SPONTANEOUS IGNITION DELAYS OF PROPANE INJECTED INTO A HOT AIR STREAM

by

Sin-Kan Fang

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Department of Mechanical Engineering
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SUMMARY

The ignition delays of propane in a flow system were found to be influenced by the manner in which propane was introduced into the air. For a multihole injector with fuel jets at 90 degrees to the air stream the delay-temperature relationship is of the form $\ln \gamma = \frac{71,800}{RT} + \text{constant}$, over the range of air/propane ratios 117 - 35:1.

This equation is dependent on the concentration of propane. Investigations showed that by decreasing air/propane ratio from 117:1 to 11:1, ignition delay increased to a maximum and then decreased to an almost constant value, for air temperatures between 1011 °K and 1062 °K. The same tendency has been observed for higher temperatures up to 1164 °K, but the variation in delay was considerably less.

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INTRODUCTION

Owing to its significant effect on fire hazards of combustible materials and the performance of internal combustion engines, spontaneous ignition has been studied since the beginning of this century. Early workers however aimed mainly at determining the ignition temperature, and it was not until recent years that ignition delay has received due attention and formed a subject of research in its own right.

Dixon, Bradshaw and Campbell (Ref. 1) using an adiabatic compression apparatus in 1914, were the first to recognize the existence of a 'pre-flame period'. Tizard and Pye in 1926 further demonstrated this phenomenon occurring in a reciprocal engine by a similar equipment, comprising rapid compression of a homogeneous combustible mixture in an engine like cylinder. This technique together with the 'bomb method' in which the mixture is sealed in a closed space, have been fully developed up to the present day and have provided invaluable ignition delay data for spark ignition and diesel engines.

With the development of the gas turbine and rocket motor, information obtained under conditions akin to a continuous combustion process has become necessary. In 1946 a flow technique, originated by Dixon and his collaborators in 1909 (Ref. 2) for determining ignition temperature and later modified for ignition delay measurements, was developed by Mullins (Ref. 10). Several gaseous and liquid fuels were injected through a small port into

a hot vitiated air stream, flowing in a concentric duct. Ignition delays were determined from the distances between the port and the flame front. Temperatures up to 1320 °K were investigated and a linear delay-temperature relation was obtained. No effect of fuel concentration on delay was observed for very lean mixtures.

Dodis (Ref. 3), on the other hand with a similar equipment in a much smaller scale, found that the delay-temperature relationship for fuel-air mixtures was non-linear at the high temperature end of the range 1070 - 1330 °K. For the four gaseous fuels used, ignition delay increased with fuel concentration.

A rapid mixing flow apparatus was devised by Jackson and Brokaw (Ref. 7) and ignition delays of propane-oxygen-nitrogen mixtures were measured with a photocell relay and timer. Air and fuel were preheated separately and mixed at temperatures 798 - 1013 °K. Ignition delays were found to be inversely proportional to the 0.74 to 1.0 power of the propane concentration.

Shortage of ignition delay data for flow systems and lack of consistency in existing experimental results call for more investigations under clearly defined conditions. This report describes some phenomena observed with a small scale flow apparatus, as an introduction to an extensive study of factors that influence ignition delay, to be carried out in this laboratory. Delay-temperature relationships of propane were established for two types of fuel injectors and the effect of propane concentration was studied. To assist the interpretation of the results, 'fuel concentration' and 'velocity' profiles of the gas stream were taken at various distances along the flame tube, using nitrogen to simulate propane.

THEORETICAL CONSIDERATIONS

The Arrhenius Law

Spontaneous ignition is a process by which a combustible mixture is self ignited when its temperature is raised beyond a critical 'ignition temperature'. There is, however, a time lag before the appearance of a flame, during which the mixture reacts slowly and eventually explodes. This 'ignition delay', as it is called, is inversely proportional to the reaction rate, which is very sensitive to temperature. The variation of the specific reaction rate k of a homogeneous mixture with temperature was satisfactorily expressed by Arrhenius as

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \qquad \ldots\ldots\ldots\ldots\ldots (1)$$

which integrates to

$$\ln k = \frac{-E}{RT} + \text{constant} \qquad \ldots\ldots\ldots (2)$$

or

$$k = Ae^{\frac{-E}{RT}} \qquad \ldots\ldots\ldots\ldots\ldots (3)$$

where A is the frequency factor, E the activation energy, R the gas constant and T the absolute temperature. Equation (3) is usually referred to as the Arrhenius Law.

This law is fully valid for elementary reactions but is over simplified for some complex processes such as those involving chain reactions. However, the disintegration of many organic substances follows a series of unimolecular and bimolecular

stages and can be represented by the Arrhenius law, although the meaning and magnitude of the specific reaction rate k is now different, and E is made up of the sum of the activation energies of the elementary processes constituting the complex reactions (Ref. 14).

Hinshelwood (Ref. 5) pointed out that for reactions depending on molecular collisions at high temperatures, the variation of the root mean square velocity of the molecules $\bar{u}$ should strictly be taken into account.

Thus $k = \text{constant } \bar{u}\, e^{\frac{-E}{RT}}$, and since $\bar{u}$ varies as $T^{1/2}$,

$$k = \text{constant } T^{1/2}\, e^{\frac{-E}{RT}} \quad \ldots\ldots\ldots\ldots\ldots (4)$$

He nevertheless agreed that the term $e^{\frac{-E}{RT}}$ is the only one that varied considerably with temperature. Mullins (Ref. 10) demonstrated that for kerosene this modification is numerically negligible.

Since the heat of reaction is the difference of the activation energies of the direct and reverse reactions, it follows that in principle, E is temperature-variable also. This would cause the $\ln k$ versus $\frac{1}{T}$ plot to be curved. In practice however the variation amounts to only a few percent.

Delay-Temperature Relationship

For many homogeneous fuel-oxidant induction reactions, ignition delay may be taken to represent a given fractional completion of the reaction for the mixture (Ref. 11). The

Arrhenius Law then becomes

$$\gamma = \text{constant } e^{\frac{E}{RT}} \qquad \ldots\ldots\ldots\ldots\ldots (5)$$

Upon integration this gives

$$\ln \gamma = \frac{E}{RT} + \text{constant} \qquad \ldots\ldots\ldots\ldots (6)$$

which is identical with an equation devised by Semenov (Ref. 14).

Determination of Activation Energy

If $\ln \gamma$ is plotted against $\frac{1}{T}$ from values obtained experimentally, a straight line should be obtained, from the slope of which the activation energy E can be determined. Thus using suffixes 1 and 2 to represent any two points on the straight line, activation energy is given by the equation

$$E = \frac{R \ln (\gamma_1/\gamma_2)}{1/T_1 - 1/T_2} \qquad \ldots\ldots\ldots\ldots (7)$$

Calculation of Ignition Delay

In a flow system where fuel is injected into an air stream flowing in a parallel tube, the ignition delay may be calculated from the distance between the injector nozzle and the flame front.

Let Q = mass flow of gas mixture lb/sec

A = cross section area of tube ft^2

S = flame front distance from injector nozzle ft.

x = distance along tube from injector nozzle

T_o = preheat temperature of mixture at face of injector nozzle °K

T = preheat temperature of mixture at x °K

P = absolute pressure in tube lb/ft²

R = gas constant of mixture ft-lb/lb °K

ρ = density of mixture lb/cu.ft

t = time

V = velocity of gas mixture stream

γ = ignition delay sec.

Since $$V = \frac{Q}{\rho A} = \frac{QRT}{PA} \qquad \ldots\ldots\ldots\ldots\ldots (8)$$

therefore $$\gamma = \int_o^s dt = \int_o^s \frac{dx}{V} = \int_o^s \frac{PA}{QRT}\, dx$$

$$= \frac{PA}{QR} \int_o^s \frac{dx}{T}$$ if the gas flow is constant and

the pressure drop along the tube is negligible. Owing to heat loss from the tube caused by imperfect insulation, a temperature gradient exists in the gas stream along the tube. T therefore varies with x.

Let $$\Delta T_x = T_o - T \qquad \text{at } x$$

then $$\int_o^s \frac{dx}{T} = \int_o^s \frac{dx}{T_o - \Delta T_x} = \frac{1}{T_o} \int_o^s \frac{dx}{1 - \Delta T_x/T_o}$$

$$= \frac{1}{T_o} \int_o^s \left(1 + \frac{\Delta T_x}{T_o}\right) dx = \frac{1}{T_o} \left\{ s + \frac{1}{T_o} \int_o^s \Delta T_x dx \right\}$$

which is obtained by expanding the integrand in binominal series and neglecting terms of $\left(\frac{\Delta T_x}{T_o}\right)^2$ and higher.

Substituting this, the final expression for ignition delay becomes

$$\gamma = \frac{PA}{QR} \frac{S}{T_o} \left\{ 1 + \frac{1}{T_o} \frac{\int_o^s \Delta T_x \, dx}{S} \right\} \quad \ldots\ldots (9)$$

APPARATUS AND INSTRUMENTATION

Apparatus

The apparatus which is shown diagrammatically in Fig. 1 consists essentially of four components:

(1) slave combustion chamber (not shown)

(2) heat exchanger

(3) calming chamber

(4) flame tube

Briefly, air from the laboratory supply, is preheated to desired temperatures in the heat exchanger by exhaust gas from the slave combustion chamber. The hot air then flows through the calming chamber where it achieves uniform temperature and velocity before entering the flame tube. Fuel is injected into the hot air stream by a removable 12 gauge stainless steel tube (hyponeedle) which is concentric with the calming chamber and flame tube. After combustion the gas exhausts to atmosphere.

A more detailed description of the rig is given as follows:

(1) slave combustion chamber

The combustion chamber is made of a 2-3/8 in. I.D. alundum tube encased in a cylindrical mild steel shell and the space in between is packed with fiberfrax. Two stainless steel end plates are bolted to the shell and a stainless steel collar is welded centrally at the inner face of each to support the alundum tube. The part of the end plates exposed to the flame is lined with refractory material. Propane and air are premixed

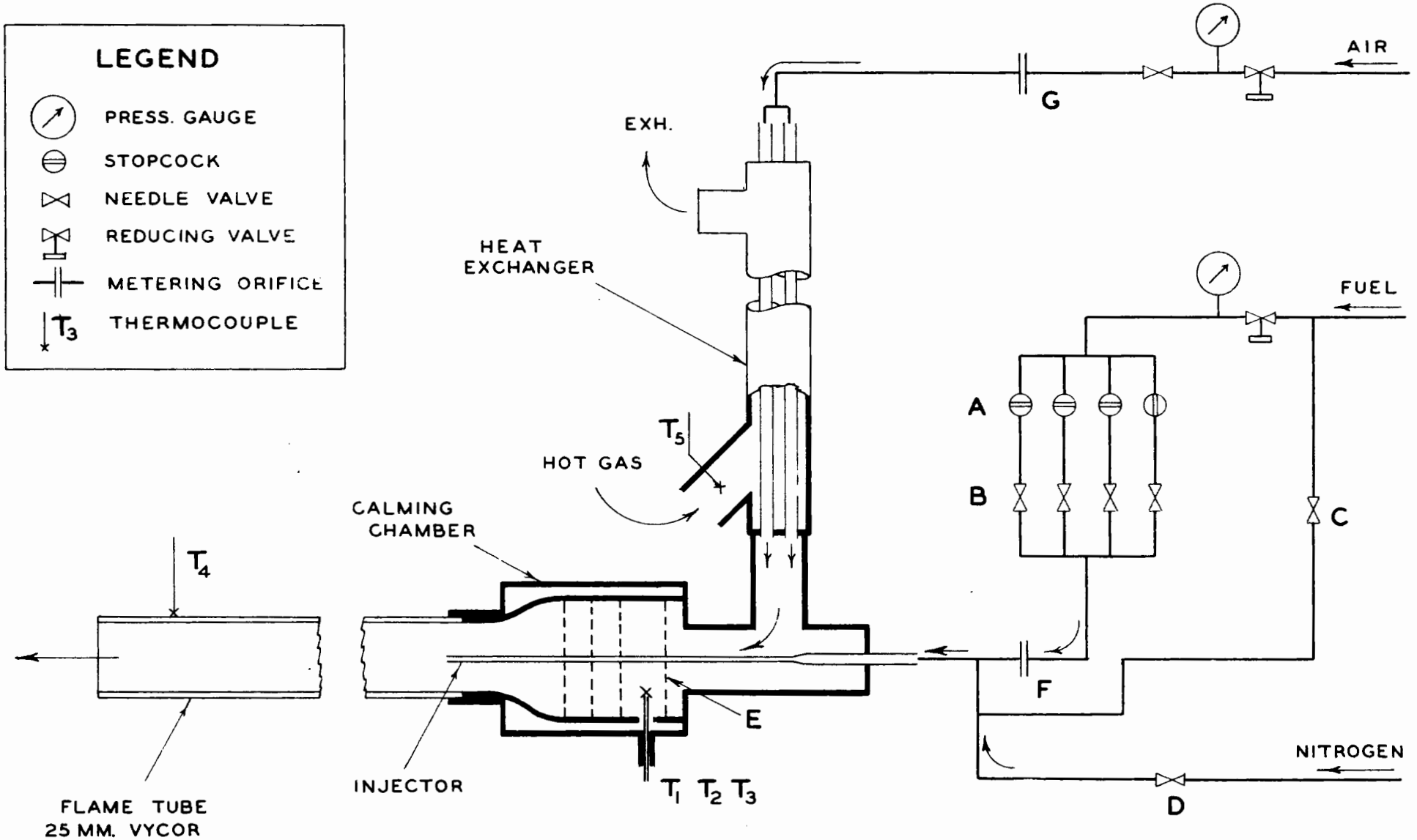


Fig. 1. Apparatus used to measure ignition delays.

and enter the chamber axially through a 3/8 in. pipe. An aircraft type spark plug is used to ignite the mixture. Secondary air is provided to improve combustion which also serves to cool the electrodes of the spark plug.

(2) Heat exchanger

At first a ceramic heat exchanger was built but it unfortunately failed after a few runs. The present one is constructed with Type 310 stainless steel, and is of the recuperative, counter flow design. Four 1/4 in. tubes with an effective length of 5 feet, serve as the air tubes while a 3/4 in. pipe is used for the outer tube through which the hot gas flows. Test air is fed into the exchanger by rubber tubes at the cold end where a sliding joint permits differential expansion between the air and the gas tubes. Connections with the slave combustion chamber and the calming chamber are made with flanges and graphite lubricated asbestos gaskets. The latter caked up after a period of tests at high temperatures, but gave a good seal as long as they were not disturbed. They were replaced occasionally. A thermocouple T_5 is placed between the combustion chamber and the heat exchanger to limit the gas temperature entering the latter to 1150 °C. This limitation is important, otherwise the exchanger is liable to be damaged.

(3) Calming chamber

This is essentially a double walled cylinder with a convergent outlet. It contains four 2-1/16 in. diameter perforated plates (E) to reduce any disturbance in the air stream caused previously, and also to even out the temperature

distribution. Three thermocouples T_1 T_2 T_3 with beads located at .40 R, .65 R and .70 R respectively are used to measure the preheat temperature. These have their wells installed on the outer wall so as to reduce lag in readings caused by conduction effects. All parts are stainless steel. The whole calming chamber and heat exchanger assembly is boxed up and insulated with fiberfrax.

(4) Flame tube

The flame burns in a 25mm Vycor tube, 36 in. long which is enclosed in a 5 in. flue pipe filled with fiberfrax. A narrow slit is cut along the pipe for flame observations. This and poor insulation unfortunately cause a temperature gradient in the gas stream along the flame tube. A metal scale is fixed parallel to the slit and the position of the flame front is determined by a sighting device. Thermocouple T_4 is used to indicate the Vycor wall temperature.

Air and fuel flows are regulated by pressure reduction valves and needle valves. In the fuel line a stopcock is added to enable a desired quantity of fuel to be preset and turned on instantly. Four such lines are connected in parallel so that several fuel flows may be preset. In high temperature tests a diffusion flame appeared at the injector nozzle upon turning on the fuel, and a very high flow was required to lift the flame. By-pass Valve (C) is incorporated for this purpose. Nitrogen is introduced to flush the injector by way of valve D after each run to prevent blockage due to fuel pyrolysis.

Two types of fuel injectors (Fig. 2) are used to study the effect of different injection methods. One has an open end, the other a closed end with four radial holes, so that the fuel flow is directed parallel or perpendicular to the air stream. They will be referred to as the straight and multihole injectors respectively.

Instrumentation

The layout of the thermocouple, orifice and pressure gauge positions is shown in Fig. 1.

All temperatures are measured with open bead type chromel-alumel thermocouples, which are calibrated against a standard platinum-platinum + 10% rhodium thermocouple connected to a Leeds and Northrup potentiometer. Air temperatures T_1, T_2 and T_3 are read on a Brown "Electronik" self balancing potentiometer type precision-indicator. Other thermocouples are connected to a Minneapolis-Honeywell millivoltmeter pyrometer.

Plate orifices are used to measure air and fuel flows. Calibrations are made with a 'Precision' wet test meter, or standard orifices in the case of higher flows.

Pressures in the fuel and air lines are indicated by Schrader bourdon-type pressure gauges.

Gas samples are taken with a pitot tube mounted on a micrometric screw mechanism, cooled and then analysed in a Hauptman and Braun oxygen meter (Fig. 3). The same tube connected to a micromanometer gives the velocities at any point in the gas stream.

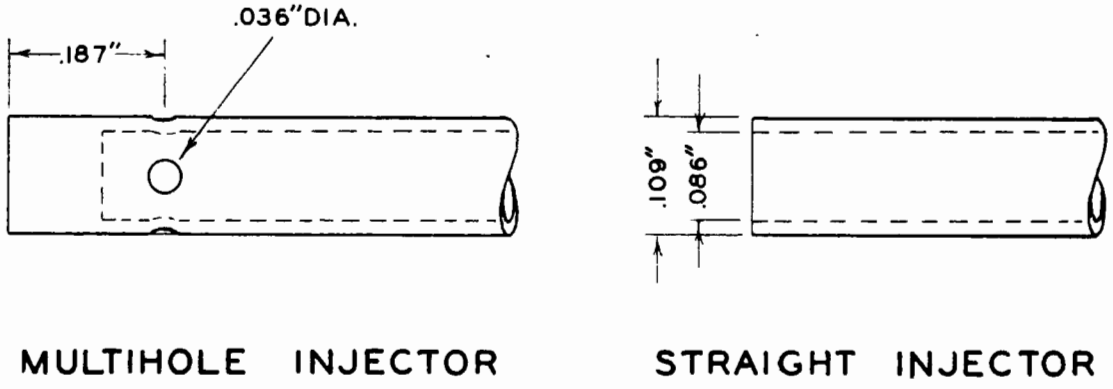


Fig. 2. Fuel injector nozzle configurations.

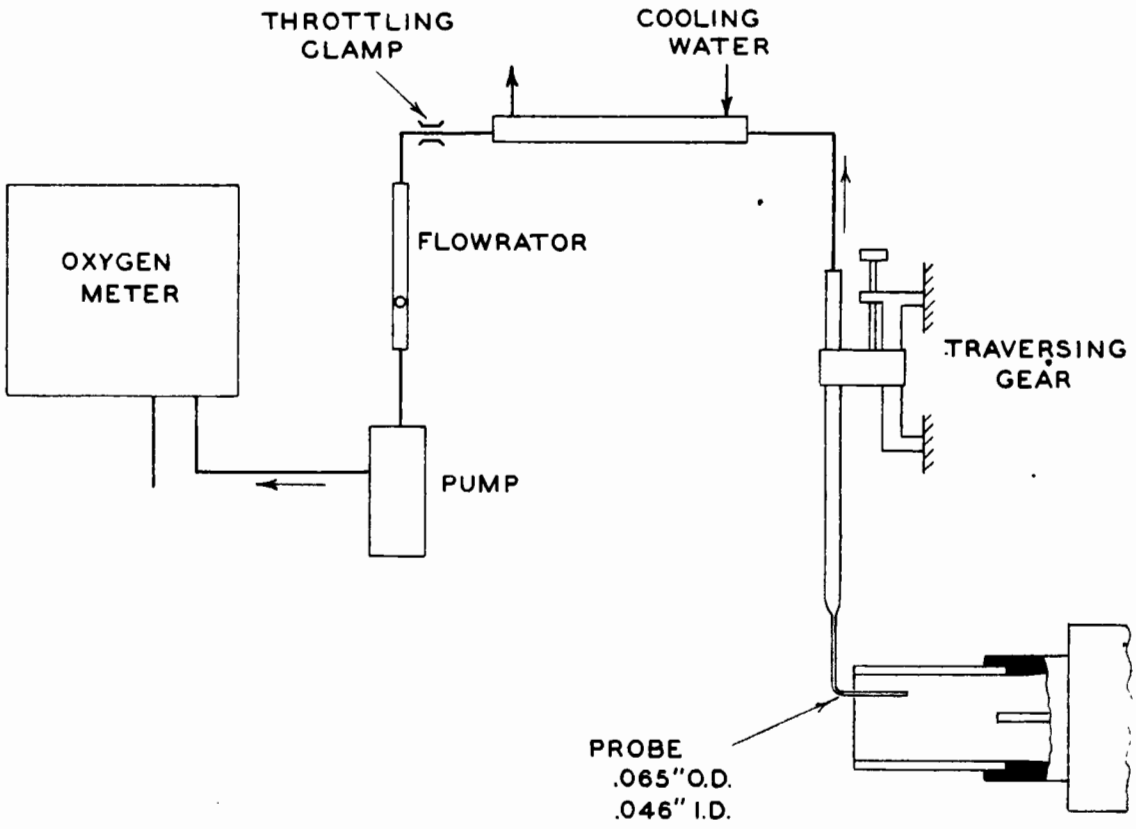


Fig. 3. Gas sampling apparatus for concentration measurements.

METHOD

The slave combustion chamber was ignited and gradually brought up to temperatures above 900 °C in about three hours. A little test air was introduced at the start which was adjusted to the correct flow as soon as the heat exchanger was fairly hot. When the desired air temperature (T_1 T_2 T_3) was reached and maintained steady, the apparatus was ready for ignition delay experiments.

With a constant air flow of .004 lb/sec throughout, (velocity of about 40 ft/sec and a Reynolds Number of 2350) two major types of tests were conducted. The variation of delay with temperature at constant fuel flow was examined by presetting the fuel and turning it on intermittently or letting it burn continuously as the air temperature was raised in steps. The continuous method caused the Vycor tube to be heated up unduly, whereas in the intermittent case it was permitted to cool down between runs, as indicated by T_4. At high fuel flows, however, the time required for the tube to cool down appreciably was too long to be practical.

The effect of fuel concentration on delay at constant temperature was determined by keeping the flame burning continuously and varying the fuel flow in small increments. All readings were taken after the air temperatures were maintained steady. Under this condition the difference between T_1, T_2 and T_3 remained almost the same for all temperatures and it was only necessary to record T_3.

The temperature gradient in the air stream was obtained by means of a 40 in. chromel-alumel thermocouple and the drop in temperature, ΔT_x, at various distances along the flame tube is shown in Fig. 4 for several air temperatures. It is assumed that the same relation would hold upstream of the flame. Using the same thermocouple, T_3 was related to T_o, the air temperature at the face of the injector nozzle (Fig. 5). Pressure drop in the flame was found to be negligible and thus the gas pressure P may be taken as atmospheric. With these readings and the flame front distances "S", ignition delays were calculated from equation (9) i.e.

$$\gamma = \frac{PA}{QR}\frac{S}{T_o}\left\{1 + \frac{1}{T_o}\frac{\int_o^S \Delta T_x\, dx}{S}\right\}$$

The correction factor $\frac{\int_o^S T_x\, dx}{S}$ due to the temperature gradient was obtained by graphical integration and was shown to have little effect on delay, approximating 5% at T_o = 1000 °K for large values of S.

Fuel concentration and velocity profiles at several distances along the flame tube were constructed by traversing the pitot tube diametrically across the tube and taking oxygen meter and micromanometer readings respectively. Short lengths of Vycor tubes were used for this purpose and it was demonstrated that the flow pattern was not affected by doing this. A mass flow of nitrogen estimated to give the same Reynolds Number in the injector as the corresponding propane flow was injected into the hot air in these tests to avoid combustion. Methods of calculating the above concentrations and velocities are illustrated in the Appendix.

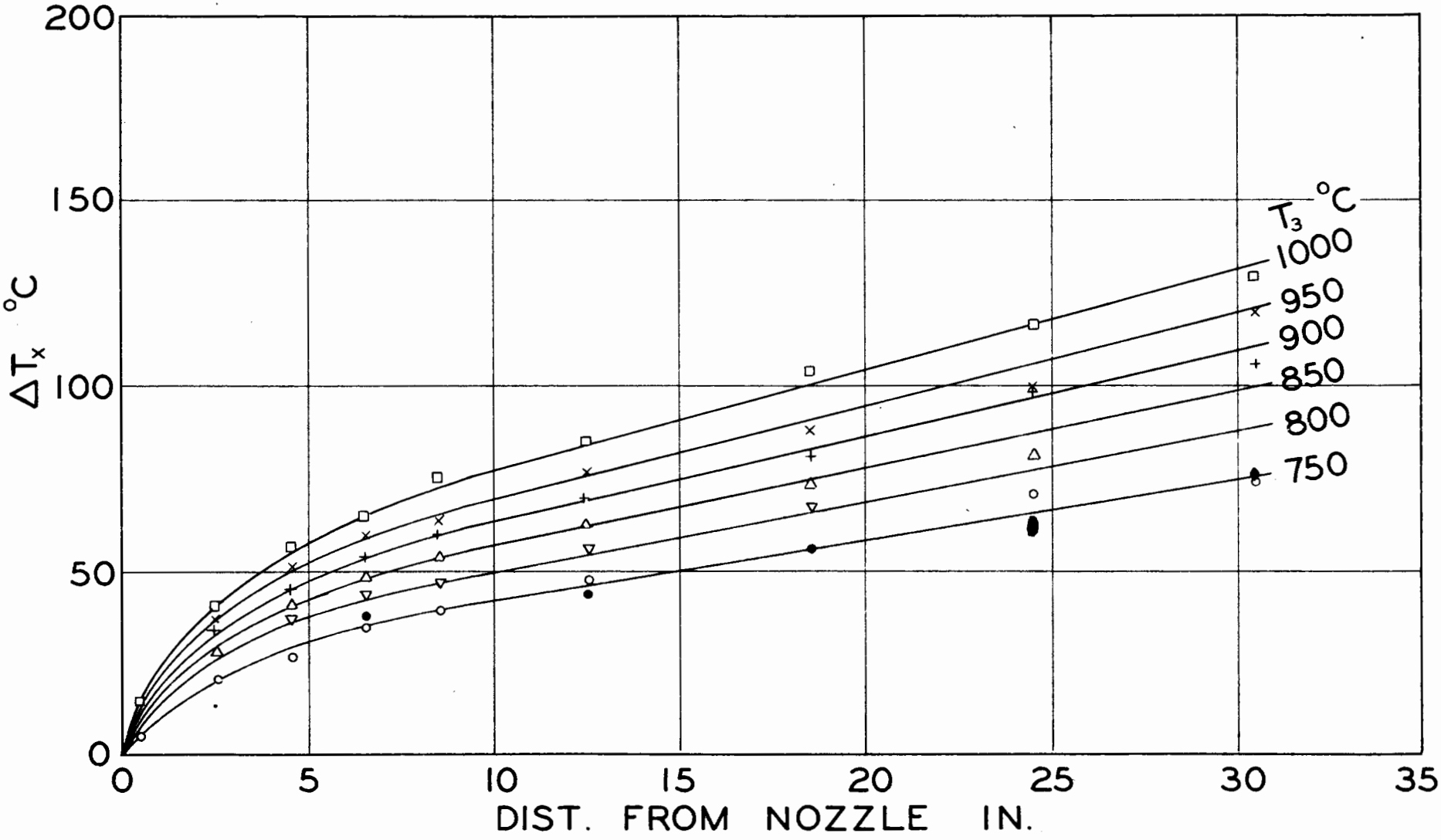


Fig. 4. Air temperature gradient along flame tube ΔT_x. Air flow .004 lb/sec.

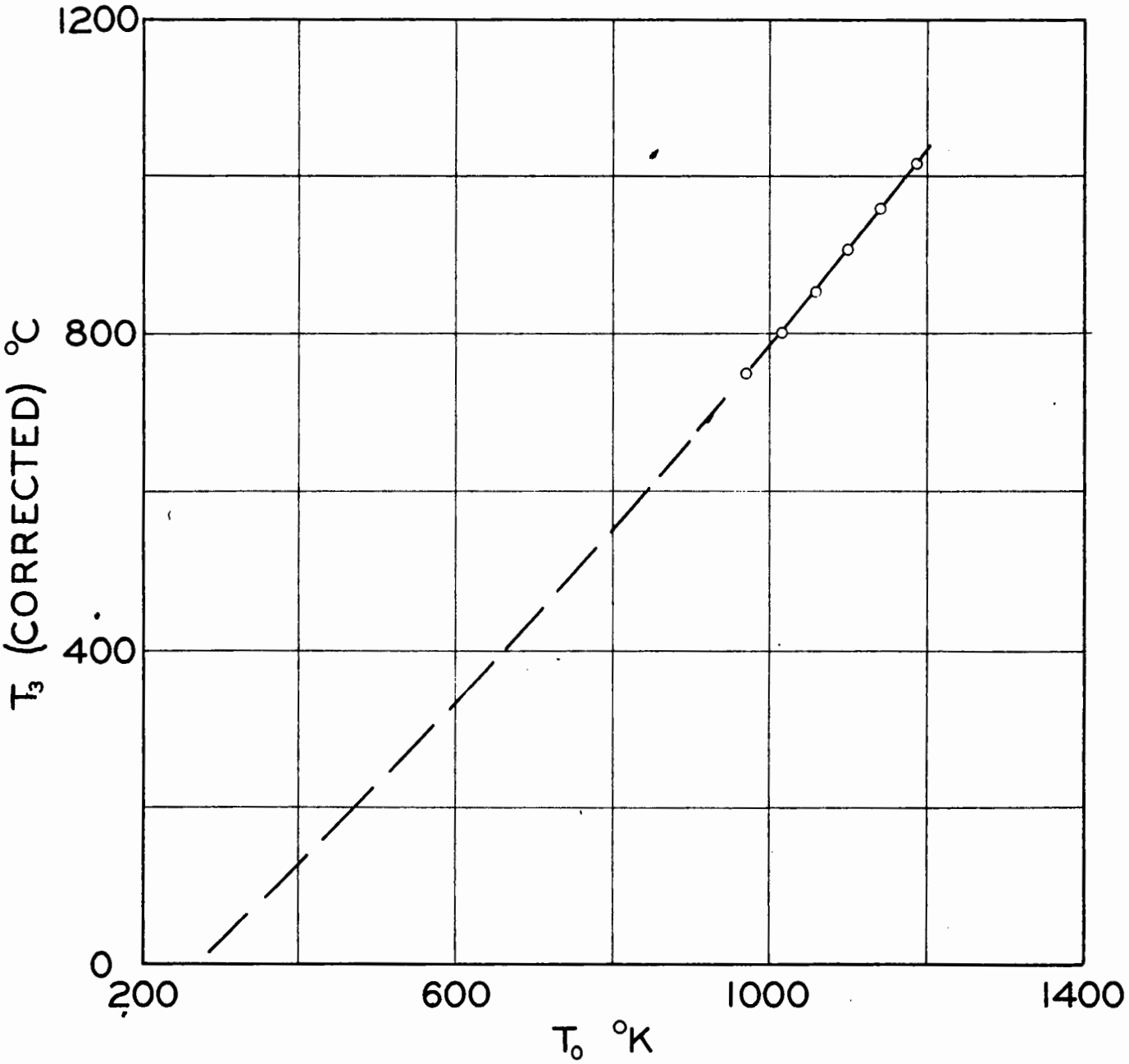


Fig. 5. Relation between mean air temperature at x = 0, T_o, and temperature in calming chamber T_3. Air flow .004 lb/sec.

The fuel tested is commercial propane supplied by Liquefied Gas Utilities Ltd., Lachine, Quebec, having the following approximate composition:-

Propane	95 %
Propylene	4 - 5 %
Butane Ethane	less than 1%

RESULTS

Variation of Ignition Delay with Propane Flow

Except for one temperature within the range T_o = 993 - 1045 °K, ignition delay increased to a maximum (transition point) and then decreased to an almost constant value, as propane flow was increased (Figs. 6 and 7). The drop after the transition was very abrupt in the case of the multihole injector. Higher temperatures up to T_o = 1164 °K were attempted for the straight injector, but results could be obtained only for flow rates lower than the transition point.

As the flame front altered in position with fuel flow several changes in its shape and character were noted. Table I and Fig. 8 describe these observations for the straight injector, and it is possible to group similar types of flame fronts in zones by replotting Fig. 6 on an ordinate of flame front distance. Briefly in Fig. 9, zone (1) contains a purely violet spontaneous flame and (2) an explosive type tailed by an orange cone. The explosions became increasingly violent and noisy, and the cone longer at higher flows until zone (3) was reached. Then after a series of less frequent but louder explosions a rather sudden transition to a quiet, steady and inclined front occurred. The latter remained in zone (4) but became louder and more turbulent as the propane flow was increased and filled the whole tube with an orange flame. Zone (3) was similar to (2) except that the cone was yellow in color. Finally a blue torroidal front followed by a thin long yellow cone was observed in zone (6). Fewer flame types

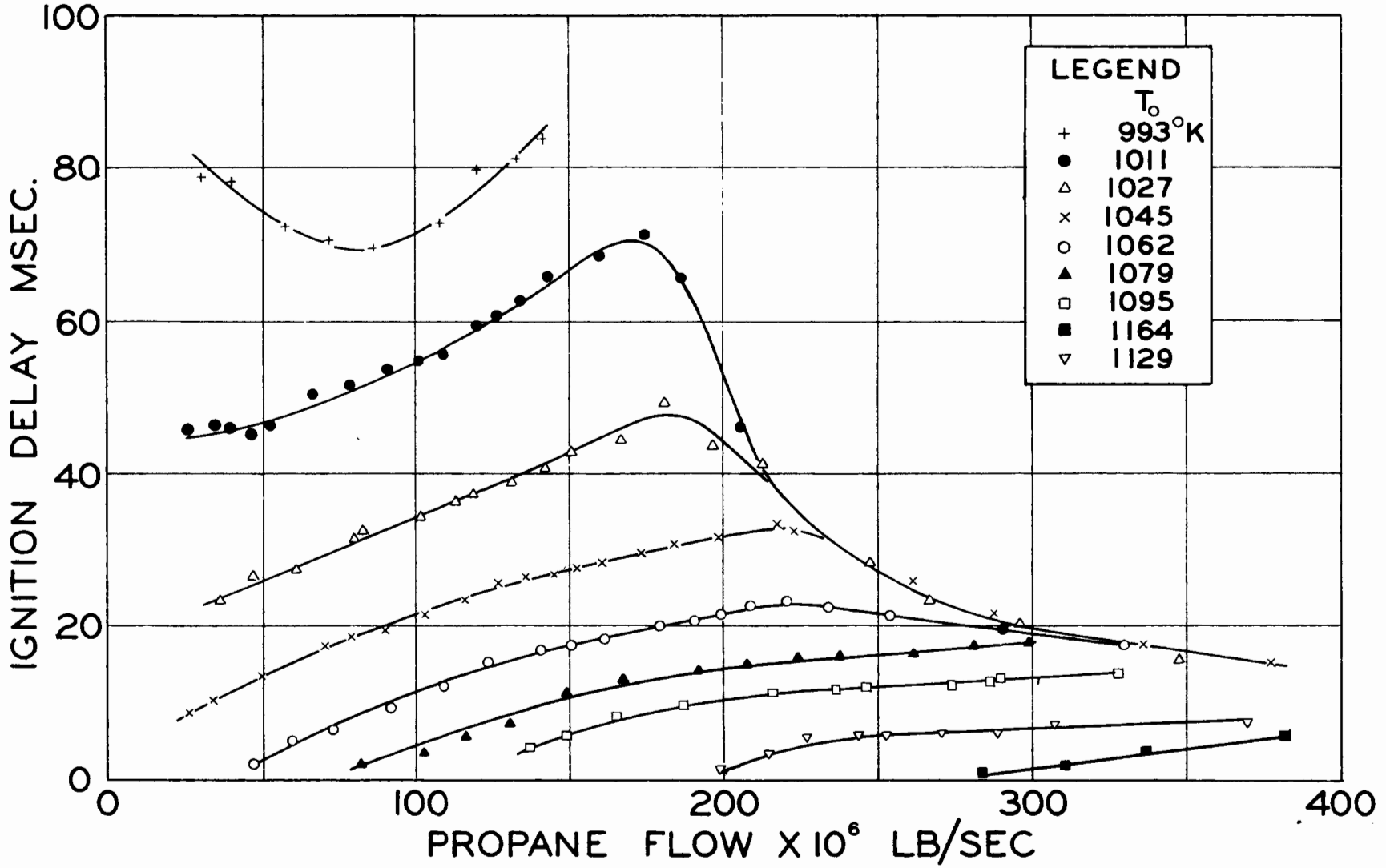


Fig. 6. Variation of ignition delay with propane flow at various air temperatures, straight injector. Air flow .004 lb/sec.

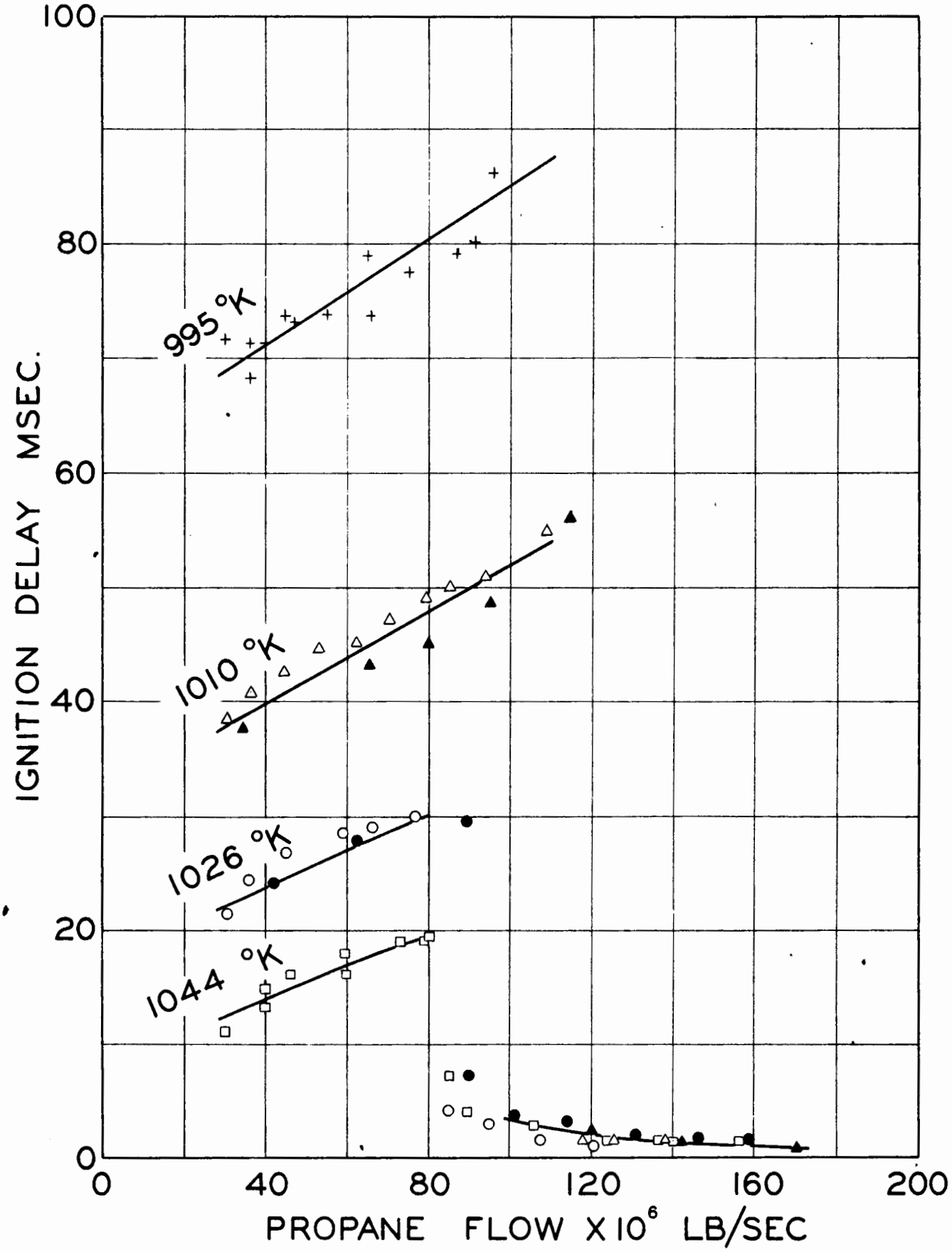


Fig. 7. Variation of ignition delay with propane flow at four air temperatures, multihole injector. Air flow .004 lb/sec.

TABLE I: FLAMES OBSERVED DURING IGNITION DELAY/FUEL FLOW TEST WITH STRAIGHT INJECTOR

T_o °K	Propane Flow lb/sec x 10^{-6}	Observation	Flame Front Type (Fig. 8)
993	28	Quiet violet flame forms spontaneously, oscillating slowly.	A
	57	Orange cone forms behind front. Louder.	
	72 - 133	Flame front now violent, loud, oscillating. Appears to be series of explosions. Well defined orange cone. Base more bluish in color.	B
	155	Explosions less rapid. Orange cone disappears. Electric blue color.	
	162	Extinguishes outside flame tube.	
1010	26	Spontaneous violet flame.	A
	39	Orange cone forms, length increases.	
	47 - 67	Gradual change to explosive front.	A - B
	160	Loud, less frequent explosions. Inclined, steady flame front appears intermittently, quiet.	B, C
	187	Explosions disappear, inclined front remains. Appears to be toroidal when viewed at an angle.	C
	220	Sound and turbulence more intense.	
	290	Very loud, turbulent flame front. Orange cone or flame fills whole tube.	flame tip - D
1027	36	Small diameter, pale blue, quiet front forms spontaneously. Each explosion appears to have spherical base with small cone attached.	E
	79	Base diameter larger. Intermittent yellow cone appears, tip at 20", fluctuates from side to side.	E

TABLE I (cont'd)

T_o °K	Propane Flow lb/sec x 10^{-6}	Observation	Flame Front Type (Fig. 8)
	101	Yellow cone disappears. Louder.	
	157 - 170	Transition from explosive to inclined flame front.	B - C
	195 - 350	Characteristics similar to 1010 °K after transition.	
1045	26	Pale blue, small flame front forms, orange cone attached.	E
	49	Small yellow cone appears, tip at 10".	E
	160 - 196	Transition. Occasional unsteady yellow flash and several sparks.	B - C
1062	not recorded	Steady yellow diffusion flame starts at injector.	
	"	Tip starts to flutter.	
	"	Flame diameter increases. Turbulent brush appears 4" from nozzle.	
	329	Flame lifts from nozzle. Noisy, turbulent orange flame fills tube. (Fuel flow now reduced)	C
	233	Sound intensity less. Not as turbulent.	
	220 - 208	Change from inclined front to loud, explosive. Occasional sparks. (Transition)	C - B
	179	Explosions quieter, blend together visibly and audibly. Base diameter less.	
	161	Yellow cone forms, unsteady.	E
	72	Very small, pale blue flame front, appears to be toroidal shape. Very quiet.	F

TABLE I (cont'd)

T_o °K	Propane Flow lb/sec x 10^{-6}	Observation	Flame Front Type (Fig. 8)
	47	Drops back to nozzle. Very bright, hot diffusion flame.	
1079, 1095	-	Similar sequence of events as at 1062 °K.	
1129	369	Flame lifts from nozzle. Pale blue flame front, steady, followed by long yellow cone.	F
	180	Drops back.	
1169	-	Similar to 1129 °K. No transition observed at either temperature.	

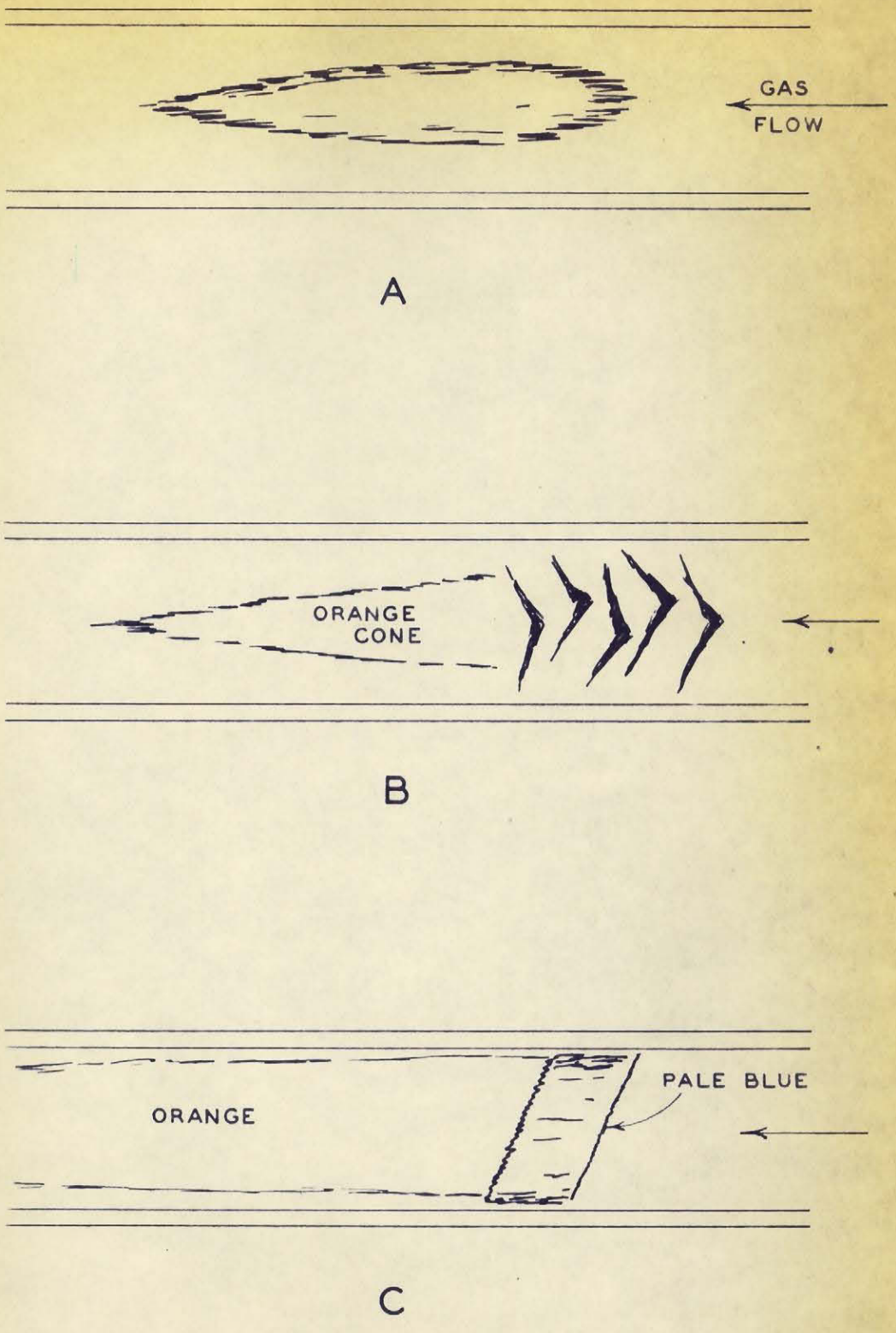
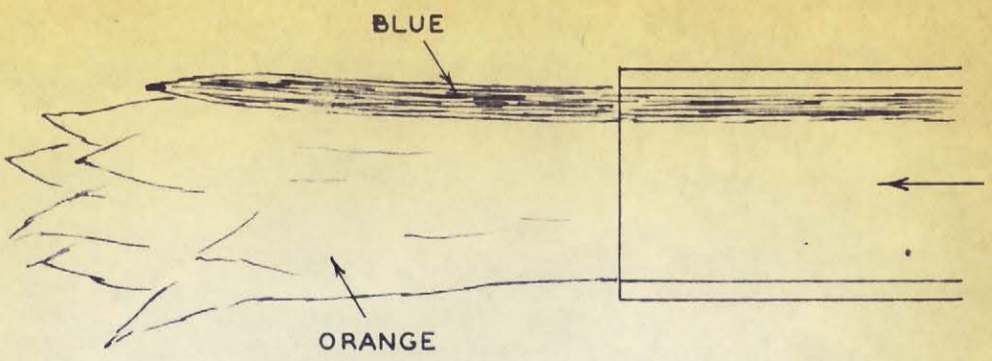


Fig. 8. Flame types observed during ignition delay/flow test, straight injector.



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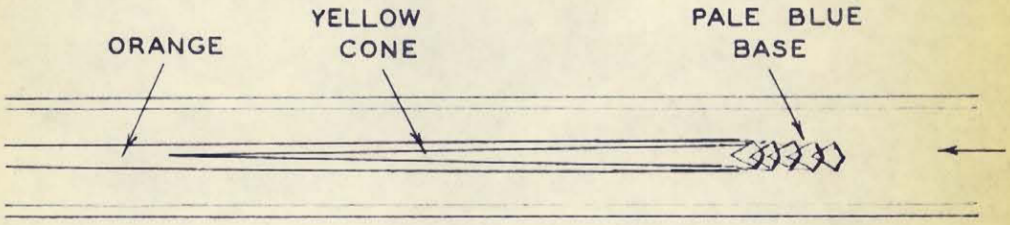

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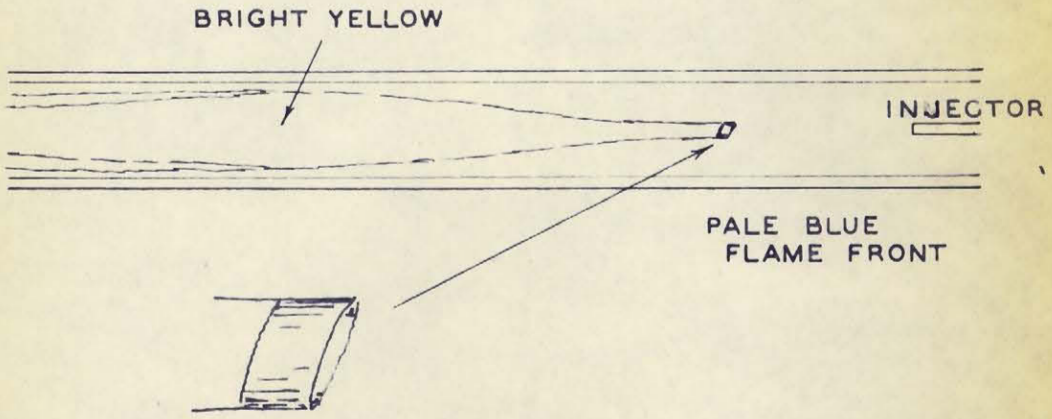

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Fig. 8 (Cont'd). Flame type observed during delay/flow test, straight injector.

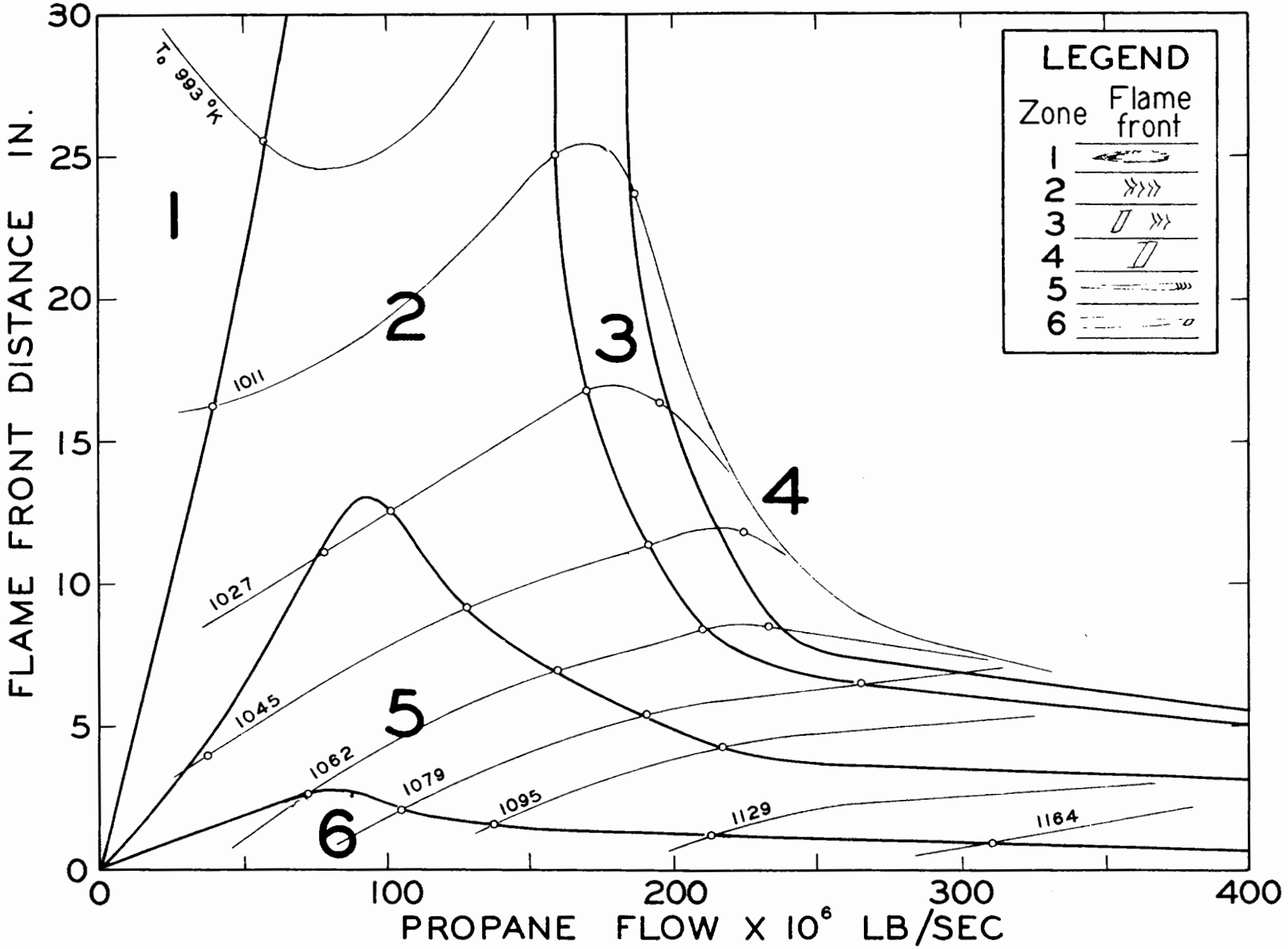

Fig. 9. Distances and flows at which different flame types appeared during delay/flow test, straight injector.

were observed for the multihole injector. Here again a distinct change from a loud explosive to a quiet inclined front took place at the transition point.

At and above T_o = 1062 °K, in the case of the straight injector, spontaneous ignition did not begin as a lifted flame, but rather as a diffusion flame burning at the nozzle. Lifting was eventually possible at a higher flow. The tip length of this type of flame was found to be directly proportional to the fuel flow up to a certain value, at which the tip began to flutter. The fuel flow at this value was close to that at the transition point of the lifted flame. This phenomenon is illustrated in Fig. 10. Because of the limitations of the apparatus, it was not possible to lift the small diffusion flames burning at the nozzles of the multihole injector, for temperatures above T_o = 1044 °K.

In a few tests it was noticed that the tip of the injector was slightly bent due to prolonged heating. This caused the position of the transition point to be shifted to a slightly lower fuel flow. These results were discarded and care was taken to keep the nozzle as straight as possible during the final tests.

Variation of ignition delay with temperature

The logarithm of ignition delay is plotted against the reciprocal absolute temperature in Fig. 11 for the straight injector. A non-linear relationship is evident for propane flows of 34, 55, 85 and 114 x 10^{-6} lb/sec (corresponding to air/fuel ratios of 117, 73, 47 and 35:1 by weight respectively).

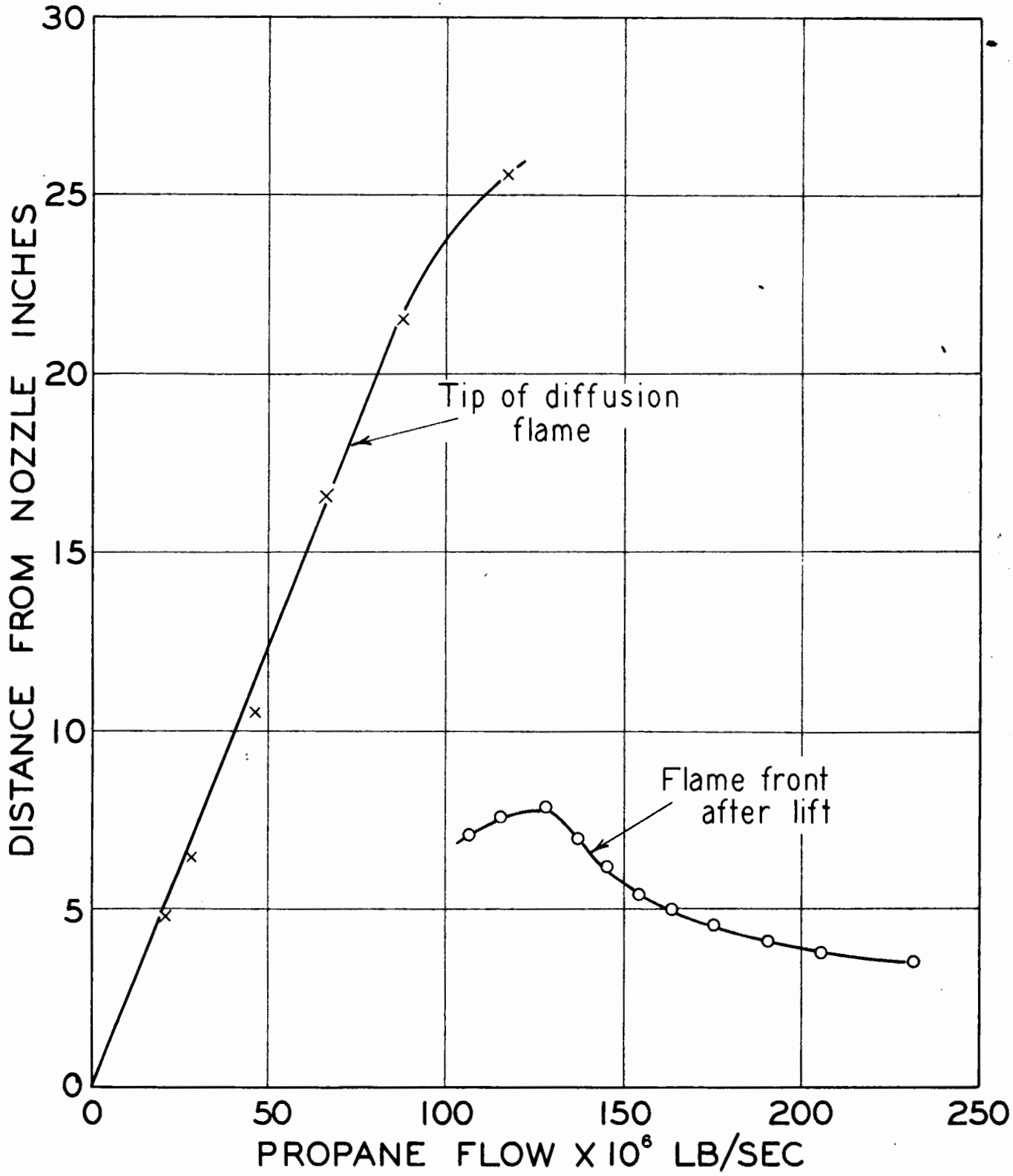

Fig. 10. Length of diffusion flame (before lifting from nozzle) and flame front distance (after lift), straight injector. Air flow .004 lb/sec.

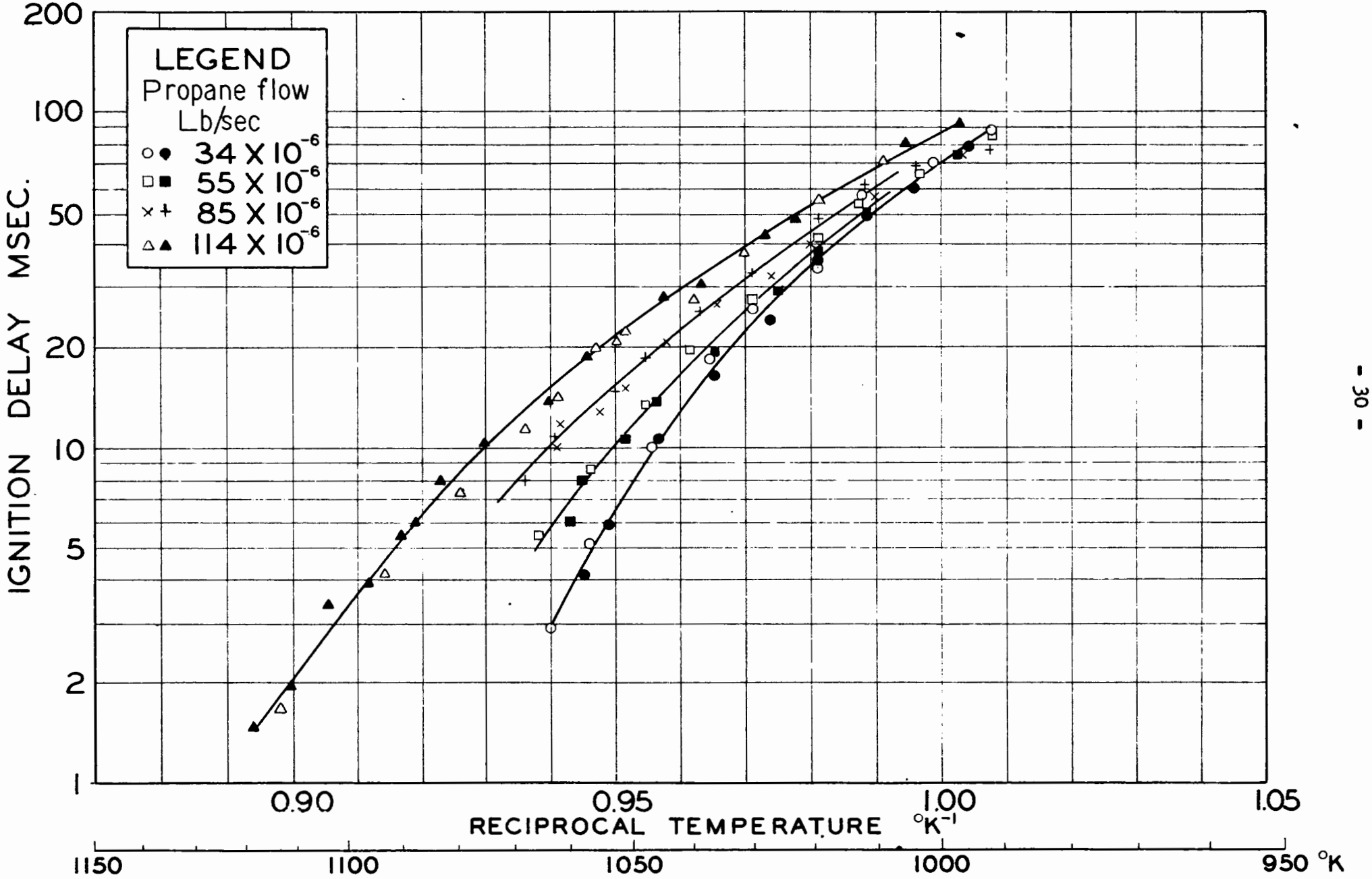

Fig. 11. Variation of ignition delay with temperature T_o, straight injector. Air flow .004 lb/sec.

The same plot for the multihole injector, on the other hand, gives a reasonably linear relationship which agrees with the integrated form of the Arrhenius equation $\ln \gamma = \frac{E}{RT} + \text{constant}$. This is illustrated in Figs. 12 and 13. The activation energy E computed from the slope of the straight lines is 71.8 K cal/mol. No spontaneously ignited flame was observed for air temperatures below about T_o = 990 °K. Typical flame front observations are described in Table II.

During some preliminary tests before the nitrogen line was installed to flush the injector, blockage in the injector by carbon deposit was experienced. This was evidence of fuel 'cracking'. Fuel temperature leaving the nozzle was estimated to be between 600°C and 700 °C.

Concentration and velocity measurements

Mixing of the air and nitrogen streams was better at higher flows and at a greater distance from the injector nozzle. Concentration profiles for the straight and multihole injectors at T_o = 1010 °K are shown in Figs. 14 - 18 and 19 - 21 respectively. A marked improvement in mixing of the multihole over the straight injector is apparent.

Similarly, velocity profiles tend to flatten at distances farther down stream. At 18" and 6" from the nozzles at the straight and multihole injectors respectively a reasonably uniform velocity was obtained for the range of nitrogen flows tested, indicating turbulent flow. Reynolds Number for air alone was 2350. Typical velocity profiles are shown in Figs. 22 - 25.

'Cool' flame observations

It is known that the ignition of most hydrocarbons in air is a two stage process and exhibits the phenomenon of 'cool' flames. As a matter of interest an experiment was conducted at night to observe the cool flame. (Table III) The multihole injector was used and propane was injected intermittently at increasing temperatures.

TABLE II: TYPICAL FLAME OBSERVATIONS IN IGNITION DELAY/TEMPERATURE TESTS FOR PROPANE FLOW = 34 x 10^{-6} lb/sec

Type of Injector	T_o °K	Observation
Straight	996	Faint violet flame begins spontaneously well down observation tube.
	1011	Faint orange glow follows flame front.
	1027	Now pale blue flame front, explosive, fills tube.
	1036	Diameter of flame front less. Yellow cone forms. Quieter.
	1045	Flame front very small, 1/4 - 3/8" diameter yellow cone extends to 7".
	1051	Base now slightly larger than injector diameter. Very quiet, bright yellow cone.
	1058	Flame drops back to nozzle.
Multihole	1050	Quiet blue flame appears spontaneously down the tube. No clearly defined base.
	1063	Pale blue flame front followed by pink cone.
	1073	Flame front unsteady, cone turning orange.
	1087	Purple explosive flame front.
	1103	Base becomes small and spherical in shape oscillates 1 inch. Quiet.
	1113	Drops back suddenly to about 2-1/2 in. from nozzle. Inclined, steady flame front.
	1118	Vycor wall red hot at flame front, difficult to observe.

TABLE III: COOL FLAME OBSERVATIONS WITH MULTIHOLE INJECTOR

T_o °K	Observation
830	Nil.
870	A faint thin glow, presumably 'cool flame', develops at tube axis extending 6" beyond tube end.
880	Brighter but remains same length. Shortens and eventually disappears with increase in fuel.
930	Tip begins to flutter. Brighter still and color faintly yellowish. Fuel flow is about 70 x 10^{-6} lb/sec and is maintained at this value from now on.
942	Slightly bluish. Faint odor noticed.
958	Pale blue. Length and diameter increases.
972	Color and length same. Increase in fuel changes color to yellowish but does not affect length. The 'cool flame' is invisible under laboratory light.
990	Tip about 2" beyond tube; flutter unsteadily and becomes darker blue. A normal flame is now visible at tip of 'cool flame' under lights which is typical of the spontaneously ignited flames observed in daylight. Audible.
995	Normal flame noisier and recede into tube. An orange cone is formed. 'Cool flame' still exists but fainter.
995-1083	Flame front moves upstream and eventually drops back to nozzle.

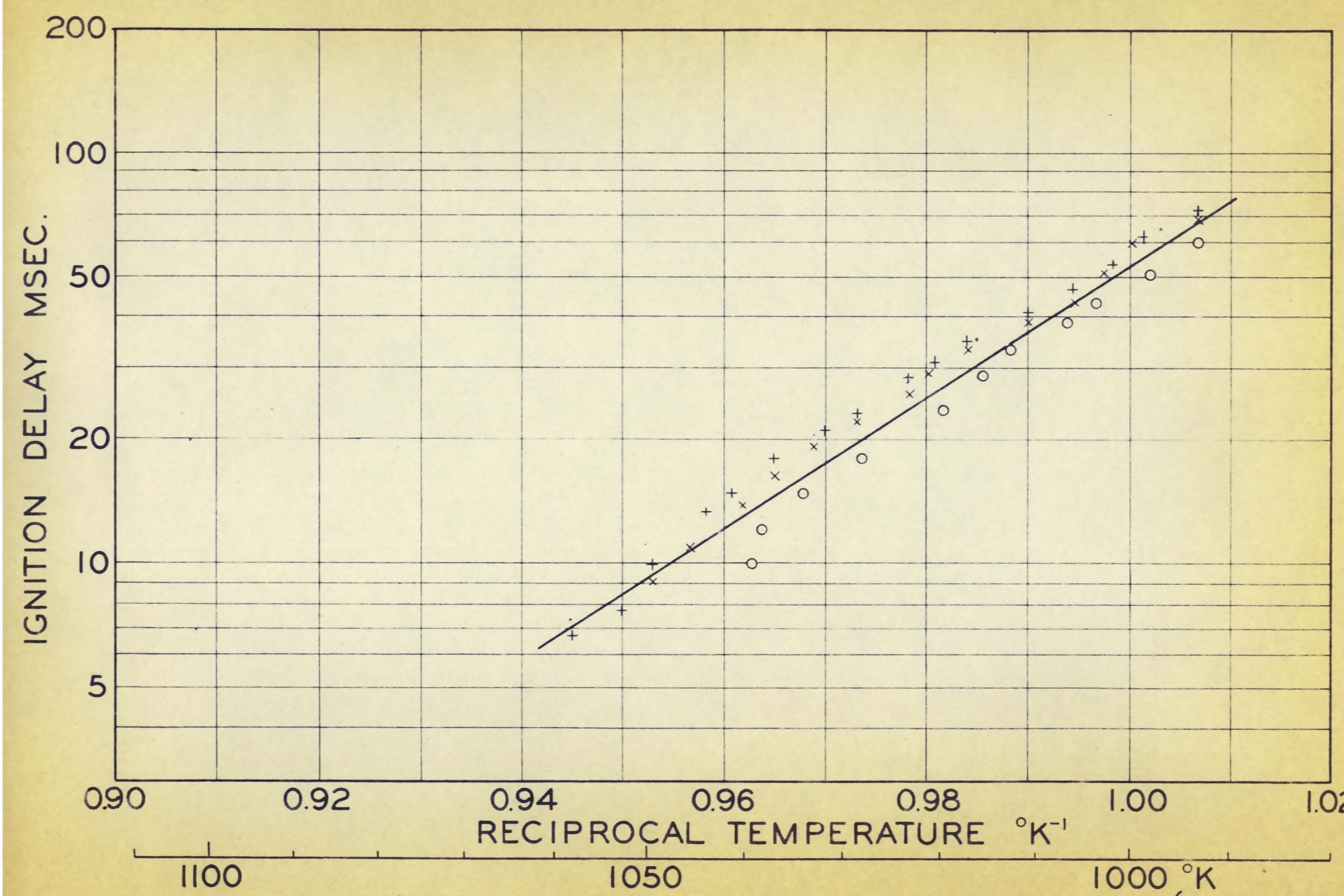

Fig. 12. Variation of ignition delay with temperature T_o, multihole injector. Propane flow 34 x 10^{-6} lb/sec. Air flow .004 lb/sec.

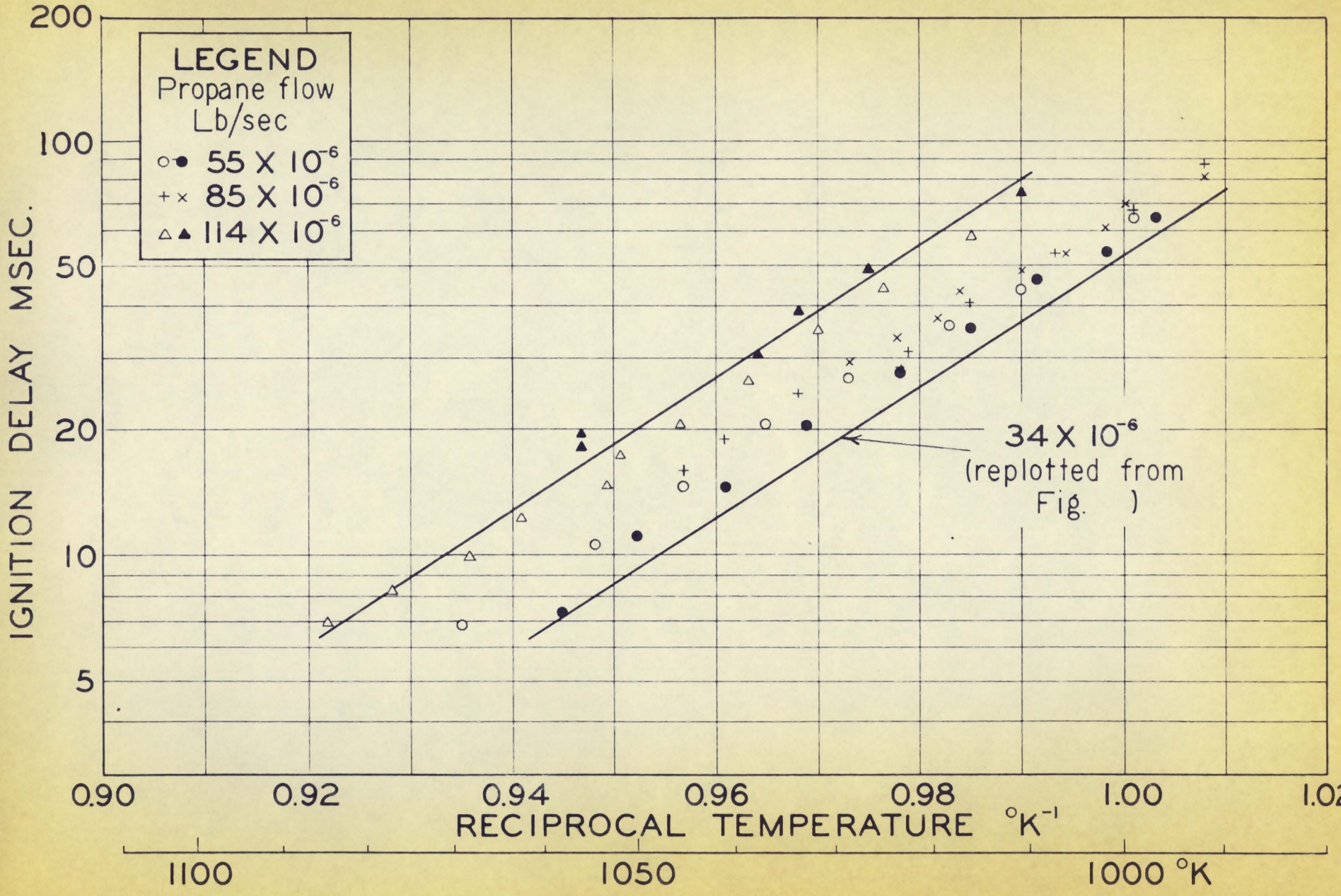

Fig. 13. Variation of ignition delay with temperature T_o, multihole injector. Air flow .004 lb/sec.

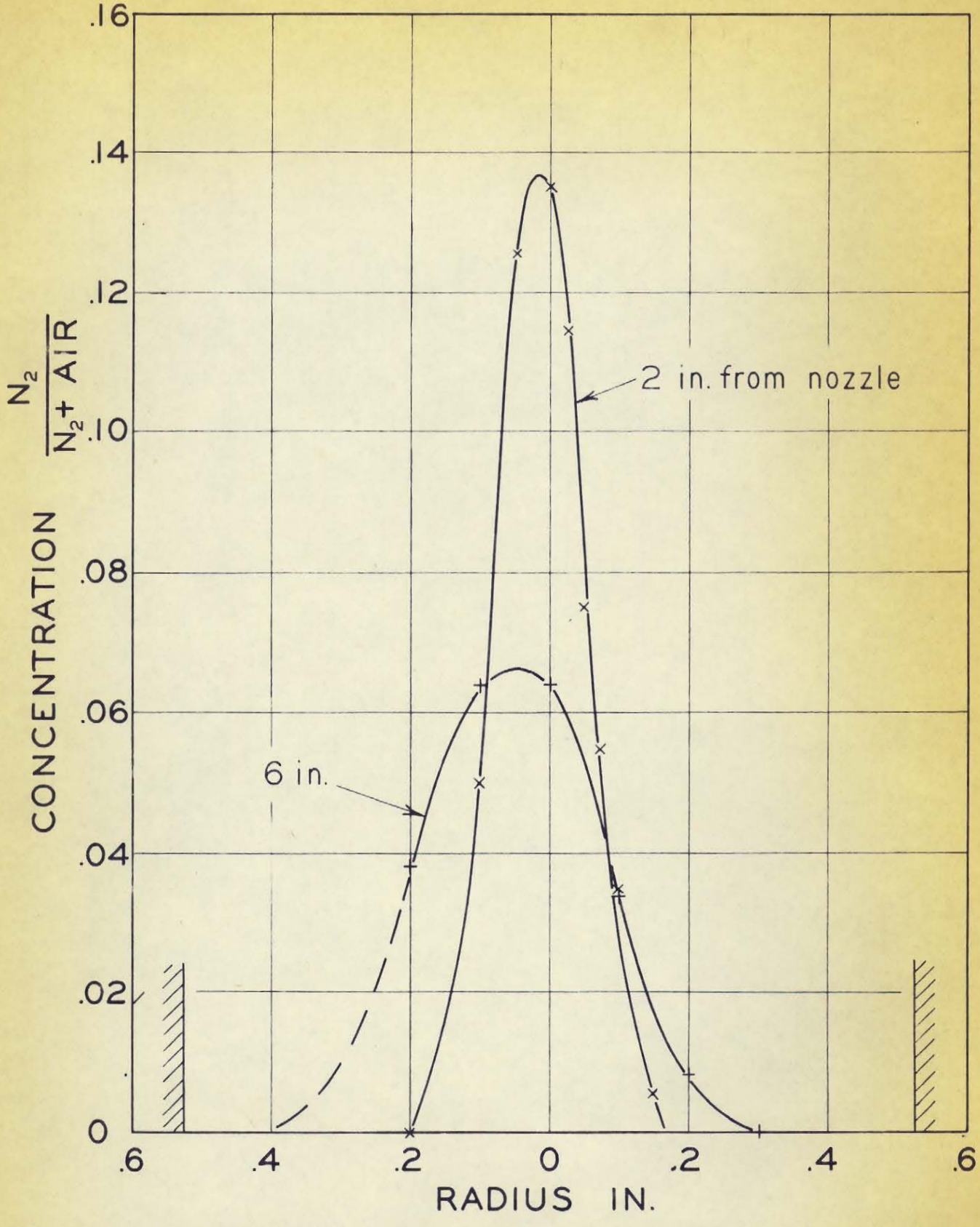

Fig. 14. Concentration profiles, straight injector. Nitrogen flow 29 x 10^{-6} lb/sec. corresponding to 15 x 10^{-6} lb C_3H_8/sec. Air flow .004 lb/sec. Air temperature T_o 1010 °K.

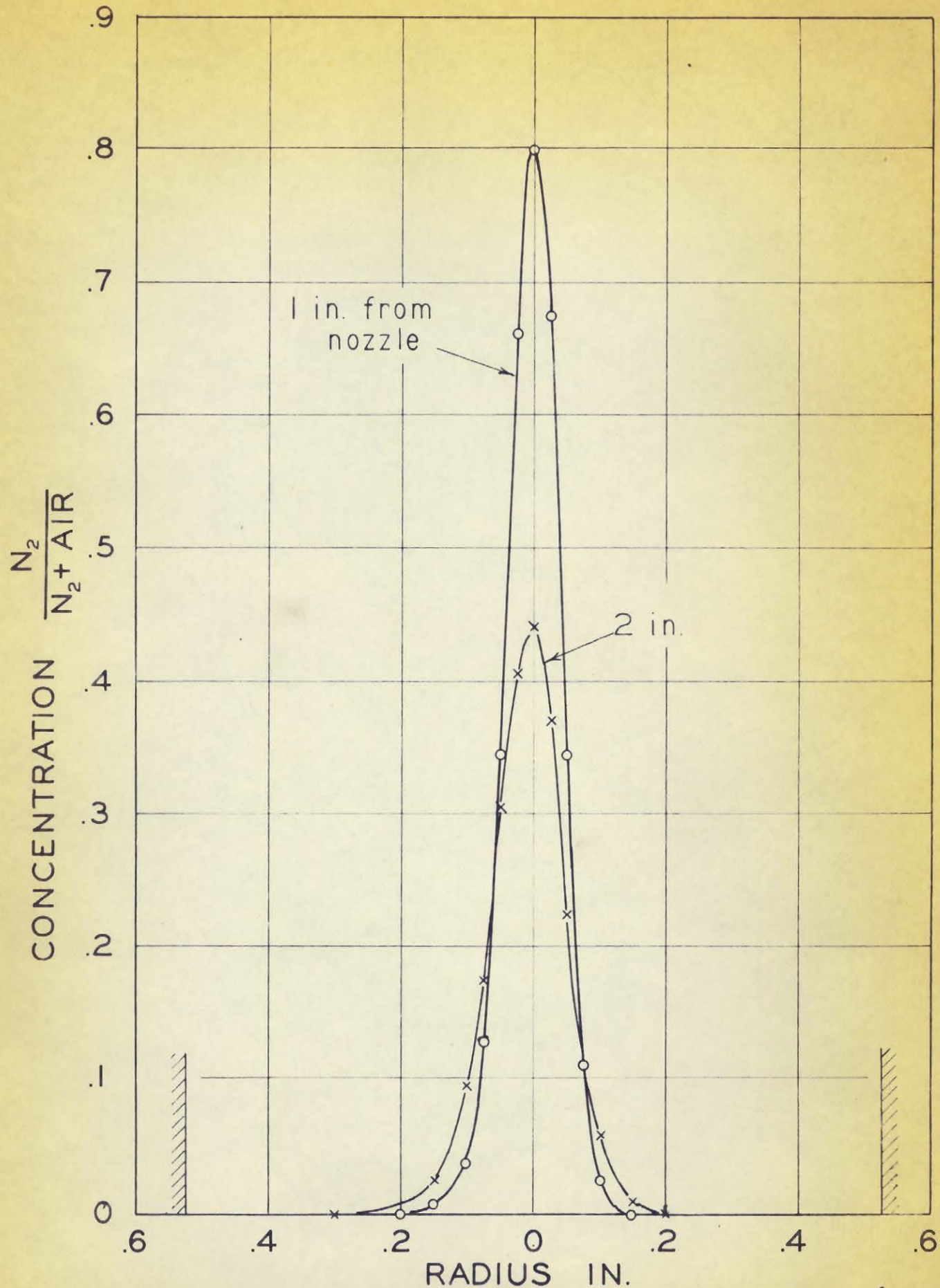

Fig. 15. Concentration profiles, straight injector. Nitrogen flow 66 x 10^{-6} lb/sec (34 x 10^{-6} lb C_3H_8/sec). Air flow .004 lb/sec. T_o= 1010 °K.

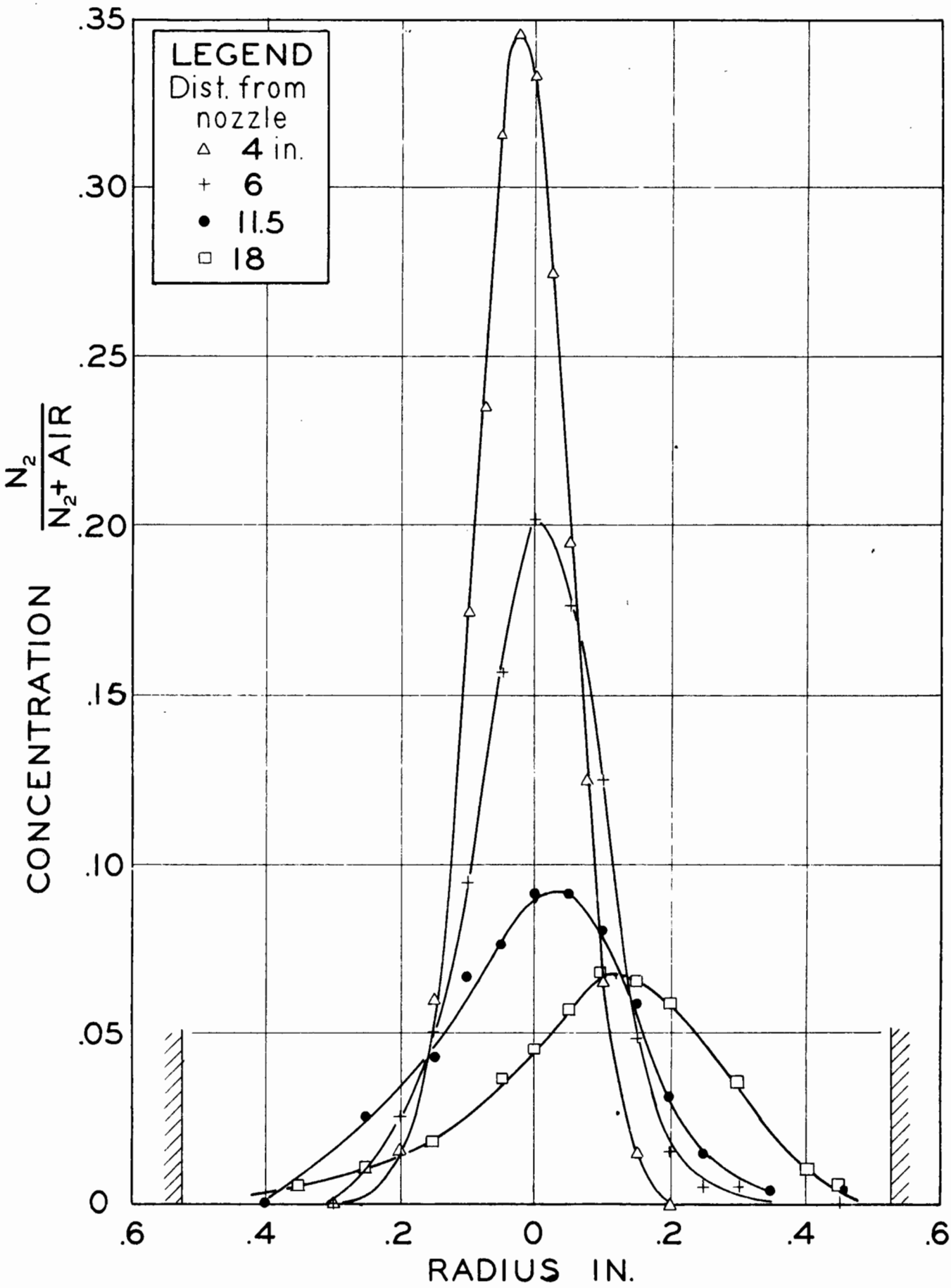

Fig. 16. Concentration profiles, straight injector. Nitrogen flow 66 x 10^{-6} lb/sec (34 x 10^{-6} lb C_3H_8/sec). Air flow .004 lb/sec. T_o = 1010 °K.

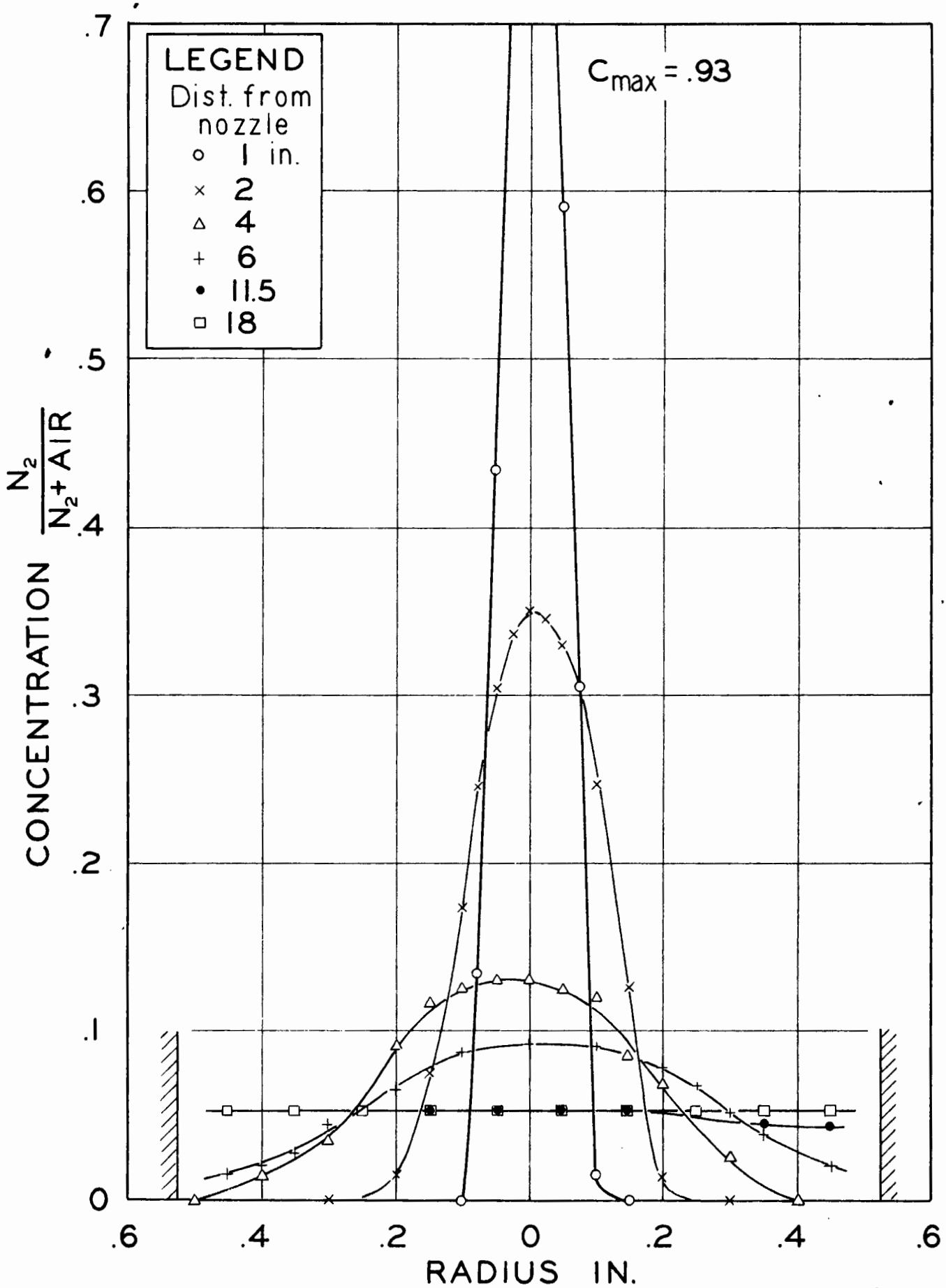

Fig. 17. Concentration profiles, straight injector. Nitrogen flow 222 x 10^{-6} lb/sec (114 x 10^{-6} lb C_3H_8/sec). Air flow .004 lb/sec. T_o = 1010 °K.

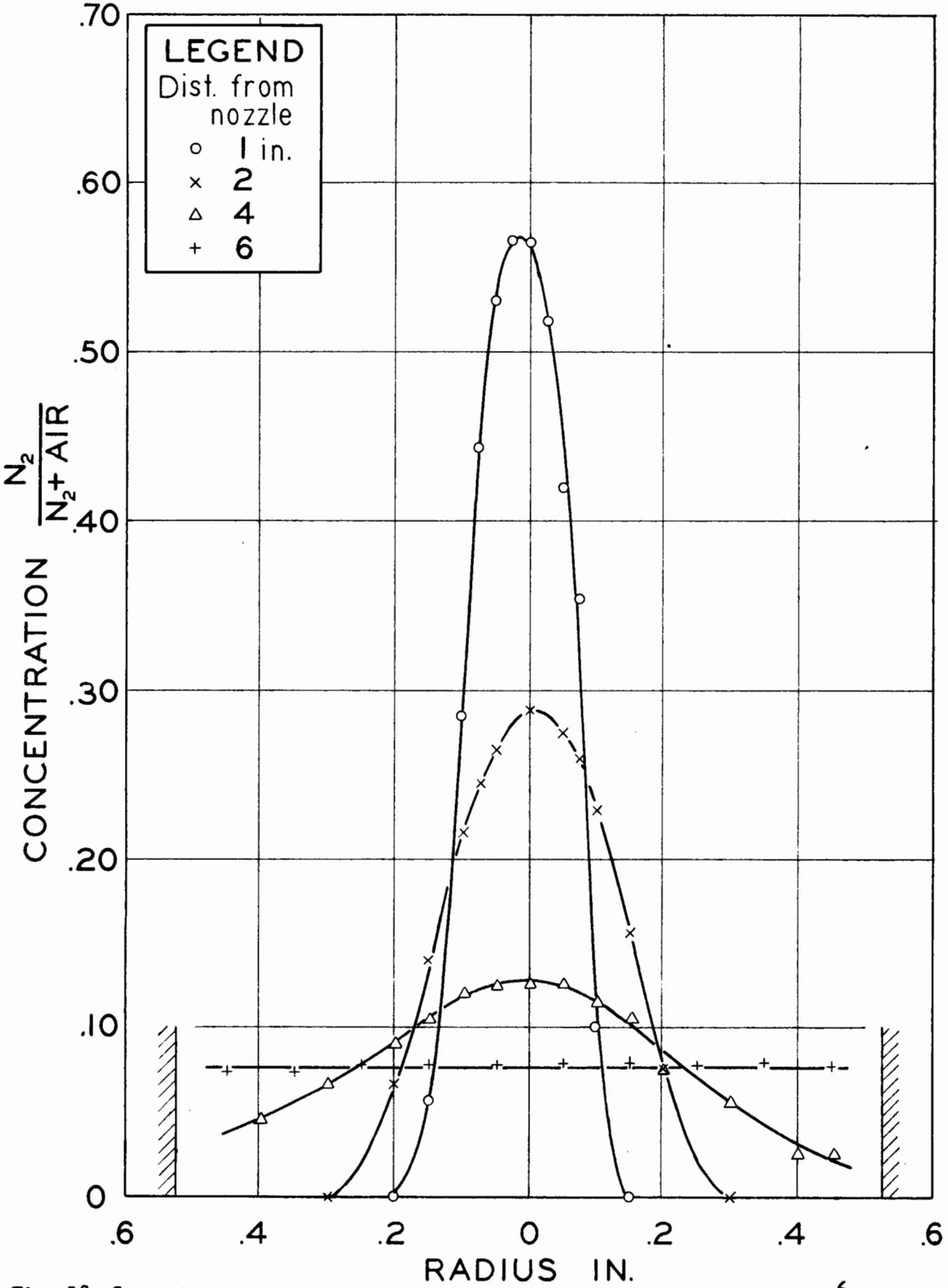

Fig. 18. Concentration profiles, straight injector. Nitrogen flow330 x 10^{-6} lb/sec (175 x 10^{-6} lb C_3H_8/sec). Air flow .004 lb/sec. T_o = 1010 °K.

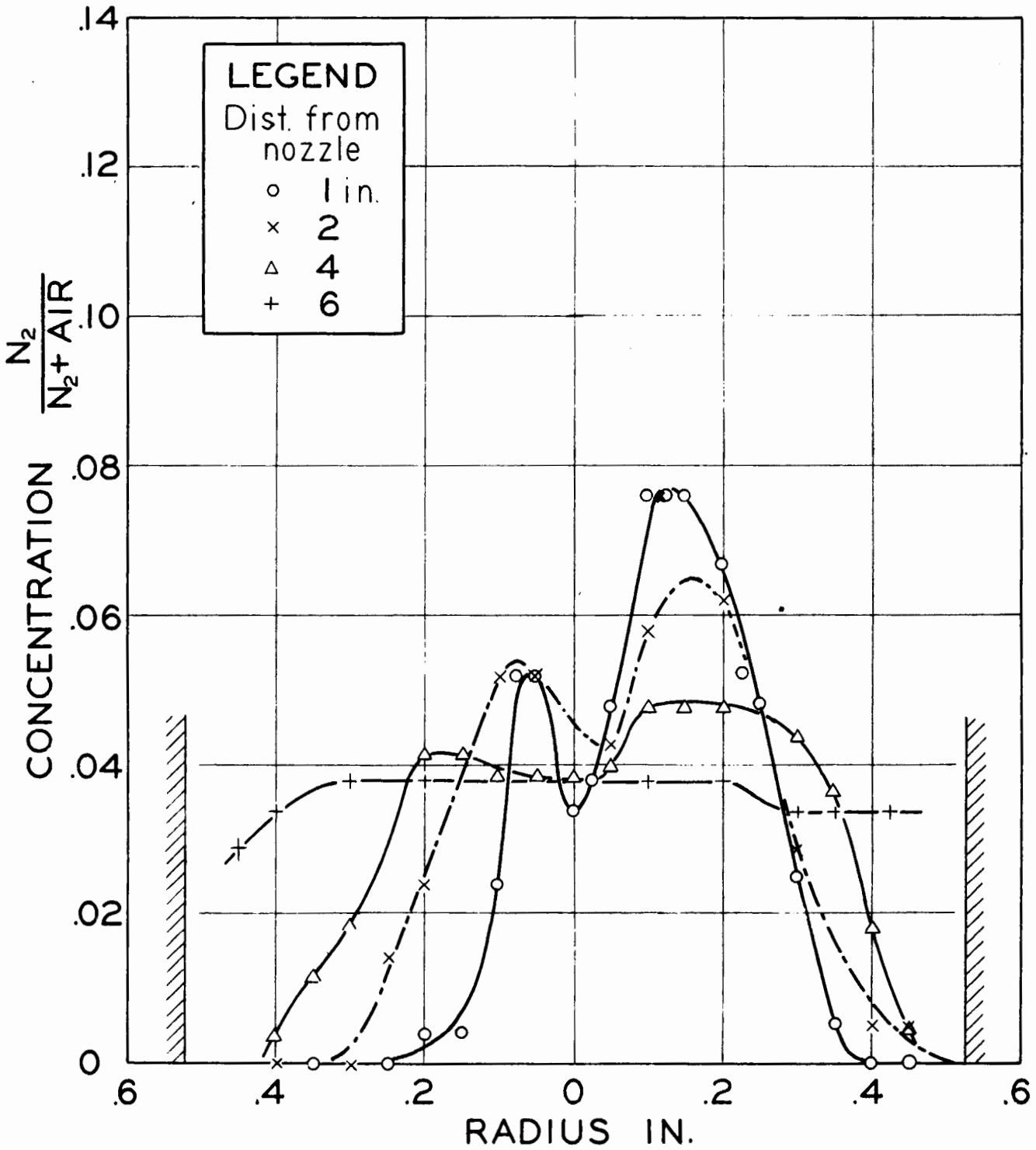

Fig. 19. Concentration profiles, multihole injector. Nitrogen flow 66 x 10^{-6} lb/sec corresponding to 34 x 10^{-6} lb C_3H_8/sec. Air flow .004 lb/sec Air temperature T_o 1010 °K.

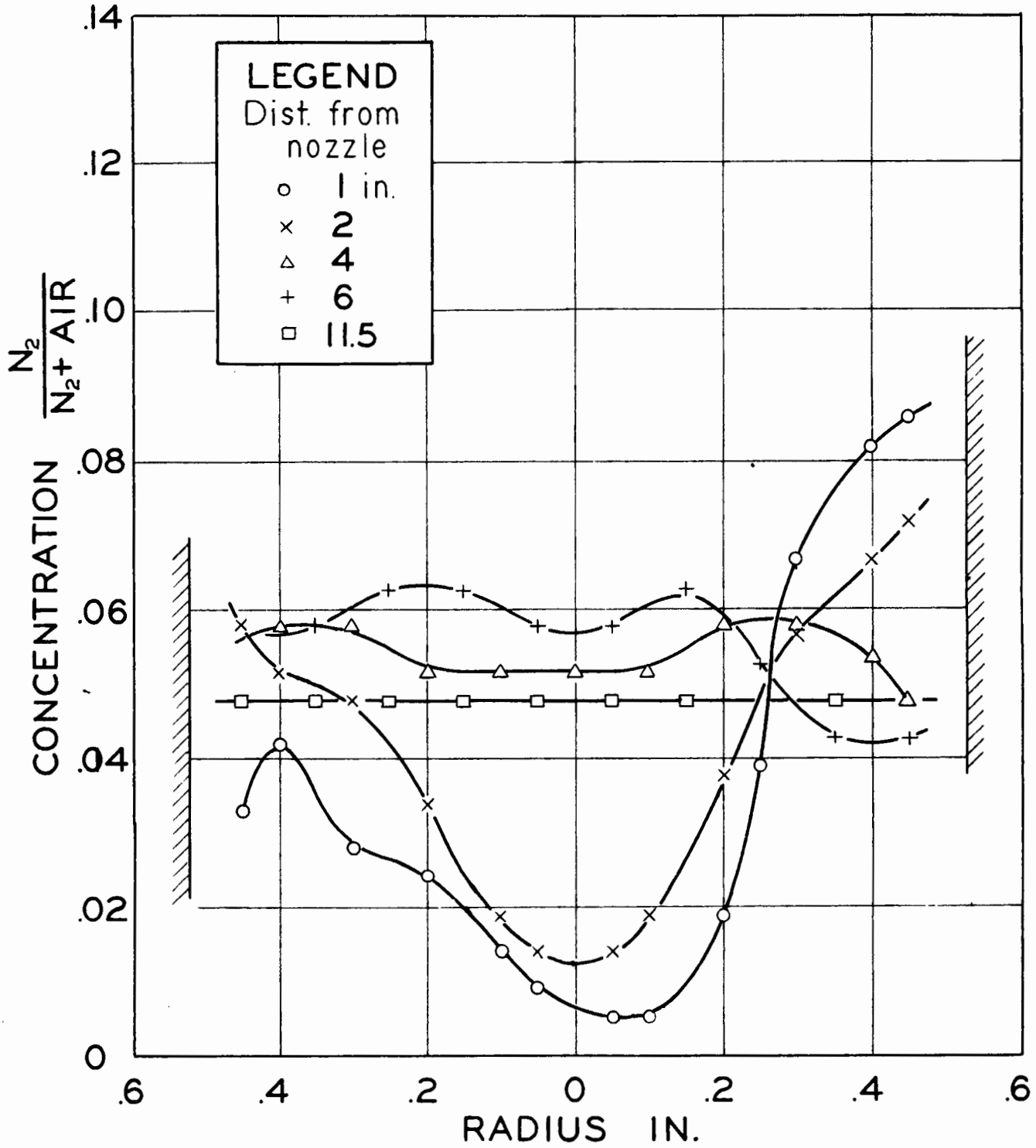

Fig. 20. Concentration profiles, multihole injector. Nitrogen flow 222 x 10^{-6} lb/sec (114 x 10^{-6} lb C_3H_8/sec). Air flow .004 lb/sec. T_o = 1010 °K.

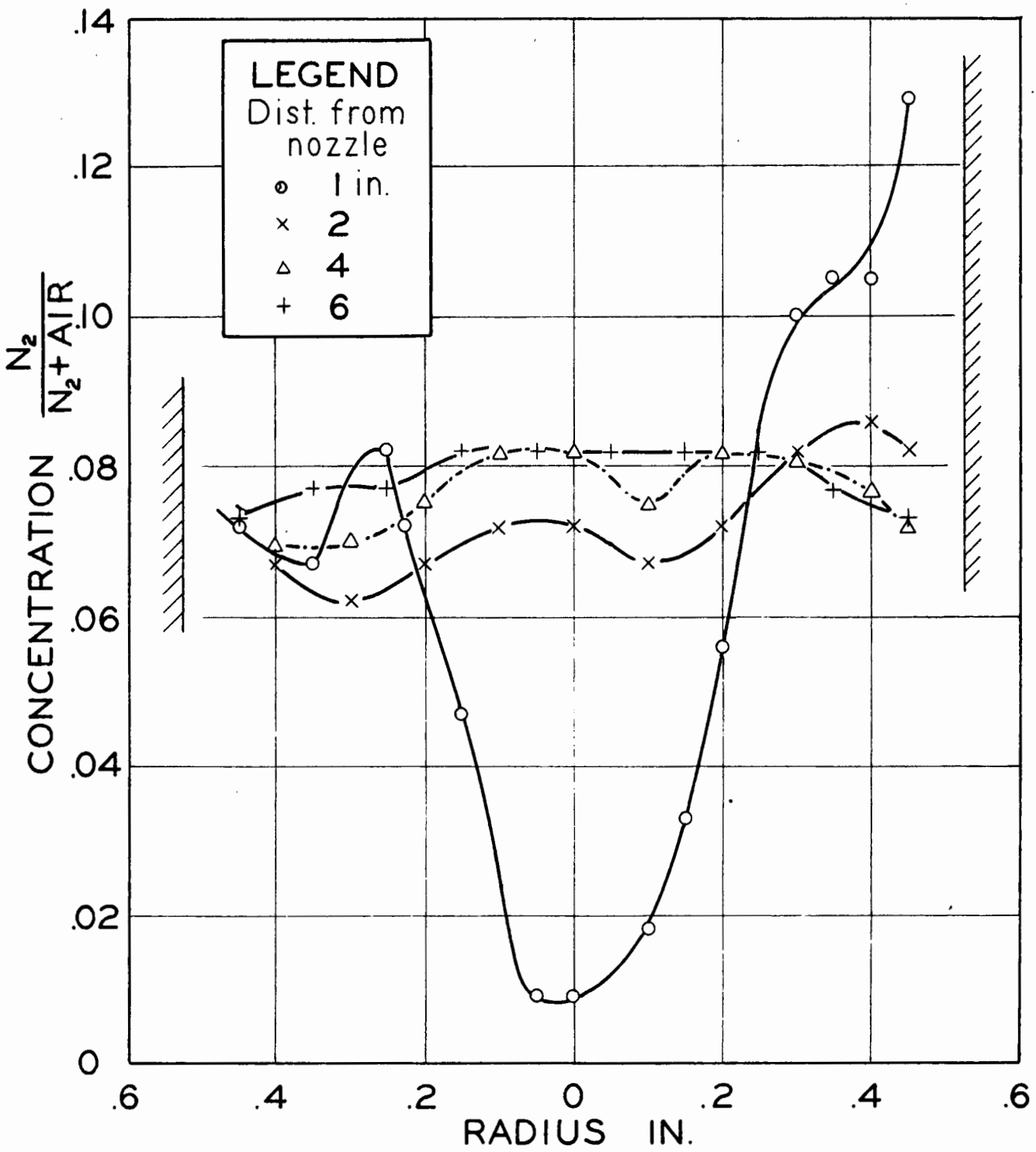

Fig. 21. Concentration profiles, multihole injector. Nitrogen flow 330 x 10^{-6} lb/sec (175 x 10^{-6} lb C_3H_8/sec). Air flow .004 lb/sec. T_o = 1010 °K.

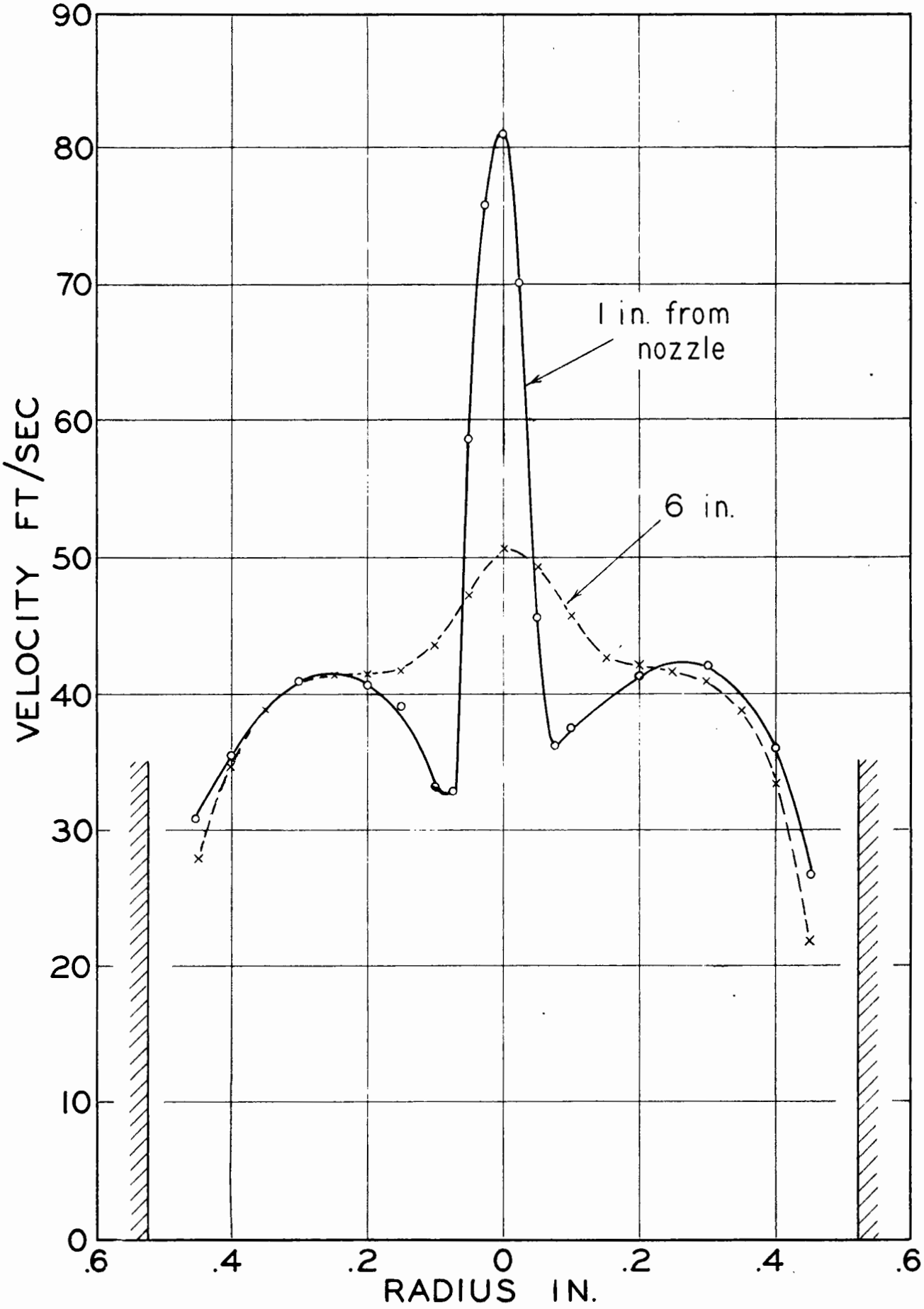

Fig. 22. Velocity profiles, straight injector. Nitrogen flow 66 x 10^{-6} lb/sec Air flow .004 lb/sec. T_o = 1010 °K.

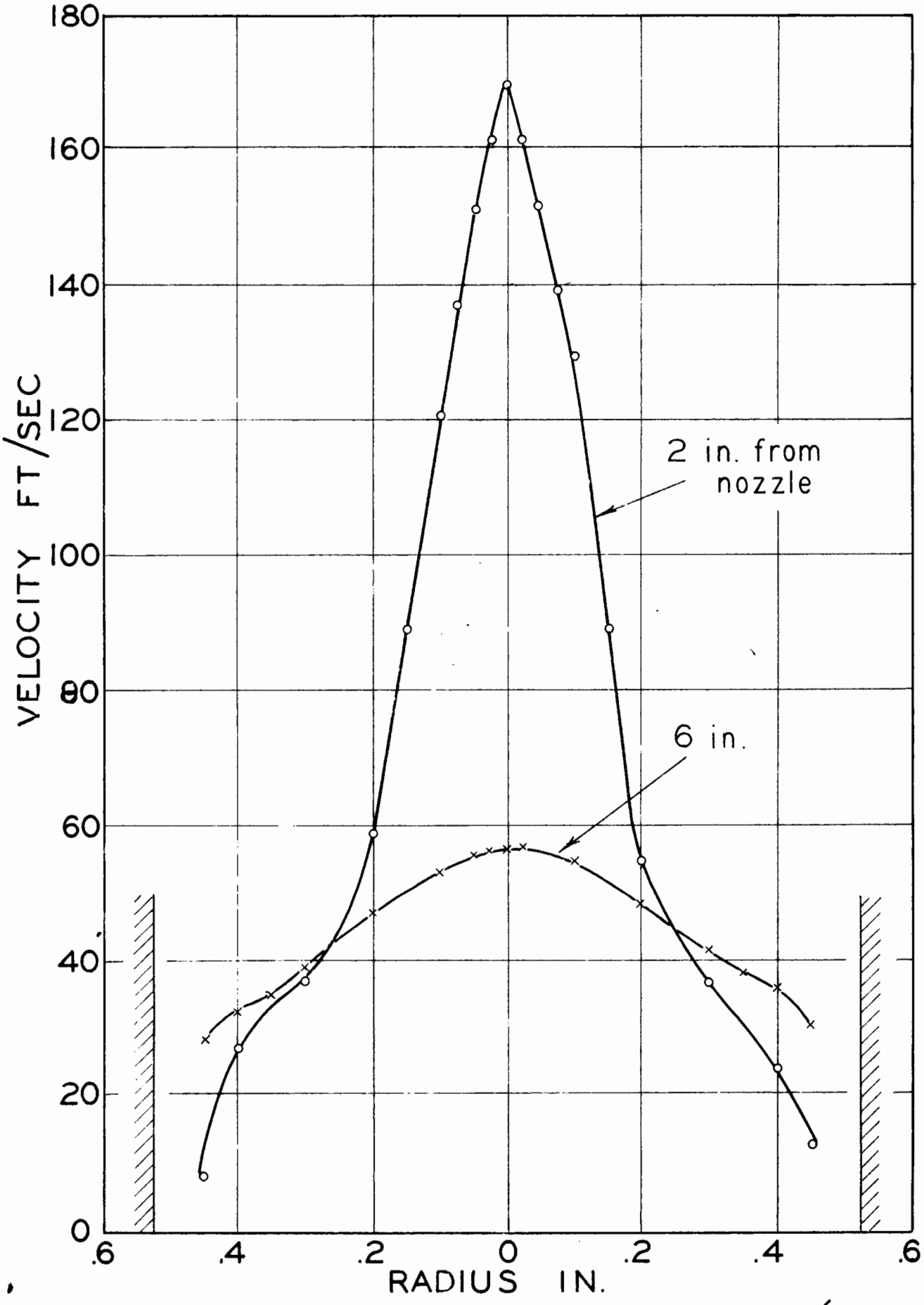

Fig. 23. Velocity profiles, straight injector. Nitrogen flow 330 x 10^{-6} lb/sec. Air flow .004 lb/sec. T_o = 1010 °K.

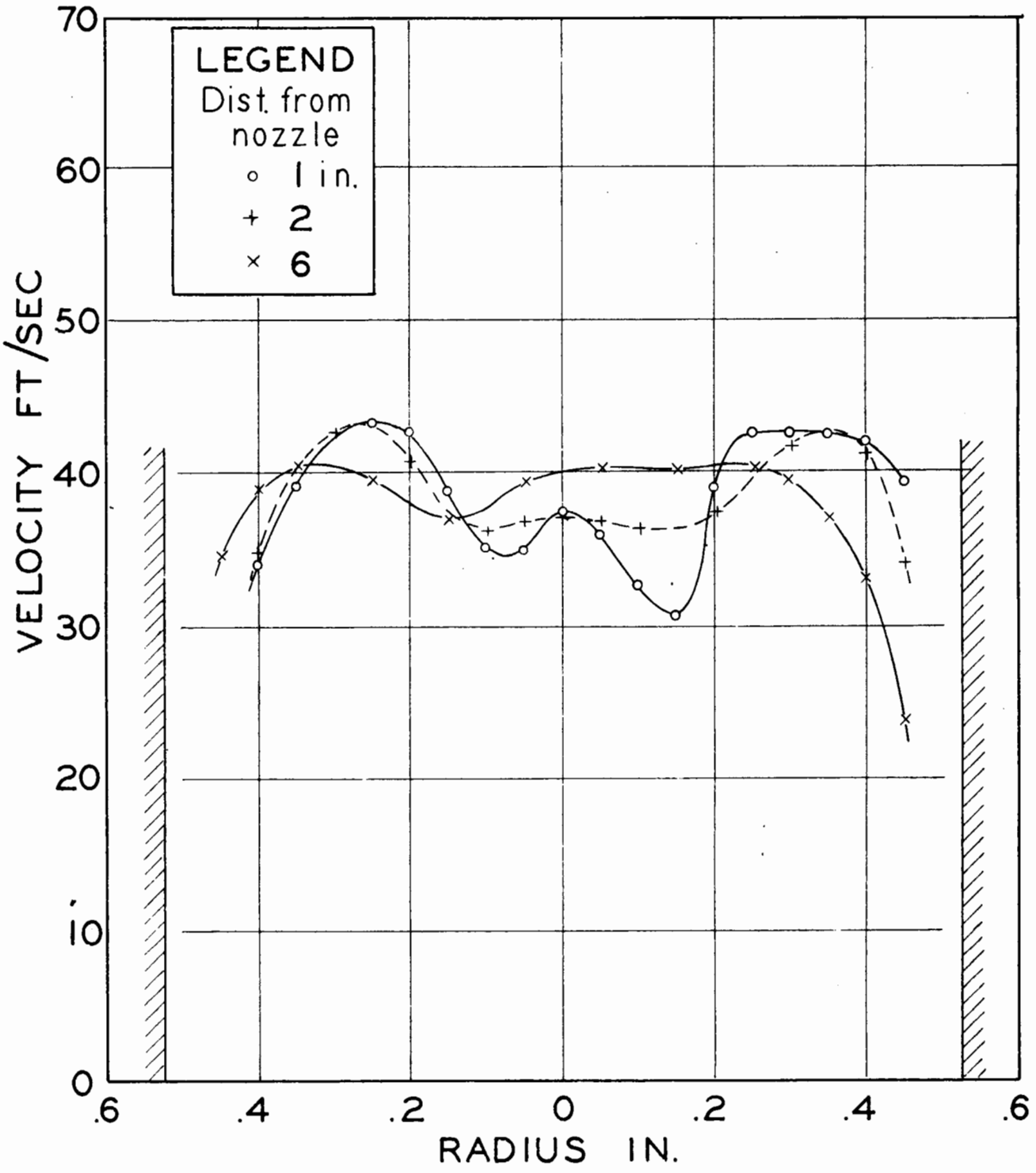

Fig. 24. Velocity profiles, multihole injector. Nitrogen flow 66 x 10^{-6} lb/sec. Air flow .004 lb/sec. T_o = 1010 °K.

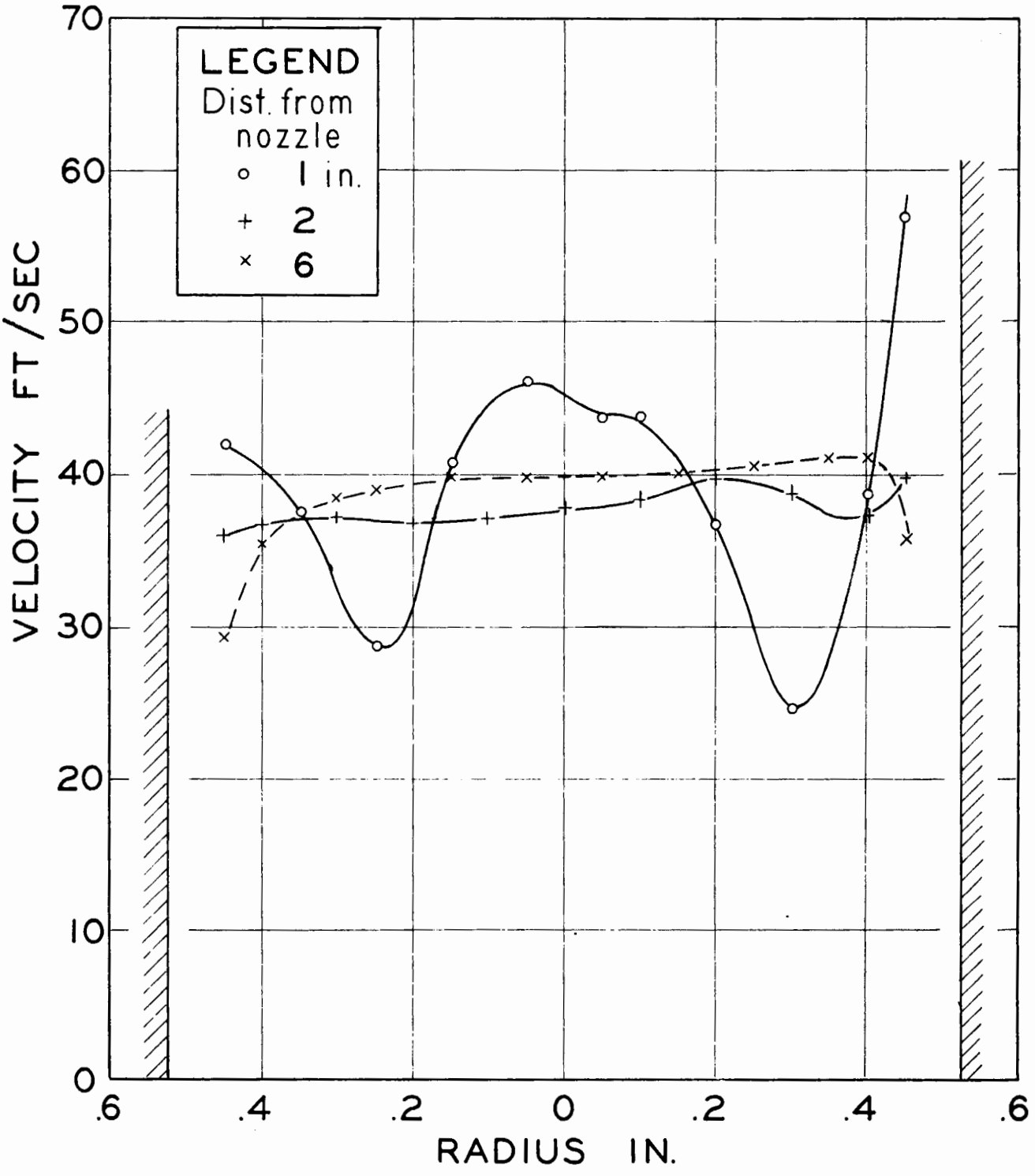

Fig. 25. Velocity profiles, multihole injector. Nitrogen flow 330 x 10^{-6} lb/sec. Air flow .004 lb/sec. T_o = 1010 °K.

DISCUSSION

Comparing the results obtained for the straight and multihole injectors, it is apparent that the aerodynamic configuration of the system plays an active part in determining ignition delay. Thus it is necessary to examine the data in two respects, the physical as well as the chemical.

Multihole injector

Nearly all significant flame front distances measured are greater than 5" from the nozzle. Since the concentration profiles show that at these distances the mixture is homogeneous, the effect of mixing is not appreciable. Delays obtained may therefore be considered as mainly due to chemical kinetics. The linearity of the delay-temperature relationship (Figs. 12 and 13) confirms the argument.

Owing to the preheating of the propane within the injector to temperatures above that for decomposition, it is postulated that ignition delay is determined by the process of thermal decomposition rather than oxidation. The mechanism is probably a very complex one and consists of a chain of reactions involving free radicals initiated by the decomposition of propane. This postulation seems to be supported by the high value obtained for the activation energy (71.8 K cal/mol) which is comparable to the value of 63.3 K cal/mol quoted by Steacie (Ref. 15).

The increase of delay with fuel flow up to the transition point (Fig. 7) may be explained as follows. As the propane flow is increased, the time available for decomposition within the

injector is less. In effect the concentration of free radicals is reduced which decreases the reaction rate or increases the delay period.

The steep drop back of the flame front to a very short delay of about 1.5 m sec (at approximately 0.5" from the nozzle) beyond the transition point cannot be regarded as an ignition delay phenomenon. At these high fuel flows the four tiny jets penetrate to the wall, and cause such turbulence as to stabilize the flame at or near the nozzle. The penetration of a jet perpendicular to an air stream depends on its initial momentum MV (Ref. 16). As velocity V is proportional to temperature, mass flow M must be less at a higher temperature to give the same penetration. If stabilization of the flame begins at this degree of penetration, then it is understandable that at higher temperatures the fuel flow necessary for the drop back is less.

Straight injector

Deviation of the delay-temperature plot from a straight line at the higher temperature end (Fig. 6) is influenced by the mixing process. Concentration profiles at various distances along the tube may be represented simply in Fig. 26, and it is assumed that these do not vary much within the experimental temperature range. If C_1 and C_2 are the inflammability limits (assumed constant) then the shaded areas are regions where reactions are appreciable. Fuel concentration in these regions is shown to increase towards the nozzle up to the distance x_s. The position of the flame front also moves in the same direction as temperature

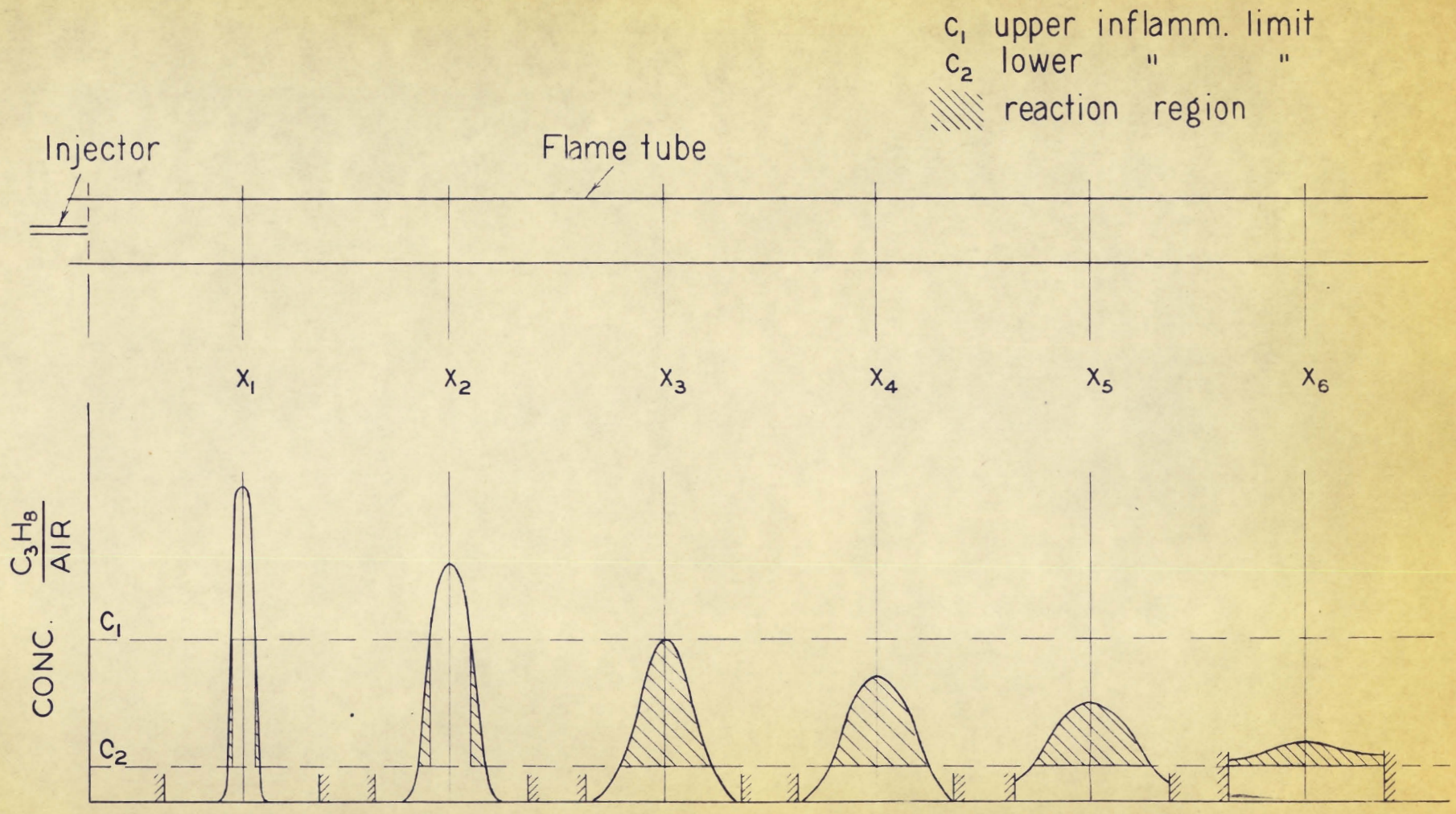

Fig. 26. Approximate concentration profiles at various distances along flame tube, straight injector.

increases. Since reaction rate is proportional to the average fuel concentration in the induction region, it can be seen that for the same temperature at the higher end, the ignition delay should be shorter for the existing flow pattern than one which gives a homogeneous mixture at all distances. In fact inflammability limits widen at higher temperatures which creates a more favourable condition for this explanation. However, lack of concentration measurements for the whole range of temperatures hinders the assurance that profiles such as those at distance x_1 and x_2 are not obtained at the higher temperature end of the delay-temperature plot.

The reason given for the increase of delay with fuel flow up to the transition point for the multihole injector also applies in this case. In addition there is an effect of radial temperature gradient in the flame tube. Air temperature measurements across the tube show that there is an appreciable temperature gradient from the axis to the wall. The delay time, being sensitive to temperature would therefore be shorter if the concentration favourable for reaction were nearer the axis. It is presumed that the region suitable for reaction is near the axis at low flows, and approaches the wall as the flow is increased. This is caused by the expansion of the fuel jet at increased velocity.

The gradual decrease of delay with fuel flow after the transition point in this case is an ignition delay phenomenon. As fuel flow is increased beyond the value at transition, the building up of the average fuel concentration in the induction region becomes

the predominant factor causing the induction period to be shortened. Another factor is the turbulence in the gas stream caused by mixing. As mentioned in Ref. 6 when fuel is injected into still air at a low velocity, the gas flow is laminar and mixing occurs by molecular diffusion. A flame burns at the nozzle which increases in length as the jet velocity is increased until at a certain value the tip begins to flutter. Further increase in the jet velocity causes a turbulent brush to be developed which is clearly separated from the laminar portion of the flame. This is due to mass transfer between the air and fuel streams. The turbulent portion of flame lengthens and the 'breakpoint' moves towards the nozzle at higher jet velocities until eventually it maintains a constant distance from the nozzle. These phenomena are in many ways analogous to the diffusion flame (Fig. 10) and flame types at temperatures above T_o = 1062 K (Table I and Fig. 8) observed in the present experiment. It is suggested that the flame front coincides with the turbulent 'breakpoint' and behaves similarly.

Factors affecting ignition delay measurements

In these experiments several factors may have influenced the results, of which the following two are of more importance:

1. Presence of propylene in fuel.

Satterfield and Reid (Ref. 12) found that when the inlet propylene concentration was increased, the induction period of the oxidation of propane and propylene mixtures decreased for the temperature range 375 °C - 475 °C. This was more pronounced at the higher temperatures. Since the test fuel used in this experi-

ment contains 4 - 5 % propylene the ignition delays measured are expected to be slightly lower than if pure propane were used.

2. Heterogeneous effects.

A bimolecular surface reaction between propane and oxygen might be involved, thus producing, regenerating or reflecting active centers in a truly catalytic manner. Erbe and his associates (Ref. 4) investigated the possible effect of various wall materials on the combustion of premixed fuel and air in insulated tubes. Silica was shown to exhibit a positive effect. Jackson and Brokaw on the other hand found that ignition delay of propane was unaffected by changing the Vycor tube size under comparable flow conditions. Experiments should therefore be directed to settle the controversy.

CONCLUSIONS AND RECOMMENDATIONS

A small scale continuous flow apparatus yielding preheat air temperatures up to about 1000°C has been built and successfully used to measure ignition delays of propane.

With rapid mixing (multihole injector) the relation between delay and temperature obeyed the Arrhenius Law, whereas a nonlinear relationship was obtained for slower mixing (straight injector). It is therefore evident that the method of fuel injection is an important physical factor and deserves careful consideration when designing a combustion chamber in which spontaneous ignition is present.

In the region of rich mixtures, ignition delay decreased with decrease in air/fuel ratio. This is reasonable since reaction rate is directly proportional to the concentration of the reactants by chemical kinetics. Jackson and Brokaw (Ref. 7) observed a similar effect.

The increase in delay at lower air/fuel ratios for lean mixtures cannot be regarded as a general phenomenon, but rather attributable only to this particular arrangement where fuel is decomposed in the fuel injector.

From the experience gained in these experiments the following comments and suggestions are put forward as a guide for future tests:

1. The stainless steel counter flow type heat exchanger is a satisfactory means of preheating air to about 1000 °C.

2. The calming chamber should be reduced in size and better insulated because heat loss caused a drop of about 70 °C from the position of thermocouples T_1, T_2 and T_3 to the face of the injector nozzle.
3. To eliminate the physical delay due to mixing in delay/temperature tests, a number of multihole injectors may be installed perpendicular to the flame tube axis. The ignition delays measured can then be taken as purely chemical and may be explained in terms of chemical kinetics. Concentration profiles should be obtained for a range of temperatures to facilitate analysis.
4. The fuel injector system should be modified to provide independent control of the fuel temperature. The effect of fuel pyrolysis within the injector can thus be examined.
5. Isothermal conditions in the flame tube should be achieved as much as possible. The catalytic effect of the Vycor wall on ignition delay may be ascertained by using several sizes of flame tubes.
6. Pure fuel should be used. It is hoped that the results obtained have contributed towards a better understanding of the combustion mechanism and that the small scale apparatus has piloted a flow system suitable for ignition delay measurements.

APPENDIX

Calculation of Concentration

Fuel concentration is determined by injecting nitrogen instead of propane into the hot air.

Let suffix 'a' refer to air

then $$\frac{O_{2a}}{O_{2a} + N_{2a}} = 0.208 \qquad \ldots\ldots\ldots (1)$$

The Oxygen meter reading R indicates the percentage of Oxygen in the air-nitrogen mixture.

i.e. $$R = \frac{O_{2a}}{O_{2a} + N_{2a} + N_2}$$

where N_2 is the amount of nitrogen injected

N_{2a} is the amount of nitrogen in the air

$$N_2 = \frac{O_{2a}}{R} - O_{2a} - N_{2a} \qquad \ldots\ldots\ldots (2)$$

Concentration

$$C = \frac{N_2}{O_{2a} + N_{2a} + N_2}$$

$$= \frac{\frac{O_{2a}}{R} - O_{2a} - N_{2a}}{O_{2a} + N_{2a} + \frac{O_{2a}}{R} - O_{2a} - N_{2a}} \qquad \text{by Eq. (2)}$$

$$= \frac{\frac{O_{2a}}{R} - O_{2a} - N_{2a}}{\frac{O_{2a}}{R}} = 1 - R\left(\frac{O_{2a} + N_{2a}}{O_{2a}}\right)$$

$$= 1 - \frac{R}{.208} \qquad \text{by Eq. (1)}$$

$$= 1 - 4.81\ R \qquad \ldots\ldots\ldots (3)$$

Calculation of Velocity

For low gas velocities in a pitot tube, the total pressure p_t is the sum of the static pressure p_s and the velocity head

i.e. $$p_t = p_s + \frac{\rho V^2}{2}$$

or $$V = \sqrt{\frac{2\,(p_t - p_s)}{\rho}}$$

where ρ = density of gas

V = velocity of gas

Let ΔH = micromanometer reading in. H_2O

ρ' = the density of the monometer liquid (water)

T = Temperature of the gas °K

then $$V = \sqrt{\frac{2\,\rho'\,\Delta H}{\rho}} = \sqrt{2\rho'\,\Delta H\,\frac{RT}{p_s}}$$

$$= \sqrt{\frac{2 \times 32.2 \times 62.4 \times 29.92 \times 96}{144 \times 14.7 \times 12}\,\frac{\Delta HT}{p_s}}$$

$$= 21.3\sqrt{\frac{\Delta HT}{p_s}}$$

Since the pressure drop in the flame tube was measured to be only .008 in. H_2O at an air flow of .004 lb/sec, p_s is taken as atmospheric. (in. Hg)

BIBLIOGRAPHY

1. Dixon, H. B., Bradshaw, L. and Campbell, C. : Firing of Gases by Adiabatic Compression. J. Chem. Soc. 105 (1914) 2027-36.

2. Dixon, H. B. and Coward H. F. : Ignition Temperature of Gases. Proc. Chem. Soc. London 26 (1909) 514.

3. Dodis, N. G. : Spontaneous Ignition Measurements of Some Gaseous Fuels Injected into a Hot Air Stream. M. Eng. Thesis McGill University, 1955.

4. Erbe, P. E., Grey, J.T., Ball, J. L. : The Influence of Wall Material on Combustion. Technical Memorandum Cal-40, Cornell Aeronautical Lab. 1952.

5. Hinshelwood, C. N. : Kinetics of Chemical Change. Clarendon Press, Oxford 1940.

6. Hottel, H. C. and Hawthorne, W. R. : Diffusion in Laminar Flame Jets. Third Symposium on Combustion.

7. Jackson, J. L. and Brokaw, R. S. : Variation of Spontaneous Ignition Delays with Temperature and Composition for Propane-Oxygen-Nitrogen mixtures at Atmospheric Pressure. N.A.C.A. RM E54B19.

8. Laidler, K. J. Chemical Kinetics McGraw Hill Inc. 1950.

9. Lewis, B. L. and von Elbe, G. : Combustion, Flames and Explosions of Gases. Academic Press Inc., N. Y. 1951.

10. Mullins, B. P. : Spontaneous Ignition of Fuels Injected into a Hot Gas Stream. N.G.T.E. Reports R 89, 93.

11. Mullins, B. P. : Spontaneous Ignition of Liquid Fuels. AGARDograph No. 4 Butterworths Scientific Publications, London 1955.

12. Satterfield, C. N. and Reid, R. C. : The Role of Propylene in the Partial Oxidation of Propane. Fifth Symposium (International) Combustion.

13. Saunders, O.A. : The Chemistry and Physics of Combustion Part II. Chemical and Physical Factors Centrolling the Rate of Combustion. Paper presented at the Joint Conference on Combustion A.S.M.E. I. Mech. E. 1955.

14. Semenov, N. N. : Thermal Theory of Combustion and Explosion N.A.C.A. Technical Memo No. 1024, from Progress of Physical Science (USSR) vol 23, No. 3, 1940.

15. Steacie, E. W. R. : Atomic and Free Radical Reactions. Reinhold Publishing Co., New York 1954 Second Edition.

16. Sullivan, L. J. : The Mixing of Cold Air Jets with a Hot Gas Stream in a Varying Area Duct. M. Eng. Thesis, McGill University, 1953.

17. Tizard, H. T. and Pye, D.R. : Ignition of Gases by Sudden Compression. Phil. Mag. (7) 1 (1926) 1094-1105.

18. Townsend, D. T. A. and Maccormac, M. : The Inflammation of Hydrocarbon-air Mixtures. Paper presented at a Meeting of the Inst. of Petroleum 1939.