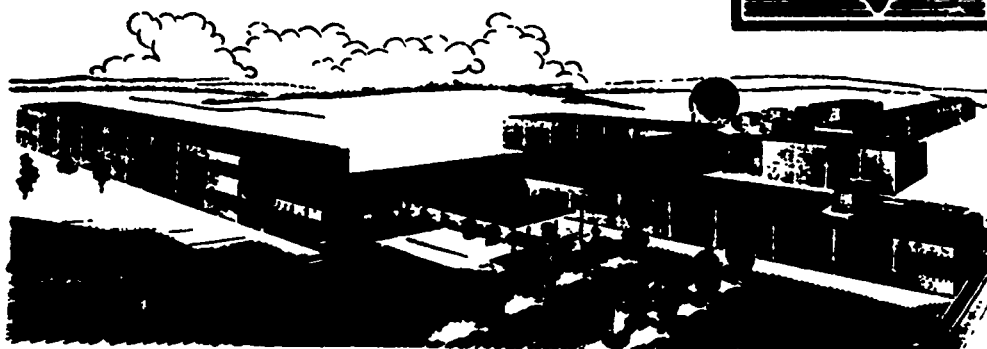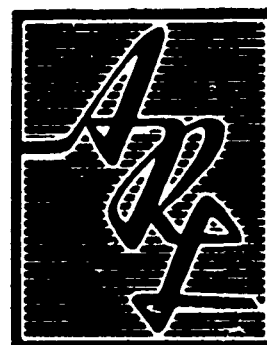63-1-6

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EXPLOSION LIMIT STUDIES OF NITROUS OXIDE AND NITROUS OXIDE – NITROGEN – AIR MIXTURES TO 200 ATM. AND 1800°R

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SEPTEMBER 1962

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AND NITROUS OXIDE–NITROGEN–
AIR MIXTURES TO 200 ATM. AND 1800°R

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FOREWORD

This technical documentary report was prepared by Juris O. Krisjansons, Loren E. Bollinger and Rudolph Edse of the Department of Aeronautical and Astronautical Engineering of The Ohio State University on Contr.t Number AF 33(616)-5615, Project 7065, "Aerospace Simulation Techniques Research", Task 7065-01, "Fluid Dynamics Facilities Research." The research on this task was administered under the direction of the Aeronautical Research Laboratories, Office of Aerospace Research, Wright-Patterson Air Force Base, Ohio, with Mr. Robert G. Dunn, Fluid Dynamics Facilities Laboratory, as Project Scientist.

This report covers one phase of the investigation on Contract AF 33(616)-5615.

ABSTRACT

Explosion limits have been determined in a 117.5 cm^3 cylindrical reaction chamber for pure nitrous oxide and mixtures consisting of $N_2O + 0.25$ AIR, $N_2O + 0.88N_2$ and $N_2O + 0.88N_2 + 0.50$ AIR. Two types of ignitors were employed; a 0.005-inch copper wire was melted by applying 31 volts DC to its terminals and a 0.020-inch diameter platinum glow wire was heated with approximately 210 watts AC. Results of these experiments are presented in the form of pressure-temperature explosion limit diagrams. The explosion limit curve for nitrous oxide follows an exponential path for both ignitors.

Explosions could not be produced in the $N_2O + 0.25$ AIR mixture. However, slow reactions were observed between $593^{\circ}K$ and $887^{\circ}K$. These results follow a characteristic pattern as shown in the pressure-temperature diagram. No reactions could be initiated in the $N_2O + 0.88N_2$ and $N_2O + 0.88N_2 + 0.50$ AIR mixtures.

Pressure-time relationships of the reactions in pure nitrous oxide and in the $N_2O + 0.25$ AIR mixture were obtained by using a quartz crystal, high-frequency response pressure transducer together with an appropriate oscilloscope and camera. These pressure traces aided in studying the individual reactions more closely and in determining their reaction times.

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LIST OF ILLUSTRATIONS

LIST OF SYMBOLS

a   Surface area of reaction vessel

A, B   Coefficients that are approximately constant

K   Heat transfer coefficient

M   Third body

p   Absolute gas pressure

q   Thermal energy of gas in vessel

Q   Heat of reaction per mole of gas decomposed

r   Number of moles reacting per unit time per unit volume

t   Time

t_1 Time interval from the end of T_1 to the plateau after the initial rapid increase in pressure

t_2 Time interval of the pressure plateau (starting at $T_1 + t_1$)

t_3 Time interval from the end of t_2 to the maximum pressure

T   Average gas temperature in vessel

T_0 Wall temperature of vessel

T_1 Time interval between activation of ignitor and initial pressure rise

T_2 Time interval between the initial pressure rise and the maximum pressure. $T_2 = t_1 + t_2 + t_3$.

V   Volume of vessel

SECTION I

INTRODUCTION

Nitrous oxide _s of technical interest because it decomposes exothermally, and the primary products of decomposition consist of nitrogen and oxygen. Aside from the academic interest in this type of exothermal decomposition reaction, it is possible that nitrous oxide may prove feasible as a working fluid for hypersonic wind tunnels. High stagnation temperatures are available because of the decomposition reaction which enables high Mach numbers to be obtained without liquefaction of the tunnel fluid. The addition of 0.88 mole of nitrogen to nitrous oxide gives a gas resembling air very closely. Since nitrous oxide decomposes on a self-sustaining basis if sufficient heat is added initially, this compound will explode when the appropriate pressure and temperature conditions prevail. These explosions, of course, are highly undesirable in technical applications where nitrous oxide is employed (e.g., wind tunnels). Therefore, it is necessary to know the conditions of pressure and temperature at which explosions will occur. At present, the theoretical analysis of the explosion mechanism of nitrous oxide is not developed sufficiently to permit accurate prediction of the conditions at which explosions will occur. Therefore, it was necessary to conduct experiments to determine the explosion regions and explosion limits of nitrous oxide; other experiments were conducted too with nitrogen and air added to nitrous oxide.

These experiments were conducted in a cylindrical stainless steel reaction vessel which had a volume of 117.5 cm^3 (see Appendix I for a description of the experimental apparatus). Nitrous oxide (or nitrous oxide plus nitrogen and/or air) was injected into the chamber; after the gas reached temperature equilibrium, ignition was attempted by means of special ignitors. The progress of the reaction was determined by measuring the initial pressure, the initial pressure rise and the final pressure.

The experimental research was divided into five different phases; each dealt with a specific type of gas mixture, type of ignition and/or technique of experimental observation. Besides investigating pure nitrous oxide, three different mixtures were studied also. They consisted of $N_2O + 0.88N_2$, $N_2O + 0.88N_2 + 0.5$ AIR and $N_2O + 0.25$ AIR.

An exploding-wire ignitor and a glow-wire ignitor were utilized for the two methods of ignition. For comparison, both methods of

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ignition were employed with pure nitrous oxide gas but only glow-wire ignition was employed with the mixtures.

Initially, the experimental results were determined by measurement of the pressure and temperature with Bourdon-type gauges and thermocouples respectively. Later, a high-frequency response, quartz pressure transducer was incorporated to permit a more detailed examination of the reaction mechanism as a function of time during the explosion-limit experiments.

SECTION II

THEORY

This discussion is concerned with the theory of explosion limits of gases in closed vessels. The forced ignition phase is of particular interest for these studies of nitrous oxide and nitrous oxide - nitrogen - air mixtures. Most of this material is based on discussions of this subject by Lewis and von Elbe (Ref. 1), Jost (Ref. 2), Hinshelwood (Ref. 3) and Hunter (Ref. 4).

Heat released by an ignition source causes the gas molecules in its vicinity to dissociate into atoms and to form free radicals. These particles may act as chain initiators and carriers in the resulting chemical reaction. The flow of heat and the diffusion of chain carriers from the reacting gas layers near the ignition source may initiate chemical reactions in a layer adjacent to the ignitor. If this process is continued, the reaction is propagated and may lead to an explosion.

If the explosive rate of the reaction is due to the heat released by the reaction, this process is called a thermal explosion. On the other hand, if chains are involved, most explosions result from branching chains which may be material or energy chains.

For a purely thermal propagation of the reaction the region of slow reaction can be determined from the condition that no heat is accumulated in the reaction vessel. This condition can be expressed by the equation

$$\frac{dq}{dt} = QVr - aK (T - T_o) = 0 \qquad (1)$$

where q is the thermal energy of the gas in the vessel, Q is the heat of reaction per mole of gas decomposed, V is the volume of the vessel, r is the number of moles reacting per unit time per unit volume, a is the surface area of the reaction vessel, K is the heat transfer coefficient, T is the average gas temperature in the vessel, and T_o is the temperature of the wall. The first term on the right hand side of

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Eq. (1) is the rate of heat evolution, and the second term is the rate of heat loss to the surroundings. The rate r is a complicated function which is determined by the reaction mechanism. If Eq. (1) has a real root involving T, the system will come to equilibrium at this temperature, and the reaction will take place on a steady-state basis until the reactants are consumed. If T_o is increased suffi-

ciently, the equation will not have a real root in T, and $\frac{dq}{dt}$ will

always be positive. Under these conditions the temperature will increase, and the process of self-acceleration of the reaction, i.e., an explosion, will occur. A critical temperature is reached when the wall temperature T_o is sufficiently high to ignite the gas. This

temperature, which is a function of various parameters, can be called the ignition temperature of the system. Since r is dependent on the pressure, the relationship of ignition temperature and pressure generally may be expressed in this form

$$\log p = \frac{A}{T_o} + B \tag{2}$$

where A and B are coefficients that are nearly constant. A represents an over-all activation energy divided by the gas constant, and B depends upon vessel parameters and other factors. Equation (2) agrees with the experimental results presented in Ref. 1, however, it does not serve as a criterion to distinguish between thermal and chain-branching explosion limits because the temperature-pressure relationship of a chain-branching explosion frequently is given by Eq. (2).

SECTION III

EXPERIMENTAL STUDIES AND DISCUSSION OF RESULTS

A. N_2O IGNITED BY AN EXPLODING WIRE.

Experiments with nitrous oxide were conducted at initial temper-atures of 296, 348, 373, 423, 473, 523, 573 and 623°K with initial pressures ranging from 2 to 48 atmospheres.

The ignitor consisted of a 0.005-inch diameter copper wire which was melted by applying 31 volts DC to its terminals. The resulting electric current melted the copper wire very quickly thereby producing a concentrated heat source for ignition.

The initial experiments were carried out at low pressures (two atmospheres) and at ambient temperature (296°K). In later experiments the temperature was maintained constant while the pressure was elevated gradually from experiment to experiment until an explosion

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was obtained. For a given initial temperature, measurements were
made up to pressures well within the explosion region to make sure
that the explosion limit actually had been reached. Then, the
temperature was elevated and the experiments were repeated. This
procedure was continued up to a temperature of $623°K$ which was the
maximum temperature obtainable with the experimental equipment at
that time. Later, the cooling system of the reaction vessel was
improved so that temperatures up to $1000°K$ could be reached. At
$623°K$, the explosion limit occurred at two atmospheres. Experiments
with nitrous oxide which were conducted at higher temperatures are
described in part B of this section.

The experimental results are depicted graphically by a temper-
ature versus pressure diagram shown in Fig. 1. Only measurements in
the immediate neighborhood of the transition region between explo-
sions and slow reaction are included. These points define the
explosion limit curve as being the dividing line between conditions
of temperature and pressure above which heat addition from the
ignitor initiates an explosion and below which such an explosion
is not formed. The explosion limit curve is exponential in shape
from the point of $623°K$ $(350°C)$ and two atmospheres to $298°K$ $(25°C)$
and 47 atmospheres. Theoretically, the explosion limit line is the
locus of points of the unstable equilibrium conditions at which an
explosion can be initiated by the addition of a minute amount of
energy and above which an auto-explosion will occur. Since the
amount of heat added by the "exploding" wire ignitor was more than
just a small amount, it is probable that the limiting conditions
occur at pressures higher than those obtained in these experiments.
This assumption was affirmed by experiments with a glow wire ignitor
which gives an explosion limit curve that is displaced to temperature
and pressure conditions higher than those obtained with the exploding
wire ignitor. With the glow wire ignitor, the amount of heat added
during ignition can be adjusted. However, such adjustment is not
possible with the exploding wire ignitor since a minimum voltage is
required for melting the wire.

After injection of the gas into the reaction chamber, the gas
temperature increased by as much as $20°C$. At first it appeared that
this temperature increase might have been caused by a limited
exothermal decomposition initiated when nitrous oxide came into
contact with the hot walls of the reaction chamber. Further study
of this phenomenon showed, however, that this temperature increase
resulted from convective heating of the thermocouple hot junction
by gases at the bottom of the reaction chamber which were at a
higher temperature. Measurements showed that the lower region of
the reaction vessel was appreciably warmer than the upper section
because of excessive cooling at the top which resulted in an
undesirable temperature gradient throughout the reaction chamber.
To eliminate this temperature gradient the reaction vessel was
modified so that it could be operated without a cooling jacket.

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The experimentally observed reactions were characterized by an initial rapid increase of pressure that began to decay immediately after it had reached its peak. The stable value that resulted was 30 to 45 per cent higher than the initial pressure. The exact pressure variations during the reaction could not be obtained because the instrumentation needed for such rapid pressure changes was not available at that time. Since the explosion limit curve obtained was similar to curves established for thermal reactions in other systems, the decomposition of nitrous oxide is probably a thermal explosion. An explosion based on a chain mechanism is hard to visualize for this decomposition. The experiments were performed in a rather small chamber. Different results may be obtained in larger chambers or in chambers of different geometry.

In order to study the ignition characteristics of nitrous oxide with a low energy ignitor, various ignitor-wire configurations were tried with AC voltage energizing sources. However, these methods did not produce any consistent results. In subsequent experiments, therefore, a platinum glow wire ignitor was used as described in the following part of this section.

B. N_2O IGNITED BY A GLOW WIRE.

Explosion limits of pure nitrous oxide were determined at various temperatures between 423 and $1035°K$. In this temperature interval, a pressure range from two to 75 atmospheres was investigated.

Experiments were performed in a heavy walled stainless steel cylindrical reaction vessel. The volume of the reaction vessel was 117.5 cm^3. This vessel and the flow controls, ignition mechanism and temperature controls are described in the Appendix.

The first step in the experimental procedure was to heat the reaction chamber to the desired temperature level and to stabilize it at this temperature by adjusting the voltage control manually. After the reaction vessel was evacuated and then filled with nitrous oxide, sufficient time was allowed for the gas to reach temperature equilibrium. Ignition was attempted by energizing the 0.020-inch diameter platinum glow wire with a power of approximately 210 watts from an AC source. It was believed that a flame front could be initiated with the platinum glow wire which was able to propagate through the volume of gas and possibly could result in an explosion. This aspect will be discussed more fully in part D.

After the ignitor wire was activated, the amount of the reaction was determined from pressure changes indicated by Bourdon-type pressure gauges. The ignitor wire was heated for approximately one to two seconds. When ignition of the nitrous oxide gas occurred, the gas pressure rose rapidly and markedly. The pressure increase consisted of two very definite steps the first of which was of relatively short duration. After a short lag the first step was followed

by a second step in which the pressure rose much more than in the first step, and the slope of the second step was considerably steeper. Finally, the pressure decreased and asymptotically approached a value that exceeded the initial pressure by approximately 30 to 45 per cent. The maximum pressure during the explosion exceeded the initial value by a factor of two to three.

The experimental technique was not suitable to determine the reaction period accurately at the time that these measurements were made. However, an improved mechanism was incorporated later which permitted reaction times to be measured.

The experimental results are represented by the temperature-pressure diagram as depicted by Fig. 2. Not all results are included in this graph because only the data of experiments in the neighborhood of the transition region between no reactions and explosions are shown. The explosion limits were determined by attempting ignition of the nitrous oxide at a constant temperature over a wide range of pressures. From Fig. 2 it can be seen that the explosion limit curve is exponential in the temperature region between 390 and 720°C. The pressure was approximately three atmospheres at 993°K (720°C) and increased to 25.5 atmospheres at 663°K (390°C). Between 663°K (390°C) and 513°K (240°C), experimental results were very inconsistent. In this temperature range, sometimes the gas exploded and sometimes it did not react, so that a sharp limit could not be established. These results were not reproducible. A more detailed investigation of the reaction mechanism in this region was made later with a high-frequency pressure transducer.

At temperatures below 513°K (240°C), the explosion limit curve was considerably more linear than the branch above the irregular region. This explosion limit curve in the lower temperature region starts at a temperature of 513°K (240°C) and a pressure of 23 atmospheres and falls off to 423°K (150°C) and 72 atmospheres. Experiments below 423°K were not performed because the present study concerned itself only with explosion limits at higher temperatures.

Some experiments with nitrous oxide were attempted at 1035°K. At this temperature an ignitor was not needed because auto-ignition took place approximately one second after the gas had entered the reaction chamber. These auto-explosions were observed at 3.5, 3.7 and 3.9 atmospheres (at 1035°K). Higher initial pressures were not investigated at this temperature.

In order to learn more about the reaction mechanism of nitrous oxide, a high-frequency pressure transducer was incorporated into the experimental equipment. The Kistler quartz pressure transducer was connected to a high-frequency oscilloscope through a transistorized charge amplifier to decouple the high impedance source. The pressure transducer was attached to the 1/8-inch stainless steel tube connecting the reaction chamber with the conventional pressure gauges. The

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crystal detector of the transducer was placed as close as possible to
the reaction chamber in order to obtain adequate frequency response.
Since the pressure transducer was located in a high-temperature area,
a cooling mechanism was incorporated to prevent damage to the crystal.
The output signal of the transducer was photographed with a Polaroid
camera attached to the oscilloscope (Tektronix Model 555).

Experiments with pure nitrous oxide were performed with this
transducer system at 498, 566, 618, 745, 805, 828 and 887°K for a
wide range of pressures. At 745, 828 and 887°K, experiments with
the N_2O + 0.25 AIR mixture were performed at the same initial pres-
sures that were employed with nitrous oxide in order to compare the
reaction times of the mixture and the pure nitrous oxide gas. These
results are shown in Figs. 3, 4 and 5. Pressure-time traces, depicted
in Fig. 6, were obtained also during experiments with nitrous oxide
in the "inconsistent" range, that is, between 513°K (240°C) and 663°K
(390°C).

These pressure-time histories of the reactions exhibit certain
basic characteristics. The pressure increase with time did not
follow a uniformly rising path in the initial phase. Instead, the
reaction period between ignitor activation and the time when maximum
pressure was attained can be divided into two intervals T_1 and T_2
(see upper tracing in Fig. 6). The first interval T_1 started when
the ignition wire was activated and terminated when a reaction in
the gas was first noticed as evidenced by a measurable increase in
pressure. The second time interval T_2 started where T_1 ended and
terminated when the pressure reached its maximum value, that is,
completion of the primary reaction. During the time interval T_2
the reaction was composed of several phases distinguished by differ-
ent rates of pressure rise. At the end of time interval T_1, a rapid
increase in pressure was observed which lasted for approximately
0.05 second (call this time interval t_1) during most experiments.
This increase was followed by a slower pressure rise, essentially
a plateau, lasting for an interval t_2. At the end of period t_2,
however, the primary reaction accelerated and came to an end at
the peak during time interval t_3.

Since the platinum glow wire ignitor contributed only heat to
the nitrous oxide gas, the initial gas reaction, which lasted for
the time period t_1, was of a thermal nature. This reaction did not
start until the ignitor wire was activated for a period of time T_1
which varied from 0.1 to 1.5 seconds. For lower pressures at
temperatures below 663°K, the period T_1 was as long as 15 seconds.

During the period t_2 it is difficult to specify the type of
reaction which took place. This interval appears to be a transition

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region between the reaction started by the ignitor and the final self-sustaining reaction mechanism which lasted for a period t_3. The period t_2 was of the order of 0.05 to 0.2 second although values up to 0.6 second were obtained for temperatures below $663°K$. From the rate of pressure increase, it appears that the reaction during the final period t_3 was similar to the initial reaction, that is, a thermal reaction. For higher temperatures at a certain pressure level, or vice versa, the reaction time t_2 becomes noticeably shorter and the intermediate reaction almost disappears. Consequently the decomposition reaction seemed to go from the initial thermal reaction directly into the final thermal reaction resulting in an overall short reaction time T_2. The experimental results showed that this reaction time T_2 varied between 0.2 and 0.4 second. Since the pressure pulses from the reaction area had to travel a distance of 9 1/2-inches through 0.074-inch diameter tubing before they reached the pressure transducer, a time lag resulted which distorted the measured reaction times and amplitudes. Because of the relatively long time periods involved, however, frequency and amplitude response were satisfactory.

For the decomposition of N_2O, a chain-branching reaction can be formulated although it is unlikely

$$N_2O* \rightarrow N_2 + O \qquad \text{initiation}$$

$$\left. \begin{array}{l} O + N_2O \rightarrow N_2 + O_2* \\ \\ O_2* + N_2O \rightarrow N_2O* + O_2 \end{array} \right\} \text{chain}$$

$$N_2O* + M \rightarrow N_2O + M* \qquad \text{chain breaking}$$

$$O_2* + M \rightarrow O_2 + M* \qquad \text{chain breaking}$$
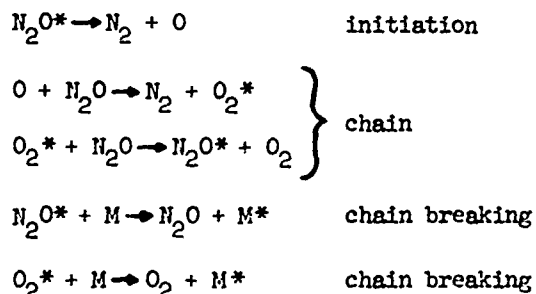
because of the breaking of chains the chain will not propagate. The * indicates excess thermal energy.

It is concluded, therefore, that the decomposition of nitrous oxide involves no chain reaction, and thus the explosions are of purely thermal nature.

The pressure versus time traces definitely show that at temperatures below $663°K$ the reaction times were longer than those determined at higher temperatures as expected. Some typical pressure-time traces obtained in this region are depicted in Fig. 6.

C. N_2O + 0.25 AIR IGNITED BY A GLOW WIRE.

Experiments with the N_2O + 0.25 AIR mixture were conducted at initial temperatures of 508, 594, 648, 744, 832 and $887°K$. For these

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temperatures respectively, pressure ranges of 6 to 62.2, 21 to 61.7, 21 to 61.7, 6 to 27, 2.7 to 21.4 and 4.4 to 21.4 atmospheres were investigated. At the lower temperatures most of the experiments were conducted at relatively high pressures, up to approximately 62 atmospheres; at the higher temperatures, however, the lower pressure region was studied more closely. This procedure was chosen because the ignition limits of explosive gases usually follow this pattern.

The experimental apparatus was the same as that employed for the measurement of explosion limits of pure nitrous oxide. However, additional flow controls were necessary to obtain the nitrous oxide - air mixture. A flow of the premixed gases at the required concentrations was established; then they were bypassed from the reaction chamber through a vent for a sufficient period of time to purge the flow system of any foreign gases. Next, the vent valve was closed and the gas mixture was admitted to the reaction chamber, which had been evacuated previously. When the desired pressure level was reached, the reaction chamber was sealed off from the remainder of the system. To minimize the danger involved when the reaction vessel was pressurized with explosive gases, filling and venting operations were controlled remotely.

Experimental results are presented in Fig. 7 by a temperature-pressure diagram. Numerous experiments were necessary to identify the critical pressure range. No ignition was obtained at a temperature of $593^{\circ}K$ or lower. At a temperature of $887^{\circ}K$ ignition was secured for all pressures investigated. The range between $593^{\circ}K$ and $887^{\circ}K$ included the transition region between ignition and no ignition (Fig. 7) which is described by an exponential curve. Either of two types of process was observed when the gas mixture ignited. The first type of process was a very limited one which resulted in a final pressure increase of approximately five per cent; the peak was approximately 20 per cent greater than the initial pressure. Since the reaction time was relatively long and the pressure increase was small, probably this decomposition was incomplete. The glow wire ignited the surrounding gas layer thus causing a modest increase in pressure as observed; however, insufficient heat was available to ignite the adjacent layer. Thus, the flame was extinguished. This process is characterized by pressure-time traces obtained at $593^{\circ}K$ (Fig. 8). The other process that was observed developed a much greater increase in pressure as depicted in the pressure-time traces at 648 and $887^{\circ}K$ in Fig. 8. For these experiments the maximum pressure rise was approximately a factor of two. The average final pressure increase was 26 per cent. From these pressure rises it seems probable that the decomposition went to completion. Further supporting evidence was derived from the pressure-time histories of the decompositions which indicated that their rates increased with time.

Pressure-time histories (Figs. 3, 4, 5 and 8), determined with the pressure transducer - oscilloscope system, indicated that all decompositions investigated were relatively slow. The reaction process can be divided into certain definite time intervals T_1 and T_2 as defined in the last section. At the end of time interval T_1 the rapid pressure

increase was observed to last for approximately 0.1 second (t_1). This fast pressure rise was followed by a slower pressure increase which continued for 0.5 to 1.4 seconds (t_2). This latter pressure rise was followed by the final pressure increase interval (t_3). Although the decomposition process started as a slow burning flame, it is possible that the decomposition which took place during the final time interval t_3 was a thermal explosion. But, since the volume of the reaction chamber was small, this decomposition did not continue for a sufficiently long time to identify its character clearly. Although these various phases of the decomposition were obtained too during the experiments with pure nitrous oxide, the intervals T_1, t_1, t_2 and t_3 were longer (particularly t_2 and t_3) for the nitrous oxide - air reactions which indicated a slower reaction rate which is to be expected. From Figs. 3, 4, 5 and 8 it can be seen that the reaction time T_2 $(t_1 + t_2 + t_3)$ decreased with increasing temperature (from 1.8 to 0.6 seconds) indicating an acceleration in the reaction mechanism with increased temperature. The time T_1 also decreased in the same manner, however, a few inconsistencies occurred.

Since the reaction times for the $N_2O + 0.25$ AIR mixtures were relatively long, it is concluded that explosions were not initiated in these gas mixtures. More likely the observed decompositions were of the slow-burning type.

D. $N_2O \sim 0.88N_2$ IGNITED BY A GLOW WIRE.

The mixture $N_2O + 0.88N_2$ was investigated to determine whether nitrous oxide diluted by an inert gas, such as nitrogen, could be forced to ignite and explode. This particular concentration was chosen because, if the decomposition did go to completion, the product would be air $(3.76 N_2 + O_2)$.

Since it is known that inert gases such as nitrogen tend to prevent the formation of explosions, most of the experimentation was conducted at higher temperatures и l pressures where a reaction is more likely to take place. Ordinarily, for these experiments the platinum glow wire ignitor was activated for periods of five seconds; quite frequently, however, the activation period was extended to 30 seconds. Experiments were initiated at $573^{\circ}K$ and 10 atmospheres. Then the temperature was increased stepwise until $1000^{\circ}K$ was reached. At each individual temperature level a pressure range from 10 to 68 atmospheres was investigated. Experiments were attempted at $1087^{\circ}K$ $(1957^{\circ}R)$, but they could not be completed because some of the pressure seals, the gas injection mechanism and the thermocouple hot junction were destroyed at this high temperature. No explosions or slow reactions were observed at any single combination of these temperatures and pressures.

For experiments in the temperature range from 889°K to 1000°K, pressures from 75 to 200 atmospheres were investigated. Even at these extreme conditions, no reactions could be initiated even though the amount of power delivered to the ignitor was increased to the point where the wire melted. A small temperature increase in the gas was measured during the experiments which could have indicated that a limited reaction had taken place. However, since no measurable pressure rise accompanied the temperature increase, it is unlikely that a reaction was initiated. The temperature rise was attributed to heating of the thermocouple hot junction by the glow-wire ignitor because of long periods of activation. A sizeable amount of heat was emitted by the ignitor which was located close to the thermocouple hot junction.

From the experimental investigation of the $N_2O + 0.88N_2$ gas mixture, it is concluded that nitrogen is very efficient in preventing the formation of explosions. The region of investigation for the various temperatures and pressures is summarized in Fig. 9.

E. $N_2O + 0.88N_2 + 0.50$ AIR IGNITED BY A GLOW WIRE.

Experiments with the mixture $N_2O + 0.88N_2 + 0.50$ AIR were performed in order to learn how the addition of one half mole of air affects the $N_2O + 0.88N_2$ mixture which was investigated previously. With this latter mixture it was demonstrated experimentally that the addition of nitrogen to pure nitrous oxide negates the formation of explosions under the conditions employed. Air, being an oxidizer, will support combustion or explosion reactions. It is obvious that if the decomposition of N_2O with $0.88N_2 + 0.50$ AIR goes to completion, the end product will be air and, therefore, such a reaction is of technical interest (see Section I). The ignition method and experimental procedure was similar to that employed with the nitrous oxide - nitrogen mixture described previously.

The initial experiments were performed within the temperature interval of 673 to 1000°K at pressures which ranged from 12 to 82 atmospheres. Since no decompositions were obtained with these temperature and pressure conditions, further experimental efforts were concentrated in the region up to and including the maximum temperature and pressure of 1000°K and 200 atmospheres respectively. At these high temperatures and pressures numerous difficulties were encountered with the flow controls and the reaction vessel. However, they were overcome and the experiments were conducted successfully.

From the experimental results obtained, no explosions or even slow, limited reactions are to be expected at any one of the previously specified combinations of temperature and pressure. It is concluded, therefore, that the addition of one-half mole of air to the mixture $N_2O + 0.88N_2$ has no effect in counteracting the effect of inert nitrogen gas in preventing ignition in nitrous oxide.

The experimentally investigated temperature and pressure conditions are summarized in Fig. 10 which shows a temperature-pressure plot.

CONCLUSIONS

From Figs. 1 and 2, it can be seen that the "ignition" temperature T_o (below which no explosions can be initiated for a fixed pressure) decreases with increasing pressure for nitrous oxide as predicted by theoretical analysis for a thermal explosion. The experimental points defining the explosion limit follow an exponential path. Although the explosion limit is drawn as a sharp line, it is more likely a band of a given thickness. When ignition was attempted by melting the copper wire, a portion of the wire was vaporized. Conceivably the vapor could initiate a reaction with nitrous oxide such as $Cu + N_2O = N_2 + CuO$. Besides having a different value of heat input, this possible reaction was another reason for substituting the platinum glow wire for the exploding wire as an ignitor. A comparison of the results obtained with the two ignitors shows that a higher explosion limit curve was obtained when the platinum wire was used. In Fig. 2 it can be seen that a thermal explosion limit curve was obtained between 663 and 998°K. The decomposition time, as obtained from pressure-time traces, was of the order of 0.2 to 0.4 second. These reaction times are long for explosive reactions, however, modest attenuation occurred because the pressure transducer was located some distance from the reaction chamber. At best, these decompositions can be classified as slow thermal explosions. Below 663°K (including the inconsistent points in the region from 513 to 663°K), the pressure-time traces show that a relatively slow decomposition took place.

Experiments with the $N_2O + 0.25$ AIR mixture produced only relatively slow decomposition or no decomposition. Reaction times (T_2) were between 0.6 and 1.8 seconds which are too long to allow the decomposition to be classified as explosions. Therefore, it is concluded that the platinum glow wire ignitor could initiate only a slow decomposition in the $N_2O + 0.25$ AIR mixture. Reaction times in the $N_2O + 0.25$ AIR mixture and N_2O gas can be compared in the diagrams depicted in Figs. 3 through 5. These diagrams show that the reaction periods T_1 and T_2 are longer and that the maximum and final pressures are smaller for the $N_2O + 0.25$ AIR mixture than for pure N_2O. It is concluded, therefore, that the decomposition of N_2O in the $N_2O + 0.25$ AIR mixture is slower than in the pure nitrous oxide.

No explosion or reactions of any kind were observed in the $N_2O + 0.88N_2$ mixture. Therefore, it was concluded that the inert gas is

very effective in preventing reactions in nitrous oxide in the temperature and pressure limits investigated. No reactions occurred in a $N_2O + 0.88N_2 + 0.50$ AIR mixture. This result shows that the half mole of air does not promote the ignition of the $N_2O + 0.88N_2$ mixture with the glow wire ign .or.

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3. Hinshelwood, C. N., "The Homogenous Thermal Decomposition of Nitrous Oxide," Proc. Roy. Soc. London, Series A, 106, 1924.

4. Hunter, E., "The Thermal Decomposition of Nitrous Oxide at Pressures up to 40 Atmospheres," Proc. Roy. Soc. of London, Series A, 144, 1934.

APPENDIX

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The explosion limit reaction vessel (Fig. 11) was fabricated from type 304 stainless steel. It was designed to contain the reactive gas mixture in a 1 1/2-inch diameter by 4 1/16-inch long reaction chamber. The lower part of the reaction vessel (which has a wall thickness of two inches) was heated by an electric heater (described below) which had a manual temperature control; the upper part was cooled by circulating cold water through a cooling jacket which functioned satisfactorily. However, the cooling system had to be eliminated after it was found that excessive temperature gradients were introduced into the reaction chamber. Because of the internal stresses created in the reaction vessel during welding, it was stress relieved prior to initiating the experiments.

The reaction chamber was closed tightly by means of a copper seal; in addition, this lid supported the shaft which contained the ignition mechanism, a thermocouple and a 1/8-inch diameter tube through which the reaction chamber was filled with the gas mixture. Since experiments were to be performed at temperatures up to 1300°R and pressures up to 200 atmospheres, the ignitor lead had to be sealed and insulated with materials that were capable of withstanding high temperatures and pressures simultaneously. It was found that a suitably modified spark plug served this function very well. Six studs were embedded in the top of the reaction vessel to secure the lid.

The reaction was initiated by adding heat to the nitrous oxide gas (or gas mixture) through an ignitor mechanism that consisted of an ignitor wire fastened between two terminal posts at the end of the shaft. One post was grounded and the other was connected by an insulated lead to the voltage source. This type of ignition mechanism was adaptable to the use of either the exploding wire or the platinum glow wire. For the experiments wherein exploding wires were used, a 31-volt DC potential was employed. When the circuit was completed, the 0.005-inch diameter copper wire melted very quickly with a bright flash resulting in the rapid addition of energy.

Later experiments employed a glow wire which was activated with AC power that could be adjusted with a Variac to increase or decrease the amount of heat emitted by the glow wire.

Since the glow wire could be used repeatedly for succeeding experiments without being replaced, the reaction chamber did not have to be opened between experiments. Thus, the problem of handling the components of the reaction vessel at the extreme temperature conditions was avoided. An ammeter was inserted in the ignitor circuit to allow constant current settings to be made by the Variac. Also, the ammeter served as a convenient detector to ascertain whether or not the glow wire had burned out.

The temperature in the reaction vessel was determined with a chromel-alumel thermocouple in a stainless steel sheath which was inserted into the chamber through a groove on the shaft. A conventional ice-bath cold junction was employed and a portable potentiometer was used to measure the thermocouple voltage. This thermocouple was employed to determine the gas temperature before and after ignition was attempted, however, it could not be employed to obtain a temperature-time history of the reaction because of its poor frequency response.

The reaction vessel was heated electrically to the required temperature. Details of the heater and the vessel are given in Fig. 12. This heater was constructed from a six-inch inside diameter Alundum tube which was grooved on the outside to hold 100 feet of 14-gauge, chromel-A heating wire; the tube was placed around the 5.5-inch outside diameter reaction vessel. The heating wire was covered with a refractory cement and the whole system was insulated with fire brick on the top and bottom and with asbestos along the sides. A 12-inch diameter Transite tube held the insulation in place. With a Variac type of power control, a continuously variable range of reaction-vessel temperatures could be obtained. Using 220 volts AC across the heater, the reaction chamber could be heated to 1100°K in approximately three hours. This temperature was above the maximum value required in these experiments. A second chromel-alumel thermocouple was installed to ascertain the temperature near the heating wires of the reaction vessel.

A Bourdon-type gauge, filled with mercury to decrease pressure losses from the reaction chamber because of expansion, was used to determine the pressure in the chamber before and after the reaction took place. Since the experiments covered a pressure range from one to 200 atmospheres, a number of pressure gauges with different ranges was selected and filled with mercury beforehand so that they could be quickly and easily incorporated into the system when needed. For the experiments at maximum pressure, a 10,000-pound per square inch mercury-filled gauge was installed to measure the final pressure while a gauge with a lower pressure range was employed to determine the initial pressure more accurately. The reaction vessel was evacuated with a conventional pump before filling operations began.

A schematic diagram of the experimental apparatus and a flow diagram of the system employed to determine the explosion limits are shown in Figs. 13 and 14. Figure 15 is a photograph of the apparatus. One-eighth-inch diameter stainless steel tubing was used from valve 1 to the reaction vessel and from valve 2 to valves 3, 4, 6 and 15 and to the pressure gauges. The small diameter tubing was employed to reduce pressure losses during experiments because of tubing volume. All other tubing was 1/4-inch diameter stainless steel. The flow controls, regulators and so forth were made from stainless steel to prevent corrosion.

15

Before the experiments could be initiated, the temperature of the reaction chamber was stabilized at the desired temperature level. First, the heater controls were adjusted so that the reaction vessel would be heated rapidly to a value close to the desired temperature. Then the voltage was decreased to prevent overshoot of the temperature; usually it could be maintained within a range of $\pm 10^{\circ}K$ without the use of an automatic regulator.

When the desired temperature was reached, the system was evacuated with valves 2 and 7 open and with all other valves closed. After a satisfactory vacuum was obtained, valves 2 and 7 were shut off, valves 5 and 1 were opened (in sequence) and nitrous oxide was admitted to the reaction chamber from a commercial storage cylinder containing the gas at a pressure of approximately 1000 pounds per square inch. The filling process was regulated by a control system that was located in the adjoining corridor. The reaction chamber was filled to the desired pressure and valve 1 was shut off. Deviations from the desired pressure could be corrected by bleeding the excess gas through valve 4 into the venting system. Then valve 4 was closed and the reaction-chamber temperature was checked. Next, ignition of the nitrous oxide gas was attempted by melting the 0.005-inch diameter copper wire or by activating the 0.02-inch platinum wire with AC potential. The experimental results were observed with the pressure gauge and/or temperature values from the thermocouple readings and a high-frequency pressure transducer arrangement (described below).

Venting was accomplished by opening valve 2. After the pressure reached one atmosphere, valve 3 was closed and the system was flushed with high-pressure air by opening valve 6. Next, the ignition wire was replaced if necessary and filling operations for the next experiment could be started. During the higher temperature experiments it was necessary to replace the copper pressure seals frequently.

During the experiments with mixtures, the flow rate of each component was controlled and metered separately. A uniform mixture was obtained by passing the individual gases through the mixing chamber located near the experimental area in order to decrease the danger from an accidental explosion during the mixing process. The gas flowed from the mixing chamber through valves 10 and 8 into the vent line in order to purge the flow lines of any foreign gas. Then valve 8 was closed, valves 1 and 9 were opened and the evacuated reaction chamber was filled with the desired gas mixture. The remainder of the experimental procedure for mixtures was the same as that employed for experiments with pure nitrous oxide.

To determine the pressure-time history of these reactions, a Kistler quartz pressure transducer was employed together with a high-frequency oscilloscope. The oscilloscope traces were photographed with a Polaroid camera attachment. This observation technique was employed only for experiments with pure nitrous oxide and nitrous oxide - air mixtures since reactions were obtained only for these

16

gases. This apparatus functioned satisfactorily after some initial difficulties with drift in the transistor-zed amplifier were overcome. To prevent damage to the Kistler pressure transducer at high temperatures, a cooling mechanism was constructed to maintain it near ambient temperature.

Nitrogen and air at high pressures (up to 200 atmospheres) were obtained by using a 4000-pound per square inch compressor. To obtain high-pressure nitrogen, the gas was expanded from a standard commercial cylinder through a regulator to a large tank which was maintained at atmospheric pressure. Nitrogen from this tank was recompressed to 4000-pounds per square inch and was stored in a high-pressure tank from which the gas was taken for the experiments. Also the compressor was used to pump high-pressure air to a separate storage system.

The high-pressure nitrous oxide was produced by a liquefaction cycle using freon 22 as the refrigerant in the heat exchanger. Nitrous oxide was liquefied in a stainless steel tank containing the heat-exchanger coils and then drained into a stainless steel storage vessel located in a water bath. High-pressure nitrous oxide was obtained by raising the temperature of the liquid in the storage vessel above $98^{\circ}F$, the critical temperature, by means of electric heaters.
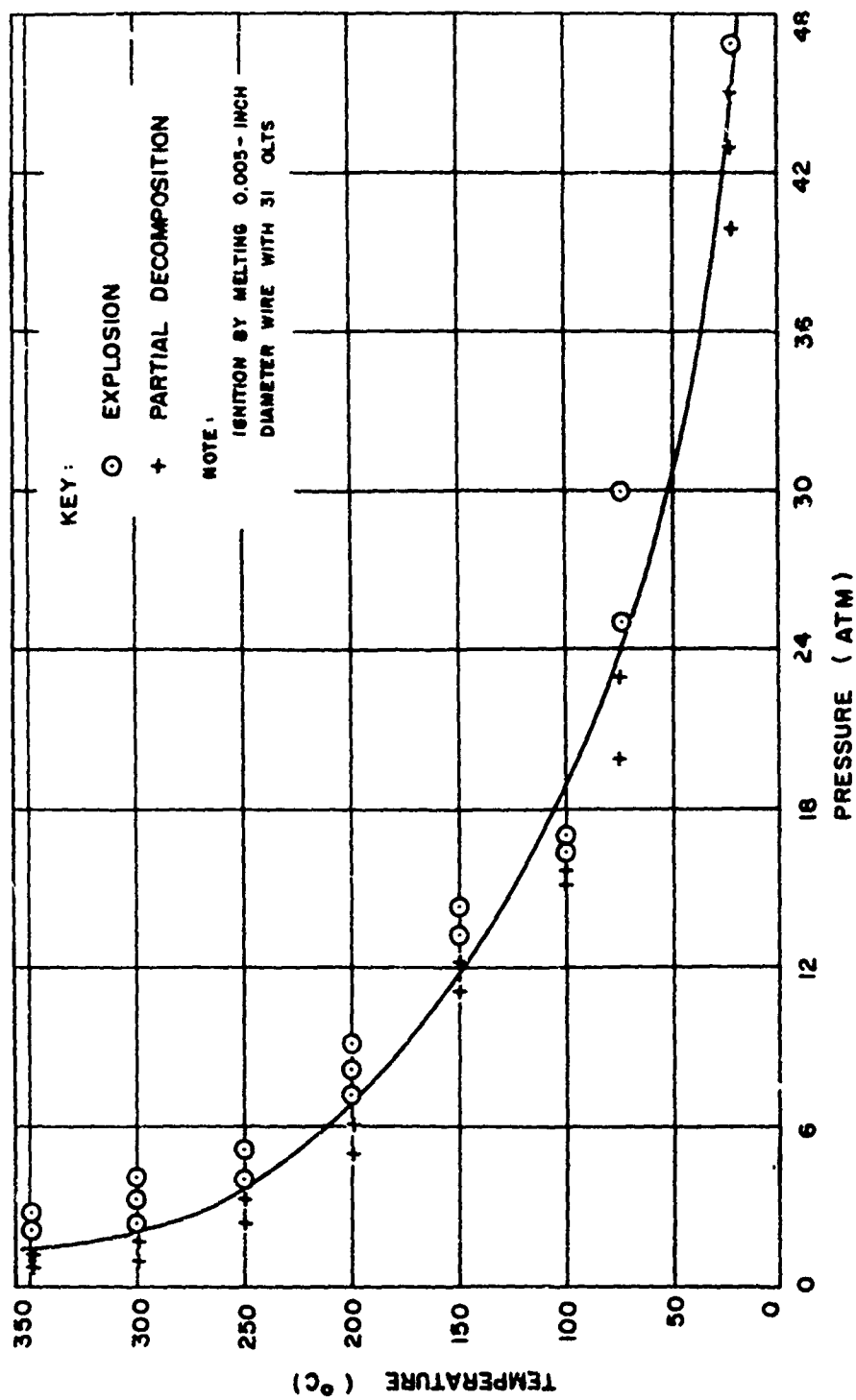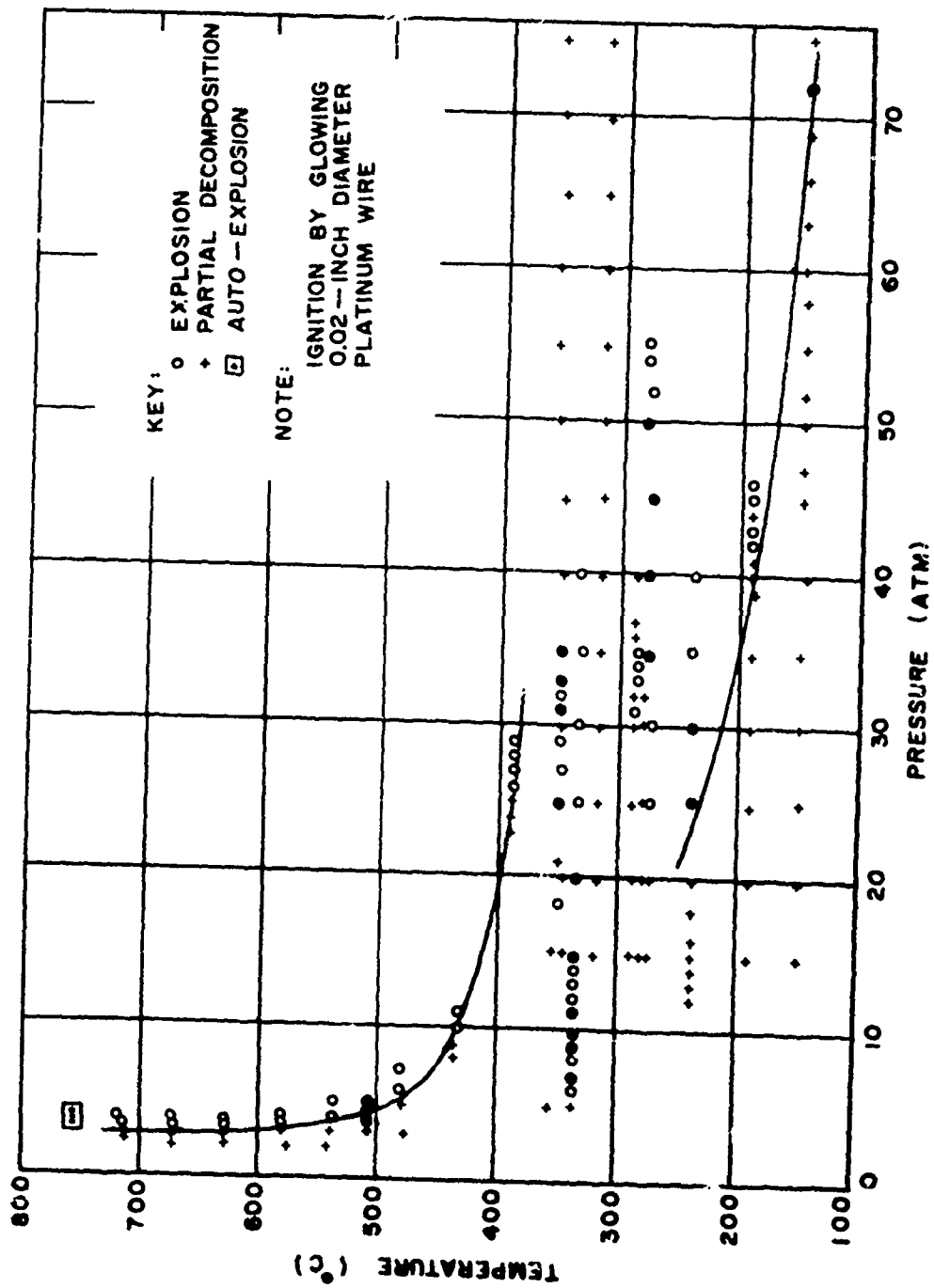
KEY:

⊙ EXPLOSION

+ PARTIAL DECOMPOSITION

NOTE:

IGNITION BY MELTING 0.005-INCH
DIAMETER WIRE WITH 31 OLTS

FIG. I   MEASURED EXPLOSION LIMITS OF N_2O

TEMPERATURE (°C)

PRESSURE (ATM)

18

FIG. 2   MEASURED EXPLOSION LIMITS OF N_2O

KEY: o EXPLOSION
      + PARTIAL DECOMPOSITION
      ☒ AUTO-EXPLOSION

NOTE: IGNITION BY GLOWING
       0.02-INCH DIAMETER
       PLATINUM WIRE

PRESSURE (ATM)

TEMPERATURE (°C)

19

N₂O

T = 745 °K

6 ATM

9 ATM

14 ATM

19 ATM

24 ATM

678
560
442
324
206
88

722
604
486
368
250
132

796
678
560
442
324
206

869
751
633
515
397
279

943

PRESSURE , (psia)

N₂O + 0.25 AIR

6 ATM

9 ATM

14 ATM

19 ATM

24 ATM

678
560
442
324
206
88

722
604
486
368
250
132

796
678
560
442
324
206

869
751
633
515
397
279

943
825

PRESSURE , (psia)

20
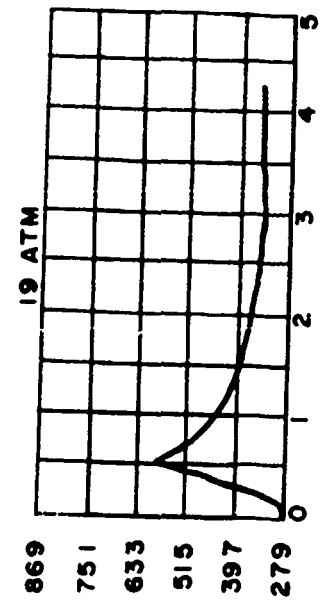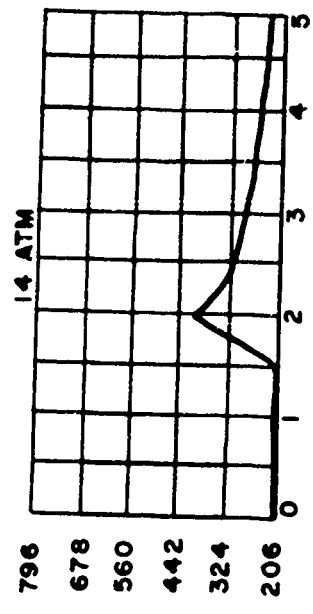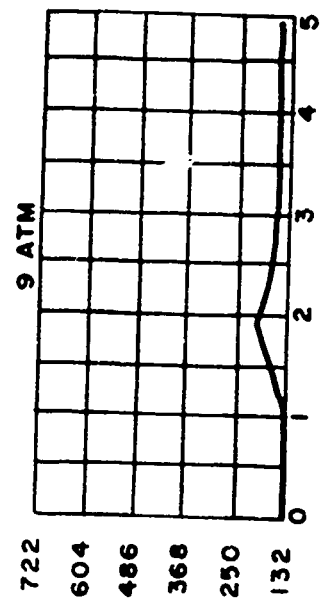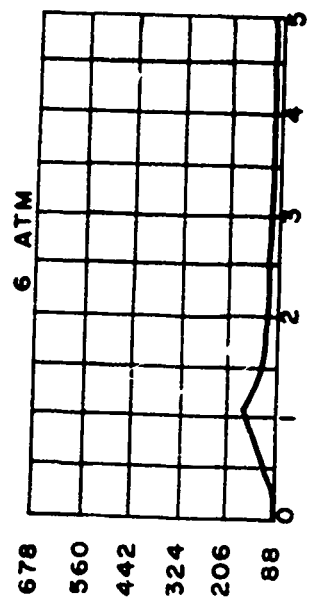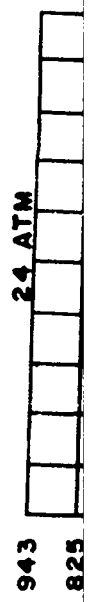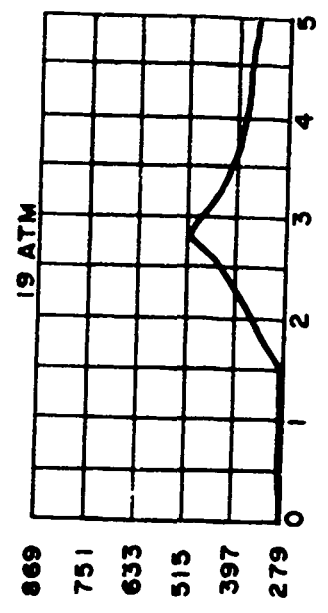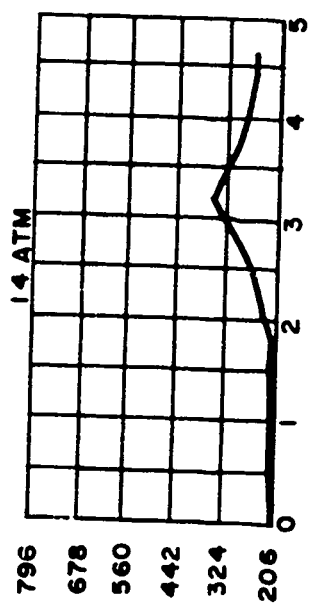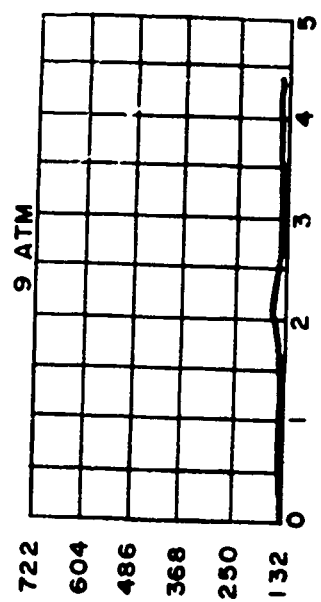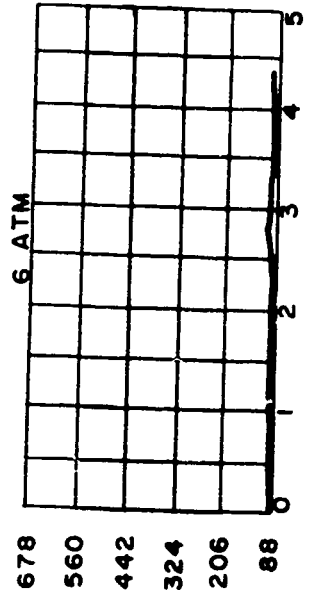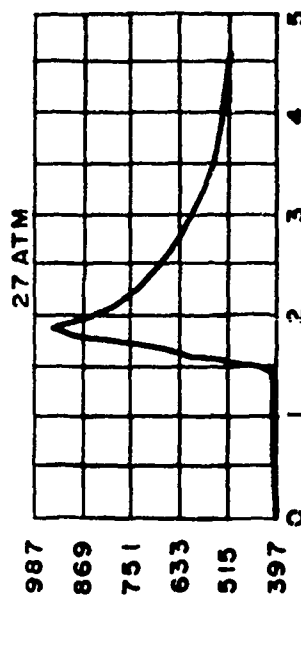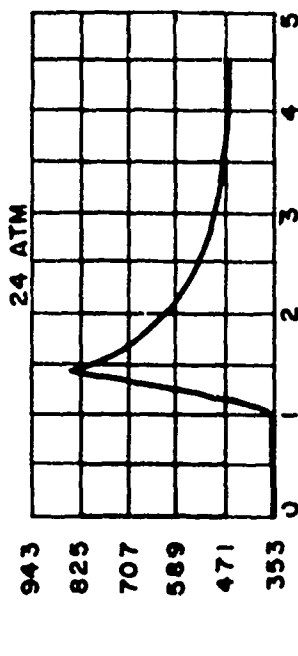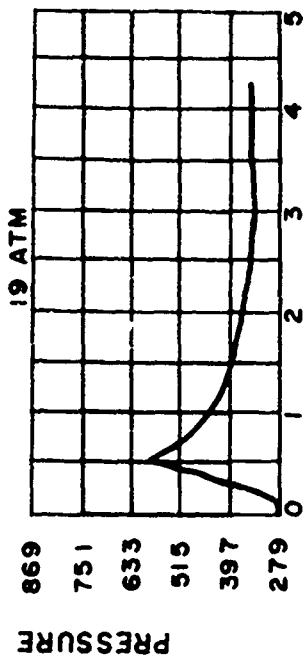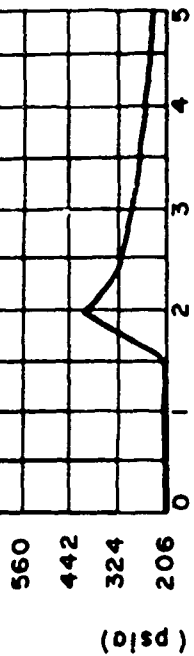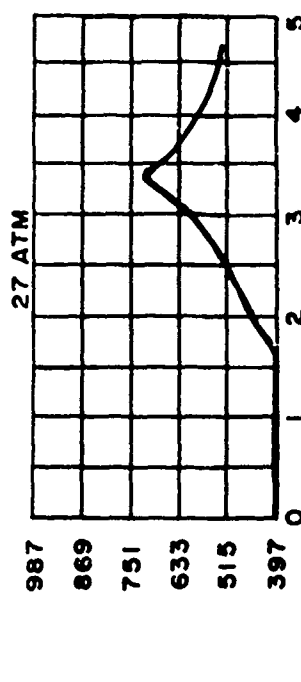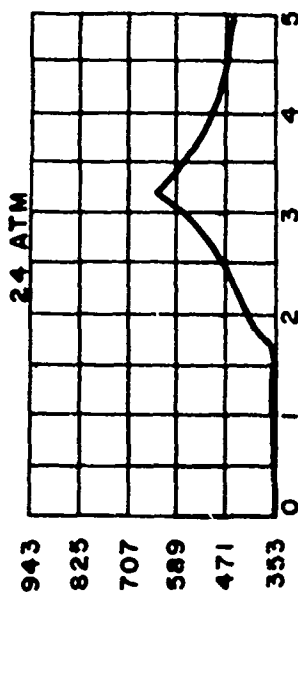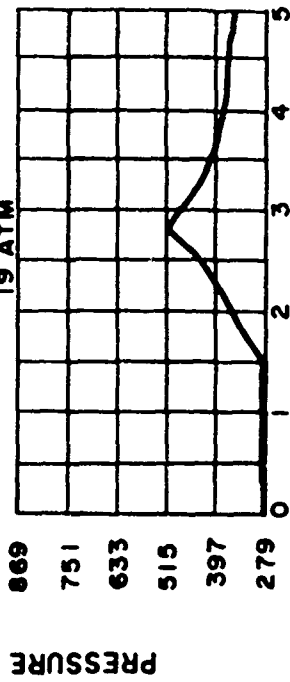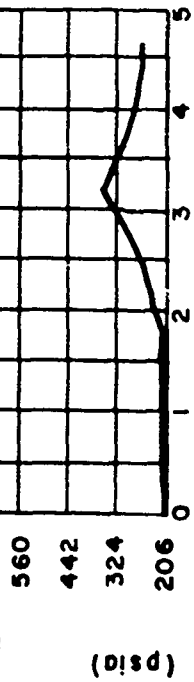
FIG.3 PRESSURE VS. TIME DIAGRAMS FOR DECOMPOSING N_2O AND $N_2O+0.25$ AIR

MIXTURE WITH FORCED IGNITION AT 745 °K

NOTE:
INITIAL PRESSURE IN ATM

N₂O
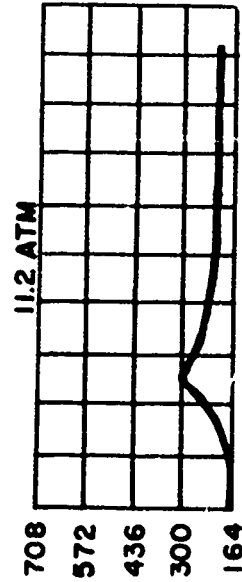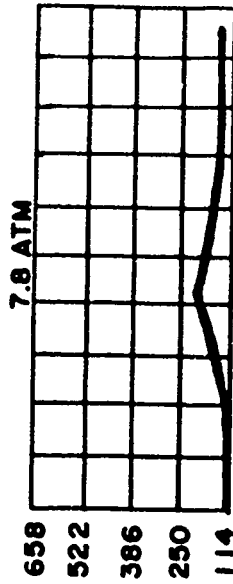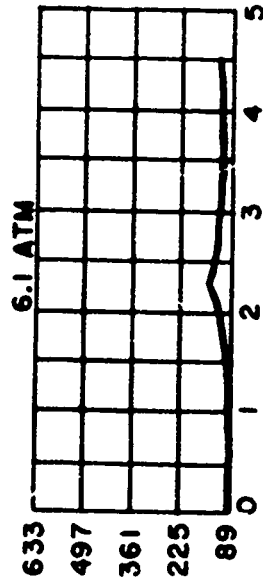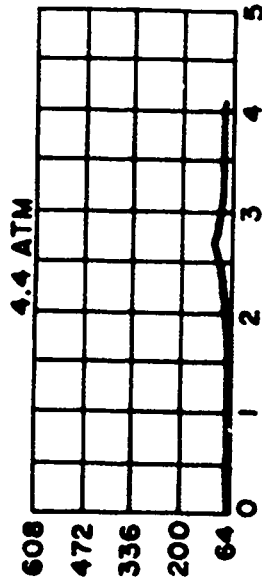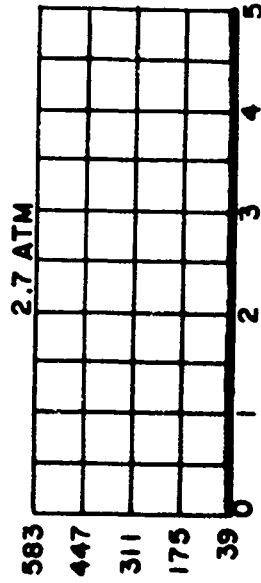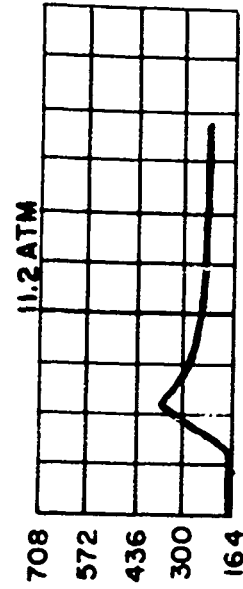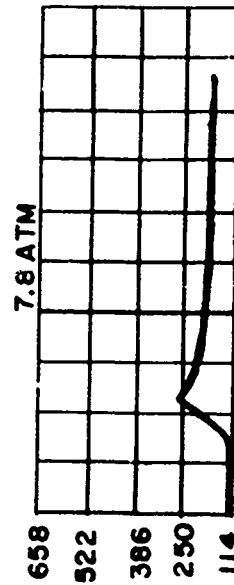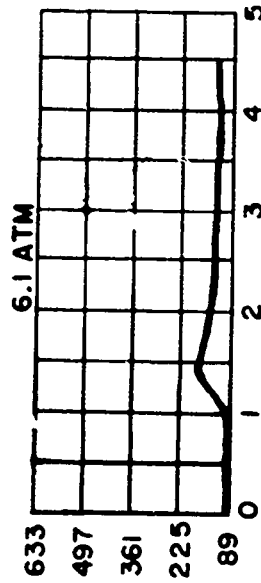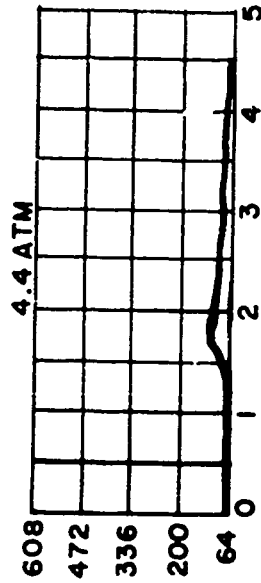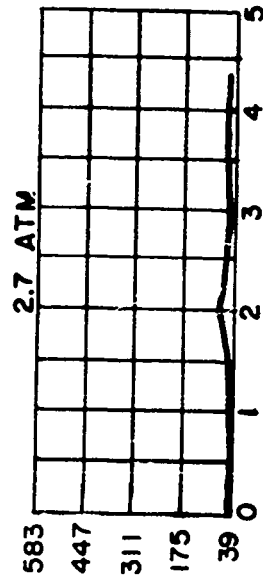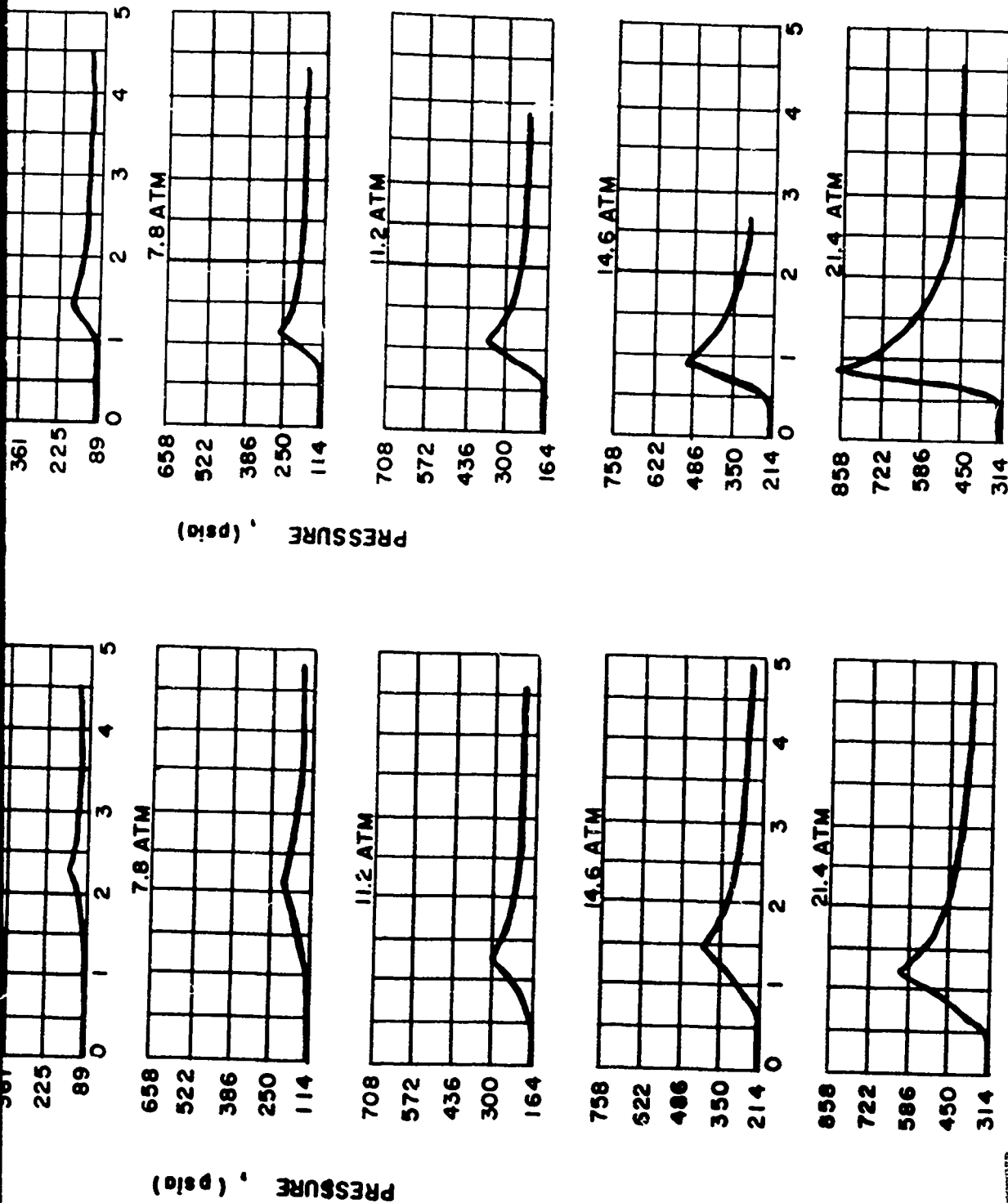
T = 830 °K

N₂O + 0.25 AIR

FIG. 4 PRESSURE VS. TIME DIAGRAMS FOR DECOMPOSING N_2O AND $N_2O + 0.25$ AIR MIXTURE WITH FORCED IGNITION AT 830 °K
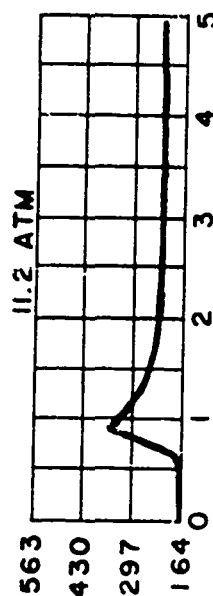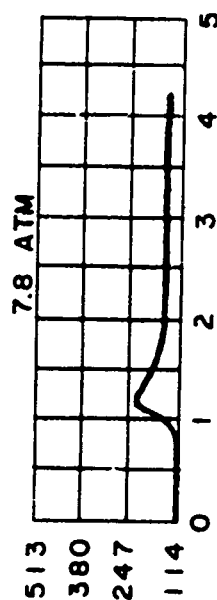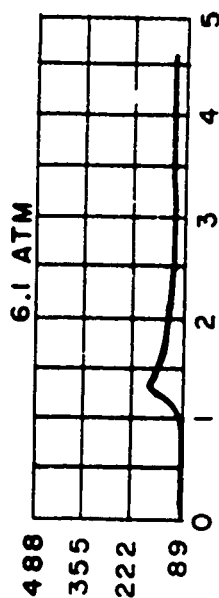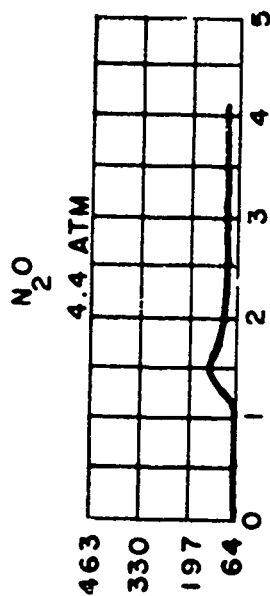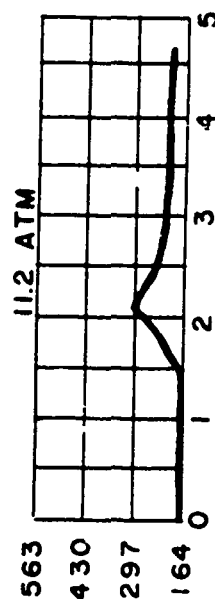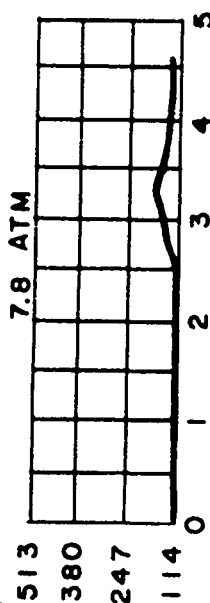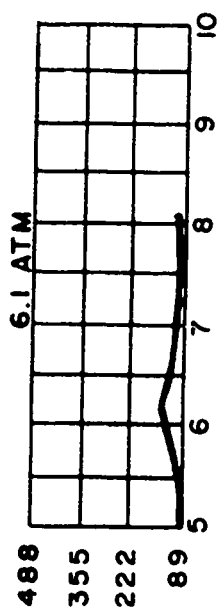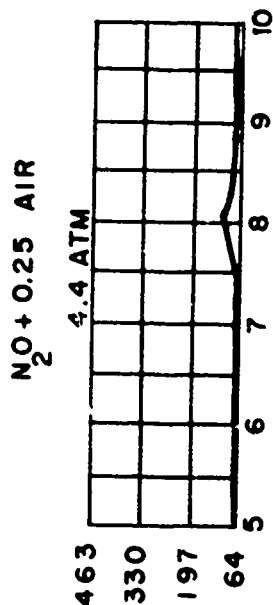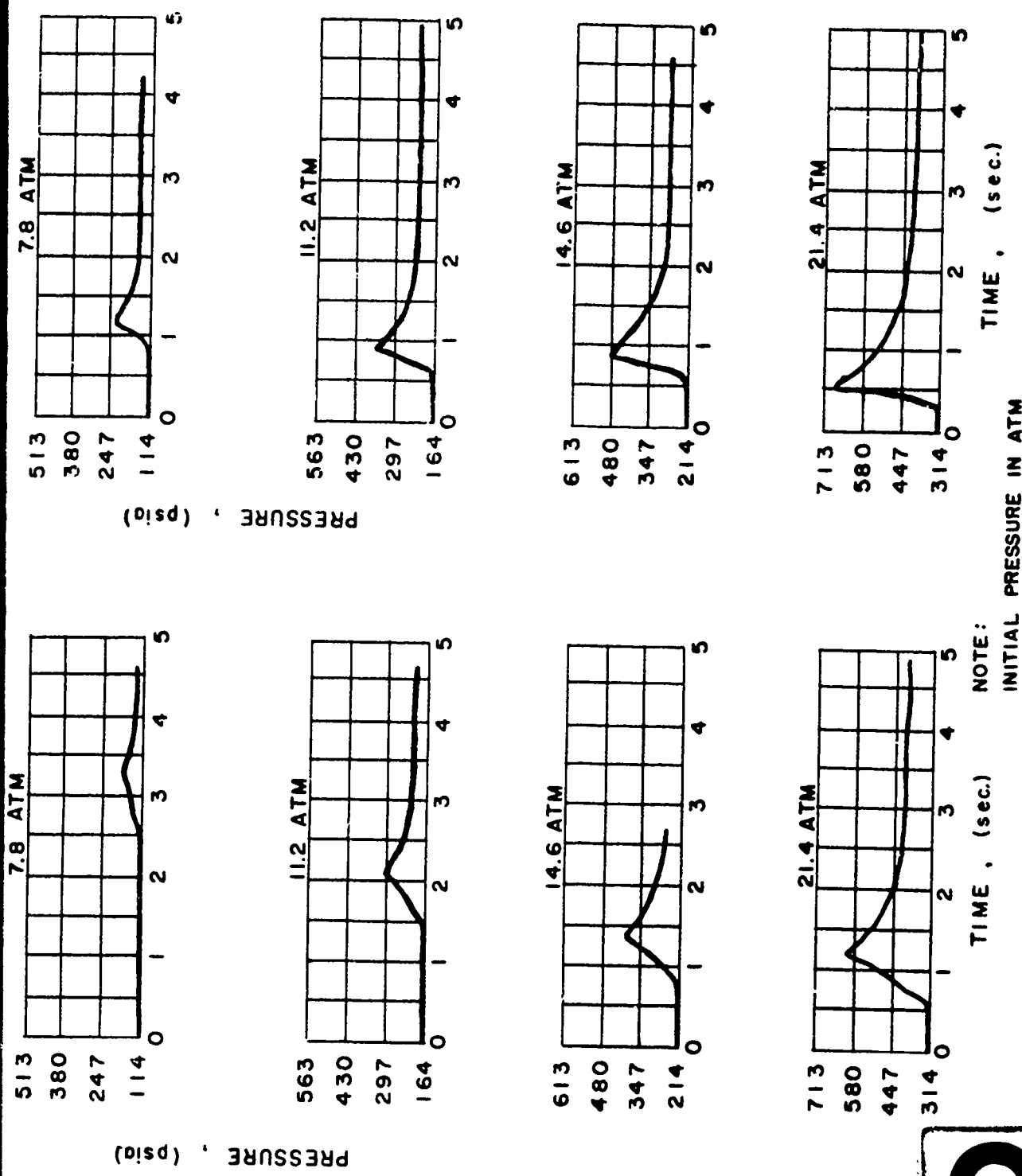
NOTE:
INITIAL PRESSURE IN ATM

T = 887 °K

N₂O

N₂O + 0.25 AIR

22

FIG. 5   PRESSURE VS. TIME DIAGRAMS FOR DECOMPOSING N_2O AND $N_2O + 0.25$ AIR
MIXTURE WITH FORCED IGNITION AT $°K$

NOTE:
INITIAL PRESSURE IN ATM

FIG. 6   PRESSURE   VS.   TIME   DIAGRAMS   FOR   DECOMPOSING N_2O

NOTE:

IGNITION BY GLOWING 0.02-INCH
DIAMETER PLATINUM WIRE

23
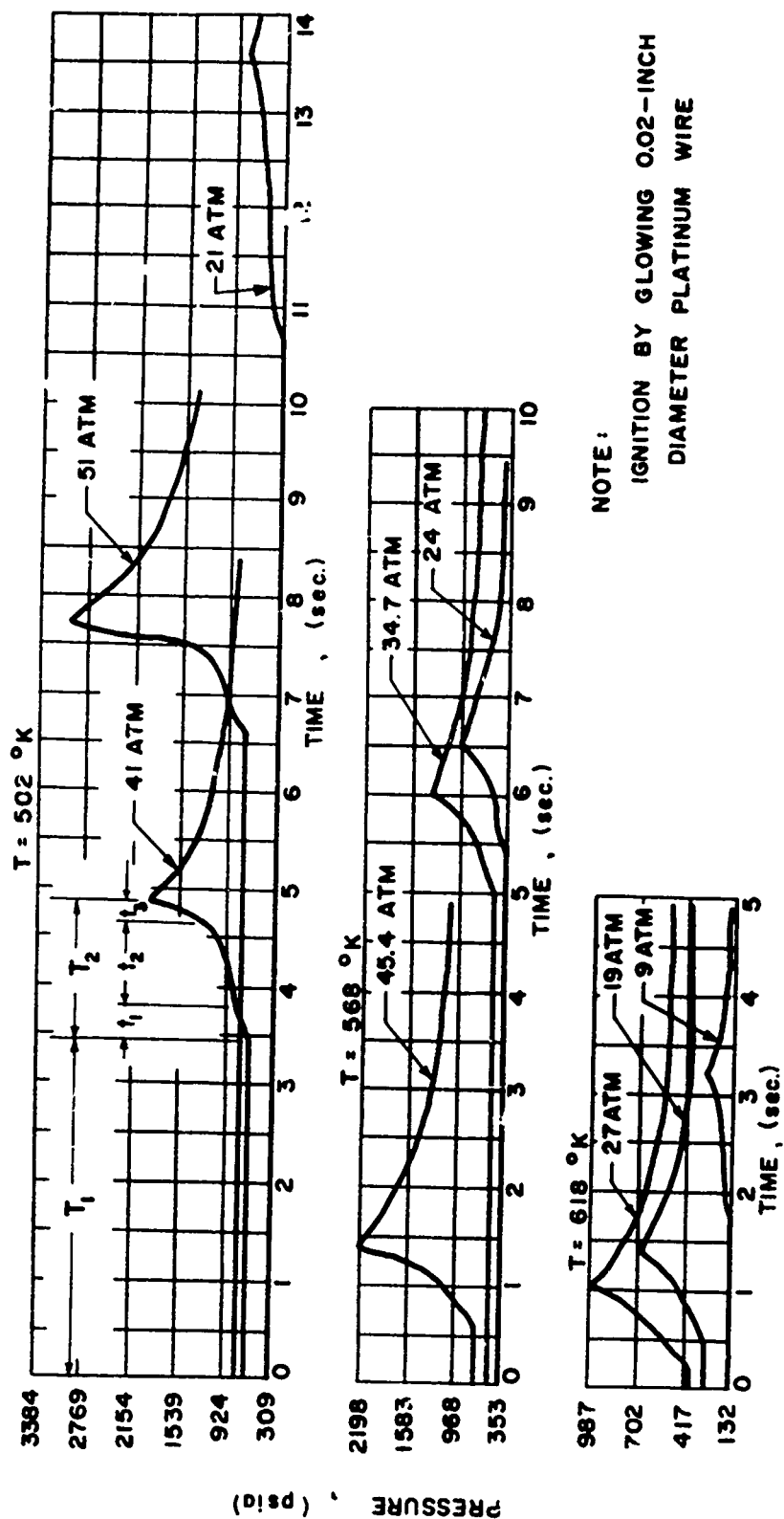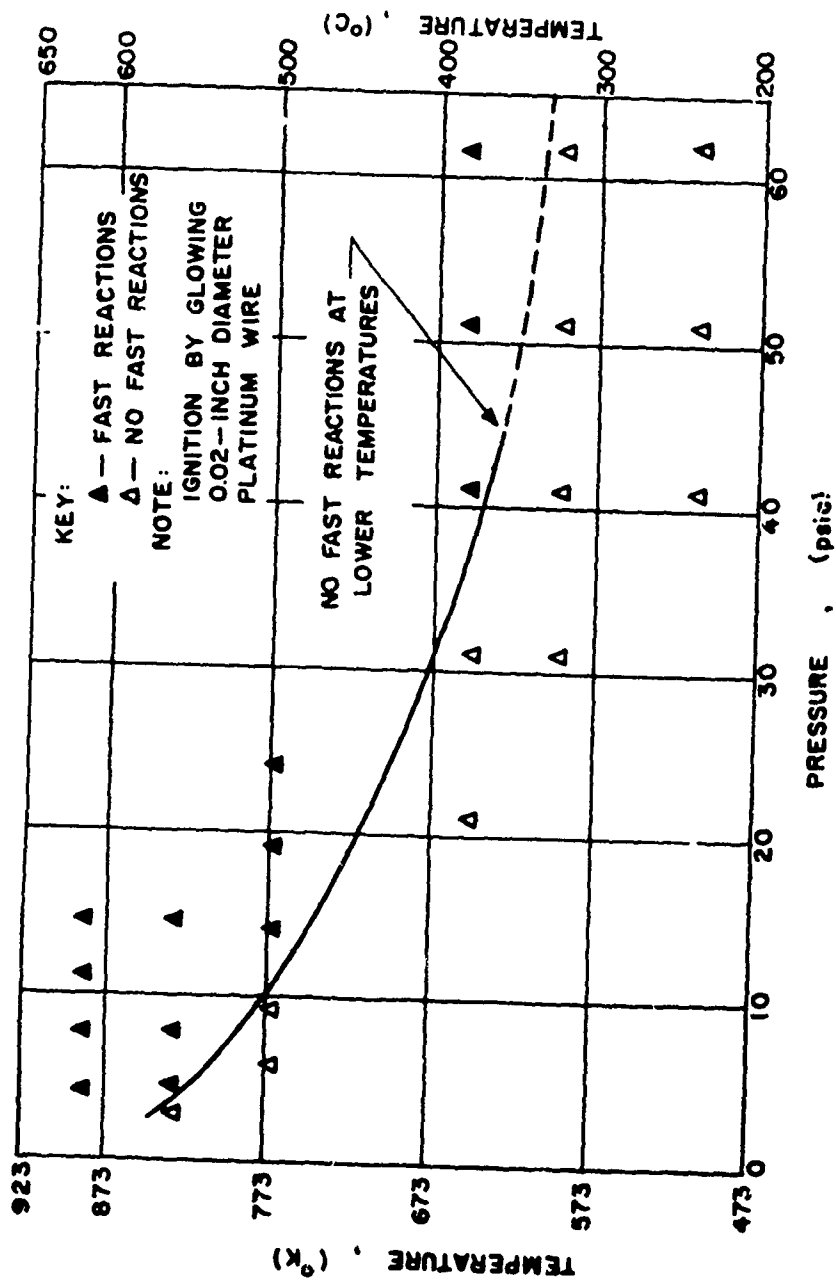
FIG.7   MEASURED IGNITION LIMITS OF $N_2O + 0.25$ AIR MIXTURE

KEY:
▲ — FAST REACTIONS
△ — NO FAST REACTIONS

NOTE:
IGNITION BY GLOWING
0.02—INCH DIAMETER
PLATINUM WIRE

NO FAST REACTIONS AT
LOWER TEMPERATURES

PRESSURE , (psig)

TEMPERATURE , (°C)

TEMPERATURE , (°K)

24

FIG. 8   PRESSURE VS. TIME DIAGRAMS FOR DECOMPOSING $N_2O + 0.25$ AIR
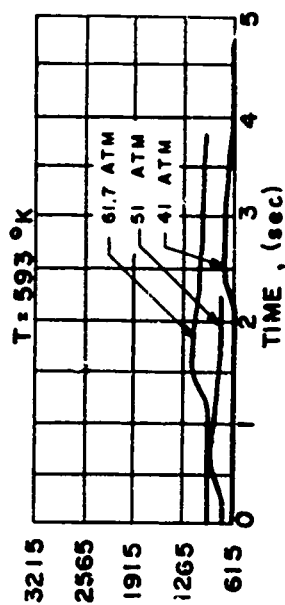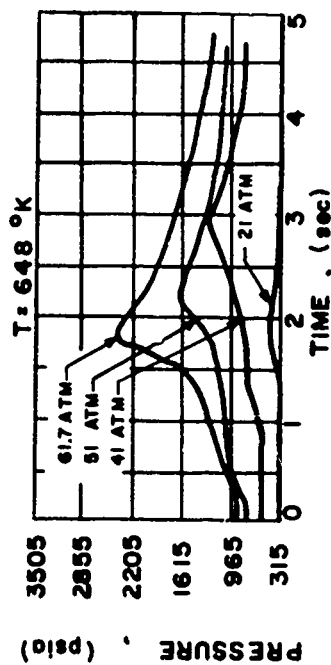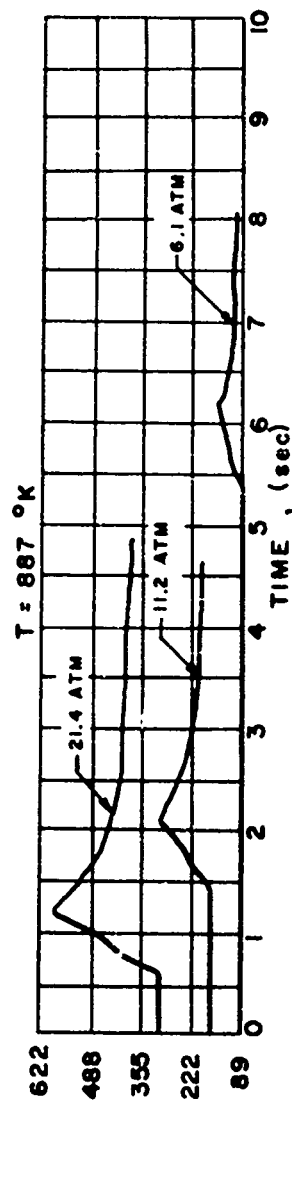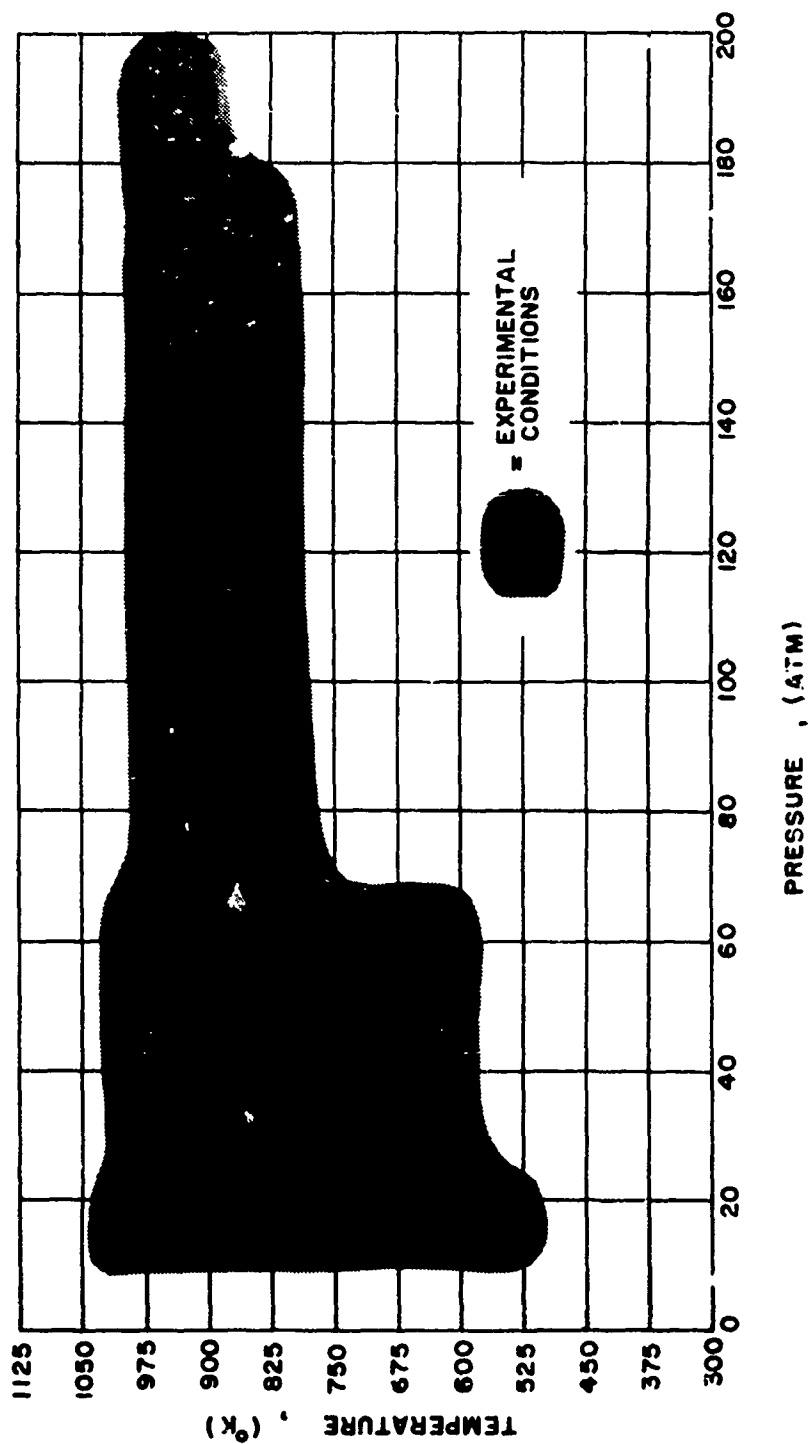
NOTE:
IGNITION BY GLOWING 0.02−INCH
DIAMETER PLATINUM WIRE

FIG. 9   PRESSURE –TEMPERATURE REGION OF EXPERIMENTS CONDUCTED WITH
$N_2O + 0.88 N_2$

PRESSURE , (ATM)

TEMPERATURE , (°K)

■ = EXPERIMENTAL
CONDITIONS
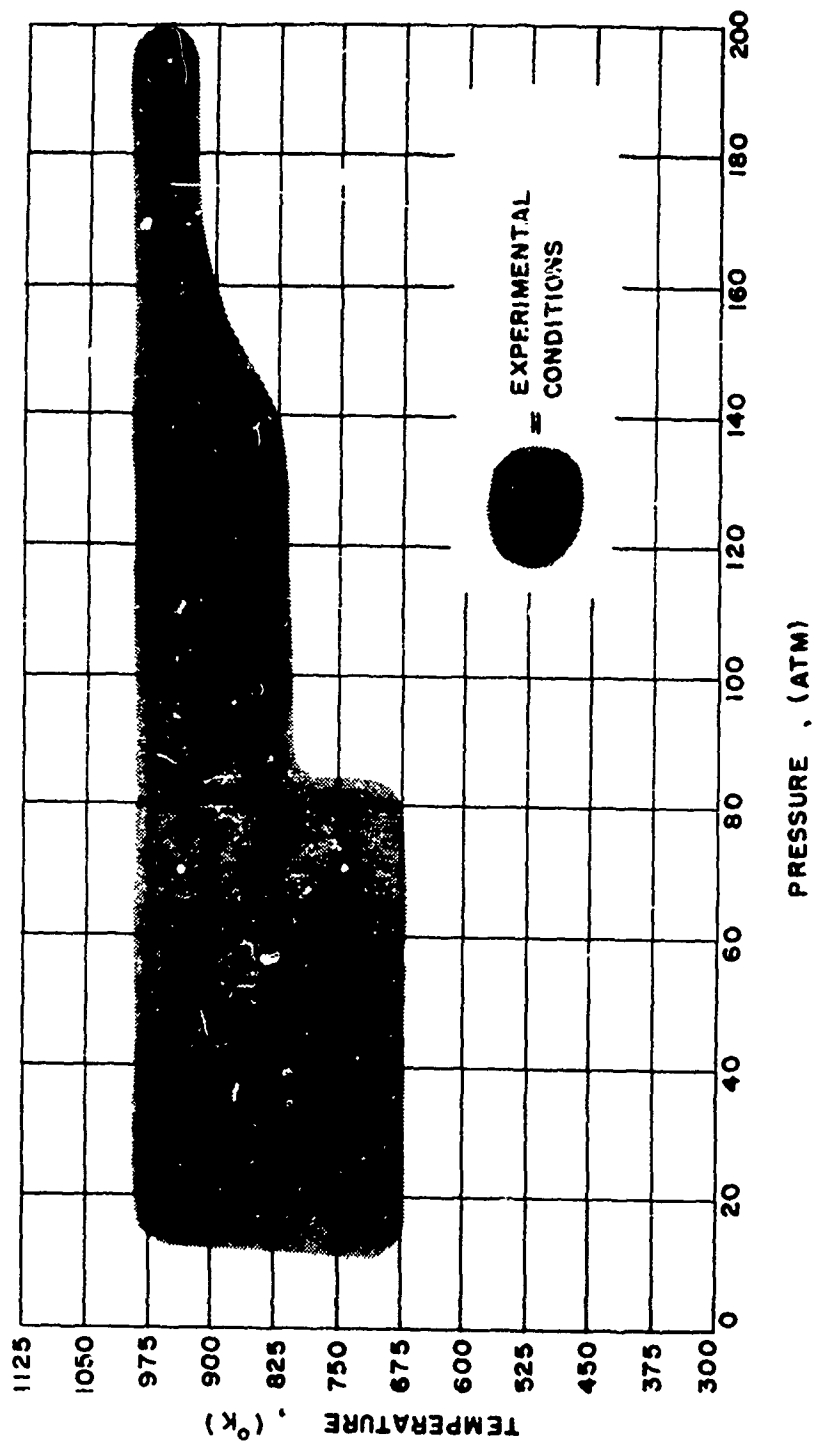
FIG. 10 PRESSURE – TEMPERATURE REGION OF EXPERIMENTS CONDUCTED WITH
$N_2O + 0.88N_2 + 0.50$ AIR

27

NOTE.
    ALL DIMENSIONS IN INCHES

IGNITOR TERMINAL
MODIFIED SPARK PLUG
NITROUS OXIDE
THERMOCOUPLE
COPPER O-RINGS
LID
IGNITOR WIRE
REACTION CHAMBER
1.50

$12\frac{1}{4}$

$4\frac{15}{16}$

$5\frac{1}{2}$
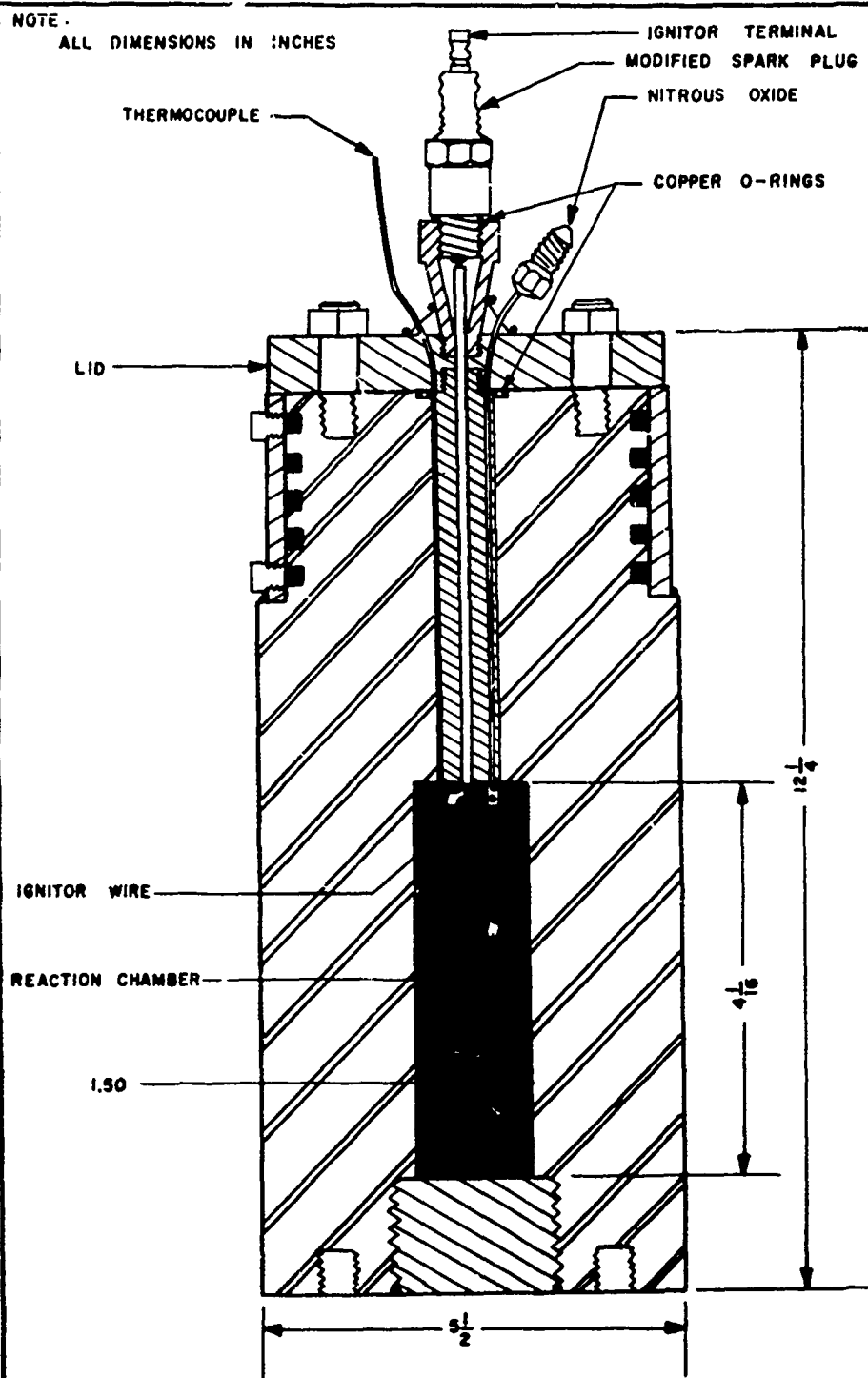
FIG. II   EXPLOSION   LIMIT   REACTION   VESSEL
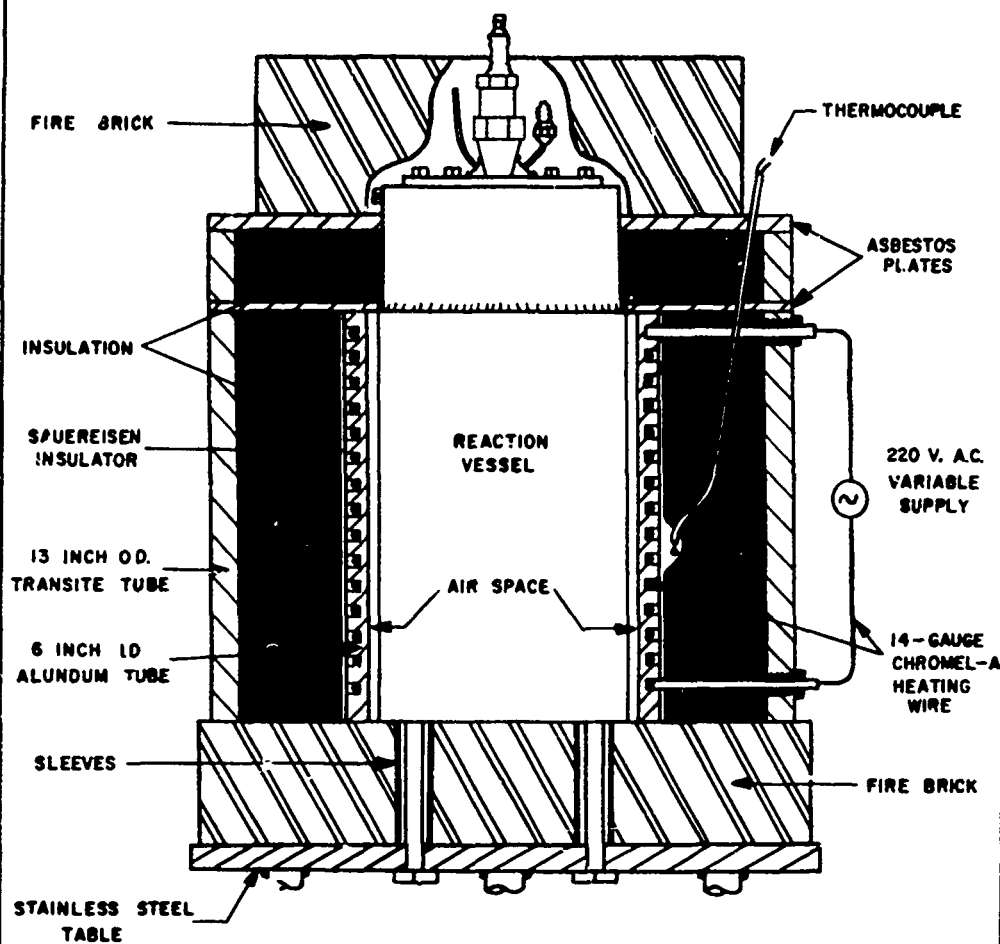
FIG. 12   REACTION VESSEL FOR NITROUS OXIDE EXPLOSION
LIMIT   MEASUREMENTS
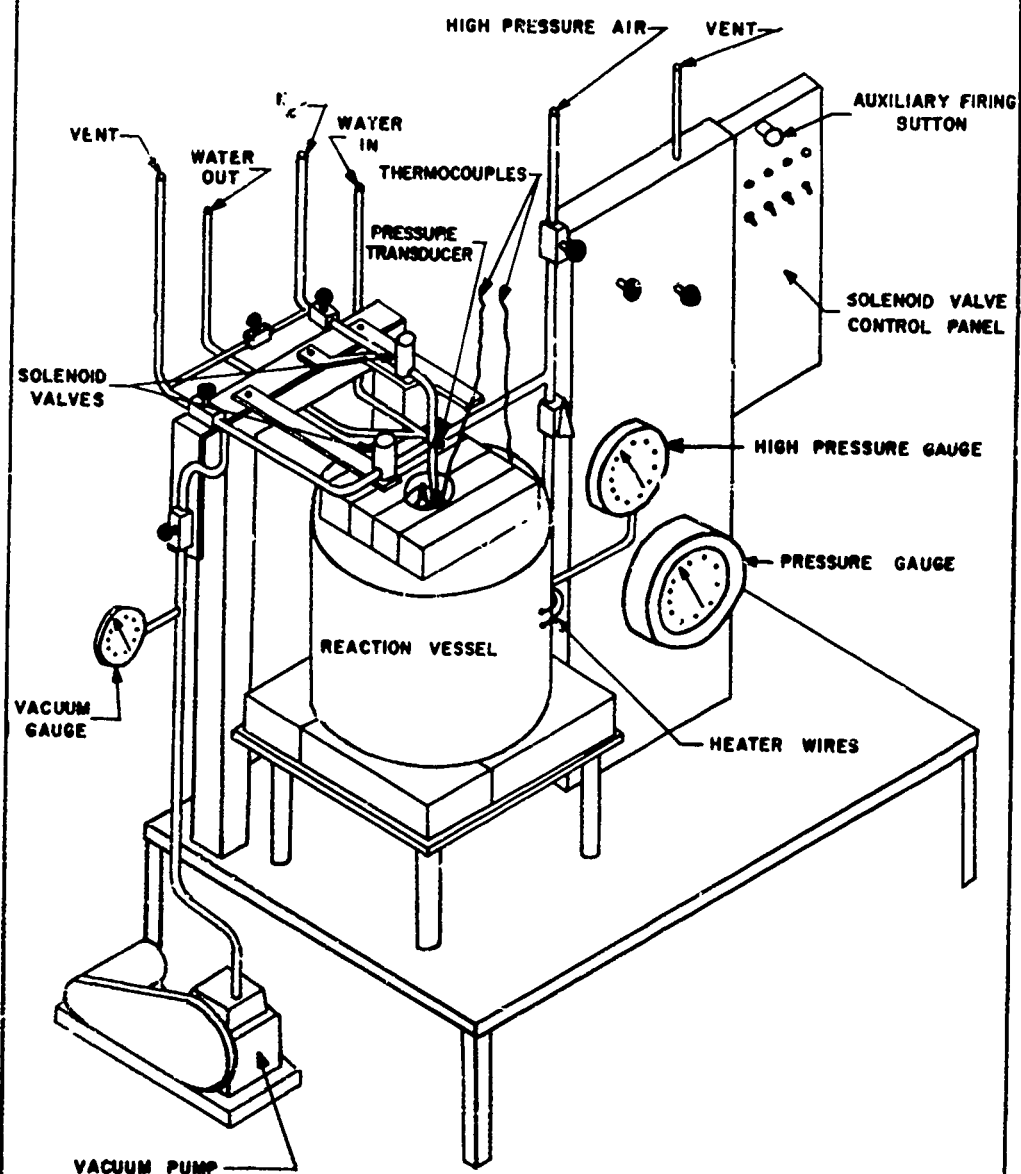
FIG.13 SCHEMATIC VIEW OF EXPERIMENTAL EXPLOSION LIMIT
EQUIPMENT

30
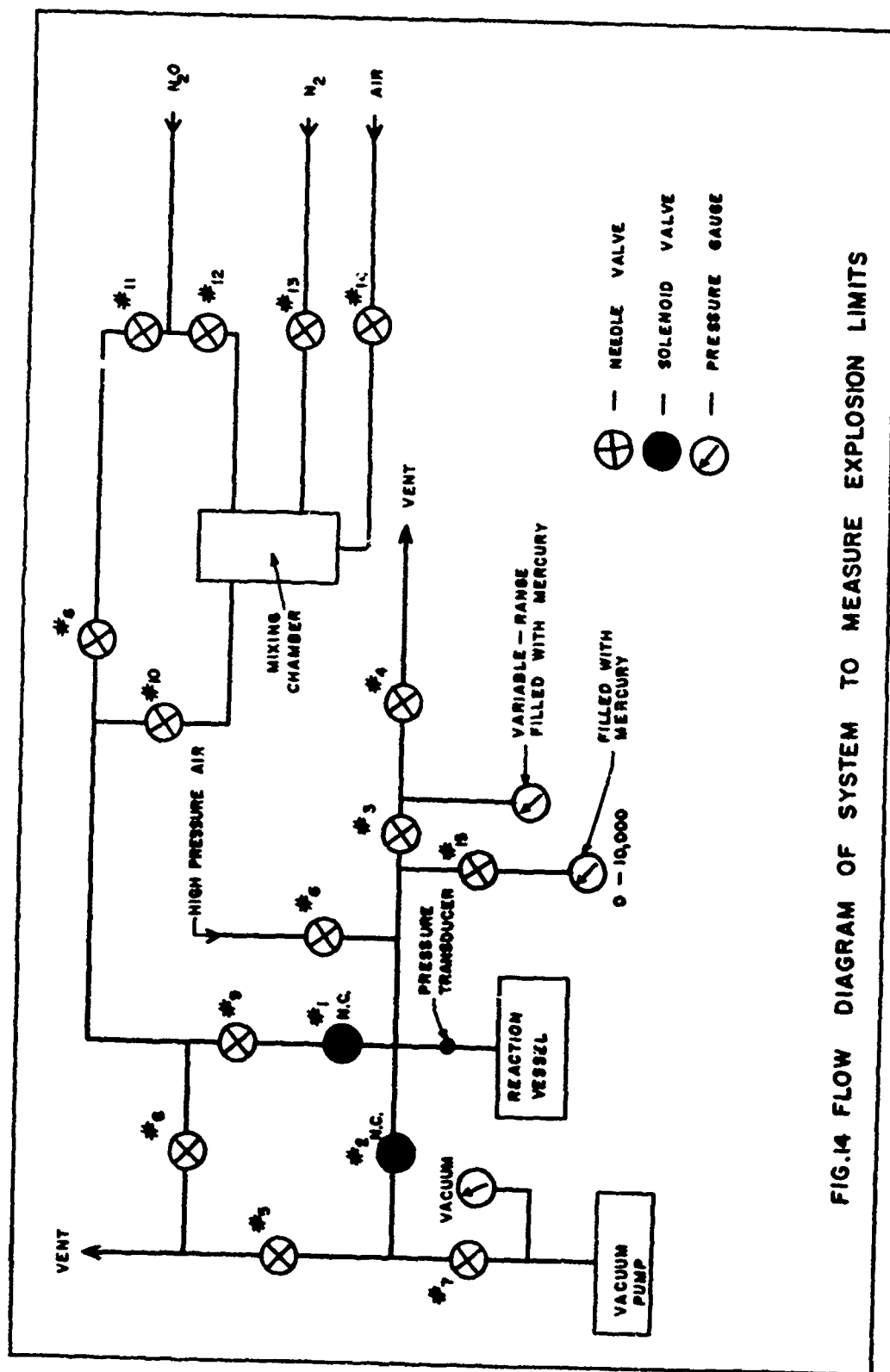
FIG.14 FLOW DIAGRAM OF SYSTEM TO MEASURE EXPLOSION LIMITS

FIG. 15 PHOTOGRAPH OF EXPERIMENTAL APPARATUS USED TO DETERMINE EXPLOSION LIMITS

Aeronautical Research Laboratories. Wright-Patterson AFB, Ohio EXPLOSION LIMIT STUDIES OF NITROUS OXIDE AND NITROUS OXIDE-NITROGEN-AIR MIXTURES TO 200 ATM. AND 1800°R by J.O. Krisjansons, Loren E. Bollinger. Rudolph Ohio State U. Columbus, O. September 1962. 31 p. incl illus. (Project 7065,Task 7065-01) (Contract AF 33(616)-5615) (ARL 62-431)
Unclassified Report

Explosion limits have been determined in a 117.5 cm³ cylindrical reaction chamber for pure nitrous oxide and mixtures consisting of $N_2O + 0.25$ AIR, $N_2O + 0.88N_2$ and $N_2O + 0.88N_2$, and $N_2O + 0.88N_2 + 0.50$ AIR. Two types of igniters were employed; an 0.005-inch copper wire was melted by applying 31 volts DC to its terminals and an
(over)

0.020-inch diameter platinum glow-wire was heated with approximately 210 watts AC. Results of these experiments are presented in the form of pressure-temperature explosion limit diagrams. The explosion limit curve for nitrous oxide follows an exponential path for both ignitors.