FEASIBILITY STUDY OF
OXYGEN/HYDROGEN
POWDERED METAL IGNITION

FINAL REPORT

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Report 25,179

BII STUDY OF OXYGEN/HYDROGEN POWDERED METAL IGNITION

(TMC Project 358)

This report was prepared by The Marquardt Corporation under Contract No. NAS8-11250, "Feasibility Study of Oxygen/Hydrogen Powdered Metal Ignition", for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Propulsion and Vehicle Engineering Laboratory of the George C. Marshall Space Flight Center.

ABSTRACT

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Theoretical and experimental studies were performed on the subject of producing low temperature H_2/O_2 ignitions by the use of catalytic and/or pyrophoric powdered metals.

Interest centered on the use of Raney nickel powder, which is both catalytic for H_2/O_2 ignition, and pyrophoric with oxygen. Tests with this material produced a large number of ignitions with cold gaseous hydrogen and liquid oxygen. Ignition times of the order of 10 milliseconds were observed under favorable conditions, and this does not appear to be a limit. The Raney nickel powder was entrained in the hydrogen stream, by passing the latter through a fluidizer assembly just upstream of the injector.

It was demonstrated that Raney nickel powder, stored under an atmosphere of hydrogen, should have indefinite shelf life in the activated state, being able to produce ignitions at any time upon contact with oxygen.

It is considered that the most promising application would take the form of the Raney nickel powder stored under these conditions in a side tank near the rocket engine. A bleed stream from the main hydrogen flow would entrain some of the nickel powder as it passed through this fluidizer. This hydrogen stream would then be hypergolic with either liquid or gaseous oxygen. The low cost of Raney nickel (in comparison with noble metal catalysts) lends support to this application.

The data of this report appear to justify continued testing on a larger scale, comparable to actual rocket engine operating conditions.

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PREFACE

For planning purposes, the subject research program was divided into four phases, as follows:

Phase I	Analytical Studies
Phase II	Planning of Experimental Program
Phase III	Experimental Study
Phase IV	Evaluation of Experimental Data

The results of the program are discussed in the text in the above order.

I. ANALYTICAL STUDIES

A. General Consideration of Ignition Mechanisms

Theoretical and experimental studies since 1928 have established that the reaction between gaseous hydrogen and gaseous oxygen is a branched-chain reaction. Beginning with Gibson and Hinshelwood (Reference 1) in 1928 and the experimental work of Kovalskii (Reference 2), numerous experimental studies have established that the general nature of the reaction can be interpreted in terms of Reactions (1-14) listed below (References 3-5).

$H_2 + M \rightarrow 2\,H + M$	Initiation	(1)
$O_2 + M \rightarrow 2\,O + M$	Initiation	(2)
$H_2 + O_2 \rightarrow 2\,OH$	Initiation	(3)
$H_2 + O_2 \rightarrow H + HO_2$	Initiation	(4)
$O + H + M \rightarrow OH + M$	Addition	(5)
$H + O_2 \rightarrow OH + O$	Chain-branching	(6)
$O + H_2 \rightarrow OH + H$	Chain-branching	(7)
$OH + H_2 \rightarrow H_2O + H$	Propagation	(8)
$2\,OH \rightarrow H_2O + O$	Propagation	(9)
$H + OH + M \rightarrow H_2O + M$	Termination	(10)
$OH + \text{wall} \rightarrow \frac{1}{2} O_2 + \frac{1}{2} H_2 + \text{wall}$	Termination	(11)
$H + \text{wall} \rightarrow \frac{1}{2} H_2 + \text{wall}$	Termination	(12)
$O + \text{wall} \rightarrow \frac{1}{2} O_2 + \text{wall}$	Termination	(13)
$H + O_2 + M \rightarrow HO_2 + M$		(14a)
$HO_2 + \text{wall} \rightarrow \frac{1}{2} H_2 + O_2 + \text{wall}$	Termination	(14b)

Reaction (4) represents an initiation step in hydrogen-oxygen combustion, in which a hydrogen atom is generated by a pair of molecules reacting with sufficient activation energy. Reactions (6) and (7) represent very important steps in the further reactions occurring between hydrogen and oxygen molecules and atoms, and hydroxyl free radicals. In these steps, chains are branched. That is, they produce two reactive atoms or free radicals, (O, H, OH) by the reaction of one atom or free radical (O, H, OH) with a molecule (H_2, O_2). Thus, when a hydrogen atom is produced, as by Reaction (4), a series of chain-branching and propagation reactions (6-9) are then initiated, which quickly culminate in an extremely rapid oxidation. The chain-branching steps may be rapidly terminated by the hydroxyl radical (OH), or the hydrogen atom or the oxygen atom, striking the wall of the vessel and losing its chemical energy, as in Reactions (11-13). The termination reactions of the type of (11-13) may also occur by these same atoms or radicals striking hydrogen or oxygen molecules, which are not in the activated energy state required to react and branch, thus losing their energy as by Reaction (14) or the reverse of Reactions (1-3).

This sequence of reactions will not spontaneously initiate the chain process at low temperature. One possibility would be to excite Reaction (4) by heating, An alternative approach is to essentially bypass Reaction (4) by otherwise providing atoms or free radicals to promote Reactions (6-7). Based upon well-known concepts of bond energy, it is easier to prepare hydrogen atoms than oxygen atoms. With this view, the appropriate way to induce the chain process outlined by Reactions (6-9) is by means of chemical process which can readily generate hydrogen atoms.

It is well established chemically that hydrogen molecules can be readily dissociated on selected catalysts into hydrogen atoms, as by the following reaction. ,

$$H_2 \longrightarrow 2\,H \text{ (chemisorbed on catalyst)} \qquad (15)$$

This process has been well established as occurring on the noble metal catalysts, such as platinum, palladium, and the like, and on certain other transition metals, such as nickel. These types of metal catalysts must, therefore, be considered as potential ignition catalysts.

The use of pyrophoric metal powders to obtain ignitions generally represents a case in which a reaction similar to (4) above is caused to occur, as a result of the high temperature which the pyrophoric metal powders attain. This high temperature is a result of the heat release associated with the reaction of the pyrophoric metal particles with oxygen.

B. Basic Approach

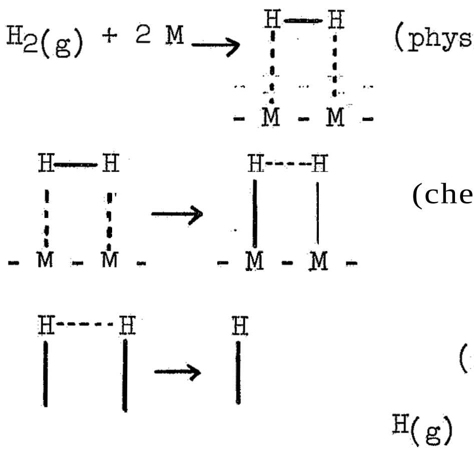
It was considered desirable that this research program emphasize the study of powdered metal ignition agents which would be applied in the form of an entrained powder in one of the propellant streams, since a considerable amount of work has already been performed utilizing fixed catalyst beds, It was also of interest to evaluate the use of materials considerably less expensive than the noble metal catalysts normally employed in ignition studies of this type.

These considerations, and others, led to the selection of active nickel powders of the "Raney nickel" type Tor evaluation. The reasons for considering this material are discussed below. It should be noted, however, that, for completeness of study, work was also performed on fixed bed catalysts, both noble metal and nickel.

C. Mechanism of Raney Nickel H_2/O_2 Ignitions

The following discussion is concerned with utilizing a preformed layer of chemisorbed hydrogen on a powdered metal substrate to initiate combustion. This method combines to some extent the characteristics of both catalytic and pyrophoric powdered metal ignition.

Catalytic ignition in the H_2/O_2 system is normally considered to operate through a mechanism of hydrogen chemisorption. That is, the H_2 molecule is adsorbed so strongly to the surface of the catalyst that the H-H bond is partially or wholly ruptured, being replaced by H-M bonds, where M denotes the catalyst. In schematic equation form,



(physical adsorption) (16)

(chemisorption) (17)

(free radical formation) (18)

The process of chemisorption is the sum of Reactions (16) and (17). Reaction (18), the generation of free H radicals, is shifted far to the left; i.e., the concentration of free H atoms is very small. However, only small amounts of H atoms are necessary to initiate reaction.

Reaction (16), physical adsorption, normally occurs rapidly, even at low temperatures. Chemisorption, however, is usually associated with an energy of activation. Thus, only that fraction of H_2 molecules possessing this energy can undergo chemisorption. As is well known, the fraction of molecules possessing a given energy decreases exponentially with the absolute temperature. At the cryogenic temperatures concerned in this study, this fraction may become so small that the kinetics of chemisorption may be too slow to initiate combustion in the desired time interval.

This slow kinetic step could be eliminated if one could provide a pre-formed layer of chemisorbed hydrogen on the catalyst surface. A chemisorbed layer of hydrogen can be deposited readily enough on a number of metal surfaces at ambient, or slightly higher, temperature. A question arises, however, concerning the feasibility of protecting this layer, Depending on the nature of the hydrogen chemisorption process, this might involve storing the catalyst under an atmosphere of hydrogen until it enters the ignition chamber.

If a metallic catalyst were sufficiently finely divided, it might behave as a pyrophoric metal powder; i.e., the powdered metal would itself be oxidized, initiated by the heat release of the catalytic reaction, and would no longer, strictly speaking, be only a catalyst. It should be noted that the pyrophoricity in this case would be due to the adsorbed hydrogen layer.

Early in this project, it appeared that Raney nickel, and similar materials, satisfy these requirements. The term "Raney nickel" refers to a form of nickel obtained by leaching the aluminum from a nickel-aluminum alloy by reaction with sodium hydroxide. The resulting finely divided nickel powder contains large amounts of bound hydrogen, presumably in the chemisorbed state. It was considered likely that the pyrophoric properties of Raney nickel are due to the presence of this chemisorbed layer of hydrogen, the evolution of the latter being primarily responsible for the gradual loss in activity observed when Raney nickel is stored under an inert atmosphere.

Raney nickel has long been known to be a very active catalyst for many applications. It has been utilized almost exclusively, however, in the field of organic chemistry, for a variety of purposes, such as hydrogenation of esters, desulfuration of thiazoles, etc. It is likely that this close association with specialized organic reactions has tended to obscure the fact that Raney nickel (and modifications thereof)-.is a very promising catalyst for inorganic reactions in which a source of active hydrogen is required. In particular, it appears that past applications of this material have not been concerned with its properties as a source of hydrogen atoms at cryogenic temperatures. In the form in which it is usually described in the literature, Raney nickel is stored under an inert carrier, such as ethanol, until use. In addition to being an inconvenient arrangement for the present application, Raney nickel stored in this manner has a limited active life, generally a few weeks at most. It was therefore necessary to develop new techniques for handling and storing dried Raney nickel powders.

It was also necessary to verify the above postulated mechanism of the H_2/O_2 ignitions obtained from Raney nickel powders.

These goals were achieved by a variety of tests, reported in more detail below. The results are summarized here briefly.

It has been clearly demonstrated that it is a pre-chemisorbed layer of hydrogen on the Raney nickel powders which is responsible for its catalytic activity. It has been demonstrated that the basic mechanism of H_2/O_2 ignition obtained from Raney nickel is catalytic in nature. The pyrophoricity of the Raney nickel represents a secondary process; namely, the oxidation of the nickel powders due to the heat generated by the reaction of oxygen with this chemisorbed hydrogen. Upon removal of the chemisorbed hydrogen layer (by vacuum desorption), the material is no longer catalytically active for the cryogenic temperature ignition of hydrogen and oxygen, and is no longer pyrophoric. The low temperature catalytic activity (and the associated pyrophoricity) can be restored by redeposition of a layer of chemisorbed hydrogen.

It has also been shown that the reaoted, oxidized nickel powders can be reactivated, This is accomplished by hydrogen reduction of the nickel oxide, followed by degassing and subsequent hydrogen chemisorption. The resulting material is pyrophoric.

Based upon this theoretical and experimental model, active Raney nickel powders should have indefinite shelf life when stored under an atmosphere of hydrogen. Experimental observations made during this project are in agreement with this hypothesis.

Samples of dry Raney nickel powder stored under these conditions for nearly five months have produced cryogenic temperature ignitions at the end of this period.

D. Literature Survey

A literature survey was conducted early in the program. The initial emphasis of this survey was placed on reviewing the preparation of catalytic agents which are specific for the chemisorption of hydrogen. The resulting partial dissociation of hydrogen molecules into atoms should initiate the H_2/O_2 combustion reaction, as discussed above, It is well known that catalysts prepared in the laboratory are more active for this purpose than many commercially available materials. Much information is available in the chemical literature describing very active hydrogen catalysts, prepared for a wide variety of uses. Accordingly, the literature was studied for preparative techniques which appeared feasible for this application. References 6-21 constitute a partial list of publications which contain pertinent information on catalytic activity of the desired type. Based on this survey, platinum, palladium, and nickel catalysts have been prepared and evaluated in cryogenic ignition tests under the subject program. These catalysts have been in the form of both agglomerates and finely divided powders.

A literature survey concerning pyrophoric metal powders was also performed. This survey was directed primarily towards experimental methods of preparing certain metal powders in very finely divided states. References 22-34 comprise a partial list of publications which describe both experimental techniques and theoretical considerations of interest to the proposed application of pyrophoric metal powders.

II. PLANNING OF EXPERIMENTAL PROGRAM

A. General Approach

The basic experimental approach followed throughout this contract has been directed toward the object of reducing the time required between inception of an idea and its experimental verification. Accordingly, experimental testing, utilizing small-scale laboratory apparatus, was initiated very early in the program. The first tests were of a preliminary, proof-of-principle nature, with simplicity and straightforward experimental techniques being paramount. As the program progressed and more information became available, the experimental arrangements became more complex, in order to make more accurate measurements under more severe operating conditions. The scale of testing was kept at the laboratory level. This was done primarily for the following reasons.

1. Wide ranges of variables were required to be experimentally evaluated in this program. These included the type of catalyst to be used; method of its preparation and utilization; effect of mixture ratio, temperature, and pressure; etc. It was believed that a greater body of meaningful experimental observations could be gathered by restricting the physical scope of the test arrangements. This reduced the time required for design, fabrication, and pre-run checkout of larger, more inflexible apparatus.

2. Early in the program, it was planned to include a certain amount of testing utilizing a larger scale set-up at The Marquardt Corporation's Magic Mountain Remote Test Facility. These tests were intended to serve as "hardware-size" duplication of the main laboratory study. Certain factors caused this approach to be discontinued, however, The main factor was the continued delay in delivery of necessary hardware for the liquid hydrogen system. The purchase order for this critical hardware was cancelled after the third successive delivery due date expired, with no prospect of rapid delivery.

B. Description of Ignition Test Apparatus

This sub-section describes the experimental apparatus used during this program. The presentation and discussion of the data obtained are given in following sections.

1. Preliminary Apparatus Using Fixed Bed Catalysts

The first tests were performed in the Mark I igniter, shown schematically in Figure 1. The catalyst, contained on either glass wool or a 200-mesh nickel screen, was mounted in a small glass tube, positioned behind a safety-glass shield. The hydrogen and oxygen control valves (located at the flowmeter inlets) were adjusted to provide the desired flow rates upon activation of the solenoid salves. Each gas was passed through a copper coil into a Dewar flask, in which liquid nitrogen or another cooling medium was placed. The insulation around the-top of the ignition tube provided a reservoir for liquid nitrogen, to obtain more effective chilling of the inlet gases and the ignition tube. Copper/constantan thermocouples were installed in the oxygen and hydrogen lines just upstream of the ignition tube inlet.

Glass wool was used to mix the gas streams before contact with the catalyst. The flow rates of oxygen and hydrogen were set at low values so that the ignitions were not violent. A purge of nitrogen was used before and after each ignition test.

Initial tests with this apparatus used visual detection of ignition. Later, a platinum/platinum-rhodium thermocouple (0.005 in. dia.) was also used for this purpose. The output of the latter, suitably amplified, was displayed on a Hewlett-Packard Model 130A oscilloscope. Using small amounts of a platinum-powder catalyst prepared by a method similar to that of Reference 10, ignition was demonstrated with both hydrogen and oxygen gases cooled to cryogenic temperatures. The ignition tube, with catalyst, was also chilled substantially by the liquid nitrogen in these tests. Re-ignition was repeatedly obtained under these conditions.

The next experimental set-up, the Mark II igniter, permitted insertion of the entire assembly, including catalyst and gas inlet lines, into a liquid nitrogen Dewar. This permitted more uniform control for low-temperature tests. This apparatus is shown in Figure 2. With the fast-response thermocouple in the position shown, the oscilloscope trace indicated the initial temperature rise of the catalyst bed caused by the water formation reaction. Using this more rugged apparatus, higher gas flow rates (with more vigorous ignitions) could be tested.

With this apparatus and the same type of platinum catalyst mentioned above, it was demonstrated that ignitions could be obtained when the catalyst, the hardware, and both gases were at approximately 90°K (162°R), the boiling point of liquid oxygen.

The next apparatus, the Mark III igniter, provided more positive control and measurement of the temperature of the gases and of the catalyst. This device is shown in Figure 3 and 4. It also reduced the time lag involved from activation of the solenoid valves to the establishment of steady flow of both gases past the catalyst zone. This was accomplished by utilizing small diameter conduits for all gases, up to the sudden enlargement at the catalyst zone.

The main body of this device was brass. The lower body portion was a tube with three slots cut through the wall. The thin body wall and the slots reduced the thermal path, allowing a measure of temperature control of the gases and catalyst by varying the immersion depth of the apparatus in liquid nitrogen.

The oxygen and hydrogen entered the unit from opposite sides into a central port, and then flowed into the catalyst zone. A copper/constantan thermocouple placed in the central port measured the gas temperature.. The nitrogen entered through a side port, purging the reaction zone.

Both ports opened into a sudden enlargement, which contained the catalyst and two thermocouples, all of which were held in place between two sections of 200-mesh nickel screen. One thermocouple was copper/constantan, to measure the catalyst temperature. The second was a fast response Pt/Pt-10% Rh thermocouple (0.005 in. dia.) to measure the response time of the reaction.

The position of the catalyst was maintained by a support ring which was placed over the top section of nickel screen. The copper exhaust tube was positioned by slipping onto the brass base unit.

The outputs of the two copper/constantan thermocouples were measure by two Leeds and Northrop millivolt potentiometers. Due to the small diameter gas conduits used, the temperatures of the hydrogen and oxygen gas streams were quite sensitive to the temperature of the surrounding metal. The output of the Pt/Pt-10% Rh thermocouple was amplified by a Kintel Model 111BF voltage amplifier, and portrayed on a Tektronix Type 564 storage oscilloscope. Photographs of the latter were made with a Tektronix C-12 oscilloscope camera.

When operating at low temperatures, gas temperatures were measured by flowing only one propellant at a time. This was necessary to avoid heating of the catalyst bed, since there was some reaction at the catalyst with the Mark III igniter even with the nitrogen purge flowing. During low temperature runs, the reading of the top copper/constantan thermcouple (placed near the catalyst) was normally about 10-15°F higher than that of the gas temperature thermocouple.

This apparatus was used in a large number of cryogenic ignitions utilizing platinum and Raney nickel fixed-bed catalysts.

The Mark IV Igniter, shown in Figures 5 and 6, was a revision of the Mark III apparatus, with provisions for operating under full or partial vacuum conditions. A secondary catalyst bed, maintained at ambient temperature, was provided to prevent explosive mixtures of hydrogen and oxygen from entering the vacuum pump.

2. coaxial Injector Utilizing Fixed Bed Catalysts

In order to more closely simulate the actual J-2 and RL-10 motor conditions, a new ignition device was designed and fabricated; it is shown in schematic form in Figure 7. The motor simulation was based upon a request by NASA personnel. This device incorporated a coaxial injector nozzle. In order to reduce flow transients associated with initiation and termination of flow, 3-way solenoid valves with balancing flow resistance legs were incorporated in the laboratory flow system. In this manner, propellant flow was maintained continually and was diverted rapidly to the ignition device. The switching time of the solenoid valves was less than 20 milliseconds, as determined by flow response at the pressure transducer. Also, a high-response thermocouple was inserted in the coaxial injector nozzle to determine the propellant temperature prior to ignition. A photograph of the coaxial ignition device may be seen in Figure 8. In the nozzle employed in the laboratory device, the oxygen flowed through a 1/16-in. tube with an inner diameter of 0.040 in. This tube was positioned concentrically in a 1/8-in. tube with interior diameter of 0.101 in. The tip of the exterior tube was formed into a converging nozzle of 0.082-in. inside diameter. This insured contact of the hydrogen, flowing in the annulus, with the oxygen. Figure 9 is a top view showing the coaxial nozzle and the various sensors, located radially about the reaction zone at 90° separation. Included are the quartz crystal transducer, the fast-response Pt/Pt-Rh thermocouple, and a copper/constantan thermocouple. Also seen are the 0.005-in.-diameter thermocouple used to measure the inlet gas temperature, and the inlet nitrogen purge line. The relative placement of ther sensors may be better visualized from Figure 7.

Due to the larger physical dimensions of the coaxial ignition device as compared to the Mark III apparatus, the minimum obtainable propellant temperature, utilizing gaseous propellants, was approximately 115°K.

Using this apparatus, a large number of cryogenic ignitions were obtained using fixed-bed catalysts of platinum, palladium, and Raney nickel.

3. Coaxial Injector Utilizing Entrained Raney Nickel Powder

The apparatus described in the preceding subsection yielded a great deal of useful information concerning cryogenic ignitions utilizing a fixed-bed catalyst.

The method of application of greatest interest to the present program, however, involved the entrainment of the dry nickel powders in the hydrogen stream. With this arrangement, ignition occurs when this stream, with its entrained nickel powder, comes into contact with the oxygen stream. Accordingly, testing with fixed-bed catalysts was discontinued, and the emphasis was placed on entrained powder ignitions.

The initial fluidizer arrangement is shown schematically in Figure 10. The catalyst fluidizer section was loaded in a dry box, under an atmosphere of nitrogen, with the Raney nickel powder. In the arrangement shown in Figure 10, the Raney nickel powder was protected from contact with the air by burst diaphragms.

Upon activation of the three-way hydrogen solenoid valve, gas pressure ruptured these diaphragms, causing some of the fine Raney nickel powder to be entrained in the hydrogen gas stream, as it left the fluidizer and entered the coaxial injector.

In another arrangement, the burst diaphragms were replaced by check valves. This change was made in order to simulate more closely the operation of a system possessing multiple restart capability. Both fluidizer arrangements produced low-temperature ignitions.

As can be seen from Figure 10, this apparatus was basically the same as the Mark V version, with the addition of the fluidizer assembly. Accordingly, the Mark VI device was subject to the same temperature limitation, i.e., the injection of gaseous propellants at approximately 115°K.

The next step, therefore, was the modification of the apparatus to permit the injection of liquid oxygen and cold gaseous hydrogen; both being cooled to the temperature of liquid nitrogen. This was accomplished by modifying the Mark VI apparatus to position the oxygen inlet line in liquid nitrogen, thereby assuring liquefaction of the flowing oxygen. This arrangement (Mark VII) is shown schematically in Figure 11. The depth of immersion in liquid nitrogen was greater, with this device, in order to ensure that both propellants, and the injector hardware, were at liquid nitrogen temperature. The Mark VII device had the feature that the catalyst fluidizer assembly was also immersed in liquid nitrogen, thereby providing information on the functioning of this component at cryogenic temperatures. The fluidizer, together with its associated check valves, functioned in a normal manner under these conditions.

Using this arrangement, ignitions were obtained with liquid oxygen and Raney nickel entrained in the cold gaseous hydrogen stream. It was also determined, by visual observation, that the Raney nickel powders were pyrophoric in the presence of liquid oxygen.

The only remaining experimental requirement was to further lower the temperature of the cold gaseous hydrogen. Since safety regulations precluded the use of liquid hydrogen in the Physical Chemistry Laboratory, this was accomplished by utilizing liquid helium for cooling purposes. The overall system schematic of the arrangement used to achieve this goal is shown in Figure 12. A more detailed schematic of the ignition assembly itself is given in Figure 13. The salient features of this arrangement are as follows:

The ignition device was located within a double Dewar arrangement. The outer Dewar contained liquid nitrogen, This served to chill and liquefy the oxygen stream, and to chill the nitrogen purge. It also served as a pre-chill for the hydrogen stream. The latter was then directed into the inner Dewar, which was futher cooled by the flow of cold gaseous helium. The helium was obtained from a commercial liquid helium Dewar. The temperature inside the inner Dewar (as measured by the copper/constantan thermocouple, T.C. 2) was controlled by adjusting the rate of addition of cold helium from the liquid helium source. It was found that this technique permitted a convenient control of temperature in this region over the desired range.

The temperature of the cold hydrogen was measured by another copper/constantan thermcouple, T.C. 1, just prior to entering the coaxial injector. Hydrogen flowed through the annulus of this injector, through a 0.111-in. bore. The inqer, oxygen line was 0,035 in. O.D. by 0.019 in. I.D. The oxygen and nitrogen purge streams were normally not cooled excessively by the cold gaseous heilium, since these lines passed straight from the liquid nitrogen Dewar to the injector assembly. This tended to place a lower limit on the hydrogen temperature, however, since the oxygen stream could conceivably approach its freezing temperature (55°K) if the temperature of the hydrogen stream were permitted to get too low. This became even more important at the lower mixture ratios, at which the oxygen flow rate, and hence the effective thermal mass of the flowing oxygen stream, was reduced.

Both propellants were obtained from pressurized, ambient-temperature gas cylinders. Referring to Figure 12, hydrogen flow rates were determined from the gas rotameter, F_1, which was also at ambient temperature, A three-way solenoid valve, V_1, diverted the hydrogen flow to the bypass line except when an ignition test was being performed. The fluid resistance of the bypass line was adjusted by the needle valve, V_2, to match that of the injection line. This provided a smooth flow transition when the three-way valve was activated to the ignition mode. Downstream of the three-way solenoid valve was the catalyst fluidizer. In this device the hydrogen stream entrained a small amount of Raney nickel powder. The contents of the fluidizer were protected by check valves, C_1 and C_2, or, in certain tests, by burst diaphragms.

The hydrogen line downstream of the fluidizer was purged and pre-chilled by a portion of the hydrogen bypass flow, by activation of the two-way solenoid valve, V_3. The hydrogen line was then passed into the outer Dewar for pre-chill.

The oxygen system was straightforward. Flow rates were measured by the gas rotameter, F_2. The gaseous oxygen flow was vented to the bypass line by the three-way solenoid valve, V_4, except when flow to the injector was desired. The fluid resistance of the oxygen bypass linecwas adjusted to match that of the injection line by means of the needle valve, V_5. The gaseous oxygen was then liquefied by passing through a coil of 1/16-in.-O.D. tubing immersed in liquid nitrogen in the outer Dewar, and then flowed as a liquid to the injector.

The pre-cooled, gaseous nitrogen purge normally flowed continually, except during ignition periods. Provisions were made, by means of valves V_7 and V_8, to purge each propellant system with nitrogen,

Output data, consisting of thermocouple and pressure transducer traces, were recorded on a Tektronix Type 564 Four Channel Storage Oscilloscope, and photographed by a Tektronic C-12 Oscilloscope Camera.

The nominal flow rates used in these ignition tests were as follows:

	NOMINAL MIXTURE RATIO, O/F			
	0.5	1.5	4.0	6.0
O_2 flow, g/min	0.283	0.85	2.22	2.22
SCFM	7.00×10^{-3}	0.0210	0.055	0.055
H_2 flow, g/min	0.566	0.566	0.555	0.370
SCFM	0.222	0.222	0.218	0.1455

4. Ignition Sensing

Two types of instrumentation were used for ignition sensing; (1) one or more 0.005-in. Pt/Pt-10% Rh fast response thermocouples, and (2) a Kistler 601-H quartz crystal pressure transducer. The unshielded thermocouple beads were mounted directly in the ignition zone. The quartz transducer was mounted at one end of a 2-in. long, 1/8-in. dia. tube; the open end of the latter was mounted directly over the injector. It is of interest to compare the information gained from these two sources. The pressure transducer output was the primary signal, since this program was concerned with the establishment of a well-defined detonation wave. The latter was positive evidence that an ignition had occurred which should have been capable of producing combustion in a large engine. The thermocouple output provided useful supporting information concerning the mechanism of this ignition; e.g., whether or not a finite pre-ignition reaction occurred. It also provided information concerning the local temperature developed in the immediate vicinity of the ignition zone.

The response time of the pressure transducer plus amplifier was of the order of 10 microseconds, and was therefore negligible for the purpose of this program. With this as a basis, one can then estimate the response time of the 0.005-in. Pt/Pt-10% Rh thermocouple. Analysis of the experimental results, discussed subsequently, reveals that the response time of this thermocouple to a detonation wave was too short to be measured at the oscilloscope trace speeds utilized in this study (generally 100-200 milliseconds/cm) and could not have been greater than about 5 milliseconds. Moreover, the present experimental data verify that, with Raney nickel catalysts at the higher mixture ratios, the initial rise of the thermocouple output signal corresponds to the detonation wave. The subsequent behavior of the thermocouple trace was strongly dependent on the particular geometry prevailing for the test in question. In some cases the trace continued smoothly up to the maximum temperature; in others, there was a lag or discontinuity in the trace. The indicated maximum temperature accompanying ignition was normally about 2000°K, but was sometimes much lower. Thermocouple failure (due to melting) occurred in a few cases, generally associated with tests in the Mark IV apparatus. This was presumably due to the altered flow patterns prevailing in the ignition area, as a result of the modified exhaust line. Otherwise, thermocouple burnout was not a problem during this study.

The outputs of these instrumentation probes, suitably amplified, were portrayed on a storage oscilloscope. Polaroid photographs of the latter provided permanent records of ignition data.

The radio noise associated with the activation of the solenoid valves produced a pip on the oscilloscope track. This provided the basis for computing ignition delay times. The delay due to gas lead time was determined by blank runs in which only one gas was flowing. The gas lead time represents the time interval between the valve "on" pip and the pressure transducer response. This lead time (approximately 20 milliseconds for the hydrogen stream) was subtracted from the overall ignition delay time.

All temperature measurements of the cryogenic propellants were made with copper/constantan thermocouples, with room temperature reference compensation. These thermocouples were not individually calibrated, since a high degree of accuracy was not required in these measurements. The temperature vs. emf relationship at the cryogenic conditions involved was based on the data of NBS Circular 561, extrapolated with the aid of a calibration curve for a specific copper/constantan thermocouple.

C. Ignition Mechanism and Storage Characteristics of Raney Nickel

As mentioned previously, it was necessary to develop new storage methods for Raney nickel powders, and to determine the mechanism responsible for the ignitions obtained from this material. This was accomplished by a series of observations involving desorption and re-adsorption tests, as described in the following section.

D. Gas Adsorption Studies

Gas adsorption studies were made on samples of Raney nickel powder. These studies were performed by a modification of the classical B.E.T (Brunauer-Emmett-Teller) volumetric method. The purpose was to gain information concerning the surface area of these powders and to observe the hydrogen adsorption characteristics at various temperatures. Although only limited time was available for these tests, interesting data were obtained. These data are presented and discussed in the following sections.

III. EXPERIMENTAL STUDY

This section presents the experimental data obtained during the program, together with a brief description of the experimental conditions under which they were taken, Analyses of these data, and a discussion of the significance of the results, are also given in the following section.

The ignition data of this section are given in approximately chronological order. Initial data therefore represent the more qualitative, proof-of-principle results, while the latter body of data gives the more quantitative, precise results. The ignition data are grouped into the same headings as utilized in the preceding section.

A. Experimental Ignition Data

1. Preliminary Ignitions Using Fixed Bed Catalysts

Ignition devices Mark I and Mark II were uged to demonstrate ignitions utilizing a platinum catalyst. The latter was prepared by a method similar to that of Reference 10, which involved the formaldehyde reduction process. The catalyst was in the form of an agglomerated powder. The activity of this material decreased very noticeably with temperature. Ignitions were demonstrated, however, at temperatures near that of liquid oxygen, 90°K (162°R). These preliminary items of apparatus also served to check out the technique of recording ignitions by means of fast response Pt/Pt-10% Rh thermocouples.

The Mark III apparatus (Figures 3 and 4) was used for the preliminary evaluation of Raney nickel powders. The Raney nickel was prepared by modifications of the procedures given in References 11 and 18. In these initial tests the nickel was stored in the form of a sludge under methanol. Since this material became pyrophoric when dry, it was necessary to protect it from contact with oxygen until time for an ignition test. This was done in the following manner: With the Mark III device at ambient temperature, a small amount (1-2 grams) of the Raney nickel-methanol sludge was placed in the ignition zone (see Figure 3). The exhaust tube was quickly slipped on, and the nitrogen purge started. This served to vaporize the methanol, leaving the dry, pyrophoric Raney nickel behind. The latter was broken up into a powdery form by insertion of a stainless steel spatula down the exhaust tube. Liquid nitrogen was then added to the containing Dewar, and the entire apparatus chilled. During this period the nitrogen purge protected the Raney nickel by excluding air and moisture, Ignition was accomplished by activating the hydrogen and oxygen solenoid valves. These preliminary ignition data are listed in Table I.

For the initial series of tests described in Table I, in no case was an attempted ignition unsuccessful at atmospheric pressure. Normally, four or five ignitions could be obtained from the sample of Raney nickel before the nickel powders became completely oxidized.

Some of the attempted vacuum runs failed to produce an indication of ignition. In every case, however, post-run inspection revealed that the nickel powders had been oxidized, with the liberation of considerable heat. It is likely that this occurred during the process of evacuating the system, since a small leak would permit atmospheric oxygen to come into contact with the pyrophoric powder. Subsequent tests have indicated that the geometric arrangement of the ignition chamber may be an important variable. Photographic results of some of these runs are shown in Figures 14 and 15.

Table I indicates that the majority of ignitions occurred with a time lag of the order of 200-500 milliseconds, with a few runs proving that more rapid ignitions are possible under favorable circumstances. Control measurements with the pressure transducer output showed that only a negligible fraction of this delay could be attributed to thermocouple response time.

The response times of the solenoid valves, and of the fluids concerned, were next considered. Information on this subject is given in Figure 16, which shows the response of the pressure transducer to flow of each separate gas with the Mark III ignition device. The response times for the valves were negligible for present purposes, but the times required for the gas flows to become established were not negligible. It can be seen from Figure 16 that the hydrogen flow required about 120 milliseconds to reach steady state, while the oxygen flow took about 440 milliseconds for steady state to be obtained. It is of course readily possible to obtain ignitions before steady-state flow has been attained. An inspection of Figure 16 indicates, however, that certain minimum time intervals are required before gas flow becomes significant. These minimums appear to be, roughly, 20 milliseconds for hydrogen and 50 milliseconds for oxygen. Since an oxygen lead was normally used, 20 milliseconds were subtracted from the overall ignition times.

Slight irregularities in the flow pulses, which occurred when one or both of the solenoid valves were activated, could well have delayed the attainment of a suitable mixture ratio in the ignition zone. This factor is possibly one of the main reasons for the scatter in the observed ignition times. The problem was alleviated in the coaxial injection device.

In Run 114, performed at a pressure of 2.2 psia, the initial rise of the thermocouple trace was not clearly defined. The pressure transducer was not installed for this test. There was no detectable audible signal accompanying the ignition.

These tests with the Mark III device demonstrated that ignitions could be routinely attained at temperatures down to about 90°K (162°R) utilizing Raney nickel.

2. Coaxial Injection Utilizing Fixed Bed Catalysts

In accordance with requests of the contracting agency, further ignition testing was restricted to devices employing coaxial injection of the propellants.

The first of these, the Mark V ignition device (Figures 7-9), continued the fixed catalyst bed tests described previously. In addition to Raney nickel, tests were performed with various types of platinum and palladium catalysts, primarily for comparative purposes. These tests are summarized in Table 11. Some of the catalysts listed therein are not of direct applicability to this program. They were included in the test schedule, however, in order to afford a basis of comparison, and to demonstrate the effectiveness of various in-house activation treatments.

It should be noted that the corrected ignition times reported in Table II represent the observed total ignition delay time, minus the gas lead time, which was of the order of 20 milliseconds for these tests.

As can be seen from Table II, these systems have demonstrated feasibility for low-temperature ignitions, with corrected ignition times in the vicinity of 10 milliseconds having been measured. Oscilloscope traces of two of these runs are shown in Figure 17.

The reliability of the attempted ignitions utilizing Raney nickel as a fixed bed was exceptionally good, yielding successful results for all attempts. An inspection of Table II reveals that ignition delays of the order of 40-50 milliseconds can be obtained with this material, with results in the 10-20 millisecond range under optimum conditions. An average of 11 ignitions was obtained from each sample before the nickel powders were deactivated. However, in many instances the catalyst would need to be repositioned over the coaxial injector to get minimum ignition delays. It is likely that this factor was responsible for the scatter observed in the ignition times. This indicated that the optimum catalyst bed geometry had not yet been ascertained. However, no effort was directed toward optimizing this parameter, as it was felt that the fluidized bed concept offered greater potential.

Two types of noble metal catalysts were also evaluated. One was in the form of essentially pure platinum black, prepared by a method similar to that of Reference 10. The other was a commercial 5% palladium on activated alumina. Both materials consistently produced ignitions at ambient conditions. Attempts to use the same catalysts at cryogenic temperatures, however, produced no ignitions.

Portions of both materials were subjected to a process of evacuation, followed by exposure to ambient hydrogen gas. This treatment made a marked improvement, particularly for the palladium catalyst, as shown by Runs 145-157 in which ignitions were obtained at 134°K. This is in keeping with the postulate that pre-chemisorbed hydrogen is responsible for the cryogenic catalytic activity of noble metal catalysts for H_2/O_2 ignition. In this regard, it is believed that the basic mechanism of ignition obtained from Raney nickel is similar to that of noble metal catalysts.

The observations of this program therefore indicate that there is a problem area associated with the exposure of fixed-bed catalysts of this type to the vacuum of space. Desorption of hydrogen will result (and will be greatly speeded up if the catalyst bed is still warm from previous engine firing). According to the mechanism postulated in this report, it will be necessary to deposit a new layer of chemisorbed hydrogen before the catalyst will be capable of producing cryogenic ignitions.

It is, of course, possible that certain noble metal formulations may chemisorb hydrogen more rapidly than the materials investigated in this program. Based upon quite general kinetic considerations, however, it does not appear likely that this adsorption process will occur extremely rapidly (a few milliseconds or less) at cryogenic temperatures for any practical system.

The implication is, therefore, that a fixed-bed, noble metal catalyst would have to be protected from exposure to space vacuum in order to provide cryogenic restart capability.

This condition does not affect the application of Raney nickel, since it is proposed to utilize the latter by fluidization into the hydrogen stream, rather than as a fixed bed catalyst.

A modified form of Raney nickel was utilized in some of the fixed-bed tests. This material was prepared in a manner similar to that used with earlier batches, except that the final stage of washing with methanol (and subsequent storage under methanol) was omitted. That is, the process was stopped after the water rinse stage and the final product was stored under distilled water. The reason for doing this was as follows: During the water rinse stage, the Raney nickel exists in the form of relatively large particle agglomerates, with no fines present. It is only after the material is rinsed with absolute (anhydrous) alcohol that the particle size becomes very small (approaching colloidal size). It is likely that this pronounced particle size reduction is due to a combination of surface tension effects, and the strong affinity of the anhydrous methanol for any bound water which may be associated with the particle agglomerates. The result is that the coarse agglomerates are broken up into their constituent fine particles.

The effect of stopping at the water rinse stage is, therefore, the production of Raney nickel in a coarser particle form, which has perhaps more bound hydrogen than in the form used previously. This modified form of Raney nickel produced ignitions which were among the most rapid observed. In this application, the material was present in the ignition zone as a fixed bed. Although quite active catalytically, this form was less pyrophoric than the others, due to its coarser particle (or agglomerate) size. This provided a larger thermal mass and a smaller surface-to-mass ratio. The heat of reaction between oxygen and the chemisorbed hydrogen could thus be dissipated more readily.

3. Coaxial Injection Utilizing Entrained Raney Nickel Powder

Initial data of this type were obtained from the Mark VI ignition device (Figure 10) in which the *dry* Raney nickel powder was entrained in the hydrogen stream. This unit operated with gaseous propellants, cooled down to near the boiling point of oxygen, 90°K (162°R). These data are summarized in Table III. They demonstrated the feasibility of obtaining rapid ignitions by the use of dry Raney nickel powders entrained by fluidization in the H_2 stream.

The ignition delay times initially obtained by this method were subject to scatter, as shown in Table III. It is believed that this was primarily a matter of mechanical design of the fluidizer chamber, rather than a fundamental limitation. This statement is supported by the fact that the most rapid ignition times (of 20-30 milliseconds) reported in Table III (Runs 191 and 192, Figure 18), compare favorably with the best results obtained from the fixed bed technique.

A pronounced difference in the ignition characteristics as a function of mixture ratio was observed. Ignitions obtained at a mixture ratio (O/F) of 6.0 were consistently exemplified by a sharp, well-defined detonation pulse. At the oscilloscope trace speeds used in these studies, the ignition pressure surge appeared as a sharp, vertical pip on the pressure transducer trace {see Figure 18). On the millisecond scale, there was no appreciable pre-ignition reaction time.

The situation was quite different at the lower mixture ratio of 1.5, however. These ignitions were of a much milder nature, with indications of a reaction pressure buildup stage lasting on the order of 200 milliseconds. In addition, it was found, by visual observation of the interior of the ignition tube (by means of a prism), that most ignitions were occurring well downstream of the region in which the ignition at O/F = 6.0 occurred.

This factor was doubtless one of the major reasons for the apparent scatter and nonuniformity observed in the ignitions at O/F = 1.5 (Runs 214 through 228 of Table III). The pressure rises accompanying these more gentle ignitions were so slight that, unless the exhaust tube was firmly stoppered, they did not register on the pressure transducer trace. Also, the ignitions sometimes occurred sufficiently far downstream of the fast-response thermocouple that no signal was obtained from the latter.

These points are illustrated in Figure 19. The top photo therein shows the pressure transducer trace for a calibration run in which hydrogen gas alone was flowing. Note that the pressure buildup curve has a negative second derivative (i.e., the curve is concave to the time axis). This characteristic was observed in all calibration runs, wherein the pressure buildup was due solely to the gas flow.

The bottom photograph of Figure 19 depicts an ignition (at O/F = 1.5) obtained with the exhaust tube stoppered. This run had an oxygen lead, as indicated by the slight rise in pressure prior to opening the hydrogen valve. After actuation of the latter valve, the pressure buildup curve showed a positive second derivative (i.e., convex to the time axis). This was due to the more rapid pressure rise resulting from the H_2/O_2 combustion reaction, which began shortly after the hydrogen gas (with entrained Raney nickel) entered the ignition zone. This ignition pressure rise continued at an increasing rate for approximately 240 milliseconds before the detonation pulse occurred. The latter blew out the restriction which had blocked the exhaust tube, causing the pressure trace to decrease to its base line valve. The fact that the thermocouple trace did not respond indicates that the ignition occurred considerably downstream of the injector.

The next phase of testing involved the injection of liquid, rather than gaseous, oxygen. This was accomplished with the Mark VII apparatus (Figure 11). The ignition data are given in Table IV, with selected ignition traces shown in Figures 20 and 21.

All of the ignitions (15) recorded in Table IV were obtained from a single charge of Raney nickel (about 4 grams). In addition, there were approximately as many ignitions obtained from this sample which were not recorded. The charge of Raney nickel had not been depleted when these tests were discontinued. Upon disassembly, there appeared to be approximately one gram of nickel powder remaining.

Liquid oxygen was visually observed (by means of a prism) to be welling out of the oxygen tube or injector. Generally, sparking could be heard (and usually seen) almost immediately upon opening of the hydrogen valve. This was due to the pyrophoric reaction which occurred when small particles of Raney nickel contacted liquid oxygen. These sparks could not be detected by the instrumentation. At times, the pronounced detonation wave accompanying ignition was delayed, presumably until sufficient mixing of the propellants had occurred. This delay could be reduced considerably by providing a brief oxygen lead. Positive results (either sparking or a clearly defined ignition) were obtained in every attempt. If complete mixing prevailed, the ignition would proceed catalytically. Strictly speaking, the combustion process would be well underway before the Raney nickel powders themselves react pyrophorically with the oxygen. Should incomplete mixing permit the nickel powders to be in a localized zone which is very oxygen rich, the powders would become incandescent before the ignition proper occurred. The latter would be delayed by the mixing time required to transport the incandescent particles into a region of favorable mixture ratio. Thus, although ignitions will be obtained in both cases they will be more rapid and uniform under conditions which provide for thorough mixing in the immediate vicinity of the injector.

The corrected ignition time for Run 246 (Figure 21) was approximately 10 milliseconds. This represents one of the most rapid ignitions of the program. It should be noted that this is the total time from admission of H_2 gas to the attainment of steady-state combustion. As discussed previously, at a mixture ratio (O/F) of 6.0, the detonation wave accompanying ignition was virtually simultaneous (on the millisecond scale) with the initial rise of the thermocouple trace. This is shown in the traces for Runs 242 and 243 (Figure 20), which yielded corrected ignition times of about 60 and 15 milliseconds, respectively. The pressure trace was not operative in Run 246. The corrected ignition times were obtained by subtracting the H_2 gas lead time (approximately 20 milliseconds) from the total time interval between the H_2 valve "on" pip and the ignition. These data demonstrate that the ignition characteristics of Raney nickel in the presence of liquid oxygen are at least as favorable as those when gaseous oxygen is used.

The firings reported in Table IV were obtained with all injector hardware, including the fluidizer, at liquid nitrogen temperature, approximately 77% (138°R). Both the liquid oxygen and gaseous hydrogen were also at this temperature.

It is also of interest to note that the fluidizer, using standard check valves, operated satisfactorily at 77°K. No problems were encountered with the downstream check valve, which was exposed to the stream of gaseous hydrogen with entrained Raney nickel powder. It therefore appears that the concept of utilizing entrained Raney nickel should not present unusual hardware and plumbing problems.

The final experimental stage involved cooling the hydrogen stream with helium, in order to obtain ignition data with the hydrogen temperature in the range of 40-140°R (approximately 22-78%). This was accomplished with the Mark VIII device (Figures 12 and 13). These data are given in Table V. Figures 22 and 23 show some of the ignition oscilloscope traces.

The first group of data in Table V (Runs 250-264) were made at liquid nitrogen temperature (propellants plus hardware). It can be seen that the ignition times reported therein are consistently longer than those obtained with the former apparatus under these same experimental conditions (see Table IV). It appears, therefore, that the geometry of the Mark VIII device did not promote rapid mixing of the propellants as well as did its predecessor, the Mark VII device.

Runs 265-274 were performed with liquid helium cooling of the hydrogen stream. The hydrogen temperatures reported in Table V were measured with the thermocouple designated T.C. 1 in Figure 13. With this procedure, ignitions were obtained in the contractual temperature range. The ignition times observed in Runs 265-274 were of the same magnitude as those of Runs 250-264. There was no observable effect on ignition of the lower temperature of the hydrogen stream.

The lowest hydrogen temperature at which an ignition occurred was 57°K (103°R), in Run 270, shown in Figure 22. The exact ignition time could not be determined in this case, due to the failure of the hydrogen valve "on" pip to register on the oscilloscope. The ignition was normal, however, and could not have required over 500 milliseconds, i.e., the same order as other ignitions obtained with this apparatus.

Referring again to Figure 13, it can be seen that the coaxial injection feature, combined with the low flow rates of these laboratory devices, places a minimum on the permissible hydrogen inlet temperature. Recalling that the freezing temperature of liquid oxygen is about 55°K (99°R), it can be appreciated that hydrogen temperatures substantially lower than this could lead to partial plugging of the oxygen flowing in the central tube of the injector. It appears, therefore, that hydrogen inlet temperatures much below that of Run 270 would not be feasible with this apparatus. Additional information on this subject may be gained from Runs 275-278. In Run 275, an ignition was obtained at 64°K. Following this, the flow rate of cold gaseous helium to the inner Dewar was increased, in order to lower the temperature. When the hydrogen gas temperature read 48°K, an ignition was attempted, but was unsuccessful (Run 276). On permitting the hydrogen temperature to rise slightly, ignitions were again obtained. Although one cannot say with certainty what prevented the ignition in Run 276, it is likely that partial or complete plugging of the oxygen line, due to freezing, was responsible.

This effect could have been minimized in the existing apparatus by introducing the hydrogen and oxygen streams separately into the ignition zone. The preferred coaxial injector approach was followed, however, in accordance with requests of the contracting agency.

It will be noted in Figures 22 and 23 that a second thermocouple trace appears on the oscilloscope traces. The middle trace is due to the Pt/Pt-10% Rh fast-response thermocouples located in the ignition zone immediately downstream of the injector. The bottom trace is the output of a similar thermocouple located further downstream, in the exhaust tube. The latter thermocouple was useful for detecting ignitions at low mixture ratios and at partial vacuum conditions, as Run 279 (Figure 23) demonstrates.

The results obtained under partial vacuum conditions (such as Runs 279-283) were more difficult to interpret. The ignitions detected by the instrumentation usually occurred after relatively long delays (several hundred milliseconds). In several cases, however, post-run inspection clearly showed that ignitions had occurred which were not picked up by the instrumentation, presumably due to the fact that they occurred downstream of the thermocouple installations. It appears, therefore, that considerable work would still have to be done in evaluating the effect of ignition zone geometry on mixing efficiency under vacuum conditions.

It is interesting to note that ignition Runs 279-283 were obtained from a sample of Raney nickel which had been stored for almost five months (under hydrogen gas) prior to this use. The material used in these tests gave every indication of being as active as the other samples.

B. Ignition Mechanism and Storage Characteristics of Raney Nickel

Raney nickel is prepared by reacting a nickel-aluminum alloy (in the form of a fine powder) with sodium hydroxide. The reaction is

$$NiAl_2 + 2NaOH + 4H_2O \rightarrow 2Na(H_2AlO_3) + Ni + 6[H] \qquad (19)$$

The nascent (atomic) hydrogen is therefore formed in close proximity to the newly exposed nickel surface. Most of this nascent hydrogen forms molecular hydrogen and escapes; a small part is chemisorbed on the fresh nickel surfaces. In simplified notation,

$$Ni + H \rightarrow (Ni\text{-}H)_{chemisorbed} \qquad (20)$$

Thus the Raney nickel contains some chemisorbed hydrogen as a direct result of its method of preparation.

In the usual application, the product is stored under an inert carrier, such as ethanol, until ready for use. During this period, slow but continual evolution of hydrogen may be observed. This doubtless represents the gradual desorption of the chemisorbed hydrogen. In a period of a few weeks, at most, the Raney nickel loses its activity.

It was evident, therefore, that a more suitable storage technique would have to be developed which would permit long-term storage of the material in the active state. Theoretical considerations indicated the desirability of storage under an atmosphere of hydrogen, preferably in the form of the dry nickel powder under hydrogen gas at ambient conditions. This was done, with indications of a virtually indefinite storage life under these latter conditions. The experimental arrangement was as follows:

Eight samples were withdrawn from a common source of Raney nickel-methanol sludge. One sample was placed in each of eight flasks, and immediately covered with methanol. Next, the eight flasks were simultaneously evacuated to dryness. The exact pressure was not measured, but was approximately $100\,\mu$Hg. Hydrogen gas was then admitted simultaneously to the eight flasks, to approximately atmospheric pressure, These flasks were then set aside, to serve as long-term storage tests. At various times throughout the remainder of the contract period, these flasks were opened and tested for pyrophoricity in ambient air. Some of these samples were also used in cryogenic-temperature ignition tests.

The results of these tests were as follows:

Sample No.	Total Storage Time Under Ambient H_2 Gas	Condition when Opened	Remarks
1	7 Days	Intensely pyrophoric	
2	14 Days	It t?	
3	29 Days	tt tt	
4	58 Days	tt tt	Used successfully in entrained metal ignition tests, Runs 190-194
5	86 Days	If tt	Low-temperature ignitions obtained
6	120 Days ($\approx$ 4 months)	tt tt	
7	159 Days ($\approx$ 5 months)	tt tt	Used successfully in low-temperature vacuum ignitions, Runs 279-283

The procedure in opening these flasks was to quickly evacuate to a crude vacuum (to remove the bulk of the gaseous hydrogen, and back-fill with nitrogen gas. The contents could then be transferred, under an inert atmosphere, into the fluidizer, These observations represent, as far as is known, the longest storage periods attained with Raney nickel. Qualitatively, each of these samples was immediately pyrophoric upon contact with air, with no observable decrease in activity with storage time. According to the theoretical model described earlier, there should be no reasonable limit to the shelf life of Raney nickel powder stored under these conditions.

It was next necessary to demonstrate conclusively that the pyrophoricity of the Raney nickel being used in these tests is due to a chemisorbed layer of hydrogen, rather than simply being a result of the small particle size of the nickel powder. This was accomplished by the following simple experiment.

Two different samples were withdrawn from a common batch of Raney nickel stored under methanol; this parent batch of nickel was shown to be pyrophoric just before the samples were withdrawn. The two samples were then evacuated to dryness (at approximately 100 μHg), and then back-filled with ambient nitrogen gas. After a short period of time, both samples were exposed to the air and found to be completely inactive (nonpyrophoric). These same two samples were then returned to the vacuum desiccator and re-evacuated, followed by back-filling with ambient hydrogen gas. Two days later, these samples were exposed to air (after pumping off the hydrogen gas) and found to pyrophoric. These results are in complete agreement with the theoretical model presented previously.

Additional verification came from tests in which reacted, oxidized Raney nickel (now in the form of nickel oxide) was regenerated. This was done by reducing under hydrogen at about 300°C and removing the water formed by the reaction:

$$NiO + H_2 \rightarrow Ni + H_2O.$$

Upon chemisorbing a layer of hydrogen onto the reduced nickel powder, the latter was again made active, as evidenced. by its pyrophoricity.

As a result of the preceding observations, the ignition mechanism of Raney nickel may be summarized as follows:

The catalytic activity of Raney nickel for low temperature H_2/O_2 ignition is due solely to a pre-existing layer of chemisorbed hydrogen. This serves to produce ignitions by one or both of two main paths. The first is based on the fact that the chemisorbed hydrogen has a small but finite tendency to desorb, producing an extremely small concentration of hydrogen atoms in the vicinity of the nickel surface. This is the same as Reaction (18), discussed previously. This very small concentration of free hydrogen atoms may react with oxygen molecules to initiate the combustion process by Reactions (6-10) described in Section I. Alternatively, the oxygen molecules may react directly with the chemisorbed hydrogen atoms, to produce free radical species, such as OH, which could then desorb and trigger the combustion reaction by a similar process.

The heat release associated with these reactions, which occur either on or very near the nickel surface, raises the temperature of the nickel particles. The latter, due to their small thermal mass, quickly attain a temperature sufficient to promote the direct oxidation reaction between elemental nickel and oxygen; i.e., the nickel powders are pyrophoric. Although this pyrophoricity may be quite useful in promoting an ignition, it definitely represents a secondary process, resulting from the primary catalytic reaction involving the chemisorbed hydrogen. Upon removal of the latter, with no change in particle size or configuration, the nickel is no longer pyrophoric.

C. Gas Adsorption Studies

One of the purposes of the gas adsorption studies was to obtain information concerning the surface area of the Raney nickel powders. This was done in a volumetric apparatus, using standard B.E.T. nitrogen adsorption techniques (35).

The surface area determined by this method for two different batches of Raney nickel powder was approximately 50 m^2/g (square meters per gram of nickel powder). In comparison, a sample of the pure platinum catalyst used earlier in the program had a surface area of 6 m^2/g. This is in accordance with the greater activity observed for the Raney nickel at low temperatures as compared to the platinum black.

Additional information on this subject is provided from the data of Figures 24 and 25, which show hydrogen adsorption isotherms for these two materials.

The present discussion is concerned with the adsorption isotherms at ambient temperature (298-300°K), since these curves may be expected to represent the desired phenomenon of chemisorption (as opposed to the physical adsorption which may occur at lower temperatures).

It can be seen from these curves that the Raney nickel chemisorbs considerably more hydrogen per unit weight than the platinum black. Even on the basis of catalyst volume (to take into account the greater density of platinum) the Raney nickel adsorbs more hydrogen..

The significance of these curves is that the amount of chemisorbed hydrogen is a measure of the amount of free hydrogen atoms which may be available to produce a catalytic ignition.

It must be emphasized that the field of adsorption measurements is a complex one, particularly as it applies to the Raney nickel powders. After a rapid initial uptake of hydrogen, long periods of time (2 days or more) were sometimes required to reach final equilibrium. This could represent a specific type of activated chemisorption, complicated by the diffusion processes involved in permeating through the nickel powder. Further work would be required in order to provide unambiguous interpretation of the data shown in Figures 24 and 25.

IV. EVALUATION OF EXPERIMENTAL DATA

The preceding section gave brief analyses of each group of data, at the time those data were presented. The purpose of this section is to relate all the previously reported observations with the general question of the feasibility of producing reliable low-temperature ignitions in full-size rocket engines.

A. General Summary and Conclusions

One of the main goals of this program was to investigate novel, unconventional methods of producing low-temperature H_2/O_2 ignitions. Since the fluidized metal powder concept was of prime interest (rather than a fixed catalyst bed), a matter of some concern was the development of catalytic and/or pyrophoric metal powders of much lower cost than the noble metals such as platinum and palladium.

Theoretical considerations early in the program led to interest in materials of the Raney nickel type. It was decided to investigate the low-temperature ignition characteristics of Raney nickel, and to simultaneously determine if this material could be put into a form possessing indefinite shelf life in the activated state.

Results of both of these tasks were highly encouraging. Using finely divided Raney nickel powders entrained in the hydrogen gas stream, a large number of cryogenic ignitions with liquid oxygen were obtained. Ignition times of the order of 10 milliseconds were observed in the most favorable conditions. This represents the time from admission of hydrogen gas into the ignition zone to the detonation pulse accompanying a clearly defined ignition. The most rapid of the ignitions observed in this program were of the same order as certain limiting conditions, primarily the hydrogen gas lead time. The above figure of 10 milliseconds does not, therefore, appear to represent a limit. It represents, rather, the smallest time increment in which the ignition process could be sub-divided by the instrumentation in use in this program, which was primarily of a screening nature.

The lowest hydrogen gas temperature (measured at the injector) at which an ignition was recorded was 57°K (130°R). Again, this does not appear to represent a fundamental limit, but rather reflects limitations imposed by the specific apparatus and experimental conditions involved. In particular it should be noted that the coaxial injection technique utilized, together with the small flow rates involved, tends to place limitations on how low the hydrogen gas temperature may be in the immediate vicinity of the injector. Chief of these is the fact that the liquid oxygen, flowing in the central tube, may approach its freezing point (approximately 55°K) should the temperature of the surrounding hydrogen, flowing through the annulus, be substantially colder.

It is believed that ignitions could be obtained with lower hydrogen temperature, provided that different injection techniques, or larger flow rates, were employed.

It is further believed that the observed variation in ignition times is primarily a function of the degree of mixing attained in the ignition zone. It appears that development work is necessary on the details of ignition zone geometry, particularly with regard to vacuum ignitions.

The second major task has produced conclusive theoretical and experimental observation to demonstrate that Raney nickel powder may be stored indefinitely in the form of a dry powder under an atmosphere of hydrogen. A variety of means might be employed to introduce this catalytic (and also pyrophoric) agent into the ignition zone. The technique utilized in this program involved entrainment into the hydrogen stream (from a catalyst fluidizer) just upstream of the injector. The price of Raney nickel powder is sufficiently low to justify this approach.

B. Itemized Discussion of Results

This sub-section presents a brief itemized discussion of the results of this program as they apply to the specific items listed in the Scope of Work.

1. Analytically investigate the feasibility of using metal powders as catalysts for hypergolic ignition of hydrogen-liquid oxygen mixtures.

This was performed during the literature survey at the beginning of the program. This analytical investigation resulted in interest in Raney nickel, which possesses both catalytic and pyrophoric properties.

2. Select the metal powders which appear most promising theoretically, then experimentally determine the ignition characteristics of hydrogen-liquid oxygen combustion ignited through the use of each type of powder, the parameters to be varied according to the following:

a. Hydrogen temperature, 40°R to 140°R.

b. Combustion chamber pressure, 0.5 psia to 15 psia.

c. O/F ratios, 4.0 to 6.0 and 0.5 to 1.5.

d. Powder concentration be varied as required to achieve satisfactory ignition.

This was performed, primarily for Raney nickel, which was the material of major interest in this program. Experimental work was also performed on certain types of platinum and palladium catalytic powders.

Other types of metal powders were also considered, including Raney cobalt and finely divided pyrophoric aluminum. There was not sufficient time to evaluate all of these materials, however, since special preparative techniques would generally be required. It was decided that, although other materials are also of interest, Raney nickel appeared to represent the best compromise.

Hydrogen temperatures were investigated in the designated range. For reasons specified previously, equipment and experimental conditions placed a practical lower limit on the hydrogen temperature (at the injector) of about 50°K (90°R). An ignition was obtained at a hydrogen inlet temperature of 57°K.

The majority of testing was done at atmospheric pressure. Ignitions were obtained under partial vacuum conditions (down to about 2 psia), but these were more difficult to interpret than those at ambient pressure. It is believed that the ignition zone geometry is a critical variable here.

Ignitions were obtained at nominal mixture ratios covering the above range. The evidence of this report is that more reliable, rapid ignitions are obtained with Raney nickel at the higher mixture ratios, particularly at O/F = 6.0.

The concentration of Raney nickel powder in the hydrogen stream did not seem to be an important variable. It was visually observed during cryogenic tests that the individual particles of Raney nickel would become incandescent upon contact with liquid oxygen (due to their pyrophoricity). Strictly speaking, even one such incandescent particle should be sufficient to produce ignition. The efficiency of the mixing process in the immediate vicinity of the injector appears to be the critical parameter in this regard.

3. Investigate the effect of variables which might be a problem in actual rocket engine systems using powdered metal ignition. A list of these variables includes, but is not restricted to:

a. Partial oxidation of the powder.

b. Powder particle agglomeration.

c. Powder particle size.

Since Raney nickel powders are pyrophoric, it is evident that contact with a given mass of air will result in the oxidation of a stoichiometric amount of the nickel powders. The oxidized nickel powder has no catalytic activity for the proposed application. In practical terms, consider the recommended installation in which the Raney nickel is stored as a dry powder under an atmosphere of ambient hydrogen gas. Consider now the consequences of three different types of failure conditions (which may reasonably be expected to cover the range of possible occurrences).

(1) Complete and sudden exposure of the contents of the fluidizer vessel to the atmosphere (due to a hypothetical mistake, or to total mechanical failure of the vessel).

(This condition was simulated at various times during this contract when sealed samples of Raney nickel were exposed to air to test for pyrophoricity.)

The entire mass of Raney nickel powder would be oxidized in a very rapid reaction. This reaction would be initiated in, at most, a very few milliseconds after exposure to air. During the reaction, there is a ball of flame surrounding the powders, which persists on the order of one to a few seconds. This phenomenon is doubtless due primarily to the oxidation of the large amount of chemisorbed hydrogen present on the surface of the metal particles.

Although the reaction is very rapid, accompanied by a large heat release, it does not constitute an explosion. There are two reasons for this. The main reaction product is a solid (nickel oxide). Also, the nickel powders are so reactive in the presence of air that the particles would be oxidized before sufficient time could elapse for them to disperse throughout an area as a dust suspension. The latter is the condition normally associated with explosions involving finely divided powders.

The hydrogen atmosphere, under which the powder had been stored, would of course ignite at once; it should be noted, however, that the actual mass of hydrogen gas required for this function would be relatively quite small. That is, essentially all the inner bulk volume of the fluidizer would be occupied by the nickel powders. The free hydrogen gas would occupy only the inter-particle void volume. This hydrogen gas could therefore be expected to be consumed in essentially a single sheet of flame. The latter would occur simultaneously with the combustion reaction of the nickel particles.

Summarizing this worst possible case, one may state that the results would be essentially as follows.

(a) complete and rapid combustion of the fluidizer contents, associated with one to a few seconds of visible flame, and large heat release

(b) no explosion

(2) Moderate leak of air into the fluidizer interior (due to hypothetical improper assembly, for example) but overall mechanical integrity of fluidizer not impaired.

This condition would result in a rapid temperature rise of the contents of the fluidizer, perhaps to 300-400°C, depending on the severity of the leak. The temperature should not rise high enough to damage metal components, but would be sufficient to damage or destroy rubber or plastic materials in the immediate vicinity (i.e., 'O' rings, gaskets, etc.). There would be very little likelihood of open flame or an explosion, since the oxygen of the air would be quantitatively consumed as it passed over the closely packed nickel powders. An air leak of this magnitude could be expected to render the fluidizer contents catalytically inactive within a few minutes to an hour. The onset of such an occurrence could readily be detected by standard means (i.e., a thermocouple activated relay).

(3) Very small air leak into fluidizer contents.

Such a process, if permitted to continue unchecked, could lead to oxidation and deactivation of the nickel powders over a period of hours or days. There would be no significant external effects. It appears likely, however, that a sensitive thermocouple, located within the fluidizer, could detect quite small air leaks, due to the heat release associated with the pyrophoric reaction of Raney nickel.

It should be pointed out that a small positive pressure of hydrogen gas within the fluidizer could be expected to effectively eliminate this source of contamination.

Regardless of how it could conceivably occur, however, partial oxidation of the nickel powders would be detrimental. Ignitions could still be obtained, but more of the fluidizer contents would have to be entrained into the combustion zone in order to obtain an equivalent amount of active powder. This would require longer, and less uniform, ignition time delays. The magnitude of this effect would of course be a function of the extent of powder oxidation.

Based upon the observations of this program, it appears that, qualitatively, partial oxidation amounting to at least a few percent of the total could perhaps be tolerated. This statement is based on the fact that ignitions were obtained in cases in which it was certain that a fraction of the Raney nickel powders had been oxidized.

There was no agglomeration tendency of the dry Raney nickel powders observed at any time during this program. Should the powders come into contact with water, they would form a sludge. In the absence of moisture or grease contaminants, however, the evidence of this work is that particle agglomeration should not be a problem area with the use of Raney nickel powders as prepared in this program.

Quantitative data are not available at this time concerning the absolute magnitude of the Raney nickel particle size. Practically speaking, however, the particle size is controlled directly by the method of formation of the Raney nickel, and by the particle size of the original nickel-aluminum alloy used. The chemical procedures involved in the formation of Raney nickel are straightforward. The experience of this program is that minor variations in the specific procedure used had no observable effect on the particle size of the final dried Raney nickel powder. The nickel-aluminum alloy used as starting material is a widely available commercial product which appears to be quite uniform in character. There was no observable difference between any of the several batches of Raney nickel prepared during this contract. Every batch of Raney nickel powder tested in the fluidizer was successfully entrained in the hydrogen stream. It should be noted that the fluidizer used in this work was by no means an optimum design.

4. Consider the relative merits of:

   a. Mixing powder with liquid hydrogen in the propellant tank, and

   b. Injecting powder into the combustion chamber or hydrogen feed line, and also consider the effects of metal powders on turbine bearings, valves, etc.

As mentioned previously, the only method of entrainment used experimentally in this program was that of fluidization of the nickel powders in the gaseous hydrogen upstream of the injector.

The possibility of storing the Raney nickel as a powder mixed with the liquid hydrogen in the main propellant tank was considered analytically. The feasibility of this approach did not appear high, however, primarily due to the very large density difference (a factor of 127) between the nickel powders and liquid hydrogen. Only if very fine particle sizes were utilized (of the order of 10-100 Å in diameter) would the phenomena associated with Brownian motion be expected to allow the particles to remain in suspension. The preparation and stabilization of particulate matter of such dimensions does not appear to be feasible at present. Experimental study of this subject would represent a substantial program in itself. If liquid hydrogen can be gelled, this might be a means of suspending the Raney nickel powders. However, the amount of gellant required might compromise the performance potential of the hydrogen.

Observations were made in all tests concerning any problems which might arise due to the action of the metal powders on valves and other fittings. The indications of this program were that this is potentially a problem area, but one which can be surmounted by proper design. For example, standard check valves were exposed to the flow of hydrogen gas plus entrained nickel powders. Some plugging and valve sticking occurred, but this was largely eliminated by such simple expedients as enlarging port areas and increasing annular clearances. More work on this subject is needed, but it appears that the very small particle size and non-agglomerating character of the Raney nickel powder render this system amenable to use with a wide range of hardware components.

C. Recommendations

It is believed that this program has demonstrated the feasibility of obtaining reliable low-temperature ignition of hydrogen and oxygen by the use of Raney nickel powder entrained in the hydrogen stream. Based on this work, the following system is proposed. Dry Raney nickel powder is contained in a small fluidizer vessel located near the rocket engine. The fluidizer, filled with the nickel powders, is maintained under a slight positive pressure of ambient temperature hydrogen gas. Upon engine start, gaseous hydrogen is caused to flow through the fluidizer, entraining nickel powders in the process. This hydrogen stream may be obtained as a bleed from the main hydrogen flow, or it may be desired to tap off directly from the main hydrogen tank.

The hydrogen stream leaving the fluidizer flows into the injector, where it mixes with a suitable flow rate of either liquid or gaseous oxygen, producing an ignition.

This basic concept has been demonstrated by the ignitions obtained in this program. A system such as this would possess multiple restart capabilities under space conditions, and would not be significantly affected by wide variations in the range of propellant inlet conditions.

The main areas in which further work would be required are:

a. optimum fluidizer design

b. attainment of thorough mixing, in the immediate vicinity of the injector, between the entrained powder hydrogen stream, and the corresponding oxygen stream.

It appears that the limitations which were encountered during this program were due primarily to limitations of the laboratory scale hardware involved, and that even more encouraging results would be obtained from larger-scale tests. It is also recommended that experimental study be continued on the subject of the optimum method of introducing the Raney nickel powder into the ignition zone.

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PRELIMINARY H_2 - O_2 IGNITION ASSEMBLY

MARK I

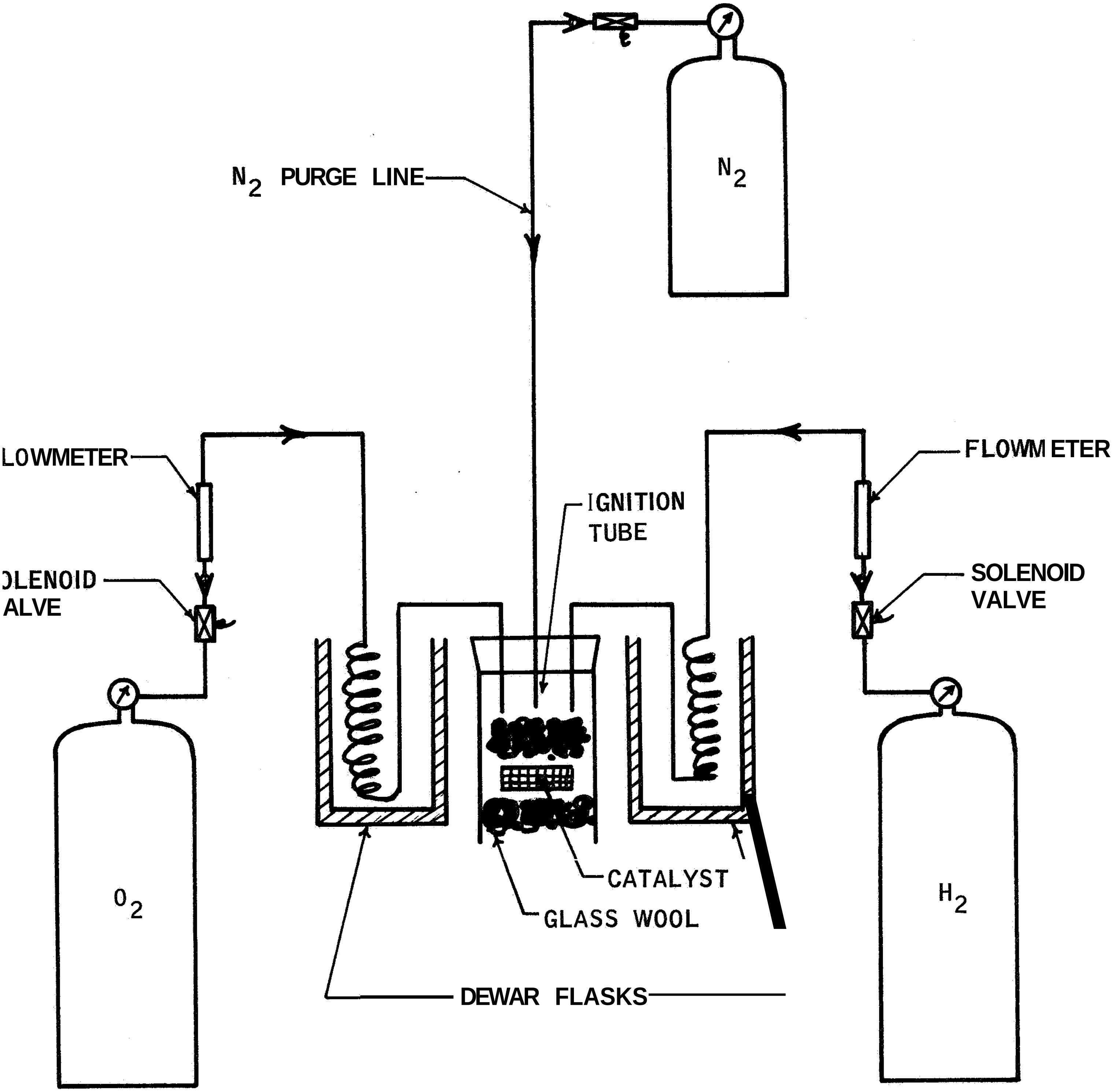
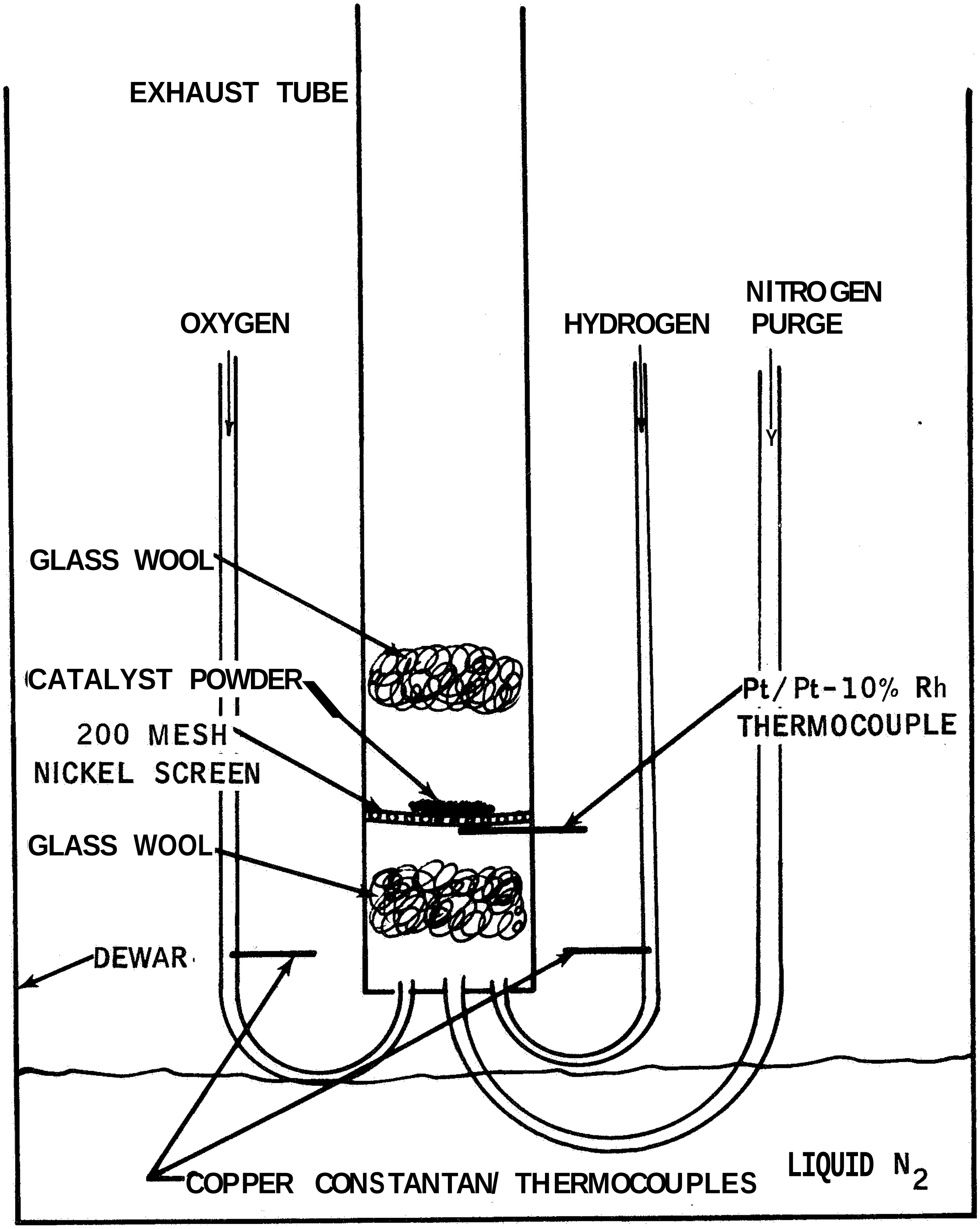


Figure 1

IGNITION DEVICE
MARK II



R-19,174

Figure 2

IGNITION DEVICE
MARK III

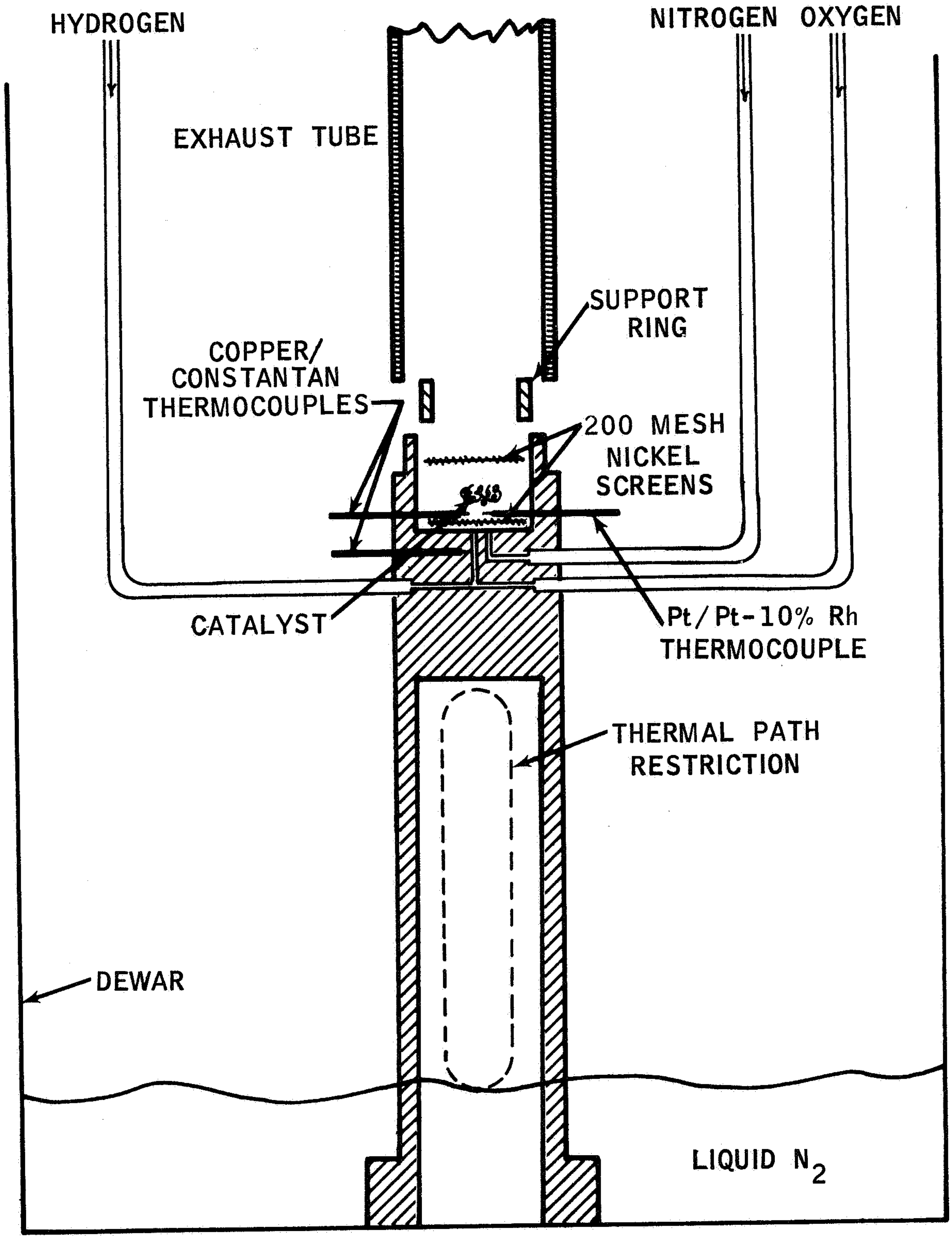
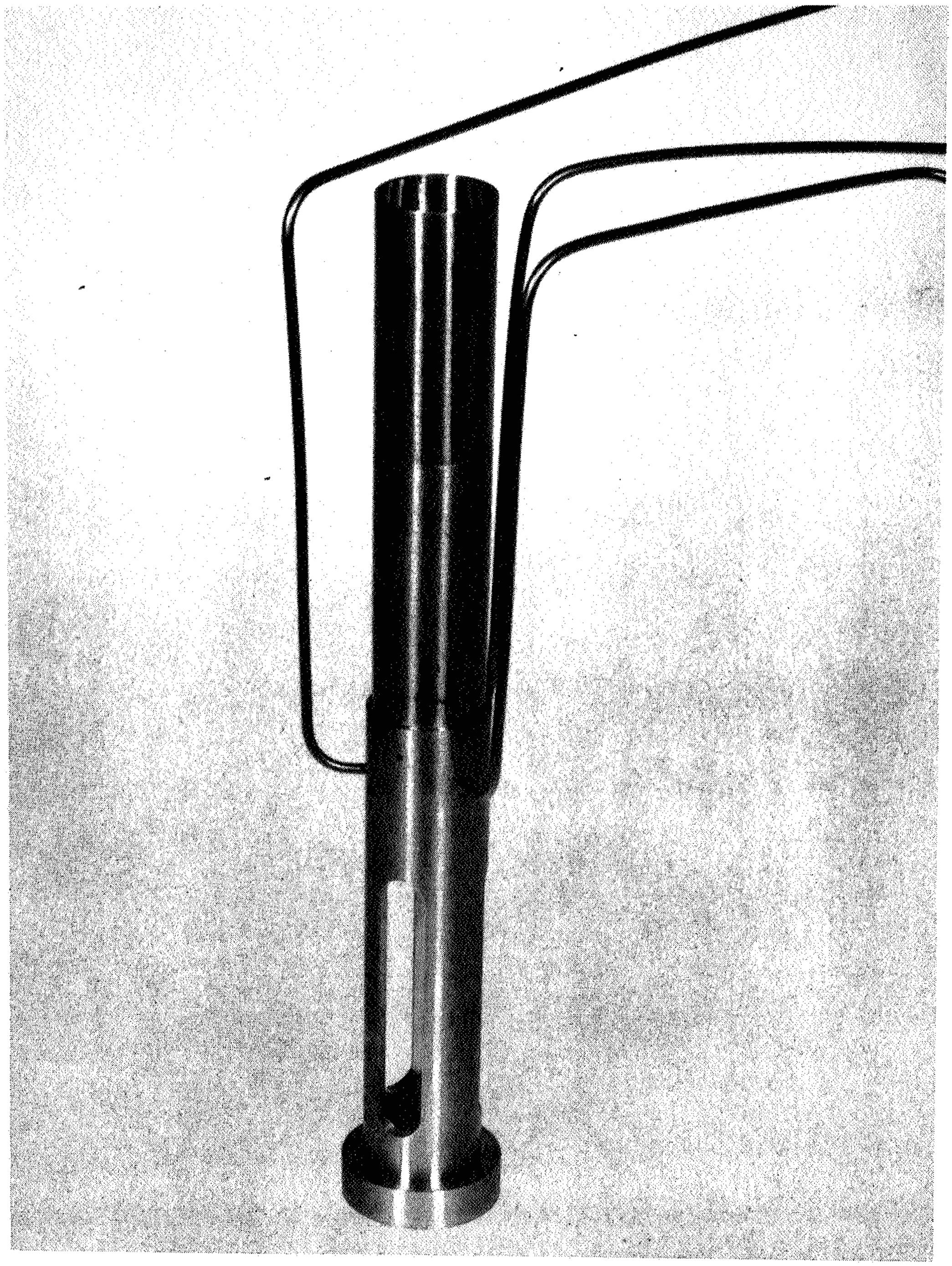


Figure 3

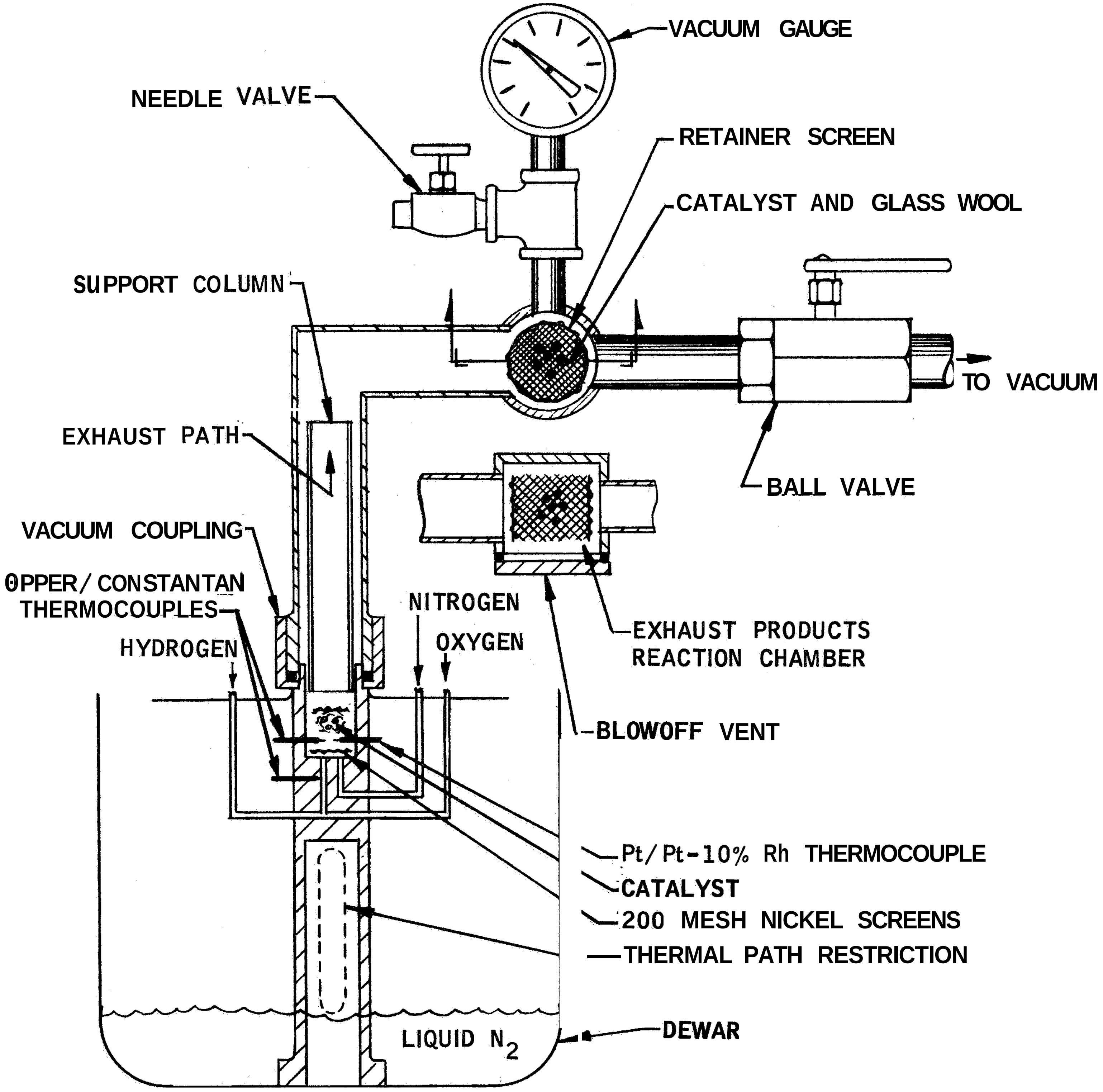
IGNITION DEVICE
MARK III



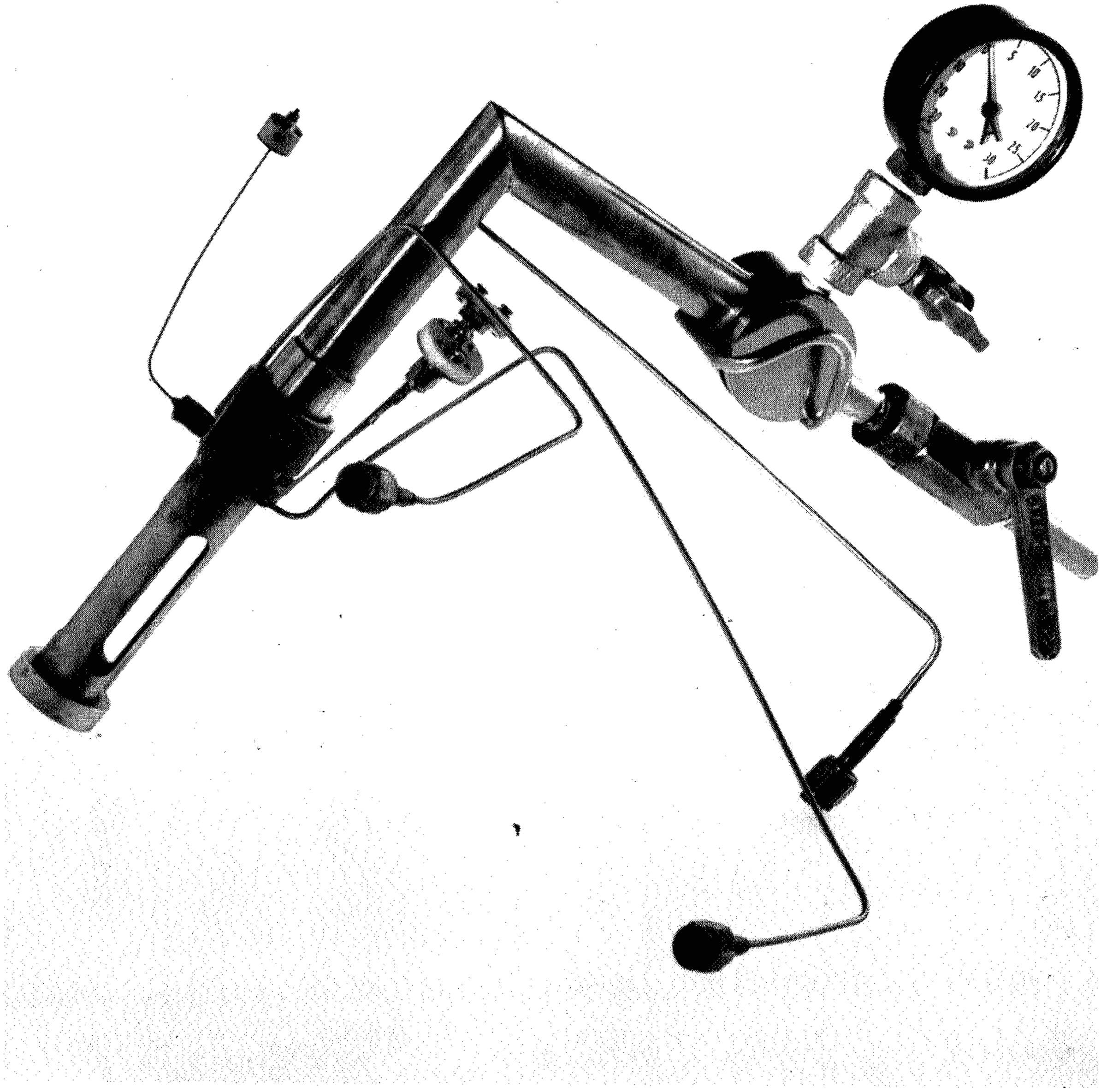
R-19,170
Neg. 6494-2

Figure 4

IGNITION DEVICE
MARK IV (SCHEMATIC)



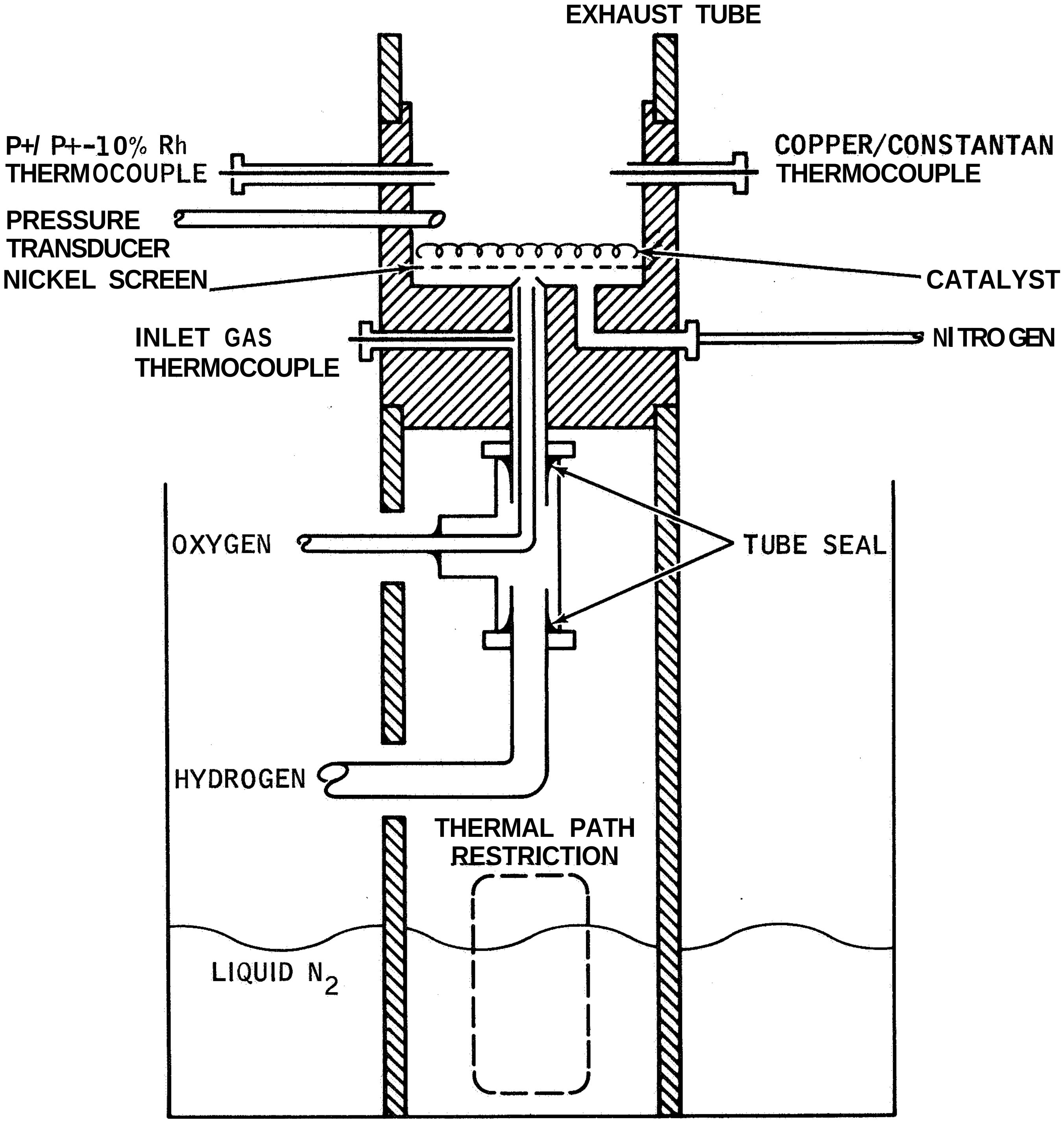
IGNITION DEVICE
MARK IV (ASSEMBLED)



R-19, 244
Neg. 6542-2

Figure 6

COAXIAL IGNITION DEVICE
MARK V

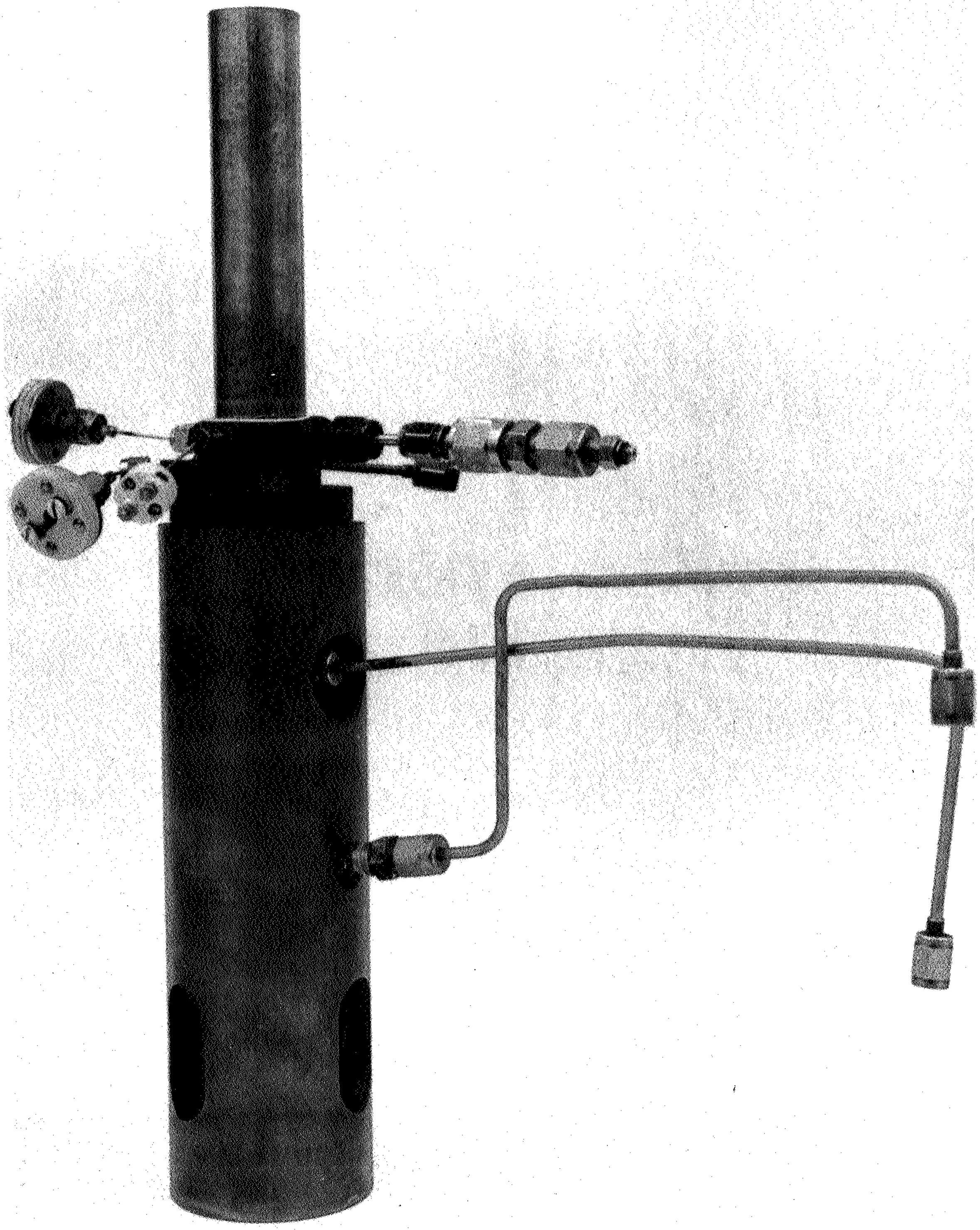


R-19,817

Figure 7

COAXIAL IGNITION DEVICE

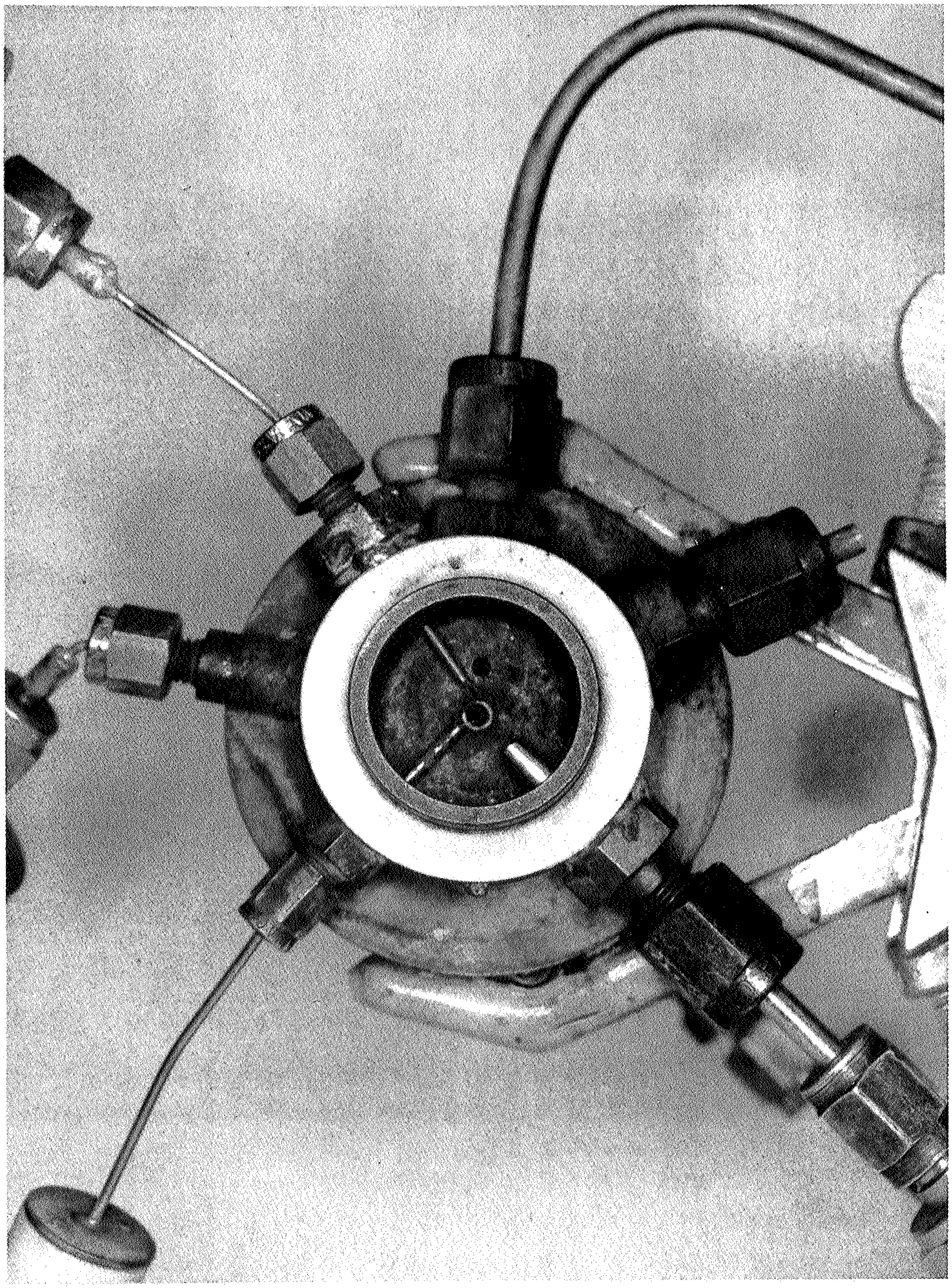
-MARK V



R-19,474
Neg. 6655-1

Figure 8

COAXIAL INJECTOR NOZZLE AND SENSORS
MARK V

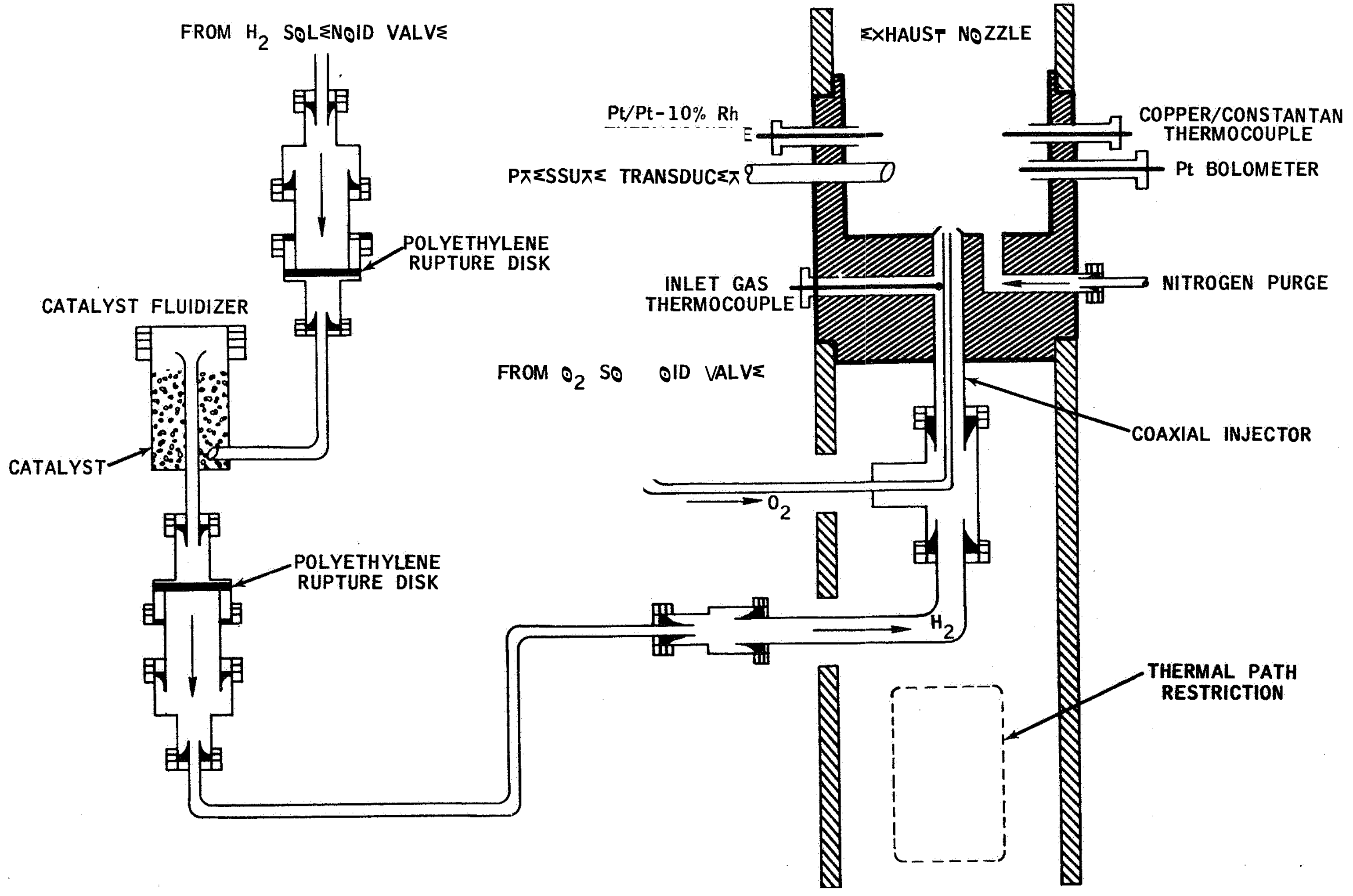


R- 19,476
Neg. 6655-3

Figure 9

H_2/O_2 CATALYTIC IGNITION DEVICE

MARK VI



R-19,945

Figure 10

COAXIAL IGNITION DEVICE

MARK VII

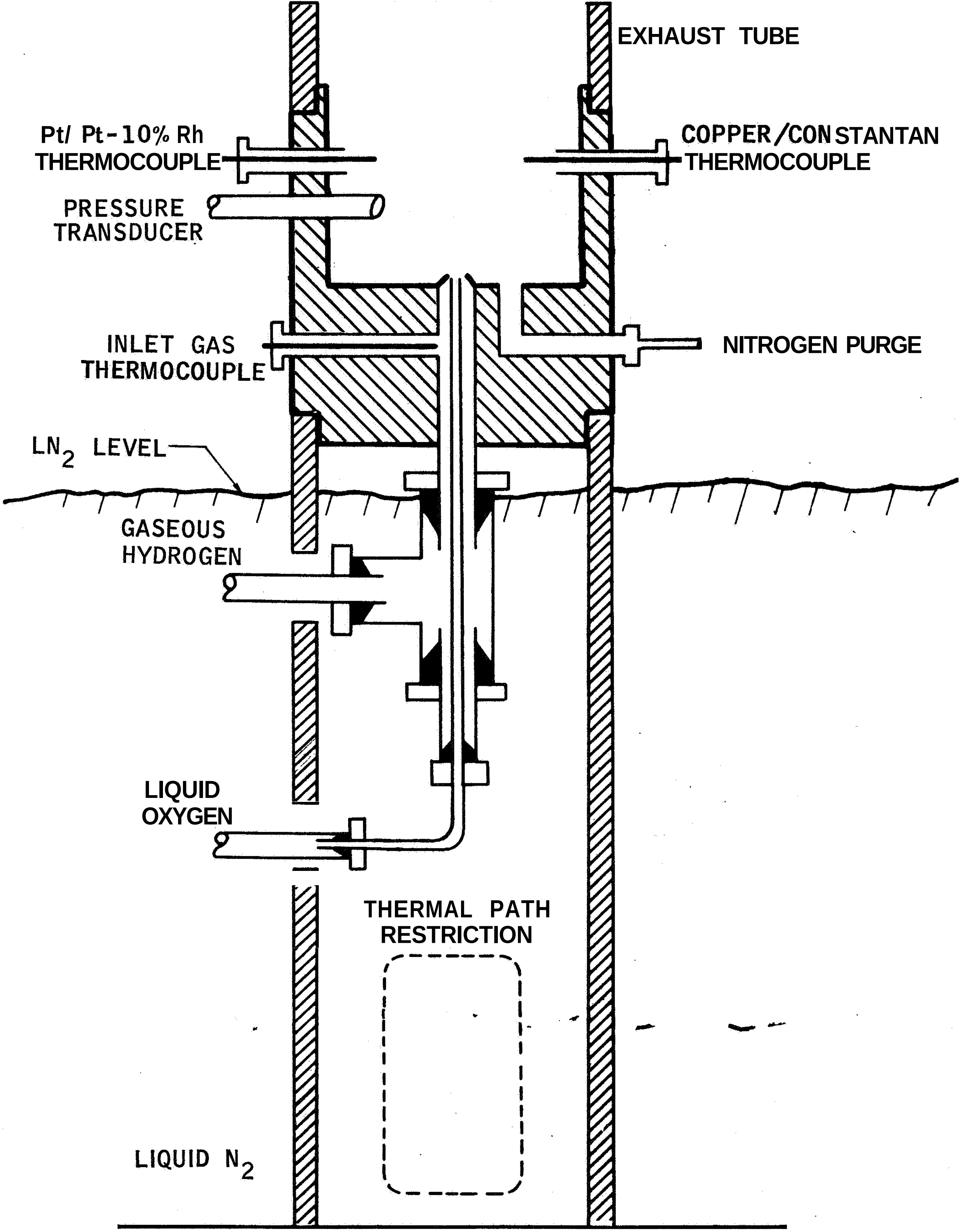


Figure 11

SCHEMATIC OF MARK VIII IGNITION ASSEMBLY

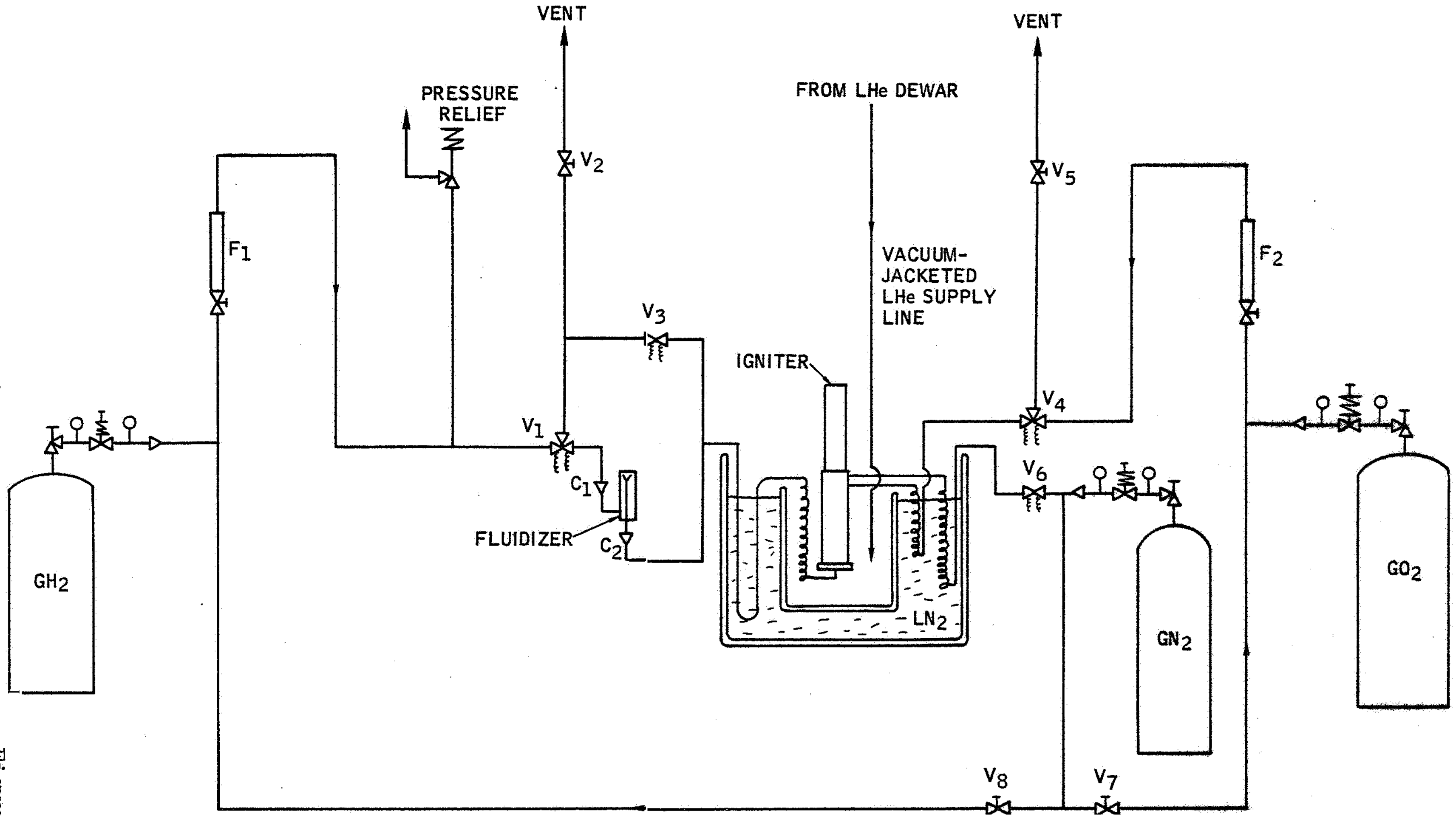


Figure 12

DETAIL OF MARK VIII IGNITER

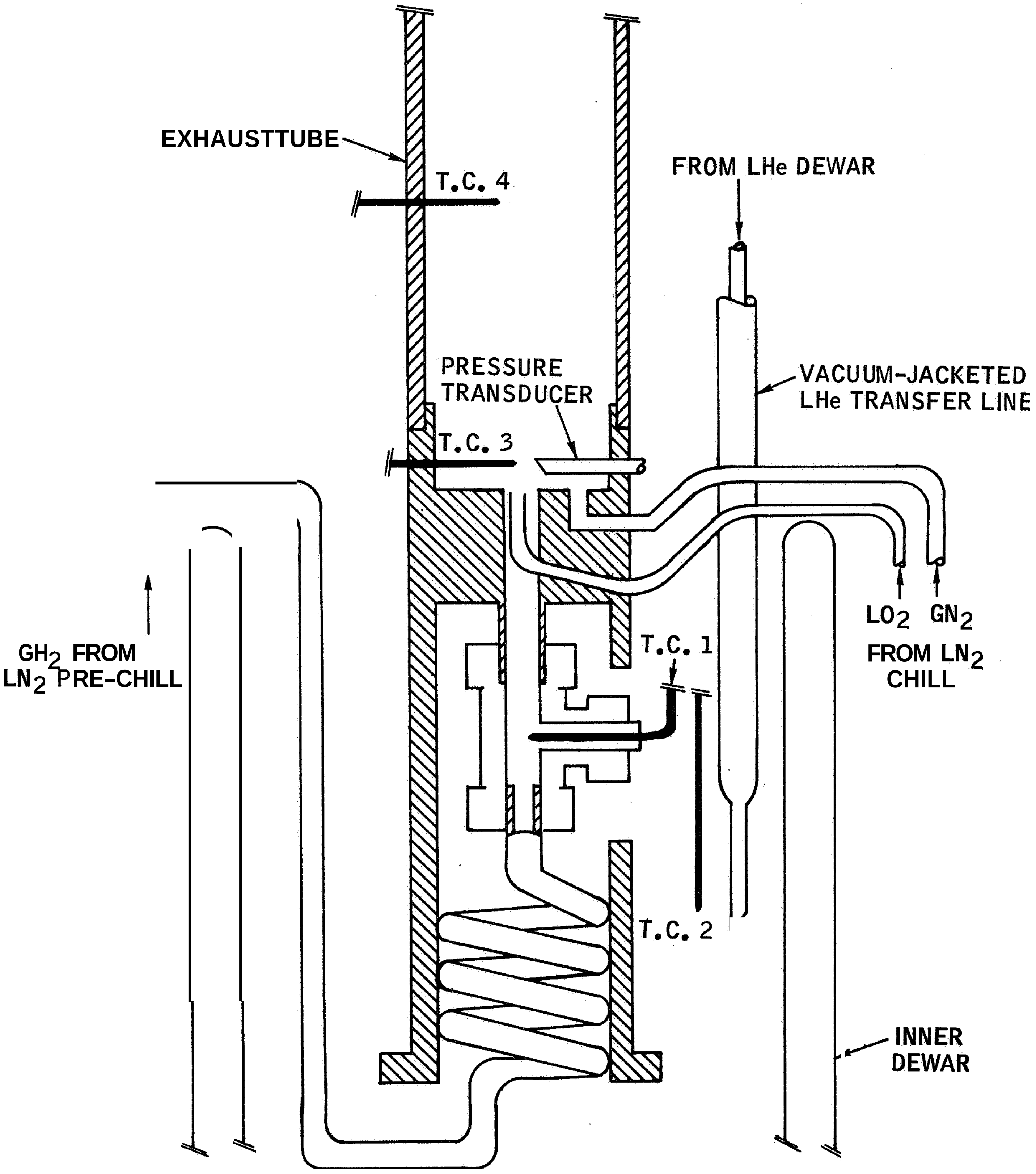
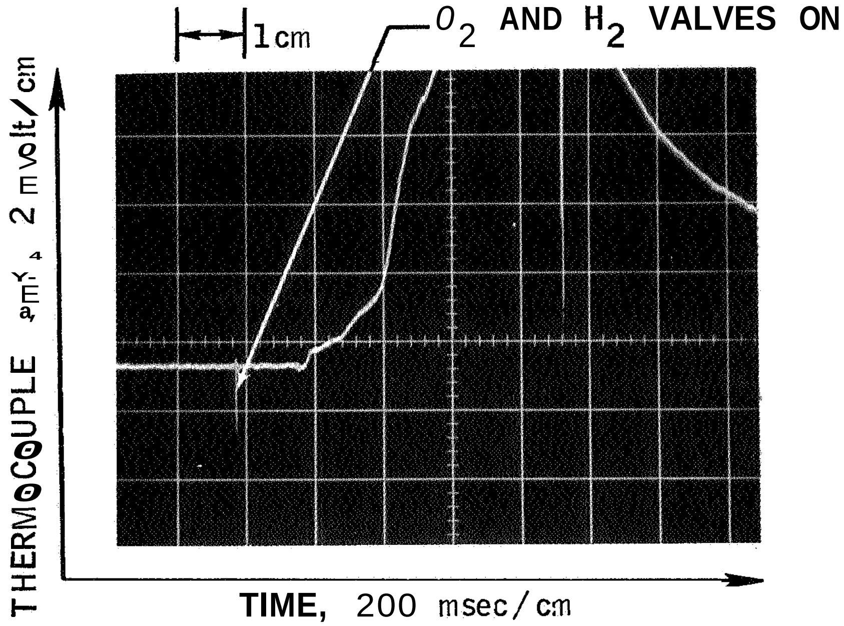


Figure 13

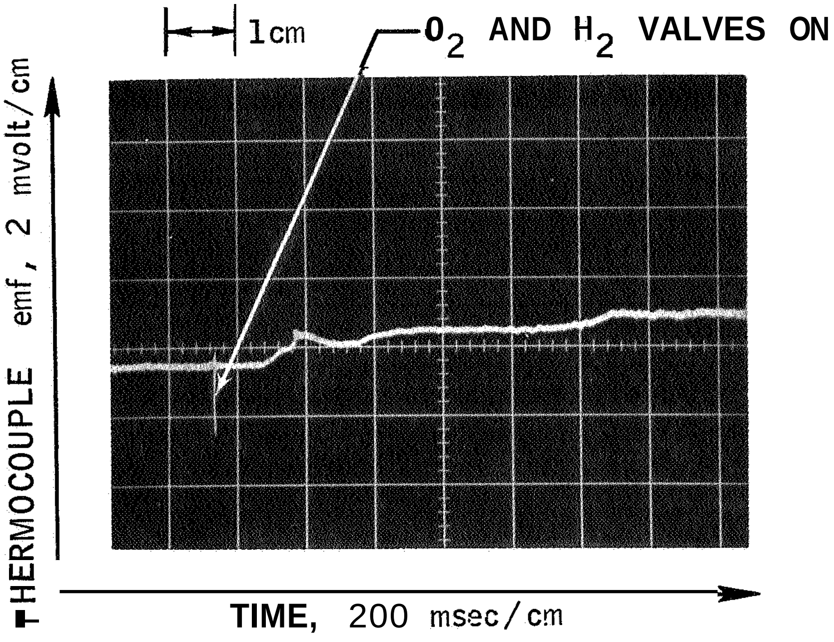
OSCILLOSCOPE IGNITION TRACES

PRELIMINARY TESTS WITH FIXED BED RANEY NICKEL CATALYST



RUN 110; 98°K (176°R), 1 atm

CORRECTED IGNITION TIME = 180 msec



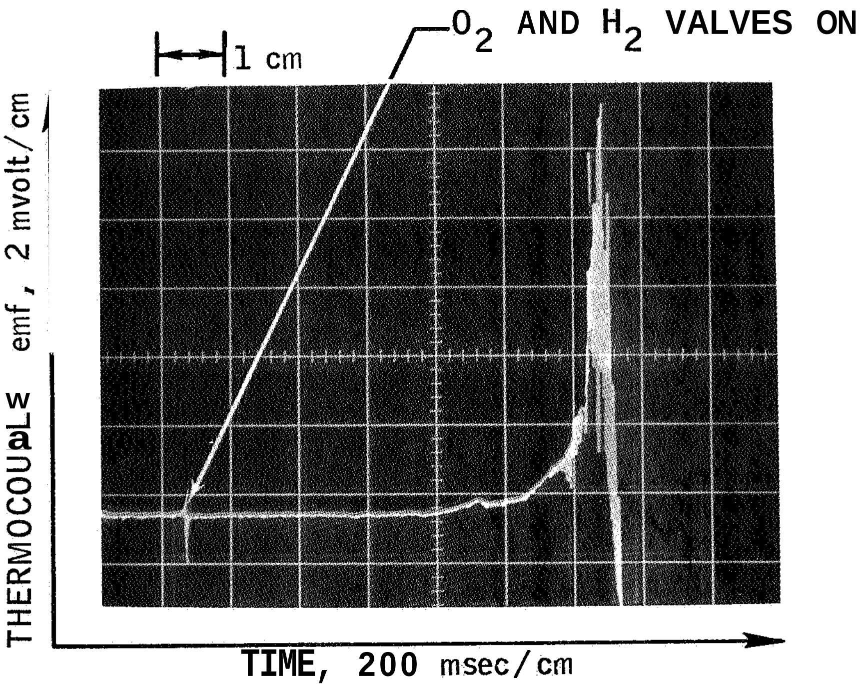
RUN 108; 95°K (171°R), **1** atm

CORRECTED IGNITION TIME = 130 msec

Figure 14

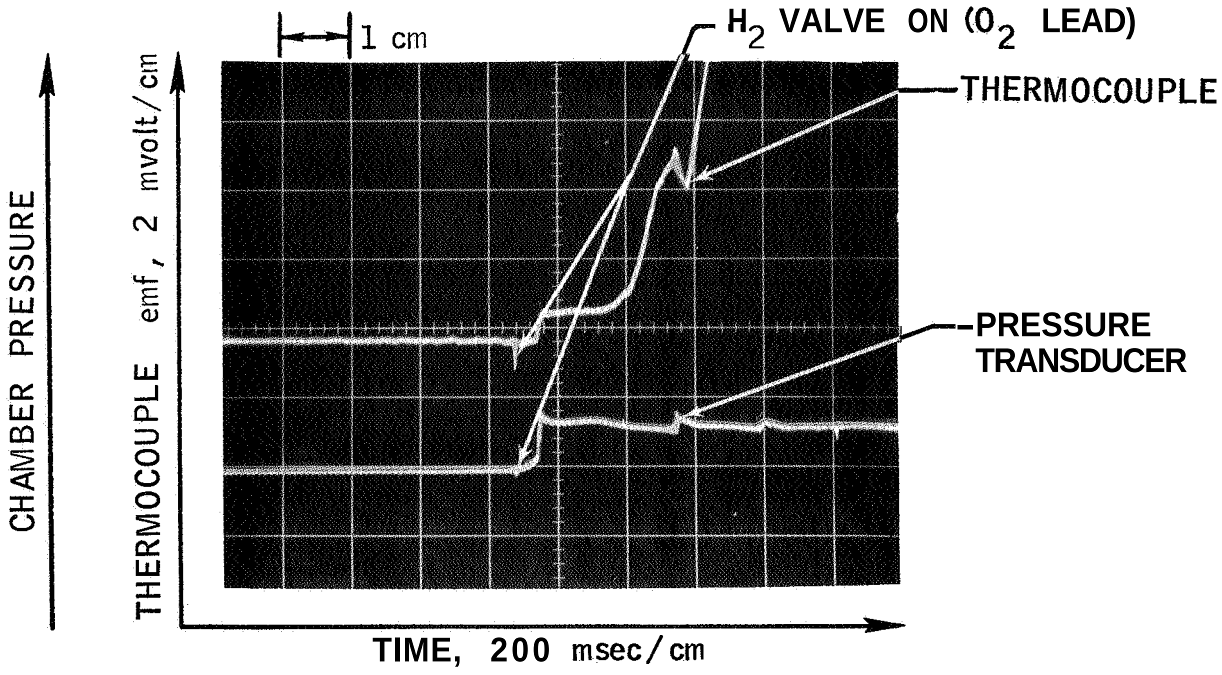
OSCILLOSCOPE IGNITION TRACES

PRELIMINARY TESTS WITH FIXED BED RANEY NICKEL CATALYST



RUN 114; 97°K (175°R); p = 2.2 psia

CORRECTED IGNITION TIME = 700 msec



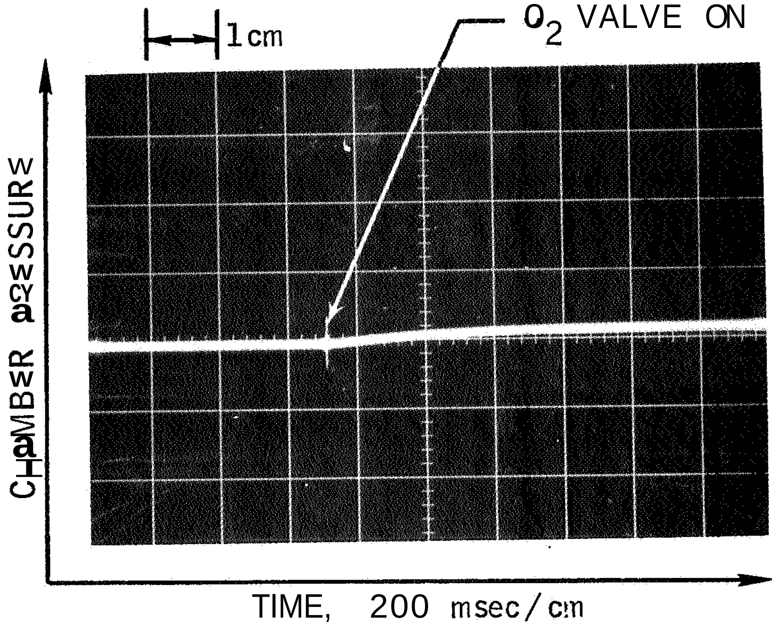
RUN 126: 91°K (164°R); 1 atm

CORRECTED IGNITION TIME = 45 msec

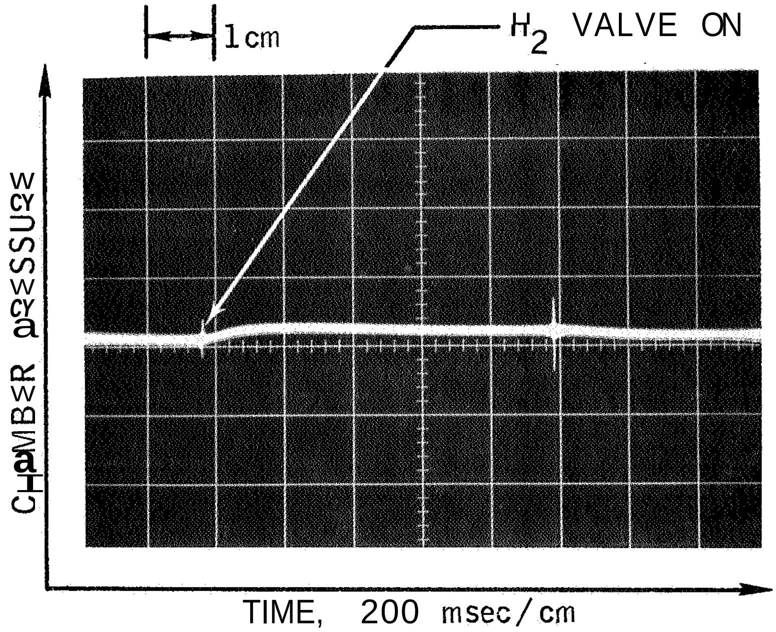
Figure 15

GAS FLOW CALIBRATION RUNS
MARK III

ATMOSPHERIC PRESSURE, AMBIENT TEMPERATURE



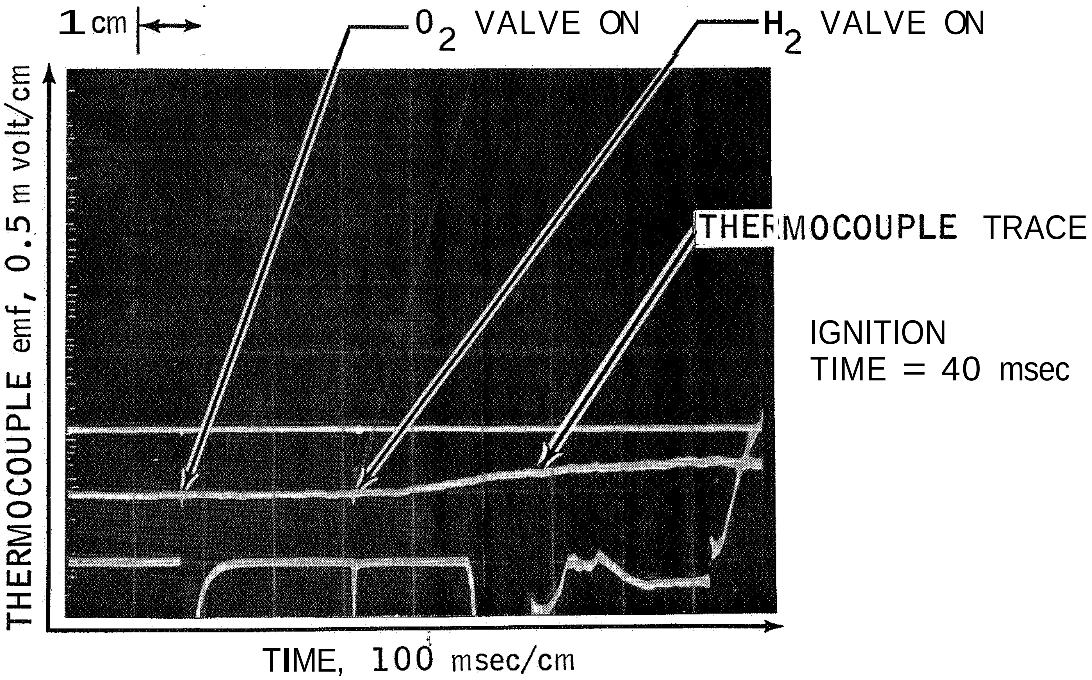
RUN 115; O_2 FLOW ONLY (STEADY STATE FLOW = 7.9×10^{-3} g/sec)



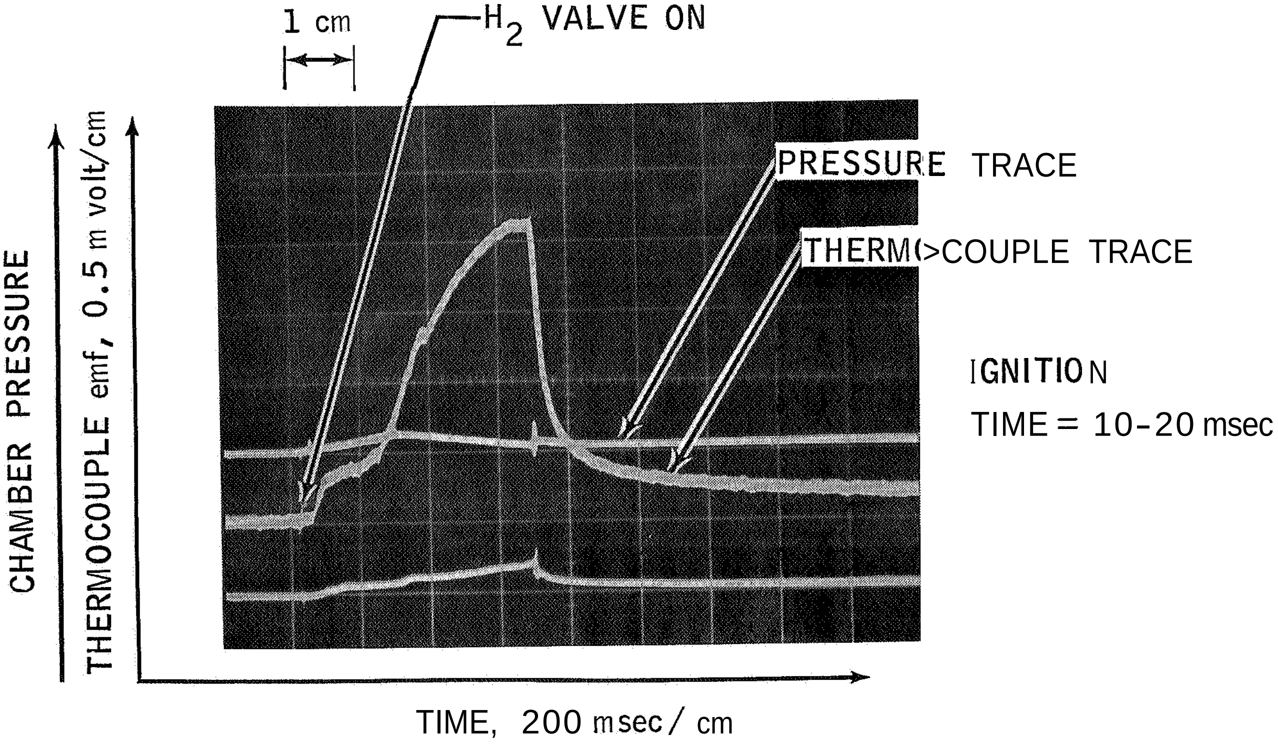
RUN 116; H_2 FLOW ONLY (STEADY STATE FLOW = 1.3×10^{-3} g/sec)

Figure 16

OSCILLOSCOPE IGNITION TRACES
FIXED BED CATALYSTS; COAXIAL INJECTION



RUN 164, 126°K, 1 atm
RANEY NICKEL (MODIFIED PREPARATION)

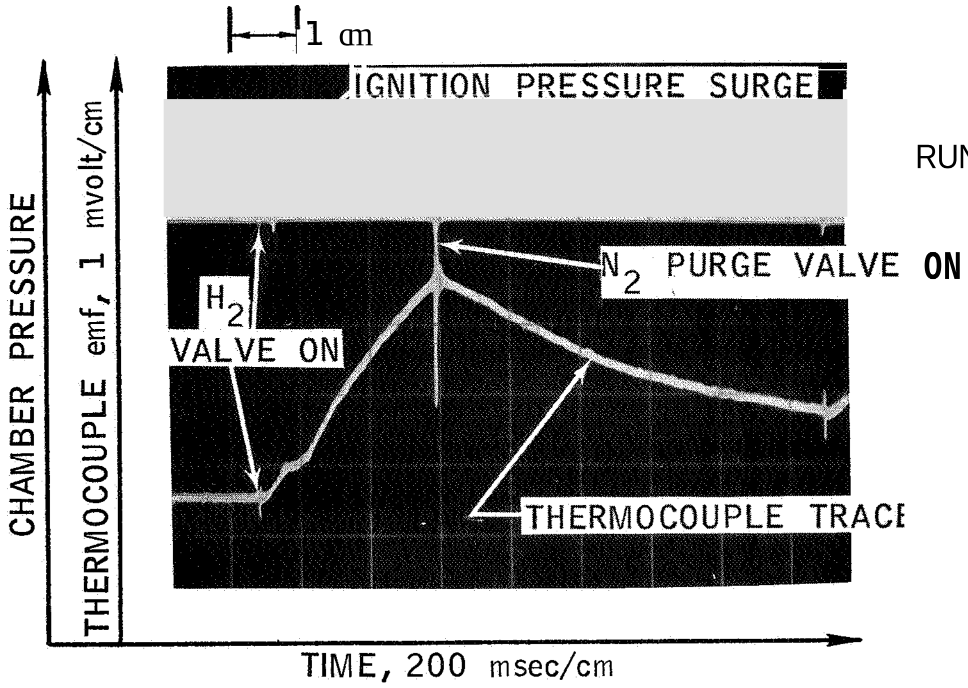


RUN 146, 134°K, 1 atm
5% PALLADIUM ON ACTIVATED ALUMINA (MODIFIED)

Figure 17

OSCILLOSCOPE IGNITION TRACES

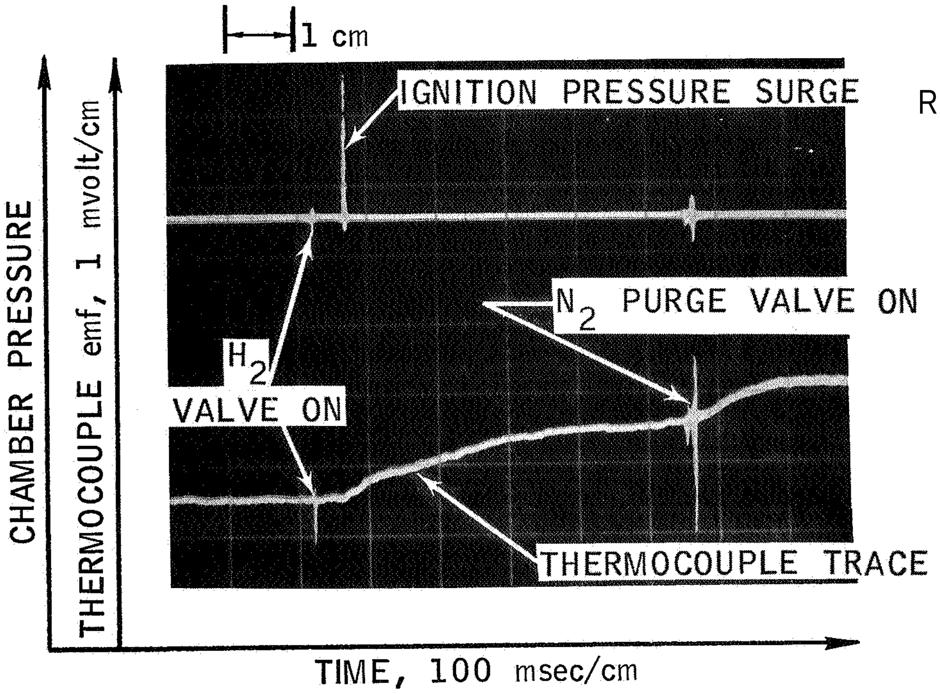
RANEY NICKEL POWDER ENTRAINED IN H_2 STREAM



RUN NO. 191, 90°K, 1 atm

O/F = 6.0; O_2 LEAD

CORRECTED IGNITION
TIME = 20 msec



RUN NO. 192, 90°K, 1 atm

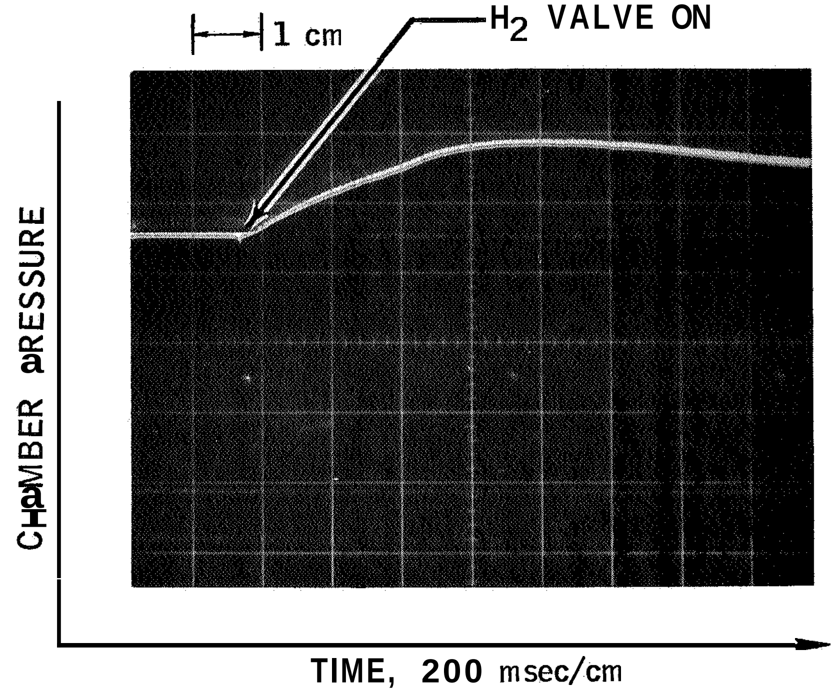
O/F = 6.0; O_2 LEAD

CORRECTED IGNITION
TIME = 30 msec

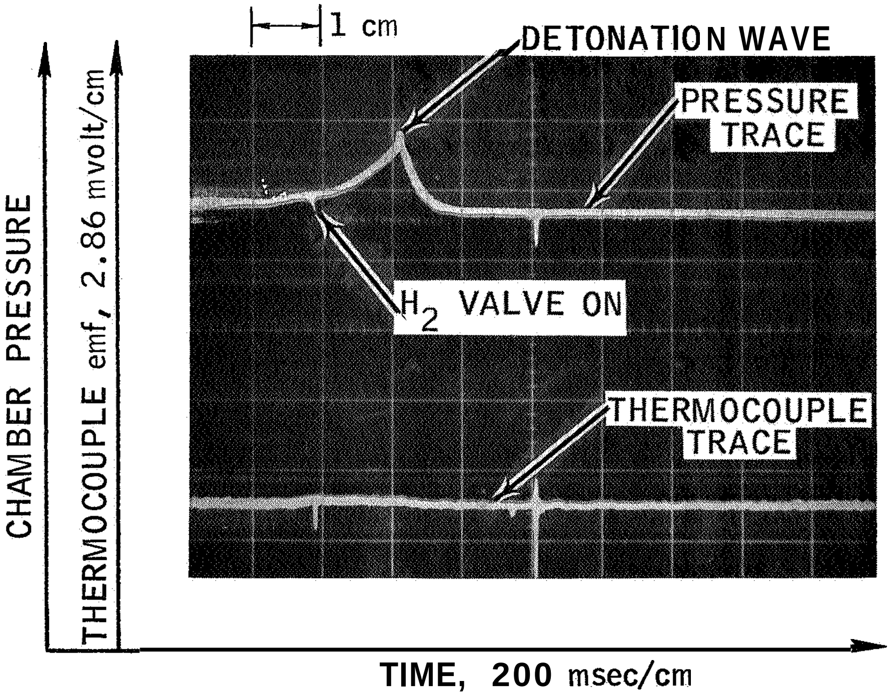
Figure 18

OSCILLOSCOPE IGNITION TRACES

RANEY NICKEL POWDER ENTRAINED IN H_2 STREAM



RUN NO. 213
CALIBRATION RUN,
H_2 GAS ONLY FLOWING,
AMBIENT



RUN NO. 219,
90°K, 1 atm

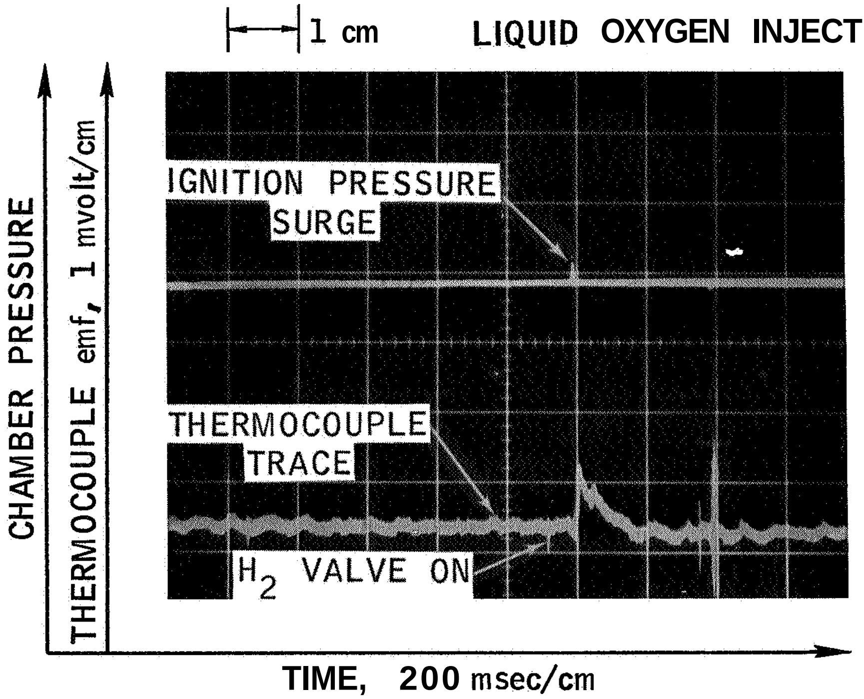
O/F = 1.5; O_2 LEAD

Figure 19

OSCILLOSCOPE IGNITION TRACES

RANEY NICKEL POWDER ENTRAINED IN H_2 STREAM

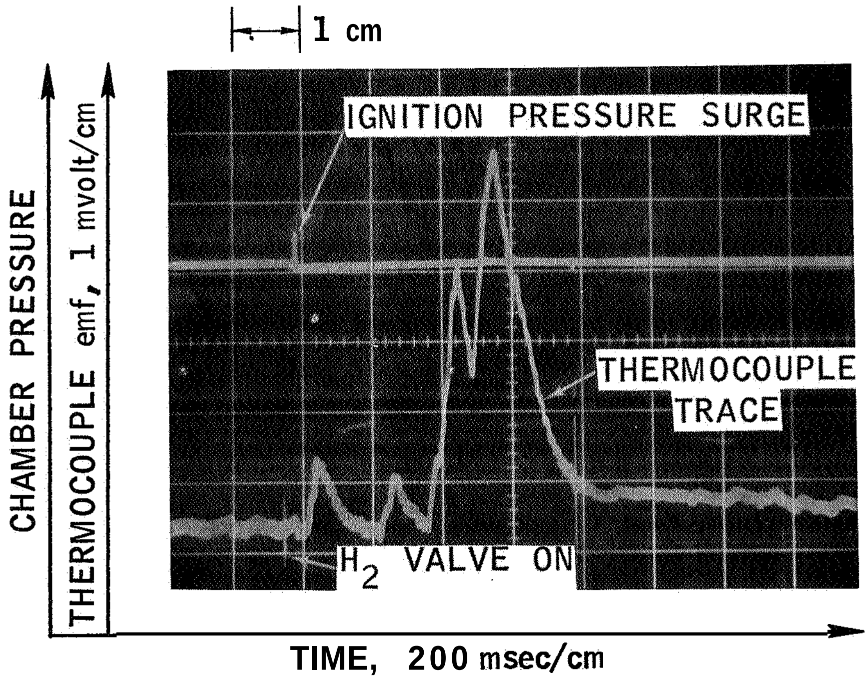
LIQUID OXYGEN INJECTION



RUN NO. 242, 77°K, 1 atm

$O/F = 6.0$, LO_2 LEAD

CORRECTED IGNITION TIME = 60 msec



RUN NO. 243, 77°K, 1 atm

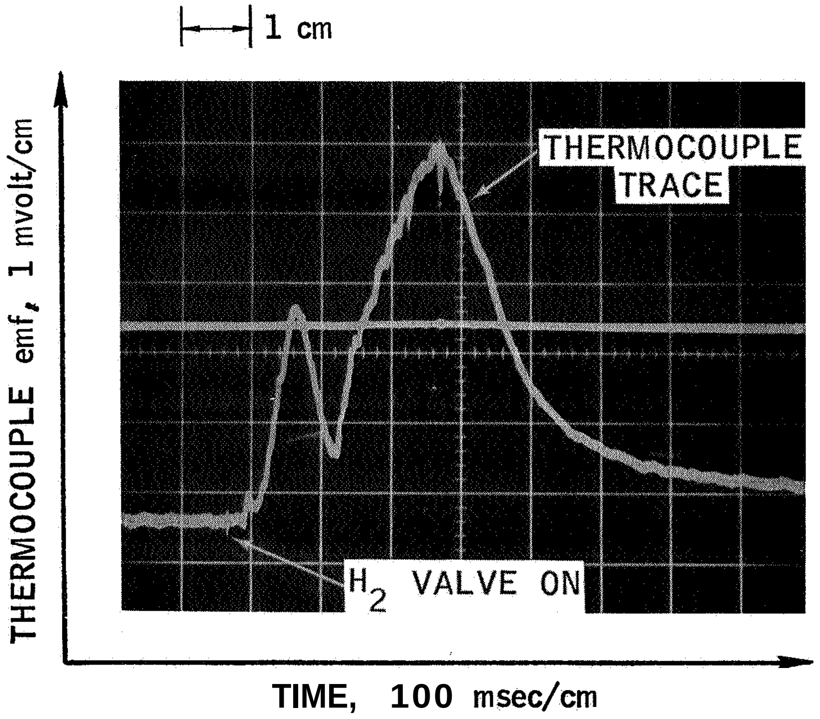
$O/F = 6.0$, LO_2 LEAD

CORRECTED IGNITION TIME = 15 msec

Figure 20

OSCILLOSCOPE IGNITION TRACES

RANEY NICKEL POWDER ENTRAINED IN H_2 STREAM
LIQUID OXYGEN INJECTION



RUN NO. 246, 77°K, 1 atm

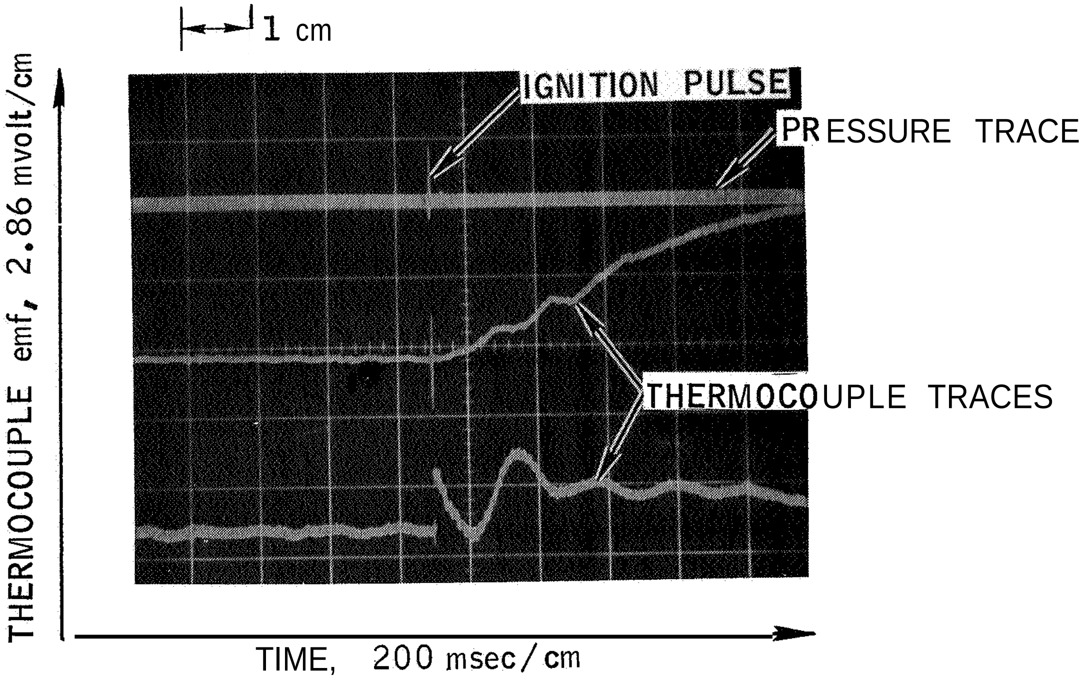
O/F = 6.0, O_2 LEAD

CORRECTED IGNITION TIME = 10 msec

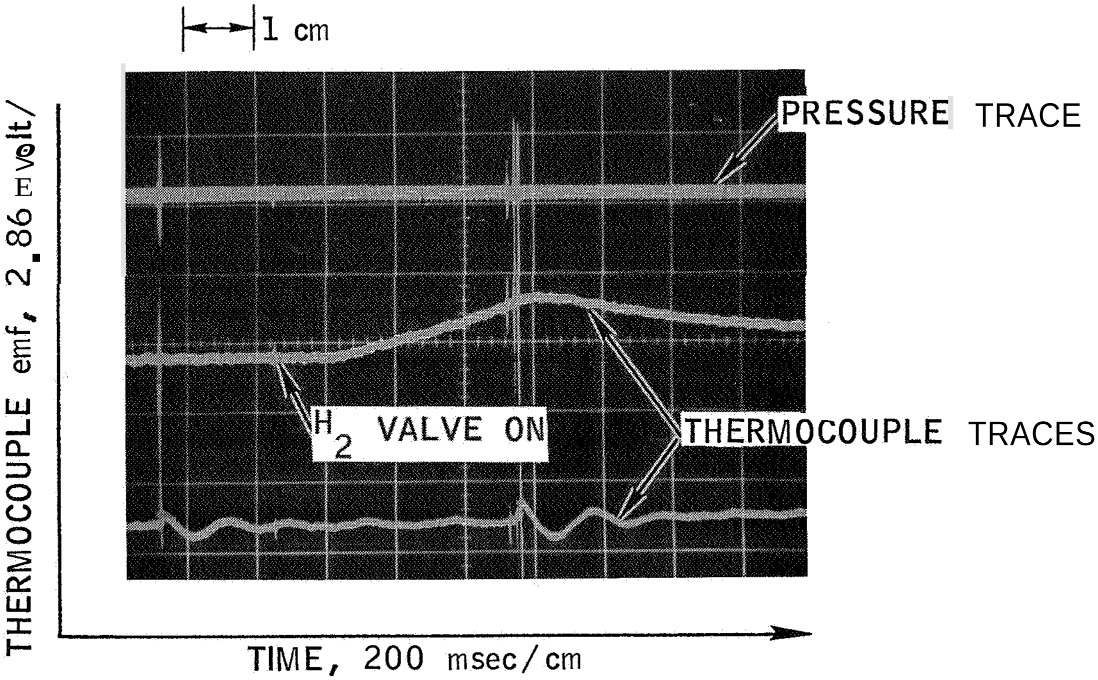
(CHAMBER PRESSURE TRACE NOT OPERATIVE)

OSCILLOSCOPE IGNITION TRACES
MARK VIII

RANEY NICKEL POWDER ENTRAINED IN H_2 STREAM



RUN 270; 57°K (103°R), 1 atm



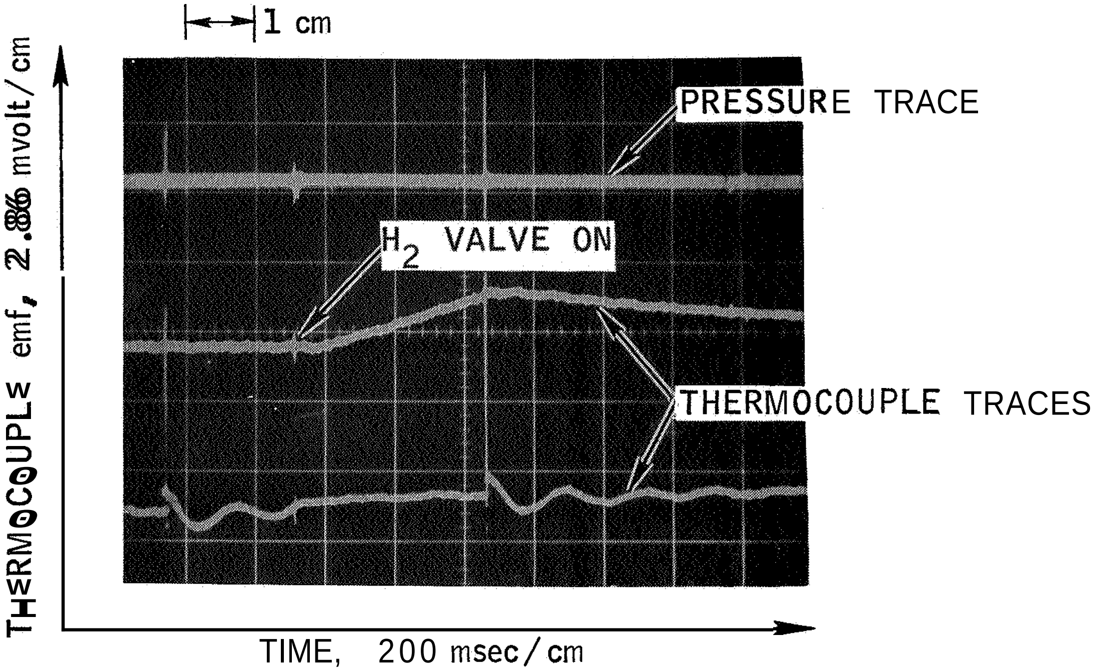
RUN 273; 64°K (115°R), 1 atm

CORRECTED IGNITION TIME = 130 msec

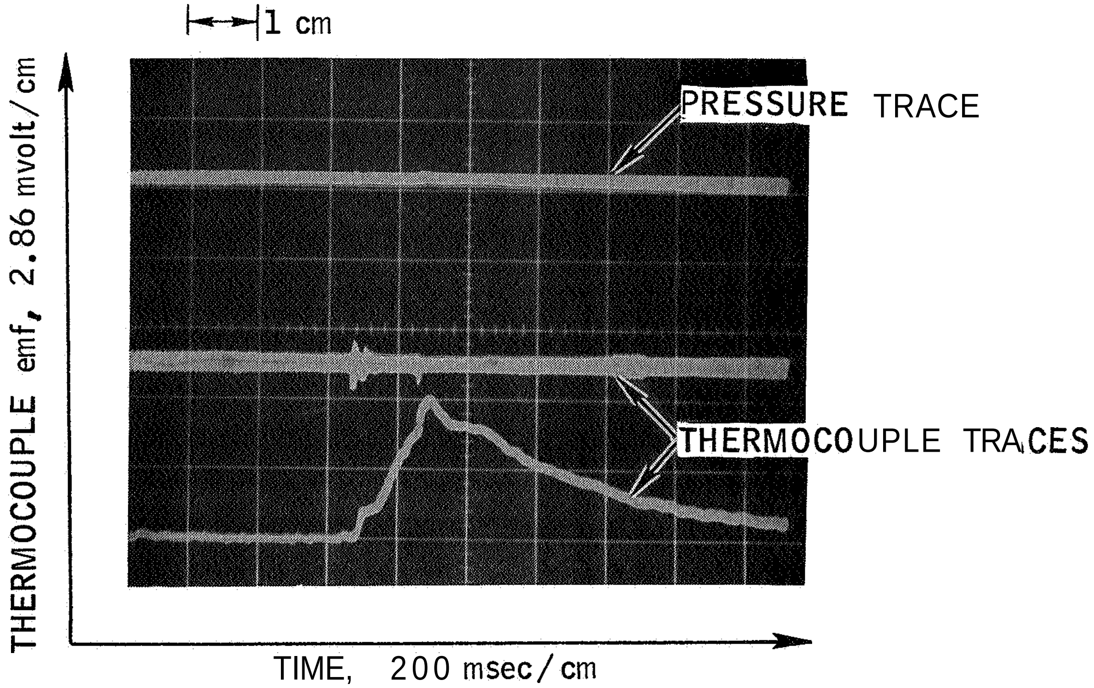
Figure 22

OSCILLOSCOPE IGNITION TRACES
MARK VIII

RANEY NICKEL POWDER ENTRAINED IN H_2 STREAM



RUN 274; 63°K (113°R), 1 atm
CORRECTED IGNITION TIME = 70 msec



RUN 279; 76°K (137°R), p = 4.9 psia

Figure 23

HYDROGEN ADSORPTION ISOTHERMS ON RANEY NICKEL

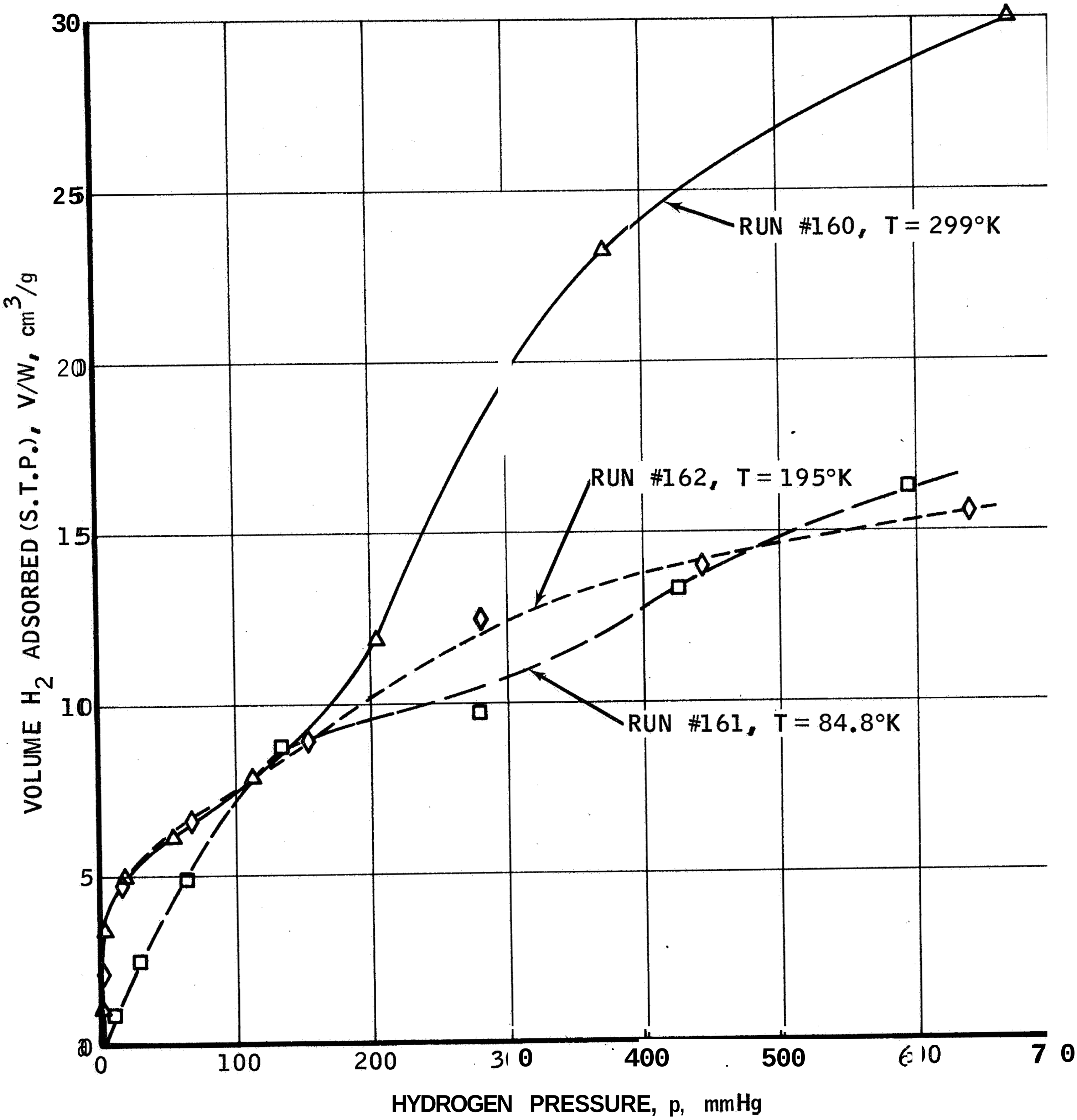


Figure 24

HYDROGEN ADSORPTION ISOTHERMS ON PLATINUM BLACK

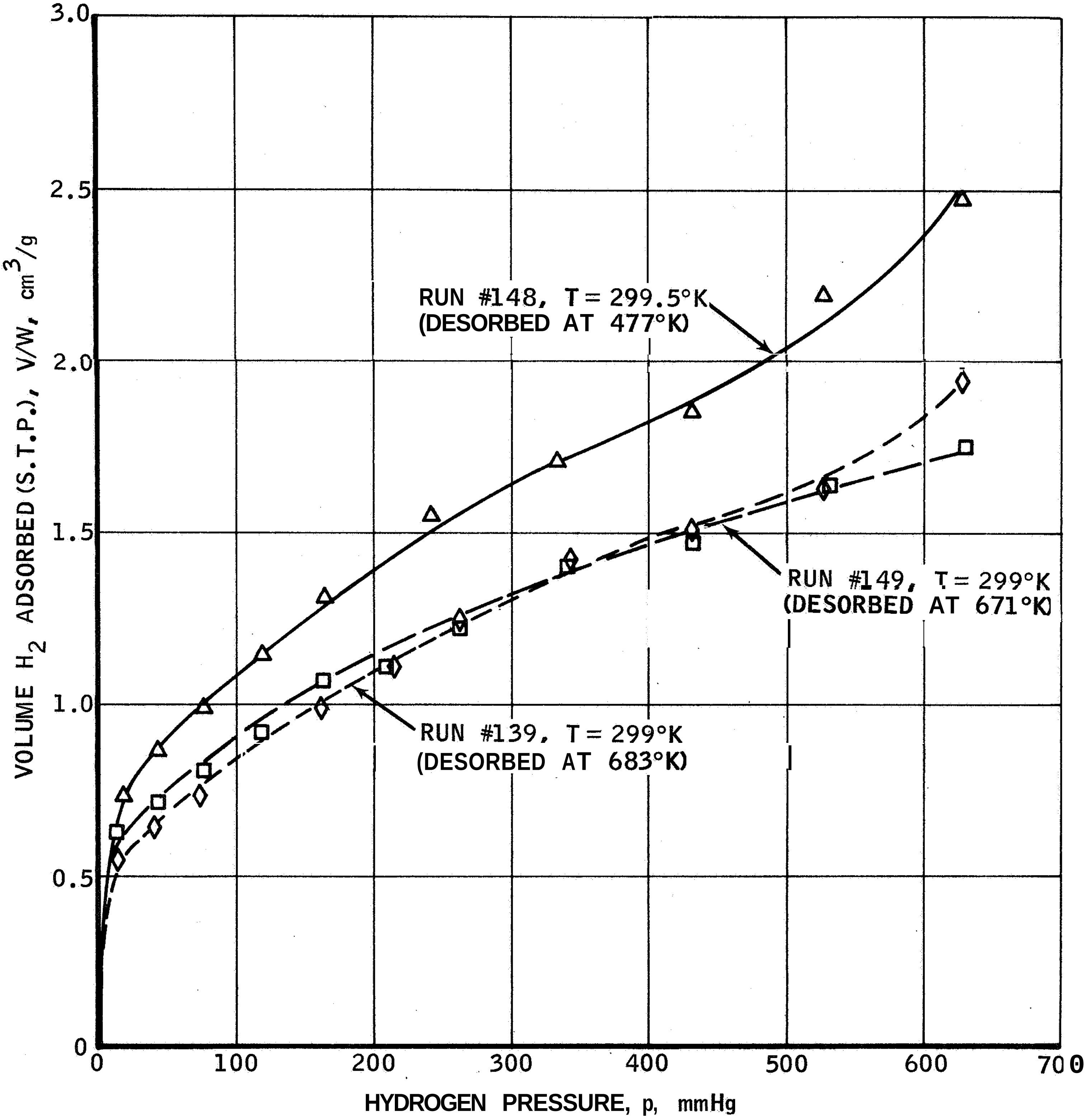


Figure 25

TABLE I

PRELIMINARY IGNITION TESTS WITH RANEY NICKEL

FIXED BED CATALYST

Nominal Mixture Ratio: $O_2/H_2 = 6.0$
Apparatus: **Mark** III

Catalyst Sample No.	Ignition Run No.	Gas Temp(1) °K	**Flow** Sequence	Corrected Ignition Time milliseconds	Remarks
#1	101	134	No lead	1000	Normal
	102	135	H_2 lead	510	Normal
	103	108	H_2 lead	480	Normal
#2	104	92	H_2 lead	220	Strong detonation Catalyst deactivated
#3	105	89	No lead	180	Normal
	106	88	No lead	720	Normal
	107	90	No lead	500	Normal
	108	95	No lead	130	Normal
	109	93	H_2 lead	380	More violent ignition than #108
#4	110	93	No lead	150	Normal
	111	91	No lead	480	Normal
	112	88	No lead	1050	Normal
	113	93	H_2 lead	340	More violent ignition than #112
#5 Mark IV (Vacuum Run)	114	97	H_2 prepurge; no **lead;** N_2 still flowing	700	p = 2.2 psig T.C. burned out
----	115	300	O_2 only	--	**Flow** calibration checks
	116	300	H_2 only	--	
	117	300	N_2 only	--	

TABLE I (Continued)

Catalyst Sample No.	Ignition Run No.	Gas Temp(1) °K	Flow Sequence	Corrected Ignition Time milliseconds	Remarks
#6	118	97	No lead	180	Normal
	119	95	No lead	280	Normal
	120	95	O_2 lead	800	Strong detonation
	121	95	H_2 lead	240	Normal
	122	94	O_2 lead	260	No pressure rise; only T.C. rise
#7	123	95	No lead	800	Normal
	124	95	H_2 lead	440	Normal
	125	94	H_2 lead	820	Normal
	126	91	O_2 lead	45	Normal
	127	93	O_2 lead	560	Normal
See Table II for Runs 128-137					
#10	138	122	No lead	700	Normal
	139	122	No lead	700	Normal

Notes:

(1) Gas temperature measure by Cu/Constantan thermocouple. This was approximately equal to the temperature of the ignition device and of the catalyst in the fixed bed.

TABLE II

COAXIAL INJECTION IGNITION TESTS USING FIXED BED CATALYSIS

Nominal Mixture Ratio: O/F = 6.0
Apparatus: Mark V

Catalyst and Sample No.	Ignition Run No.	Gas Temperature °K	Flow Sequence	Corrected Ignition Time milliseconds
Platinum No. 1	128	299	No lead	1500
	129	299	No lead	1400
	130	299	No lead	1500
	131	299	No lead	1300
	132	299	No lead	1500
	133	299	No lead	1500
	134	299	No lead	600
	135	299	No lead	1100
Raney Nickel No. 8	136	142	No lead	1200
Raney Nickel No. 9	137	143	No lead	680
Palladium No. 1 (unactivated commercial)	140	283	No lead	180
	141	283	No lead	430
	142	283	No lead	80
	143	283	No lead	20
	144	283	No lead	40
Palladium No. 2 (activated comercial)	145	134	No lead	1000
	146	134	O_2 lead	20
	147	134	No lead	680
	148	134	No lead	160
	149	134	No lead	320
	150	134	No lead	180
	151	134	No lead	180
	152	134	No lead	90
	153	134	No lead	160
	154	134	No lead	160
	155	134	No lead	40
	156	134	No lead	100
	157	134	O_2 lead	20

TABLE II (Continued)

Catalyst and Sample No.	Ignition Run No.	Gas Temperature °K	Flow Sequence	Corrected Ignition Time milliseconds
Raney Nickel No. 11	158	131	O_2 lead	380
	159	131	O_2 lead	130
	160	131	O_2 lead	160
	161	128	N_2 lead	330
Raney Nickel No. 12 (Modified preparation)	162	126	O_2 lead	280
	163	126	N_2 lead	330
	164	126	O_2 lead	40
	165	126	O_2 lead	10
	166	126	O_2 lead	130
	167	126	O_2 lead	10
	168	126	O_2 lead	40
	169	126	O_2 lead	20
	170	126	O_2 lead	230
Platinum No. 2 (activated)	171	126	O_2 lead	230
	172	290	N_2 lead	100
	173	290	N_2 lead	130
Palladium No. 1 (activated)	174	300	N_2 lead	80
	175	300	N_2 lead	120
	176	300	N_2 lead	130
	177	300	O_2 lead	100
	178	300	O_2 lead	100
Raney Nickel No. 13	179	128	O_2 lead	80
	180	128	O_2 lead	90
	181	128	O_2 lead	100
	182	128	O_2 lead	40
	183	128	O_2 lead	50
	184	128	O_2 lead	60
	185	128	O_2 lead	70
	186	128	O_2 lead	50
	187	128	O_2 lead	10
Palladium No. 3 (Modified preparation)	189	287	N_2 lead	80

TABLE III

IGNITION TESTS USING DRY RANEY NICKEL POWDER ENTRAINED IN H_2 STREAM

Gaseous Propellant Injection
Apparatus: **Mark** VI

Catalyst	Ignition(1) Run No.	Nominal M.R. O/F	Flow Sequence	Corrected(2) Ignition Time msec	Remarks
Raney Nickel Batch RNi-5 (5) stored under H_2 gas 58 days prior to use; single catalyst charge; burst diaphragms used.	190	6.0	O_2 Lead	110	Normal; two previous ignitions obtained but not recorded on oscilloscope.
	191	6.0	O_2 Lead	20	Normal
	192	6.0	O_2 Lead	30	Normal
	193	6,0	O_2 Lead	120	Normal
	194	4.0	O_2 Lead	530	Violent ignition; this run presumably expended the charge of Raney nickel,
	195-207				Calibration runs to measure gas lead times utilizing fluidizer with check valves.
Raney Nickel Batch RNi-8 (2)	208	1.5	O_2 Lead	≈ 1400	Mild ignitions; difficult to detect due to ignition apparently occurring downstream of thermocouple and pressure pickups,
	209	1.5	O_2 Lead	600	
	210	1.5	O_2 Lead	500	
	211-213				Gas lead time calibration runs.

TABU III (Continued)

Catalyst	Ignition$^{(1)}$ Run No.	Nominal M.R. O/F	Flow Sequence	Corrected$^{(2)}$ Ignition Time msec	Remarks
Raney Nickel Batch RNi-8 (2) (new charge)	214	1.5	O_2 Lead	Not Measured	Rapid ignition on H_2 valve actuation. Mild ignition, appeared to occur before thermocouple response.
	215	1.5	O_2 Lead	400	
	216	1.5	O_2 Lead	Not Measured	These ignitions also appeared to occur down — of the instrumentation zone, precluding accurate sensing.
	217	1.5	O_2 Lead	Not Measured	
	218	1.5	O_2 Lead	Not Measured	
	219	1.5	O_2 Lead	10-20 msec to initiation of reaction $\approx$ 40 msec to detonation pulse.	Exhaust tube exit blocked, permitting pressure transducer output to be detecable. No thermocouple response.
Raney Nickel Batch RNi-9 (1)	220	1.5	O_2 Lead	Not Measured	Normal ignition, but H_2 valve "on" pip did not print out, precluding accurate measurement of ignition time,
	221	1.5	O_2 Lead	Not Measured	Rapid ignition, no instrumentation response. Visual. observation of the exhaust tube interior confirmed that most of the ignitions were occurring downstream of the instrumentation zone, precluding ignition sensing.
	222	1.5	O_2 Lead	Not Measured	
	223	1.5	O_2 Lead	Not Measured	
	224	1.5	O_2 Lead	Not Measured	
	225	1.5	O_2 Lead	Not Measured	
	226	1.5	O_2 Lead	$\approx$ 600	
	227	1.5	H_2 Lead	$\approx$ 600	Delayed, violent ignition,
	228	1.5	H_2 Lead	100	

TABLE III (continued)

Catalyst	Ignition(1) Run No.	Nominal M.R. O/F	Flow Sequence	Corrected(2) Ignition Time msec	Remarks
Raney Nickel Batch RNi-9 (1) (new charge)					This charge of Raney nickel had been in the fluidizer ≈ 18 hrs prior to use.
	229	6.0	O_2 Lead	Not Measured	Delayed ignition, strong detonation pulse.
	230	6.0	O_2 Lead	Not Measured	Rapid ignition.
	231	6.0	O_2 Lead	≈ 620	Sparks were observed in the ignition chamber before H_2 admitted.
	232	6.0	O_2 Lead	≈ 1000	Strong, delayed ignition.
	233	6.0	O_2 Lead	Not Measured	Strong, delayed ignition.
	234	6.0	O_2 Lead	Not Measured	Strong, delayed ignition.

(1) Gas temperatures not measured; experimental conditions were such that both gas temperatures were near the boiling point of LO_2 (90°K).

(2) Corrected times obtained by subtracting 20 msec (H_2 gas lead time) from overall ignition time.

TABLE IV

IGNITION TESTS WITH LIQUID OXYGEN

Apparatus: Mark VII

Test Conditions:

(a) Dry Raney nickel catalyst entrained in hydrogen stream (single batch of Raney nickel used)

(b) Fluidizer, catalyst, hardware, and both propellant streams at a temperature of ≈ 77°K (138°R)

(c) Nominal Mixture Ratio (O/F) = 6.0

(d) Liquid Oxygen Lead

Ignition Run No.	Corrected Ignition Time(1) Millisec.	Remarks
235	not measured(2)	Local, undetected ignition occurred prior to main ignition
236	60	Rapid ignition, not picked up by instrumentation
237	not measured	
238	not measured	
239	400	Sparking occurred prior to ignition
240	75	
241	not measured	Rapid ignition, not recorded
242	60	Normal ignition
243	15	Normal ignition
244	not measured	Normal ignition
245	not measured	Normal ignition
246	10	Normal ignition
247	not measured	Normal ignition
248	not measured	Normal ignition
249	220	Normal ignition

TABLE IV (Continued)

(1) Corrected ignition time obtained by subtracting the hydrogen gas lead time (≈ 20 millisec) from the time of hydrogen valve opening to ignition pressure peak.

(2) Certain ignition times were not measured for one of the following reasons:

(a) Hydrogen valve "on" pip did not appear on the oscilloscope trace.

(b) Ignition occurred off the oscilloscope time scale.

(c) Ignition not detected with sufficient clarity by instrumentation.

TABLE V

IGNITION TESTS WITH MARK VIII IGNITER

Test Conditions:

(a) Dry Raney nickel catalyst entrained in hydrogen stream

(b) Liquid oxygen injection; $T_{O_2} \approx 77°K$ (138°R)

Ignition Run No.	H_2 Temp. °K	Nominal Mixture Ratio, O/F	Ignition Characteristics	Remarks
250	ambient	6.0	Normal	Ambient temperature
251	ambient	6.0	Normal	Check **runs**
252	77	6.0	Strong, delayed ignition, LO_2 lead	Runs 252-264 were performed with LN_2 cooling only
253	78	6.0	Normal, 140 msec	
254	78	6.0	Normal, 140 msec	
255	77	8.0	Delayed ignition	30 min. delay between Runs 254 and 255
256	77	6.0	Strong ignition, 180 msec	
257	77	6.0	Delayed ignition, 400 msec	
258	77	6.0	Normal, 180 msec	
259	77	1.5	Delayed ignition, 360 msec	Poor mixing was apparently encountered at O/F = 1.5; ignitions often occurred upon opening the N_2 purge valve
260	77	1.5	Delayed ignition, 500 msec	
261	77	1.5	Delayed ignition, 800 msec	
262	75	1.5	Delayed ignition, 600 msec	1 hr. delay between Runs 261 and 262
263	75	1.5	Delayed ignition, 500 msec	
264	75	1.5	Delayed ignition, 500 msec	
		0.5	Several unrecorded ignitions obtained, very similar to those of Runs 259-264	Single charge of Raney nickel (≈ 4 grams) used for the above ignitions.

TABLE V (Continued)

Ignition Run No.	H_2 Temp. °K	Nominal Mixture Ratio, O/F	Ignition Characteristics	Remarks
265	71	6.0	Strong, delayed ign.	Runs 265-274 performed using LHe cooling of the H_2 stream.
266	70	6.0	Strong, delayed ign., 500 msec	
267	79	6.0	Normal	Single charge of Raney nickel (≈ 4 grams) used for Runs 266-274. Several unrecorded ambient temperature check firings also obtained.
268	71	6.0	Normal, ≈ 300 msec	
269	63	6.0	Normal, 400 msec	
270	57	6.0	Normal	≈ 500 msec; could not get exact time due to failure of H_2 valve "on" pip to appear on trace
271	64	6.0	Strong ignition, 540 msec	N_2 flow left on
272	63	6.0	Normal, 520 msec	Prior ignition audible, but did not appear on scope
273	64	6.0	Normal, 130 msec	
274	63	6.0	Normal, 70 msec	Raney nickel presumably expended
275	64	4.0	Strong, delayed ignition, 600 msec	New charge of Raney nickel
276	48	4.0	No ignition obtained	Lowest temp. reached in this test series; O_2 flow may have been impeded by this low H_2 temp. Shortly afterward, supply of LHe was exhausted.
277	85	4.0	Strong ignition	
278	75		Normal, 400 msec	Tests discontinued due to depletion of LHe

TABLE V (Continued)

Ignition Run No.	H_2 Temp. °K	Nominal Mixture Ratio, O/F	Ignition Characteristics	Remarks
279	76	6.0	p = 4.9 psia; ignition occurred after N_2 purge was turned on	Runs 274-283 were conducted under partial vacuum, with LN_2 cooling.
280	76	4.0	p = 2.5 psia, normal ignition	Ignitions obtained in Runs 280-283 were delayed several hundred msec after H_2 valve opening.
281	76	1.5	p = 2.5 psia, normal ignition	
282	76	1.5	p = 2.5 psia, normal ignition	
283	76	0.5	p = 4.9 psia, normal ignition	