NASA CONTRACTOR REPORT

NASA CR-2896

INVESTIGATION OF HYDROGEN-AIR IGNITION SENSITIZED BY NITRIC OXIDE AND BY NITROGEN DIOXIDE

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • OCTOBER 1977

1. Report No. NASA CR-2896	**2. Government Accession No.**	**3. Recipient's Catalog No.**

4. Title and Subtitle INVESTIGATION OF HYDROGEN-AIR IGNITION SENSITIZED BY NITRIC OXIDE AND BY NITROGEN DIOXIDE	**5. Report Date** October 1977 **6. Performing Organization Code**
7. Author(s) M. Slack and A. Grillo	**8. Performing Organization Report No.**
9. Performing Organization Name and Address Grumman Aerospace Corp. Bethpage, NY 11714	**10. Work Unit No.** 505-05-41-02 **11. Contract or Grant No.** NAS1-14348
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546	**13. Type of Report and Period Covered** Contractor Report **14. Sponsoring Agency Code**

15. Supplementary Notes

Langley technical monitor: Charles J. Schexnayder, Jr.

Final report

16. Abstract

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Addition of both NO and NO_2 reduced the measured induction times. The experimental data are interpreted in terms of H_2-O_2-NO_x oxidation reaction mechanisms.

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17. Key Words (Suggested by Author(s)) Ignition Reaction Kinetics Nitrogen Oxides Shock Waves	**18. Distribution Statement** Unclassified - Unlimited Subject Category 25

19. Security Classif. (of this report) Unclassified	**20. Security Classif. (of this page)** Unclassified	**21. No. of Pages** 42	**22. Price*** $4.00

* For sale by the National Technical Information Service, Springfield, Virginia 22161

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SUMMARY

The sensitization of stoichiometric hydrogen-air ignition by NO, NO_2, and a mixture of NO and NO_2 has been investigated behind reflected shock waves in a shock tube. Induction times were measured in the pressure range 0.273 to 2.02 x 10^5 N/m^2 (0.27 to 2.0 atm), temperature range 800 to 1500°K, and for NO or NO_2 mole percent between 0.0 and 4.5. Emission from OH (3064Å) and H_2O (2.7μ) was monitored, together with static pressure.

Addition of both NO and NO_2 reduced the measure induction times. Sensitization was most pronounced in the vicinity of the second explosion limits. At temperatures below 1000°K and for a pressure of 2.02 x 10^5 N/m^2, 0.5% of either NO or NO_2 reduced the observed induction times by more than an order of magnitude. The experimental data are interpreted in terms of H_2-O_2-NO_x oxidation reaction mechanisms. Comparison is made with current numerical predictions and predictions by Strokin and Khailov.

The incidental presence of NO_x will assist ignition in a hydrogen-fueled combustor test conducted in an arc-heated facility. Consequently, such tests will not ensure the development of a successful engine operating in relatively clean air, unless the influence of NO_x upon the ground tests is carefully assessed and a meaningful extrapolation is made to flight conditions. The influence of NO_x upon a NASA Langley supersonic combustion ramjet (SCRAMJET) combustor test, conducted in an arc-heated facility, is assessed.

1. INTRODUCTION

Ground tests of high performance airbreathing engine combustors require that the enthalpy in the facility duplicate the flight enthalpy and that the pressure of the test stream be the same as the pressure produced by the engine inlet in flight. Generation of this high enthalpy air may be accomplished by either pebble bed heaters, vitiated air heaters or arc heaters. Testing of a SCRAMJET combustor, burning gaseous hydrogen, is in progress at the NASA Langley Research Center (Ref. 1) with an arc heater supplying the high enthalpy inlet air. Since an arc heater also generates substantial oxides of nitrogen (typically 3% NO_x by volume) it is important to understand the impact of this incidental NO_x upon the hydrogen-air ignition kinetics. If the NO_x inhibits ignition, poor combustion efficiencies can be expected from the ground test. Conversely, if NO_x sensitizes ignition, a successful ground test will not ensure the development of a successful engine operating in relatively clean air. Therefore the influence of NO and NO_2 upon the ignition delay times of hydrogen-air is vitally important to the interpretation and scaling of combustor ground tests in which the high enthalpy inlet air is simulated with an arc heater.

It is well established (Refs. 2 to 6) that traces of NO_2 lower the ignition temperature of hydrogen-oxygen mixtures, and that ignition occurs only if the pressure of NO_2 lies between a lower and upper limit. These early investigations are summarized by Ashmore (Refs. 7, 8), and Ashmore and Tyler (Ref. 9). Ashmore (Ref. 8) has also observed that the lower and upper sensitizer limits of ignition are substantially the same whether the original additive is NO, NO_2, NOCl or a mixture of NO and NO_2.

A theoretical study by Strokin and Khailov (Ref. 10) predicts that NO impurities will significantly increase the induction time (or ignition delay time) of hydrogen-air, through termination reactions which remove O, H, or OH. In contrast, the mechanism proposed by Ashmore and Tyler (Ref. 9) would predict a reduction of induction times, through NO attack upon the HO_2 chain terminator. Furthermore, in the experimental study of Glassman and Sawyer (Ref. 11) upon H_2-O_2-N_2-NO mixtures, NO caused both inhibition and sensitization in the reaction zone depending on the NO/O_2 ratio. Clarification of the role played by NO is clearly desirable both from a fundamental and practical viewpoint.

We report here on a shock tube investigation into the influence of NO upon the induction times (τ_i) of stoichiometric hydrogen-air. The influence of NO_2 and of a mixture of NO + NO_2 were also investigated. A low pressure rapid mixing technique was employed so that prior to each test the contact time of NO and O_2 was minimal and the oxidation of NO to NO_2 was negligible. Induction times were measured between 800 and 1500°K, at pressures of 0.273 to 2.02×10^5 N/m^2 (0.27 to 2.0 atm)

4.25 mole percent. The experimental data are interpreted in terms of oxidation reaction mechanisms and the influence of NO_x upon a NASA Langley SCRAMJET test (Ref. 1) is assessed.

2. EXPERIMENTAL TECHNIQUE

Stoichiometric hydrogen-air mixtures together with NO or NO_2 additives were heated by reflected shock waves in a 38.1 mm i.d. stainless steel shock tube. This facility has previously been described (Refs. 12 and 13) and is shown in Fig. 1. The various mixtures which were investigated are listed in Table 1. Gas purities were as follows: H_2, 99.95%; O_2, 99.95%; N_2, 99.999%; NO, 99.2%; and NO_2, 99.5%. The driven section of the shock tube was pumped down to about 3×10^{-6} torr before being filled with the test gas. The leak rate varied between 3.3 and 5×10^{-6} torr/sec and the shock tube was fired typically 30 seconds after closing the vacuum valves. Initial pressures of the reactants ranged from 3 to 100 torr.

If nitric oxide were premixed and stored with hydrogen-air, the fast reaction

$$NO + NO + O_2 = NO_2 + NO_2 \tag{1}$$

would completely convert NO to NO_2. This problem was overcome by a rapid, but thorough, mixing technique which relies on the residence time of NO and O_2 contact prior to shock heating being at least an order of magnitude lower than the half life of reaction 1. Hydrogen and oxygen were premixed in a steel cylinder while nitrogen and NO were premixed in a separate cylinder. The desired partial pressures of these mixtures were admitted via a "pepper pot" inlet tube to an evacuated 4.4 litre stainless steel mixing chamber, where mixing was promoted by a stainless steel paddle, turning at 75 rpm. Residence times in the mixing chamber were limited to 2 minutes after which the evacuated shock tube driven section was filled with the test mixture and the shock tube immediately fired. This residence or contact time is compared in Table 2 to the half life ($t_{1/2}$) of reaction 1 at typical pretest conditions. The rate coefficient for the oxidation reaction was taken from Baulch et al (Ref. 14)

$$k_1 = 2.4 \times 10^9 \exp(1046/RT) \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1} \tag{2}$$

and the half life of a termolecular reaction, as derived by Benson (Ref. 15), is

TABLE 1 INITIAL MIXTURE COMPOSITION *

Mixture No.	Mole Percentage				
	H_2	O_2	N_2	NO	NO_2
1	29.6	14.8	55.6	-	-
2	29.6	14.8	55.1	0.5	-
3	29.6	14.8	54.6	1.0	-
4	29.6	14.8	53.35	2.25	-
5	29.6	14.8	51.1	4.5	-
6	29.6	14.8	54.85	-	0.75
7	29.6	14.8	54.1	-	1.50
8	29.6	14.8	52.04	-	3.56
9	29.6	14.8	53.65	1.1	0.85

*In the case of NO, the composition following rapid mixing is indicated.

$$t_{1/2} = \frac{2}{k_1(2\,[O_2] - [NO])}\left\{\frac{1}{[NO]} - \frac{\ln(2 - [NO]/2[O_2]))}{2\,[O_2] - [NO]}\right\} \qquad (3)$$

Even though oxidation of NO may be limited in this manner, it should be remembered that at the time of firing the conversion of a small fraction of NO to NO_2 is inevitable and that tests with $\alpha = [NO_2]/[NO] = 0$ are not feasible. However, very low values of α were achieved, as presented in Table 2.

Validation of the rapid mixing technique was accomplished in the following manner. Premixed CO_2 (1%) in argon (99%) was shock heated and infrared radiation at 4.3 μ was monitored at a station 10 cm from the end wall of the shock tube. An oscilloscope record of the 4.3 μ emission is shown in Fig. 2a; insufficient collimation of the IR emission, together with internal reflections, is responsible for the poor resolution at the shock front. The IR emission is optically thin and a time distance transformation yields the distribution of CO_2 between the diaphragm and the measurement station, which in the case of a premixed gas, is uniform. A mixture of 0.5% CO_2 in argon was then prepared by rapidly mixing 1% CO_2 in argon (premixed) with equal parts of pure argon. The final mixture was shock heated and the observed IR emission signal (Fig. 2b) was reduced 50%, but had the same profile as in the premixed case, which indicated a uniform distribution of CO_2 along the shock tube and therefore satisfactory uniform mixing. As a further test of the rapid mixing technique, measured induction times for CH_4-O_2-Ar mixtures prepared by rapid mixing were compared to earlier results (Ref. 12) with premixed gases. A 2% CH_4 + 4% O_2 + 94% argon mixture was prepared and rapidly mixed with equal parts of pure argon, before shock heating. The measured induction times were identical to our earlier results (Ref. 12) from premixed 1% CH_4 + 2% O_2 + 97% argon.

TABLE 2 INITIAL CONDITIONS AND NITRIC OXIDE OXIDATION HALF LIFE*

Mixture	Ø	$P_1(N/m^2)$	$T_1(^oK)$	$P_5(N/m^2)$	$T_5(^oK)$	$t_{1/2}$(sec)	α
H_2-Air	1.0	4.93E3	300	1.013E5	840	11520	9.8E-3**
+ 1% NO	1.0	3.33E3	300	1.013E5	1010	25440	4.5E-3
	1.0	1.99E3	300	1.013E5	1330	75840	1.6E-3
H_2-Air	1.0	4.93E3	300	1.013E5	840	2880	39.2E-3
+ 4% NO	1.0	3.33E3	300	1.013E5	1010	6360	18.0E-3
	1.0	1.99E3	300	1.013E5	1330	18960	6.4E-3

*Suffix 1 refers to initial conditions, suffix 5 to reflected shock test conditions.

**$\alpha = NO_2/NO$, after 120 sec rapid mixing; $9.8E\text{-}3 \equiv 9.8 \times 10^{-3}$

Mixtures of hydrogen-oxygen, nitrogen-nitric oxide, or hydrogen-air-nitrogen dioxide were prepared manometrically, stored separately in steel cylinders for at least 24 hours prior to use, and mixture composition was verified by gas chromatography.

Photometric observations of the shock heated gas mixtures were made through two flush-mounted diametrically opposed sapphire windows in a plane 3 mm from the shock tube end wall. Emission from OH (3064 Å) was isolated by an interference filter, collimated by 1 mm slits, and monitored with a photomultiplier tube. Emission from H_2O (2.7 μ) was also isolated by an interference filter and monitored with a liquid nitrogen cooled InSb detector. Reflected shock static pressures, 3 mm from end wall, were measured with a flush-mounted Kistler 601A transducer, whose deadweight calibration was confirmed by dynamic calibration against shock waves in argon.

Incident shock velocities were measured using flush-mounted thin film platinum heat transfer gauges and electronic chronometers. Thermodynamic properties of the chemically frozen gas behind the reflected shock were then computed (Ref. 16), using as input the measured incident shock velocity, initial pressure, mole fractions of the reactants, and JANAF thermochemical data. Maximum estimated uncertainties in the reflected shock temperature were $\pm 10^{\circ}$K. Vibrational equilibrium was assumed behind the reflected wave for all species; this assumption is only reasonable in a nitrogen-hydrogen mixture where the hydrogen is more than three orders of magnitude more efficient than nitrogen in transferring vibrational energy to the nitrogen molecule (Ref. 17).

Induction times (τ_i) were measured between the reflected shock pressure rise and the maximum positive rate of change of the OH emission signal, as shown in the sample oscillograms of Fig. 3. Identical induction times were also defined by a rapid increase in the pressure signal or by the onset of H_2O emission.

An upper limit on the measurement of τ_i is the duration of the steady reflected shock conditions, terminated by disturbances from the reflected shock-contact surface interaction. This limit is a function of pressure and temperature but was typically 1.5 ms. A lower limit on τ_i is the ability to resolve short induction periods (see Fig. 3) and this limit was about 10 μs. The conditions of low pressure and high temperature (0.27 atm and $T > 1100^{\circ}$K) required very low initial pressures, P_1. These conditions favor boundary layer growth and therefore the results will be least reliable in terms of the absolute values of τ_i. However, the relative influence of NO_x can still be determined. In addition, the low pressure conditions ($P = 0.273 \times 10^5$ N/m^2) were limited to temperatures above 900°K; lower temperatures required diaphragm pressure ratios below the controllable lower limit of the facility.

The experimental test matrix is given in Table 3; temperatures and pressures quoted are the chemically frozen values behind the reflected shock prior to any oxidation. The pressures given are mean values; the majority of the data deviated from the mean by less than ± 5%. Results deviating more than 10% from the mean pressure were discarded.

TABLE 3 TEST MATRIX

Temperature* (^oK)	Pressure ($10^5 N/m^2$) 0.273	0.507	1.013	2.026	% NO	% NO_2	Mixture No.
800-1500	X	X	X	X	0	0	1
800-1500		X		X	0.5	0	2
800-1500	X	X			1	0	3
800-1500	X	X		X	2.25	0	4
800-1500		X			4.5	0	5
800-1500		X		X	0	.75	6
800-1500		X			0	1.50	7
800-1500		X		X	0	3.56	8
800-1500		X			1.1	0.85	9
1000			X		**	0	2-5

* Nominal Range

** NO% = 0.5, 1, 2.25, 4.5

3. OBSERVATIONS

Measured induction times for stoichiometric H_2-Air are presented in Fig. 4, for H_2-Air-NO mixtures in Figs. 5 through 9, for H_2-Air-NO_2 mixtures indicated in Figs. 10 through 13, and for a H_2-Air-NO-NO_2 mixture in Fig. 14. In all cases NO or NO_2 sensitized the induction period chemical kinetics, reducing the induction time (τ_i). Experimental results for the different mixtures are discussed below.

Stoichiometric Hydrogen-Air

Measured ignition delay times are presented in Figs. 4a and 4b for the four pressures of the present study. The unusual pressure dependence is a result of the reaction kinetics operating near to the second explosion limit (see Section 4). At $2.02 \times 10^5 N/m^2$ (2.0 atm) the present data agree with earlier measurements by Snyder (Ref. 18). At higher temperatures ($T > 1300^{\circ}K$) the present data are in good agreement with a correlation by Moore and White (Ref. 19).

Influence of NO Additive

The temperature dependence of measured induction times at initial pressures of 2.02, 0.507 and $0.273 \times 10^5 N/m^2$ (2.0, 0.5, and 0.27 atm) are shown in Figs. 5, 6, and 7. The addition of NO to the stoichiometric H_2-Air reduced the induction times in all cases. This reduction was most pronounced at $2.02 \times 10^5 N/m^2$ (2 atm) and at temperatures below $950^{\circ}K$ where τ_i was down by an order of magnitude. The influence of NO was minimal at higher temperatures, i.e., $T > 1000^{\circ}K$.

The effect of increasing the mole percentage of added NO is shown in Figs. 8 to 10; additional data at $1.01 \times 10^5 N/m^2$ (1.0 atm) and $1000^{\circ}K$ only are presented later (Fig. 17). At initial temperatures $\geq 1000^{\circ}K$, an increase in NO mole percent above 0.5 did not cause any further sensitization of induction times. At $2.02 \times 10^5 N/m^2$ (2 atm) and below $1000^{\circ}K$, increases in NO lengthened the induction times and created a minimum in plots of τ_i against mole percent NO. At 0.273 and $0.507 \times 10^5 N/m^2$ (0.5 and 0.27 atm), τ_i was insensitive to increases in NO mole percent above 0.5, see Figs. 9 and 10.

Influence of NO_2 Additive

Measured induction times at initial pressures of 2.02 and $0.507 \times 10^5 N/m^2$ (2 and 0.5 atm) are presented in Figs. 11 and 12, as a function of temperature. Earlier shock tube measurements by Snyder et al. (18) are included in Fig. 11 and are in good agreement with the present data. Snyder et al. premixed NO with stoichiometric hydrogen-air, and the NO would have reacted with O_2 (see Reaction 1) to form NO_2. Consequently, we interpret their data to show the influence of NO_2 and not NO, as originally claimed (Ref. 18). Figures 11 and 12 show that NO_2 sensitized the ignition of stoichiometric hydrogen-air, the sensitization being most pronounced at $2.02 \times 10^5 N/m^2$ (2 atm) and temperatures below $1100^{\circ}K$ where τ_i was reduced by more than an order of magnitude.

The effect of increasing the mole percentage of added NO_2 is shown in Figures 13 and 14, for initial pressures of 2.02 and $0.507 \times 10^5 N/m^2$ (2.0 and 0.5 atm), respectively. At $2.02 \times 10^5 N/m^2$ (2.0 atm), a minimum induction time occurs at about 0.5 mole percent NO_2, and increases in the mole percent of NO_2 then reduces its sensitizing influence until above 4% the induction times were insensitive to any further increase up to the limit of Snyders data (Ref. 18). At an initial pressure of $0.507 \times 10^5 N/m^2$ (0.5 atm) no minimum was observed in the range 0.75 to 3.56 mole percent of added NO_2, where τ_i was reduced typically by 27%.

Although there were specific differences between the influence of NO and NO_2, these differences were outweighed by the similarities in the two data sets.

Influence of NO + NO_2

Induction times for stoichiometric hydrogen-air, at $0.507 \times 10^5 N/m^2$ (0.5 atm) and to which a mixture of 1.1% NO and 0.85% NO_2 was added, are presented in Figure 15. Sensitization was observed and the results were similar to those with 2.25 mole percent NO, see Fig. 6. Below 900°K, the additives reduced τ_i by a factor of three, while at temperatures around 1250°K a reduction of 35% was observed.

4. INDUCTION PERIOD CHEMICAL KINETICS

In this section we briefly examine the reaction kinetics governing the induction periods and interpret the present experimental data in terms of these reactions. The well known kinetics of H_2-Air are treated first, followed by a discussion of the kinetics applicable to the addition of NO or NO_2.

Hydrogen-Air Kinetics

The mechanism of $H_2 - O_2$ ignition is well established (Ref. 20) and the important gas phase reactions during the induction period are

$$H_2 + OH = H_2O + H \tag{4}$$

$$H + O_2 = OH + O \tag{5}$$

$$O + H_2 = OH + H \tag{6}$$

$$H + O_2 + M = HO_2 + M \tag{7}$$

Competition between reactions (5) and (7) is essentially responsible for the second explosion limit and for the unusual relationship between τ_i and pressure, as shown in Fig. 4.

Ignition delay times were computed with the NASA General Chemical Kinetics Computer Code (Ref. 21) using the sixteen reaction set and rate coefficients reported by Slack (Ref. 22) in an earlier study of H_2-O_2 ignition. Numerical predictions of τ_i at pressures of 0.507 and 2.02 x 10^5 N/m^2 (0.5 and 2.0 atm), agreed well with experimental observations as shown in Fig. 16. The agreement at 2.02 x 10^5 N/m^2 (2.0 atm) is to be expected, since Slack (Ref. 22) used this experimental data to back out a rate coefficient for reaction (7).

H_2-Air-NO Kinetics

Sensitization of the induction period kinetics by NO can be explained by the fast catalytic chain

$$HO_2 + NO = OH + NO_2 \tag{8}$$
$$NO_2 + H = OH + NO \tag{9}$$

which converts the hydroperoxyl chain terminator to hydroxyl, a chain initiator. The influence of HO_2, in lengthening τ_i at conditions near the second explosion limit, is thereby negated and the formation of OH promotes positive chain branching. This is entirely consistent with the observations of the preceeding section, which show maximum sensitization at low temperatures and high pressures, i.e., at experimental conditions where reaction (7) effectively competes with reaction (5) for hydrogen atoms and where HO_2 formation is favored in the absence of NO.

A more complete mechanism was proposed by Ashmore and Tyler (Ref 9) to explain the influence of NO upon the H_2 -O_2 ignition limits and includes the following reactions

$$HO_2 + NO = OH + NO_2 \tag{8}$$
$$NO_2 + H = OH + NO \tag{9}$$
$$NO + OH + M = HNO_2 + M \tag{10}$$
$$NO_2 + OH + M = HNO_3 + M \tag{11}$$
$$H_2 + NO_2 = HNO_2 + H \tag{12}$$
$$O + NO_2 = NO + O_2 \tag{13}$$

At low temperature and high pressure, increasing τ_i with increasing NO concentration (see Fig. 8) can be qualitatively explained by the termination reactions (10) and (11) that produce HNO_2 and HNO_3, while removing OH.

Ignition delay times were computed with the NASA General Chemical Kinetics Computer Code (Ref. 21) using a sixteen reaction H_2-O_2 mechanism together with the reactions and rate coefficients of Table 4. These predictions (for stoichiometric hydrogen-air, $1.0 \times 10^5 N/m^2$ (1.0 atm), 1000^oK, and various NO sensitizer levels) are compared with measured data from the present investigation in Fig. 17. Theory and experiment have the same qualitative trend (i.e., NO sensitizes ignition) and were in reasonable agreement. Above $\frac{1}{2}$% of additive, our theoretical ignition delays were insensitive to further increases of NO. Increases in k_8 made no difference to the predicted delay times. We conclude that once sufficient NO (about $\frac{1}{2}$%) has been added to optimize the removal of HO_2 via reaction (8), then neither an increase in sensitizer nor an increase in k_8 will further accelerate ignition. The reaction now proceeds via the H_2-O_2 chain, with the $H + O_2 + M = HO_2 + M$ termination reaction effectively neutralized and with the H_2-O_2 branching reaction rate coefficients well defined (Ref. 23).

TABLE 4 NO - H_2 - O_2 RATE COEFFICIENTS

Reaction No.	Reaction	Rate Coefficient* A	n	E	Source
8	$HO_2 + NO = OH + NO_2$	3.0 E 12	0.5	2400	Kondratiev (Ref. 24)
9	$NO_2 + H = OH + NO$	3.5 E 14	0	1480	Baulch (Ref. 15)
10	$NO + OH + M = HNO_2 + M$	8.0 E 15	0	-2200	Hampson (Ref. 25)
11	$NO_2 + OH + M = HNO_3 + M$	1.3 E 16	0	-2200	Hampson (Ref. 25)
12	$H_2 + NO_2 = HNO_2 + H$	9.6 E 12	0	24000	Estimate
13	$O + NO_2 = NO + O_2$	1.0 E 13	0	600	Baulch (Ref. 15)

*Rate coefficient, $k = AT^n \exp(-E/RT)$

Despite minor quantitative differences, the overall agreement between our predictions and data in Fig. 17, supports the mechanism first proposed by Ashmore - reactions (8) to (13).

Strokin and Khailov (Ref. 10) have also predicted τ_i for hydrogen-air-NO. They used a 21 reaction mechanism which, in addition to the usual H_2-O_2 reactions and N_2-O_2 reactions, included

$$H + NO + M = HNO + M \tag{14}$$

$$HNO + H = H_2 + NO \tag{15}$$

$HNO + OH = H_2O + NO$ (16)

$NO + O + M = NO_2 + M$ (17)

$NO_2 + H = NO + OH$ (18)

The above reactions remove radicals from the H_2 -O_2 chain, reducing the branching rate and increasing the induction time. These predictions of τ_i, by Strokin and Khailov (Ref. 10) are also shown in Fig. 17 but they are significantly higher than the current measurements. At 4% NO, Strokin and Khailov predict an induction time more than two orders of magnitude higher than the experimental data. Their mechanism lacks the important catalytic chain, reactions (8) and (9).

Further comparison between the experimental data and numerically predicted induction periods are required to test the validity of the reactions in Table 3 and their associated rate coefficients.

H_2-Air-NO_2 Kinetics

We anticipated that the Ashmore and Tyler mechanism (Ref. 9) would apply to this system. However, the presence of NO_2 introduces a fast initiation step

$H_2 + NO_2 = HNO_2 + H$ (12)

and preliminary computations indicate that the H_2 -NO_2 reactions (Ref. 26) then play a dominant role in the induction period of the H_2 -O_2 -NO_2 system. The H_2 -NO_2 reactions include the initiation step, reaction (12), and a rapid chain

$NO_2 + H = NO + OH$ (9)

$H_2 + OH = H_2O + H$ (4)

where H and OH are the chain carriers. Termination occurs via the reactions

$NO + OH + M = HNO_2 + M$ (10)

$NO_2 + OH + M = HNO_3 + M$ (11)

which become important at higher pressures and higher NO_2 concentrations, and which lengthen the induction time. This could account for the minima in the plots of τ_i against NO_2 mole percent, as shown in Fig. 13. Alternatively, termination could occur via the recombination reactions

$NO + H + M = HNO + M$ (14)

$NO_2 + H + M = HNO_2 + M$ (19)

A thorough quantitative investigation, beyond the scope of the present study, is needed to support the foregoing preliminary assessment, and should include comparisons of numerical predictions with measured induction times and adjustments of both the mechanism and associated rate coefficients.

5. INFLUENCE OF NO_x ON NASA SCRAMJET TESTS

Addressing first the general question of NO_x influence on combustion tests in an arc-heated facility, combustion will be assisted by the presence of NO_x, particularly in the vicinity of the second explosion limit (see Fig. 18). The NO_x acts to reduce the ignition delay time (in some cases by more than one order of magnitude) thereby improving measured combustion efficiencies in a ground test. Consequently, caution should be exercised in the interpretation and scaling of a successful ground test since the full scale combustor, with clean air as the oxidizer, could have very low combustion efficiencies resulting from long ignition delay times.

In connection with the specific NASA Langley SCRAMJET combustor tests (Ref. 27), Table 5 lists the local temperature, pressure, and velocity for injection bays Nos. 6, 10, and 14 of the subscale hydrogen-burning SCRAMJET combustor, shown in Fig. 19.

TABLE 5 COMBUSTOR IGNITION DELAY TIME ESTIMATES*

Bay	P	T	V	Ignition Delay (sec)		Characteristic Length (m)	
	(x $10^5 N/m^2$)	(^oK)	(m/s)	NO = 0%	NO = 2%	NO = 0%	NO = 2%
10	0.271	800.	1846.	$>4.0 \times 10^{-3}$	0.9×10^{-3}	>7.4	1.7
14	0.247	722	1896.	**	**	**	**
6	0.176	657	1935.	**	**	**	**

*Injection bay thermodynamic properties from Ref. 27. Ignition delays from extrapolation, using numerical predictions, of data in Fig. 7.

**Extrapolation of present data to these conditions considered unreliable.

Ignition delays and characteristic lengths for bay 10 are presented in Table 5. The characteristic length is computed as the product of ignition delay and velocity. A nominal 2% NO was selected for comparison with the clean air condition (i.e., NO = 0%). The temperature at bay 10 was below the experimental range in Fig. 7, and numerical predictions were employed to extend the data to lower temperatures.

For stoichiometric hydrogen-air, numerically predicted τ_i rose rapidly at temperatures below 900°K (because the second explosion limit was being approached) and at 800°K ignition had not yet occurred for numerical predictions carried out to 4 ms, which placed a lower bound on τ_i. Comparison of the ignition delays in Table 5 showed that the ignition delay time at bay 10 will be reduced at least 78% by the presence of 2% NO.

Extrapolation of the present data to the thermodynamic condition of injector bays 6 and 14 was considered unreliable. However, since the local temperatures are well below the second explosion limit temperatures (833 and 811°K for bays 14 and 6 respectively), 2% NO would be expected to play a major role in promoting ignition.

Recirculation behind the injection step and locally higher temperatures associated with shock wave heating at the injection station, will both reduce the ignition delays in Table 4. However, the injected hydrogen is cold and the initial mix of hydrogen and air will be colder than the local oncoming air temperatures listed in Table 4, offsetting the gains of shock heating and flame holding. Nonetheless, the presence of NO_x will be beneficial to the combustion tests and the extrapolation of test data to a full scale vehicle operating in clean air can only be made with caution.

6. CONCLUSIONS

From the present investigation, we conclude that both NO and NO_2 sensitize H_2-Air ignition, i.e., reduce the induction time, as shown in Figs. 5 to 15. Figure 18 illustrates the pressure-temperature regimes of maximum sensitization. Significant reductions - greater than an order of magnitude - occur in the vicinity of the second explosion limits. The mechanism of the H_2-Air-NO induction period kinetics is adequately described by the Ashmore and Tyler mechanism (Ref. 9). A theoretical reaction model proposed by Strokin and Khailov (Ref. 10) fails, inasmuch as it predicts inhibition whereas sensitization was observed.

A successful combustor test in an arc-heated facility, where NO_x is present, will not necessarily ensure the development of a successful engine operating in clean air. The influence of NO_x upon the ground tests must be carefully assessed before a meaningful extrapolation or scaling can be made to flight conditions. In the NASA Langley SCRAMJET tests (Ref. 27), combustion will be aided by the presence of NO_x reducing the induction time by at least 78% (see Table 5).

Additional shock tube measurements would be useful in order to assess the influence of NO_x on nonstoichiometric mixtures of hydrogen-air that will be encountered near the injectors. Furthermore, the present shock tube technique lends itself to the study of NO and NO_2 influence upon hydrocarbon-air combustion and could be extended to advanced aerospace fuels such as methane.

A limited study of the induction period kinetics has been undertaken in this investigation. A more extensive study is required in order to develop a satisfactory self consistent set of reactions and rate coefficients which can then be used to predict ignition in H_2-Air-NO-NO_2 mixtures, particularly at injector bay conditions well outside the present experimental range (i.e., bays 6 and 14 of Table 4).

The influence of NO and NO_2 upon the post induction period reaction zone requires additional investigation. The present results apply only to the induction period.

The authors are pleased to acknowledge laboratory technical assistance by J. Drauch and S. Danos. Assistance with the computations was provided by N. Robinson and J. Leng.

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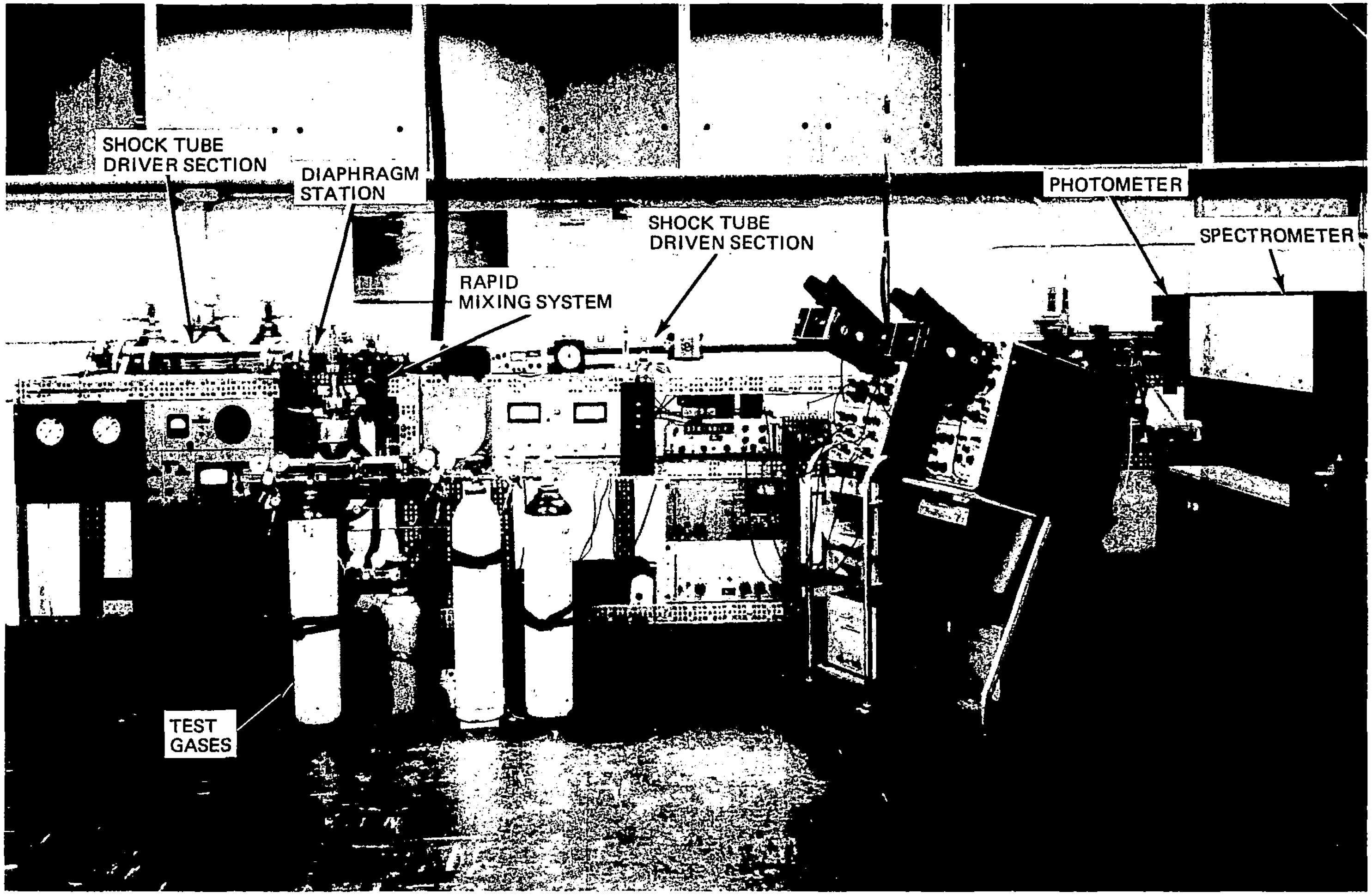


Fig. 1 Overall View of Chemical Kinetic Shock Tube

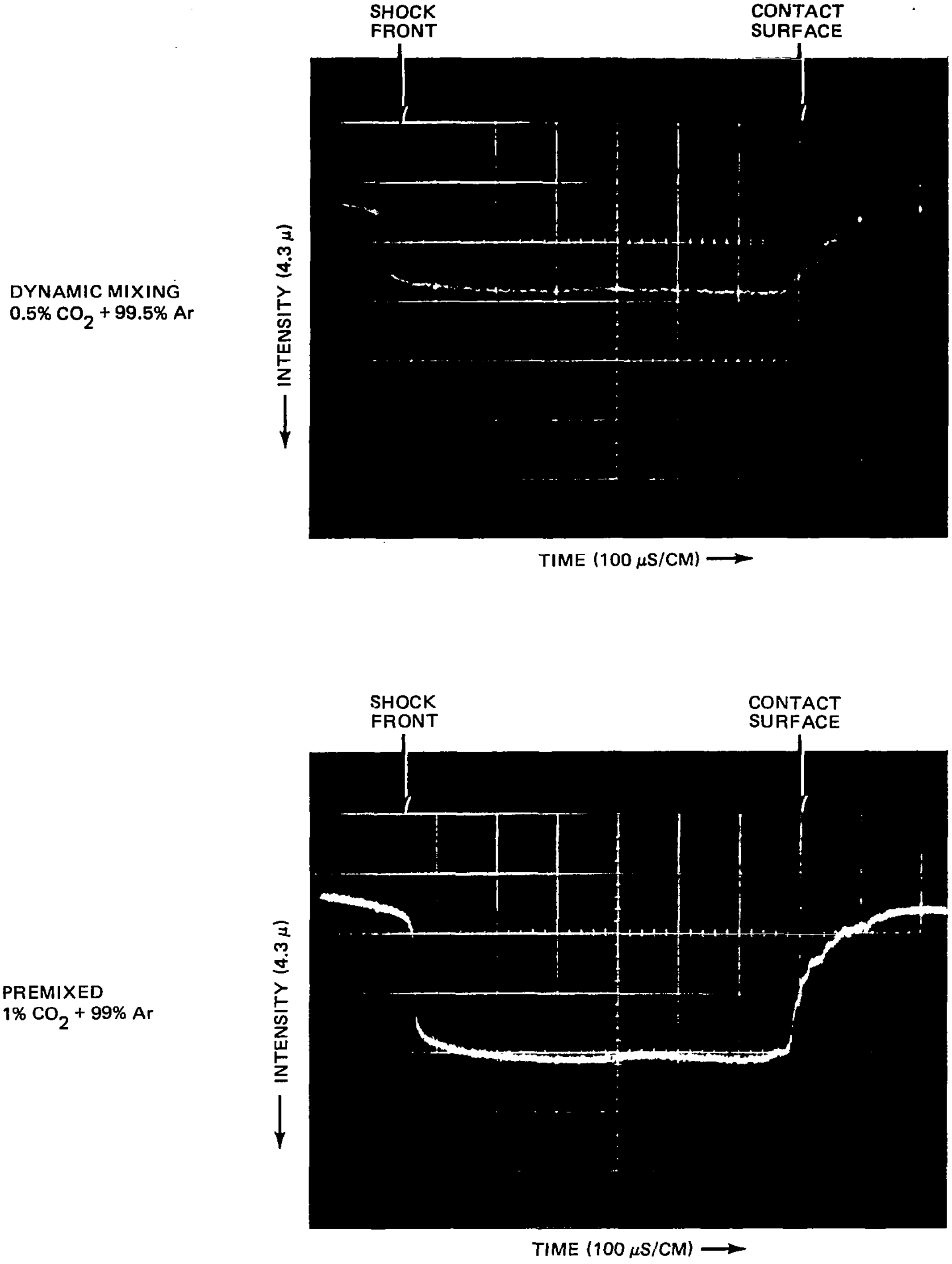
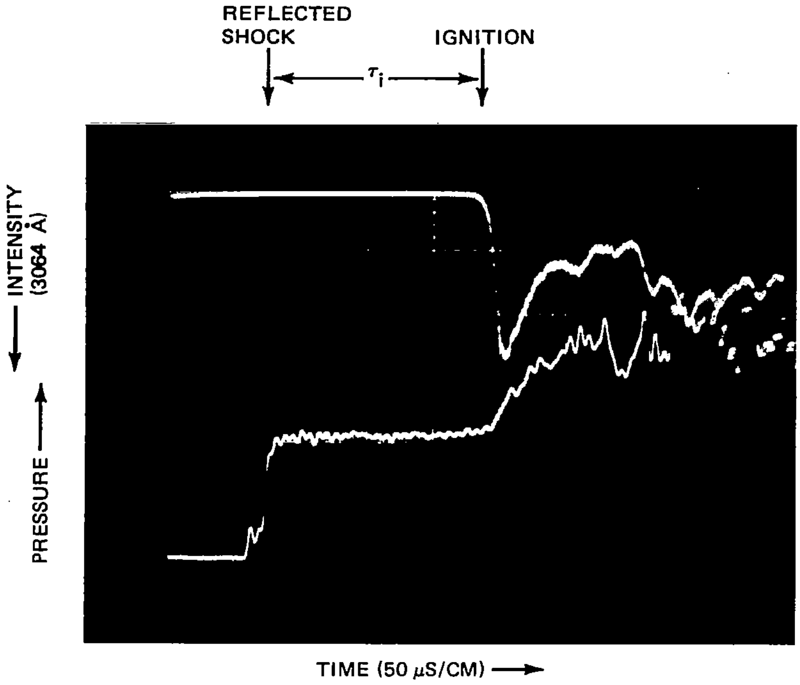
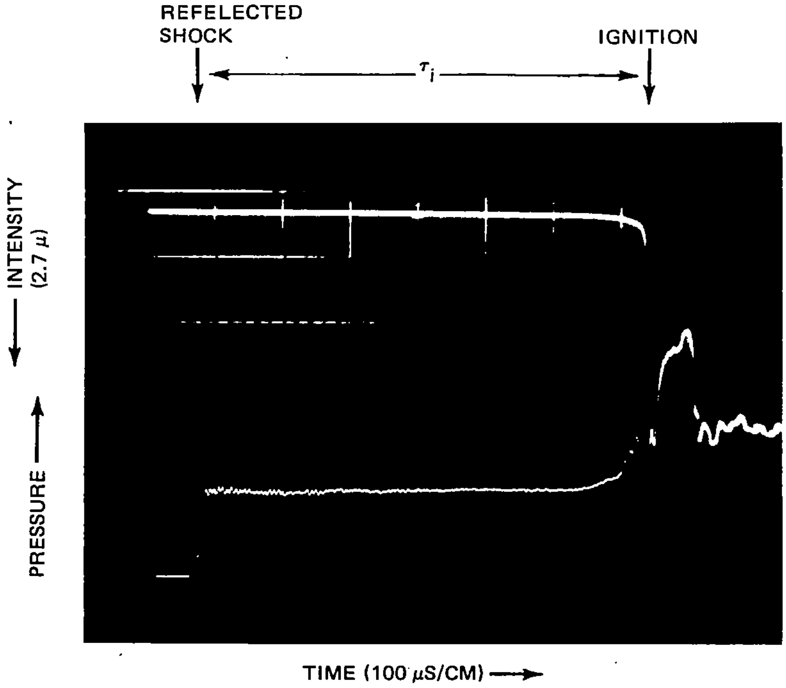


Fig. 2 Oscillogram traces of 4.3 μ Emission From The Rapid Mixing Technique Validation Tests



RUN NO. 152
0.5% NO, MIXTURE 2
T = 970°K
P = 0.51 ATM



RUN NO. 128
0.75% NO_2 MIXTURE 6
T = 845°K
P = 2.2 ATM

Fig. 3 Typical Oscillograms of Static Pressure, OH emission and H_2O emission, Illustrating Ignition in Mixtures 2 and 6 (See Table 1)

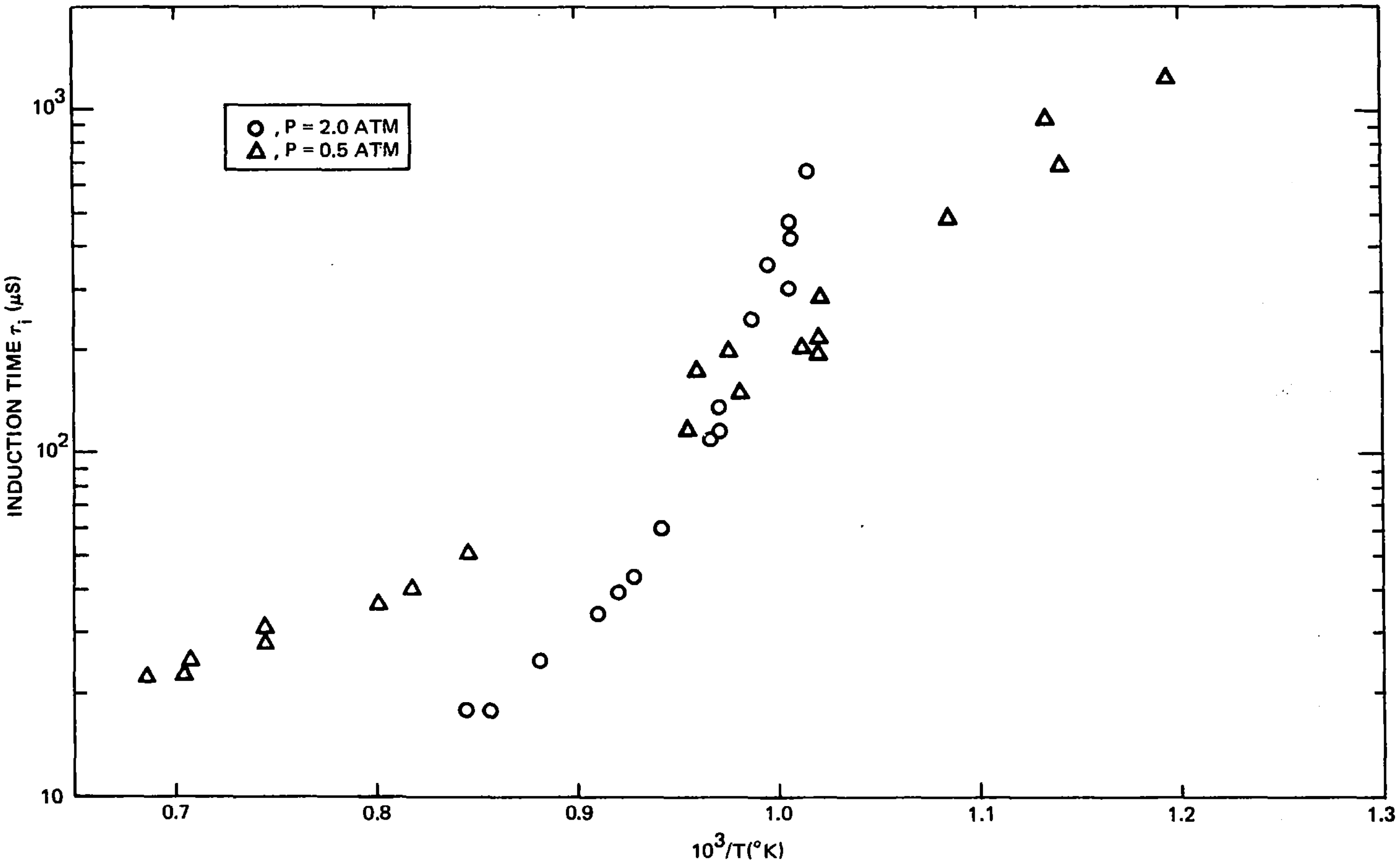


Fig. 4(a) Induction Times for Stoichiometric Hydrogen-Air vs Reciprocal Temperature; P = 0.507 x 10^5 N/m^2 (0.5 atm) and 2.02 x 10^5 N/m^2 (2.0 atm)

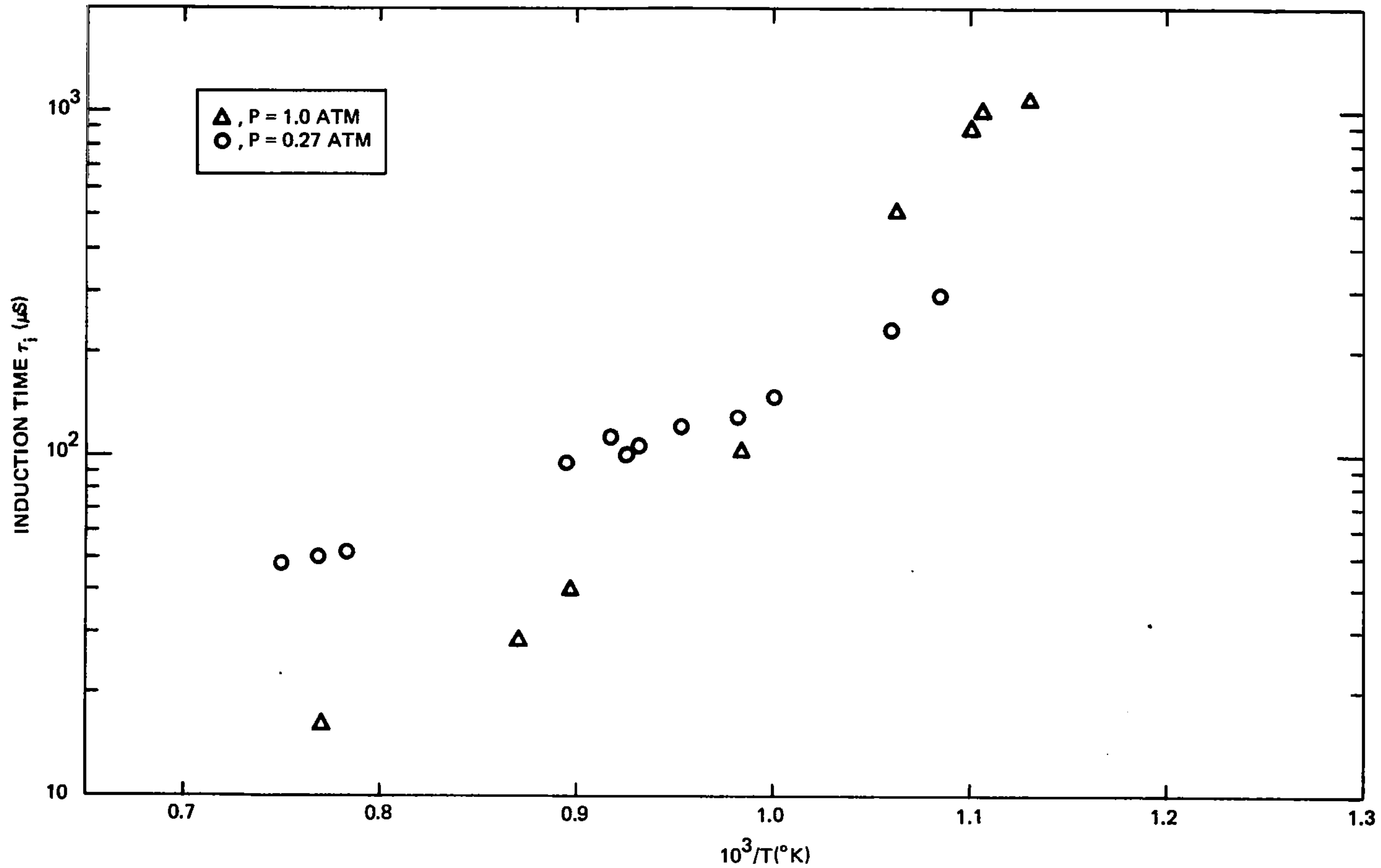


Fig. 4(b) Induction Times for Stoichiometric Hydrogen-Air vs Reciprocal Temperature; P = 0.273 x 10^5 N/m^2 (0.27 atm) and 1.01 x 10^5 N/m^2 (1.0 atm)

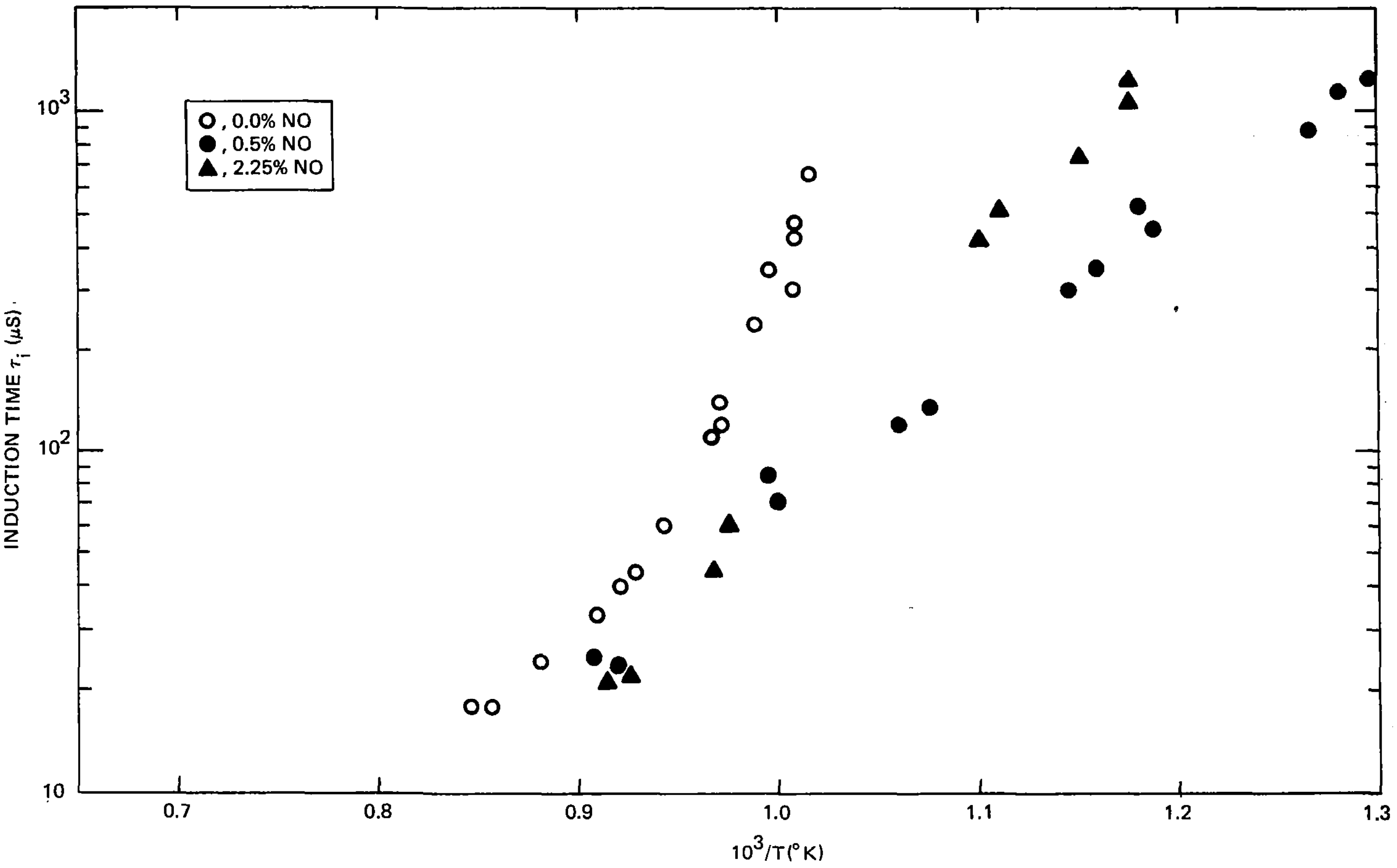


Fig. 5 Induction Times for Stoichiometric Hydrogen-Air with 0.0, 0.5, and 2.25 Mole Percent NO: P = 2.02×10^5 N/m^2 (2.0) atm

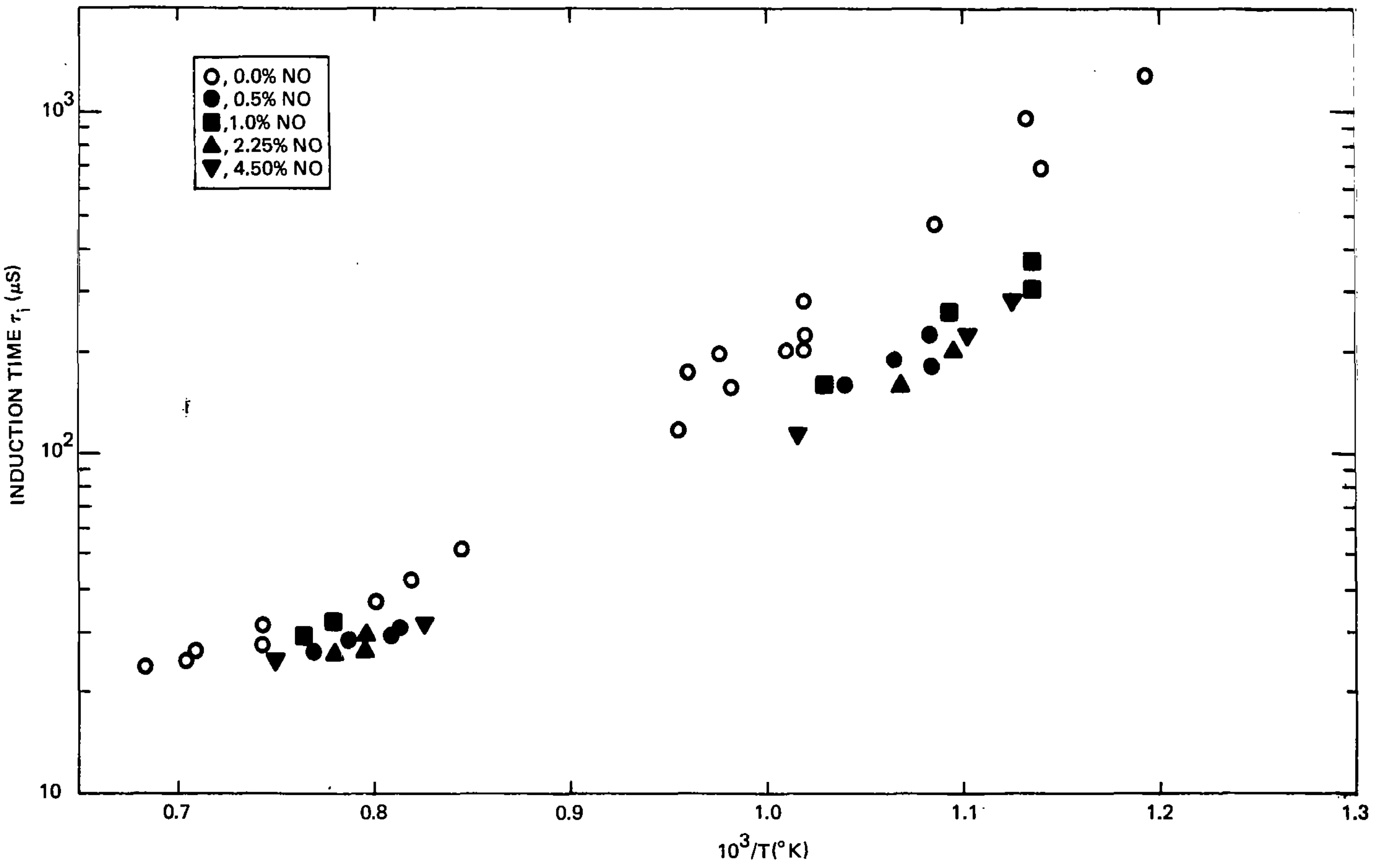


Fig. 6 Induction Times for Stoichiometric Hydrogen-Air with 0.0, 0.5, 1.0, 2.25 and 4.5 Mole Percent NO; P = 0.507 x 10^5 N/m^2 (0.5 atm)

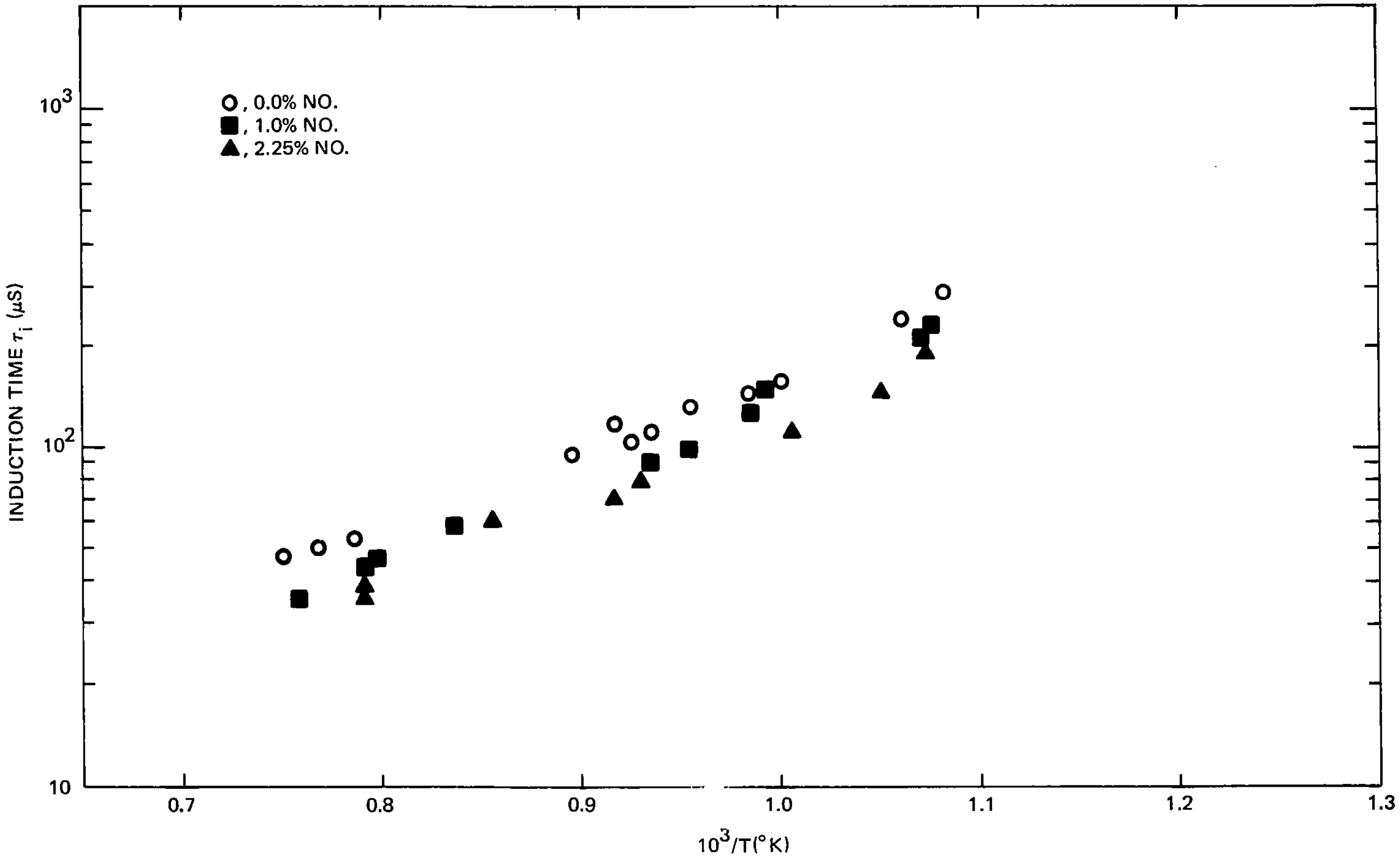


Fig. 7 **Induction Times for Stoichiometric Hydrogen-Air with 0.0, 1.0 and 2.25 Mole Percent NO; $P = 0.273 \times 10^5$ N/m^2 (0.5 atm)**

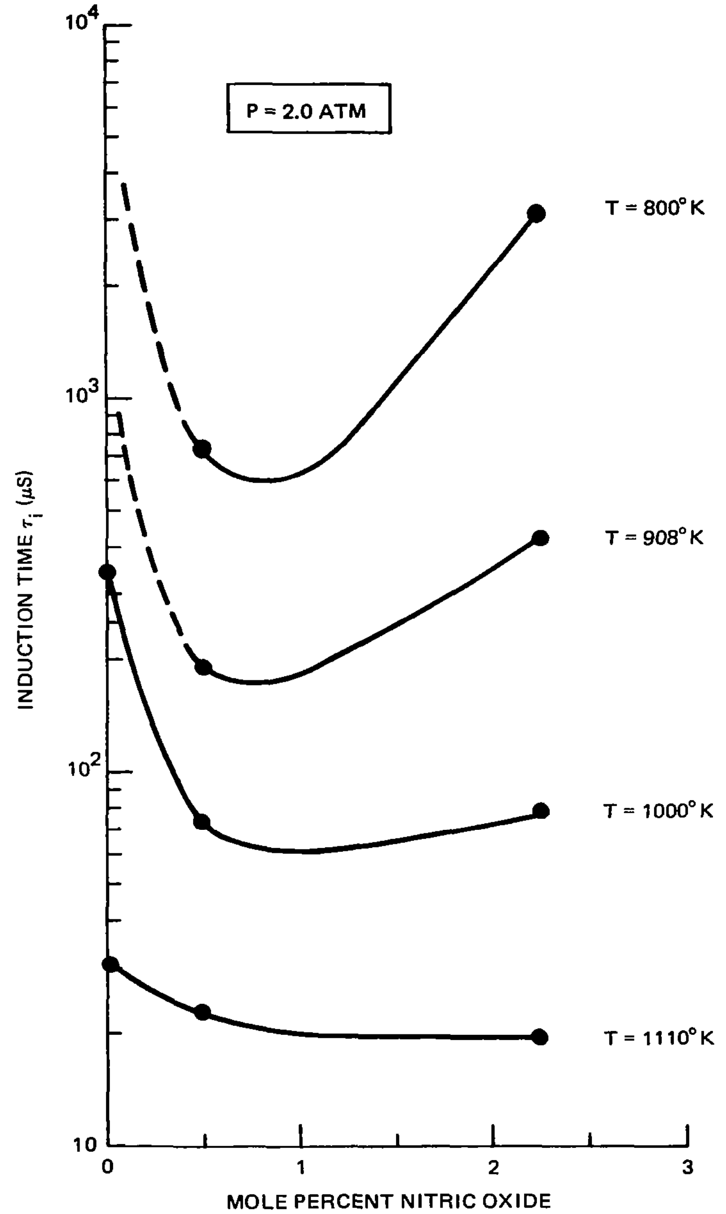


Fig. 8 Variation of Induction Times with Mole Percent Nitric Oxide, at $P = 2.02 \times 10^5$ N/m^2 (2.0 atm)

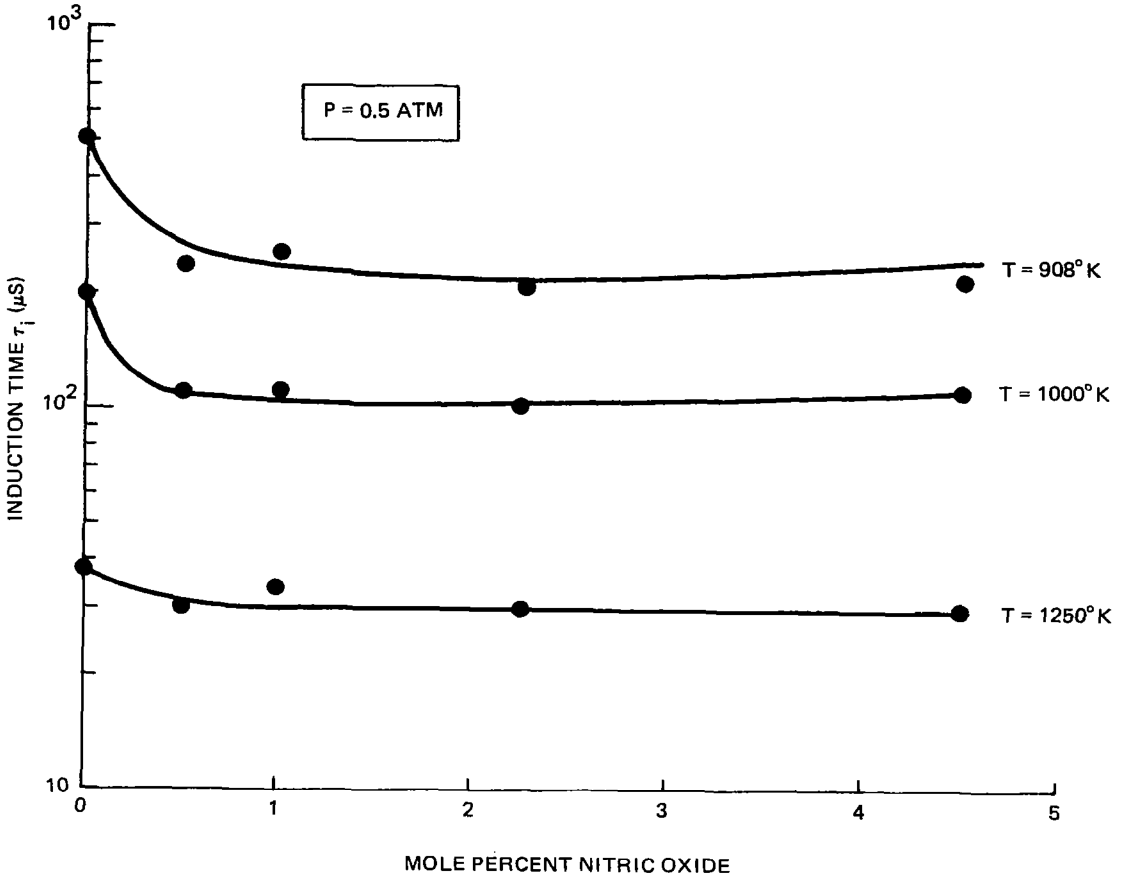


Fig. 9 Variation of Induction Times with Mole Percent Nitric Oxide, at $P = 0.507 \times 10^5$ N/m^2 (0.5 atm)

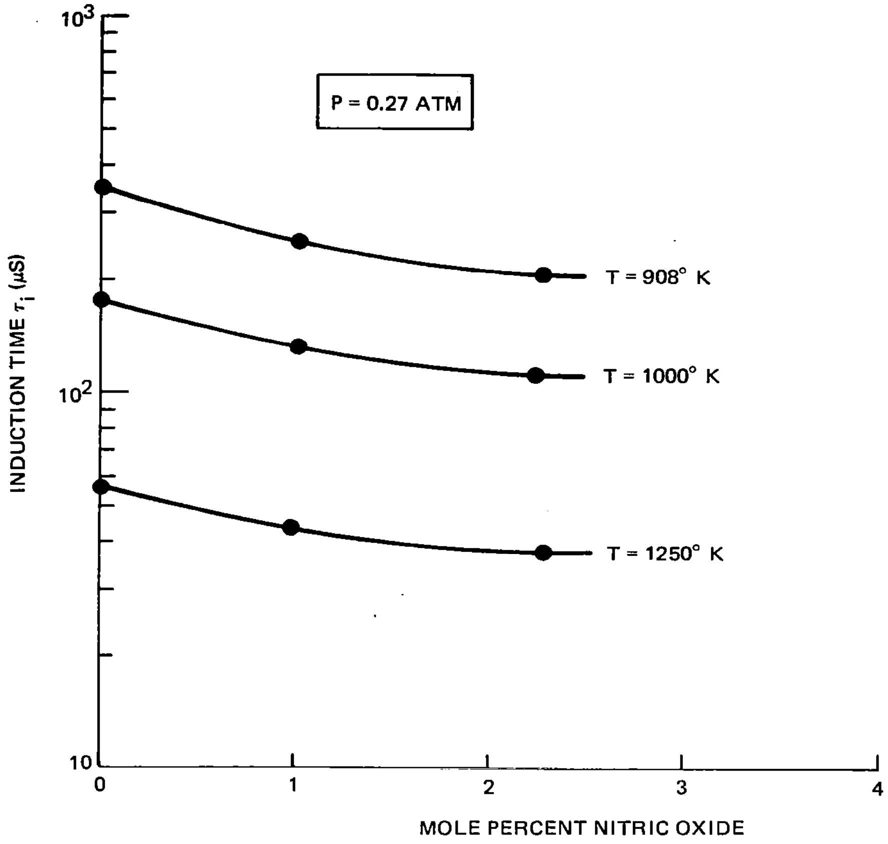


Fig. 10 Variation of Induction Times with Mole Percent Nitric Oxide; $P = 0.273 \times 10^5$ N/m^2 (0.27 atm)

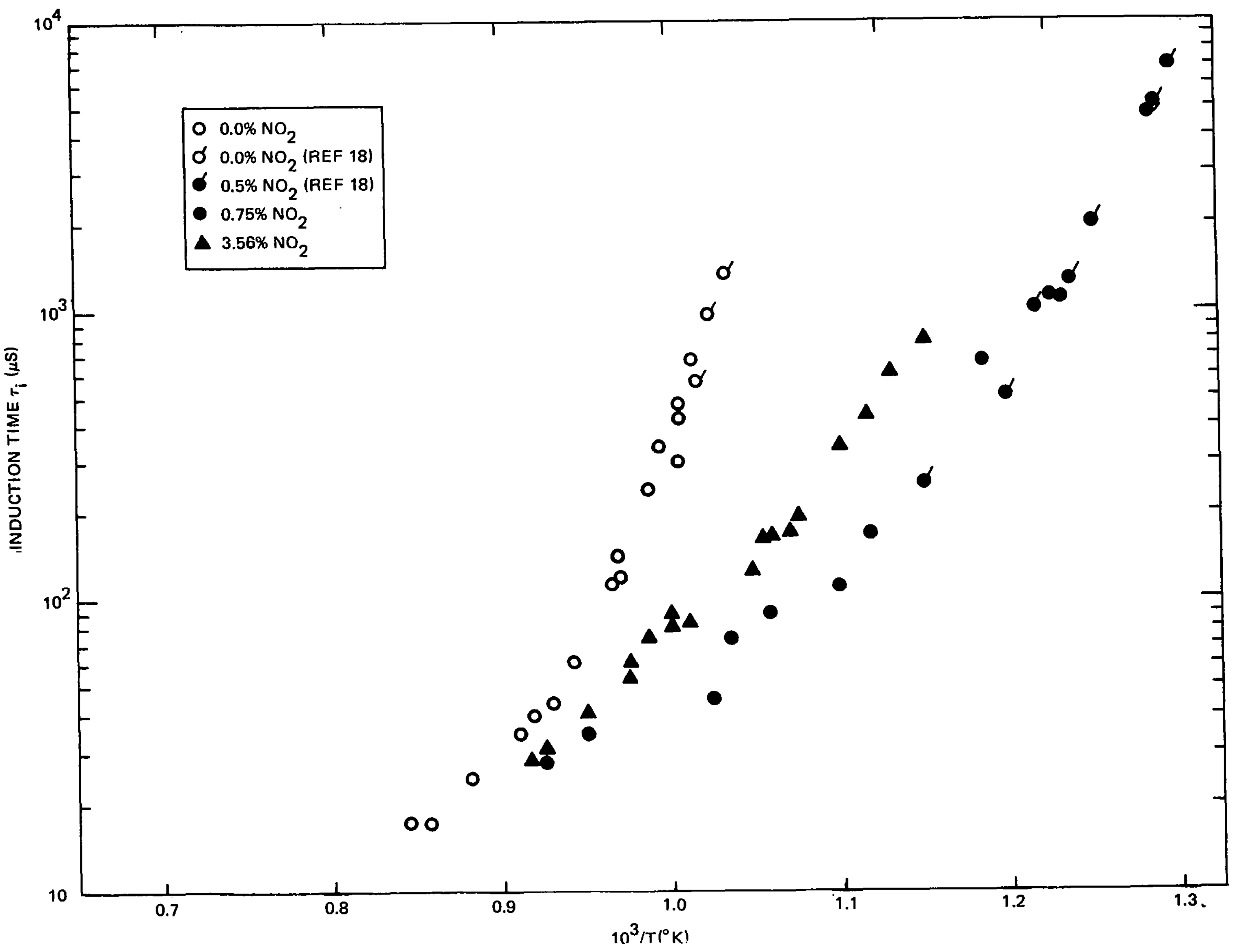


Fig. 11 Induction Times for Stoichiometric Hydrogen-Air with 0.0, 0.5, 0.75, and 3.56 Mole Percent NO_2; P = 2.02 x 10^5 N/m^2 (2.0 atm)

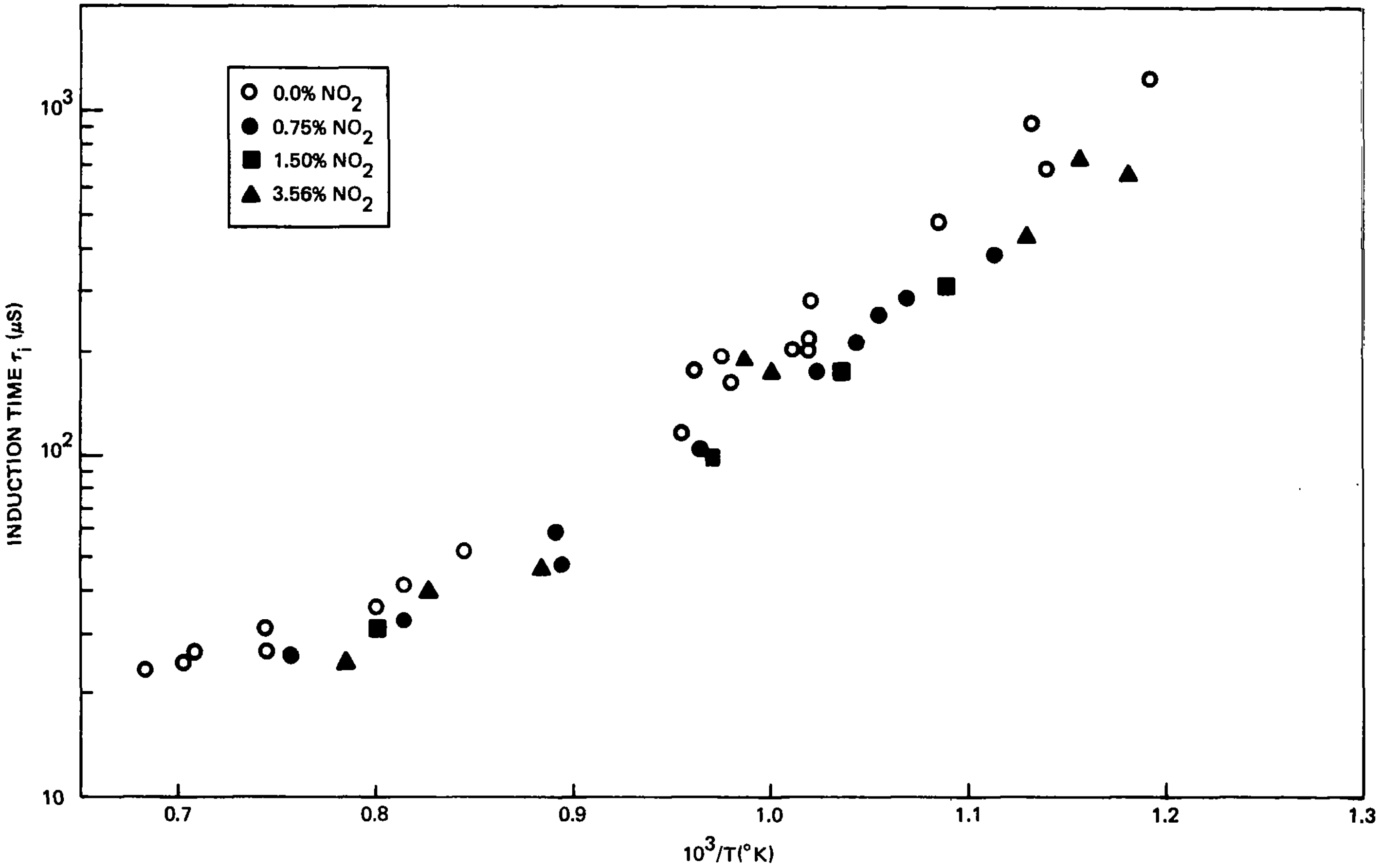


Fig. 12 Induction Times for Stoichiometric Hydrogen-Air with 0.0, 0.75, 1.5, 3.56 Mole Percent of NO_2; $P = 0.507 \times 10^5\ N/m^2$ (0.5 atm)

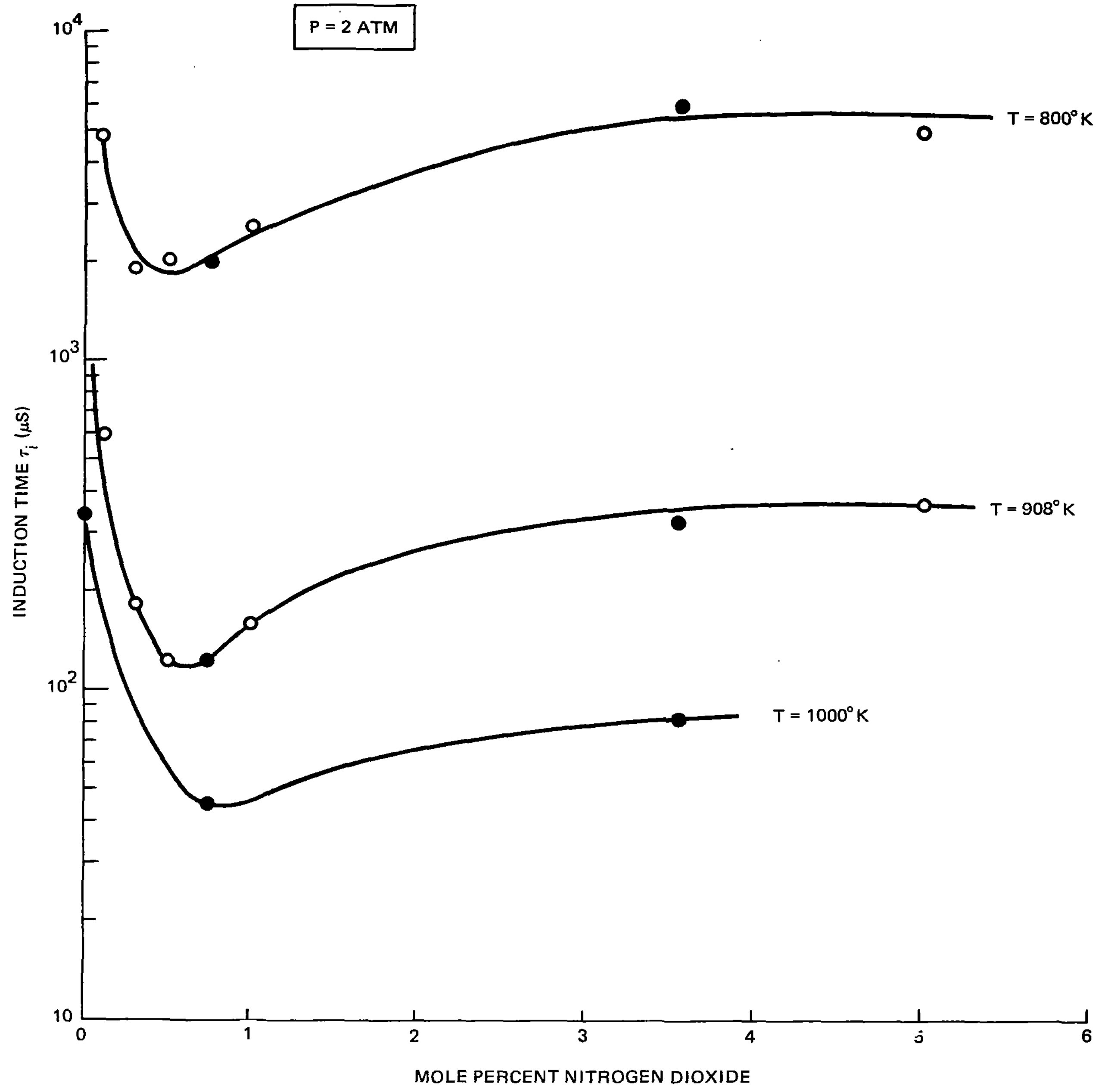


Fig. 13 Variation of Induction Times, with Mole Percent Nitrogen Dioxide. Present Investigation, Closed Symbols; Ref. 18, Open Symbols. $P = 2.02 \times 10^5$ N/m^2 (2.0 atm)

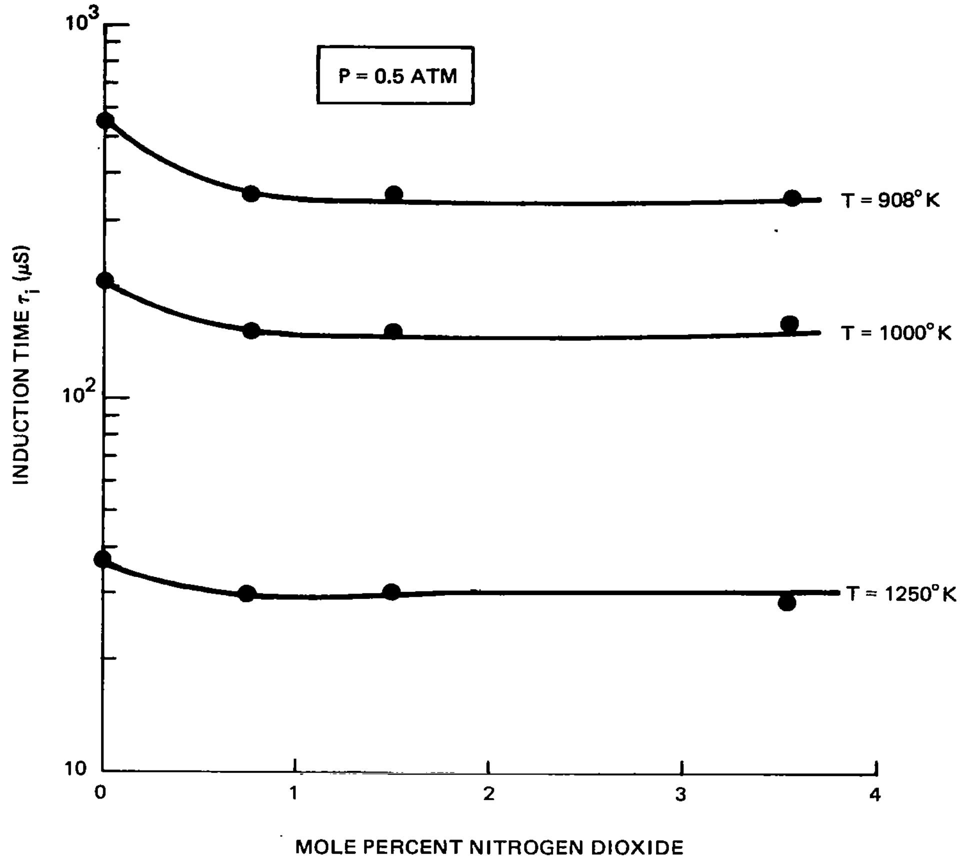


Fig. 14 Variation of Induction Times with Mole Percent Nitrogen Dioxide; $P = 0.507 \times 10^5$ N/m^2 (0.5 atm)

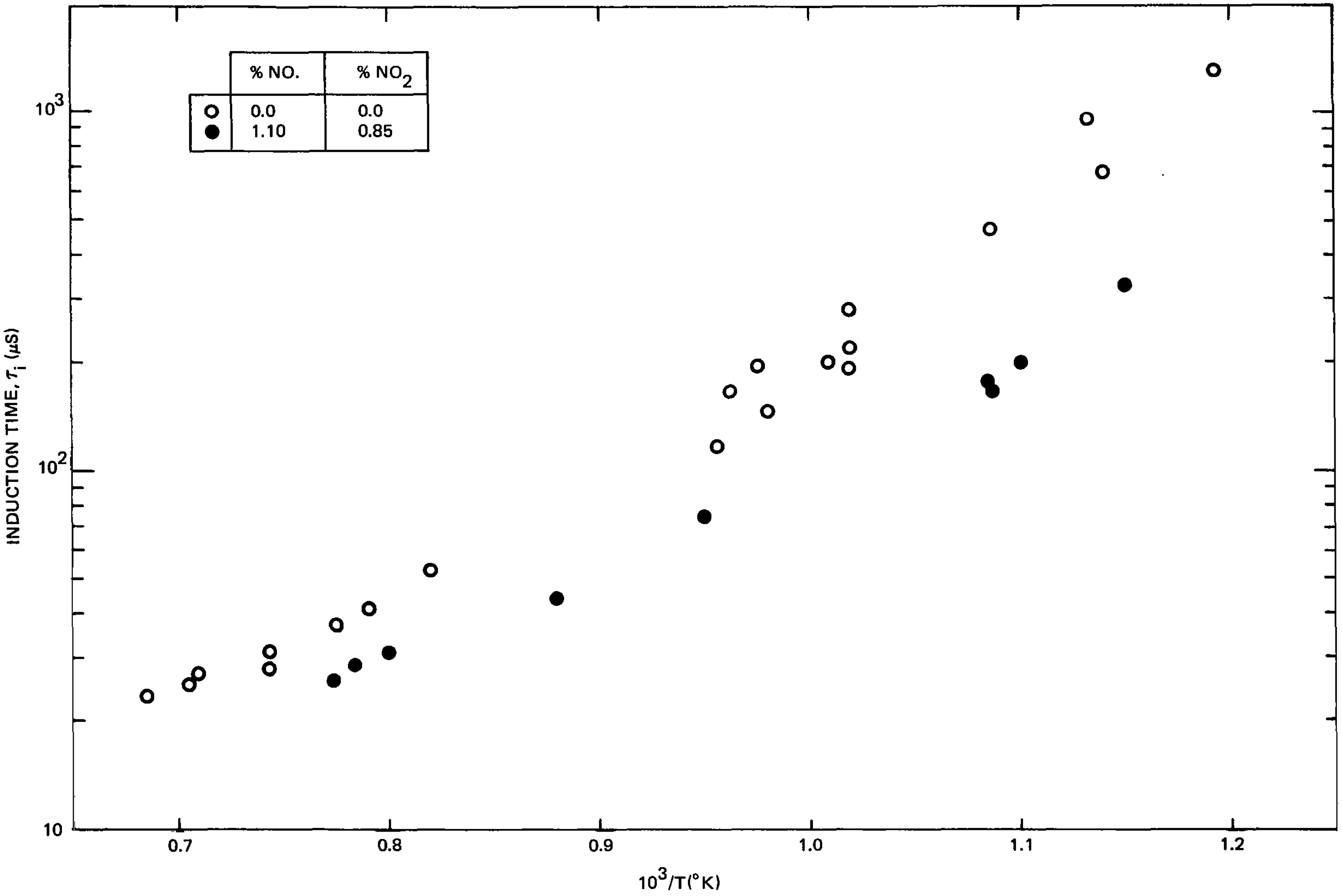


Fig. 15 Induction Times for Stoichiometric Hydrogen-Air with 1.10 Mole Percent NO Plus 0.85 Mole Percent NO_2; P = 0.507 x 10^5 N/m^2 (0.5atm)

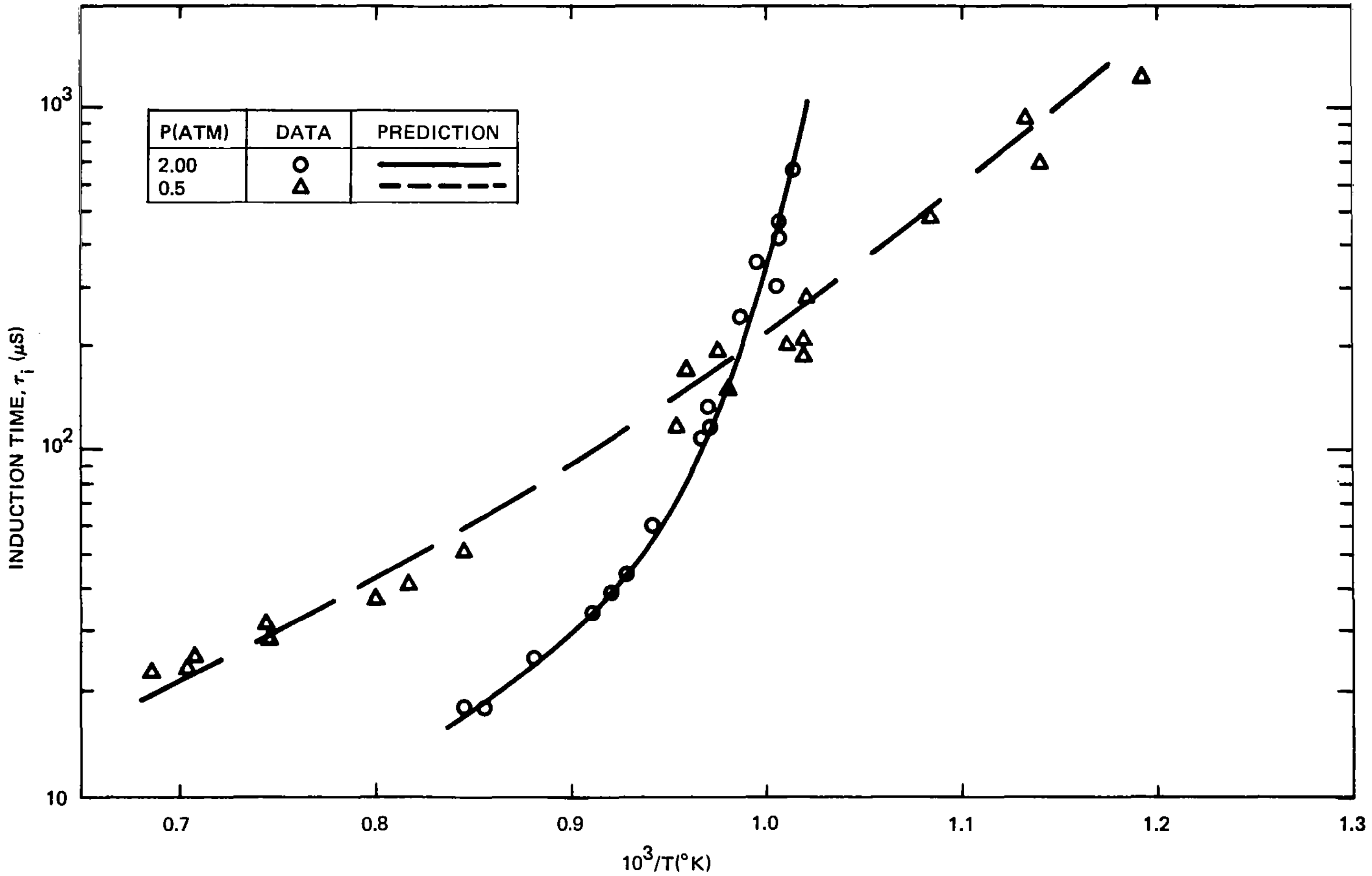


Fig. 16 Numerically Predicted Induction Times Compared with Experimental Data. Stoichiometric Hydrogen-Air at Pressures of 0.507 x 10^5 N/m^2 (0.5 atm) and 2.02 x 10^5 N/m^2 (2.0 atm)

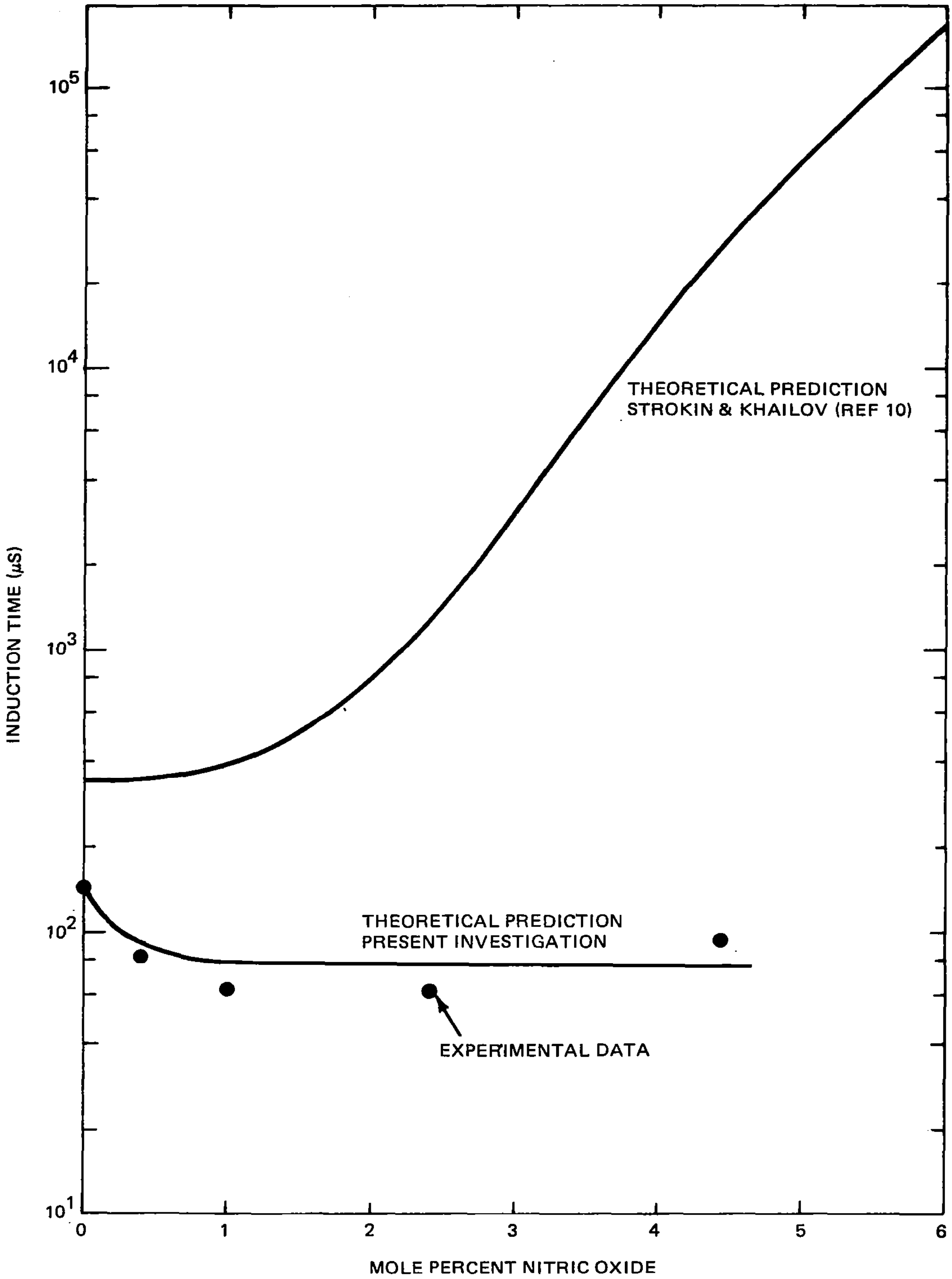


Fig. 17 Theoretical Predictions (Present Investigation and Ref. 10) of Induction Times as a Function of Nitric Oxide Mole Percent Compared with Experimental Data. Stoichiometric Hydrogen-Air, T = 1000°K and P = 1.01×10^5 N/m^2 (1.0 atm)

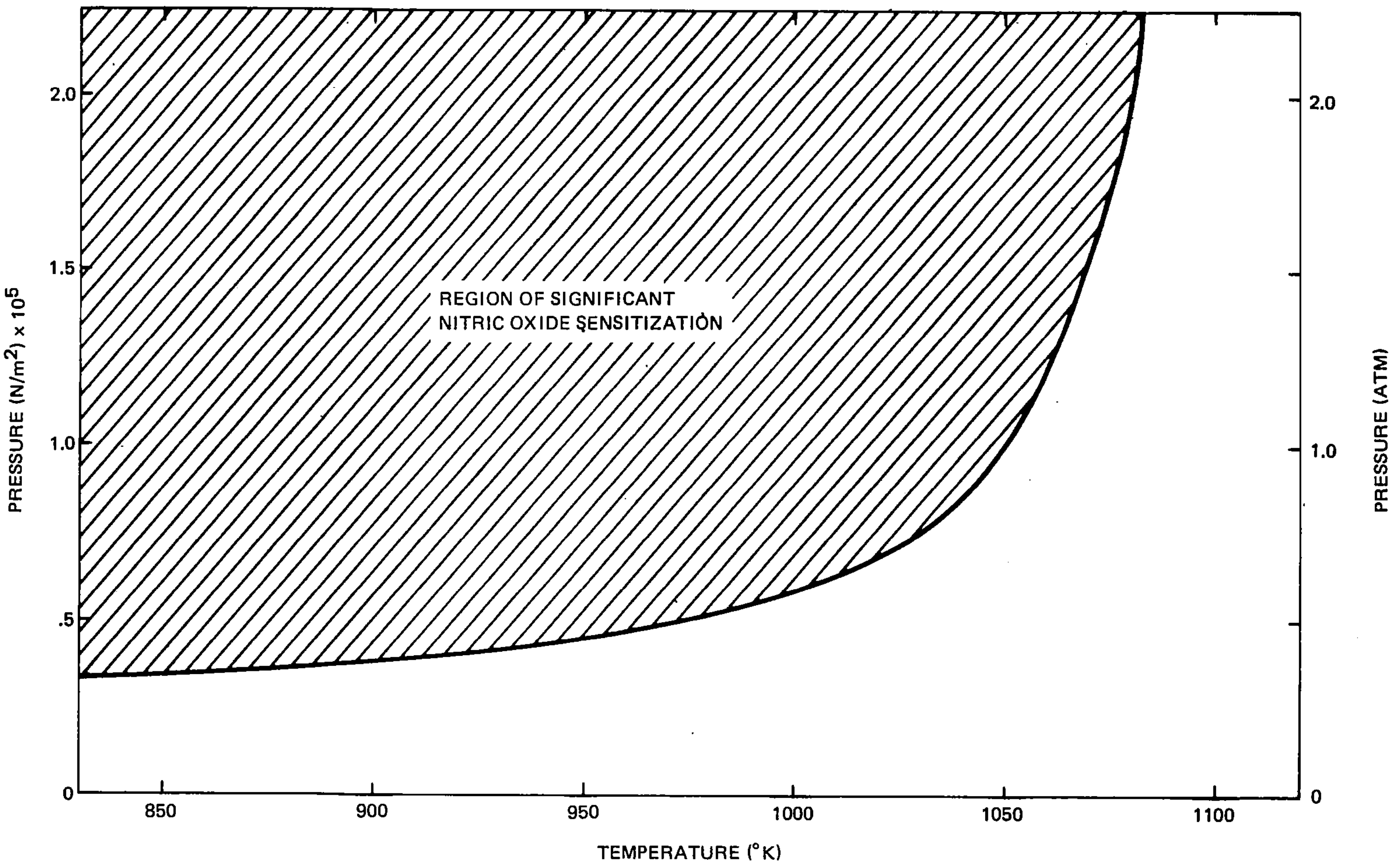


Fig. 18 Pressure-Temperature Region Where 2% NO Additive Reduces τ_i of Stoichiometric Hydrogen-Air by at Least a Factor of 2

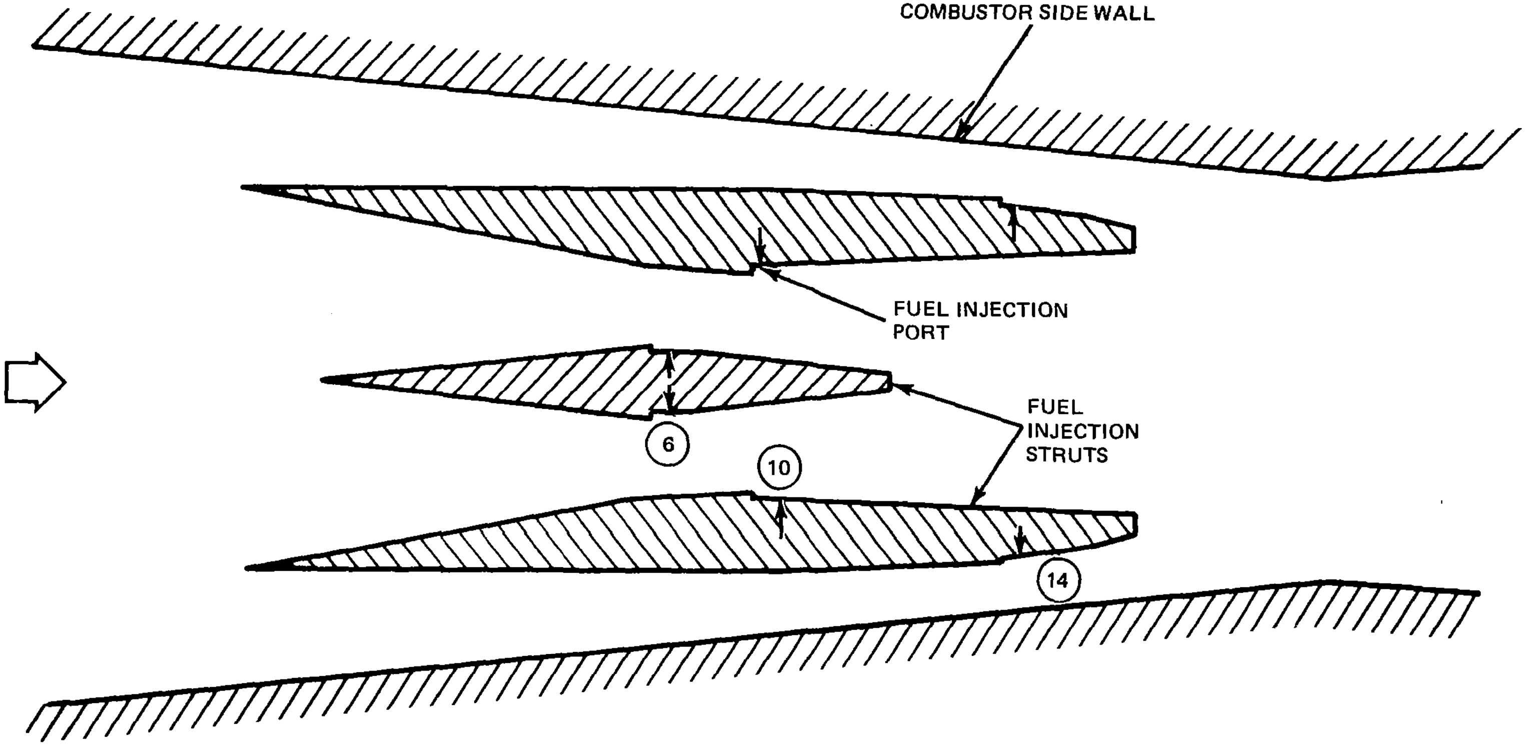


Fig. 19 SCRAMJET Combustor Section in Plane Parallel to the Cowl Plane, Illustrating Fuel Injection Ports and Injection Bay Numbers

NASA-Langley, 1977 CR-2896