NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 3624

INVESTIGATION OF THE USE OF THE THERMAL DECOMPOSITION

OF NITROUS OXIDE TO PRODUCE HYPERSONIC FLOW OF A

GAS CLOSELY RESEMBLING AIR

By Alexander P. Sabol and John S. Evans
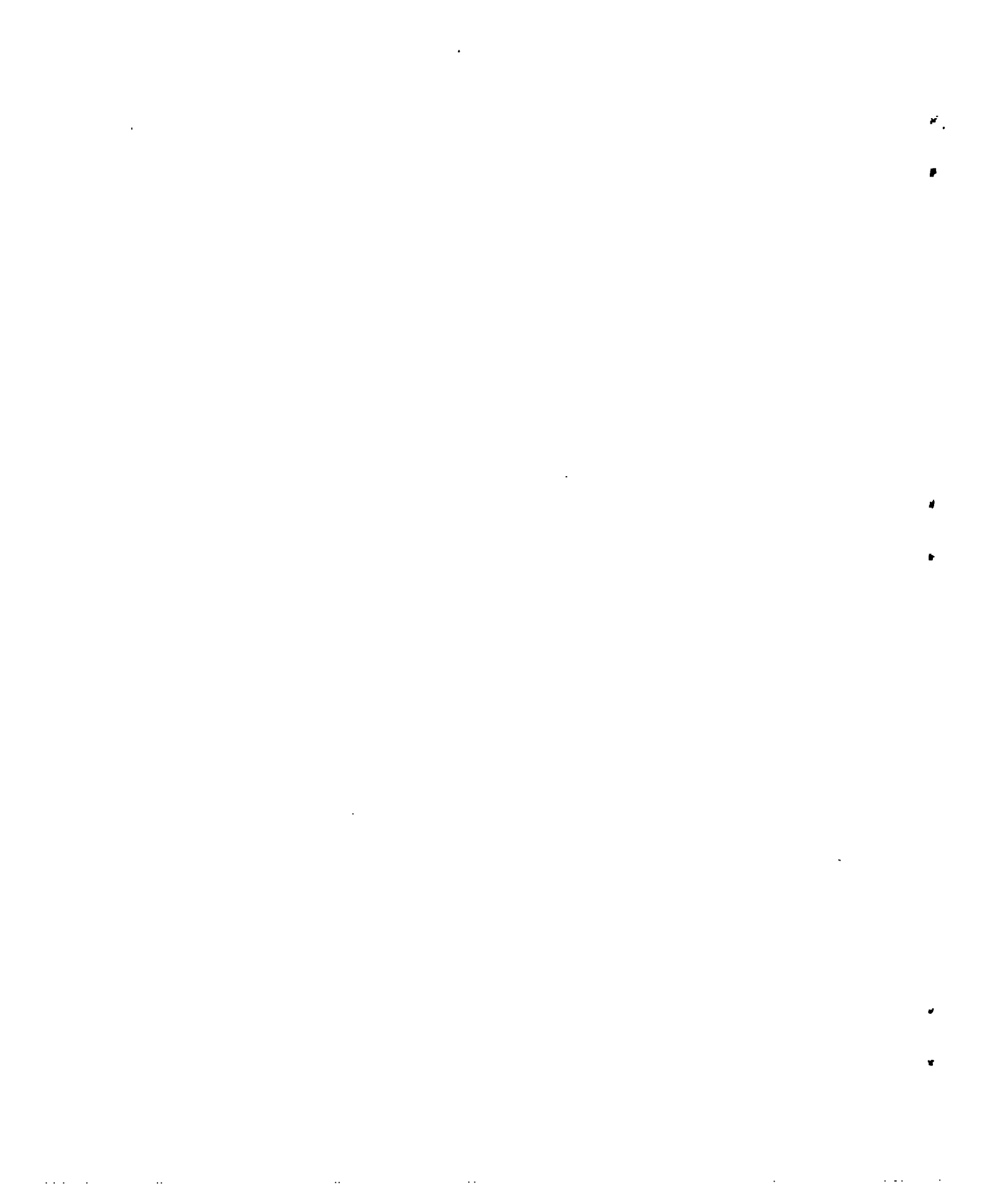
Langley Aeronautical Laboratory
Langley Field, Va.

NACA

Washington

March 1956

During the tests, measurements were made of the stagnation pressure
in the settling chamber and of the static pressures at 10 stations located
in a spiral fashion along the conical nozzle wall at intervals of approxi-
mately 6.4 millimeters. Measurements were also made of the preheat,
decomposition, and upstream stagnation temperatures. Chromel-alumel and
platinum—platinum-13-percent-rhodium thermocouples were used for this
purpose.

Flow comparison tests using constant-pressure decomposition.- Fig-
ure 9 shows the experimental static-pressure ratios obtained by operating
the nozzle with heated air at several stagnation conditions. The experi-
mental values are compared with a theoretical curve based on a one-
dimensional isentropic-flow expansion of a gas having $\gamma = 1.4$. In the
calculations of the curve, the geometric nozzle area at each pressure
station was assumed to be reduced by an amount corresponding to a reduc-
tion in diameter of twice the displacement thickness (ref. 11) because
of the growth of the boundary layer. The experimental points agree fairly
well with theory in the region extending from the throat to approximately
one-half the nozzle length. Farther downstream, flow separation (which
moves downstream as the ratio of the static pressure to the stagnation
pressure is increased) is a governing factor. (See ref. 12.) The
highest flow Mach number indicated by the ratio of the static pressure
to the upstream stagnation pressure is $M_2 = 6.9$. For this maximum flow
case, the Mach number of the flow at which the vapor pressure of H_2O
is reached is $M = 4.45$; for N_2, $M = 9.95$; and for O_2, $M = 9.51$.

Figure 10 shows the experimental static-pressure ratios obtained in
the hypersonic nozzle with decomposed and undecomposed N_2O gases. The
test results for decomposed N_2O are compared with the same theoretical
curve that was used in figure 9. The maximum decomposition pressure was
70 atmospheres. The results of the two tests of decomposed N_2O agree
with theory and show flow separation similar to that found when air was
used. The maximum flow Mach numbers upstream of the separated regions
in these two tests were 6.86 and 7.59.

Since $\gamma = 1.3$ for N_2O, the theoretical curve shown in figure 10
is suitable only for a qualitative comparison with the experimental
points obtained for undecomposed N_2O. (A new curve was not computed
because the tables of ref. 11 are restricted to $\gamma = 1.40$.) However,
consideration of the isentropic-flow equations shows that the static-
pressure ratios for $\gamma = 1.3$ should be larger than those for $\gamma = 1.4$.
The experimental data agree with this observation.

The experimental points for N_2O do not show the clearly defined
flow separation that was identified with the other curves. This estab-
lishes another difference between the undecomposed N_2O and the

Procedure and Tests

Air, decomposed N_2O, and undecomposed N_2O were tested in the same hypersonic nozzle to compare the nozzle pressure distribution obtained by use of the three different gases.

Apparatus and methods.- The hypersonic-nozzle apparatus, schematically shown in figure 8, consisted of a gas reservoir, a preheater, a stagnation chamber, and a nozzle which was connected to a vacuum pump through two low-pressure exhaust coolers. A conical ($6°$ $53'$ half-angle) stainless-steel nozzle was used which was 6.37 centimeters long and had a minimum nozzle diameter of 0.53 millimeter. The nozzle had an area ratio of 810:1 which corresponds to $M = 10.9$ for a gas having $\gamma = 1.4$. When the area ratio was corrected for boundary-layer growth, the allowable flow was reduced to $M = 8.65$.

The gases passed through the narrow, electrically heated, stainless-steel tubes of the preheater to attain temperatures as high as $728°$ K for N_2O and $963°$ K for air. For the case of air, the decomposition chamber shown in figure 8 was omitted so that the air passed directly from the preheater into the stagnation chamber, on to the nozzle, and exhausted at a low pressure through a water cooler. For the case of decomposed N_2O, the gas entered the decomposition chamber and was decomposed at constant pressure in the vicinity of the initiator which was momentarily heated at the start of the decomposition. The gases then passed through a layer of ceramic beads to aid in securing complete decomposition. Decomposition pressures up to 70 atmospheres were used. The decomposed gases then passed through the nozzle and exhausted through both a water cooler and an NO_2 trap cooled with dry ice. A sample of the decomposed gas was withdrawn downstream of the water cooler for chemical analysis. For tests using undecomposed N_2O, the same apparatus was used as for heated air.

Air was supplied to the preheater at controlled pressure from a reservoir maintained at room temperature. The measured water dewpoint of the air at atmospheric pressure was $205°$ K. The N_2O was taken directly from a commercially bottled supply. A high supply pressure of N_2O was maintained by immersing the bottles in hot water. The water dewpoint of the N_2O gas at atmospheric pressure had a measured value of $225°$ K. These values indicate that no appreciable effects due to condensation of water should be present in expansions up to about $M = 10$ (ref. 8, p. 1825).

NO, and N_2O. When such decomposition products are present in the medium of a hypersonic wind tunnel, the compounds NO and N_2O may condense in the stream at a higher temperature than is required for the condensation of oxygen. (See fig. 6.) Data for NO and N_2O in this figure were taken from reference 8.

Nitric oxide has the property of oxidizing at low temperatures to form NO_2; but, because of the long time required for the oxidation, as compared with the time of flow through the nozzle and test section, NO_2 should not be present in the test section (ref. 9). The effects of the heat addition to the flow due to condensation of NO and N_2O in a hypersonic stream can be calculated by the method of reference 10.

The results of a calculation of the effect of NO condensation on a flow at $M_2 = 14$ with $T_t = 1,700^\circ$ K are given in the following table. The effect at $M_2 = 10$ and $T_t = 1,700^\circ$ K was negligible.

M_2	Amount of NO condensed, percent of total gases present	p_3/p_2	M_3
14	1.0	1.18	12.85
14	10.0	2.56	8.75

The results of a similar calculation for N_2O are

M_2	Amount of N_2O condensed, percent of total gases present	p_3/p_2	M_3
10	1.0	1.11	9.5
10	10.0	1.24	6.92
14	1.0	2.07	12.55
14	10.0	3.04	8.00

These calculations show that the presence of even a small amount of NO or N_2O can seriously affect the operation of a tunnel when the operating conditions are such that condensation of these substances can occur.

isentropic expansion in the chamber after decomposition) as

$$t = \frac{2V}{(\gamma - 1)zA_1a_t}\left[\left(\frac{T_t}{T_{t'}}\right)^{1/2} - 1\right]$$

where T_t is the initial stagnation temperature in the chamber and $T_{t'}$ is the minimum permissible stagnation temperature in the chamber.

For typical test conditions when it is assumed arbitrarily that a 10-percent drop in initial stagnation temperature is the maximum tolerable decrease and that the end temperature is limited by the condensation criteria of figure 7, the running times for typical test conditions are

M_2	$p_{t'}$, atm	$T_{t'}$, ^{o}K	$T_t = \frac{10}{9}T_{t'}$	Running time, sec
10	200	1,110	1,230	0.11
10	2,000	1,280	1,420	.10
14	200	1,880	2,090	.42
14	2,000	2,120	2,360	.40

These calculations were based on $\gamma = 1.4$ and on arbitrarily selected values of M_2 and $p_{t'}$, with no allowance for the drop in peak pressure and temperature due to heat losses (fig. 2). Furthermore, for the calculations, the stagnation-chamber volume has been assumed to be 28.32 liters (1.0 cubic foot) and the area of the test section to be 929.0 square centimeters (1.0 square foot). Similar calculations using the experimentally obtained temperature of $1,859^o$ K and pressure of 1,465 atmospheres (see table II) show that a nozzle could be operated at a flow Mach number of $M = 13$ (maximum) for 0.30 second. Other schemes - such as a throttled flow in order to extend the running time - could be employed for venting the hot confined gases of a constant-volume decomposition to a nozzle.

Condensation effects of NO and N_2O.- Results of chemical analyses show incomplete decomposition of N_2O for both the constant-volume and the constant-pressure processes. At the high reaction temperatures, incomplete decomposition yields gaseous mixtures consisting of N_2, O_2,

Test results.- The results of the constant-pressure tests are given
in table III. They indicate that N$_2$O can be decomposed at elevated
pressures in a self-sustained manner and that the onset of decomposition
is accompanied by a sharp rise in temperature which is, however, smaller
than that predicted by theory. Decomposition was obtained during these
tests at pressures up to 37.4 atmospheres. The highest observed tempera-
ture was 1,726° K and can be compared with a theoretical value of 2,165° K
based on an initial temperature before decomposition of 550° K. The
chemical analysis showed that, in these tests, the decomposition was not
so complete as in the constant-volume tests and that the secondary prod-
uct, NO$_2$, was present in considerable quantities. Table III shows the
reaction temperatures obtained at various operating pressures and mass-
flow ratios and also the typical chemical compositions of the decomposed
mixture.

<center>APPLICATION OF N$_2$O DECOMPOSITION TO HYPERSONIC FLOW</center>

<center>Theoretical Discussion</center>

Stagnation conditions required for hypersonic wind tunnels using
air.- When the appropriate stagnation conditions are not maintained in
a hypersonic wind tunnel, condensation can occur in the test section
because of the large flow expansions. Condensation conditions can be
avoided by maintaining the partial pressures of oxygen and nitrogen in
the test section below their vapor pressures. (The relationship of the
partial pressure of oxygen to the temperature, obtained from ref. 7, is
shown in fig. 6.) The necessary upstream stagnation conditions can then
be computed by using the isentropic-flow equations. Figure 7 shows the
stagnation requirements where the partial pressure of oxygen was assumed
to be 21.2 percent of the air pressure.

Use of constant-volume decomposition.- Since the composition of the
products of the N$_2$O decomposition resembles air, either a constant-
volume or a constant-pressure process can be substituted for a heated-
air supply and applied to the operation of a hypersonic nozzle. The
application of the former process is examined theoretically for the case
of complete decomposition. The application of the constant-pressure
decomposition is considered experimentally and will be described subse-
quently. For the constant-volume decomposition, the reactor can be used
as the settling chamber and the gases vented directly through the nozzle.
Because of the fixed stagnation-chamber volume, the stagnation pressure
and temperature drop continually during operation as the remaining gases
expand and cool. The running time (in seconds) can be expressed (assuming

loading density used, the amounts of NO_2 and N_2O present were 0.43 percent and 2.24 percent, respectively.

Constant-Pressure Decomposition

A constant-pressure decomposition has been produced at approximately atmospheric pressure by Whittingham (ref. 4), who observed the reaction in a quartz tube electrically heated to about $1,173^\circ$ K. Although he did not report the occurrence of a self-sustained reaction, the quantity of heat released during decomposition suggested that it could take place. Experiments were performed to ascertain whether the reaction could be self-sustained and whether it could occur at elevated pressures as well as at atmospheric pressure.

Theoretical conditions.- The complete thermal decomposition of N_2O into molecules of nitrogen and oxygen is accompanied by 20,000 cal/mole of heat released (ref. 1). This heat is sufficient to raise the temperature of the final gas mixture from 300° K to $1,964^\circ$ K in a constant-pressure decomposition. (See appendix A.)

Apparatus and test procedure.- The constant-pressure N_2O decomposition apparatus used is schematically shown in figure 5. It consisted of a steel tube which enclosed a gas preheater, a decomposition chamber, and an exit orifice. The preheater, a 61-centimeter-long brass tube with an inside diameter of 1.9 centimeters, was electrically heated with Nichrome V wire. The chamber had an inside diameter of 3.8 centimeters and was 20 centimeters long; it contained a 0.3-centimeter-thick ceramic liner. Nitrous oxide was drawn at a controlled pressure from an unheated reservoir and led into the preheater where the gas temperature was brought up to a value below the initiating temperature (which was found to be about 750° K in the range of pressures used). The preheated gas impinged on the electrically heated initiator in the decomposition chamber, about which a steady decomposition took place once started. In order to avoid burning out the heater wire wrapped about the initiator, the current was shut off immediately after decomposition began. The reaction zone was prevented from entering the preheater by two perforated insulators, one made of brass and the other made of pressed asbestos. The initiation was accompanied by a noticeable rise in the stream temperature, and the decomposition maintained the initiator at an elevated temperature. The gas temperatures were measured at various stations in the reactor by use of platinum—platinum-13-percent-rhodium and chromel-alumel thermocouples. The gas passed from the reactor into the atmosphere through the orifice. The mass flow was altered by using orifices of different sizes. For the larger mass flows, decomposition took place only on the downstream side of the initiator. The mass flow was calculated from the observed pressure and temperature near the exit orifice and the nominal area of the orifice. A sample of the gas was taken at the exit.

The results show that the decomposition of N_2O at constant volume
can be initiated by either an electrically fused copper wire or a
heated wire to yield a nitrogen-oxygen mixture at a high temperature
and pressure. Typical records of the reaction-pressure time history
are shown in figure 2. The peak pressures were obtained from such
curves and they are plotted for the "cold wall" tests in figure 3 and
for the "hot wall" tests in figure 4. The terms "cold wall" and "hot
wall" refer to initial reactor wall temperatures which are, respectively,
below and above the critical temperature of N_2O. The peak pressure
obtained for hot-wall tests was 1,930 atmospheres. The peak reaction
temperatures were determined from equation (1) (corrected) by use of
measured values of peak pressure and loading density. Tables I and II
show the peak reaction pressures obtained for various loading densities
and the resulting peak temperatures. The chemical analyses of the products
of representative tests are shown.

When there was no initial N_2O condensation because of the low
loading densities, the peak pressures increased with the loading density
as predicted. However, in the cold-wall tests at higher loading densi-
ties, the peak pressure rise failed to correspond to theory (eq. (1)
corrected). For these tests the chemical analysis of the final gas
mixture showed the presence of a large proportion of undecomposed N_2O.
(See table I.) In all tests the measured pressures were lower than the
theoretical pressures. For example, figure 4 shows that at a loading
density of 5.3 g-moles/liter the peak pressure was 1,465 atmospheres as
compared with the theoretical value of 2,080 atmospheres. The loss in
pressure is attributed to incomplete decomposition and to heat losses
due to convection and radiation. A comparison of tests made with the
two types of initiators showed no observable difference in the results.
(See table II.)

The highest observed temperature for the cold-wall tests was
$1,504^\circ$ K where the initial temperature before decomposition was 283° K.
For this case, theory indicates a peak temperature of $2,429^\circ$ K. In the
hot-wall tests, the maximum observed value of the peak temperature
was $1,859^\circ$ K for an initial temperature of 361° K. Theory indicated a
temperature of $2,507^\circ$ K.

A chemical analysis of the cooled, decomposed gas mixture from the
hot-wall tests showed 1.83 percent NO_2 and 21.1 percent N_2O present
by volume at the smallest loading density used. (In addition to N_2 and
O_2, a small amount of NO was formed in the decomposition. This oxidized
to NO_2 when the mixture cooled.) As the loading density increased, the
decomposition became more complete and the amounts of NO_2 and N_2O
present in the final nitrogen-oxygen mixture decreased. At the largest

metal-to-metal seal, (2) a head piece with a neoprene rubber "O" ring
in addition to a screw pressure-loaded copper ring, (3) an electrical
lead which contained a Teflon element designed to obtain a gas seal by
the internal gas pressure acting on an unsupported area of the plastic,
and (4) all lubricants removed, and commercial gland packings in all
valves replaced by similarly shaped packing made of Teflon. (Teflon
was used because of its nearly total chemical inertness.)

In order to remove any condensed water vapor from the reactor
chamber and prepare it for testing, the air in the chamber was evacuated
while hot water was circulated through the jacket. Cold water (at a
temperature of approximately 280° K) was then used to lower the wall
temperature in order to facilitate filling the reactor from a small
portable N_2O reservoir. The portable reservoir was weighed before
and after each filling to determine the amount of N_2O used in the
test. A loading density of 10.22 g-moles/liter would completely fill
the reactor with liquid N_2O if the temperature were raised to the
critical value (T = 309.8° K). The water temperature was then altered
to suit the test conditions. Sufficient time was allowed for the reactor
temperature to equalize with that of the water. Thus, the reactor tem-
perature before decomposition began was obtained from measurements of
the water temperature.

The decomposition process was initiated by either heating or fusing
a wire initiator. The heated wire initiator consisted of approximately
75 centimeters of Brown and Sharpe No. 22 gage Nichrome V wire. The
wire was supported by a mica slab and was electrically grounded inside
the reactor. An electric current of 13 amperes at 80 to 85 a-c volts
was applied to this element for 20 seconds during a test. The fused wire
initiator was made from 0.25 centimeters of Brown and Sharpe No. 36 gage
copper wire which was fused by applying current at 110 a-c volts at the
time of test.

During the tests, the gas pressure in the reactor was measured by
use of a Baldwin SR-4 strain gage. The cell was joined in a vertical
position to the base of the reactor, and the connecting tubing was
filled with mercury to help transmit rapid pressure changes to the
pressure cell and to reduce the dead space in the reactor. The pressure
history of the decomposition was recorded on photographic film by a
recording oscillograph. Approximately 1 minute after initiation, the
gas mixture was vented from the reactor to the atmosphere and a sample
of the gas mixture was obtained for chemical analysis. The method of
chemical analysis used is explained in appendix B.

Test results.- The results of the constant-volume-decomposition
tests are shown in tables I and II for two initial wall temperatures.

Constant-Volume Decomposition

The results of the tests given in references 1, 2, and 4 indicate the possibility that the high pressures and temperatures which are required for hypersonic wind tunnels may be obtained by the rapid thermal decomposition of N_2O at constant volume. Some of the tests show that the decomposition can be nearly complete, in which case the properties of the decomposed nitrogen-oxygen mixture would approximate the properties of air. Experiments were performed to determine the temperature of the reaction products and to obtain more information about their chemical composition.

Theoretical conditions.- The ideal temperature and pressure of the products of the constant-volume reaction can be readily computed from available data and are used as a basis for comparison with the experimental results. The heat released by the complete thermal decomposition of N_2O, given in reference 1 as 20,000 calories/mole, can raise the temperature of the final mixture from $300°$ K to $2,448°$ K. (See appendix A.) Since this temperature is independent of the amount of N_2O used, the final pressure computed by the perfect gas law is directly proportional to the initial pressure or to the gas density in the reactor; thus,

$$p_f = \left(\frac{3T_f}{2T_i}\right)p_i = \left(\frac{3RT_f}{2}\right)\rho_i \qquad (1)$$

where ρ_i is the weight of charge divided by the volume of the reactor (in g-moles/liter), $R = 0.08207$ liter-atm/$°$K, and $T_f = 2,448°$ K when $T_i = 300°$ K. The value of p_f given by equation (1) is too low and must be corrected by multiplying it by the compressibility factor (refs. 5 and 6).

Apparatus and test procedure.- The constant-volume reactor is shown in figure 1. It consisted of a high-pressure steel chamber fitted with an exterior water jacket, a removable headpiece, and a gas inlet. The headpiece contained an insulated electrical lead and an opening for pressure instrumentation. The internal volume of the chamber was 0.45 liter, 2.0 percent of which was contained in a portion of the gas-inlet tubing and a valve. The reactor was designed for a maximum working pressure of 2,000 atmospheres. The internal surfaces, including the threads on the headpiece, were chromium plated to prevent corrosion.

Four types of closures were used with the reactor. They were as follows: (1) connecting tubing with a standard cone-shaped

t'   minimum stagnation conditions upstream

1   nozzle minimum section

2   test section before condensation

3   test section after condensation

Chemical symbols:

CO_2 carbon dioxide

H   hydrogen

H_2O water

KOH   potassium hydroxide

N   nitrogen

NO   nitric oxide

NO_2 nitrogen dioxide

N_2O nitrous oxide

O   oxygen

Conversion factor:

1.0 g-mole per liter of N_2O = 2.747 lb/cu ft of N_2O

TESTS

In an attempt to verify and extend the available information on the thermal decomposition of nitrous oxide, experimental observations were made of the decomposition at both constant volume and constant pressure. The principal interest was in the conditions necessary to initiate rapid reactions, in the temperature and pressure of the products, and in the chemical composition of the products. On the basis of the results obtained, a hypersonic nozzle was constructed and was operated to compare the use of air and the products of the thermal decomposition of N_2O as flow mediums.

SYMBOLS

A	area
a	velocity of sound
B	arbitrary constant (see appendix B)
b,c,d,e, f,g,i	arbitrary constants (see appendix B)
M	Mach number
h	enthalpy
p	pressure
R	universal gas constant
T	temperature
t	time
u	internal energy
V	settling-chamber volume
z	constant, $\left(\dfrac{2}{\gamma + 1}\right)^{\frac{\gamma+1}{2(\gamma-1)}} = 0.57870$ (for $\gamma = 1.4$)
γ	ratio of specific heat at constant pressure to specific heat at constant volume, 1.4 for a diatomic molecule
Δ	incremental amount
ρ	density

Subscripts:

i	before decomposition
f	after decomposition
t	stagnation conditions upstream

A summary of the conclusions drawn from the examination of the literature on the thermal decomposition of N_2O is as follows:

(1) Nitrous oxide can be made to decompose within a confined volume or to decompose in a steady stream by heating it to a temperature of the order of 1,000° K.

(2) An explosive reaction can be produced by local heating of the confined gas, such as is produced by a spark following the electrical fusion of a wire, by introducing the gas into a preheated vessel or by rapid compression.

(3) The explosion limit apparently is a function of temperature and pressure.

(4) Under certain conditions, the decomposition is approximately complete.

(5) The temperature and pressure of the reaction products rise sharply during a rapid constant-volume decomposition but these quantities have not been measured.

(6) A self-sustained constant-pressure decomposition of N_2O has not been reported.

(7) The continuous decomposition of N_2O has been reported only for a reactor operating at atmospheric pressure.

In an attempt to evaluate the feasibility of applying the decomposition of N_2O to the operation of a hypersonic wind tunnel, an exploratory program of research was carried out. The objectives were as follows:

(1) To verify and extend the available information on the thermal decomposition of nitrous oxide

(2) To determine the theoretical and experimental end conditions of constant-volume and constant-pressure decompositions and to consider the application of these decompositions to the operation of a hypersonic nozzle

(3) To design and construct a small hypersonic nozzle based on the information obtained and, for comparison purposes, to operate it on both heated air and decomposed nitrous oxide

the thermal decomposition of which is governed by the equation

$$2N_2O \rightarrow 2N_2 + O_2 + Heat$$
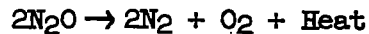
was selected for study because of the relative ease with which it could be decomposed and because the ratio of N_2 to O_2 in the decomposition products (2:1) is closer to the ratio of N_2 to O_2 in air (4:1) than is the ratio of the decomposition products of NO (1:1).

The thermal decomposition of nitrous oxide has been studied by a number of investigators. Of particular interest in the application of nitrous-oxide decomposition in hypersonic wind tunnels are results of investigations conducted at rapid reaction rates. Several methods were found to produce such decompositions. In their study of the heat of formation of N_2O, Carlton-Sutton, Ambler, and Williams obtained rapid constant-volume decompositions that were accompanied by an increase in both temperature and pressure of the gas (ref. 1). They reported that a mild explosion can be caused in N_2O gas by the electrical fusion of a small wire. However, the reaction is not propagated in the gas when the initial gas pressure is below 13 atmospheres. Chemical analysis of reactions initiated at approximately 42 atmospheres indicated 90- to 95-percent decomposition. Hunter accidently produced explosions in N_2O at initial pressures between 40 and 70 atmospheres (ref. 2). In his investigations of reaction rates, the gas was introduced into a reinforced quartz tube preheated to approximately 930° K. In working with low gas pressures, Zeldovich and Jacovlev produced explosive reactions in N_2O when it was confined in a quartz tube heated to temperatures between 1,100° to 1,300° K (ref. 3). Another means of initiating the rapid decomposition of N_2O was found by Berthelot who rapidly compressed N_2O gas to 1/500 of its original volume. (This experiment is mentioned in ref. 1.) Under such conditions, the ideal adiabatic temperature of compression causing the reaction was calculated to be approximately 1,860° K.

The continuous decomposition of N_2O at constant pressure (approximately atmospheric) in an electrically heated quartz tube was demonstrated by Whittingham (ref. 4). In his experiments, the decomposition was controlled to produce a luminous glow similar to a flame. In order to obtain a steady decomposition, the rate of flow was adjusted in the tube (which was 3 centimeters in diameter and 20 centimeters long) to give a time of contact of about 1 second. As the tube was heated to 1,023° K, the brown color of other nitrogen oxides was visible in the exit gases. A pale yellow-green luminescence appeared in the tube at about 1,123° K and a vivid luminescence at about 1,173° K.

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INVESTIGATION OF THE USE OF THE THERMAL DECOMPOSITION

OF NITROUS OXIDE TO PRODUCE HYPERSONIC FLOW OF A

GAS CLOSELY RESEMBLING AIR

By Alexander P. Sabol and John S. Evans

SUMMARY

An investigation was made of a method for producing hypersonic flow in a wind tunnel by using the hot gaseous products obtained from the thermal decomposition of nitrous oxide (N_2O). Tests are described of N_2O decompositions made at constant volume and at constant pressure. Decomposition temperatures up to $1,859°$ K $(3,346°$ R) at pressures up to $1,930$ atmospheres were obtained by the constant-volume process, whereas theory indicated a temperature of $2,507°$ K $(4,510°$ R). Temperatures up to $1,726°$ K $(3,107°$ R) at pressures up to 70 atmospheres were obtained by the constant-pressure process, whereas theory indicated a temperature of $2,165°$ K $(3,898°$ R). Results of comparison tests made in a divergent conical nozzle operated at Mach numbers up to about 7 on air and on the products of N_2O decomposed at constant pressure showed no significant difference in the wall static pressures.

INTRODUCTION

One requirement of wind tunnels operating at very high supersonic Mach numbers is a high stagnation temperature in order to avoid adverse effects due to oxygen or nitrogen condensation. The temperature range of electrical heaters, which are generally used for this purpose, is limited because of material properties. In an attempt to obtain higher temperatures, chemical energy obtained from rocket fuels burned within a settling or mixing chamber has been used by some investigators. Since high-temperature air obtained in this way is contaminated with the products of combustion, the characteristics of the gas are not those of air.

In order to avoid heater limitations and flow-contamination problems, the use of chemical energy obtained from the decomposition of either NO (nitric oxide) or N_2O (nitrous oxide), both of which contain only nitrogen and oxygen, appeared suitable for heating purposes. The compound N_2O,

decomposed N_2O. The absence of visible separation can probably be attributed to the smaller difference in upstream stagnation pressure and exhaust stagnation pressure required for a given area change where a gas having $\gamma = 1.3$ is substituted for one having $\gamma = 1.4$. For these tests the stagnation-pressure ratios were essentially the same in both cases.

A comparison between the static-pressure distributions for heated air and decomposed N_2O is shown in figure 11. In one case they are compared at approximately equal temperatures; in the other case they are compared at approximately equal pressures. The agreement between the curves for air and for decomposed N_2O is very good before the onset of separation.

CONCLUSIONS

An investigation of the feasibility of using the thermal decomposition of nitrous oxide (N_2O) to produce a source of high-pressure and high-temperature gas (closely resembling air) for hypersonic-flow studies indicates the following conclusions:

(1) The constant-volume thermal decomposition of nitrous oxide produces a gaseous mixture which is chiefly nitrogen and oxygen. In the tests described, pressures up to 1,930 atmospheres and temperatures up to $1,859^\circ$ K ($3,346^\circ$ R) have been observed. As high loading densities are approached, the decomposition tends to be more complete and the observed temperature approaches the theoretical value ($2,507^\circ$ K for an initial temperature of 361° K).

(2) The constant-pressure thermal decomposition of nitrous oxide produces a similar mixture in a self-sustained manner, and, in the tests described, has occurred at pressures up to 70 atmospheres. The highest observed temperature was $1,726^\circ$ K ($3,107^\circ$ R). In the reactors used, the decomposition was not so complete as in the constant-volume experiments. As a result, the observed temperatures compared less favorably with the theoretical temperatures ($2,165^\circ$ K for an initial temperature of 550° K).

(3) On the basis of the tests described, the use of the hot decomposition products of nitrous oxide in a hypersonic nozzle appears feasible. The static-pressure distribution in a hypersonic conical nozzle using the products of constant-pressure decomposition of N_2O shows good agreement when compared with the distribution obtained with air in the same nozzle. Upstream of the point of flow separation, both pressure distributions agree with predicted values based on one-dimensional

isentropic-flow expansion corrected for boundary-layer growth. When undecomposed N_2O is used in the same nozzle, the static-pressure distribution differs from that of air.

Langley Aeronautical Laboratory,
        National Advisory Committee for Aeronautics,
            Langley Field, Va., December 2, 1955.

APPENDIX A

IDEAL DECOMPOSITION TEMPERATURES

The complete decomposition of two moles of N_2O into nitrogen and oxygen is expressed (ref. 1) by

$$2N_2O \rightarrow 2N_2 + O_2 + 40{,}000 \text{ calories}$$
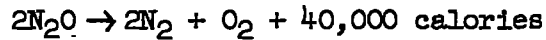
The heat released is assumed to be retained in the decomposed mixture. The temperature for a constant-volume process is found by equating the internal-energy increase of the mixture to 40,000 calories. The following table is presented for the case where the initial temperature is $300°$ K.

T, °K	Internal energy, calories, for -		
	$2N_2$	O_2	$2N_2 + O_2$
300	2,978	1,492	4,470
2,400	28,375	15,110	43,485
2,450	29,049	15,473	44,522

By interpolation between the values of the increase in internal energy, that is, $\Delta u = 39{,}015$ calories and 40,052 calories, the final temperature is $2{,}448°$ K. (Energy values in this table were obtained from ref. 13.)

The temperature for a constant-pressure process is found by equating the enthalpy increase of the mixture to 40,000 calories. For the case where the initial temperature is $300°$ K, the following table is presented.

T, °K	Enthalpy, calories, for -		
	$2N_2$	O_2	$2N_2 + O_2$
300	4,170	2,087	6,257
1,950	30,120	15,772	45,892
2,000	30,979	16,223	47,202

By interpolation between the values of the increase in enthalpy, that is, $\Delta h = 39{,}635$ calories and 40,945 calories, the final temperature is $1{,}964°$ K. (Energy values in this table were obtained from ref. 13.)

APPENDIX B

## CHEMICAL ANALYSIS OF REACTION PRODUCTS

Both qualitative and quantitative methods were used for the chemical analysis of reaction products. The qualitative analysis was made during the constant-pressure tests and immediately following the constant-volume tests. The decomposed mixture was passed through a trap cooled by liquid nitrogen until a sufficient quantity of condensate was collected. The temperature of the trap was then allowed to return to room temperature while the temperature of the condensate was recorded. The presence of N_2O was indicated by a plateau in the boiling-point record, and the presence of NO_2 was detected by its characteristic color and odor. (Warning: NO_2 is toxic.)

The quantitative analysis was conducted as follows: A 200-milliliter sample of the decomposed mixture was obtained at atmospheric pressure and temperature and then cooled by CO_2 snow to approximately -80° C. At this temperature, the vapor pressure of NO_2 was about 0.05 millimeter of mercury (see ref. 6); this was low enough to prevent it from leaving the sampling bottle while a portion of the uncondensed gases was withdrawn and placed in a gas microanalyzer. The use of this microanalyzer is described in reference 14.

The chemical equation expressing the decomposition at elevated temperatures is
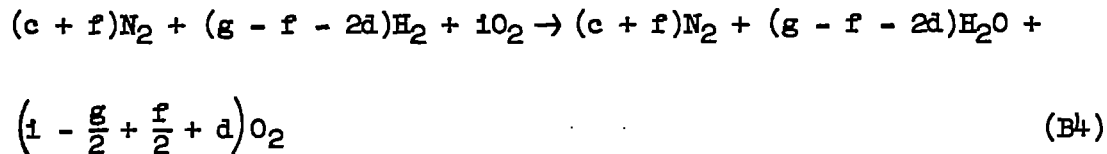
$$bN_2O \rightarrow fN_2O + cN_2 + (d + e)O_2 + 2eNO \tag{B1}$$
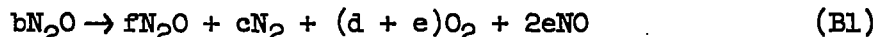
When the condensate was cooled to room temperature, NO was oxidized to NO_2 so that

$$bN_2O \rightarrow fN_2O + cN_2 + dO_2 + 2eNO_2 \tag{B2}$$
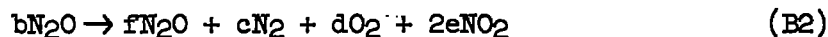
After removal of NO_2 by cooling with CO_2, the remaining products were placed in the microanalyzer and burned with an excess of H_2:

$$fN_2O + cN_2 + dO_2 + gH_2 \rightarrow (c + f)N_2 + (f + 2d)H_2O + (g - f - 2d)H_2 \tag{B3}$$
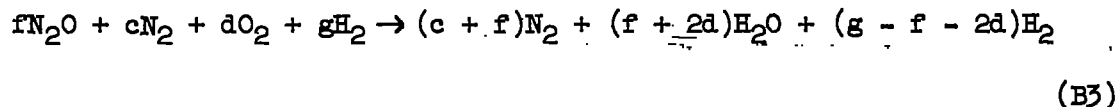
Water was removed by inserting a bead of KOH for a few minutes. The remaining products were burned with an excess of O_2:

$$(c + f)N_2 + (g - f - 2d)H_2 + iO_2 \rightarrow (c + f)N_2 + (g - f - 2d)H_2O +$$

$$\left(i - \frac{g}{2} + \frac{f}{2} + d\right)O_2 \qquad\qquad\qquad (B4)$$

Water was again removed so that the final products were

$$(c + f)N_2 + \left(i - \frac{g}{2} + \frac{f}{2} + d\right)O_2 \qquad\qquad (B5)$$
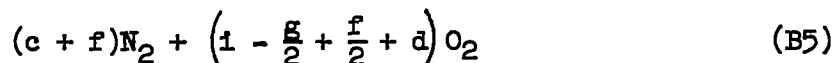
According to the conditions of the analysis, all the gases could be considered perfect gases. Thus, the number of moles and the volume were taken to be directly proportional. The following outline shows the volume measurements made with the gas analyzer as the quantitative analysis was carried out.

1. Gas sample minus NO_2 placed in analyzer; volume measured (eq. (B2)) was $c + d + f$.

2. Hydrogen added; volume measured (eq. (B3)) was $c + d + f + g$.

3. Mixture burned; water removed; volume measured (eq. (B3)) was $c + g - 2d$.

4. Oxygen added; volume measured (eq. (B4)) was $c + g - 2d + i$.

5. Mixture burned; water removed; volume measured (expression (B5)) was $c + d + \frac{3f}{2} - \frac{g}{2} + i$.

From this analysis, the volumes $(c + d + f)$, $\left(c + d + \frac{3f}{2}\right)$, and $(c - 2d)$ were found. These constituted a system of three linear equations in the three desired unknowns. Thus, c, d, and f were easily calculated. By observing that the total number of atoms of a given kind is conserved in a reaction, equation (B2) leads to an expression for e; that is,

$$e = \frac{1}{3}(c - 2d) \qquad\qquad\qquad (B6)$$

The percent by volume of each component in the original sample taken from the reactor was calculated by using the following formulas:

$$\text{Percent} \quad O_2 = \frac{d}{B} \times 100 \tag{B7}$$

$$\text{Percent} \quad N_2 = \frac{c}{B} \times 100 \tag{B8}$$

$$\text{Percent} \quad N_2O = \frac{f}{B} \times 100 \tag{B9}$$

$$\text{Percent} \quad NO_2 = \frac{2e}{B} \times 100 \tag{B10}$$

$$B = c + d + 2e + f \tag{B11}$$

Since in the test results the percent of NO_2 present was relatively small, the percent of NO originally present in the hot gas can be considered to have approximately the same value. Or, more precisely,

$$\text{Percent} \quad NO = \frac{2 \times \text{Percent} \quad NO_2}{2 + \dfrac{\text{Percent} \quad NO_2}{100}} \tag{B12}$$

which was derived by comparing the following expression with equation (B10):

$$\text{Percent} \quad NO = \frac{2e}{c + d + 3e + f} \times 100 \tag{B13}$$

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TABLE I.- CONDITIONS OBTAINED BY DECOMPOSING N_2O

WITHIN A FIXED VOLUME

[Theoretical peak temperature of 2,429° K based
on an initial wall temperature of 283° K]

Test	Loading density, g-moles / liter	Peak pressure, atm	Peak temperature, T_f, °K (a)	Chemical analysis of cooled products, percent by volume, of -				$\dfrac{O_2}{N_2}$
				N_2	O_2	NO_2	N_2O	
1	1.51	256	1,371	-----	-----	-----	-----	-----
2	1.62	268	1,337	-----	-----	-----	-----	-----
3	2.27	432	1,504	59.5	28.8	1.19	10.7	0.485
4	3.10	520	1,311	58.60	28.20	1.735	11.00	0.481
5	3.52	581.5	1,276	-----	-----	-----	-----	-----
6	3.61	524	1,129	-----	-----	-----	-----	-----
7	4.21	592	1,084	-----	-----	-----	-----	-----
8	4.52	585	1,015	60.30	29.6	0.39	9.55	0.491

[a]Based upon peak-pressure measurements.

TABLE II.- CONDITIONS OBTAINED BY DECOMPOSING N_2O

WITHIN A FIXED VOLUME

[Theoretical peak temperature of 2,507° K based
on an initial wall temperature of 361° K]

Test	Loading density, g-moles / liter	Peak pressure, atm	Peak temperature, T_f, °K (a)	Chemical analysis of cooled products, percent by volume, of -				$\frac{O_2}{N_2}$
				N_2	O_2	NO_2	N_2O	
b1	1.56	257.8	1,390	52.40	24.80	1.83	21.10	0.474
2	1.56	295	1,530	58.65	28.37	1.276	11.71	0.4837
3	1.67	309	1,490	-----	-----	-----	-----	------
4	2.27	476	1,637	60.70	29.92	0.58	8.85	0.4935
c5	2.54	541	1,649	-----	-----	-----	-----	------
6	2.92	622	1,631	60.29	29.27	1.16	9.27	0.486
c7	3.09	------	-----	64.70	29.40	3.92	1.96	0.455
b8	3.45	742	1,605	61.40	30.10	0.75	7.80	0.491
9	3.61	770	1,585	62.21	30.21	1.204	6.38	0.4854
10	4.18	990	1,707	62.50	30.59	0.77	6.04	0.491
c11	5.31	1,465	1,859	-----	-----	-----	-----	------
12	7.13	1,930	1,712	65.0	32.2	0.43	2.24	0.497

aBased upon peak-pressure measurements.
bInitial temperature of approximately 348° K.
cOnly these tests were initiated by an electrically fused wire.

TABLE III.- CONDITIONS OBTAINED BY DECOMPOSING N_2O

WITHIN A CONSTANT-PRESSURE REACTOR

Run	Pressure, atm	Preheat temperature, °K	Maximum temperature, °K (a)	Approx. flow rate, g/sec	Chemical analysis of cooled products of reaction, percent by volume, of -				$\dfrac{O_2}{N_2}$
					N_2	O_2	NO_2	N_2O	
1	25.5	586	1,692	2.36	56.5	16.8	15.2	11.7	0.298
2	37.4	540	1,645	0.44	58.5	25.50	3.94	11.25	0.436
3	27.9	554	1,726	2.58	------	------	------	------	------

aTheoretical temperature of approximately 2,165° K based on a preheat temperature of 550° K.
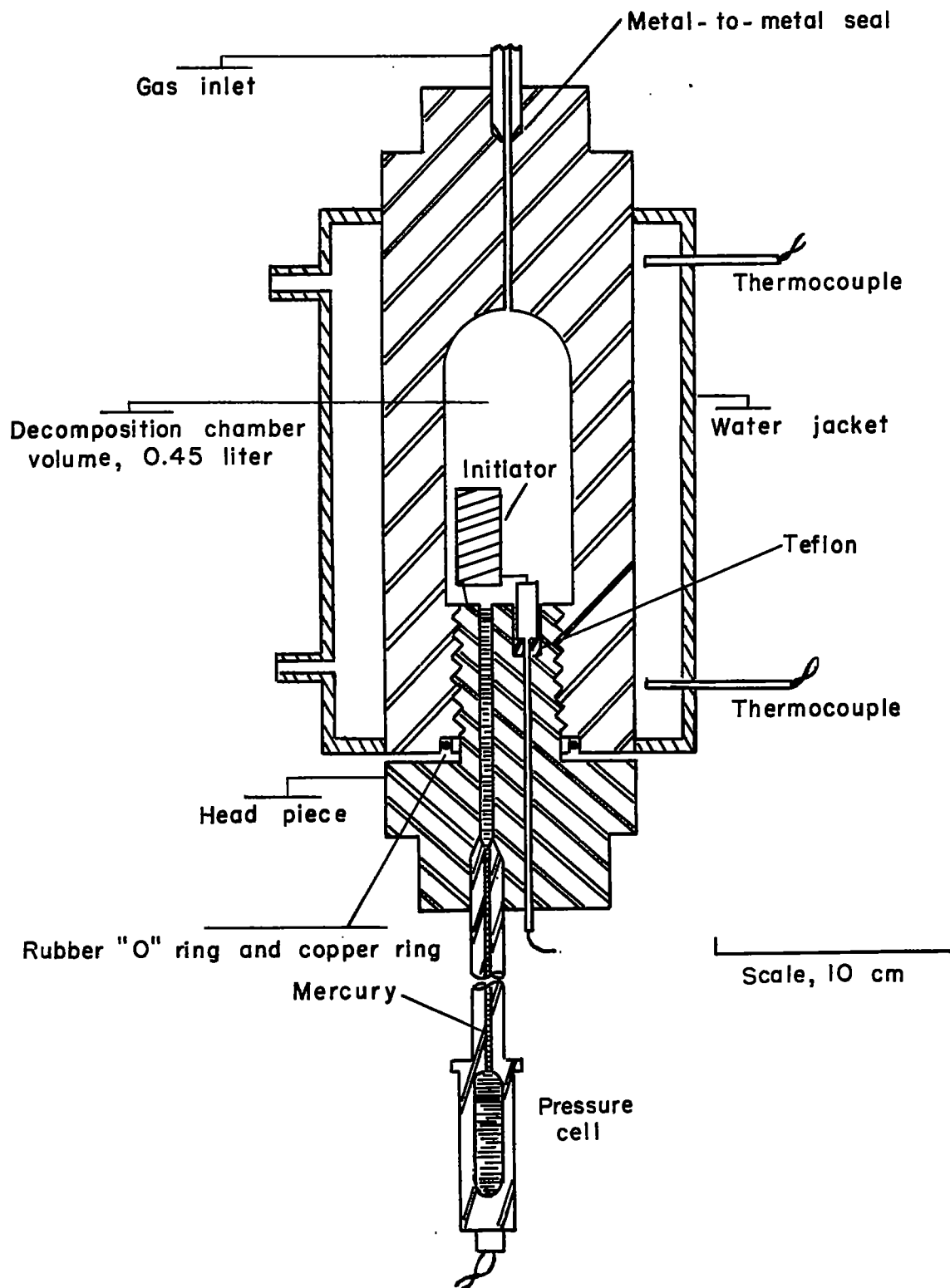
Figure 1.- Schematic drawing of constant-volume reactor.
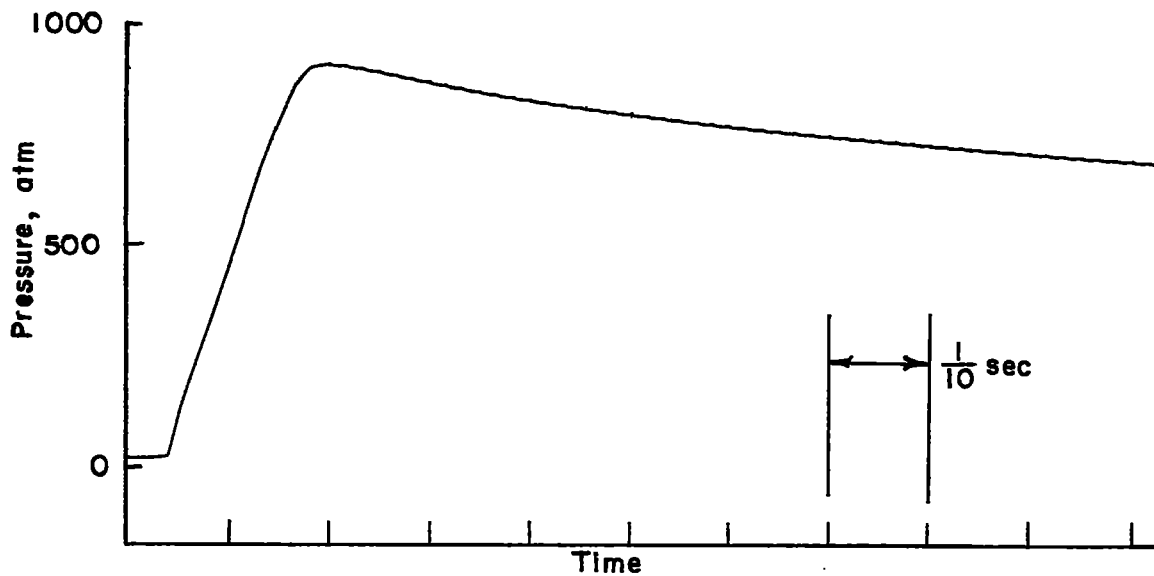
(a) Hot-wall test.   Loading density, 4.18 g-moles/liter.
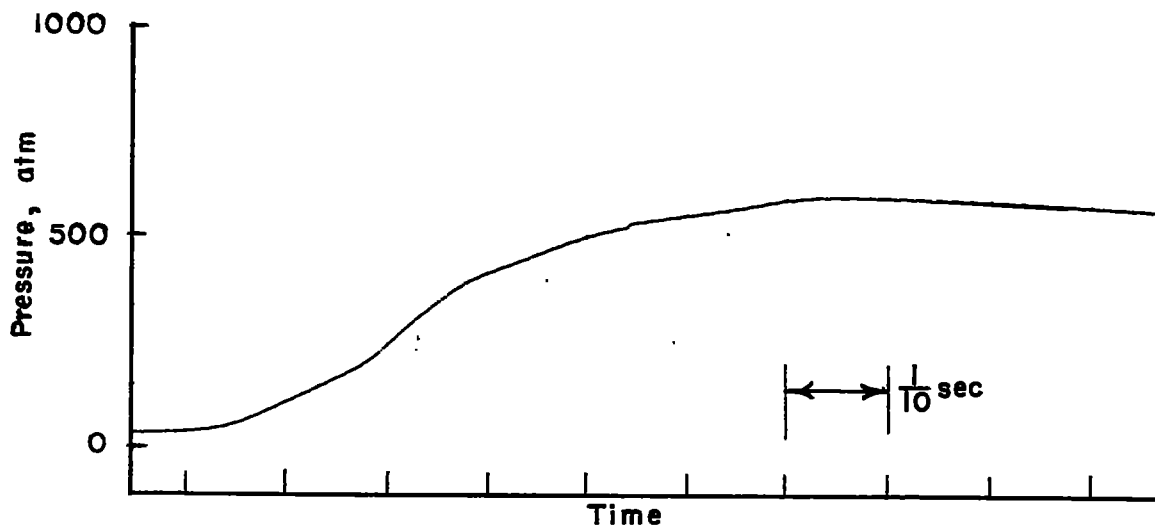
(b) Cold-wall test.   Loading density, 4.21 g-moles/liter.

Figure 2.- Pressure time history during constant-volume reaction.
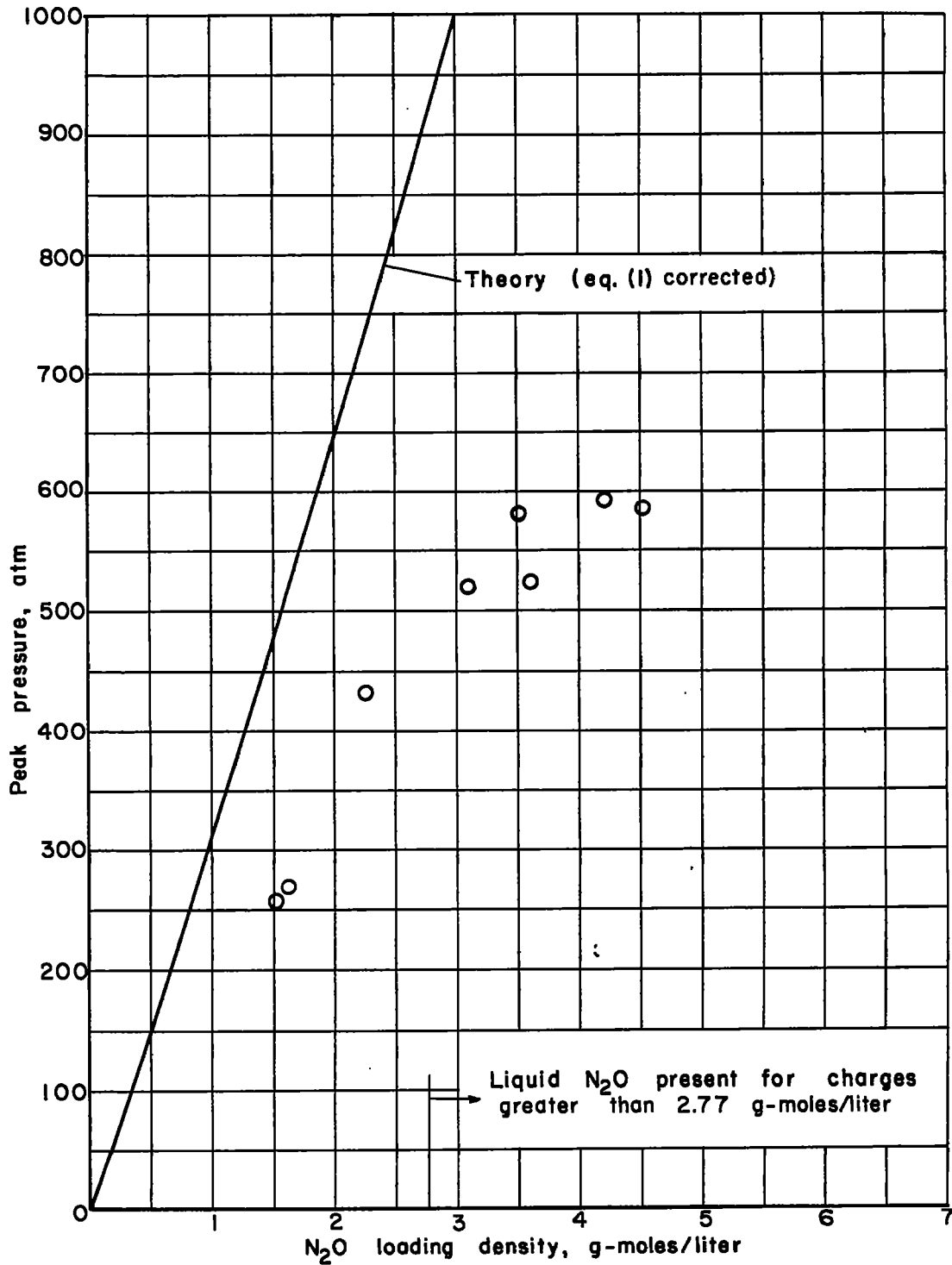
Figure 3.- Peak pressures for constant-volume reactions. Initial wall
temperature, 283° K.
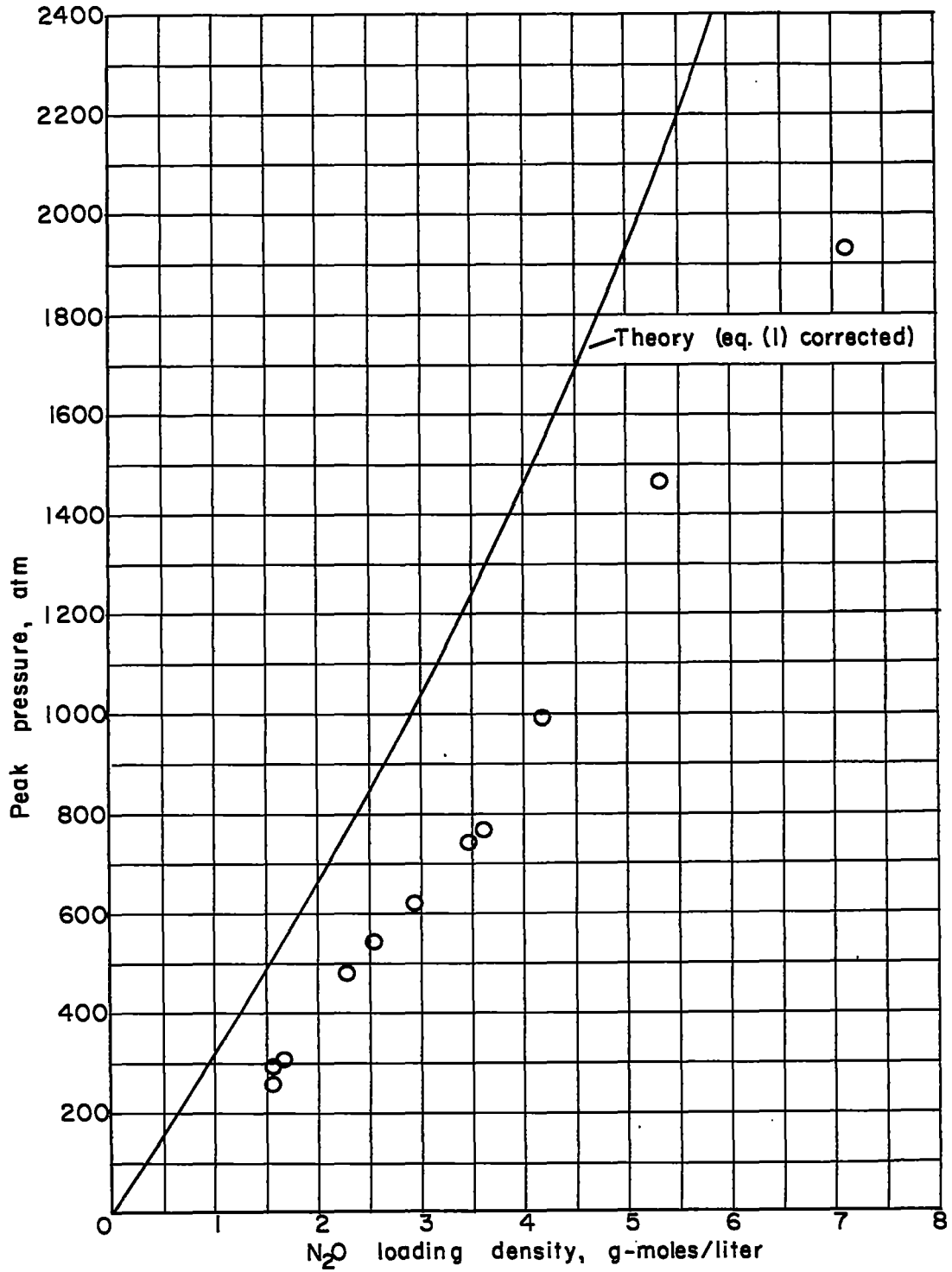
Figure 4.- Peak pressures for constant-volume reactions.   Initial wall
temperature, 361° K.
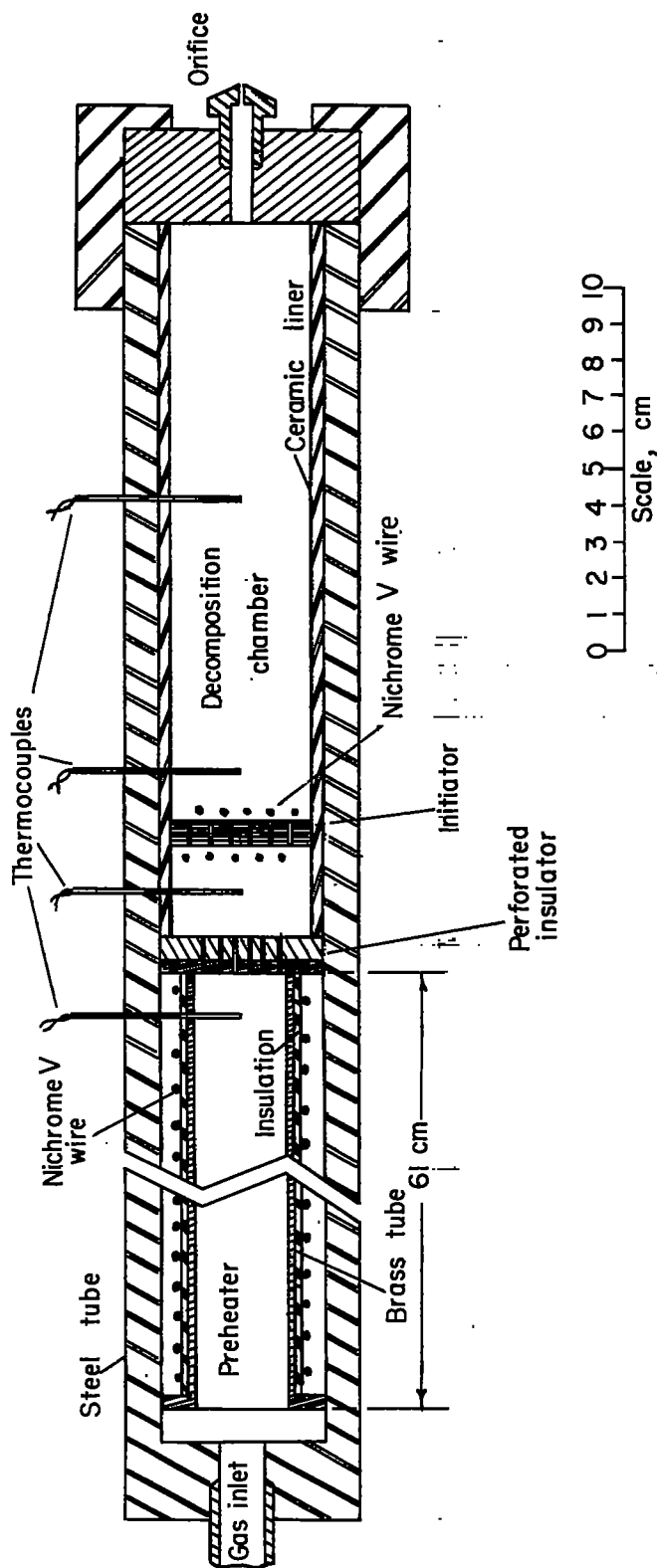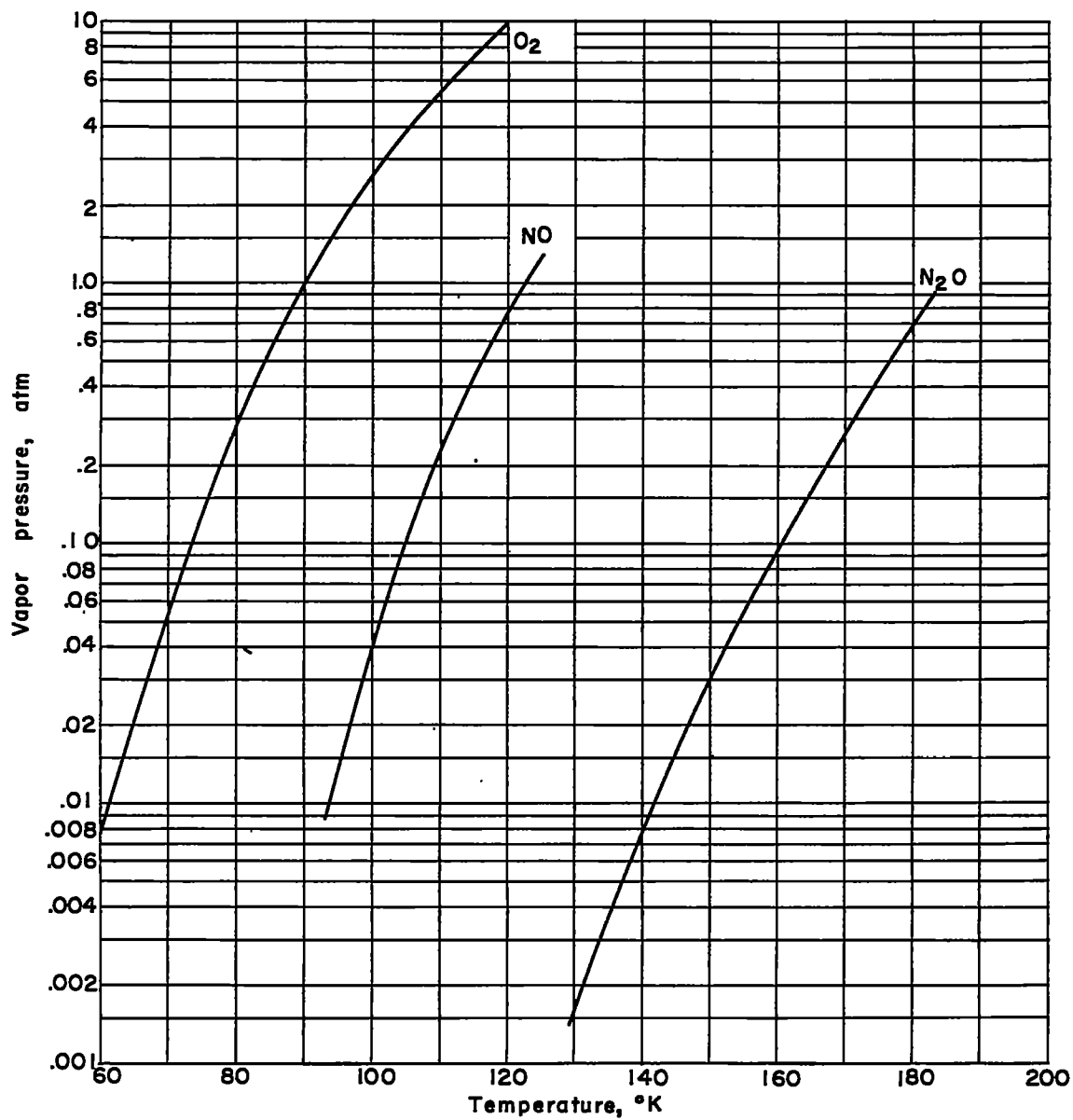
Figure 5.- Schematic drawing of constant-pressure reactor.

Figure 6.- Variation of vapor pressure with temperature for oxygen (O_2), nitric oxide (NO), and nitrous oxide (N_2O). Data for O_2 are from reference 7; data for NO and N_2O are from reference 8.
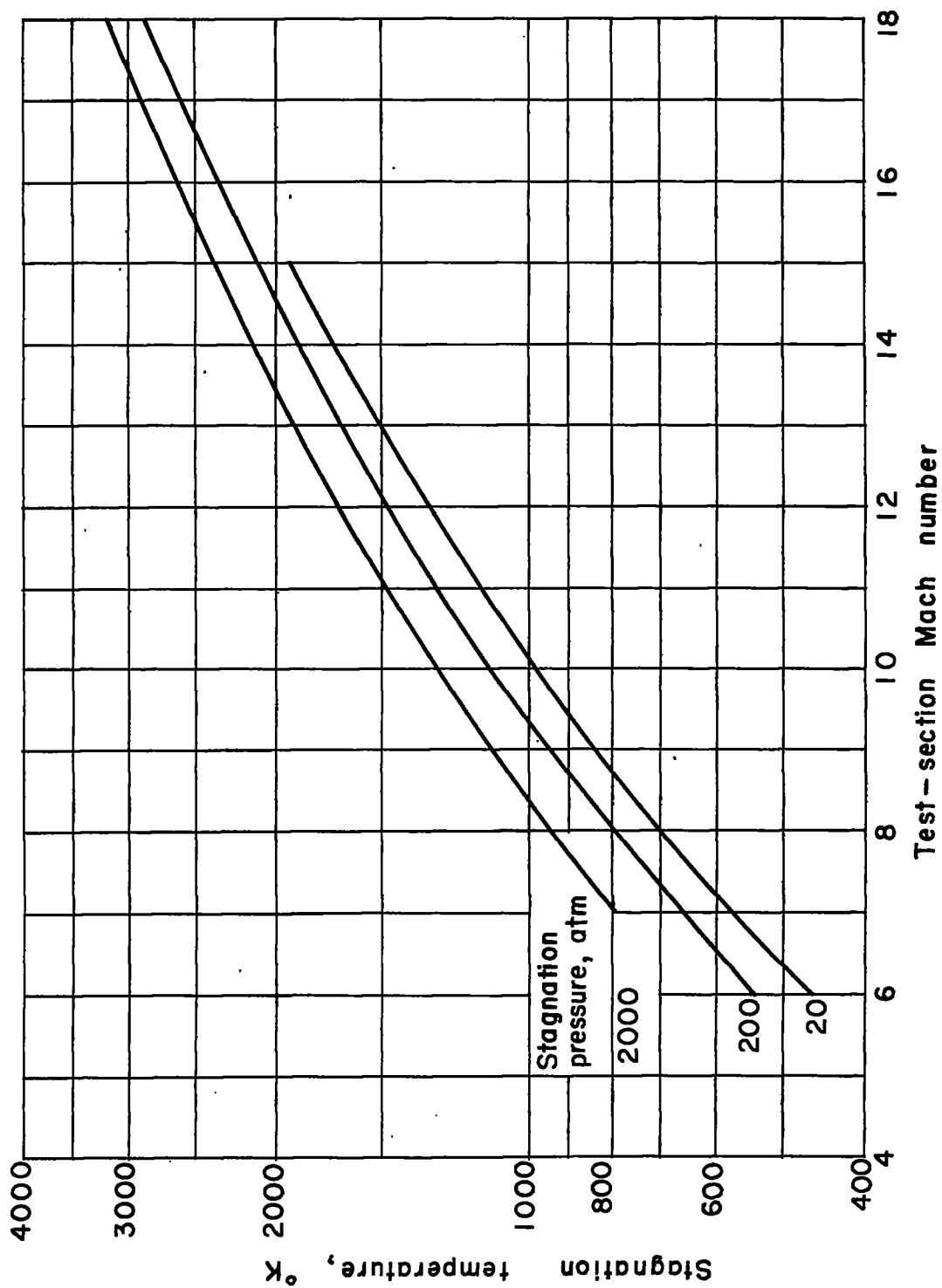
Figure 7.- Stagnation-temperature requirements for air at various stagnation pressures to avoid condensation in a wind tunnel.
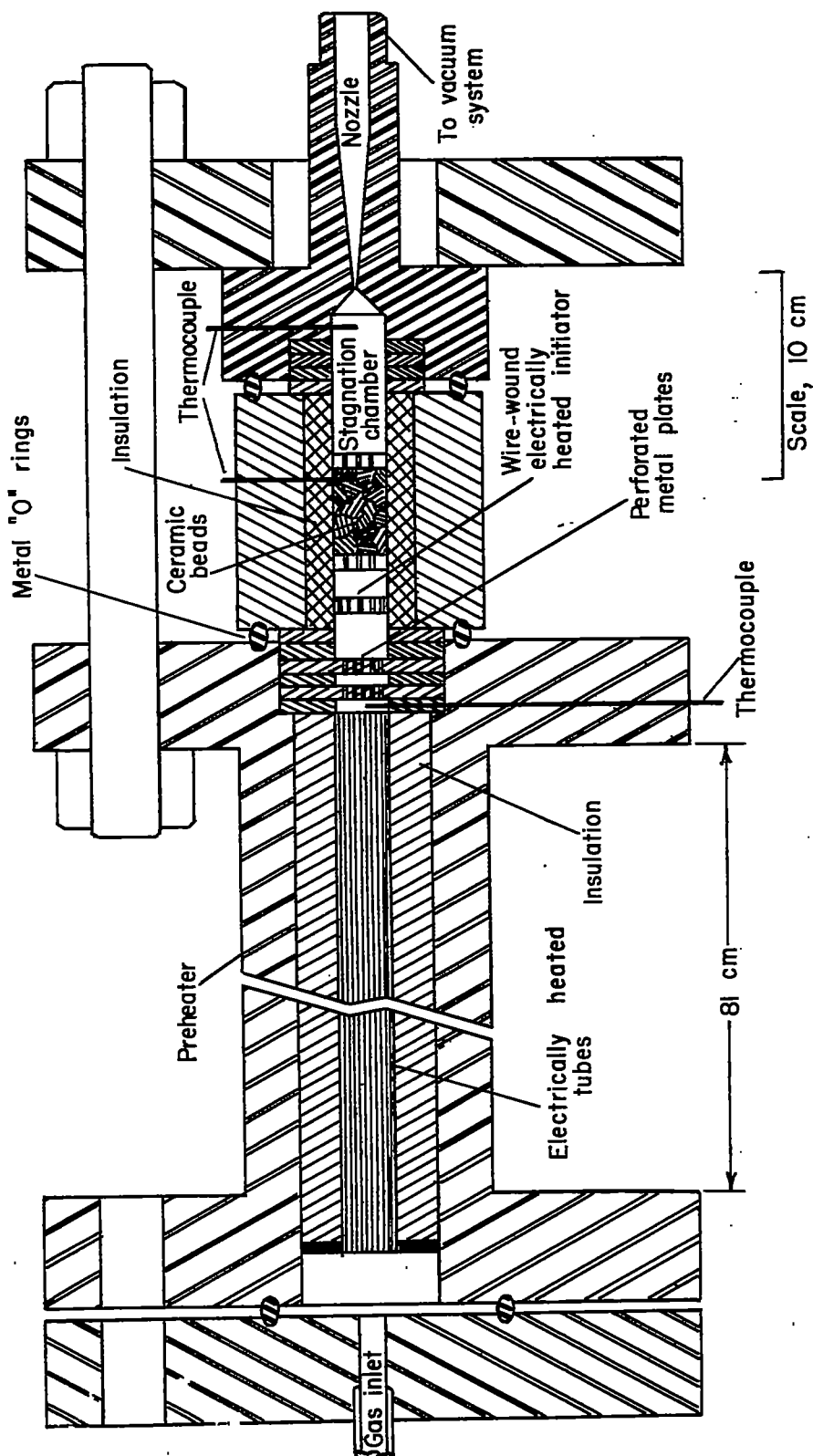
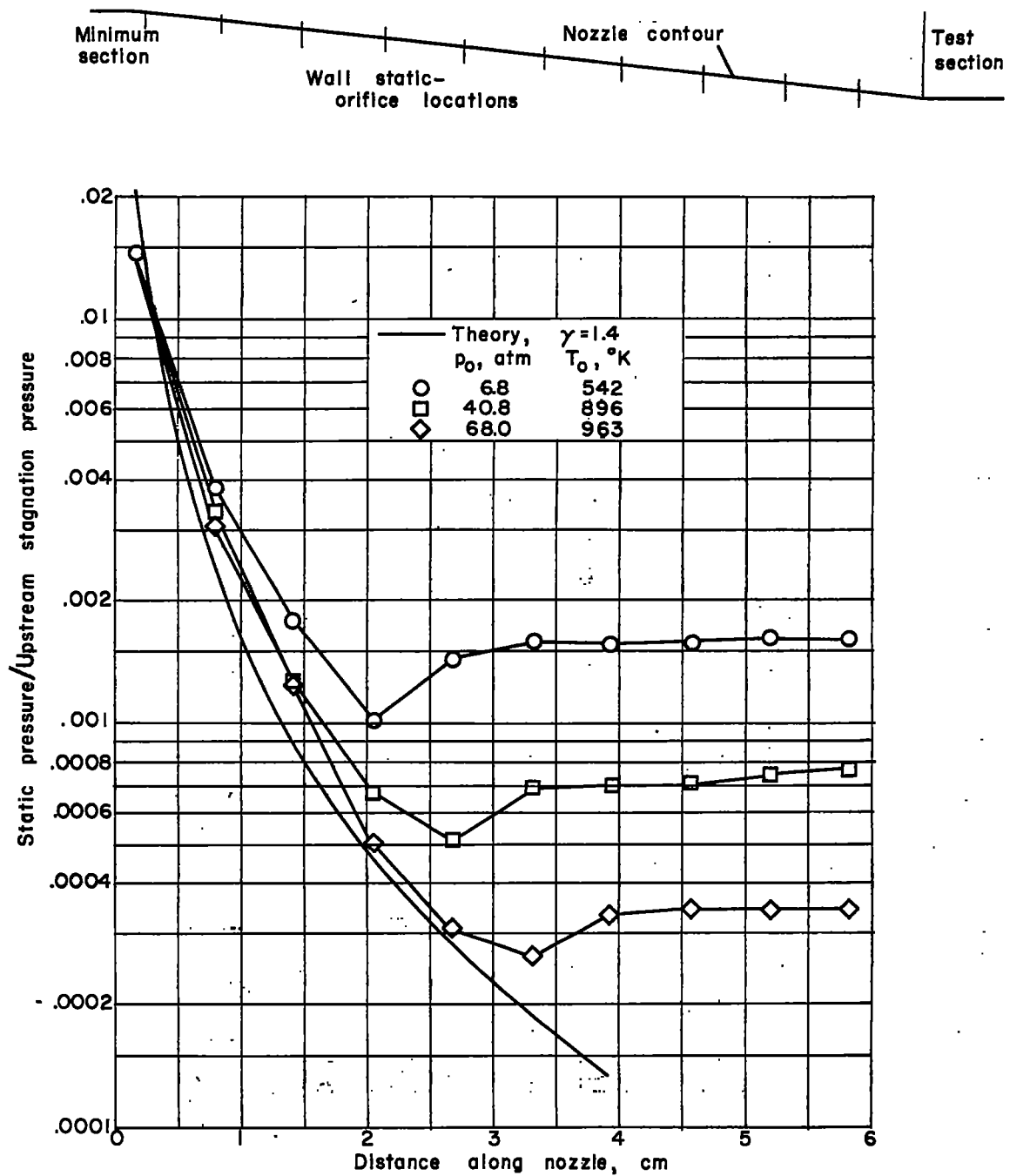Figure 8.- Schematic drawing of hypersonic-nozzle apparatus.

Figure 9.- Comparison of static-pressure distributions along nozzle for tests using air.
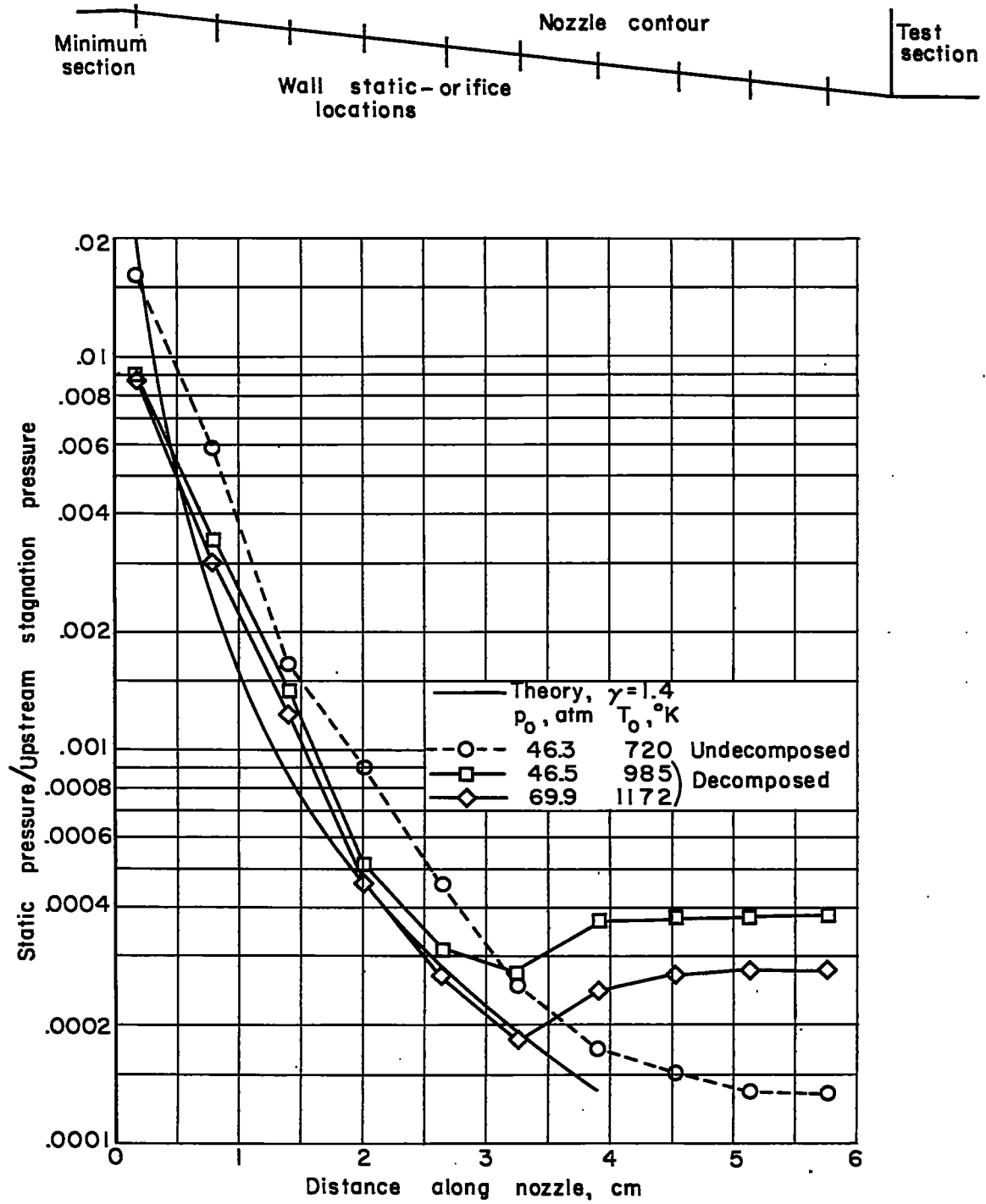
Figure 10.- Comparison of static-pressure distributions along nozzle for tests using decomposed and undecomposed N_2O.
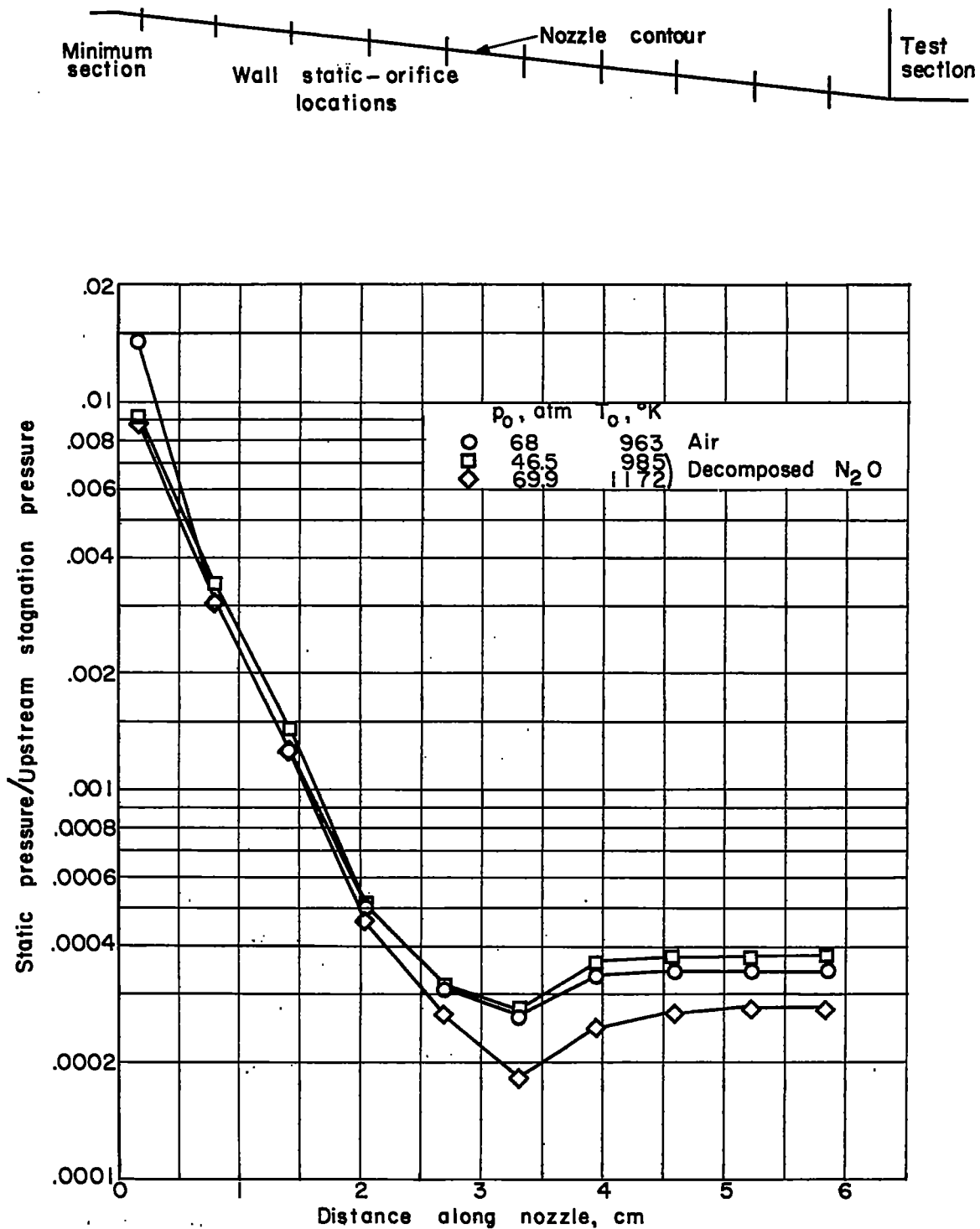
Figure 11.- Comparison of static-pressure distributions along nozzle for tests using air and decomposed N_2O.