material goes directly out the nozzle. This stream of two-phase liquid hydrogen was visually observed on hydrogen leads through the remote TV monitor. Similarly when LOX was the lead material very little material was observed to flow from the nozzle, probably because the spray from the impinging streams was more uniformly deposited upon the motor chamber walls. As a result, the amount of hydrogen that flowed into the engine and remained there for sufficient time for reaction cannot be computed with reasonable accuracy. The results appear to indicate that the change in L* from 58.7 to 26 may not have influenced the ignition delay. Statistically there are insufficient test numbers to be absolutely precise. However, one anomaly which may in part contradict this is the fact that the correlation line for atmospheric ignition delays lies above that for altitude ignitions, which is the opposite effect shown by data developed with the vortex injector. Note that under both atmospheric and altitude starts, data for each engine L* configuration plot within the scatter of data from the other. On this basis it is unlikely that the L* change influenced the delays significantly either at altitude or at atmospheric pressure.

e. Altitude Ignitions with the Vortex Injector

In Test Series 9 the vortex injector was used to attempt a more definitive correlation between atmospheric and vacuum firings. The engine was maintained at ambient temperatures for these tests. The data are compared in Fig. 15 to those of Series 6 which were mostly altitude ignitions, whereas in Series 9 both ambient and altitude pressures were tried. As with the triplet injector, the effect of $\overset{o}{O}/\overset{o}{F}$ variation at atmospheric pressure is not as pronounced as at altitude, i.e., ignition delays change less with change in pressure. However with the vortex injector the correlation line lies below that for altitude ignitions and would indicate that the atmospheric ignitions are faster, for the same $\overset{\circ}{O}/\overset{\circ}{F}$ ratio, than those measured with the triplet injector. It will be observed that many of the ignitions obtained using the Vortex igniter at ambient pressure were significantly faster than those for the corresponding O/F ratio under altitude conditions. It appears that, with one important exception, the ambient data can be correlated with a line of lower slope than the altitude data. The outlying data point in question (O/F ratio of 8.5) if examined by the Dixon outlyer criteria appears to be excluded from the data population by a probability of 98%. However, if this point is included in the data population, no satisfactory correlation coefficient can be obtained.

f. O_3F_2 Concentration Level

In Test Series 9 the planned experiment was to change $\overset{\circ}{O}/\overset{\circ}{F}$ by reducing the flow of hydrogen, thereby increasing $\overset{\circ}{O}/\overset{\circ}{F}$ upwards in the 20 to 30 range. This required an overnight shutdown to change cavitating venturis on the hydrogen side. It also necessitated mixing a new tank of LOX/O_3F_2. When the melting point and color criteria for acceptance of each flask containing O_3F_2 were applied on the second day's run, so many of the extra samples did not melt that only half the usual amount was judged to be of satisfactory quality. In all other runs, including the prior days' firings on Series 9, approximately twice the theoretical amount to saturate the LOX run tank was added to the mix tank. The two initial test runs resulted in no ignition under conditions where ignition would be predicted. The flow setup was then changed back to the higher rates used the previous day. Although ignition delay data were obtained, the ion gage instrumentation indicated that the ignition was outside. It was concluded tentatively that the smaller amount of O_3F_2 caused the ignitions to occur outside the engine and hence the resulting delays did not correlate with $\overset{\circ}{O}/\overset{\circ}{F}$ relationship. These data are given in Fig. 16.

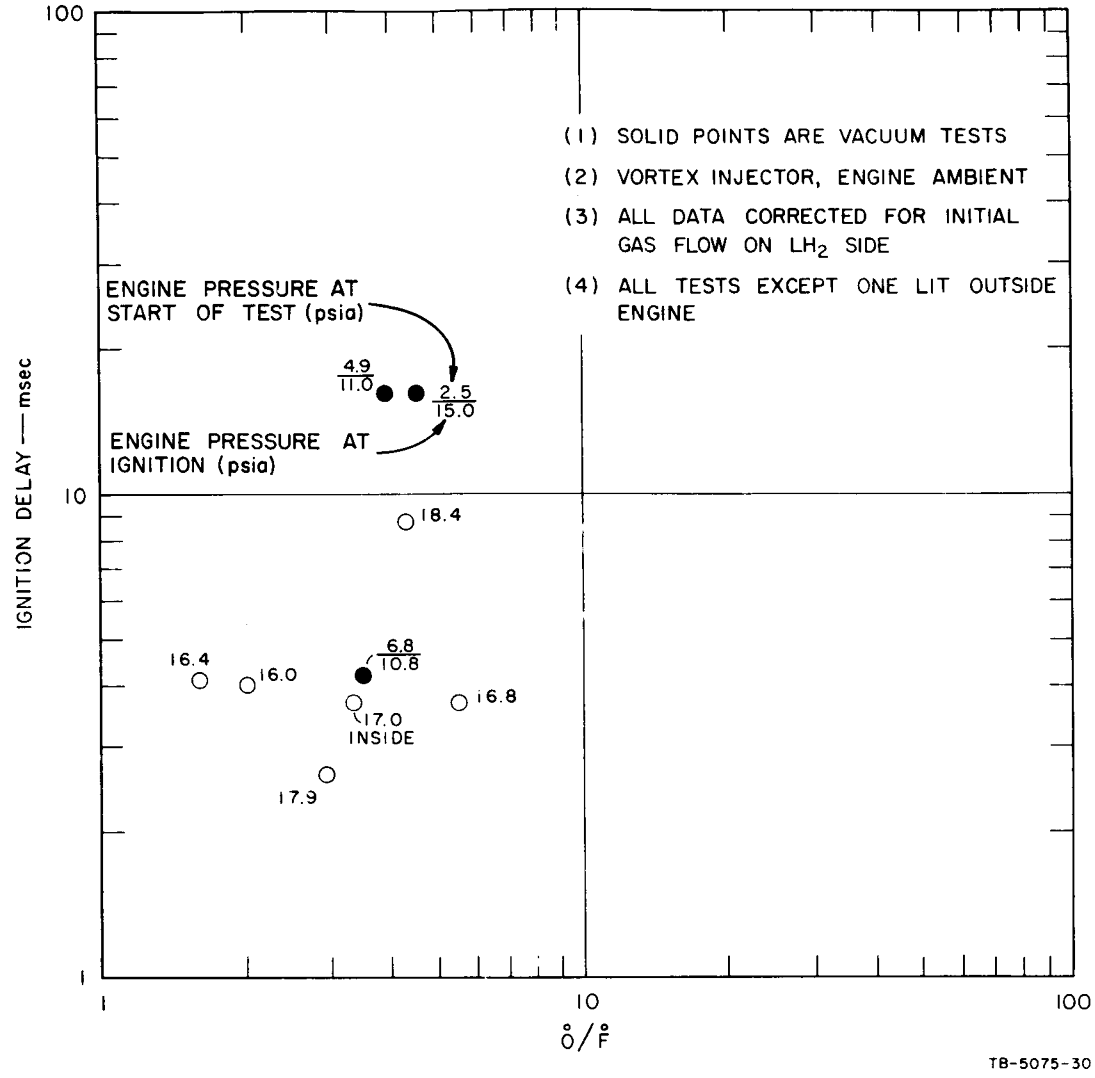


FIG. 16 EFFECT OF O_3F_2 CONCENTRATION ON IGNITION DELAY

Subsequently two causes for the ignitions outside the engine were advanced. One postulated that the slower ignitions resulted from the reduction in spray droplet size and mixing action produced by decreasing the hydrogen flow from 0.23 lb/sec to 0.07 lb/sec; the other, that the reduced amount of O_3F_2 charged to the mix tank resulted in an insufficient concentration being delivered to the engine to function as a hypergol.

Since the reduction in total flow from 1.0 lb/sec to 0.77 lb/sec was so slight, and ignitions continued outside the engine after changing back to the higher flow, it seemed doubtful that the injector spray efficiency was seriously impaired. However, in order to reduce the number of possible causes, a cryogenic cold flow test was carried out under identical environmental conditions as in Test Series 9, except that the O_3F_2 was not mixed with LOX and the engine was disassembled from the injector to allow high speed movies to be taken of the spray pattern. Analysis of the results from flow tests at full and reduced flow indicated that the atomizing action of the injector had been impaired by reducing the hydrogen flow. However, it was not possible to definitely pinpoint this as the cause of tardy ignition.

The next experiment proposed involved mixing an excess amount of O_3F_2 into LOX and sampling the material after it flowed through the lines and into the engine under the same experimental conditions as in Series 9.

In our experimental runs the total amount of LOX used in the mixing tank was 37 liters. To achieve saturation, assuming no losses, 37 grams of O_3F_2 was required. For most ignition studies the LOX mixing tank was charged with an excess of O_3F_2 in order to ensure saturation at a LOX temperature of 90°K. The extent of melting of the frozen O_3F_2 before charging was variable and between 60 and 80 cc of O_3F_2 were usually added to the mix tank. Since the density of O_3F_2 is much greater than LOX, it was believed that the excess would settle out during the 15-minute period of no agitation which was standard procedure on each tank mixed.

Experiments were conducted to determine the concentration of O_3F_2 in the mixture after transfer through the system, i.e., to determine what portion of O_3F_2 was lost in the transfer process. Therefore, effluent mixtures were assayed colorimetrically after being processed through the mixing-transfer cycle used in the ignition studies.

Two different mixtures were prepared for assay. In the first, the tank of LOX contained approximately 35 grams O_3F_2; in the second, 80 grams.

Samples of each mixture were collected from the ignition chamber in small prechilled dewar flasks to minimize evaporation of LOX. (O_3F_2 is not volatile at 90°K.) To prevent LOX evaporation at the exhaust valve, the exhaust pressure was maintained at atmospheric pressure. Samples of known relative concentrations were also prepared for these tests. Figure 17 shows the colorimetric analysis calibration curve obtained from experimental data; the photocell in the colorimeter gives an out of balance voltage which is correlated with O_3F_2 concentration.

In the flow tests using a 35-gram charge of O_3F_2 in 37 liters of LOX the samples taken at the engine assayed at 60% of the saturation value rather than at 95% which was anticipated on the basis of solubility data. For the samples which flowed from the tank containing 80 grams of O_3F_2, the analysis data indicated greater than saturation. Voltages in excess of 15 volts were recorded. The samples examined were turbid, thus indicating that probably some O_3F_2 was being delivered as a colloidal suspension in all of the test series except Series 9B where a reduced amount was charged to the mix tank. The analytical reading obtained would be invalidated by light scattering in the turbid solutions.

To confirm that suspended particles would produce this result, we prepared in the laboratories a saturated solution of LOX/O_3F_2 at 88°K. This temperature was chosen to minimize boil-off of LOX. This solution was assayed by the colorimeter; the concentration was very near that for saturation at 90°K. The clear solution was then rapidly cooled to 77°K by immersing the container in liquid nitrogen. The solution became turbid and exhibited a marked Tyndall effect when examined with a light beam. The output voltage (used to determine concentration) from the colorimeter was 19.5-20V during the first five minutes after cooling and dropped to 15V after 10 minutes. This value was well above that which would indicate saturation and arose from light scattering. It was concluded that:

1. The nominal 100% excess of O_3F_2 in the mixing tank delivered a saturated solution containing also an excess of colloidally suspended particles to the ignition test chamber. It should be noted that transfer during mixing and delivery to the test chamber involves the application of elevated pressures and rapid solution and precipitation can well explain the undesirable excess obtained.
2. Over-all losses during transfer may have been as high as 40% of the amount needed to saturate liquid oxygen at its boiling point. These losses may be attributed in part to passivation of the tank walls, reaction with impurities in the LOX, impurities in the O_3F_2, or decomposition during transport through the flow system.
3. Although the precise analytical amount of O_3F_2 in the LOX delivered to the engine was not determined at the time of each test series because the required test method was not available until the end of the program, it is considered that the use of excess O_3F_2, together with consistency of processing procedures and times would insure that the same amount would be delivered each time. It has been clearly shown that the delivery of less than a saturated solution can be detrimental by causing ignitions outside the engine.

In Series 9, liquid oxygen/liquid hydrogen, attempts were made to measure both the engine pressure and environmental vacuum chamber pressure at ignition. During atmospheric pressure tests, the engine pressure increased from approximately 14.5 to 16-17 psia, indicating a non-choked nozzle. Under high altitude conditions, i.e., vacuum pressure in the dump tank less than 2.5 psia, the engine pressure increased to about 15 psia before ignition, thus indicating a choked-nozzle condition.

g. Study of Gaseous Hydrogen Feed

In Test Series 10 gaseous hydrogen in the range 140-190°K was used to simulate the RL-10 and J-2 engine start conditions. The hydrogen was cooled from ambient temperature gas by passing it through a 10-in dia. x 15 in-long stainless steel tank immersed in liquid argon. This required a vortex injector redesigned for gaseous flow. Ambient engine temperatures were varied down to 190°K. Both ambient and vacuum starts were investigated. Again the pressure measurements indicated the engine was choked under vacuum conditions, but it was not choked under ambient pressure start conditions. Here our O/F correlation (Fig. 18) produced a positive slope for vacuum starts, compared to the negative slope usually encountered and also observed in this series for the sea-level pressure tests.

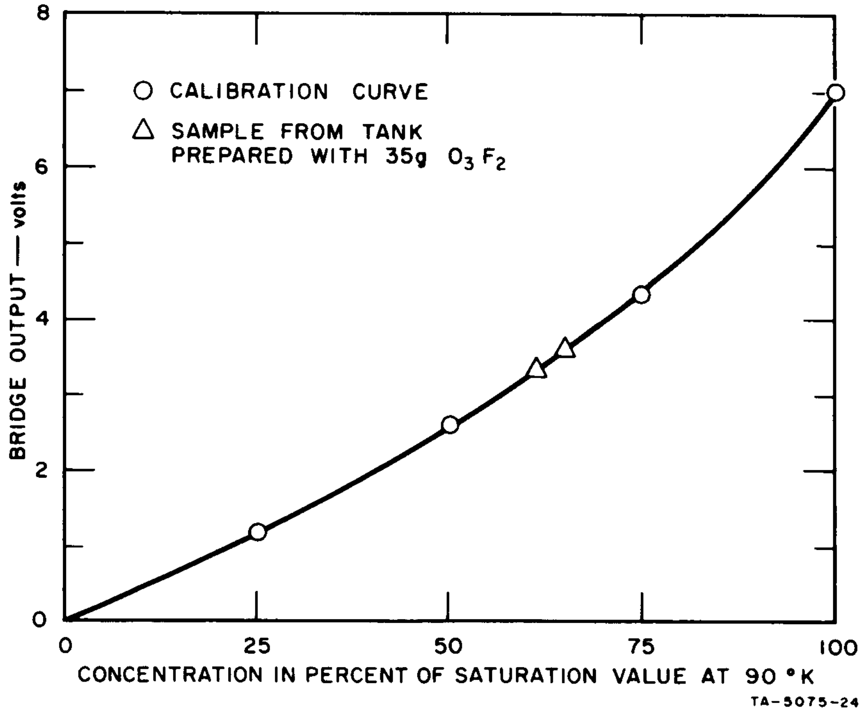


FIG. 17 ANALYSIS OF LOX/O_3F_2 SOLUTION DELIVERED AT THE ROCKET ENGINE

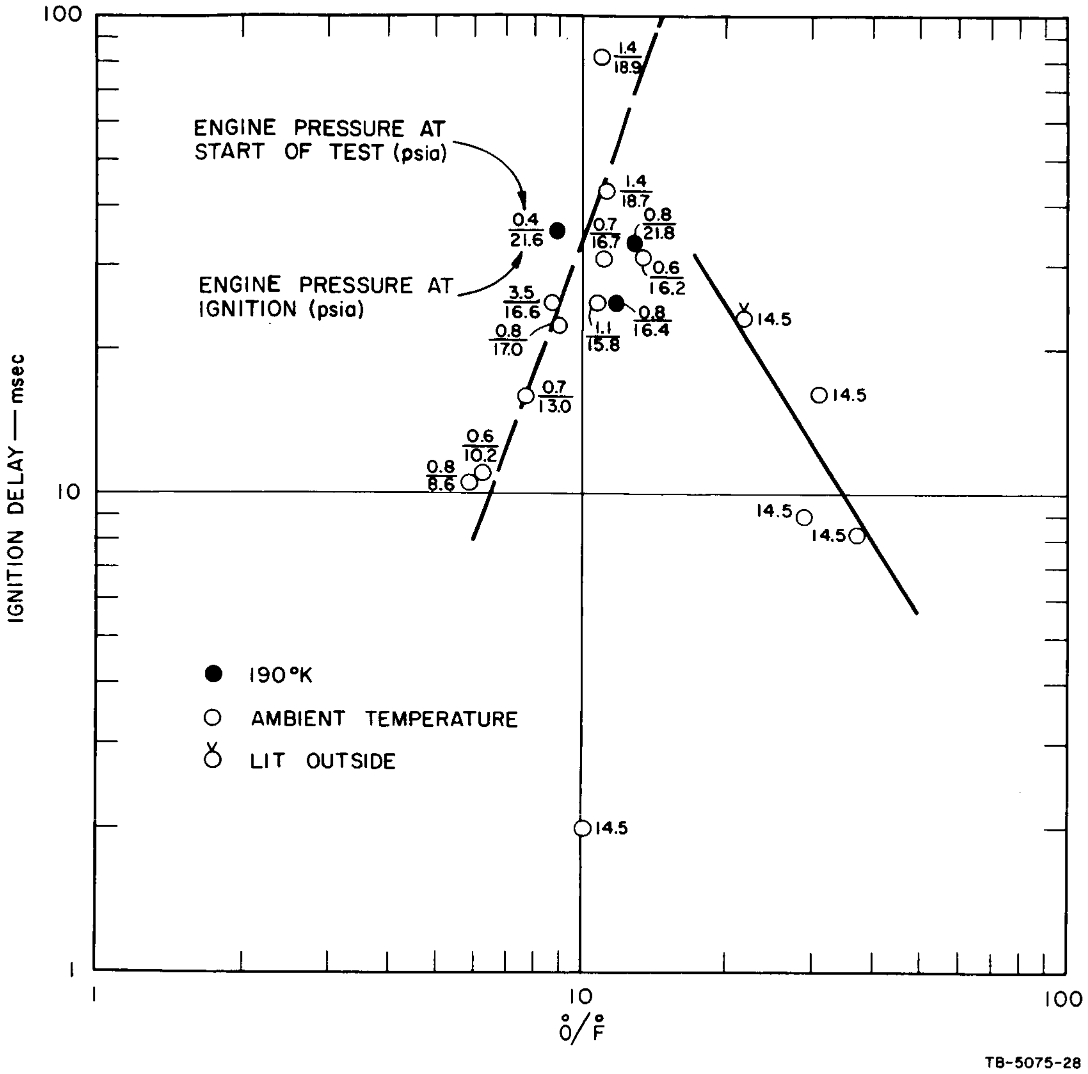


FIG. 18 IGNITION DELAYS OBTAINED USING GASEOUS HYDROGEN

The anomalous data correlation observed for the vacuum firings is related to the fact that the pressure drop across the injector orifices is used to calculate the total flow rate under vacuum conditions; whereas in the liquid flow measurements the cavitating venturi meter was used to compute total flow. Since the flow rate with gas flow under altitude conditions is dependent upon ΔP across the injector orifices, the longer the ignition delay, the more gas flows through the injector; this results in the $\overset{\circ}{O}/\overset{\circ}{F}$ shifting to a higher value. In prior tests the liquid flow rate was computed from the upstream pressure only, and the downstream density and was therefore independent of ΔP across the injector orifices. (Consequently, a plot of ignition delay against $\overset{\circ}{O}/\overset{\circ}{F}$ would be expected to have a positive slope. The line is dotted to emphasize this experimental anomaly.) The real factor controlling the onset of ignition in the vacuum tests using gaseous hydrogen cannot be ascertained from the available experimental data. Certainly the ignitions occurred inside the chamber at unexpectedly short delay times; this favorable result may have ensued from the expanding supersonic flow out of the injector orifices and the interaction of associated downstream shocks with the LOX/O_3F_2 spray or the increased enthalphy contributed by the hydrogen feed stream. The latter appears more probable.

The effect of reducing the engine temperature to 190°K using gaseous hydrogen in the 140 to 190°K range was insignificant, since light-off still occurred within the engine and the data fell within the scatter of that from ambient temperature tests. Note that with liquid hydrogen feed with the engine at 190°K, ignition occurred outside the engine. An increase in engine starting pressure to 14.5 psia was inconclusive because of insufficient data.

C. Discussion of Results

1. Ignition and Combustion Aspects

We must first consider the validity of correlating ignition data with the total mixture ratio $\overset{\circ}{O}/\overset{\circ}{F}$ which represents the ratio of mass inputs to the engine. Two recent reports have indicated that ignition characteristics are functions of the mixture ratio. Marquardt[5] reports

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[5] Feasibility Study of Oxygen/Hydrogen Powdered Metal Ignition, Report No. 25, 179, NASA Contract No. NAS 8-11250, 16 Sept. 1964 to 15 Sept., 1965, p. 20.

this phenomenon in its feasibility study of the ignition of oxygen/hydrogen with powdered metals. Pratt & Whitney[6] reported a similar correlation for the hypergolic ignition of light hydrocarbon fuels with FLOX mixtures.

In the former case the observation was qualitative; for the latter, ignition delay was correlated with an equivalence ratio defined as the stoichometric mixture ratio divided by the mixture ratio at ignition. The derivation of theory has not been attempted nor discussed. The reason is obvious since there has been so little work on the development of theoretical models for unsteady flow conditions. The lack of a theoretical background, however, would not preclude the use of such correlations if experimentally one can vary engine and operating parameters and detect the effect of the change.

In the case of H_2/LOX:O_3F_2 we have postulated that thermal decomposition of O_3F_2 produces active radicals, [O], which initiate the hydrogen-oxygen chain reaction. It is thus reasonable that the onset of ignition will be favored by a high concentration of [O] which is associated with a high relative concentration of O_3F_2; this in turn is favored by a high O/F.

Another factor in this study which, however, can be only gaged in a qualitative manner, is the transfer of thermal energy from the usually relatively warm combustor. Thus it was found that blow-back ignitions occurred when the combustor was held at temperatures close to 100°K; similarly a liquid hydrogen lead may be undesirable since it would precool the combustor and lower temperatures would inhibit thermal decomposition of O_3F_2.

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[6] Hypergolic Ignition of Light Hydrocarbon Fuels with Fluorine-Oxygen (FLOX) mixtures, Paper presented at Western States Section. The Combustion Institute, Santa Barbara, Calif., 22-26 Oct. 1965 by S. A. Mosier, R. E. Dotson and O. K. Moehrbach.

While it is not to be inferred that the test results from the small combustor used are directly scalable to large rocket engines, it is pertinent to examine the trends obtained. First, as a result of the tests where the engine ambient temperature was in the range of 77 to 200°K, it is concluded that ignitions will occur outside the engine whenever altitude ignitions are attempted. The effect of engine thrust rating upon this conclusion cannot be stated positively since the only thrust variable was with the single triplet injector going from 100 to 300lb thrust. From 230°K to 290°K (ambient temperatures), O_3F_2 gives satisfactory hypergolic ignitions at altitude if gaseous hydrogen at 140°K upwards is used. Ignitions under these conditions ranged from 10 through 80 milliseconds with the majority being under 40. If liquid hydrogen feed to the injector is used, only engine temperatures in the ambient region will give reliable ignitions at altitude. The reaction appears to be kinetically limited below 230°K.

Injector design influences the time to ignition at sea level by changes in mixing energy and spray break-up. Unfortunately these factors are intimately concerned with combustion instability (See analysis in Appendix A). The vortex injector with fuel entering radially and oxygen flowing axially appears to be unstable in a spinning tangential mode. With LOX/hydrogen, the combustion wave travels at the detonation velocity of about 2600 meters/sec. Changes in O/F ratio will cause velocities as high as 3000 meters/sec.

It is significant that O_3F_2 does not inhibit combustion instability. One of the puzzling aspects of our experiments is the predominance of higher-amplitude pressure oscillations when LOX leads were employed.

Most investigators have reported the increase in ignition delay with altitude of almost all hypergolic propellant combinations. Hydrogen LOX/O_3F_2 proved to be no exception. However, it appears that careful engine design combined with O/F programming can keep the delay at a satisfactory level.

It appears that the relatively long delays (10-80 ms) may pose problems in small inpulse bit devices; in large engines the apparent detonation of accumulated unreacted propellants may not be acceptable unless a prechamber and propellant flow programming are utilized.

2. Factors Relating to Use in Large Rocket Engines

The current program with its large number of test series was satisfactorily carried out using liquid hydrogen in combination with an oxidant which was hypergolic with any combustible material. The successful use of a flow facility with no major operational problems indicates that LOX/O_3F_2 imposes no more serious hardware problems than associated with those encountered with fluorine.

It does not appear that the storage stability is completely adequate for some purposes. In particular, the flow test studies show that, in mixing and transporting LOX/O_3F_2, up to 40% of a nominally saturated solution may be lost. In this study it was considered that losses in O_3F_2 content could arise from: (1) impurities in the neat LOX, (2) variable purity of the neat O_3F_2, and (3) interaction with the flow facility.

The approach taken to minimize these losses by mixing an obviously large excess of O_3F_2 with the LOX does not appear desirable for large scale preparation of LOX:O_3F_2.

The thermal instability of O_3F_2 obviously poses problems since heat leakage into cryogenic storage systems often occurs at points where corrosion must be minimized, as, for example, the discharge ports. The requirement that cold LOX/O_3F_2 ($\sim 90^\circ K$) would be injected into the combustion chamber will pose additional problems in flow system design since inadvertent delivery of a gaseous oxygen slug could cause a system malfunction. Excessively long complex chill-down requirements in stop-start operation of any type of engine will obviously result in weight penalties and negate other advantages of hypergolic ignition, such as simplicity and short preparation time.

Small attitude control devices might be thought to be well suited to gaseous hydrogen/LOX:O_3F_2 operation. It appears that the thermal instability of O_3F_2 will be a problem in small flow lines; thus fluorine/hydrogen mixtures which are hypergolic in the gaseous form appear far more desirable.

Another point to consider is that hypergolicity may eliminate the blast hazard resulting from premixing and subsequent explosion of fuel and oxidant. It is certainly true that LOX:O_3F_2 can be of service in this manner but so equally can FLOX and neat fluorine.

In discussing the relative merits of LOX:O_3F_2, FLOX, and fluorine, it appears that the material reactivity problems are the same for all three. However, in the case of LOX:O_3F_2 the low concentration of O_3F_2 in solution may be eliminated completely by slow reactions in storage or transfer. The only advantages LOX:O_3F_2 may have are lower toxicity and perhaps lower cost. Whether cost is a factor awaits a detailed cost analysis of O_3F_2 preparation, LOX:O_3F_2 solution mixing, large scale storage studies, and development of quality control procedures.

TABLE II

TEST SERIES 2

Test	LH_2						LO_2						Engine										Remarks
	T_i	T_L	P_L	P_T	P_i	$\dot{W}$	T_i	T_L	P_L	P_T	P_i	$\dot{W}$	T_{c1}	T_{c2}	T_{c3}	P_c	P_a	Lead (ms)	$\dot{O}$	$\dot{F}$	$\dot{O}/\dot{F}$	Ignition Delay (ms)	
53	75 120	127 131	290 290	300 300	- 135	0.0550	88 110	78 85	345 340	335 335	- 60	0.257	*	*	*	20	14.5	O_2 30	0.0286	0.0040	7.15	70	
54	73 60	67 65	288 288	267 267	- 127	0.0549	88 115	103 102	308 308	330 330	- 92	0.225	*	*	*	-	14.5	O_2 34	0.0287	0.0055	5.22	93	
55	LH_2 valve didn't open																						
56	LH_2 valve didn't open																						
57	75 94	102 105	295 290	340 340	- 195	0.0550	96 120	87 104	380 380	337 337	- 125	0.250	*	*	*	-	14.5	O_2 50	0.0248	0.0033	7.52	56	
58	75 -	98 -	58 -	105 -	- -	-	93 113	108 108	140 -	145 -	- 70	0.126	*	*	*	-	14.5	O_2 37	-	-	-	No Ignition	
59	LH_2 valve didn't open																						
60	LH_2 valve didn't open																						
61	LH_2 valve didn't open																						
62	LH_2 valve didn't open																						
63	LH_2 valve didn't open																						

NOTE: The first line for each test indicates value before ignition (start); the second, value at ignition (1) SERIES 2, SMALL TRIPLET INJECTOR; LIQUID NITROGEN BATH AROUND ENGINE

* Not measured.

TABLE III

TEST SERIES 3

Test	LH$_2$						LO$_2$						Engine										Remarks
	T_i	T_L	P_L	P_T	P_i	$\dot{W}$	T_i	T_L	P_L	P_T	P_i	$\dot{W}$	T_{c1}	T_{c2}	T_{c3}	P_c	P_a	Lead (ms)	$\dot{O}$	$\dot{F}$	$\dot{O}/\dot{F}$	Ignition Delay (ms)	
64	75 -	112 108	215 -	270 -	- -	0.0478	95 -	131 115	220 -	350 -	- -	0.149	*	*	*	-	14.5	O_2 40	-	-	-	No Ignition	
65	75 105	- -	190 190	240 240	- 50	0.0450	90 122	134 101	250 250	370 370	- 10	0.204	*	*	*	-	14.5	O_2 40	-	-	-	After Shutdown	Outside
66	75 74	73 66	270 273	320 320	- 170	0.0533	80 116	87 105	275 276	375 375	- 10	0.208	*	*	*	45	14.5	O_2 42	0.0162	0.0030	5.40	68	
67	75 75	77 77	295 292	345 345	- 230	0.0551	87 127	111 127	320 320	377 377	- 40	0.140	*	*	*	20	14.5	O_2 39	0.0083	0.0018	4.61	32	
68	75 75	77 75	310 310	360 360	- 240	0.0568	84 125	92 125	390 418	380 380	- 40	0.199	*	*	*	18	14.5	O_2 44	0.0127	0.0022	5.77	37	
69	75 75	80 80	360 360	310 310	- 275	0.0568	87 112	83 112	390 395	380 380	- 90	0.239	*	*	*	20	14.5	O_2 135	0.0309	0.0031	9.97	27	
70	75 80	92 97	285 287	335 335	- 210	0.0547	89 107	82 105	395 380	380 380	- 100	0.249	*	*	*	20	14.5	O_2 135	0.0368	0.0041	8.97	43	
71	75 74	72 71	260 257	310 310	- 203	0.0520	87 111	83 114	395 390	380 380	- 87	0.231	*	*	*	20	14.5	O_2 136	0.0303	0.0032	9.47	32	
72	76 79	- -	245 245	295 295	- 130	0.0508	76 127	95 124	360 360	355 355	- 365	0.179	*	*	*	70	14.5	O_2 27	0.0169	0.0025	6.76	75	
73	76 75	- -	250 247	300 300	- 200	0.0510	75 108	88 110	365 355	360 360	- -	0.228	*	*	*	35	14.5	O_2 20	0.0117	0.0014	8.36	40	
74	76 60	76 76	315 310	365 365	- 165	0.0568	75 90	84 106	450 450	440 440	- 305	0.271	*	*	*	20	14.5	H_2 37	0.0107	0.0059	1.81	60	
75	87 87	- -	205 205	255 255	- -	0.0468	87 117	104 127	345 335	335 335	- 390	0.149	*	*	*	10	14.5	O_2 56	0.0082	0.0010	8.20	3	Engine in liquid Argon
76	87 65	- -	205 -	250 -	- -	0.0468	90 104	97 110	345 -	335 -	- -	0.225	*	*	*	-	14.5	O_2 45	-	-	-	No Ignition	Nozzle O-Ring failure
77	87 68	- -	210 -	257 -	- -	0.0471	90 97	94 102	345 -	335 -	- -	0.241	*	*	*	-	14.5	O_2 31	-	-	-	No Ignition	Nozzle O-Ring failure

NOTE: The first line for each test indicates value before ignition (start); the second, value at ignition (1) SERIES 3, SMALL TRIPLET INJECTOR; LIQUID NITROGEN ENGINE BATH EXCEPT TEST 75

* Not measured.

TABLE IV

TEST SERIES 4

Test	LH_2						LO_2						Engine										Remarks
	T_i	T_L	P_L	P_T	P_i	$\dot{W}$	T_i	T_L	P_L	P_T	P_i	$\dot{W}$	T_{c1}	T_{c2}	T_{c3}	P_c	P_a	Lead (ms)	$\dot{O}$	$\dot{F}$	$\dot{O}/\dot{F}$	Ignition Delay (ms)	
78	77 65	70 46	250 260	200 200	- 119	0.178	83 107	90 108	245 240	250 250	- 68	0.704	*	*	*	130	14.5	O_2 43	0.0439	0.0042	10.45	27	
79	76 60	73 38	250 255	200 200	- 115	0.178	78 100	94 101	245 240	255 255	- 100	0.766	*	*	*	90	14.5	O_2 57	0.0695	0.0047	14.79	29	
80	76 64	69 49	345 365	335 335	- 205	0.218	84 95	92 100	365 350	350 350	- 213	0.877	*	*	*	145	14.5	O_2 52	0.0617	0.0043	14.35	23	
81	77 65	73 49	365 380	345 345	- 165	0.227	80 100	80 80	360 340	370 370	- 215	0.965	*	*	*	-	14.5	O_2 53	0.0635	0.0039	16.28	22	
82	87 74	x	350 355	345 345	- 250	0.221	87 107	91 98	+	360 360	- 165	0.921	*	*	*	115	14.5	O_2 49	0.0453	0.0034	13.32	19	
83	83 68	x	335 335	350 350	- 215	0.223	87 107	90 97	+	345 345	- 120	0.901	*	*	*	155	14.5	O_2 56	0.0502	0.0023	21.83	14	
84	81	x	345	350	-	0.223	95	84	+	345	-	0.890	*	*	*	-	1.1	O_2 50	-	-	-	252	Ignition after shutdown
85	79 49	x	340 330	350 350	- 195	0.223	84 95	85 92	+	345 345	- 175	0.909	*	*	*	-	1.1 1.8	O_2 45	0.0985	0.0149	6.61	70	
86	80	x	340	350	-	0.223	85	89	+	350	-	0.893	*	*	*	-	1.1 4.6	H_2 58	-	-	-	309	Ignition after shutdown
87	78 73	77 57	330 330	330 330	- 185	0.217	83 106	85 107	+	350 350	- 55	0.869	*	*	*	110	14.5	O_2 48	0.0614	0.0078	7.87	38	
88	77 77	70 70	330 335	330 330	- 0	0.217	80 107	90 112	355 385	350 350	- 40	0.855	*	*	*	130	14.5	O_2 63	0.0476	0	-	0.030	Pre-Ignition
89	77 63	59 45	390 370	385 385	- 185	0.231	89 100	108 117	355 360	355 355	- 125	0.900	*	*	*	130	14.5	O_2 65	0.0544	0.0040	13.60	21	
90	87 64	59 44	355 350	350 350	- 120	0.223	96 107	98 112	355 355	355 355	- 75	0.864	*	*	*	110	14.5	O_2 55	0.0673	0.0067	10.04	35	
91	87 84	58 55	340 325	340 340	- 93	0.219	98 115	123 135	355 370	360 360	- 80	0.842	*	*	*	122	14.5	O_2 58	0.0503	0.0012	41.92	10	

NOTE: The first line for each test indicates value before ignition (start); the second, value at ignition.
(1) TESTS 82-86, 90-91 engine dewar contained liquid argon; all others, liquid nitrogen
(2) TESTS 78-86, triplet injector; 87-91, coaxial injector
(3) TESTS 78-91, lit outside

x Open thermocouple
+ Frozen pressure tap
* Not measured

TABLE V

TEST SERIES 5

Test	LH$_2$						LO$_2$						Engine										Remarks
	T_i	T_L	P_L	P_T	P_i	$\dot{W}$	T_i	T_L	P_L	P_T	P_i	$\dot{W}$	T_{c1}	T_{c2}	T_{c3}	P_c	P_a	Lead (ms)	$\dot{O}$	$\dot{F}$	$\dot{O}/\dot{F}$	Ignition Delay (ms)	
97	77 69	76 43	385 385	380 380	- 250	0.226	78 93	78 82	375 200	380 380	- 35	0.880	~180	254	264	155	14.5	H_2 12	0.0100	0.00279	3.58	12	
98	75 46	76 29	365 340	360 360	- 232	0.221	78 103	67 103	380 370	385 385	- 134	0.889	~180	267	270	190	0.5	H_2 20	0.0287	0.00743	3.86	34	
99	75 47	75 29	365 380	360 360	- 236	0.221	83 110	73 117	380 395	390 390	- 156	0.836	~180	268	270	185	0.5	H_2 5	0.0311	0.00802	3.88	43	
100	74 49	73 34	390	380	-	0.226	77 101	75 101	360	365	-	0.851	~170	197	198	-	0.1	H_2 12	-	-	-	750	Ignition after shutdown; dry ice
101	75 67	70 54	375 360	365 365	- 269	0.223	78 102	82 81	360 195	365 365	- 40	0.858	~170	196	197	-	14.5	H_2 7	0.0113	0.00268	4.22	14	
102	75 54	65 36	375 380	370 370	- 229	0.224	78 107	82 109	360 320	370 370	- 250	0.846	~170	196	196	-	14.5	H_2 3	0.0242	0.00847	2.86	41	
103	74 52	70 37	385	375	-	0.225	79 103	67 108	360	365	-	0.805	~160	197	198	-	0.5	H_2 12	-	-	-	~3800	Ignition after shutdown; dry ice
104	81 82	87 88	390 390	370 370	- 266	0.224	79 112	80 110	350 350	350 350	- 95	0.845	~180	252	260	154	14.5	O_2 45	0.0406	-	-	5	$\dot{F}$ unattainable
105	75 46	90 30	380 380	365 365	- 245	0.223	75 100	105 100	350 350	350 350	- 140	0.836	~180	265	268	138	0.2	O_2 60	0.129	0.0217	5.94	108	
107	75 67	77 55	380 380	370 370	- 275	0.224	74 113	84 115	350 350	350 350	108	0.862	~180	266	269	170	2.7	O_2 7	0.0254	0.00329	7.72	25	
108	74 43	68 62	430 430	410 410	- 320	0.234	75 95	80 110	350 350	350 350	- 225	0.868	~170	265	267	-	0.3	O_2 7	0.0150	0.00238	6.30	16	
109	75 74	73 73	375 375	360 360	- 292	0.221	75 90	94 103	345 345	350 350	- 90	0.866	~180	264	267	-	3.6	O_2 10	0.00875	0.000807	10.84	9	
110	76 88	93 110	375 375	360 360	- 293	0.105	77 100	107 123	330 330	335 335	- 73	0.752	~170	261	266	-	3.0	O_2 5	0.0131	0.00158	8.29	15	Hydrogen gas
111	77 86	109 124	375 375	360 360	- 297	0.101	77 105	112 127	330 330	335 335	94	0.704	~170	262	266	-	0.6	O_2 7	0.0131	0.00131	10.00	13	Hydrogen gas
112	81 89	104 125	375 375	360 360	- 283	0.098	82 110	107 123	330 330	335 335	100	0.805	~170	250	260	-	14.5	O_2 13	0.0191	0.00118	16.19	12	Hydrogen gas

NOTE: The first line for each test indicates value before ignition (start); the second, value at ignition.
(1) SERIES 5, TRIPLET INJECTOR, AMBIENT BATH EXCEPT TESTS 100 AND 103

TABLE VI

TEST SERIES 6

Test	LH$_2$						LO$_2$						Engine										Remarks
	T_i	T_L	P_L	P_T	P_i	$\dot{W}$	T_i	T_L	P_L	P_T	P_i	$\dot{W}$	T_{c1}	T_{c2}	T_{c3}	P_c	P_a	Lead (ms)	$\dot{O}$	$\dot{F}$	$\dot{O}/\dot{F}$	Ignition Delay (ms)	
113	114 109	67 68	375	375	- 90	0.224	86 103	95 102	340	350	- 54	0.847	155	252	260	105	14.5	O_2 55	0.0500	-	-	2.3	$\dot{F}$ unattainable
114	62 55	87 45	375	375	- 223	0.224	76 103	95 108	340	350	- 70	0.862	155	252	260	-	4.0	O_2 10	0.0201	0.00305	6.6	20.5	
115	64 64	73 70	365	365	- 270	0.222	73 99	99 114	345	355	- 62	0.855	155	252	260	135	1.7	O_2 27	0.0104	0.00085	12.2	9	
116	60 35	83 32	395	390	- 240	0.228	65 105	78 102	350	355	- 45	0.856	162	268	273	180	3.8	O_2 14	0.0495	0.00882	5.6	50	
117																							Pre-Ignition
118	62 70	83 53	425	425	- 257	0.237	69 103	80 120	350	355	- 79	0.872	162	264	270	215	7.8	O_2 14	0.0364	0.00401	9.1	31.5	
119	61 52	51 46	365	360	- 275	0.221	73 106	77 106	350	355	- 56	0.832	135	231	236	137	0.4	O_2 19	0.0395	0.00570	6.9	36	
120																							Pre-Ignition
121	70 34	79 30	350	345	- 205	0.217	69 105	80 106	340	350	- 55	0.856	140	235	236	180	7.9	O_2 28	0.0649	0.00916	7.1	54	
122	61 74	80 62	350	345	- 200	0.217	62 95	90 100	340	350	- 72	0.836	140	235	237	205	2.8	O_2 22	0.0298	0.00234	12.7	27	
123	61	78	390	385	-	0.227	65	80	345	350	-	0.836	140	201	204	29	0.1	O_2 20	-	-	-		Ignition after shutdown; dry ice temperature

NOTE: The first line for each test indicates value before ignition (start); the second, value at ignition.
(1) VORTEX INJECTOR (Series 6)
(2) TESTS 119, 121, 122 FREON 12 BATH
TESTS 114-118 AMBIENT BATH

TABLE VII

TEST SERIES 7

Test	LH_2						LO_2						Engine										Remarks
	T_i	T_L	P_L	P_T	P_i	$\dot{W}$	T_i	T_L	P_L	P_T	P_i	$\dot{W}$	T_{c1}	T_{c2}	T_{c3}	P_c	P_a	Lead (ms)	$\dot{O}$	$\dot{F}$	$\dot{O}/\dot{F}$	Ignition Delay (ms)	
124	92 34	79 33	365	370	- 230	0.224	75 100	76 97	350	355	- 130	0.860	166	254	267	190	14.5	O_2 105	0.123	0.00832	14.78	53	
125	124 33	75 33	365	365	- 232	0.223	104 96	79 93	350	355	- 164	0.884	175	260	264	161	14.5	O_2 66	0.104	0.01077	9.66	65	
126	68 32	75 32	350	355	- 250	0.220	61 100	85 94	350	350	- 207	0.879	183	262	266	171	0.9	O_2 68	0.168	0.0215	7.81	117	
127	86 76	78 77	350	350	- 245	0.219	77 103	81 97	350	360	- 253	0.875	173	223	227	150	14.5	O_2 55	0.0703	0.00185	38.00	26	
128	96 52	77 37	350	350	- 241	0.219	92 103	85 95	350	355	- 183	0.877	161	222	226	145	14.5	O_2 58	0.0903	0.00542	16.66	42	Lit outside
129	70 34	77 33	400	405	- 269	0.232	62 100	96 95	350	360	- 190	0.881	167	224	228	154	1.0	O_2 52	0.104	0.01309	7.94	71	Lit outside
130	85 74	74 72	355	355	- 252	0.220	30 104	78 95	360	365	- 182	0.883	140	176	181	147	14.5	O_2 62	0.0760	0.00170	44.71	23	
131	65	73	360	360	-	0.221	60	81	355	360	-	0.875	143	179	184	27	1.0	O_2 60	-	-	-		Ignition after shutdown
132	108 51	73 41	370	370	- 215	0.224	110 100		355	365	- 185	0.883	140	177	182	140	14.5	O_2 58	0.0947	0.00660	14.35	47	TL-O opened

NOTE: The first line for each test indicates value before ignition (start); the second, value at ignition.

(1) TESTS 124-126 AMBIENT BATH
TESTS 127-129 LIQUID FREON BATH
TESTS 130-132 DRY ICE BATH

(2) TRIPLET INJECTOR (SERIES 7)

TABLE VIII

TEST SERIES 8

Test	LH_2						LO_2						Engine										Remarks
	T_i	T_L	P_L	P_T	P_i	$\dot{W}$	T_i	T_L	P_L	P_T	P_i	$\dot{W}$	T_{c1}	T_{c2}	T_{c3}	P_c	P_a	Lead (ms)	$\dot{O}$	$\dot{F}$	$\dot{O}/\dot{F}$	Ignition Delay (ms)	
134	90 33	75 30	400	380	- 138	0.226	92 98	85 95	330	350	- 185	0.862	188	262	276	160	14.5	O_2 80	0.1222	0.01102	11.09	65	Lit outside
135	97 71	77 72	360	340	- 234	0.215	82 105	83 121	330	350	- 122	0.866	185	256	268	150	14.5	O_2 27	0.04679	0.00159	29.43	23	
136	61 33	75 31	360	340	- 147	0.215	61 98	94 96	330	350	- 215	0.866	188	272	275	170	0.3	H_2 7	0.07751	0.01648	4.70	96	
137	56 33	75 32	365	340	- 180	0.215	60 95	89 95	335	350	- 195	0.862	186	270	274	150	0.2	H_2 3	0.1429	0.03248	4.40	177	
138	95 62	74 56	365	340	- 223	0.215	86 91	93 95	335	350	- 237	0.866	185	254	268	165	14.5	H_2 12	0.00777	0.00185	4.20	9	
139	58 43	68 40	380	355	- 153	0.220	60 92	81 96	335	350	- 130	0.874	185	268	274	-	0.1	H_2 10	0.04272	0.00962	4.44	52	
140	89 77	79 79	365	340	- 212	0.215	96 96	98 103	330	345	- 75	0.840	186	255	266	-	14.5	H_2 2	0.01362	0.00095	14.34	16	
141	97 29	69 27	365	340	- 170	0.215	80 94	95 97	335	350	-	0.856	193	257	267	- 44	14.5	H_2 38	0.01583	0.00451	3.51	19	Lit outside
142	56 32	73 29	370	345	- 160	0.217	58 102	81 102	335	350	- 195	0.859	184	267	271	-	0.6	O_2 11	0.04488	0.00629	7.14	46	
143	59 -	69 -	370	345	- -	0.217	59 -	84 -	335	350	- -	0.856	183	268	271	-	0.4	O_2 70	-	-	-	-	Ignition after shutdown
144																							Pre-Ignition

NCTE: The first line for each test indicates value before ignition (start); the second, value at ignition.
(1) SERIES 8, TRIPLET INJECTOR, AMBIENT ENGINE BATH

TABLE IX

TEST SERIES 9

	LH_2						LO_2						Engine										Remarks
Test	T_i	T_L	P_L	P_T	P_i	$\dot{W}$	T_i	T_L	P_L	P_T	P_i	$\dot{W}$	T_{c1}	T_{c2}	T_{c3}	P_c	P_a	Lead (ms)	$\dot{O}$	$\dot{F}$	$\dot{O}/\dot{F}$	Ignition Delay (ms)	
145	90 77	79 78	120 -	125 -	- 86	0.145	76 94	79 129	- 430	- 445	- 65	0.897	158	249	271	93	14.5	H_2 25	0.00569	0.000768	7.41	7.5	
146	82 58	76 65	155 -	165 -	- 112	0.166	83 109	85 102	- 430	- 445	- 67	0.904	156	249	265	95	14.5	0	0.0393	0.00462	8.51	45	
147	60 38	76 45	155 -	160 -	- 123	0.164	67 98	80 96	- 430	- 445	- 130	0.899	163	263	269	90	3.9	H_2 3	0.118	0.0202	5.84	140	
148	58 44	75 52	150 -	160 -	- 182	0.164	62 110	80 110	- 430	- 445	- 200	0.891	162	264	270	86	1.5	H_2 6	0.0610	0.0102	5.98	73	
149	85 86	100 100	235 -	240 -	- 160	0.195	77 96	81 114	- 330	- 345	- 87	0.771	151	245	262	85	14.5	0	0.00426	0.000298	14.3	6	
150	85 82	83 81	235 -	240 -	- 225	0.195	78 98	78 110	- 330	- 340	- 77	0.783	159	247	261	100	14.5	H_2 2	0.00708	0.000870	8.14	12	
151	84 80	83 80	430 -	440 -	- 440	0.254	78 94	78 102	- 155	- 160	- 37	0.549	160	248	262	95	14.5	H_2 4	0.00647	0.00246	2.63	13	
152	82 58	81 59	430 -	435 -	- 385	0.252	78 101	82 105	- 155	- 160	- 48	0.537	161	249	262	100	14.5	H_2 14	0.0130	0.00625	2.08	28	
153	80 87	98 97	350 -	355 -	- 265	0.232	83 95	81 103	- 160	- 165	- 40	0.547	159	248	261	105	14.5	H_2 3	0.00776	0.000986	7.87	14.5	
154	82 86	101 100	350 -	355 -	- 240	0.232	78 104	115 113	- 155	- 160	- 68	0.529	160	250	261	105	14.5	O_2 7	0.00752	0.000823	9.14	14	
155	94 -	61 -	440 -	445 -	- -	-	129 -	80 -	- 245	- 250	- -	-	169	268	285	-	14.5	H_2 20	-	-	-	-	Ignition after shutdown
156	88 -	73 -	440 -	440 -	- -	-	131 -	77 -	- 245	- 250	- -	-	174	266	284	-	14.5	H_2 25	-	-	-	-	Ignition after shutdown
157	86 31	92 34	260 -	260 -	- 175	0.202	120 103	80 101	- 345	- 350	- 100	0.806	170	257	274	130	14.5	H_2 10	0.0643	0.0150	4.29	88	Lit outside

TABLE IX (Concluded)

Test	LH$_2$						LO$_2$						Engine										Remarks
	T_i	T_L	P_L	P_T	P_i	$\dot{W}$	T_i	T_L	P_L	P_T	P_i	$\dot{W}$	T_{c1}	T_{c2}	T_{c3}	P_c	P_a	Lead (ms)	$\dot{O}$	$\dot{F}$	$\dot{O}/\dot{F}$	Ignition Delay (ms)	
158	59 32	76 35	260 -	255 -	- 195	0.200	68 97	82 99	- 340	- 345	- 140	0.806	169	274	279	125	2.5 15.0	H$_2$ 15	0.131	0.0292	4.49	160	Lit outside
159	60 -	90 -	260 -	255 -	- -	0.200	67 -	82 -	- 340	- 345	- -	-	168	263	277	-	0.4	0	-	-	-	-	No ignition
160	71 42	77 45	260 -	255 -	- 250	0.200	68 90	81 95	- 340	- 345	- 330	0.810	167	272	276	118	4.9 11.0	H$_2$ 9	0.112	0.0286	3.92	160	Lit outside
161	60 48	86 57	260 -	255 -	- 282	0.200	70 96	81 102	- 340	- 345	- 126	0.803	168	271	275	140	6.8 10.8	H$_2$ 10	0.0265	0.00755	3.51	42	Lit outside
162	88 67	89 73	260 -	255 -	- 210	0.200	122 102	80 106	- 340	- 345	- 147	0.803	176	256	272	137	14.5	0	0.0222	0.00405	5.48	37	Lit outside
163	82 30	80 33	255 -	250 -	- 185	0.199	117 99	80 104	- 340	- 345	- 115	0.803	173	257	270	135	14.5	H$_2$ 58	0.0260	0.0160	1.62	41	Lit outside
164	82 31	82 35	260 -	250 -	- 188	0.199	118 102	80 105	- 340	- 345	- 98	0.803	170	257	270	138	14.5	H$_2$ 43	0.0255	0.0127	2.01	40	Lit outside
165	82 53	82 63	375 -	360 -	- 275	0.233	117 105	83 112	- 340	- 345	- 91	0.785	167	254	268	174	14.5	H$_2$ 11	0.0176	0.00599	2.94	26	Lit outside
166	82 40	75 48	460 -	445 -	- 347	0.255	111 100	80 105	- 340	- 345	- 73	0.794	165	256	268	170	14.5	H$_2$ 14	0.0254	0.00753	3.37	37	
167	65 -	79 -	370 -	360 -	- -	0.232	68 -	80 -	- 350	- 355	- -	-	163	270	273	-	0.1	H$_2$ 17	-	-	-	-	No ignition

NOTE: The first line for each test indicates value before ignition (start); the second, value at ignition.
(1) TESTS 145-167 AMBIENT BATH; VORTEX INJECTOR

TABLE X

TEST SERIES 10

Test	LH_2						LO_2						Engine										Remarks
	T_i	T_L	P_L	P_T	P_i	$\dot{W}$	T_i	T_L	P_L	P_T	P_i	$\dot{W}$	T_{c1}	T_{c2}	T_{c3}	P_c	P_a	Lead (ms)	$\dot{O}$	$\dot{F}$	$\dot{O}/\dot{F}$	Ignition Delay (ms)	
173	78 86	90 100	235 -	230 -	- 50	0.110	70 72	- -	325 -	340 -	- 29	0.869	159	255	273	150	14.5	H_2 8.5	0.00154	0.000150	10.27	2	
174	81 105	87 125	260 -	255 -	- 116	0.131	64 94	78 104	327 -	338 -	- 80	0.867	157	256	276	141	14.5	H_2 1.0	0.0174	0.000802	21.70	23	Lit outside
175	81 85	83 96	250 -	247 -	- 49	0.108	65 76	81 103	330 -	340 -	- 75	0.815	152	260	275	132	14.5	H_2 0.3	0.00551	0.000149	36.98	8.2	
176	77 102	107 127	236 -	231 -	- 74	0.094	65 92	82 106	248 -	255 -	- 76	0.731	156	263	276	-	14.5	H_2 0.5	0.0113	0.000365	30.96	16	
177	65 128	97 140	240 -	236 -	- 140	0.103	48 98	78 109	270 -	278 -	- 109	0.737	175	275	285	110	0.8 17.0	H_2 12	0.0156	0.00175	8.91	22.5	
178	61 143	130 161	254 -	248 -	- 150	0.103	49 102	83 107	263 -	270 -	- 112	0.719	177	275	285	113	1.1 15.8	H_2 6	0.0170	0.00159	10.69	25	
179	60 130	161 168	296 -	291 -	- 140	0.134	49 88	76 101	200 -	208 -	- 63	0.676	170	275	285	117	0.8 8.6	H_2 12	0.00673	0.00115	5.85	10.5	
180	70 150	177 182	276 -	270 -	- 160	0.115	48 96	92 112	244 -	250 -	- 111	0.707	168	274	285	115	0.6 10.2	H_2 14	0.00738	0.00118	6.25	11	
181	72 153	143 172	280 -	275 -	- 175	0.116	50 95	77 106	288 -	297 -	- 99	0.773	164	272	284	115	0.7 13.0	H_2 11.5	0.0117	0.00152	7.70	16	
182	64 151	79 162	215 -	210 -	- 118	0.078	65 107	107 98	328 -	343 -	- 89	0.858	180	291	298	148	0.6 16.2	H_2 10.5	0.0274	0.00202	13.56	31.5	
183	65 158	94 165	238 -	233 -	- 133	0.092	63 105	93 100	326 -	340 -	- 86	0.851	166	288	297	115	1.4 18.9	H_2 12	0.0673	0.00615	10.94	82	
184	68 160	90 163	241 -	236 -	- 137	0.093	62 105	85 102	326 -	340 -	- 89	0.851	166	288	297	139	1.4 18.7	H_2 9	0.0349	0.00311	11.22	43	
185	72 145	99 159	247 -	241 -	- 137	0.098	67 95	84 98	326 -	340 -	- 150	0.855	166	284	294	145	3.5 16.6	H_2 8	0.0145	0.00166	8.73	25	
186	161 148	117 136	253 -	247 -	- 71	0.098	118 92	84 97	327 -	340 -	- 58	0.851	167	275	290	124	14.5	H_2 3.5	0.00709	0.000245	28.94	9	
187	72 145	97 160	244 -	239 -	- 136	0.093	62 93	84 95	333 -	346 -	- 182	0.858	166	279	291	126	0.7 16.7	H_2 4	0.0198	0.00178	11.12	31	
188	75 143	164 173	293 -	285 -	- 167	0.128	66 111	104 107	291 -	302 -	- 96	0.789	160	205	212	131	0.8 16.4	H_2 3	0.0193	0.00164	11.77	25	
189	75 160	168 180	293 -	285 -	- 167	0.122	64 115	115 110	291 -	303 -	- 116	0.799	162	206	213	139	0.8 21.8	H_2 1.5	0.0261	0.00203	12.86	33.5	
190	75 178	114 182	284	277	- 164	0.118	64 108	87 106	291	303	- 90	0.782	156	207	213	137	0.4 21.6	H_2 10.5	0.0262	0.00296	8.85	35.5	

NOTE: The first line for each test indicates value before ignition (start); the second, value at ignition
(1) TESTS 188-190, DRY ICE BATH
TESTS 173-187, AMBIENT BATH

V GENERAL CONCLUSIONS

LOX:O_3F_2 can be utilized to promote hypergolic ignition of liquid hydrogen provided the combustion chamber is at normal ambient temperature. When gaseous hydrogen is used, satisfactory ignition times (10-80 milliseconds) can be obtained at sea level and high altitude environments.

Ignition delay has been found under most conditions to correlate with integrated O/F ratio, in agreement, but perhaps for different reasons, with studies made on Hydrocarbon/FLOX hypergols.[6]

The study of engineering considerations shows that LOX/O_3F_2, while comparable with FLOX and fluorine, has an additional problem associated with its use since O_3F_2 has appreciable rates of decomposition at temperatures in excess of 100°K.

From the over-all standpoint, it appears that LOX:O_3F_2 does not offer many advantages over LOX, FLOX, or fluorine; the complications associated with the use of FLOX or fluorine are combined with the lower performance of LOX. A very careful system study of all candidate ignition systems, engine/flow system design, and factors such as reliability and storage life needs to be made. This present study justifies consideration of LOX:O_3F_2 since it has shown that predictable behavior can be obtained if great care is exercised.

ACKNOWLEDGEMENTS

The valuable discussions with Erwin Edelman and Riley Miller of NASA, Lewis Research Center; G. Dale Roach, formerly of NASA; and H. Burlage, Jet Propulsion Laboratory (formerly of the Advanced Research and Technology Office), are gratefully acknowledged.

The relevance of current modelling theories to transient flow in the combustor was reviewed by G. A. Marxman.

APPENDIX A

OCCURRENCE OF COMBUSTION INSTABILITY

No evidence of combustion instability was noted with the triplet and coaxial injectors. Instrumentation in all cases included Kistler gages on engine chamber and both injector feed ports. The vortex injector, however, almost always caused instability. In Fig. A-1 we show the oscilloscope playback of a typical test. It was noted that instability starts at ignition and continues through shutdown. The oscillations also feed back to the injector pressure gages, although not in phase. Consideration of the cycle time and engine geometry indicate that the instability is probably a spinning detonation wave traveling at 2640 meters/sec.

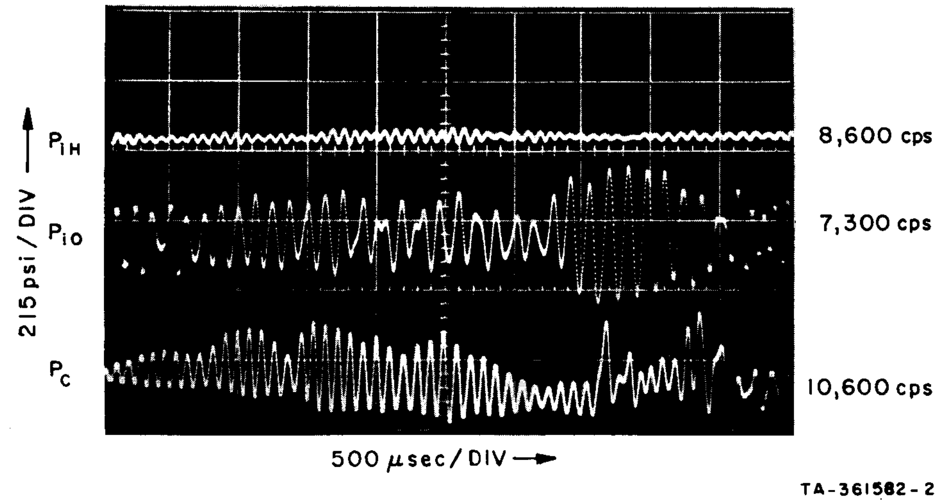

FIG. A-1 COMBUSTION INSTABILITY FEEDBACK TO INJECTOR PRESSURES, LOX/O_3F_2 LIQUID HYDROGEN ENGINE

Since we test fired the vortex injector with both liquid and gaseous hydrogen (after suitable modifications), it is of interest to compare relative severity of instability. In Table A-I we list the results for Test Series 6, 9, and 10 obtained from the tape playbacks of the Kistler gage measuring the chamber pressure. Peak-to-peak amplitudes are listed for each run. Note that for some runs the instability as measured by the amplitude of the pressure wave is very low, 5-10 psia with the mean chamber pressure in the range of 100 psia. However, the number of runs where low amplitude instability occurred amounted to only a few percent of the total.

The consideration of whether gaseous or liquid hydrogen feeds is more likely to give combustion instability can only be answered statistically. Gaseous hydrogen gave the highest peak-to-peak amplitude pressure waves; but it also resulted in a lower percentage of low amplitude firings. One of the puzzling aspects of this study was the low amplitude of most of the waves generated with liquid hydrogen in Test Series 9 where most peak-to peaks were 20 psia or lower. This was in contrast to Test Series 6 where most amplitudes were greater than 60 psia. About the only variable of significance appears to be whether oxygen or hydrogen was led. In general LOX leads appeared to generate more severe combustion instability. Among the variables which proved not to be significant were ambient pressure, engine environmental temperature, ignition delay, and mixture ratio.

TABLE A-I

PEAK-TO-PEAK AMPLITUDES OF COMBUSTION WAVES GENERATED WITH THE IMPINGING VORTEX INJECTOR

a. Liquid H_2

Series #	Test #	Peak-to-peak Pressure, psia	P_c	$\frac{\Delta P}{P_c}$	T_A, °K	P_A, psia	Ignition Delay, ms	Lead Prop. & Time, ms
6	113	75	105	0.714	-	14.3	2.3	O_2,59
6	114	105	-	-	-	4.0	20.5	O_2, 8
6	115	60	135	.444	260	1.7	9.0	O_2, 4
6	116	75	180	.417	273	3.8	50.0	O_2,14
6	117	110	185	.594	275	7.9	-	O_2,20
6	118	120	215	.558	270	7.8	31.5	O_2,15
6	119	60	137	.438	236	0.4	36	O_2,15
6	120	60	130	.461	230	14.7	-	O_2,19
6	121	140	180	.777	236	7.9	54	O_2,26
6	122	105	205	.512	237	2.8	27	O_2,16
6	123	15	29	.518	204	0.1	-	O_2,20
6 Avg. P-P		84						
9A	145	18	93	0.194	271	14.3	7.5	H_2,27
9A	146	15	95	.158	265	14.3	45	H_2, 1
9A	147	10	90	.111	269	3.9	140	H_2, 1
9A	148	10	86	.116	270	1.5	73	H_2, 7
9A	149	24	85	.282	262	14.3	6	H_2, 3
9A	150	12	100	.120	261	14.3	12	H_2, 4
9A	151	6	95	.063	262	14.8	13	H_2. 9
9A	152	15	100	.150	262	15.0	28	H_2, 9
9A	153	12	105	.114	261	14.5	14.5	O_2, 3
9A	154	75	105	.713	261	15.4	14	O_2,40
9B	155	24	-	-	285	14.3	-	H_2,20
9B	156	12	-	-	284	14.3	-	H_2,25
9B	157	20	130	.154	274	18.4	88	H_2, 8
9B	158	20	125	.160	279	2.5	160	H_2,16
9B	160	6	118	.051	276	4.9	160	H_2, 9
9B	161	18	140	.128	275	6.8	42	H_2,11
9B	162	18	137	.131	272	16.8	37	0
9B	163	10	135	.074	270	16.4	41	H_2,63
9B	164	18	138	.131	270	16.0	40	H_2,44
9B	165	40	174	.230	268	17.9	26	H_2,13
9B	166	60	170	.353	268	17.0	37	H_2, 7
9B Avg. P-P		21						

TABLE A-I (continued)

PEAK-TO-PEAK AMPLITUDES OF COMBUSTION WAVES GENERATED WITH THE IMPINGING VORTEX INJECTOR

b. Gaseous H_2

10	173	130	150	.866	273	14.5	2	O_2, 9
10	174	210	141	1.420	276	14.5	2	O_2, 1
10	175	140	132	1.060	275	14.5	8	O_2, 0.3
10	176	90	-	-	276	14.5	16	O_2, 0.5
10	177	85	110	.773	285	0.8	23	O_2,12
10	179	10	117	.085	285	0.8	11	O_2,12
10	180	15	115	.087	285	0.6	11	O_2,14
10	181	20	115	.174	284	0.7	16	O_2,12
10	182	60	148	.405	298	0.6	32	O_2,11
10	183	85	115	.739	297	1.4	82	O_2,12
10	184	115	139	.827	297	1.4	43	O_2, 9
10	185	90	145	.621	294	3.5	25	O_2, 8
10	186	20	124	.161	290	14.2	9	O_2, 4
10	187	10	126	.079	291	0.7	31	O_2, 4
10	188	35	131	.267	212	0.8	25	O_2, 3
10	189	190	139	1.367	213	0.8	34	O_2, 2
10	190	60	137	.437	213	0.4	36	O_2,11

Avg. P-P 80 psia

APPENDIX B

ROCKET USE FACTORS -- LOX/O_3F_2

INTRODUCTION

The use of trioxygen difluoride (ozone fluoride, O_3F_2) in rocket engines poses several problems to the engineers concerned with its utilization.[1,2*] This review discusses general problems, preparation and mixing, and use of the liquid oxygen solution of O_3F_2 (LOX/O_3F_2).

BACKGROUND

The utilization of liquid oxygen containing a small addition of trioxygen difluoride as a hypergolic oxidant for liquid hydrogen-fueled rocket engines is dependent to a major degree on the stability, under operation conditions, of the O_3F_2. It has been shown in previous studies that O_3F_2 solution can be satisfactorily handled in large quantities at or near the boiling point of oxygen.

Problems in the handling of LOX/O_3F_2 arise because it is an active fluorinating agent which is both thermally and photochemically unstable. Therefore equipment used with LOX/O_3F_2 or neat O_3F_2 must be passivated with gaseous fluorine. While tanks, lines, and valves of appropriate materials can be successfully used with LOX/O_3F_2, increased care is necessary during start up or shut down of a facility for testing of a combustor or engine. This is because the poor thermal instability of O_3F_2 above 110°K results in the formation of active, oxidizing species. These attack most materials used in the flow lines, even those passivated in advance. To obviate this possibility of corrosion, it is necessary to ensure that systems are chilled thoroughly with liquid oxygen (LOX) or liquid nitrogen (LN_2) prior to a run. On shutdown it is desirable that the system be purged with neat LOX and completely sealed from moisture.

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[*] Superscripts in Appendix B refer to references at the end of Appendix B.

PREPARATION AND HANDLING OF NEAT O_3F_2

Synthesis

Most syntheses of O_3F_2 are performed in some modification of the reactors shown in Fig. B-1. These are cooled by LOX or LN_2 and utilize high voltage (2,000-10,000 V, 20-40 milliamps), discharge tubes with metal electrodes of copper, aluminum, etc. Premixed reactant, 60% O_2, 40% F_2, is supplied to the reactors as required to maintain the pressure at 5-30 mm Hg. The O_3F_2 collects as a solid (below $83^\circ K$) or liquid on the walls of the reactor. Most single reactors (Figs. B-1, a-d) produce only a few cc's per hour, and usually produce some material which does not melt at the melting point of O_3F_2. Banks of single reactors and multiple reactors (Fig. B-1, e) are utilized for preparing large quantities of O_3F_2. Spark discharge[8] and ultraviolet light[3,9] synthesis methods have also been reported.

Efficient production seems to depend upon proper balancing of heat transfer characteristics to produce and condense O_3F_2 before decomposition. For large sample preparations, removal of O_3F_2 from the reactor zone is essential and is accomplished by operating above the melting point, $83^\circ K$, either intermittently or continuously. Several pounds of O_3F_2 have been prepared at both $77^\circ K$ and $90^\circ K$ utilizing a bank of four single reactors (cf. Kirshenbaum and Grosse[4]).

The reactors were operated at 77° for about $3\frac{1}{2}$ hours at which time the LN_2 baths were replaced with LOX for 5-10 minutes. This allowed the O_3F_2 to melt and drain from the reactor zone. (Longer operation without O_3F_2 removal decreases reaction rate.) Next the LN_2 baths were returned to the system and another cycle completed. This operation could be improved by using a pressurizable Dewar flask. By controlling the pressure (and therefore the temperature) of the LN_2 bath, O_3F_2 can be melted from the reactor walls without dismantling the coolant bath (the vapor pressure of nitrogen is 2 atm at $83^\circ K$). LN_2 baths also preclude leakage of O_2 into the reactor which could produce ozone.

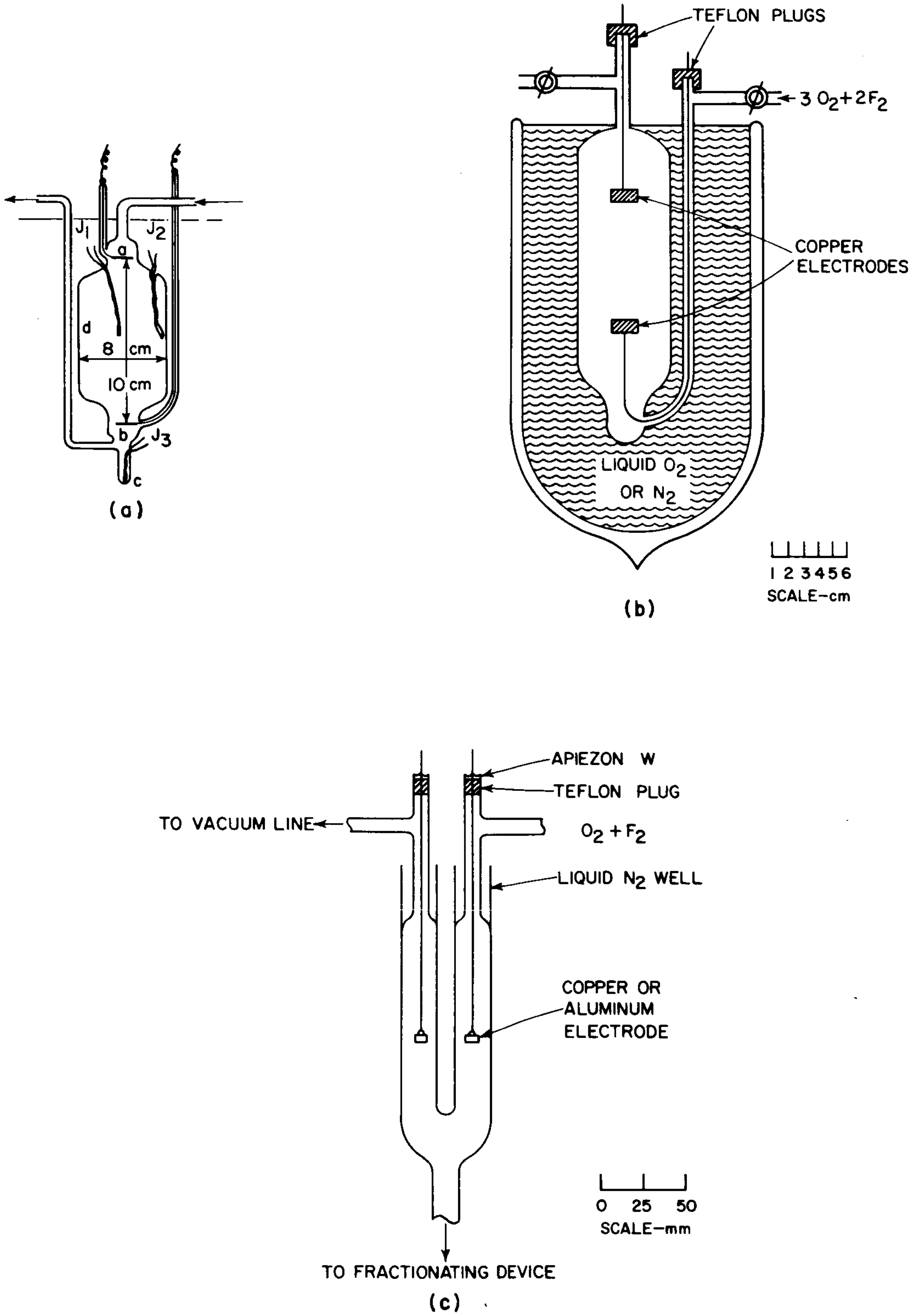

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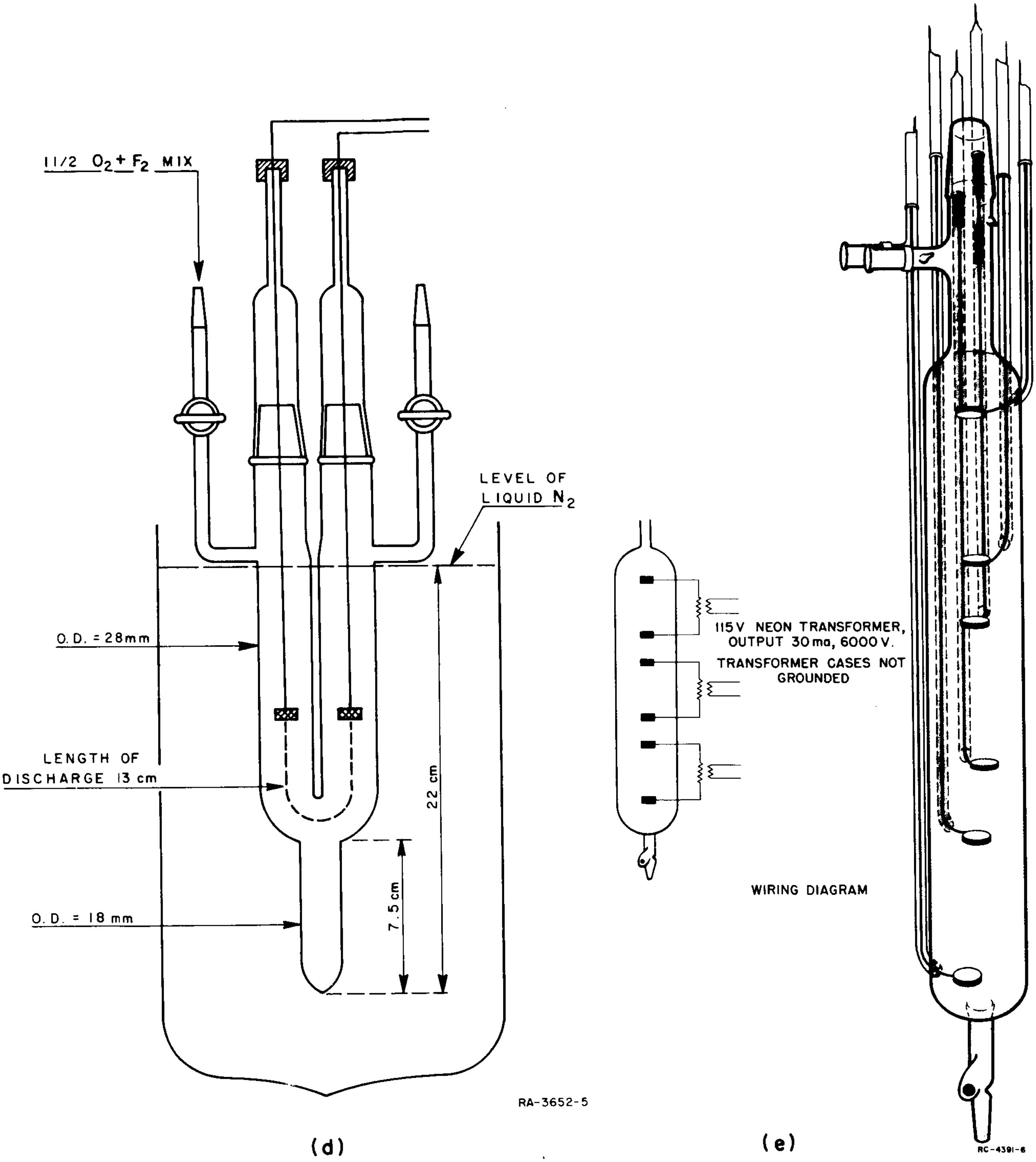
FIG. B-1 (a) APPARATUS FOR SYNTHESIS OF O_3F_2: AOYAMA AND SAKURABA (Ref. 3)
(b) APPARATUS FOR SYNTHESIS OF O_3F_2: KIRSHENBAUM AND GROSSE (Ref. 4)
(c) U–TUBE O_3F_2 REACTOR: MAGUIRE (Ref. 5)



(d)

(e)

FIG. B-1 Concluded
(d) U-TUBE O_3F_2 REACTOR: STRENG AND GROSSE (Ref. 6)
(e) MULTIPLE REACTOR (Ref. 7)

In addition to O_3F_2, some O_2F_2 (solid at $90^{\circ}K$) is also produced and must be eliminated. This is done with a removable ball valve inserted between the filled receivers and the upper reactor walls. The receivers are kept below $90^{\circ}K$ while the portion of the reactor above the ball valve is warmed. Residual matter on the wall decomposes and the resultant gases are pumped away. The receivers are then removed either by warming the Kel-F lubricated standard taper joints to room temperature or by sealing the receiver necks well above the fluid level with an oxygen torch. Standard taper receivers are sealed with Kel-F grease containing a little Kel-F oil to lower the viscosity. As soon as practical the sealed sample containers are chilled to 77° for storage.

Physical Properties

Most of the physical properties of O_3F_2 have been determined by the Research Institute of Temple University. Pertinent data taken from a review article[10] are listed in Table B-I.

Chemical Properties

Trioxygen difluoride is reported[10] to be more reactive than F_2, OF_2, or mixtures of O_2 and F_2. Liquid O_3F_2 can initiate reactions, sometimes of explosive violence, with a wide variety of fuels at $90^{\circ}K$. The dilute solution of LOX-O_3F_2 can produce similar results. A partial list of materials treated with O_3F_2 and the observed results are shown in Table B-II taken from Reference 2.

Results of open cup ignition tests[2] with O_3F_2 LOX(0.05% O_3F_2) with various fuels are shown in Table B-III. Ignition of ethyl alcohol, JP_4, U-DETA, hydrogen gas (below $90^{\circ}K$), and propane has been reported in small rocket engine tests (20-pound thrust level).[2] Other tests with 500-pound thrust level engines have demonstrated ignition of hydrogen[17,7] using fully saturated LOX-O_3F_2 solution.

TABLE B-I

PHYSICAL AND PHYSICOCHEMICAL PROPERTIES OF TRIOXYGEN DIFLUORIDE

Properties	Ref.
Appearance	
Dark red liquid at 84°K. Reddish brown solid below 83°K.	
Molecular weight	
86.000	
Melting point	
83-84°K., -189 to -190°C.	(11)
Boiling point	
213°K., - 60°C. dec.	(11)
Vapor pressure[a]	
$\log P_{mm.} = 6.1343 - 675.57/T$	
(over the temp. range of 79 to 114°K.)	
P = 0.010 mm. at 83.052°K.	
0.100 94.693°K.	
1.00 110.130°K.	
10.00 131.580°K.	
Density[b]	
Liquid, d = 2.357 - 0.00676T g./cc.	(11)
1.573 g./cc. at 116°K.	
1.749 g./cc. at 90°K.	
1.895 g./cc. at m.p.	
Molar volume	
49.3 cc./mole at 90.3°K.	
Activation energy of thermal decomposition	
3.7 kcal./mole	(11)
Rate of thermal decomposition	
3.6×10^{-5}/hr. at 77.3°K.	(11)
6.2×10^{-5}/hr. at 77.8°K.	
8.3×10^{-5}/hr. at 79.4°K.	
1.6×10^{-3}/hr. at 89.6°K.	
7.2×10^{-2}/hr. at 113.8°K.	
Heat of vaporization	
$\Delta H_{vap.} = 4.581 \pm 0.200$ kcal./mole, at 121°K.	(12)
Entropy of vaporization (Trouton's constant)	
21.51 cal/$^{\circ}$K. mole	
Hildebrand's solubility parameter at b.p.	
6.66 $(\text{cal./cc})^{1/2}$ (10.7, at 90°K.)	
Heat of formation (from the elements)	
$\Delta H_{298} = 6.24 \pm 0.75$ kcal./mole	(12)
Distillable at 0.1 to 1.5 mm (90-114°K.) with slight decomposition	(10)
Paramagnetic "in liquid Freon"	(15)
Mixes homogeneously with O_3 at 90°K.	(10)
O_3F_2 mixes homogeneously with:	(10)
O_3 at 90°K. the mixture explodes readily	
OF_2 116	
O_2F_2 116	
NO_2F 116	
CCl_2F_2 116	
$CClF_3$ 116	
ClO_3F 127	
Forms two practically insoluble layers with:	(10)
N_2 at 77°K.	
F_2 77	
NF_3 90	
ClF 90	
ClF_3 90	
CF_4 90	
Partially soluble in CCl_2F_2, $CClF_3$, and CF_4 at 90°K.	(10)
Heat of decomposition	
For the reaction:	
$O_3F_{2\,liq.} \rightarrow O_2F_{2\,liq.} + 0.5\,O_{2\,gas}$, at 121°K., $\Delta E = -2040 \pm 150$ cal./mole	(12)
For the reaction:	
$O_3F_{2\,liq.} \rightarrow 1.5O_{2\,gas} + F_{2\,gas}$, at 121°K., $\Delta E = -2160 \pm 250$ cal./mole	
For the reaction:	
$O_3F_{2\,gas} \rightarrow 1.5O_{2\,gas} + F_{2\,gas}$, at 121°K., $\Delta E = -6500 \pm 450$ cal./mole	
For the reaction:	
$O_3F_{2\,gas} \rightarrow 1.5O_{2\,gas} + F_{2\,gas}$, at 298°K., $\Delta E = -7130 \pm 750$ cal./mole	
Bond energy	
$E_{o-o} = 61.1$ kcal./bond	(13)
Specific heat	
Gas, at 121°K.,	
$C_v = 16 \pm 1.5$ cal./mole $^{\circ}$K. (estd.)	(12)
Molar extinction coefficient[c]	
18.76 (350)	
17.63 (365)	
16.59 (380)	(13)(14)
16.95 (400)	
17.28 (420)	
17.28 (430)	
15.21 (450)	
13.26 (470)	
13.94 (480)	
11.96 (500)	
5.48 (540)	
1.98 (580)	
0.12 (600)	
0.12 (625)	
0.12 (650)	
0.12 (675)	
0.00 (700)	
0.12 (750)	
Solubility in LOX	(1)
0.11 wt. % 90°K	
0.045 77	
0.188 102	(7)
0.095 90	
0.0062 77	
Surface Tension ca. 40 dynes/cm	(15)
Viscosity ca. 200 centipoises	(16)
Light-sensitive	(4)(9)(17)
Does not detonate when initiated with Tetryl or in presence of spark	(10) (1)

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[a] This equation was derived from the experimental data. The equation given in the original work and quoted in other publications is in error.

[b] Preliminary data.

[c] In the visible range for liquid O_3F_2 dissolved in a mixture of 23% (by volume) of Freon 12 + 77% Freon 13, in $cm.^{-1}$ $mole^{-1}$ (mμ).

TABLE B-II

CHEMICAL REACTIVITY OF O_3F_2 (Ref. 2)

Material	Results
anhydrous ammonia[a]	instantaneous yellow-white flame accompanied by mild explosions
liquid methane[a]	loud, sharp, powerful explosion; destroyed equipment
solid hydrazine[a]	loud, sharp, powerful explosion; destroyed equipment
red phosphorous, powder[a]	mild explosion, bright white flame
wood charcoal, powder[a]	instant yellow flame; as temperature rose, mixture exploded
sulfur, powder[a]	instant blue flame, then turned white with mild explosion
solid ethyl alcohol[a]	no reaction until warmed, then blue-white flame accompanied by mild explosion
solid bromine[a]	white flash, then mild explosion
solid iodine[a]	white flash, then mild explosion
powdered Tetryl[b]	explosion, ref. 7
solid NO_2F -- 90°K	no reaction
solid ClF_3 -- 90°K	no reaction
ClF -- 90°K	sparks
F_2 -- 77°K under electrical discharge	O_2F_2, ref. 10

[a] One drop of pure O_3F_2 added to approximately 1 to 3 gm of each of the substances at 90°K produced the results indicated.

[b] Tetryl lowered into O_3F_2 liquid at 90°K

TABLE B-III

OPEN CUP TESTS OF 0.05% O_3F_2 WITH VARIOUS FUELS (Ref. 2)

Fuel	Vol. of Fuel (ml)	Vol. of Oxidizer (ml)	Reaction Time (sec)	Remarks
JP-4	5	5	3.4	fire
JP-4	5	10	12.4	explosion
U-DETA	5	1	0	instantaneous ignition
UDMH	5	5	0	instantaneous ignition
50% (by vol.) UDMH in JP-4	5	3	0	instantaneous ignition
10% (by vol.) UDMH in JP-4	5	3	0	instantaneous ignition
5% (by vol.) UDMH in JP-4	5	5	0	instantaneous ignition
1% (by vol.) UDMH in JP-4	5	5	0	instantaneous ignition

Ignition of hydrogen under a variety of conditions has been demonstrated.[17,7,10]

O_3F_2 and its decomposition product, O_2F_2, react violently when poured on warm water or moist earth at ambient temperature.

Detonability

Neat O_3F_2 does not detonate in an open cup 1¼ inches ID x 6 inches long when subjected to strong shock with a tetryl booster.[7]

Storage

Neat O_3F_2 can be conveniently stored in liquid nitrogen cooled refrigerators (Linde LNR-25 can be used for storage of a few pounds of O_3F_2).

LOX SOLUTIONS--COMPATIBILITY AND STORABILITY

In general, O_3F_2 is compatible with materials which are not destroyed by liquid or gaseous fluorine. A partial list of materials treated with a LOX solution containing 0.05% O_3F_2 (by weight) is reproduced in Table B-IV (reference 2).

O_3F_2 is soluble in LOX to about 0.1% at 90° K and much less[*] at 77° K. These solutions are pale yellow when freshly prepared and return to the normal blue color of LOX as the O_3F_2 decomposes. Samples have been stored at 77° K and at 90° K. The solutions stored at 77° K were still pale yellow after six months. The shelf life of those stored at 90° K was approximately one month. (The normal pale yellow solution had returned to a blue LOX color.)

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[*] Kirshenbaum[2] reported 0.045% by weight when a solution is prepared at 90° K and chilled to 77° K. Solubility determination at Stanford Research Institute indicates that the figure is much less (see Table B-I) when the material is saturated at 77° K.

TABLE B-IV

COMPATIBILITY TESTS OF ENGINEERING MATERIALS WITH 0.05% O_3F_2 (BY WEIGHT) SOLUTION IN LIQUID OXYGEN

Materials	Results
Metals	
Stainless steel No.	No appreciable reaction[a]
303[b]	
303	
316	
321	
347	
Aluminum	
Copper	
Brass	No appreciable reaction; surface pitted on continued exposure
Stainless steel carpenter 20 cb[c]	No appreciable reaction
Titanium alloy β-120-VCA[c]	
Magnesium-lithium (14. 1% alloy[c]	
Magnesium-thorium alloy XK31	
Packing materials	
Kel-F elastomer (plasticized)	Delayed (50 sec.) slight reaction
Allpax 500	No appreciable reaction
Allpax 500 (fluorolube T-80 treated)	
Teflon	
JM 76	
Duroid 3400[c]	
JM "L - Flo"	
Polyethylene film	Delayed (60 sec.) ignition
Lubricants and sealants	
Fluorolube T-80, (T-45)	No appreciable reaction
Halocarbon, series 11-14	Delayed (50 sec.) slight reaction
Kel-F oil, Alkane No. 464	Delayed (50 sec.) slight reaction
Molykote "Z"[b]	No appreciable reaction
Oxylube 702[b, c]	
AR-1F, LOX lube	Delayed (50 sec.) slight reaction

[a] No appreciable reaction indicates no fire, flame, or other visible evidence of reaction. [b] These samples were tested additionally by being immersed in 0. 10% of O_3F_2-O_2 solution, which was cooled with liquid nitrogen for a specified time, then allowed to warm up and the solution evaporated. These samples again showed no tendency to react. [c] The residue indicated a possible reaction, although no obvious reaction took place during evaporation of solutions.

RECOMMENDED HANDLING PROCEDURES

General

Since O_3F_2 is a cryogenic high energy oxidizer capable of igniting almost any fuel and is sensitive to light, special handling techniques must be employed. Although O_3F_2 is prepared in an electrical discharge which produces considerable light, preparation, handling, and storage in darkness is preferred since its sensitivity to light has been demonstrated. Transfers should be made in a clean dry atmosphere because ice and condensable fuels deposit directly on the surface of the chilled liquid and container walls. Dry boxes or deep Dewar flasks have been used successfully for transfers.

All equipment (metals, etc., which are potential fuels) for containing fluorine or O_3F_2 should be degreased (LOX-cleaned), dried, and passivated as outlined in General Chemical Division, Allied Chemical Company, New York, N.Y., Product Information Technical Bulletin, TA-85411. Liquid O_3F_2 will ignite Neoprene gloves and rubber, but if care is taken that Neoprene gloves do not directly contact liquid O_3F_2 they can be used on dry boxes in the presence of gaseous fluorine. In general, the list of materials found to be compatible with liquid and gaseous fluorine can tolerate liquid O_3F_2 and LOX-O_3F_2 solutions. O_3F_2 reacts instantly and usually violently with any water available anywhere in apparatus used with it or LOX solutions containing it.

In no case should O_3F_2 be allowed to warm rapidly above its decomposition temperature in a closed system. O_3F_2 will decompose slowly in storage at 90° K in a LOX bath without generating excessive pressures because the first decomposition products, O_2 and O_2F_2, do not generate much more than the equilibrium vapor pressure for LOX. At higher temperatures, where O_2F_2 decomposes and the decomposition products O_2 and F_2 are produced, conditions exist for rapid pressure buildup, accompanied by violent ruptures, reactions, or explosions.

Clean metal pans can be used under handling equipment to catch inadvertently spilled O_3F_2. O_3F_2 decomposes rapidly without incident in an open container. Dewar flasks should be modified to remove exterior jackets or bases fabricated from combustibles such as plastic or asphalt. The latter can be removed easily by freezing it in LN_2 and scraping out the residue.

A variety of handling equipment such as LOX-cooled pipettes, funnels, and containers have been used--examples of a few simple ones are shown in Fig. B-2. Glass equipment is not as satisfactory as metal because of poor heat conductivity. Glass containing O_3F_2 often fractures when traces of O_3F_2 react on the surface with combustibles. The double copper-to-glass Housekeeper Seal pipette (Fig. B-2) was easier to handle than the LOX-cooled glass Dewar type pipette and was not as bulky. Transfers with pipettes are best accomplished inside large LOX-cooled Dewar flasks to minimize boiloff of the coolant LOX.

O_3F_2 can be poured from one container to another if great care is taken to cool completely the pouring spout. Poor cooling results in subsequent contamination of the delivery sample with material which adheres to the lip of the spout, which on warming decomposes to O_2F_2. This then melts and freezes near the surface of O_3F_2.

Utensils which have O_3F_2 adhering to the walls are potentially dangerous and the O_3F_2 is not readily washed away with LOX solvent. It is convenient to utilize extra Dewar flasks partially filled with LN as temporary storage for contaminated utensils and unused materials. It is not always convenient or practical to warm immediately each piece of contaminated equipment to room temperature; excessive haste could result in spilling O_3F_2 or O_2F_2.

Liquid transfer of O_3F_2 through LOX-cooled "U" tubes pressurized with inert gases has been accomplished but extreme care must be taken that no dirt or hot spots exist in the tube. Such conditions serve to produce oxygen-fluorine gas generators.

In many instances it has been more convenient to design small generators which produce O_3F_2 near the spot to be utilized rather than attempt to transfer small quantities and risk contamination.

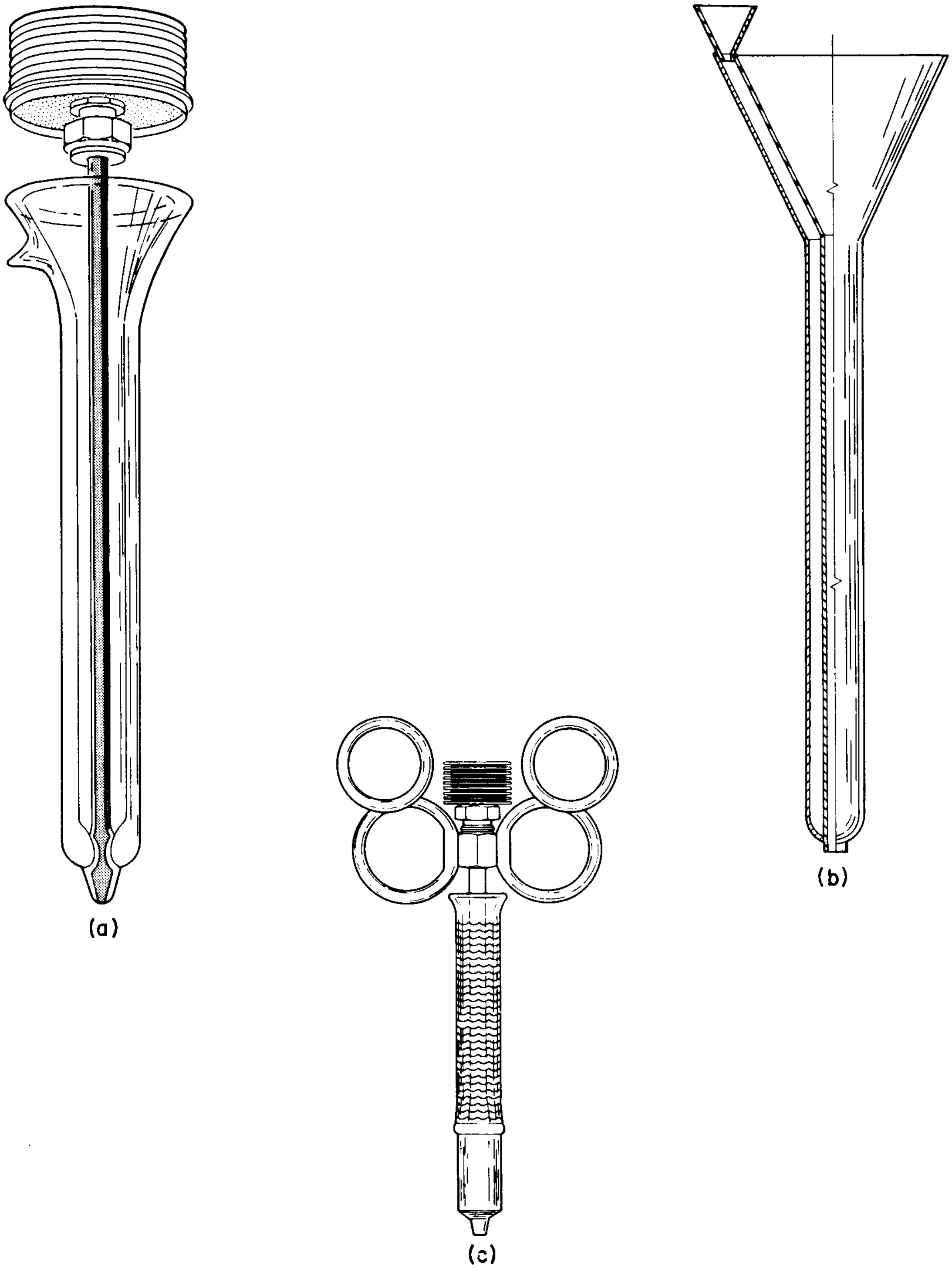

FIG. B-2 (a) LOX-COOLED GLASS PIPETTE DEWAR FLASK JACKET
(b) LOX-COOLED FUNNEL
(c) LOX-COOLED PIPETTE (Double Housekeeper Seal)

Samples of O_3F_2 or LOX-O_3F_2 can be readily sealed in glass ampoules for storage. A metal bellows soldered to Swagelock fittings having Teflon collars serves as a seal between the glass and bellows to prevent fuels from contacting the O_3F_2 when the tubes are sealed with an open flame. Pressure inside the bellows can be adjusted to cause the glass to collapse and seal when heated. This operation should be done with a minimum of exposure due to the sensitivity of O_3F_2 to light.

Facility Use of LOX/O_3F_2

LOX/O_3F_2 can be obtained at a test facility as a premixed solution or the solution can be prepared on site. The supply of premixed solutions is contemplated by one supplier. However, as some users may prefer to prepare or purchase neat O_3F_2, information on recommended mixing procedures are included.

Materials of Construction and Fabrication Processes

Materials used in flow systems include metals and various nonmetallics used for gaskets, valve seats, insulation, and combustion chambers.

Metals used in contact with LOX/O_3F_2 may be selected on the basis of usage with fluorine, Flox, or the interhalogens. It is customary to LOX-clean and passivate using gaseous fluorine or other approved procedures. An applications table of metallic materials which have proved satisfactory is given below:

PROVEN METALLIC MATERIALS

Material \ Use	Tankage and Combustors	Piping and Fittings	Valve Bodies and Seats	Valve Gates	Gaskets
Stainless Steel					
304	X				
309			X		
316		X			
321		X			
Copper				X	X

System fabrication can be carried out using welding, gasketed flanged joints, or close-tolerance compression-fit unions. Experience to date indicates that welding is satisfactory but 100% x-ray inspection of welds is mandatory. This is particularly true of super-insulated or conventional vacuum-jacketed lines where weld repair of the inner flow line after fabrication becomes difficult. (In one incident it is believed that a slag inclusion was attacked with subsequent line burnup.) A major fire occurs if LOX/O_3F_2 is drawn into a vacuum jacket and reacts with the reflective metal and plastic insulant.

Only highly fluorinated plastics have been found satisfactory for service with LOX/O_3F_2. Kel-F elastomer (non-plasticized) and Teflon are the two materials used for gaskets and valve seats. Both materials have been used but tests to date show that Kel-F is preferable. Dense carbon has been found to be of little value for service as valve gates because it reacts with O_3F_2 under field conditions.

Passivation Procedure

Prior to assembly of a system, all parts are LOX-cleaned using the standard procedure. After assembly all lines are purged to removed traces of moisture using gaseous nitrogen obtained from a cryogenic generator. The system is then checked for leaks. If no leaks are present, the system is next passivated using one of two procedures:

a) Gaseous fluorine is slowly admitted and the system pressure is allowed to increase to 5 psig after all lines are filled.

b) A mixture of 10% fluorine in helium is premixed and used in place of neat gaseous fluorine.

The first procedure has been used in experiments to date and lines and valves have withstood repeated passivation.

LOX/O_3F_2 Mixing Procedure

Small scale mixing of O_3F_2 in LOX has been carried out using a premix tank. This tank was insulated with 4 inches of polyurethane foam. A copper impeller, safety valve, dump valve, and a LOX-cooled entry port are fitted to the tank.

Mixing is achieved by taking the appropriate volume of O_3F_2 (obtained as the frozen solid in an LN_2 refrigerator) and melting it in a Dewar containing LOX. After melting, the O_3F_2 is transferred to the mix tank through a LOX-jacketed funnel. (A slight excess of O_3F_2 is normally added to ensure complete saturation of the LOX in the mix tank.)

After addition of the O_3F_2, the tank is stirred for 30 minutes to vent any pressure buildup. On completion of mixing, the LOX/O_3F_2 is transferred by pressure to the main flow tank (previously cooled with LOX).

Flow System Problems

All lines, tanks, and fittings used with LOX/O_3F_2 must be at a sufficiently low temperature, where the O_3F_2 has adequate stability. This is achieved by using prechilled lines of the super-insulated type or a LOX-jacketed line. In making test runs, the combustor preferably, but most certainly the injector must stagnate at or near LOX tank temperature.

Cooling of the injector and lines may be achieved using direct thermal conduction to the LOX tank or by regenerative cooling using LOX or LH_2 boiloff gases. Care must be taken to preclude over-cooling of the line which would lead to LOX line freezing.

The need for extra precaution with LOX/O_3F_2 and LOX is mandatory since contact of LOX/O_3F_2 with any organic matter, metallic foil (unless cleaned and passivated), and even sized glass insulation fiber results in fire.

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APPENDIX C

INSTRUMENTATION AND SYSTEMS CONTROL

Instrumentation and System Data Aquisition

In Fig. C-1, the basic instrumentation circuits are shown. The measurements made with these circuits fall into three categories each of which dictates the calibration and the environmental and frequency response requirements for the measurement. The three types of data obtained were; oxidizer and fuel supply system data, oxidizer and fuel supply flow data, and ignition delay data. Table C-I lists the measurements, transducers, signal conditioning, and method of recording. These measurements all fall into the flow and event data categories with the exception of the run tank pressure measurements.

The oxidizer and fuel supply system measurements are the standard type measurements made and were only periodically monitored to assure operation, safety, and capability of the system. Figure 1 in the main text shows the schematic of facility and the location of these measurements. Pressure measurements monitored throughout the facility were made with three types of transducers: (1) Bourdon tube with dial indicator, (2) Bourdon tube potentiometer cabled to a remote microammeter, and (3) strain gage transducer readout on the oscillograph. The facility nitrogen gas manifold and supply pressures and the regulator for both the H_2 (gas) and O_2 (gas) were read visually on the dial type gages. The regulator inlet and outlet, and tank pressures for both the H_2 (gas) and O_2 (gas) were monitored utilizing the second type of gage. The tank pressures were also recorded on the oscillograph using the strain gage transducers. The liquid levels in the run tanks were monitored using multiple thermocouples on a probe in the tank with the bottom one acting as a reference junction. The level sensors were checked during the filling operation and periodically as the tests progressed.

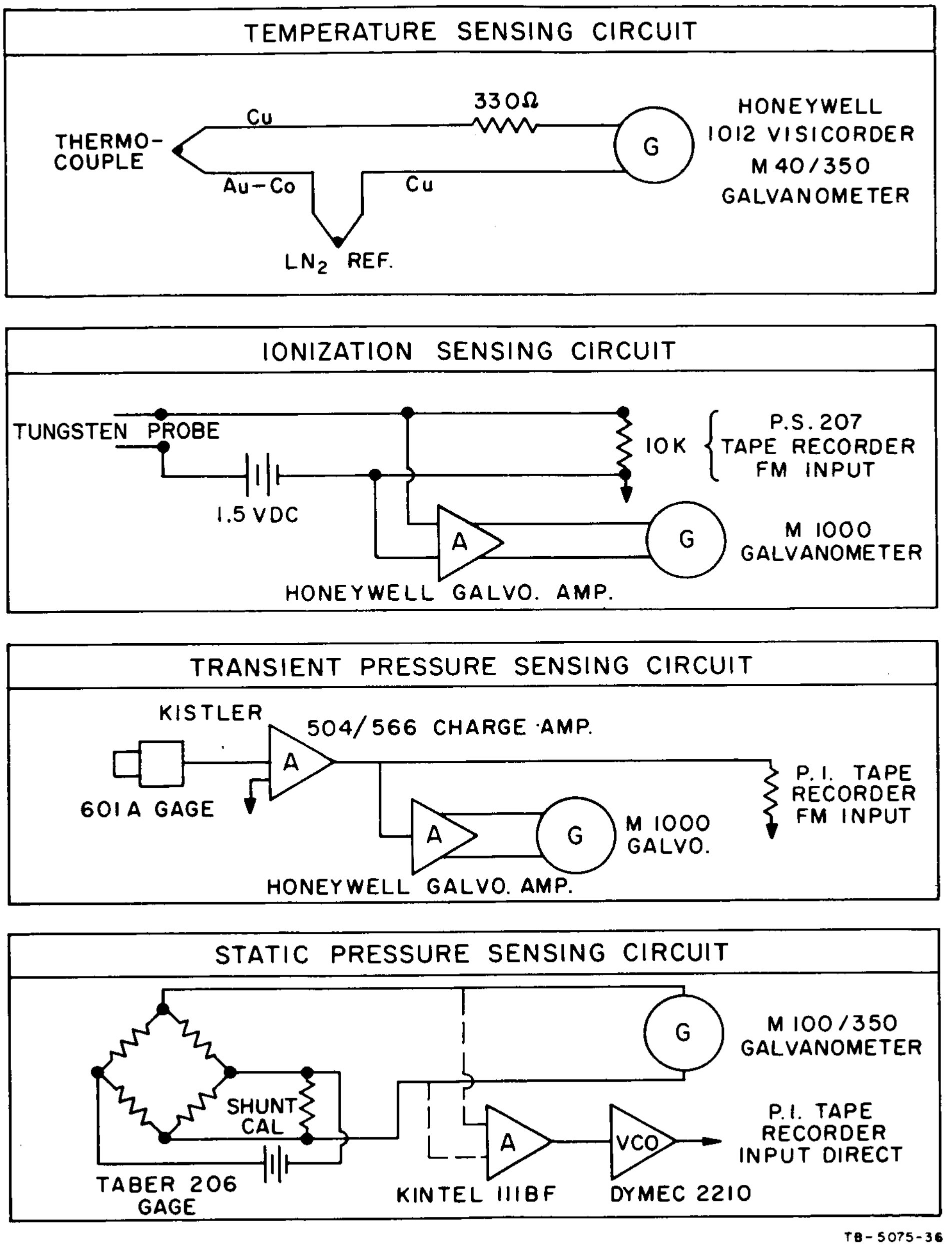


FIG. C-1 BASIC INSTRUMENTATION CIRCUITS

TABLE C-I

BASIC INSTRUMENTATION DATA

Measurement		Transducer	Signal Conditioning	Recorder
Tank Pressure LH_2 and LOX		Taber Model 206	None	Honeywell 1012 Visicorder
Line Pressure LH_2 and LOX		Taber Model 206	None	Honeywell 1012 Visicorder
Injector Pressure LH_2 and LOX		Kistler Model 601A	Charge Amplifier Kistler 504/566	P.I. 206 Tape Recorder Visicorder
Chamber Pressure	Gage	Kistler 601A	Charge Amplifier	Tape Recorder
	Abs.	Taber 227	None	Visicorder
Line Temperature LH_2 and LOX		Au-Co vs. Cu T. C. Probe	None	Visicorder
Injector Temperature LH_2 and LOX		Au-Co vs. Cu T. C. Probe	None	Visicorder
Engine Jacket Temperature		Cu vs. Constantan T. C. (welded) #1 through #3	None	Visicorder
Ionization		Tungsten Probe #1 through #4	None Galvo Amplifier	Tape Recorder Visicorder

The cryogenic flow measurements include the line and injector pressures and temperatures. These temperatures and pressures were made to determine the flow through the cavitating venturis and injector. Since the flow was transient, good frequency response of these measurements was mandatory.

In Fig. C-2, the construction of the thermocouple probes is shown. 10 Mil gold-colbalt and copper wire was used. The junctions were made by mercury arc welding. They were not enclosed or sheathed so that maximum frequency response could be obtained. Temperature calibrations are made by immersing the probe in a reference cryogenic (LOX, LN_2, and

LA_r) and recording the EMF on the oscillograph. The rise time for the thermocouple measurements is on the order of 10 milliseconds as flow is increased from zero to 20 cubic inches per second. The probes being immersed in liquid nitrogen were subjected to a maximum temperature differential of $57^{\circ}K$ on the hydrogen line and $13^{\circ}K$ on the LOX line. The reference for both LOX and liquid hydrogen temperature measurements was $77^{\circ}K$ (liquid nitrogen). The nitrogen level in the reference dewar was maintained between every test and protected from contamination by a close covering of aluminum foil, so the atmosphere above the LN_2 was gaseous N_2.

Line pressure measurements (upstream from the cavitating venturis) were made with strain-gage type pressure transducers which were thermally isolated by a length of thin wall 1/8 inch diameter stainless steel tubing. This method of coupling lowered the frequency response but since it still exceeded that of the temperature measurements it was not a prime factor. The injector pressure measurements had to have good response since the ignition delay was determined from the injector pressure rise. Piezoelectric transducers (Kistler model 601A) were used. Since the transducers were exposed to a liquid nitrogen environment, they were checked for response and calibration prior to installation. The transducers under LN_2 were coupled through a length of tubing to a Hiese gage for calibration checks. It was found that the crystal had the same sensitivity at $77^{\circ}K$ as at $296^{\circ}K$ but the zero charge was affected by temperature gradient across the crystal. The temperature difference between the sensor media and adaptor environment was at a minimum under the test conditions. The adaptor used for the injector pressure measurements is shown in Fig C-3. All pressure transducers were calibrated using a Mansfield and Green model R-100 dead-weight tester.

The "event" data determined not only the time of ignition delay from valve opening but also the location of ignition. These data were obtained from the ionization probes, chamber pressure transducer, and injector pressure transducers. The construction of the tungsten ion probes is shown in Fig. C-4. The chamber pressure measurement was made using the flush type mount as shown in Fig C-3 to obtain maximum response. The injector pressure measurements have previously been discussed. All of these measurements were recorded on magnetic tape and evaluation of the data is discussed in the text of this report.

System Control

The system schematic shown in Fig. 1 of the main text indicates the facility valving that is operated manually and that portion which can be operated remotely. Filling of the hydrogen run tank was accomplished on location by personnel manually operating the mobile dewar valving. Transfer of the LOX-O_3F_2 mixture from the mix tank to the run tank was done remotely from the control room. System pressurization, venting, and purging were done by the test conductor at the control console. The main flow and injector purge valving was handled by the automatic sequencer during the tests. These functions could be overridden by the test conductor with auxillary switching. The sequencer schematic is shown in Figure C-5. A safety-arming switch for the main flow valves enabled the preliminary setting of the time delays for the oxidizer and/or fuel. The only unique feature of the automatic operation is that of the injector purges. Normal operating procedure consisted of switching the purges to automatic during the count-down and then going back to manual after shutdown by the sequencer. The automatic cycle of the sequencer is initiated by the firing switch. The time delay units are energized and when the silicon controlled rectifier in the unit which controls the run duration is gated, the injector purge controlled rectifier is gated. As soon as the injector pressure drops below 50 psi, the purge valves are opened. The purge remains on until the controlled rectifier is reset or until the purge switches are manually switched to the OFF position.

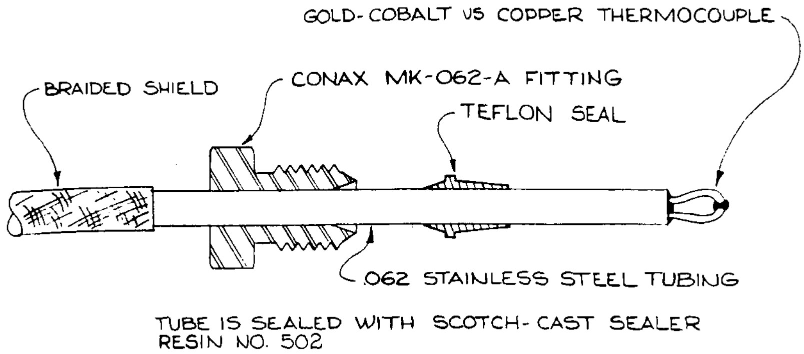


FIG. C-2 THERMOCOUPLE CONSTRUCTION

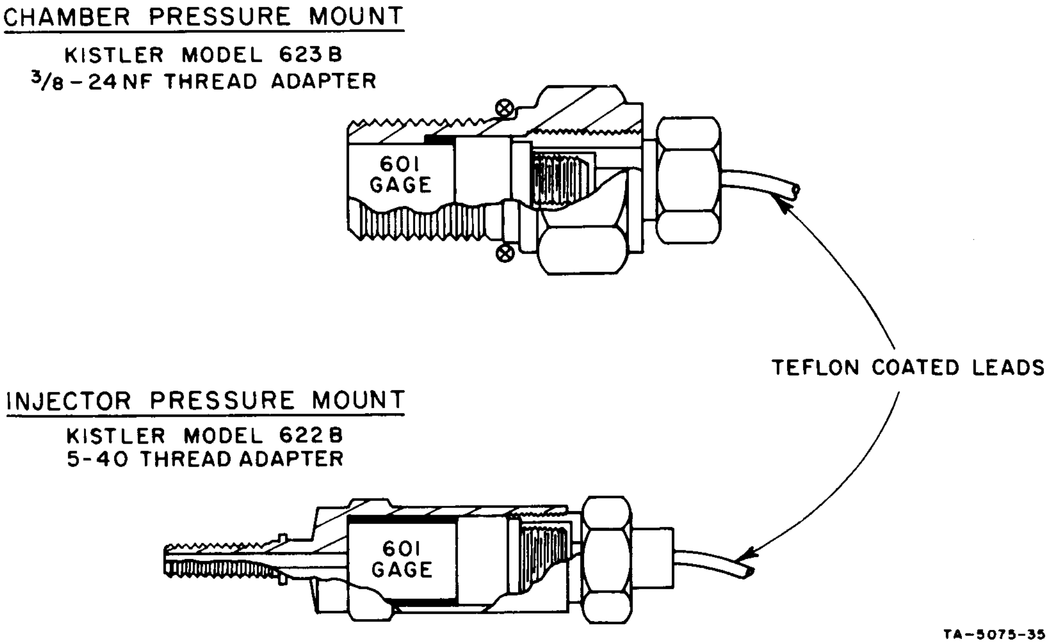
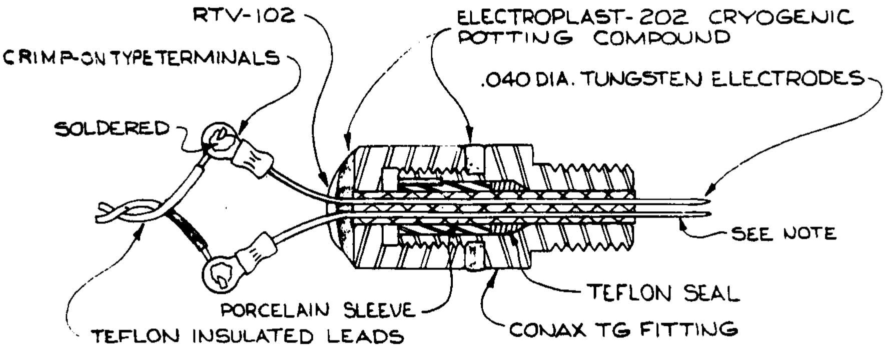
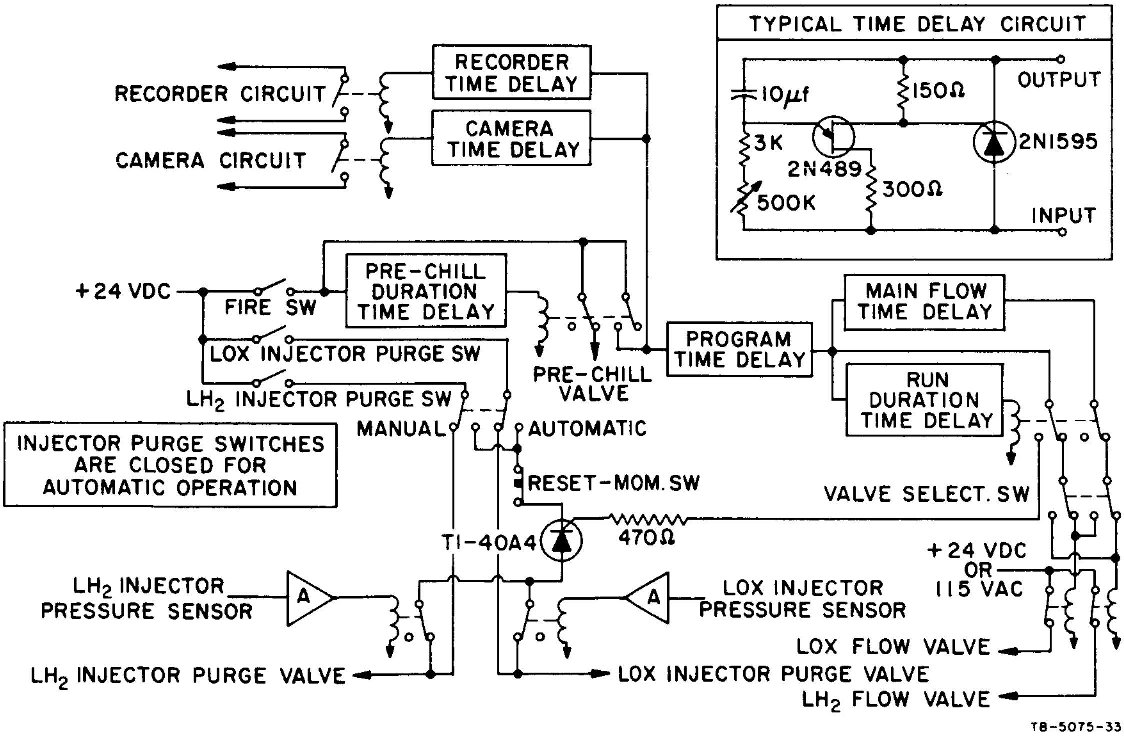


FIG. C-3 KISTLER GAGE MOUNTS



NOTE -
STANDARD ELECTRODE LENGTH 17MM
SLEEVED CHAMBER ELECTRODE LENGTH 30MM

FIG. C-4 ION PROBE CONSTRUCTION



INJECTOR PURGE SWITCHES ARE CLOSED FOR AUTOMATIC OPERATION

FIG. C-5 AUTOMATIC SEQUENCER

APPENDIX D

A SIMPLE COLORIMETER FOR ASSAY OF O_3F_2 IN LIQUID OXYGEN

A simple colorimeter was constructed for assay of O_3F_2 in liquid oxygen (LOX). Because of the problems associated with this cryogenic system, the design was somewhat different from a conventional colorimeter. The main departure from convention was the use of pyrex glass rod light pipes to conduct the light into and out of the solution. It was felt that this approach was more satisfactory than a system where the light must pass through several glass walls, as would be the case for a cell immersed in a dewar of LOX. The light source for the colorimeter was a GE 328 pilot lamp rated 6V at 0.20 amp. The lamp was powered from a 6.3 volt filament transformer whose primary is driven by a Sola constant voltage transformer. The light sensor was a Clairex CL 702L cadmium sulfide photoresistor. This cell has a peak in spectral response at 5150A, and has fairly good response down to 4000A. A Kodak gelatin filter Wratten No. 98 was used in the light source to isolate the spectral region where O_3F_2 absorbs strongly (presumed to be about 4200-4600A in the visible). A sketch of the source and detector assembly is given in Fig. D-1.

The photocell was one arm of a wheatstone bridge circuit which was powered by 66 volts regulated D.C. The bridge imbalance was read with an RCA Voltonymst vacuum tube voltmeter. A schematic of the electrical circuit is given as Fig. D-2. The imbalance voltage is proportional to the absorbance of the solutions. A calibration of the system was made using O_3F_2 in LOX solutions. The optical part of the system was operated in a dry box to avoid icing problems on the glass rods. The procedure used is as follows:

1) Immerse glass rod light pipes in LOX, and adjust the variable resistor arms to produce zero bridge output. This represents 100% transmission value.

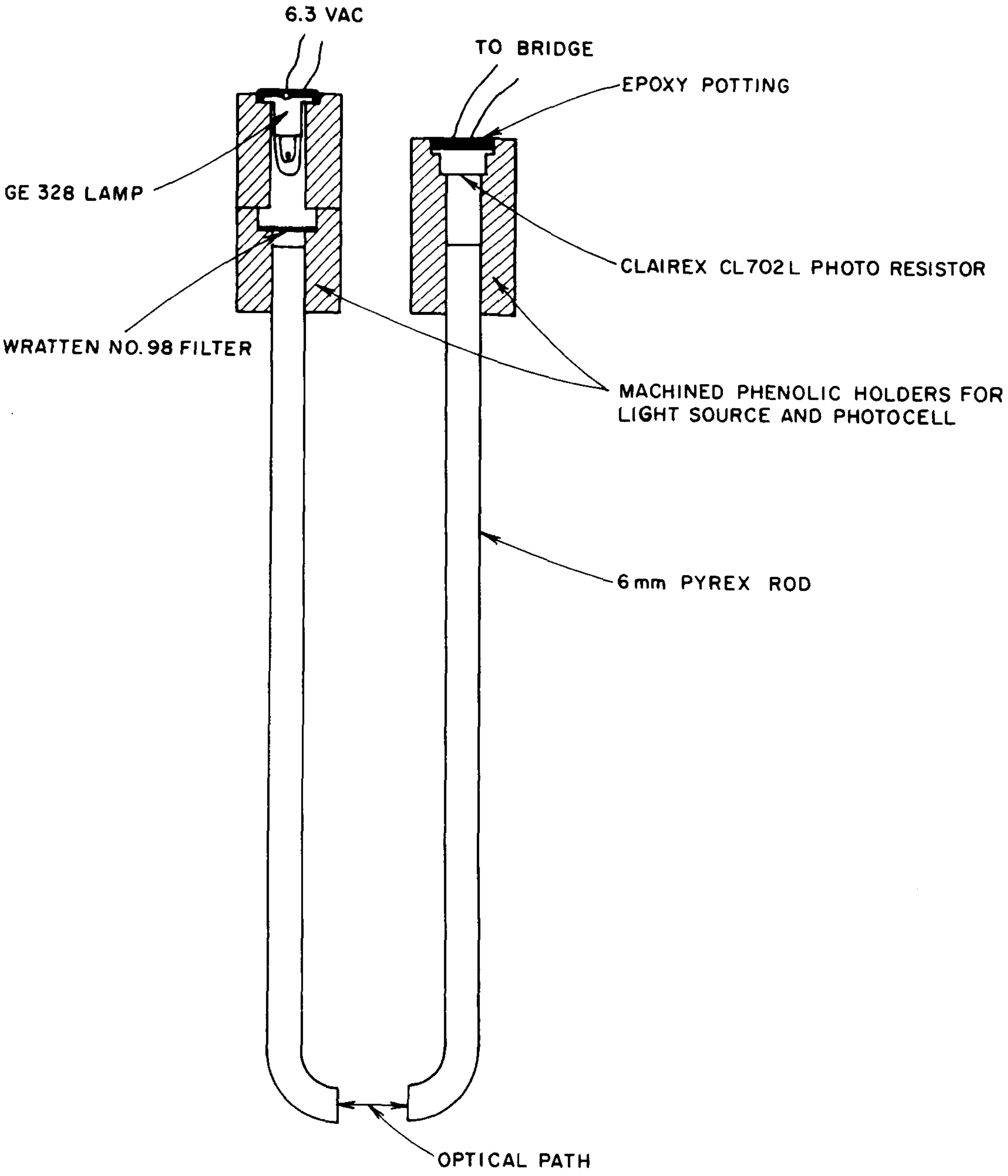


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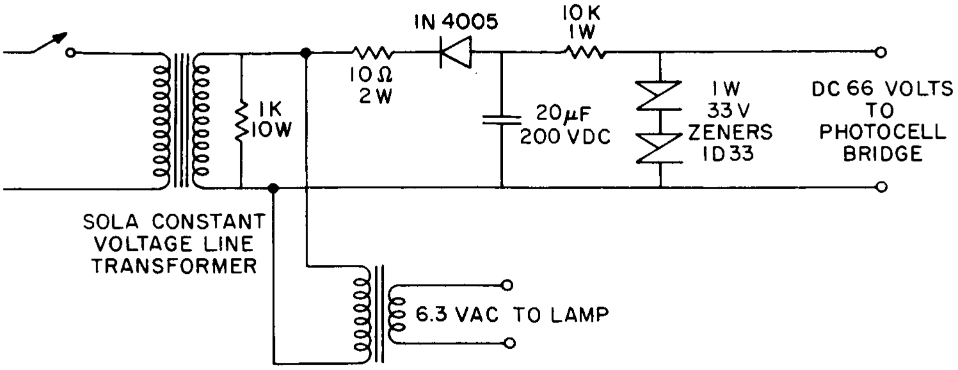
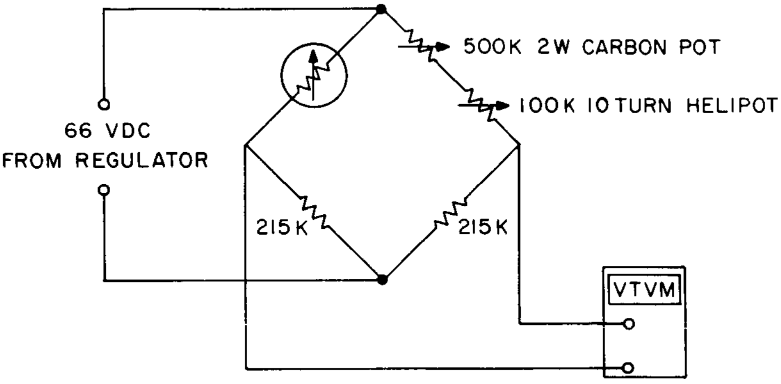
FIG. D-1 SOURCE AND DETECTOR ASSEMBLY



POWER SUPPLY



BRIDGE CIRCUIT

TA-5075-23

FIG. D-2 BRIDGE CIRCUIT

2) Replace pure LOX with solution of O_3F_2 in LOX, and read output voltage which is proportional to concentration.

The result of this calibration is given in Table D-I and Fig. D-3. The results are completely empirical, but serve the purpose intended.

Improvements that could be made in this technique, if necessary, are:

1) Construct a more stable light source using some kind of feedback regulation. Incandescent sources run on constant voltage are more stable than unregulated sources but still are subject to both short and long term variation.

2) Coat the glass rods with a reflective metal coating to increase efficiency and make them more immune to ambient light variations. We tried to use sputtered nickel on the rods but only succeeded in making them less efficient, probably because of NiO in the nickel.

3) Pick photodetector of greater stability.

TABLE D-I

CALIBRATION DATA FOR COLORIMETRIC ANALYZER

	Output Voltage	
O_3F_2 Concentration, (% of Saturation)		Average
0	0	0
25	1.22, 1.20	1.21
50	2.5, 2.7	2.6
75	4.2, 4.4	4.3
100*	7.0, 7.0	7.0

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*O_3F_2-LOX solution saturated at 90°K

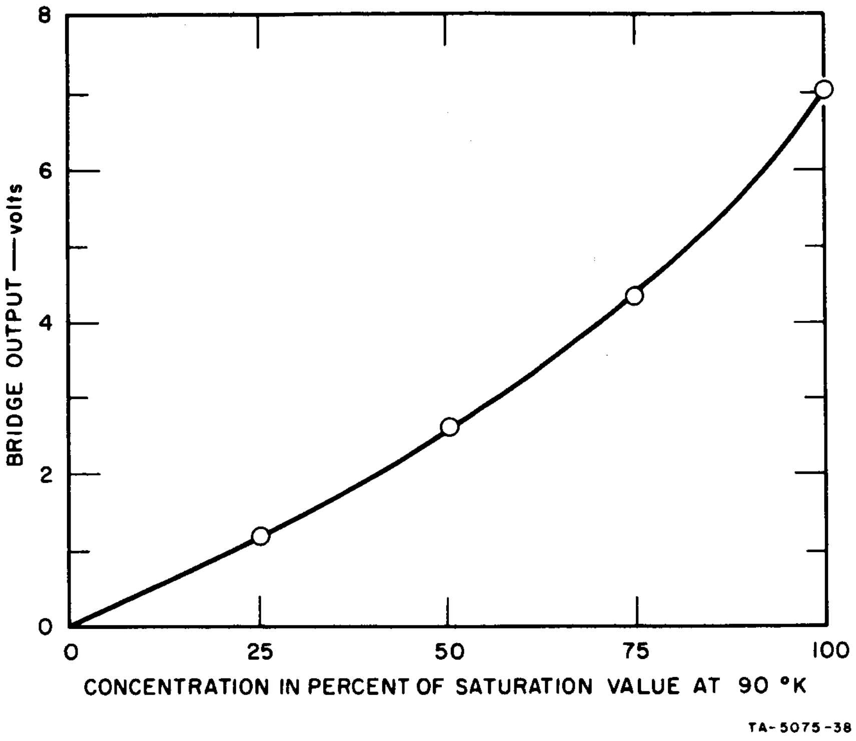

FIG. D-3 CALIBRATION DATA FOR COLORIMETRIC ANALYZER

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