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THE BURNING VELOCITIES OF HYDROCARBON - AIR MIXTURES

by
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(date(

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Bethlehem, Pa. Arthur R. DiNicolantonio
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THE BURNING VELOCITIES OF HYDROCARBON - AIR MIXTURES

by

Arthur Robert DiNicolantonio

The object of the experiments was to determine the burning velocities of Propane-air mixtures and N-Butane-air mixtures by the burner method and variations of the tube method.

Six variations of the tube method were used. Spatial velocities were measured with the tubes in a vertical position and upward flame propagation. All the variations used tubes of 44 inches in length. Variation I, utilized a 2.42 cm I.D. tube with the ignition end of the tube open, and the upstream end closed. Variation II was similar to variation I, except an orifice was fitted in the ignition end of the flame tube. Variation III, was similar to variation I except a 3.4 cm I.D. tube was utilized. Variation IV used the 3.4 cm I.D. tube with an orifice in the ignition end and the upstream end closed. Variation V used the 3.4 cm I.D. tube with an orifice in the ignition end and orifice in the upstream end of the tube. Variation VI utilized the 2.42 cm I.D. tube with an orifice in the ignition end and a cap composed of a one inch thickness of steel wool at the upstream end of the flame tube.

The author observed that flame propagation was not uniform throughout the entire length of the tube but, only over a small portion for all variations of the tube method except variation VI. In variation VI, the flame propagated uniformly throughout the entire length of the tube, and no celluar structure of the flame front was observed at any point in the flame tube.

In the burner method, burning velocities were obtained by using the total schlieren cone area.

The values of burning velocity obtained by the burner method were higher than those obtained by all variations of the tube method except variation VI. The burning velocities obtained in variation VI agreed excellently with those obtained by the burner method.

INTRODUCTION

The speed with which the combustion process occurs influences the efficiency with which the heat released in combustion can be used.

Before commencing the topic of methods of measuring burning rates it is necessary to define some terms. The spatial velocity of a flame is the velocity with which the flame moves through space. This velocity may be readily measured but it is not a fundamental property of the fuel, since it will depend to a large extent on the type and shape of the vessel in which the combustion process occurs. The spatial velocity is a vector sum of the unburned gas velocity and the transformation velocity. The transformation velocity is the speed relative to the unburned gases with which the flame front moves from the burned to the unburned gases. It is measured in a direction normal to the surface of the flame front. Because of the expansion of heated gases in the vicinity of the flame, there occurs a movement of gases in that region which displaces the flame front. The velocity of the unburned gases approaching the burning zone is called the gas velocity. Therefore, if there were no mass flow of the heated gases, then the transformation velocity would be the actual rate of advance of the flame into the unburned gas.

The terminology, stationary flame, refers to flames in which the flame front is fixed in space and the unburned mixture travels towards the burning area. This is the type of flame which occurs in a bunsen burner. A propagating flame is one in which the flame front moves through the unburned gas. This process of slow combustion is referred to as a deflagration wave.

The burning velocity or the transformation velocity defined as the linear velocity of the flame front normal to itself, relative to the unburnt gas consumed per unit time divided by the area of the flame front in which that volume is consumed. The problem then is to determine a suitable area for the flame front. This can be done easily in the case of an infinite plane flame front because the area is not dependent on how the flame surface is defined, that is, on the particular surface selected. However, this is not the case for a spherical or conical flame front. No definition of the flame surface to date has been found that is free from all possible objections. The essential difficulties are that in the case of a spherical flame front there is no particular distance from the center of combustion where the linear velocity of the gas is constant and the fact that the temperature varies continuously from the center of combustion to the flame front so that no surface can be considered to have a significance greater than any other. In the case of a conical flame front, there is no surface where the burning velocity has a constant value over the entire surface.

The problem of determining a suitable area brings us to the position of determining the structure of laminar flames in general. Simplified models suggest that the combustible wave absorbs heat until the gas temperature has risen sufficiently for the chemical reaction of combustion to become rapid. At that temperature the mixture liberates heat at a faster rate than it absorbs heat from the burned gas. Much experimental work has been concerned with the location of the region known as the reaction zone, that is the region where chemical reaction becomes rapid. Early workers considered this zone to be a surface represented by the luminous zone of the flame. They also presumed that the thickness of the luminous zone represented the distance between the initiation of combustion and its completion. While the luminous zone may be part of the total reaction zone, it is reasonable that the start of the combustion wave as indicated by a sharp temperature rise does not necessarily coincide with the occurrence of luminosity. Lewis and Von Elbe (45) have shown that the gas flow lines bend prior to the luminous zone indicating that thermal expansion begins ahead of the luminous zone, thus, the heat transfer processes begin prior to the occurrence of luminosity.

Schlieren photographs of a Bunsen flame by Van de Poll and Westerdijk (64), established that a region exists between the luminous zone and the unburned gas in which the gas density changes rapidly due to a rapid change in the temperature of the gas. As a result of many experiments at atmospheric pressure which point out that the Schlieren edge marks an initial temperature rise in the combustion wave, the Schlieren edge is considered to be the most satisfactory for burning velocity studies and is considered as the start of the reaction zone. This boundary marks a temperature in the region of about 200-300°C and is followed by a rapid rise in temperature. The luminous zone marks the region where the final flame temperature is reached and the distance between the schlieren and luminous zones may be considered as a measure of the combustion wave thickness.

II. MEASUREMENT OF BURNING VELOCITIES

Tube Method

Early flame research was carried out in glass tubes whose lengths were greater than their diameter. Mallard and Le Chatelier reported results of flame studies as early as 1883. Coward and Hartwell (8) used the following method. The gas mixture to be studied was contained in a long tube. One end of the tube was open while the other end was closed. The gas mixture was ignited near the open end and the flame propagated towards the closed end. They found that the movement of the flame front was uniform. They measured the spatial velocity and took snapshots of the flame front from which they calculated its area by matching it to a portion of ellipsoid whose plane of symmetry is in the vertical plane through the axis of the tube and whose main axis is inclined over the horizontal. By using Guoy's (32) concept of burning velocity based on the volume of the mixture burned per second divided by the flame surface area, they found that for a given mixture under a variety of conditions of tube size and direction of propagation the calculated burning velocity was constant.

According to the method of Coward and Hartwell, the area of the flame surface was calculated on the assumption that it was equal to that of a semi-ellipsoid, the axes of which were equal to (1) a line joining the points where the flame touched the top and bottom of the tube, (2) twice the perpendicular distance between that line and the point most remote from it on the photograph of the flame front, and (3) the diameter of the tube.

The area was calculated by the following formula which was derived from the integral form given by Jellette (Williamson, "Integral Calculus," 1891, p. 283):

$$A = \pi b(a^2-c^2)^{1/2} \cdot E(k\phi) + \pi bc^2(a^2-c^2)^{-1/2} \cdot F(k\phi) + \pi c^2$$

where a, b, and c are the semi-axes with, $a > b > c$ $k = e'/e$; $\phi = \sin^{-1} e$; e and e' are the eccentricities of the ellipses in the plane of the axes a & c, b & c, respectively. The values of $E(k,\phi)$ & $F(k\phi)$, the elliptic functions of the second and first kind respectively, can be obtained from math tables.

Coward and Payman (9) related the fundamental flame velocity (transformation velocity) to the spacial flame velocity by the equation:

$$U_T = (U_S - U_g)\, A_T / A_f$$

where U_g is the velocity of the unburned gas ahead of the flame. A_t is the cross sectional area of the tube and A_f is the surface area of the flame. Because of difficulty involved in measuring the unburned gas velocity, it was assumed negligible in early experiments by Coward and Hartwell.

Attempts to reproduce the experiments of Coward and Hartwell prove that the uniform flame movements occurred in only a small portion of the tube, and this location varied for different hydrocarbon mixtures.

Guenoche, Manson, and Mannot (30) placed an orifice at the ignition end of the tube and demonstrated that it reduced the pressure waves which disturb the flame and render the motion nonuniform.

Gerstein, Levine, and Wong (27) used a Pyrex glass tube 57 cm long and 2.8 cm I.D. At the ignition end of the tube they placed an 8 mm orifice. At the end of the tube towards which the flame propagated, they placed a 1.7mm orifice. The use of this second orifice increased the uniformity of the flame travel. The spatial velocity was measured by means of photocells placed six inches apart connected to an electric timer and high speed photographs taken of an oscillograph screen placed in parallel with the timer. The uniformity of flame travel was checked by a rotating drum camera. The unburned gas velocity was determined by experimental measurement of

SUMMARY OF RESULTS

Fuel	Max. U_s, cm./sec.	Max. U_t,* cm./sec.	Vol. % fuel at max. U_t
Methane	84.5	33.8	9.96
Ethane	102.8	40.1	6.28
Propane	99.5	39.0	4.54
Butane	96.2	37.9	3.52
Pentane	98.0	38.5	2.92
Hexane	98.0	38.5	2.51
Heptane	98.3	38.6	2.26
2-Methylpropane	87.5	34.9	3.48
2,2-Dimethylpropane	83.0	33.3	2.85
2-Methylbutane	92.5	36.6	2.89
2,2-Dimethylbutane	90.0	35.7	2.43
2,3-Dimethylbutane	91.7	36.3	2.45
2,2,3-Trimethylbutane	90.5	35.9	2.15
2-Methylpentane	93.0	36.8	2.46
3-Methylpentane	92.7	36.7	2.48
2,3-Dimethylpentane	92.2	36.5	2.22
2,4-Dimethylpentane	89.9	35.7	2.17
Ethene	184.5	68.3	7.40
Propene	113.4	43.8	5.04
1-Butene	111.5	43.2	3.87
1-Pentene	110.0	42.6	3.07
1-Hexene	108.5	42.1	2.67
2-Methyl-1-propene	95.0	37.5	3.83
2-Methyl-1-butene	99.5	39.0	3.12
3-Methyl-1-butene	106.9	41.5	3.11
2-Ethyl-1-butene	100.3	39.3	2.65
2-Methyl-1-pentene	101.2	39.6	2.80
4-Methyl-1-pentene	104.0	40.5	2.62
Propyne	189.1	69.9	5.86
1-Butyne	155.0	58.1	4.36
1-Pentyne	140.0	52.9	3.51
1-Hexyne	127.0	48.5	2.97
4-Methyl-1-pentyne	116.9	45.0	2.87
2-Butyne	135.6	51.5	4.36
3-Hexyne	118.0	45.4	3.05
Cyclohexane	98.4	38.7	2.65
Benzene	104.5	40.7	3.34

Results obtained by Gerstein, Levine and Wong,: J. Amer. Chem. Soc., 73, 420 (1951) the volumetric rate flow determined from photographs of the progressive growth of a soap bubble blown from a tube connected to the upstream end of the flame tube. They arrived at an equation for the unburnt gas velocity by studying the results of their experiments:

$$U_g = .236\,U_s - 10.47$$

They calculated the flame surface area from photographs taken of the flame by the method of Coward and Hartwell.

An important objection to the method of Coward and Hartwell and also that of Gerstein, Levine, and Wong is that only an average burning velocity can be obtained because cooling by the walls of the tube might be important over part of the flame surface, and thus, because of the quenching effects at the wall, the burning velocity is slower there than it is over the rest of the flame surface.

According to Guenoche (29), under conditions of uniform propagation in a tube the flame has the shape of a spoon tangent to the inner wall of the tube which takes up some position in the tube and travels the length of the tube maintaining a constant area. Guenoche and Jouy (29) placed an orifice downstream of the combustion wave in their study similar to the one used by Gerstein, Levine, and Wong, but in a discussion of their experiment by Burke, he stated that in an experiment performed by Burke and Friedman (24) orifices placed downstream of the combustion wave were found to unsatisfactory because they introduced uncertainties into the measurement of flame speeds even though they were found to reduce vibrations of the gas column.

We are at apoint now of determining how the closed end tube used by Coward and Hartwell influenced the flame shape. As explained by Lewis and Von Elbe (45b), the unburned gas ahead of the flame front forms a stationary column. The thermal expansion of the gases in the reaction zone of the flame generates a continuous flow of burned gas towards the open end of the tube, but because of the viscous drag this flow is retarded at the wall and accelerated in the center of the tube. This acceleration produces a thrust which pushes the unburned gas in the central region of the tube toward the closed end. Since the gas cannot escape there it is forced to reverse its direction so that it flows along a curved path away from the center and towards the open end. Additional curvature of the flame is caused by quenching of the flame front on the cooler walls of the tube. This effect is minimized in tubes of large diameter. Frank-Kamenetsky points out that where heat flows from the inside of the tube to the outside the flame must curve toward the unburned gas.

Ball (2) considered the hydrodynamics of a flame propagating in a tube and calculated the shape of the flame and path of the gas flow lines through the flame. He assumed flame has zero thickness, the burning velocity is constant over the entire flame surface, the gases are perfect gases, and incompressible flow exists. His calculations indicated that the tip of the flame is perpendicular to the tube axis and converging toward tangency at the tube wall. His theoretical flame shape is in good agreement with that observed in smoke track studies.

We see that in the method by Coward and Hartwell and others who used the closed end tube downstream of the combustion wave the effect of possible slight pressure increase was neglected and only compensated for by its possible effect on the flame shape. The reason for this will now be explained.

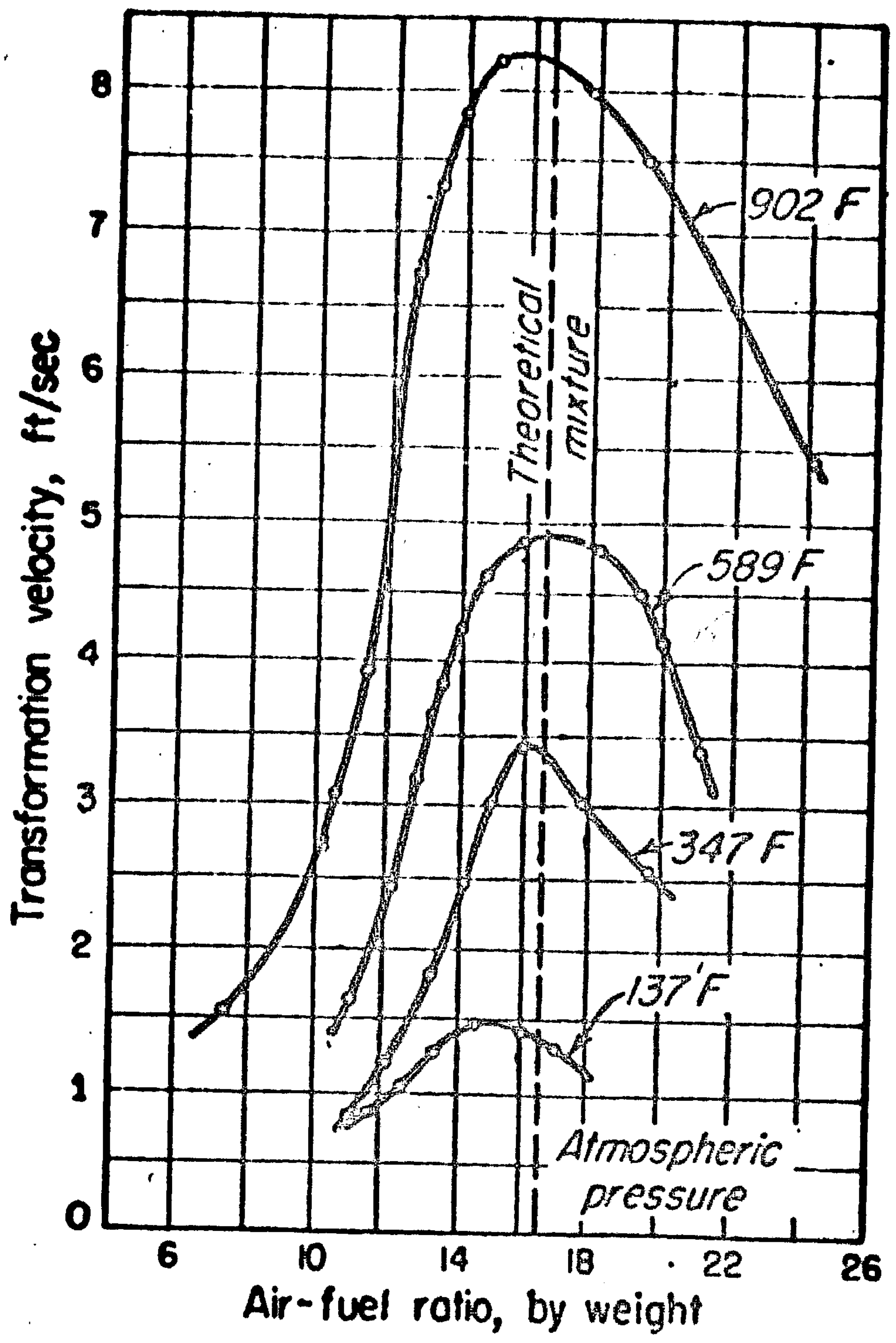
Most of the theories on flame propagation predict that $U_T \propto P^N$ where N is a positive or a negative fraction or zero. Thermal theories of Crussard (12), Jouguet (35), and Daniell (14) predict that $U_T \propto P^{1/2}$ for a second order reaction rate. Semenov (54) predicts that $U_T \propto P^{-1/2}$ for a first order reaction rate. Tanford and Pease (60) predict $U_T \propto P^{-1/4}$; theories of Boys' and Corner (6) predict $U_T \propto P^{0}$; that is that U_T is independent of pressure.

Ubbelohde and Koelliker (63) have found experimentally that $U_T \propto P^{-1/4}$ for mixtures of C_2H_2 - air, by the burner method. Linnett and Wheatley (65) have found that $U_T \propto P^{-1/4}$ for ethylene - air mixture by the burner method. Egerton (20) by using the flat flame method found that for propane $U_T \propto P^{-.3}$

As can be seen from these results the effect of pressure on the transformation velocity is very small.

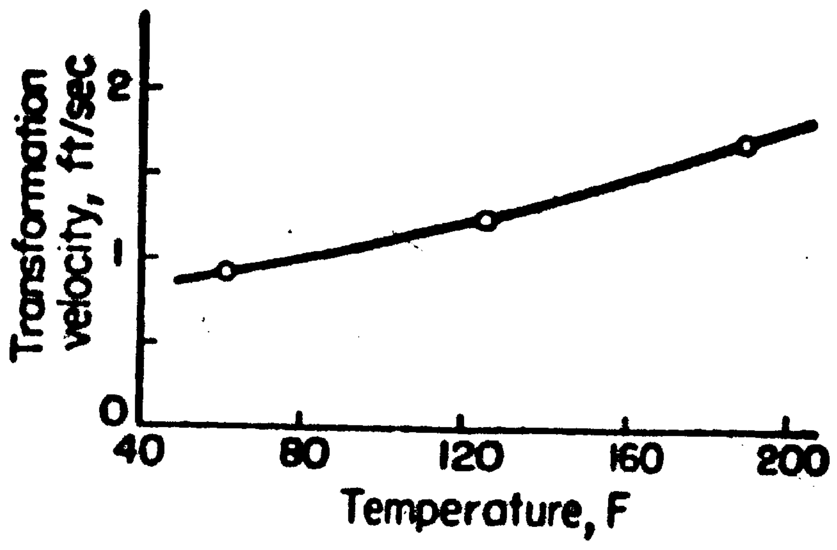
There is evidence that the combustion wave is sensitive to forces acting on the gas stream. The spatial velocity of a flame is largest for upward propagation and smallest for downward propagation as a result of the effect of gravity. The spacial velocity also increases with increasing tube diameter which indicates that the ratio of combustion wave area to tube cross section increases as the tube diameter increases.

The transformation velocity is influenced by the initial temperature of the fuel-air mixture before combustion. The higher the mixture temperature, the faster will be the transformation velocity. This was proven by results of tests conducted by Johnston (33) using various mix-



Transformation velocities for mixtures of natural gas and air at various temperatures, measured by a bunsen-burner method. (Johnston, SAE J., Dec., 1947)

FIG. 1



Variation of transformation velocity with temperature for a 31.7 per cent coal gas in air mixture, measured by a bunsen-burner method. (Sherratt and Linnett, Trans. Faraday Soc., 1948)

FIG. 2

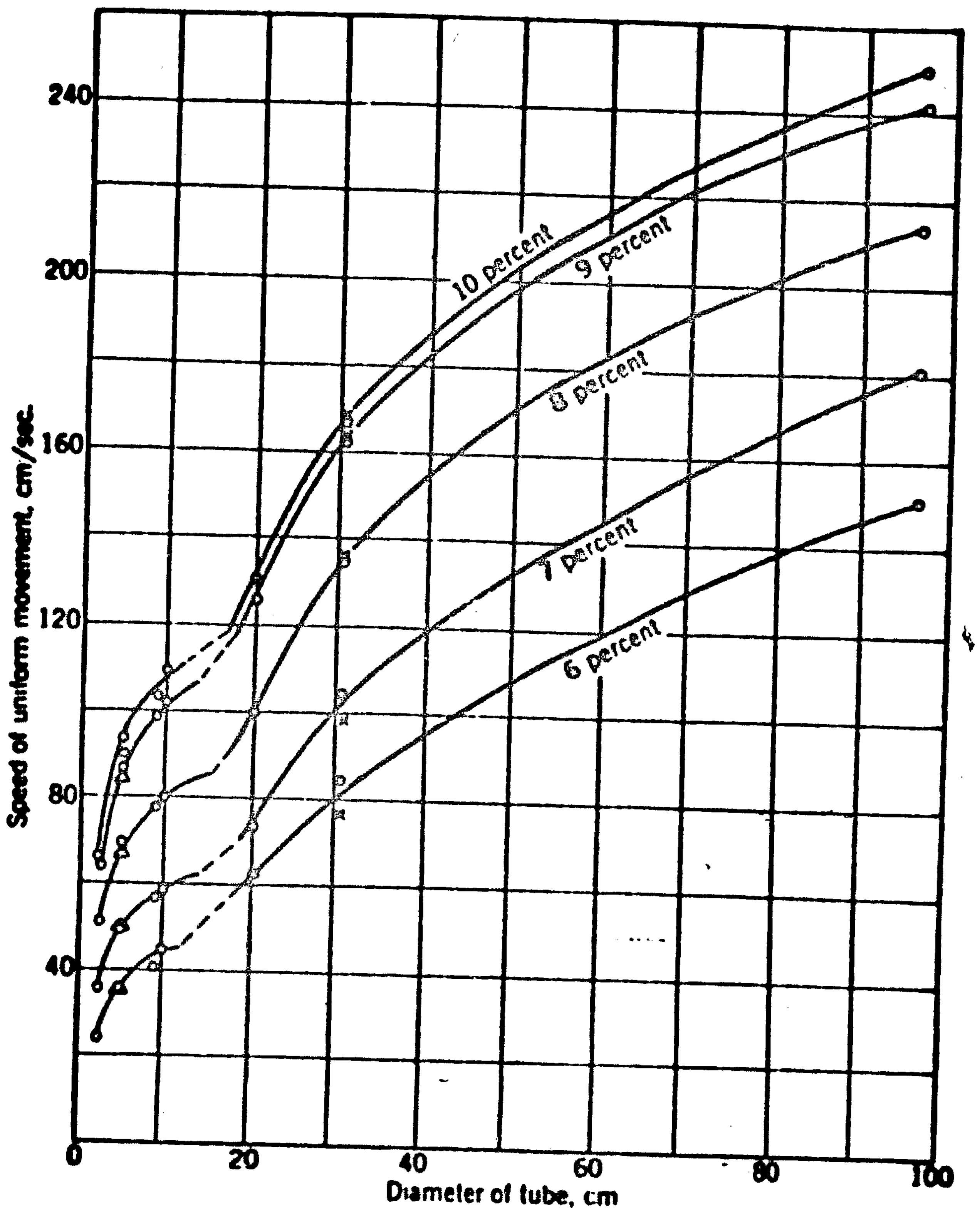
tures of natural gas and also various mixtures of acetylene and air, utilizing the bunsen burner method. The same conclusion is reached from results of tests by Sherratt and Linnett (55) utilizing coal gas-air mixture in the bunsen burner method.

a. SOME REMARKS ON TURBULENT FLAMES

Since we are studying laminar flame propagation, we are not really concerned with theories or studies of turbulent flame propagation. It will suffice, therefore, to only mention a few things about turbulence which might affect a study of laminar combustion wave propagation.

As can be seen from figure (3), ploted by Coward and Hartwell in their study of the propagation of combustion waves of methane-air mixtures in tubes, there is an increase in the spacial velocity with increasing tube diameter for the various mixtures of methane and air. The transition from laminar to turbulent flow is marked by a change in slope and has been calculated by Lewis and Von Elbe (45e) to occur at a Reynolds number of 2000.

Schmidt, Steinicke, and Neubert (53) studied the propagation of combustion waves in propane-air mixtures



Dependence of speed of uniform movement of flames of methane-air mixtures on tube diameter, (Coward and Hartwell, J. Chem. Soc., London, 1932)

FIG. 3

in a tube 109 cm long and 2.4 cm I.D. The tube was closed at one end and open at the ignition end similar to that used by Coward and Hartwell. They observed for a rich mixture of propane the following: oscillations started in the combustion wave at 1/4 of the length of the tube while the spacial velocity remained fairly constant to the center of the tube where the amplitude of oscillations increased and the flame accelerated and its speed became again constant in the last half of the tube. They explained this phenomena as follows: In the first half of the tube oscillations increased because of the ignition and were stimulated by the combustion, in the middle of the tube the oscillations reached such an amplitude that turbulence began with an increase of spacial velocity, but the turbulence did not develop fully because there was not enough time available for it to do so before the oscillations became damped, and thus, velocity again became fairly constant in the last half of the tube.

When ignition was started in the closed end of the tube, full turbulence developed because the specific volume of the burned gases being much larger than heat of the unburned gases act like a piston which accelerates the combustion wave and the gases ahead of it. When these compression waves in the unburned gas coalesce they form a shock wave if the tube is long enough.

According to Lewis and Von Elbe (45d) turbulent motion occurs in viscous fluids as a consequence of eddy formation on obstacles, of shear flow due to the retarding effect of the walls, and the mixing of streams of different velocities.

In tubes, especially those of large diameter, oscillations of the gas column cause the flame front to wrinkle and to assume the appearence of a cellular structure. This wrinkling causes an increase in surface area resulting in an increase in the amount of gas burnt per unit of time which in turn causes an acceleration of the wave, thus producing more disturbances and turbulence which aggravates the already existing condition.

Bunsen Burner Method

This method is the most common method for measuring transformation velocities of flames. In this method premixed gas flows up a tube and is burned at the mouth of the tube. Many procedures have been used for measuring the shape of the cone and determining the burning velocity. The earliest method, used by Gouy, was to divide the volume flow rate by the area of the visible cone. This method was not satisfactory since the burning velocity is different at different parts of the cone.

Dery (15) modified this method by measuring the area of the visible cone between two radii, and dividing the area by the volume flowing up the tube per second between the same two radii. By doing this he eliminated the effect of the high burning rate area at the tip of the flame and the low burning rate area at the base of the flame. The burning velocity for cylindrical burners is found from the relation:

$$V_T = 2V(r_2 - r_1)\left[1 - (r_2^2 + r_1^2)/2R^2\right]/s$$

where V is the average gas velocity in a burner of radius R. r_2 & r_1 are the radii of the base and top of the cone frustrum, respectively, and s is the slant height of the frustrum.

The main objection to the partial area method is that it is difficult to test whether the area chosen is free from the tube wall and tip effects.

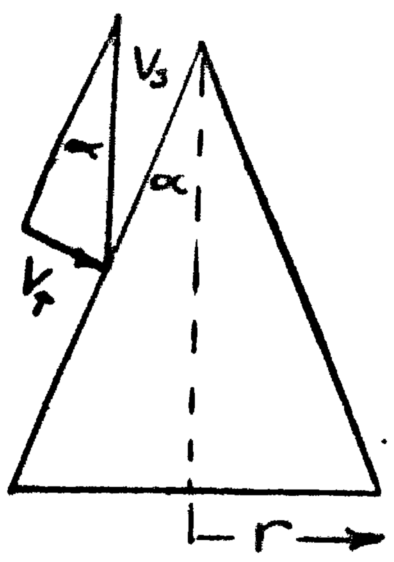
Sherratt and Linnett (55) made use of the shadow cone obtained by projecting a shadow of the Bunsen cone on to a photographic plate by using a point source of light. The shadow line is well within the luminous region of the flame, and the gas flow lines diverge at a point between the shadow and luminous cones. Their results showed that a constant value of burning velocity was found at the middle part of the cone surface. Grove, Hoare, and Linnett (28) made a study of the shadow cone method and showed that the burning velocity measured by Sherratt and Linnette was dependent upon the distance between the flame and the photographic plate and that only in extrapolation to zero distance can a true value of transformation velocity be obtained.

Conan and Linnett (6) have shown that when dust particles are introduced into the burner flame the flow lines remain parallel up to the Schlieren cone, but diverge from the tube axis before reaching the visible cone. Because of this the Schlieren cone is preferred.

Michelson (48) used hydrodynamic procedures and calculated the flame shape based on the assumption that the velocity profile in the burner tube is parabolic, the flame can be represented by a single surface of zero thickness, the burning velocity is constant over the entire flame surface, and the flow lines of the unburned gas are parallel to the axis of the tube. Michelson's theory predicted a pointed flame tip while the observed tip is rounded. The shape predicted by Michelson closely resembles the Schlieren edge of the actual burner flames but differs slightly at the base. Michelson's theory leads to the formula:

$$V_T = V_s \sin\alpha$$

where α is the angle the flame surface makes with the direction in which the gas is flowing with a velocity V_S



Smith and Pickering (57) applied this formula to the visible cone at a radius $r/\sqrt{2}$ because at this radius the flow rate is equal to the average flow rate. But because of the fact that the temperature of the gas rises and the flow ceases to be parallel to the tube axis before the visible cone is reached, it seems that their method is unsatisfactory, and Michelson's formula can only be applied to the Schlieren cone.

Andersen and Fein (1) introduced a light powder into the gas and followed the path of the particles which traced out the flow lines through the cone. They measured the angle between the direction of the particle track in the cold gas and the flame front at the point where the particle tracks pass through it. They used this angle in the Michelson formula. As is pointed out by Andersen and Fein, there is the danger that burning velocity may be affected by the particles that were introduced.

All of the above procedures do not give the same values of burning velocity for the same gas mixture. The method of using the schlieren image with the Michelson angle gives results which most closely agree with the results from the glass tube and soap bubble methods.

The shape of the burner flame is affected by the hydrodynamics of the gases and the interaction of the combustion wave with the wall of the tube. The solid rim of the burner tube acts as a heat sink so that the flame velocity vanishes near the burner rim. Particle track studies have shown that the flow lines are directed away from the tube axis by thermal expansion. Lewis and Von Elbe (45a) state that the thrust pressure is not uniform along the flame cone, but vanishes at the base where the burning velocity vanishes. Because of this, pressure gradients exist from the interior to the base of the cone, which cause the gas flow to acquire a component normal to the axis of the tube. In the region of the base of the cone the forces between adjacent stream tubes do not cancel each other and the flow acquires a component parallel to the wave layers. This produces a flow of gas directed away from the axis and contributes to the "overhang" of the cone base beyond the diameter of burner tube.

Flow lines deviate less at the flame tip than the base, but the assumption of constant velocity at the tip is not valid. Because of the small radius of curvature near the flame tip there is an increase in heat flow and also free radical transport from the flame to the unburned gases which results in an increased burning velocity. According to Lichty (46), there is a ram effect in the central lamina of the burner gas stream, and the accompanying pressure rise is much greater than the pressure rise in the burner tube so that the velocity of the central lamina is reduced in the vicinity of the flame requiring a small increase in the burning velocity at the tip of the burner flame.

Soap Bubble Method

The soap bubble method was developed by Stevens (59), in 1923. The gas mixture to be examined is contained in a spherical soap bubble and ignited by a spark in the center of the bubble so that a spherical flame spreads through the gas. The pressure remains constant. The bubble and flame is photographed along a horizontal diameter with a drum camera. The velocity thus measured is not the burning velocity but a spatial velocity because at any stage in the combustion the burnt gas behind the flame occupies a larger volume than it did as unburnt gas, and this causes the fresh gas into which the combustion is advancing to move radially outward. It has been shown that the burning velocity can be determined from the relation:

$$V_T = V_S / E$$

where E is the volume expansion ratio on burning and is assumed constant throughout the burning. This expansion ratio is obtained by measuring the initial diameter of the sphere of unburnt gas in the bubble and the final diameter of the sphere of flame at the conclusion of the outward travel of flame

In 1951 Pickering and Linnett (50) extended the method to flames of low luminosity by using a schlieren system to follow the flame front. The schlieren edge gives the same results in determining V_s as the luminous edge because the separation between the schlieren edge and visible edge remains constant once the diameter of the flame sphere is several times bigger than the flame thickness.

To determine the expansion ratio E is a difficult problem. The problem is magnified because any error in measuring the final diameter is cubed in determining E. One reason for inaccurate measurement is that the final flame edge is less sharp than the initial edge of the bubble. Another reason is that in some cases afterburning of the product gases makes the final size measurement more difficult and less accurate because on schlieren photography it is difficult to determine where the primary flame finishes and after-burning starts.

Some other disadvantages of the method are also important. Aqueous bubbles contain liquid and contaminate the mixture with an unknown amount of water. This method can be used only with fast flames because convective rise of the hot combustion gases makes the method unsuitable. Diffusion through the film may be so great in some cases that the composition of the enclosed gas changes before it is fired. In some mixtures the flame will not remain spherical as it grows but develops irregularities as observed by Markstein (47). Some gas mixtures attack the bubble and, therefore, change its composition.

Some advantages of the method are that it requires a small amount of gas, and velocity calcualtions do not require consideration of pressure effects.

Closed Spherical Vessel Method

This method was originally developed by Fiock (22). The gas is contained in a spherical vessel and ignited at the center by a spark. The outward movement of the flame is followed by a rotating drum camera. However, as a result of thermal expansion of the burned gas, the pressure rises and also has to be followed during the course of the combustion.

An advantage of this method is that only a limited amount of gas supply is needed. Some disadvantages are that the flame must idealy retain its spherical form in order to be used in this method, and the variation of the temperature and pressure of the unburnt gas during the explosion makes interpertation difficult.

During the combustion the expanding burnt gas compresses both the unburnt gas and the burnt gas. Because this process is rapid, the gases are heated by compression. Fiock, Marvin, Caldwell,and Roeder (23) assumed the compression to be adiabatic and derived a relation for the burning velocity given as:

$$V_T' = \left[1 - \frac{R^3 - r^3}{3 P \gamma r^2} \frac{\partial P}{\partial r} \right] \frac{\partial r}{\partial t}$$

where R is the radius of the vessel and r that of the spherical flame at the moment when the pressure is p. γ is the ratio of specific heats for the unburnt gas which is assumed to remain constant. The observed flame speed is $\partial r/\partial t$. Because of the fact that:

$$\frac{R^3 - r^3}{3p\gamma r^2}\frac{\partial p}{\partial r} \quad \text{is between .85-.95 an}$$

error of 1% in this term leads to an error of 10% in the burning velocity.

Lewis and Von Elbe (43) assumed that the ratio of specific heats for both the burnt and unburnt gas remains constant and thermodynamic equilibrium is established in the flame front. They arrived at an expression:

$$r^3/R^3 = \frac{P - P_i}{P_e - P_i}$$

where P_e is the fictitious pressure corresponding to combustion at constant volume computed thermodynamically. The fictitious temperature T_e corresponding to P_e is found from the relation:

$$T_e = \frac{C_{p_b} T_b}{C_{v_b}}$$

where T_b is the flame temperature computed for combustion at constant pressure P_i.

$C_{v_b} = \Sigma N C_v$ ——— molar specific heat at constant volume of burned gas.

N ——— mole fraction of constituent in the burned gas.

C_v ——— specific heat at constant volume of the constituent.

$C_{p_b} = R + C_{v_b}$

The pressure P_e is found from the relation:

$$P_e = \frac{P_i\,(M_b\ T_e)}{(M_i\ T_i)}$$

M_b the number of moles formed by combustion of m_i moles of explosive gas. Using these relations in an equation for the burning velocity given as:

$$V_T = \frac{dr/dt}{1 + (P_e/p - 1)\gamma_u}$$

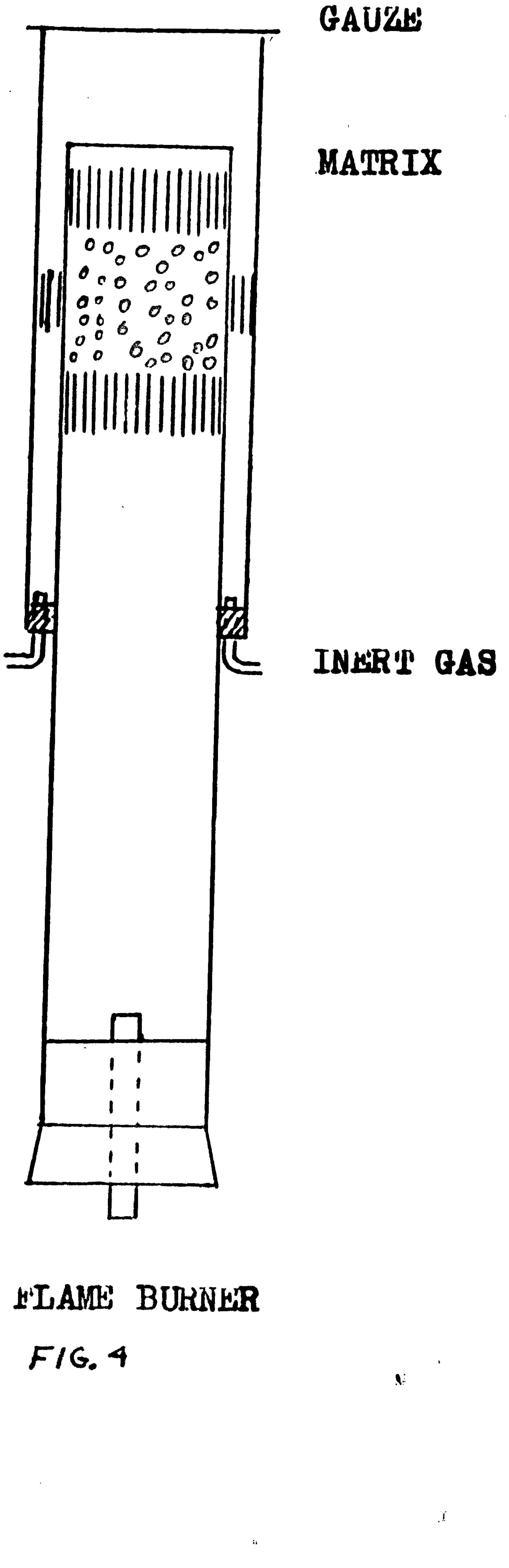
allowed the burning velocity to be determined with dr/dt the only time derivative.

Lewis and Von Elbe used a 15.295 cm I.D. vessel with a pressure indicator (of diaphram type mounted flush with the inside wall). The flame was photographed with a drum camera using a schlieren optical system. Their experimental results agreed very well with other published values for burning velocities.

Egerton - Powling Flat Flame Method

The flat flame burner was developed by Powling (51) in 1949, and modified slightly by Egerton and Thabet (19) in 1952. This burner is used for measuring low burning velocities. In this method the gas mixture enters the bottom of a vertically mounted cylindrical tube 35 cm long and about 6 cm in diameter at a known flow rate. It passes through a layer of about 4000 channels(each channel is .65 sq. mm and 22 mm long) and then through a 5 cm layer of small glass spheres, 4 mm in diameter, which break up the gas flow and deliver it evenly to another layer of channels. The burning of the gas occurs once the gas passes through the last layer of channels. The flame then passes through a wire gauze screen which is adjusted at the proper height above the tube so that the flame assumes a flat shape. The screen affects the flame by controlling the flow of the burnt gases. A stream of inert gas, such as nitrogen, is passed through a concentric tube surrounding the burner tube. The diameter of the flame is measured and its area divided into the volumetric flow rate of the gases to yield a value for the burning velocity.

This method can only be used with mixtures having burning velocities less than 12 cm/sec. because it is impossible



FLAT FLAME BURNER

FIG. 4

to obtain flat flames with mixtures having higher burning velocities. This is so because in such mixtures the flame front becomes broken into flamelets. This method makes possible the measurement of burning velocities that are so small that they cannot be measured by any other method. The lowest burning velocity that can be measured by this method is 3 cm per second.

III. LIMITS OF INFLAMMABILITY

A combustible mixture is a mixture of fuel and oxidant that is capable of sustaining combustion. Any combustible mixture can be rendered noninflammable by the addition of excess fuel, excess oxidant, or inert gases. The upper limit of inflammability is the richest mixture that will propagate a flame. The lower limit of inflammability is the leanest (least percentage of fuel in the mixture) mixture which will support combustion. The limits of inflammability are not fundamental properties of the explosive system but are affected by the method of testing.

The usual method of determining the limits is by observing the propagation of a flame in a long tube. The U.S. Bureau of Mines uses a tube 5 cm in diameter.

Wider limits are obtained for upward flame propagation than for horizontal or downward flame travel. The reason for this, as explained by Lewis and Von Elbe (45c), is that because of the force of gravity on the heavier unburned gas ahead of the flame front in upward propagation, the stream tubes open up well ahead of the combustion wave. This causes the transport of gas from the region of the tube axis to the wall to take place ahead of the thermal gradient of the combustion wave. The velocity gradient near the flame surface is diminished, thus there is less flame stretch, and therefore, the flame survives at a greater mixture dilution. In downward propagation, the velocity gradient near the flame surface is increased, leading to greater flame stretch and narrower limits.

Another reason for the wider limits in upward flame propagation is because of the effect of diffusional stratification which strongly affects the composition of the limit mixtures. The effect is particularly noticed in upward flame propagation. Stratification results in locally increased burning velocities. Diffusional stratification occurs in stoichiometrically unbalanced mixtures of fuels and oxidants in which the diffusivity of the deficient component substantially exceeds that of the excess component. The mixture stratifies on entering the combustion wave so that locally over the wave surface the burning velocity alternately increases and decreases and the wave wrinkles and acquires a cellular structure.

The limits of inflammability become wider with increasing tube diameters up to a diameter of about 2 inches. Larger diameters effect the limits very little. This has been demonstrated by Coward and Jones (10).

Temperature variations of a few degrees of the unburned gas have little affect on the limits, but temperatures considerably above room temperature cause wider limits of inflammability.

The pressure of water vapor tends to lower the upper limit of inflammability but does not affect the lower limit. Small pressure changes have negligible affect on the limits of inflammability.

Le Chatelier's (58) rule may be applied with caution to obtain an estimate of the limits of inflammability for a mixture of gases. This rule is stated as follows:

$$L = \frac{100}{(P_1/N_1) + (P_2/N_2) + (P_3/N_3)}$$

where P_1, P_2,P_3 are the percentages of each combustible gas present in the original mixture, and N_1,N_2,N_3 are the respective limits of inflammability of gaseous components.

Badami and Egerton (18) have measured the limits of inflammability using the flat flame method developed by Powling. They were able to measure lower limits than those measured by upward propagation in the tube method. They measured the limits for mixtures of hydrocarbon gases and compared the results with the limits calculated by the Le Chatelier mixing rule. Their results are shown on the following page.

Lean Limits Of Mixtures in Air

mixture of						observed lower limit in air	V at limit (cm/s)	calculated limit (Le Chatelier mixing rule)
CH_4	C_2H_6	C_3H_8	C_2H_4	CO (0-12) % H_2O)	H_2			
4·49	0·405	—	—	—	—	4·895	4·19	4·87
3·91	0·66	—	—	—	—	4·57	4·00	4·58
3·39	0·90	—	—	—	—	4·29	3·98	4·32
2·98	1·09	—	—	—	—	4·07	3·87	4·10
2·57	1·30	—	—	—	—	3·87	4·08	3·88
1·95	—	1·21	—	—	—	3·16	3·89	3·14
—	1·85	0·50	—	—	—	2·35	4·76	2·36
—	1·805	0·53	—	—	—	2·335	3·92	2·35
—	1·515	0·73	—	—	—	2·245	3·93	2·28
—	1·25	0·94	—	—	—	2·19	3·82	2·21
4·46	—	—	0·46	—	—	4·92	4·16	4·88
2·60	—	—	1·37	—	—	3·97	3·30	4·00
—	—	—	2·51	—	0·77	3·28	3·42	3·31
—	—	—	2·34	—	1·50	3·84	3·38	3·86
—	—	—	2·17	—	2·37	4·54	4·13	4·49
—	—	—	2·07	—	2·74	4·81	3·33	4·78
0·45	—	—	—	11·80	—	12·25	4·00	14·81
1·83	—	—	—	7·90	—	9·73	4·27	11·56
3·65	—	—	—	3·87	—	7·52	3·28	8·08
4·30	—	—	—	2·51	—	6·81	4·17	7·04
4·57	—	—	—	1·95	—	6·52	3·57	6·63
—	0·56	—	—	9·54	—	10·10	3·79	12·29
—	1·37	—	—	5·43	—	6·80	3·40	7·70
—	2·11	—	—	2·07	—	4·18	3·88	4·34
—	2·39	—	—	0·973	—	3·363	3·86	3·34
—	—	—	0·30	11·27	—	11·57	3·46	14·12
—	—	—	0·74	8·93	—	9·67	3·90	11·59
—	—	—	1·61	4·80	—	6·41	4·00	7·17
—	—	—	2·18	2·325	—	4·505	4·01	4·76
—	—	—	2·47	1·19	—	3·66	3·73	3·72
—	—	—	—	11·65	0·65	12·30	2·69	15·54
—	—	—	—	10·57	1·45	12·02	3·05	15·11

Data obtained by Egerton and Badami by Flat Flame method, (Proc. Roy. Soc., A228, 1955).

IV. IGNITION TEMPERATURE

Ignition temperature is defined as the minimum temperature at which a given fuel can be ignited. Ignition temperature has been proven experimentally by Coward and Guest (11), also by Jost and Muffling (34), to depend on the method of ignition and, therefore, is not a fundamental property of the combustible mixture. One general trend that has been found experimentally is that the smaller the heat source, the higher must be the temperature of that source to initiate a combustion reaction.

The ASTM, ASA, and API use a conical pyrex glass flask which is heated in a bath of molten metal and held at a known temperature level. Drops of fuel being tested are sprayed on the flask and the minimum temperature at which the fuel can be made to ignite and continue to burn is recorded as the ignition temperature. The values of ignition temperature thus obtained are useful only in comparing one fuel with another.

V. COMBUSTION REACTION MECHANISM

Combustion is the rapid, high temperature oxidation of fuels. Since we are concerned primarily with hydrocarbon fuels, burning involves the oxidation of carbon to carbon dioxide or carbon monoxide if there is insufficient oxygen for complete combustion and of hydrogen to water vapor. During a combustion process, chemical energy is liberated in the form of heat. It is this heat which renders the gases luminous which we define as a flame.

The flame front is the surface or area between the luminous region and the unburned gas region. Most of the oxidation occurs in this reaction zone while completion of burning and emission of light occurs in the luminous zone.

According to theories of chemical reaction kinetics, it is necessary for molecules of one substance to collide with molecules of another with an energy equal to or greater than a certain critical minimum before any chemical reaction can take place. For the combustion of propane and air, the theoretical combustion equation is:

$$C_3H_8 + 5O_2 + 18.8N_2 \rightarrow 3CO_2 + 4H_2O + 18.8N_2$$

This equation implies that if the reaction were to occur in one step, it would be necessary for one propane molecule to collide simultaneously with five oxygen molecules before a reaction could take place. This is highly improbable. Hence, any complex reaction involving many molecules must occur as a series of different reactions starting with the initial substance and proceeding to the final products. These series of reactions in which intermediate products are formed in one step and destroyed in a succeeding step are known as chain reactions. The intermediate products formed are known as chain carriers because they help carry the reaction to completion. Chain carriers may be free radicals which is a group of atoms having one unpaired electron, free atoms of diatomic gases, or some organic compound.

Any chain reaction consists of an initiation phase in which chain carriers are formed, a propagation phase in which the new chain carriers branch out and start a new series of reactions of its own, and a termination phase in which some chain carriers are taken out of play by another substance which reacts with or absorbs the chain carriers.

Chemical kinetics deals with the manner and speed with which a given chemical reaction will progress. The burning rate can proceed no more rapidly than the slowest reaction in the chain mechanism.

The number of collisions that occur in a gas per unit time and volume between two kinds of molecules is proportional to the concentration of each. For the total number of collisions per unit time and volume between molecules A and B with concentrations N_A and N_B, the kinetic theory of gases yields the equation:

$$Z_{A,B} = 2 N_A N_B \sigma_{A,B}^2 \sqrt{2 \pi R T \frac{M_A + M_B}{M_A M_B}}$$

where M_A and M_B are the molecular weights.

$\sigma_{A,B}$ ———— the average diameter of the colliding molecules.

R ———— is the gas constant 8.31 4 x 10^7 per degree per mole.

T ———— the absolute temperature.

Successful collisions between two reaction partners result if the two colliding molecules possess a specific degree of freedom and energy equal to or exceeding the activation energy E, and if the geometry of collision is favorable to their interaction. Thus, on a simplified basis the number of molecules reacting per unit time is given by:

$$\frac{\delta N}{\delta t} = Z_{A,B} \, e^{-E/RT} \times S$$

where E is the activation energy.

S = Steric factor (factor for geometric restrictions on collisional paths which ranges in value from 0 - 1).

When two atoms collide a diatomic molecule is not formed unless some third atom or molecule participates in the collision because the sum of the energy of reaction and kinetic energy of the colliding atoms is enough to dissociate any molecule formed. The third atom removes this excess energy and allows a bond to be formed. Two polyatomic molecules do not require a third body because the excess energy can be distributed among the various degrees of freedom of the molecules.

A reaction may occur by the decomposition of a single molecule that has the necessary energy. Such activated molecules are produced by collisions and are destroyed by collisional deactivation and by decomposition. Collisional deactivation is predominant at high pressure and negligible at low pressures.

A surface may act as a catalyst and faciliate a reaction in the gas phase or it may prevent a reaction from occurring. The property of a surface to destroy chain carriers has a very important effect on the reaction rate. This destruction may occur by a reaction with the material of the wall or by absorption followed by a heterogeneous reaction when the wall is a sink for chain carriers. The kinetics of the over all reaction is strongly dependent on the diffusion of chain carriers to the wall. The rate of surface destruction of chain carriers is ϵ times the rate at which chain carriers strike the surface where ϵ is the chain breaking efficiency of the wall and has values ranging from 0 to 1.

VI. THEORIES OF FLAME PROPAGATION

On the basis of major assumptions, theories of flame propagation are divided into three groups - comprehensive theories, thermal theories, and diffusional theories.

Thermal theories are based on the assumption that molecular heat conduction determines the rate for the combustion reaction. Most thermal theories use the concept of an ignition temperature. Heat produced by chemical reaction is conducted to the unburned gas and the temperature is raised to the ignition temperature, at which point the gas begins to react. The region of the combustion wave before the ignition point is called the preheat zone and that region following is called the reaction zone. The ignition temperature is now known to depend upon the experimental conditions under which combustion process occurs. The reaction rate in these theories is assumed to be discontinuous at the ignition point, that is, going from a zero value in the preheat zone to a finite value in the reaction zone. Present views on the subject of combustion express the idea that the reaction rate is a function of both temperature and location in the flame.

In diffusional theories the burning velocity is determined principally by diffusion. Active atoms and radicals produced by dissociation in the burned gases and by chain branching diffuse into the fresh gas and cause it to react. Diffusional theories frequently use an average value for the temperature in the reaction zone. The combustion process is usually assumed to have an induction period during which the temperature is increased and there is an accumulation of active particles because of diffusion from the burning layers. Local chemical dissociation is usually considered small during this induction period. At ignition the concentrations of the active chain carriers have become large and reaction velocities of the intermediate reactions great so that the combustion reaction suddenly accelerates.

Thermal Theories

Mallard and Le Chatelier (49) were the first to derive an expression for the burning velocity based on a thermal theory. They assumed the reaction occured at constant pressure, there was a unique ignition temperature, the unburned gas had a constant heat capacity evaluated between the initial temperature and the final flame temperature, and the temperature gradient where ignition occurs was proportional to the difference between the final temperature and the ignition temperature. They arrived at an expression for the burning velocity:

$$V_T = \frac{k}{C_p \rho \delta_r}\left(\frac{T_f - T_i}{T_i - T_o}\right)$$

where δ_r is the distance in which the temperature rises from the ignition temperature to the final flame temperature.

ρ - density

k - heat conductivity

C_p - mean specific heat of the mixture

Nusselt modified their theory by assuming the reaction velocity is constant, the velocity of the gas in the reaction zone is equal to $V_T\, T/T_o$ and arrived at the following expression for the gas burning velocity:

$$V_T = \sqrt{\frac{k\,(T_f - T_i)\,T_o\,\omega}{C_p\,\rho\,(T_i - T_o)\,T_f\,\varepsilon}}$$

where ε represents the concentration of products at the final flame temperature.

ω = reaction velocity which is constant.

Jouguet and Crussard (35, 36) and Daniell (14), arrived at theories which were essentially the same as that of Nusselt. Their theories were based upon the assumption that the unburned gas must first be brought to its ignition temperature by direct conduction of heat from the reaction zone to the gas being heated in the adjacent layer.

Damkohler (13) modified these theories and assumed that the temperature gradient at the ignition point is proportional to the average temperature gradient across the reaction zone and defined a mean velocity gradient $\bar{\omega} = N_r V / \delta_r$ where N_r is the number of reactant molecules per unit volume initially present. He arrived at an equation for burning velocity:

$$V_T = \sqrt{\frac{F K \bar{\omega} (T_f - T_i)}{C_p \rho N_r (T_i - T_o)}}$$

where F is the proportionality constant for the temperature gradient at the ignition point.

Bartholome and Sachsse (3, 3A, 52) investigated the combustion of hydrogen, hydrocarbons, alcohols, ethers, nitroparaffins, and alkyl nitrates with air, oxygen, nitrous oxide and their mixtures. They observed that gases with large differences in octane number had practically the same value of burning velocity. This indicated a weak dependence of flame velocity on reaction velocity. They observed that an increase in the unburned gas temperature caused a small increase in burning velocity. Burning velocities were found to have a strong dependence on final flame temperature for fuel air mixtures. On the basis of these observations Bartholome (3, 3b) proposed a thermal theory of burning velocity based on the assumption there is no change in the number of moles during the reaction which proceeds at constant pressure, there is no diffusion, the heat conductively k is constant, and that the ignition temperature is at least 90% of the final flame temperature. He arrived at an expression for the rate of reaction:

$$Z = N_r^{\alpha} \beta T$$

which depends on the order of the reaction α where β is a constant. For a second order reaction $\alpha = 2$ the burning velocity was found to be:

$$V_T = \sqrt{\frac{(T_f - T_o)\, T_o^2\, \beta\, K\, N_r}{(T_i - T_o)\, C\, \Sigma N}}$$

where:

$$C = \frac{C_p \rho R T}{P}$$

ΣN - total number of moles per unit volume at temperature T

E — activation energy

R — universal gas constant

P — pressure

$\beta = e^{-E/RT}/T^2$ where $T = .95\,T_f$

For the case where $\alpha = 1$

$$V_T = \sqrt{\left[\frac{T_f - T_0}{T_i - T_0} - 1\right]\frac{T_0^2\,\beta\,k\,R}{C\,P}}$$

for the case where $\alpha = 3/2$

$$V_T = \sqrt{\frac{(T_f - T_0)\,T_0^2\,\beta\,k\,(R/P)^{1/2}\,N_r/\Sigma N}{(T_i - T_0)\,C}}$$

For a stoichiometric mixture of methane and air Bartholome calculated a burning velocity of 105 cm/sec. as compared with an experimental value of 49 cm/sec.

Gaydon and Wolfhard (25) have determined from experiment that his assumption of very high ignition temperature is not valid.

The reason thermal theories are not generally accepted is because these theories depend on the questionable concept of a unique ignition temperature. Joust (34) and Muffling have stated that the ignition of a given gas may occur at a number of temperatures depending on other physical factors.

Diffusion Theories

Tanford and Pease (60,61,62) assumed that the rate of diffusion of active centers into the unburned gas determines the magnitude of the burning velocity. They proposed that burning occurs because of the presence of free radicals that are supplied to the unburned gas. They proposed two mechanisms by which these free radicals could be supplied to the unburned gas. One method is by local thermal dissociation and the other method is by diffusion from a single point at which the reaction has reached equilibrium. They determined that the effect of local dissociation was small compared to the effect of diffusion. In developing theory for combustion at constant pressure they assumed, (a) the combustion zone is at a constant mean temperature, $T_m = .7\ T_f$, (b) the diffusion coefficient has a constant value $D_m = D_o \Theta_M^2$ where Do is the diffusion coefficient for hydrogen atoms into the unburned gas at room temperature and $\Theta_M = T_M / T_o$, (c) the continuity equation could be linearized, (d) the only two reactions that occur fast enough to have an affect on the hydrogen atom concentration are:

$$H + O_2 + M \rightarrow HO_2 + M$$

$$H + H + M \rightarrow H_2 + M$$

where M represents a third body, (e) the mole fraction of oxygen molecules has a constant mean value throughout the reaction, (f) the rate of formation of product is a sum of terms for each effective radical or atom, (g) the combustible is the only species involved in the process in addition to the active particles, (h) chain branching does not occur.

They arrived at an equation for the burning velocity of carbon monoxide as follows:

$$V_T = 17 + \left\{ \frac{N_r}{\gamma_P} \left(\frac{K_H \; P_H \; D_H}{B'_H} + \frac{K_{OH} \; P_{OH} \; D_{OH}}{B_{OH}} \right) \right\}^{1/2}$$

k_i = rate constant appropriate to the i th reaction

where $N_r = .7\gamma_{co} / \Theta_m$

γ_P = mole fraction of carbon monoxide or twice the mole fraction of oxygen molecules in the initial mixture.

P_H = equilibrium partial pressure at the flame front of the hydrogen atoms.

P_{OH} = equilibrium partial pressure at the flame front of O H radicals.

B_i = $1/2 \left[1 + \left(1 - 4A^I \; D_m / v_m^2 \right)^{1/2} \right]$ where A^1 is a constant.

v_m = is the specific volume at the temperature Tm.

The values of burning velocity calculated by the equations developed in this theory for carbon monoxide mixtures was in good agreement with the values for burning velocity they measured experimentally. The maximum disagreement encountered was less than 25%.

Simon (56) modified the Tanford-Pease relation to apply to a series of hydrocarbons by including a term for the total number of moles of water and carbon dioxide which form per mole of the specific hydrocarbon. Simon assumed that H, O, and OH are the chain carriers and that they are equally effective. The relation for the burning velocity becomes:

$$V_T = \left[\frac{N\,Q'L\,K}{Q}\left(\frac{D_H P_H}{B_H} \quad \frac{D_O\,P_O}{B_O} \quad \frac{D_{OH}\,P_{OH}}{B_{OH}}\right)\right]^{1/2}$$

where -

N = number of moles of combustion product per mole of combustible.

Q' = mole fraction of combustible.

Q = mole fraction of potential combustion product.

L = number of molecules of gas at flame temperature.

k = rate of reaction of combustible.

P_i = equilibrium partial pressure of the i th active particle.

B_i = term arising from recombination of i th free radical.

k was found to have a value of $1.4 \pm .1 \times 10^{-11}$ cc/mole sec. for all hydrocarbons except ethylene. This consistancy in the value of k suggested that the rate constants are either the same for oxidation of all hydrocarbons or, unimportant in the mechanism of combustion. Simon calculated the diffusion coefficients for H, OH, and O into O_2 and N_2 by the Stefan Maxwell equation: $D = \lambda\, V/3$

λ = effective mean free path.

$V/3$ = average molecular velocity along one axis of a coordinate system.

$V = 14{,}500\ (T/_M)\ 1/2$ cm/sec.

M = molecular weight.

Values were found as follows for diffusion into air:

$D_H = 1.78$ cm/sec.

$D_{OH} = .28$ cm/sec.

$D_O = .40$ cm/sec.

B values were calculated by the method of Tanford and Pease.

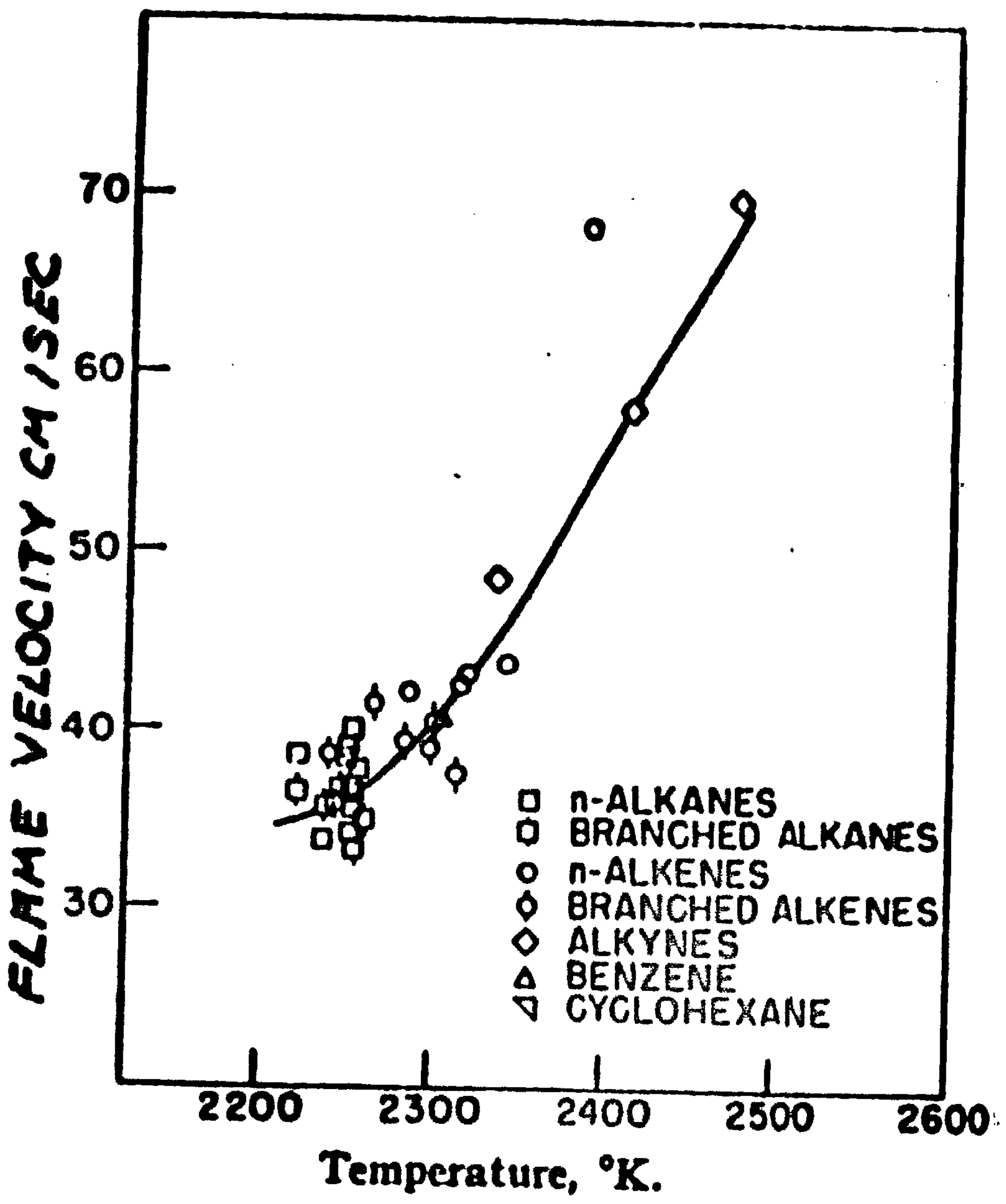
This theory was found to be consistent for thirty-four of thirty-five hydrocarbons tested by the method of Gerstein, Levine, and Wong (27). Ethylene disagreed by 25% with the experimental data. Simon points out

BURNING VELOCITIES OF HYDROCARBON FLAMES

Compounds	Vol. % hydrocarbon	T_c[a], °K.	$p_H \times 10^3$ atm.	$p_O \times 10^4$ atm.	$p_{OH} \times 10^3$ atm.	$k \times 10^{11}$, cc. molecules^{-1} sec.$^{-1}$	Flame velocity, cm./sec.	
							Exptl.	Calcd.
Methane	9.96	2235	0.57	1.42	1.98	2.36	33.8	33.9
Ethane	6.28	2246	.79	0.83	1.43	2.78	40.1	37.1
Propane	4.54	2251	.82	.80	1.37	2.56	39.0	37.7
Butane	3.52	2256	.82	.89	1.43	2.42	37.9	37.6
Pentane	2.92	2249	.82	.72	1.26	2.51	38.5	37.5
Hexane	2.51	2241	.83	.59	1.12	2.53	38.5	37.3
Heptane	2.26	2208	.80	.29	0.75	2.44	38.6	38.0
2-Methylpropane	3.48	2259	.79	1.02	1.53	2.13	34.9	36.9
2,2-Dimethylpropane	2.85	2254	.76	0.96	1.46	2.02	33.3	36.2
2-Methylbutane	2.89	2253	.80	.84	1.37	2.31	36.6	37.1
2,2-Dimethylbutane	2.43	2254	.78	.90	1.40	2.24	35.7	36.8
2,3-Dimethylbutane	2.45	2252	.80	.81	1.33	2.30	36.3	37.0
2,2,3-Trimethylbutane	2.15	2242	.80	.64	1.17	2.29	35.9	36.6
2-Methylpentane	2.46	2251	.81	.78	1.30	2.33	36.8	37.2
3-Methylpentane	2.48	2245	.82	.67	1.20	2.34	36.7	37.1
2,3-Dimethylpentane	2.22	2220	.80	.38	0.88	2.42	36.5	36.2
2,4-Dimethylpentane	2.17	2236	.80	.55	1.07	2.29	35.7	36.4
Ethylene	7.40	2387	1.56	3.51	2.95	3.97	68.3	52.9
Propene	5.04	2341	1.21	2.26	2.29	2.22	43.8	45.3
1-Butene	3.87	2320	1.14	1.64	1.92	2.43	43.2	42.8
1-Pentene	3.07	2316	1.04	1.82	2.01	2.36	42.6	42.8
1-Hexene	2.67	2287	1.04	0.96	1.43	2.43	42.1	41.7
2-Methylpropene	3.83	2315	1.06	1.71	1.95	1.90	37.5	42.0
2-Methyl-1-butene	3.12	2298	1.02	1.28	1.66	2.13	39.0	41.2
3-Methyl-1-butene	3.11	2305	1.04	1.44	1.78	2.31	41.5	42.2
2-Ethyl-1-butene	2.65	2284	1.00	0.98	1.44	2.22	39.3	40.7
2-Methyl-1-pentene	2.80	2237	.96	0.36	0.84	2.43	39.6	39.2
4-Methyl-1-pentene	2.62	2295	1.00	1.23	1.63	2.23	40.5	41.3
Propyne	5.86	2472	2.28	6.65	3.78	3.10	69.9	61.3
1-Butyne	4.36	2413	1.84	3.53	2.76	2.60	58.1	55.6
1-Pentyne	3.51	2370	1.61	2.03	2.07	2.50	52.9	51.6
1-Hexyne	2.97	2333	1.46	1.17	1.55	2.37	48.5	48.6
2-Butyne[b]	4.36	2401	1.73	3.11	2.57	2.23	51.5	53.3
Cyclohexane	2.65	2249	0.83	0.65	1.13	2.56	38.7	37.4
Benzene	3.34	2307	1.02	0.96	1.15	2.42	40.7	40.4

[a] Calculated equilibrium flame temperature. [b] 3-Hexyne and 4-methyl-1-pentyne have been omitted since accurate heat of formation data were not available.

Results obtained by, Simon, D.M., J. Amer. Chem. Soc., 73, 424 (1951)



Variation of flame velocity with equilbrium flame temperature.

Results obtained by, **Simon, D.M., J. Amer. Chem. Soc.**, 73, 425 (1951)

FIG. 5

that the calculated radical concentrations depend on the flame temperatures and that any thermal mechanism also depends on the flame temperature therefore, some mechanism which depends strongly on flame temperature might give a correlation with flame speed as good as the particle diffusion theory so that a thermal mechanism theory cannot be ruled out.

Gaydon and Wolfhard (25,26) proposed that the diffusion of atoms or radicals from the burned gas into the unburned gas is the important factor in the propagation of hot flames. They point out that since reactions involving atoms or radicals require an activation energy, heat transfer may be important. They assumed: (a) that the ignition temperature marks the beginning of appreciable exothermic reactions, (b) the temperature in the flame zone Tm is equal to the average between the final flame temperature and the ignition temperature, (c) the thickness of the total luminous region δ_r is approximately equal to $3/2\ \delta_L$ where δ_L is the thickness of the luminous reaction zone measured between point of maximum rate of change of luminosity, (d) the time required for the gas to traverse this zone of thickness δ_r is $t_r = \delta_r/V_M$ where V_M is a constant mean velocity in the flame zone equal to V_T Tm/To, (e) the diffusion of hydrogen atoms is important and the diffusion coefficient Dm is taken as equal to Do $(Tm/To)^{3/2}$ where Do is the diffusion coefficient for hydrogen atoms into a mixture of carbon dioxide and water at standard temperature and pressure.

They arrived at an expression for burning velocity given as:

$$V_T = \sqrt{\frac{D\,u\,T_i}{2\,N_r\,T_M}}$$

where u is the mean reaction velocity equal to: $\frac{N_r V_r}{\delta_r}$

$D = 2\,\delta_r^2/t_r$

N_r = number of reactant molecules per unit volume in the unburned gas.

Boys and Corner (4,7) assumed a single exothermic chemical reaction. They used three simplified models; a first order rate form of a unimolecular mechanism, a second order rate form of a bimolecular reaction, and a quasibimolecular form of a unimolecular reaction at low pressure. These models allowed analytical solutions by a method of successive approximations. They assumed constant pressure and assigned constant mean values to thermal conductivity, specific heat and diffusion coefficients. Corner (7) presents calculations which show that for typical values of diffusion rates the burning velocity calculated by neglecting diffusion is more than twice the value obtained when diffusion is considered.

Hirschfelder and Curtiss (38, 39, 40, 41) set up general equations for one dimensional steady state, non viscous, constant pressure flames in a form suitable for solution only by computing devices. Their equations are completely general with respect to the number of reaction steps, the order of the reactions, and the number of components involved. They did not use mean values for the diffusion coefficients as most other theorist have done, but used equations for diffusion in terms of the composition gradients. Chemical kinetic theory entered only in their continuity equation. In the development of their theory they introduced a mathematical flame holder at the cold boundary which acts as a heat sink and extracts a predetermined amount of heat. Numerical results were given for unimolecular and bimolecular reactions.

Comprehensive Theories

Lewis and Von Elbe (44) were the first to reject the concept of an ignition temperature and to introduce an expression for the reaction velocity as a function of temperature and concentration. They considered the affect of diffusional as well as heat conduction processes, they suggested that active atoms and radicals in the flame diffuse into the unburned gas, and are important in bringing this fresh gas to a reacting state. They assumed constant pressure and used a constant mean heat capacity. They considered the exothermic ozone to oxygen reaction:

$$O_3 = O_2 + O$$

$$O + O_2 = 2O_2$$

The diffusion coefficient for the diffusion of oxygen in the gas mixture was taken to be that for diffusion in a gas consisting entirely of oxygen molecules, and thus, being independent of composition. They also assumed that the total thermal and chemical energy per unit mass is the same at every point in the flame. Thermal dissociation of oxygen in the burned gas was neglected. The rate of formation of oxygen by chemical reaction was determined by the frequency of collision between oxygen atoms and ozone molecules and by the probability of reaction occuring upon collision. They arrived at an equation relating the change in temperature with distance into the flame front:

$$\frac{\partial t}{\partial x} = 7.17\times 10^{9} C_p P^{3/2} T^{1/2} \left\{ \int_{T_0}^{T} \frac{[T_f/T - 1]^2 e^{-15,300/T}}{[1.76\times 10^{14} e^{-12\,300} + 3.4\times 10^{9} P]^2} \right\}^{1/2}$$

the equation was integrated graphically.

The burning velocity was obtained by assuming that the number of ozone molecules entering the flame front per unit time is equal to the number reacting per unit of time:

$$V_T(N_{O_3}) = \int_{T_0}^{T_f} \frac{\omega}{1.5} \frac{\partial x}{\partial t}\, dt$$

where ω is the reaction rate given by:

$$\omega = 4 N_O N_{O_3} \sigma^2 \left(2\pi R T \frac{M_O + M_{O_3}}{M_O M_{O_3}} \right)^{1/2}$$

σ = average diameter of the molecules O and O_3

M_O and M_{O_3} are the molecular weights of the oxygen atom and ozone molecule.

N_O, N_{O_3} are the concentrations of oxygen atom and ozone molecule.

Upon introduction of the expression for $\partial r/\partial t$ the burning velocity was obtained by graphical integration. The values for burning velocity calculated by the equations developed in their theory did not agree with the values of burning velocity they measured experimentally. Even though the values did not agree, they were of the same order of magnitude and, therefore, showed some correlation. This early theory gave only a first approximation to the actual behavior and an insight into the mechanism of combustion upon which more precise theories could be based.

Zeldovich and Frank-Kamenelsky (66,67,68) have developed a comprehensive theory for flame propagation. Their theory has been discussed by Semenov (54). This theory assumes a reaction model: $NA = B + C$ for which the reaction order may be zero, first, or second with respect to A. Intermediate reactions are neglected. They divided the flame zone into two regions, the preheat region and the reaction region. In the preheat region the temperature rises from the unburned gas temperature to the ignition temperature. In the reaction region the temperature rises from the ignition temperature to the final flame temperature, and the mass flow term is considered small compared to the reaction and heat conductivity terms. These divisions were made in order to facilitate the mathematical solution for the continuity and energy equations. They assumed the reaction occurs at constant pressure and the number of molecules may change during the reaction according to the ratio of N_r/N_p (moles of reactant / moles of product by the stoichiometric equation). They further assumed that the ignition temperature is very near the final flame temperature, and that the sum of the thermal and chemical energies per unit mass of the mixture is constant in the combustion zone.

Considering the rate of reaction to be a function of temperature only, they arrived at an equation for the burning velocity given as:

$$V_T = \sqrt{\frac{2 k S e^{-E/RT_f} R T_f^2}{C_p \rho_0 A_0 (T_f - T_0) E}}$$

E - activation energy

R - gas constant

S - collision number

Ao - molecules of initial reactant

Considering the reaction rate to be a function of composition as well as temperature, they arrived at an equation given as:

$$V_T = \sqrt{\frac{2k\nu\, T_0\, e^{-E/RT}}{\rho_0\, C_p\, T_f\,(T_f - T_0)^2}\left(\frac{RT_f^2}{E}\right)^2}$$

where ν is a frequency factor.

If the number of molecules are allowed to change during the reaction in the ratio of N_r/N_p instead of remaining constant as in the previous two cases considered and the assumption that $(k/C_p)\,D = A/B$ is made, the equation for a unimolecular reaction becomes:

$$V_T = \sqrt{\frac{2k(C_p)_f\,\nu}{\rho_0\,\bar{C}_p^{\,2}}\;\frac{T_0\,N_r}{T_f\,N_p}\;\frac{A}{B}\left(\frac{RT_f^2}{E}\right)\frac{e^{-E/RT_f}}{(T_f - T_0)^2}}$$

and for a bimolecular reaction:

$$V_T = \sqrt{\frac{2k(C_p)_f^2\,\nu\,A_0}{\rho_0\,\bar{C}_p^{\,3}}\left(\frac{T_0}{T_f}\right)^2\left(\frac{N_r}{N_p}\right)^2\frac{A}{B}\left(\frac{RT_f^2}{E}\right)^3\frac{e^{-E/RT_f}}{(T_f - T_0)^3}}$$

where

$\bar{C}_p$ is the mean value for specific heat in the region.

$(C_p)_f$ is the value of specific heat at the final flame temperature.

Because of the neglect of the mass flow term in the energy equation for the reaction region, Semenov concludes that provided $(T_f - T_i) / (T_f - T_o) \leq .25$ an error of no greater than 8% is incurred in V_T. He concludes that for bimolecular reactions the solution is valid only for $RT_f/E \leq 1$. Hence, application of the equation for burning velocity is restricted to values of activation energy E greater than 40 k cal at final flame temperatures equal to 2000°C.

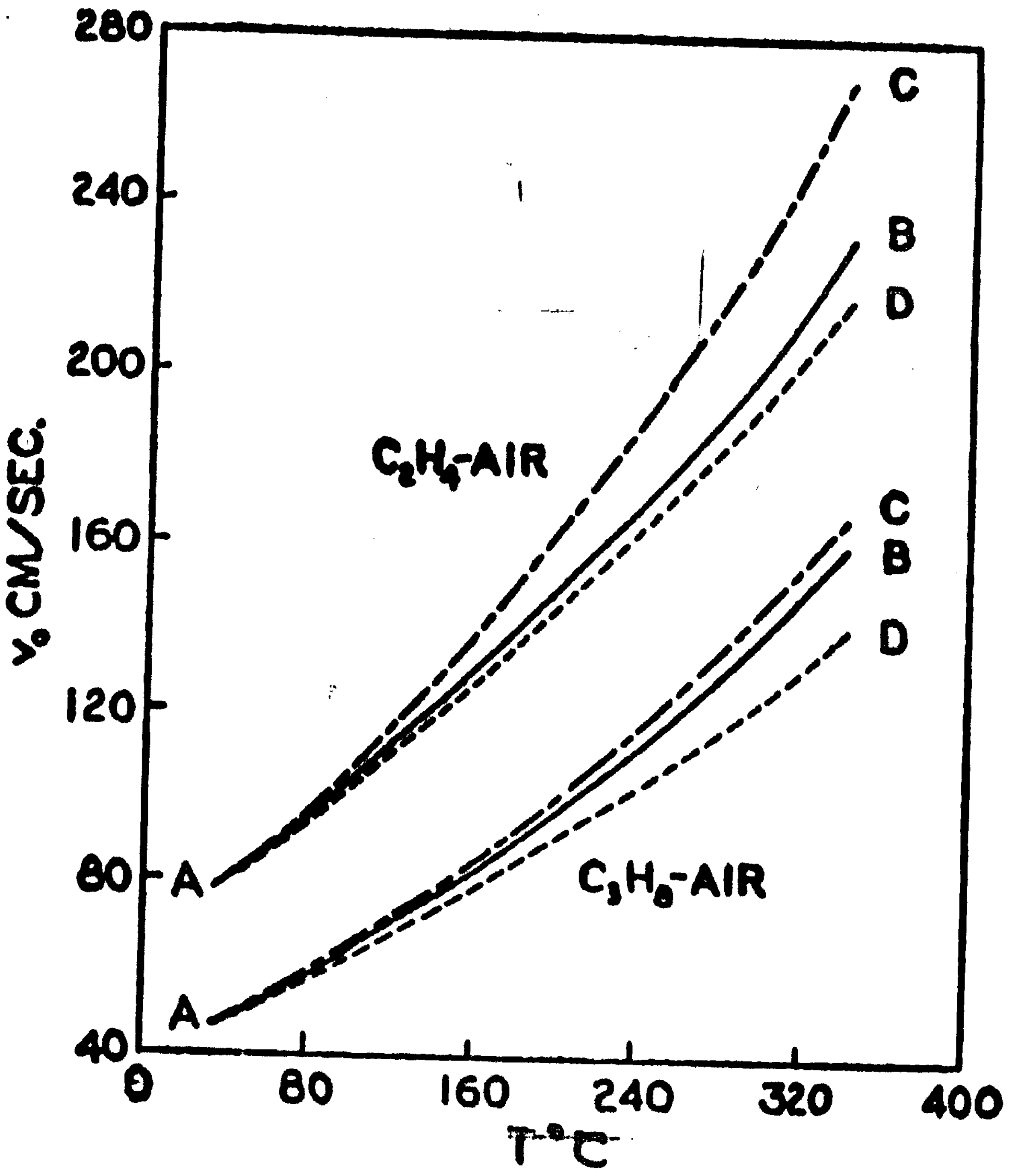
Dugger (17) measured flame velocity as a function initial temperature for propane-air and ethylene-air flames. He compared curves of experimental date with curves calculated by the Zeldovich, Frank-Kamenetsky theory and also curves calculated by the Tanford-Pease theory. He assumed a bimolecular reaction and eliminated terms not dependent upon temperature from the Zeldovich, Frank-Kamenetsky equation and arrived at an expression:

$$V_T \propto \sqrt{\frac{T_0^{2}\, T_f^{4.9}\, e^{-E/RT_f}}{(T_f - T_0)^{3}}}$$

For the Tanford-Pease theory he used:

$$\sum P_i D_{ir} = 6.5\, P_H + P_{OH} + P_O$$

As can be seen from the curves ploted in figure(6) both theories give good agreement with experimental data.



Dugger, J. Amer. Chem. Soc., (1951)

Dependence of V on T . Curves AB show experimental data by Dugger; curves AC are calculated according to the Zeldovich-Frank-Kamenetsky method; curves AD are calculated according to the Tanford-Pease method.

FIG. 6

From an analysis of all the theories for the rate of flame propagation, it is seen that there are four basic factors which most influence this rate. They are listed by Smith and Stinson (58) as:

(1). Mechanism of the reaction

(2). Kinetics of the individual reactions in the mechanism

(3). Diffusion of chain carriers, or propagating centers, from the reaction zone to the unburned gases

(4). Rate of heat transfer from the reaction zone to the adjacent heating zone of the unburned gases.

EXPERIMENTAL DETERMINATION OF THE BURNING VELOCITIES OF PROPANE-AIR MIXTURES AND N-BUTANE-AIR MIXTURES

Upon completion of the investigation into literature, the author found several questions which require an answer, They are the following:

(1), Does the flame propagate uniformly throughout the entire length of the flame tube or only over a certain part?

(2), If the flame does not propagate uniformly throughout the entire tube, over what part does it propagate uniformly?

(3), What effect do the orifices developed by Guenoche (30) and used in the ignition end of the tube have on the determination of burning velocities other than absorb pressure disturbances?

(4), Are there any significant differences in the maximum values of the burning velocity obtained by the method of Gerstein, Levine, and Wong (27) and those obtained by a method similar to that developed by Coward and Hartwell (8)?

(5), Would there by any correlation between burning velocities obtained by the burner method using the schlieren cone and some variations of the tube method if the measurements were carried out under the same environmental conditions and the same gas supply?

(6), What variation of the tube method gives the closest correlation with the bunsen burner method?

Burning Velocity Determined By The Tube Method

The apparatus used in the tube method experiments is shown in figure (E-1A). In all experiments with the tube method two tubes were used. Both tubes were 44 inches long. One of the tubes was 2.42 cm in inside diameter and the other was 3.4 cm in inside diameter. Spatial velocities of the flame propagation were measured from motion picture photographs taken of the flame front as it traversed a measured distance. The photographs were taken with a Bell and Howell camera using 16 mm Kodak Tri X film at a rate of 32 frames per second.

The fuel-air ratios used in the experiments were controlled by regulating the partial pressures of the fuel-air admitted to the mixing chamber.

The flame tube was evacuated of unwanted gases by means of a closely fitting piston which was displaced by the desired fuel-air mixture admitted to the tube under pressure.

All measurements recorded in variations of the tube method were from experiments with the tube in a vertical position and upward flame propagation. Ignition of the fuel-air mixture was accomplished by means of a 10,000 volt spark across a gap of 1/8 inch.

For each particular fuel-air mixture, 9 to 12 measurements were made to determine the spatial velocity. The range in the values obtained for each mixture are shown on the respective figures by the vertical lines.

Spatial Velocities of Propane-Air Mixtures

Spatial velocities of propane-air mixtures were measured in five variations of the tube method.

Variation I was similar to the method developed by Gerstein, Levine, and Wong. The 3.4 cm inside diameter tube was used and was fitted with a 1.27 cm orifice in the ignition end and a .238 cm orifice in the upstream end. The spatial velocity was recorded over a 9 inch distance, the center of which was located 33 inches from the ignition point. The results are shown in figure (E-2).

In variation II, the 2.42 cm inside diameter tube was used with a .795 cm orifice fitted in the ignition end and a .198 cm orifice in the upstream end. The observation point was in the same location as in variation I. The results are shown in figure (E-4).

Variation III was the same as variation II except that the observation point was a 9 inch distance, the center of which was located 11 inches from the ignition point. The results are shown in figure (E-6).

Figure (E-7), shows a comparison of the results obtained by variation II, and variation III. From this figure it appears that the maximum spatial velocity of 89 cm per second occurs at richer fuel-air ratio when measured at the top of the tube by variation II. This can be explained by considering the fact that propane has a higher molecular weight than air, and that because of this there is a tendency for it to settle out of a mixture with air, and therefore, what was recorded as a rich mixture at the top of the tube in variation II was actually leaner than recorded. For this reason, and another to be explained later, this author chose to measure all further tests over a 9 inch distance, the center of which, was located 11 inches from the point of ignition.

Variation IV was similar to the method developed by Coward and Hartwell, that is, the tube was left open at the ignition end and the upstream end was closed, The 2.42 cm inside diameter was used. The results are shown in figure (E-5).

Variation V was similar to variation IV except the 3.4 cm I.D. tube was used. The results are shown in figure (E-3).

Figure (E-8) shows a comparison of the results of variation IV and variation V. It points out the dependence of spatial velocity on the diameter of the tube used, the spatial velocity being faster in the larger diameter tube.

The unburned gas velocity for variations I, II, and III was obtained by experimental measurement of the volumetric rate of gas flow within that portion of the flame tube toward which the flame was advancing by a method similar to that used by Gerstein, Levine, and Wong. A tube was attached to the orifice in the upstream end of the flame tube. To this tube was attached a funnel of 1/2 inch diameter across which was a soap film. As the flame propagated in the flame tube, the growth of the soap bubble was photographed. The volume of the soap bubble obtained was divided by the cross sectional area of the flame tube to give an unburned gas velocity. This procedure was carried out for fuel-air ratios which gave the fastest and slowest values of spatial velocity. A linear relation was assumed between these points and the results are plotted in figure (E-16A). There was no significant difference in the values for the unburned gas velocity obtained in both the 2.42 and 3.4 cm I.D tubes. The apparatus used is shown in figure (E-1B).

Some Observations On Flame Propagation

In the method used by Gerstein, Levine, and Wong, that is, variations I, II, and III, the flame front began to accelerate about 16 inches from the ignition point. This acceleration was damped out at about 25 inches from the ignition point and the flame assumed uniform propagation again at about 28 inches from the ignition point.

In the tube method similar to that used by Coward and Hartwell, that is, variations IV and V, the flame propagated uniformaly to about 16 inches from the ignition point where it began to accelerate and assumed a cellular structure at about 22 inches from the ignition point. It retained its cellular structure for the last 22 inches of travel. At first, the author thought this phenomenon was the result of diffusional stratification, but the author tried this method with the tube in a horizontal position with rich and lean mixtures and the same phenomenon was observed. Therefore, the author concluded that it was not diffusional stratification, but a characteristic inherent in this method. Therefore, on the basis of this observed phenomena and reasons mentioned previously, in order to compare various variations of the tube method, it is necessary to measure spatial velocities over a 9 inch distance, the center of which is located 11 inches from ignition point.

SPATIAL VELOCITIES OF N-BUTANE AIR MIXTURES

Spatial velocities of N-Butane-air mixtures were measured in six variations of the tube method. Spatial velocities were measured over a 9 inch distance, the center of which was located 11 inches from the ignition point in all the variations except variation VI.

Variation I was similar to the method of Coward and Hartwell, that is, the ignition end was left open and the upstream end of the tube was closed. The 2.42 cm inside diameter tube was used. The results are shown in figure (E-9).

Variation II was similar to variation I except the tube was fitted with a .795 cm orifice at the ignition end. The results are shown in figure (E-10).

Variation III was similar to variation I except the 3.4 cm inside diameter tube was used. The results are shown in figure (E-11).

Variation IV was similar to variation III except a 1.27 cm orifice was fitted in the ignition end of the tube. The results are shown in figure (E-12).

By comparing figures E-11 and E-12, we can see clearly the effect that an orifice in the ignition end of the tube has on spatial velocity if the upstream end of the tube is closed. The reason the spatial velocity is faster when the orifice is used in the ignition end is obvious when we consider that if the orifice is to reduce pressure variations, it must also restrict flow of the burnt gases which have a much larger specific volume then the unburnt gases and which, because of this restriction, tend to act as a hot gas piston accelerating the flame front.

Variation V was similar to the method developed by Gerstein, Levine, and Wong. The 3.4 cm inside diameter tube was used with a 1.27 cm orifice used in the ignition end and a .238 cm orifice in the upstream end. The results are shown in figure (E-13A).

By comparing variation IV with variation V, shown in figure (E-15), we can see that faster spatial velocities result in variation V because of the fact that when the upstream end of the flame tube was closed, the compression waves, which were formed as a result of the hot gas effect, reflected from the closed end of the tube as compression waves, thereby causing a retardation of the propagation of the flame front. When the upstream end of the tube was fitted with the orifice some of the incident compression waves were reflected as expansion waves, which accelerated the gas particles in the direction of the propagation of the tail of the reflected expansion waves, and which resulted in an acceleration of the flame front. This orifice in the upstream end did not entirely counteract the effect of the reflected compression waves.

If in figure (E-15) we subtract the maximum value of burning velocity of curve D from that of curve C, we see that at a value of spatial velocity of 85 cm per second for curve D, the difference is 6.5 cm per second. If we enter figure (E-16) at a value of 85 cm per second for the spatial velocity, we see that to this value there corresponds an unburned gas velocity of 6.2 cm per second. As is obvious from this calculation the difference between variation IV and V is approximately a measure of unburned gas velocity. It would be a true measure except for the fact that in variation IV the flame assumes a slightly different shape because of the additional flow of gases through the flame front caused by the hot gas piston effect, and the effect of the reflected compression waves. The effect of this slight difference in flame shape, however, would be very difficult to calculate.

In variation VI, suggested by Dr. Owczarek, the 2.42 cm I.D. tube was used with the 1.27 cm orifice fitted in the ignition end of the tube. The spatial velocities were measured over a 9 inch distance the center of which was located 33 inches from the ignition point. The upstream end of the tube was fitted with a cap composed of a one inch thickness of closely packed steel wool. The purpose of this steel wool was to damp all waves which previously interfered with uniform flame propagation. This type of upstream end closure permitted uniform propagation of the flame front for the entire length of the flame tube. No acceleration or cellular flame structure was observed in this method at any point of the flame tube. The flame front was shaped like a semi-ellipsoid with a segment removed. Its semi-major axis was coincident with the axis of the flame tube. The flame shape photographed in this method was projected at double the actual size onto figure (E-17B). The values of the spatial velocity measured in this variation are shown in figure (E-13B).

The unburned gas velocity for variation VI was obtained by experimental measurement of the volumetric rate of gas flow within that portion of the flame tube toward which the flame was advancing. To the upstream end cap containing the steel wool was attached a 1½ inch long tube of 1 inch I.D. Across this tube was a soap film. As the flame propagated in the flame tube, the growth of the soap bubble was observed. The volume of the soap bubble obtained was divided by the cross sectional area of the tube to give an unburned gas velocity. The apparatus used is shown in figure (E-1C). This procedure was carried out for mixtures of 3.38% and 2.72%, N-Butane. A linear variation was assumed between these points. The results are shown in figure (E-16B).

Burning Velocity Determination In The Tube Method

In order to calculate the burning velocities from the measured spatial velocities it is necessary to know the unburned gas velocity and the flame surface area. The unburned gas velocity determination was previously described and the results were plotted in figures (E-16A and E-16B). The flame surface area was obtained from projections of photographs of the flame surface. To facilitate calculations, the flame surface was approximated by a portion of an ellipsoid with its axes aligned as shown in figure (E-17A) for the flame surface obtained in all variations of the tube method using the 2.42 cm I.D. tube except variation VI for N-Butane which is shown in figure (E-17B). The flame front geometry obtained for all variations using the 3.4 cm I.D. tube is shown in figure (E-18).

For the flame surface observed in the 2.42 cm I.D. tube, for all variations of the tube method except variation VI for Butane, we measure from figure (E-17A):

a = length of the semi-major axis = .85 in,

b = length of the semi-minor axis = .45 in.

we calculate: the eccentricity

$$e = \sqrt{1 - \frac{b^2}{a^2}} = .848$$

the area of a semi-ellipsoid is calculated from the equation:

$$A = \pi b^2 + \frac{\pi ab \sin^{-1} e}{e}$$

and we get the area: $A = 2.065 \text{ in.}^2$

Area A_2 in figure (E-17A) was approximated as a segment on the surface of a cylinder of .9 inches in diameter with its axes coinciding with the axes of the ellipsoid. Its surface area was calculated graphically to be: $A = .437 \text{ in.}^2$

The flame surface area is the difference between the surface area of the semi-ellipsoid and the segment of area A_2.

$$A_f = 2.065 - .437 = 1.628 \text{ in.}^2$$

the cross sectional of the 2.42 cm I.D. tube calculated to be: $A_t = .717$ in.^{2}

For the flame surface observed in the 3.4 cm I.D. tube, we measure from figure (E-18A):

a = length of the semi-major axis = 1.3 in.

b = length of the semi-minor axis = .65 in.

we calculate:

the eccentricity $e = \sqrt{1 - \frac{b^2}{a^2}} = .866$

the area of the semi-ellipsoid is calculated from the equation:

$$A = \pi b^2 + \frac{\pi ab}{e} \sin^{-1} e$$

we get - $A = 4.525$ in.^{2}

Area A_2 in figure (E-18) was approximated as a segment on the surface of a cylinder of 1.3 inches in diameter with its axes coinciding with the axis of the ellipsoid. Its surface area was calculated graphically from figure (E-18B), and found to be:

$$A_2 = 1.17 \text{ in.}^2$$

The flame surface area is the difference between the surface area of the semi-ellipsoid and area A_2.

$$A_f = 4.525 - 1.17 = 3.35 \text{ in.}^2$$

the cross sectional area of the 3.4 cm I.D. tube was calculated to be:

$$A_t = 1.405 \text{ in.}^2$$

In variation VI for N-Butane the flame surface was approximated as a portion of an ellipsoid with its axis coincident with the tube axis as shown in figure (E-17B).

We measure from figure (E-17B):

$a =$ length of semi-major axis $= 1.2$ in.

$b =$ length of semi-minor axis $= .477$ in.

We calculate the eccentricity:

$$e = \sqrt{1 - \frac{b^2}{a^2}} = .918$$

the area of the semi-ellipsoid is calculated from the equation:

$$A = \pi b^2 + \frac{\pi ab}{e} \sin^{-1} e$$

and we get the area $A = 2.994 \text{ in.}^2$

Area A_2 in figure (E-17B) was approximated as a segment on the surface of a cylinder of .955 in diameter whose axis is coincident with the axis of the tube. Its surface area was calculated graphically to be $A_2 = .86 \text{ in.}^2$ The flame surface area is the difference between the surface area of the semi-ellipsoid and the segment of area A_2.

$$A_f = 2.994 - .86 = 2.134 \text{ in.}^2$$

The cross sectional area of the tube was calculated to be .717 in.^{2}

The values for the burning velocity of flames that propagated in tubes which were closed at the upstream end were calculated from the formula:

$$Vb = Vs \; A_t/A_f$$

where Vb = burning velocity

Vs = measured spatial velocity

A_t = cross sectional area of the flame tube.

A_f = calculated flame surface area

For all the variations in which the upstream end of the tube was closed, it was assumed that the value of unburned gas velocity was zero.

The values for the burning velocity of flames that propagated in tubes in which there was fitted an orifice or the cap used in variation VI for N-Butane, in the upstream end of the tube, were calculated from the formula:

$$Vb = (V_s - V_{ub}) \; A_t/A_f$$

where V_{ub} = measured value of the unburned gas velocity and is obtained from figure (E-16A) for all variations of the tube method which used an orifice in the upstream end of the flame tube except for variation VI which is obtained from figure (E-16B).

The calculated values for the burning velocity of propane-air mixtures are shown in figures (E-20), (E-21), and (E-22). The values shown in figure (E-20) were obtained from the spatial velocity measured in the tube method by variation V. The values of burning velocity shown in figure (E-21) were obtained from the spatial velocities measured by variation III. The values of burning velocity shown in figure (E-22) were obtained from spatial velocities measured by variation IV.

Comparing figures (E-20, E-21, and E-22), we can see no significant difference in the values of burning velocitie obtained by the variations III, IV, and V of the tube method for propane. A maximum value of burning velocity ranging from 35.5 to 36.5 cm per second at mixtures between 4.15%and 4.25% propane, is obtained from these figures.

The calculated values for the burning velocity of N-Butane-air mixtures obtained by variations of the tube method are shown in figures (E-23), (E-24), (E-25), (E-26A), and (E-26B). The values of burning velocity shown in figure (E-23) were obtained from spatial velocities measured by variation I of the tube method for N-Butane, and those in figure (E-24) were obtained from the values of spatial velocity measured by variation II of the tube method.

Figure (E-25) shows a comparison of the values of burning velocities obtained from variation III and IV of the tube method. Curve A was obtained from variation IV and shows the effect of an orifice placed in the ignition end of the tube with the upstream end of the tube closed. As was stated previously, the orifice in the ignition end caused an increase in spatial velocity because of hot gas piston effect but, even with the increased spatial velocity, the burning velocity curves for variation III and IV should be the same. The reason variation IV shows a slightly higher burning velocity is because the same flame surface area was used in both calculations, and the value for the unburned gas velocity was assumed to be zero in both variations. The initial compression wave formed by the expansion of the burnt gases is much stronger when the ignition end contained the orifice then when the ignition end was left open. This stronger incident compression wave in variation IV caused a higher value for the unburned gas velocity than that in variation III, and therefore, the assumption of a zero value for this unburned gas velocity in variation IV by this author and others (30), who have used a similar variation is slightly in error.

Figure (E-26A) shows the values of burning velocity calculated from spatial velocities measured in variation V of the tube method for butane.

Figure (E-26B) shows the values of burning velocity calculated from spatial velocities measured in variation VI of the tube method for N-Butane-air mixtures.

Burning Velocity Determination By The Burner Method

As a result of the author's investigation into literature, the schlieren cone was chosen to be the surface to employ in determining burning velocities. The schlieren system and other equipment used in the burner method is shown in figure (E-27). The burner tube had an inside diameter of 5/16 inches. The schlieren image was photographed with Kodak Super XX panchromatic film at a shutter speed of 1/75 sec. Some typical photographs obtained are shown for propane-air mixtures in figures (E-33, E-34) and butane-air mixtures in figure (E-35). The burning velocities were calculated by dividing the volume flow rate measured by the surface area of the schlieren cone. The formula used was:

$$V_b = \frac{\text{volume flow rate}}{\pi r h / \cos\alpha}$$

where V_b = burning velocity

r = radius of the base of the cone

h = height of the cone

α = the Michaelson angle

The results of the burning velocity calculations for propane-air mixtures are shown in figure (E-28). The results for the burning velocity calculations for the butane-air mixtures are shown in figure (E-29). There was some difficulty in obtaining the values for the burning velocity of very lean mixtures of butane and air, because the flame tended to blow off the burner tube. The rich mixtures may have been diluted by the surrounding air, and what was recorded as a rich mixture was actually a leaner mixture than recorded. Two sets of points were recorded for the richer mixtures. The set of points shown at approximately 3.75% Butane would agree with those obtained by the tube method.

Comparison of Results

Figure (E-30) shows a comparison of results of burning velocities for propane-air mixtures obtained in variation V of the tube method, and the burner method by this author with those obtained by other investigators. The maximum burning velocity obtained in the burner method (curve D of figure E-30) is 40 cm per second at 4.05% propane as compared to 36.5 cm per second at 4.25% propane obtained by the tube method (curveE). From this figure it is also seen that the values obtained by this author by the burner method are higher than those obtained by Gerstein, Levine and, Wong and fall between the values obtained by the other investigators (1,5,57) who have used a variation of the burner method. It is seen that the values obtained by this author by the variations of the tube method agree very well with those obtained by Broeze who used the burner method. From a study of the results shown in figure (E-30), it is evident that the results obtained by this author compare favorably with results obtained by other investigators.

This author feels that the burning velocities obtained by the burner method are closer in value to the actual burning velocities than those obtained by the variations of the tube method.

Figure (E-31) shows a comparison of burning velocities obtained from variations of the tube method with those obtained by the burner method for N-Butane-air mixtures.

It can be seen that variation VI of the tube method (curve E) and the burner method using the total schlieren cone (curve C), yield the same value for maximum burning velocity although the maximum value for burning velocity is obtained at a leaner mixture in the burner method. Variation I (curve A), and variation V (curve D) yield a lower value for burning velocity than variation VI or the burner method. Variations I, V, and VI yield the maximum value of burning velocity at approximately 3.38% N-Butane. Variation VI and the burner method yield slightly higher values for burning velocity than those obtained by Gerstein, Levine, and Wong (27). This author feels that the results obtained by variation VI of the tube method are probably the true results.

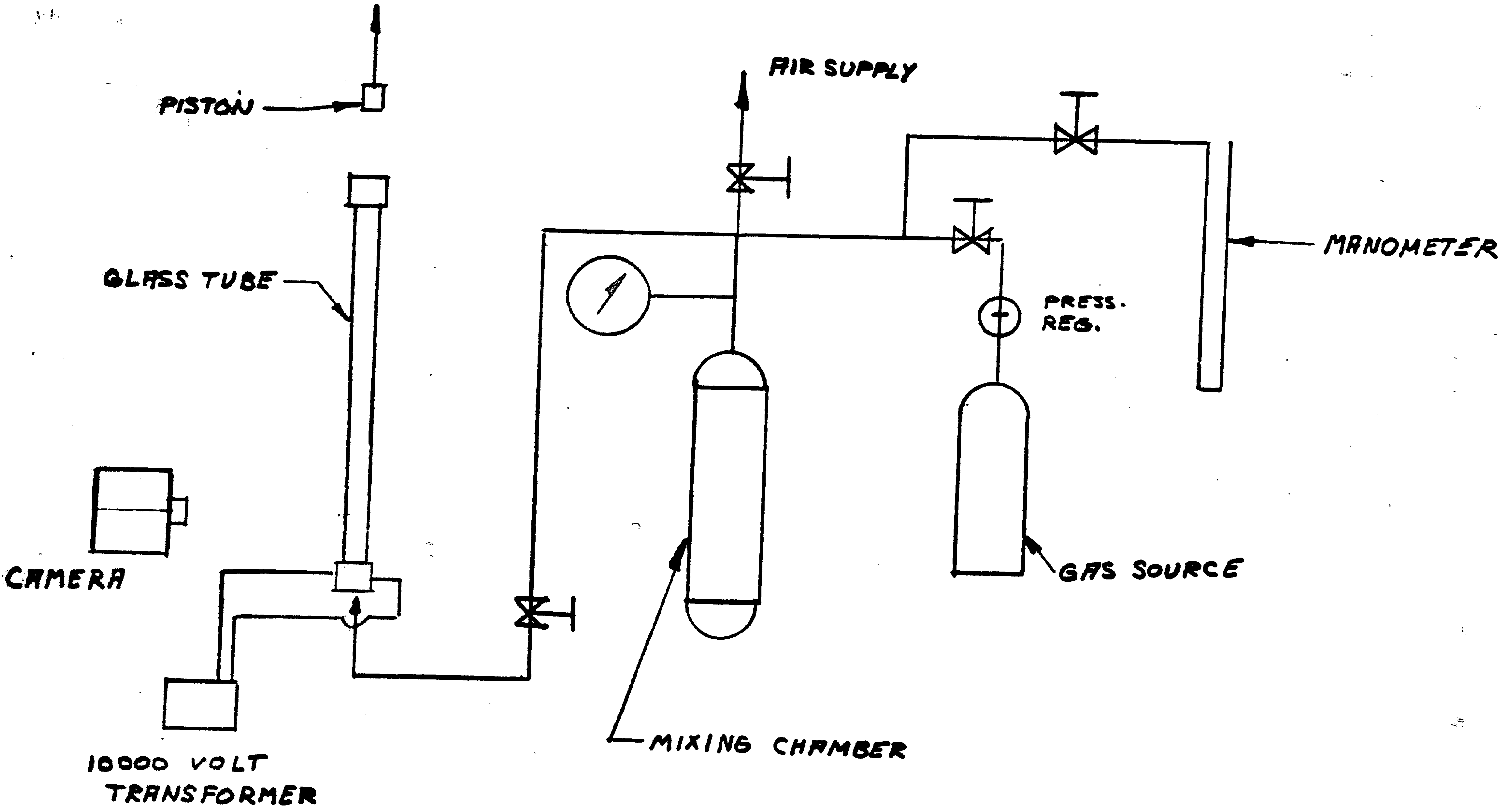
CONCLUSIONS

When an orifice is used in the ignition end of the flame tube and the upstream end of the tube is closed, such as the method developed by Guenoche (30), there is an increase in the spatial velocity caused by the restriction of the flow of the expanded burnt gases from the tube, but because of the incident compression waves, formed as a result of the hot gas piston effect, which accelerates the gas particles in the direction of the propagation of the head of the wave and the interaction of the reflected compression waves, the assumption of a zero value for the unburned gas velocity may not be valid. If this method is to be used accurately, there should be developed a method by which unburned gas velocity can be measured.

The author observed that in variations of the tube method similar to those developed by Guenoche (30) (orifice ignition end and closed upstream end) and Coward and Hartwell (8) (open ignition end and closed upstream end) flame propagation was not uniform throughout the entire length of the tube but only over a small portion. The tube method developed by Gerstein, Levine, and Wong (27), with an orifice in the ignition end and an orifice in the upstream end gave uniform propagation for a longer period of time than variations developed by Guenoche (30) or Coward and Hartwell (8). Variation VI of the tube method for N-Butane-air mixture which was suggested by Dr. Owczarek, and developed by this author, gave uniform propagation of the flame front throughout the entire length of the flame tube.

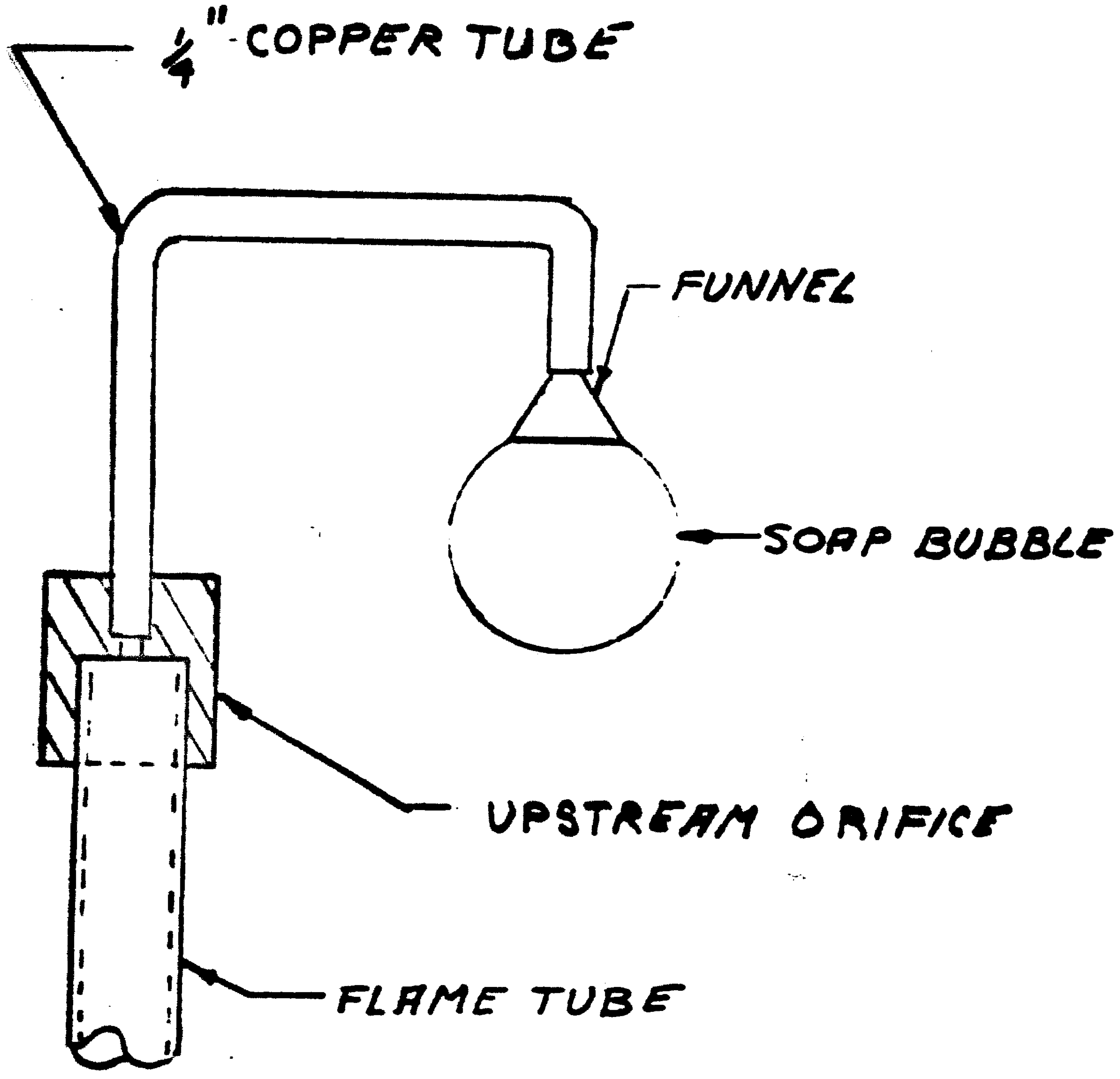
The author observed that all variations of the tube method except variation VI for N-Butane yield lower values for the burning velocity than those obtained by the burner method using the schlieren cone. Variation VI, which utilized a steel wool cap in the upstream end of the flame tube to damp out reflected waves, yielded values of burning velocity which agreed with those obtained by the burner method.

On the basis of his experiments, and information on the thoretical values calculated for burning velocities of Propane and N-Butane air mixtures, and also published literature on the experimental determined values of burning velocity, the author feels that there is excellent agreement in the values for burning velocity obtained by the burner method utilizing the schlieren cone and those obtained by variation VI of the tube method, and that these two methods yield the true values of burning velocities.



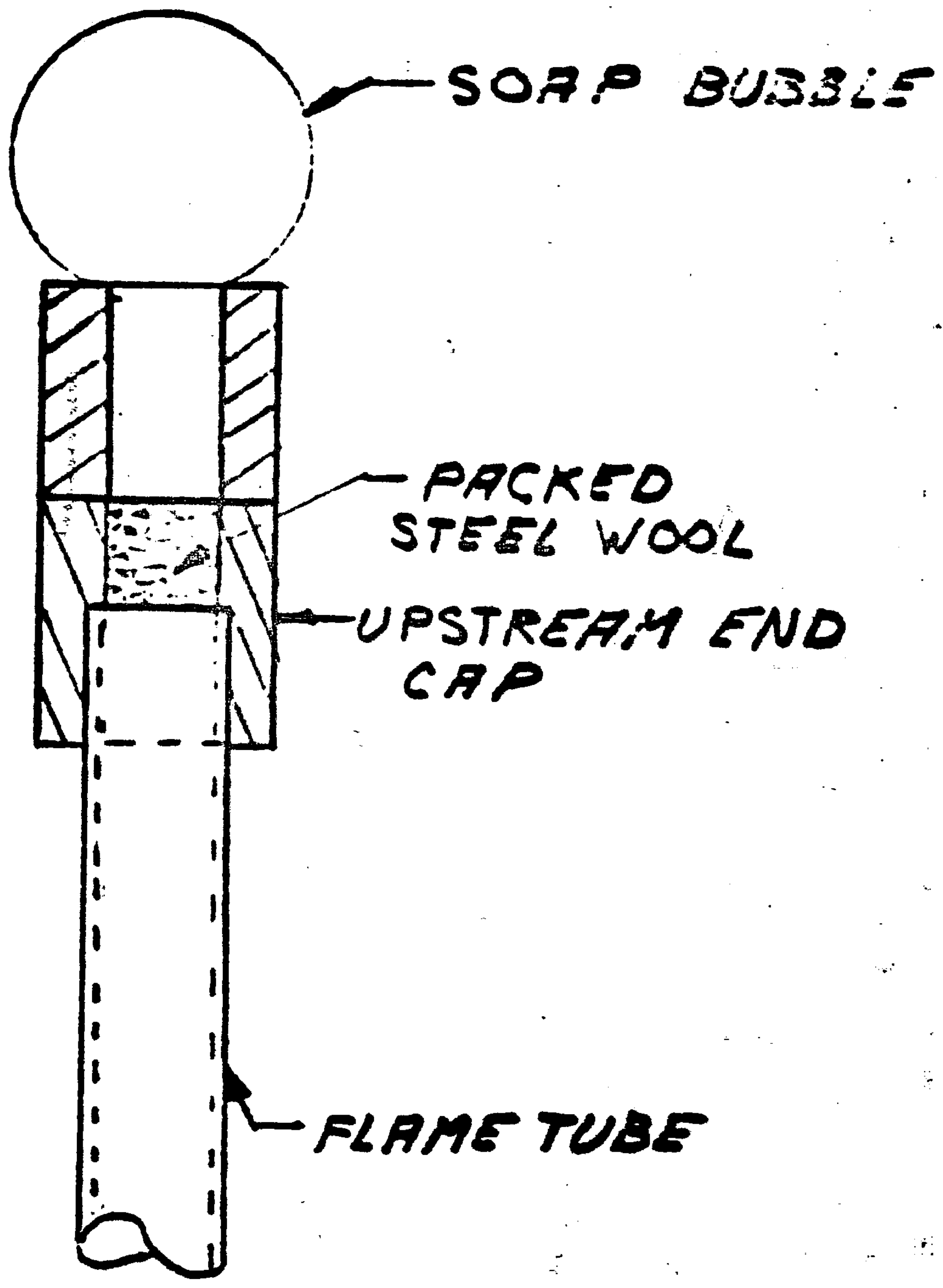
APPARATUS - TUBE METHOD

FIG. E-1A



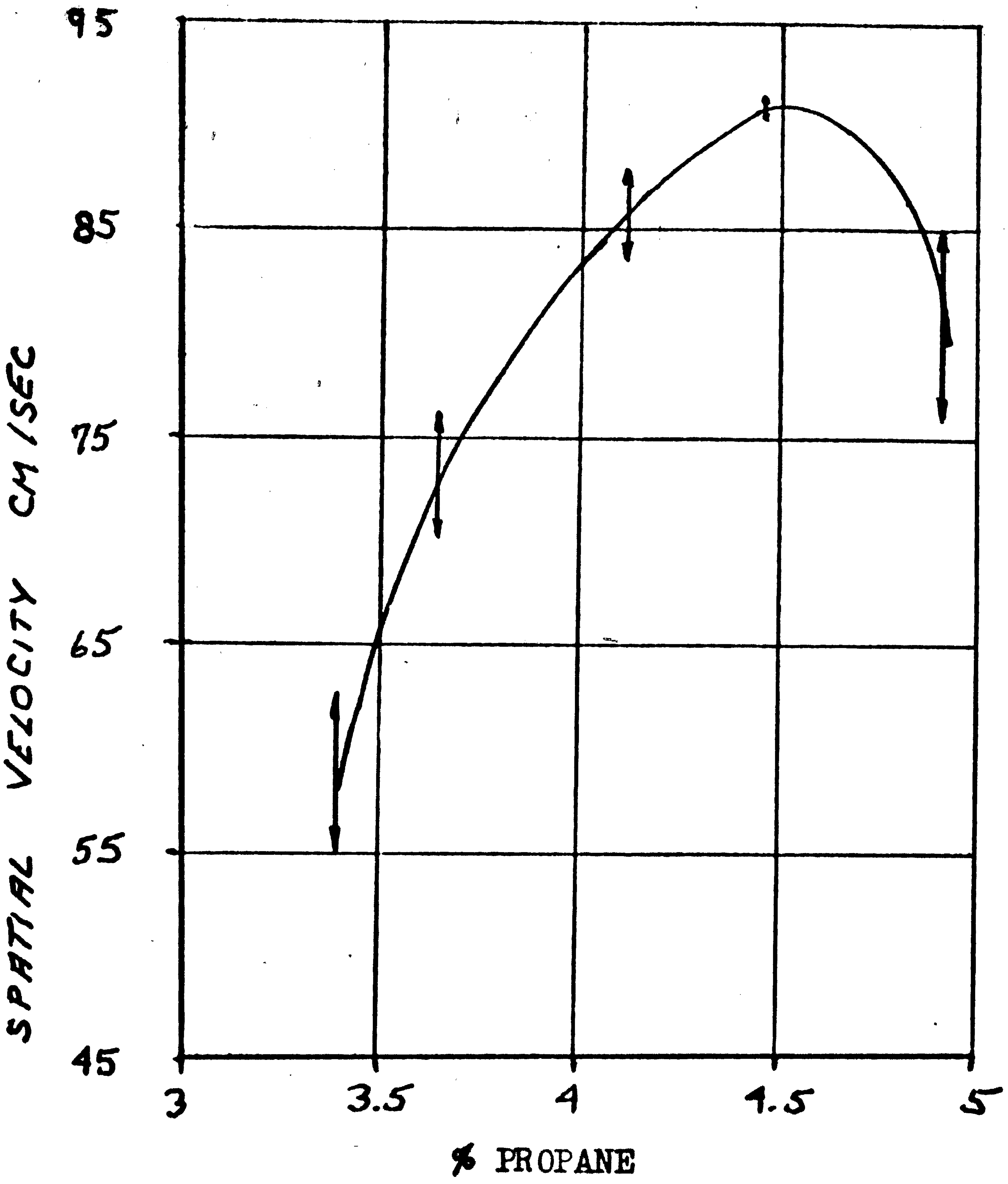
UNBURNED GAS VELOCITY
MEASUREMENT APPARATUS

FIG. E-1B



UNBURNED GAS VELOCITY
MEASUREMENT APPARATUS

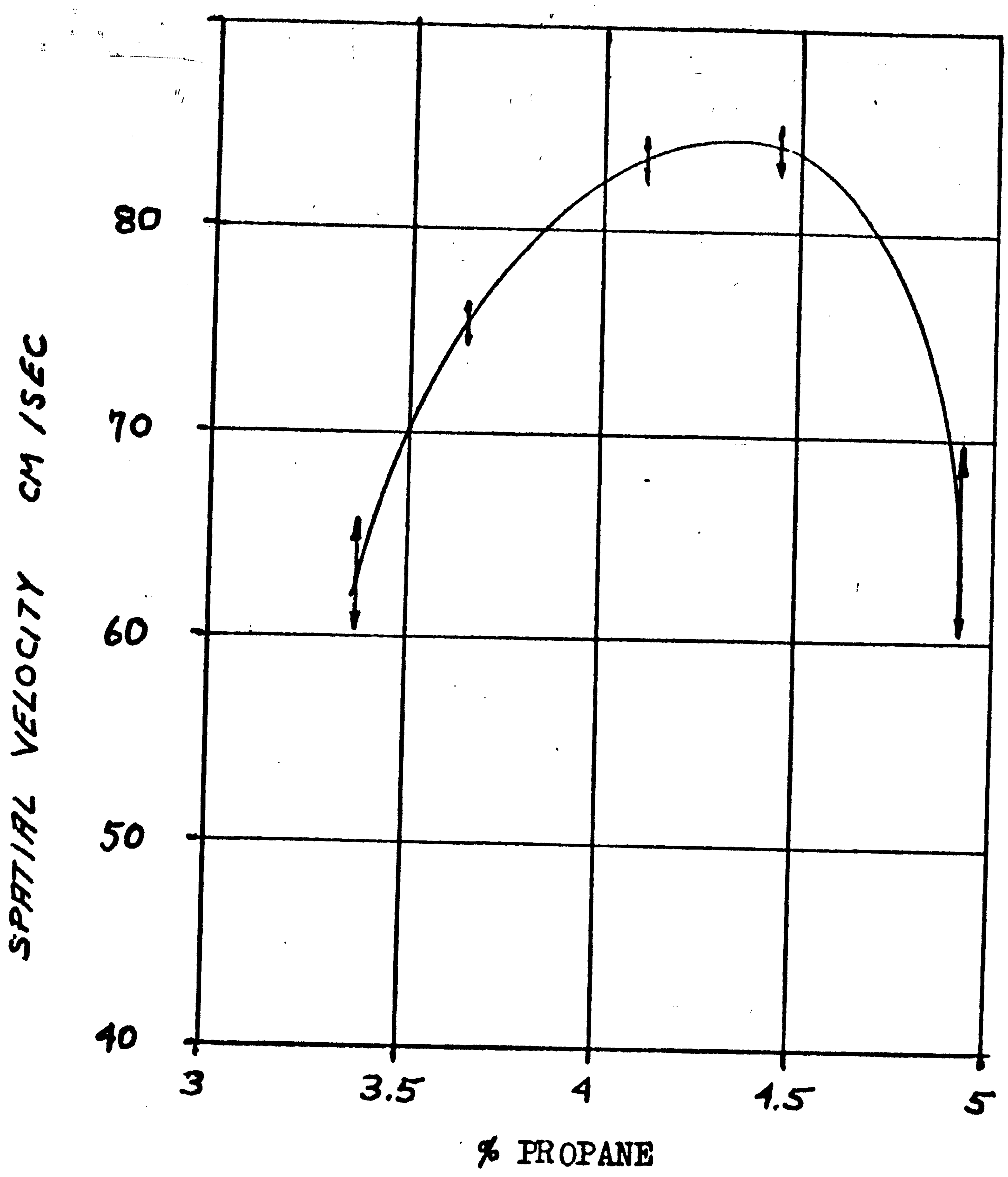
FIG. E-1C



1.27 CM ORIFICE IGNITION END
.238 CM ORIFICE UPSTREAM END
OBSERVATION POINT AT 3/4 TUBE
LENGTH FROM IGNITION POINT

3.4 CM ID TUBE

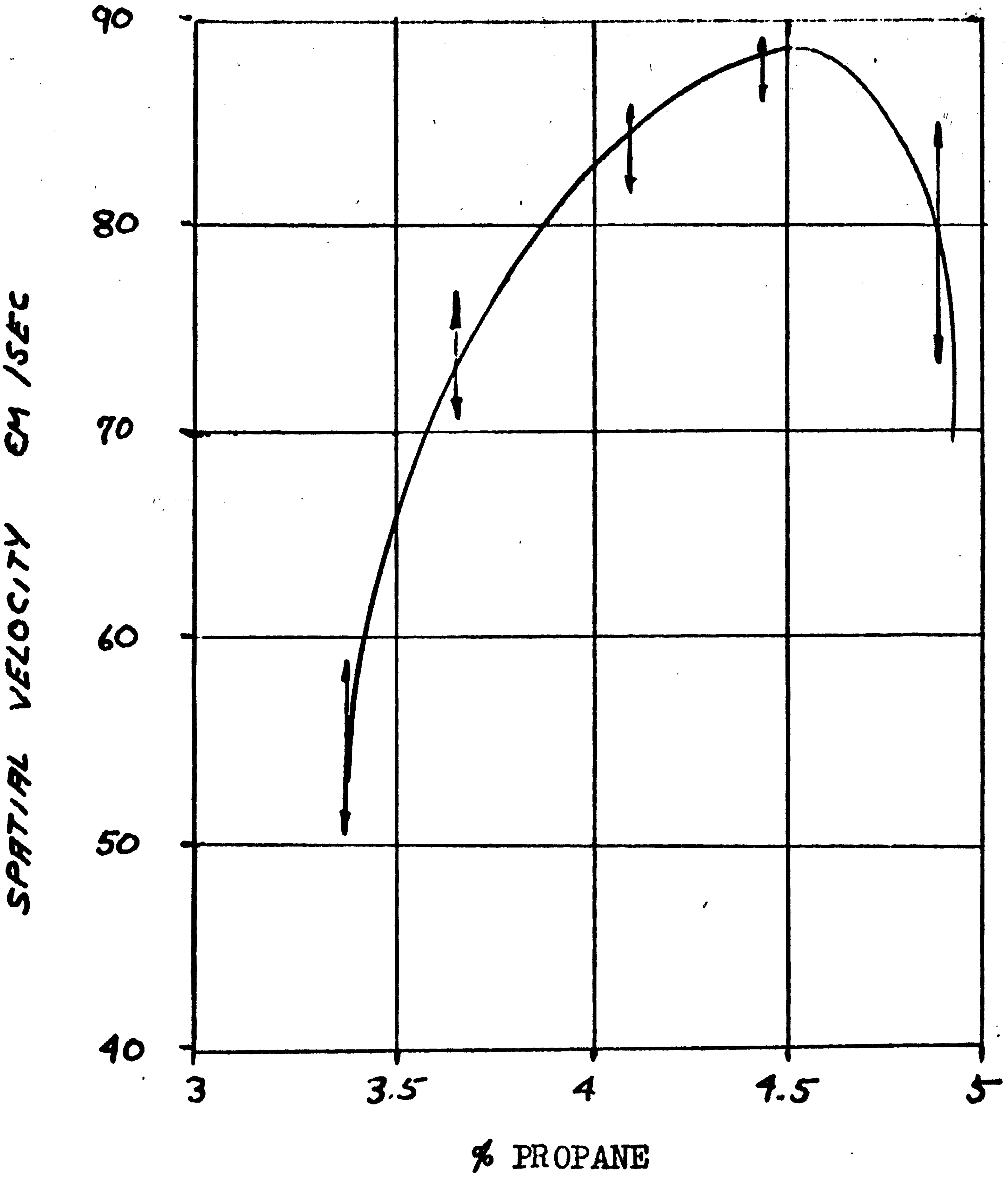
FIG. E - 2



OPEN IGNITION END (NO ORIFICE USED)
CLOSED UPSTREAM END
OBSERVATION POINT AT 1/4 TUBE
LENGTH FROM POINT OF IGNITION

3.4 CM ID TUBE

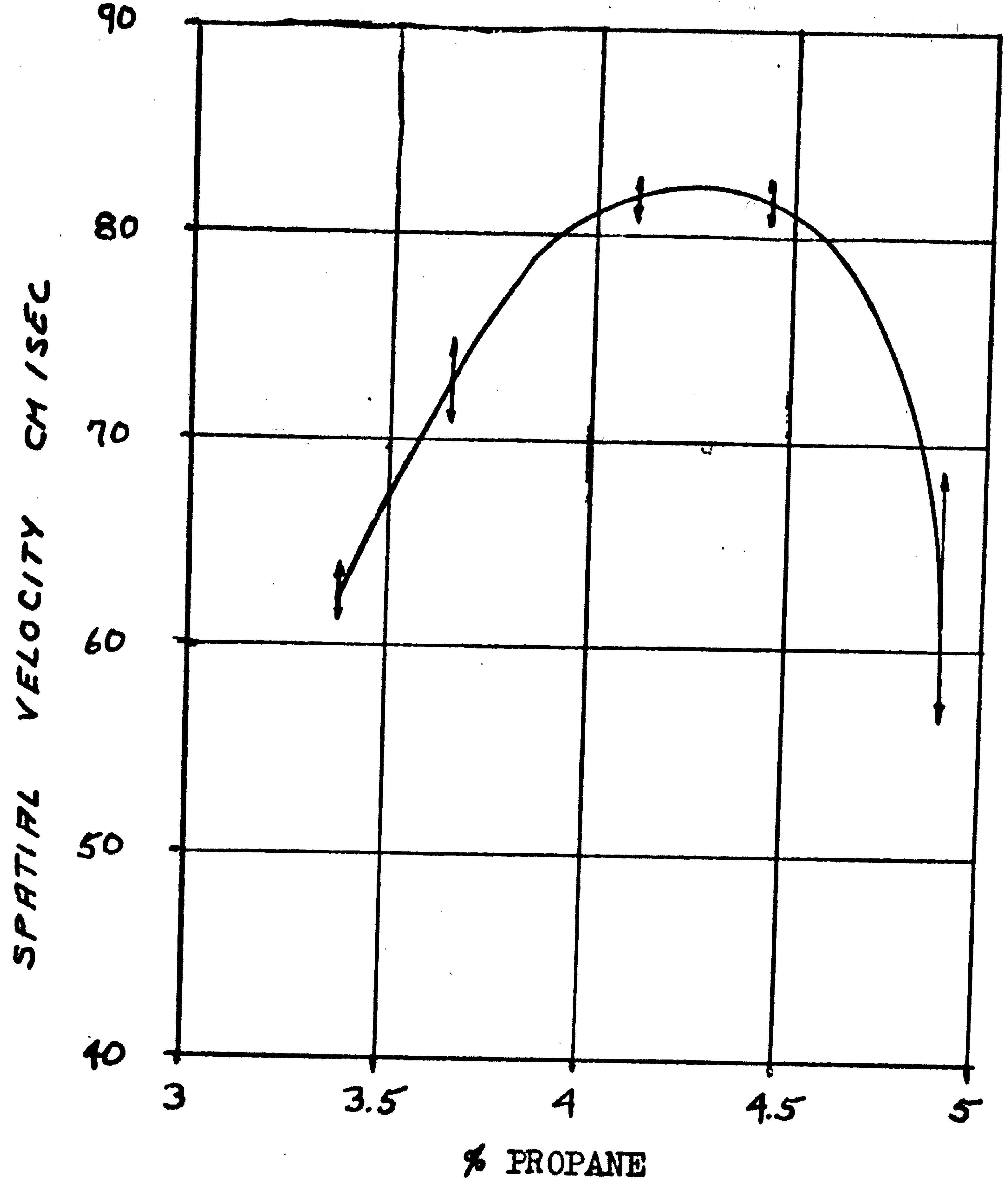
FIG. E - 3



.795 CM ORIFICE IGNITION END
.198 CM ORIFICE UPSTREAM END
OBSERVATION POINT AT 3/4 TUBE
LENGTH FROM IGNITION POINT

2.42 CM ID TUBE

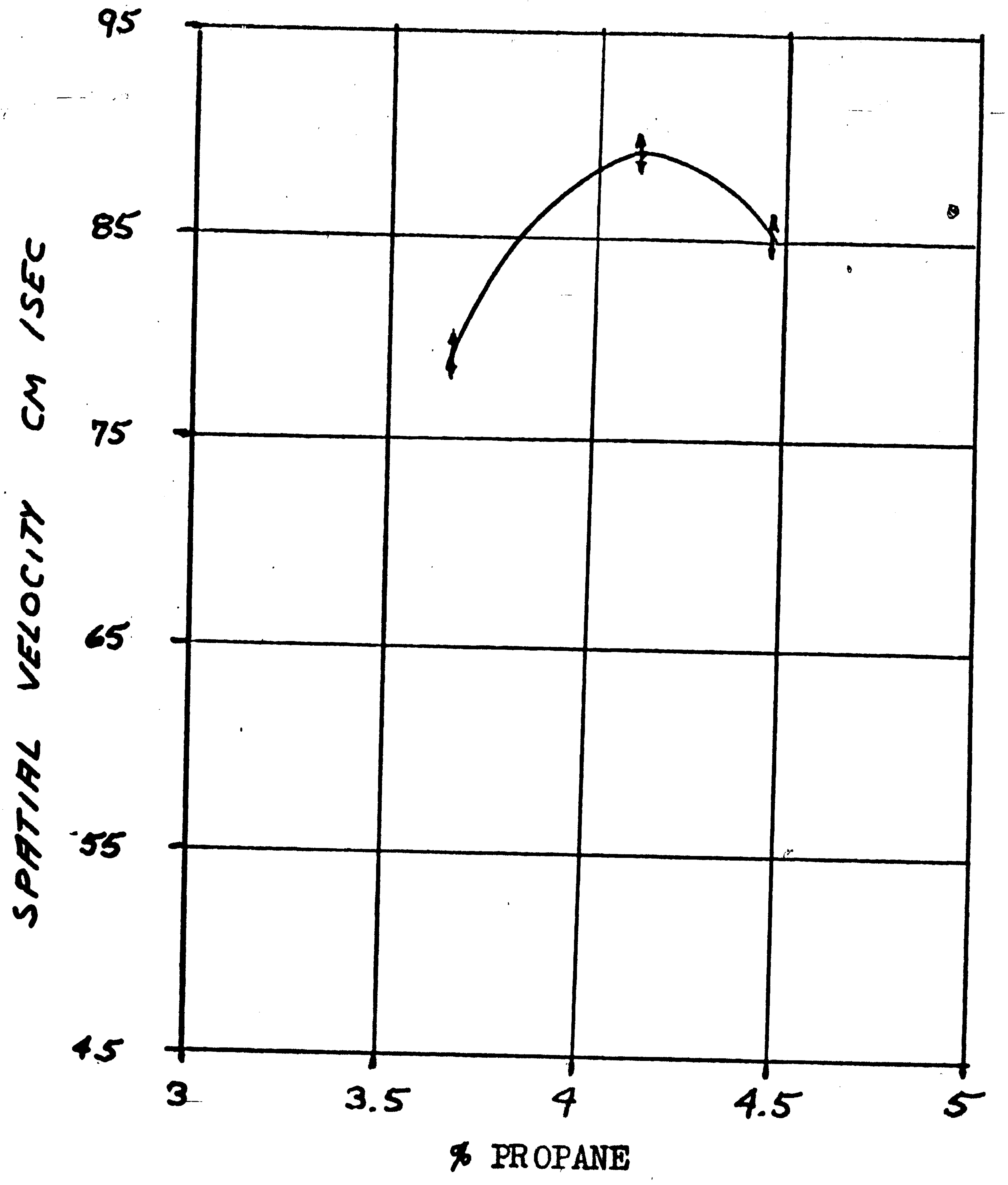
FIG. - E - 4



OPEN IGNITION END (NO ORIFICE USED)
CLOSED UPSTREAM END
OBSERVATION POINT AT 1/4 TUBE
LENGTH FROM IGNITION POINT

2.42 CM ID TUBE

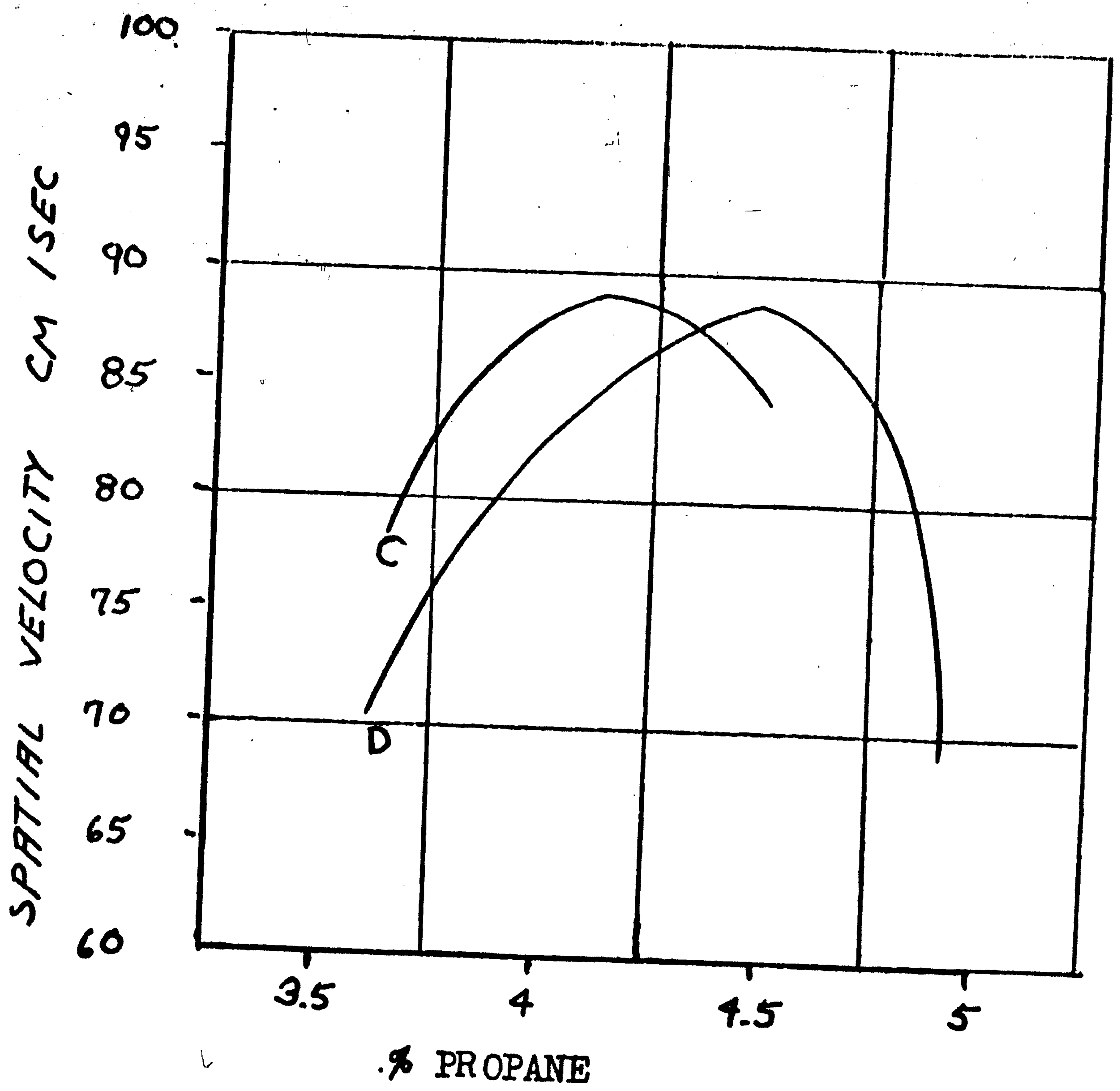
FIG. E - 5



.795 CM ORIFICE IGNITION END
.198 CM ORIFICE UPSTREAM END
OBSERVATION POINT 1/4 TUBE LENGTH
FROM IGNITION POINT

2.42 CM ID TUBE

FIG. E - 6

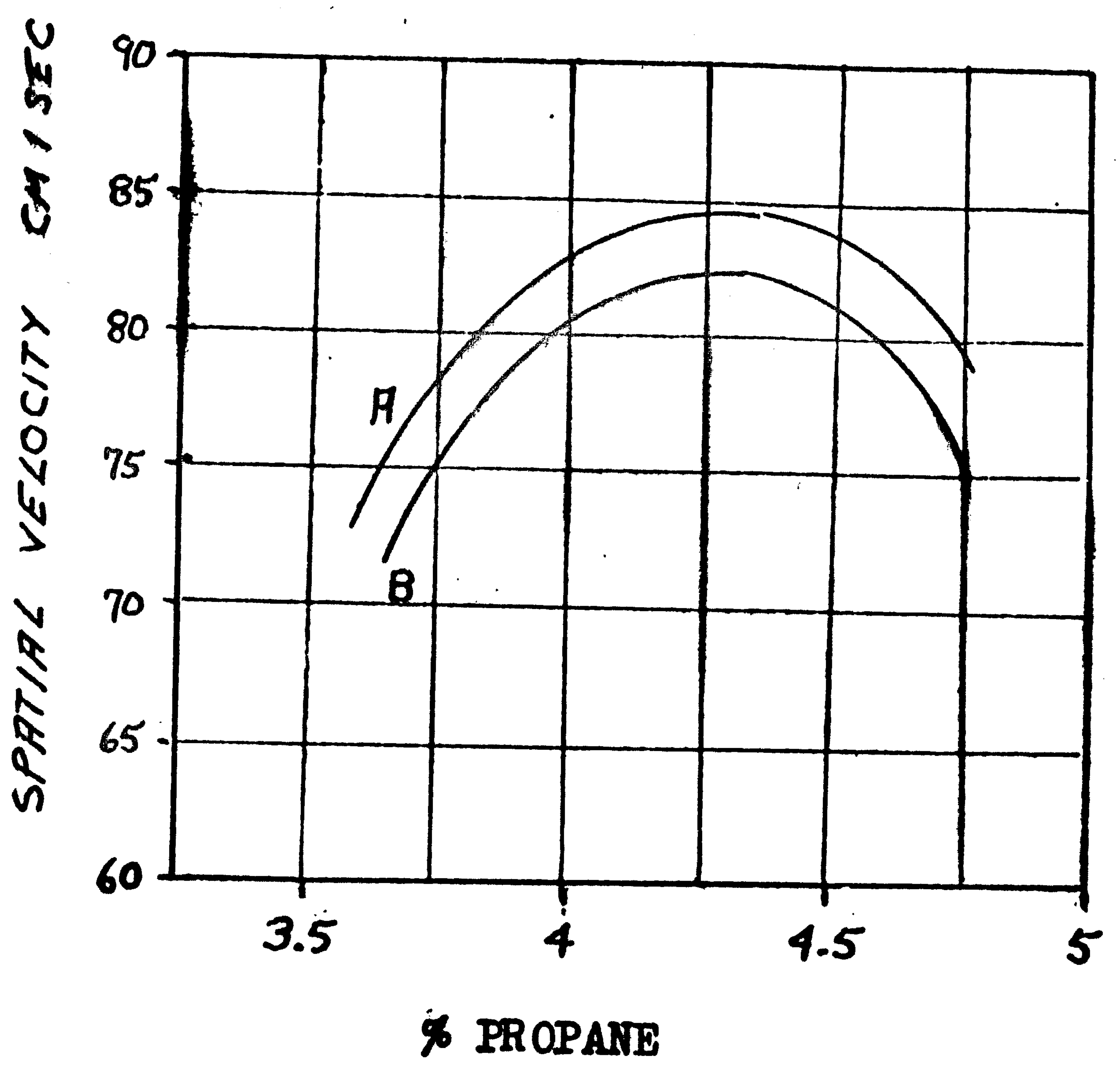


DEPENDENCE OF SPATIAL VELOCITY OF FLAMES OF PROPANE-AIR MIXTURES ON OBSERVATION POINT LOCATION

CURVE C OBSERVATION POINT 1/4 TUBE LENGTH FROM IGNITION POINT

CURVE D OBSERVATION POINT 3/4 TUBE LENGTH FROM IGNITION POINT

FIG. E - 7

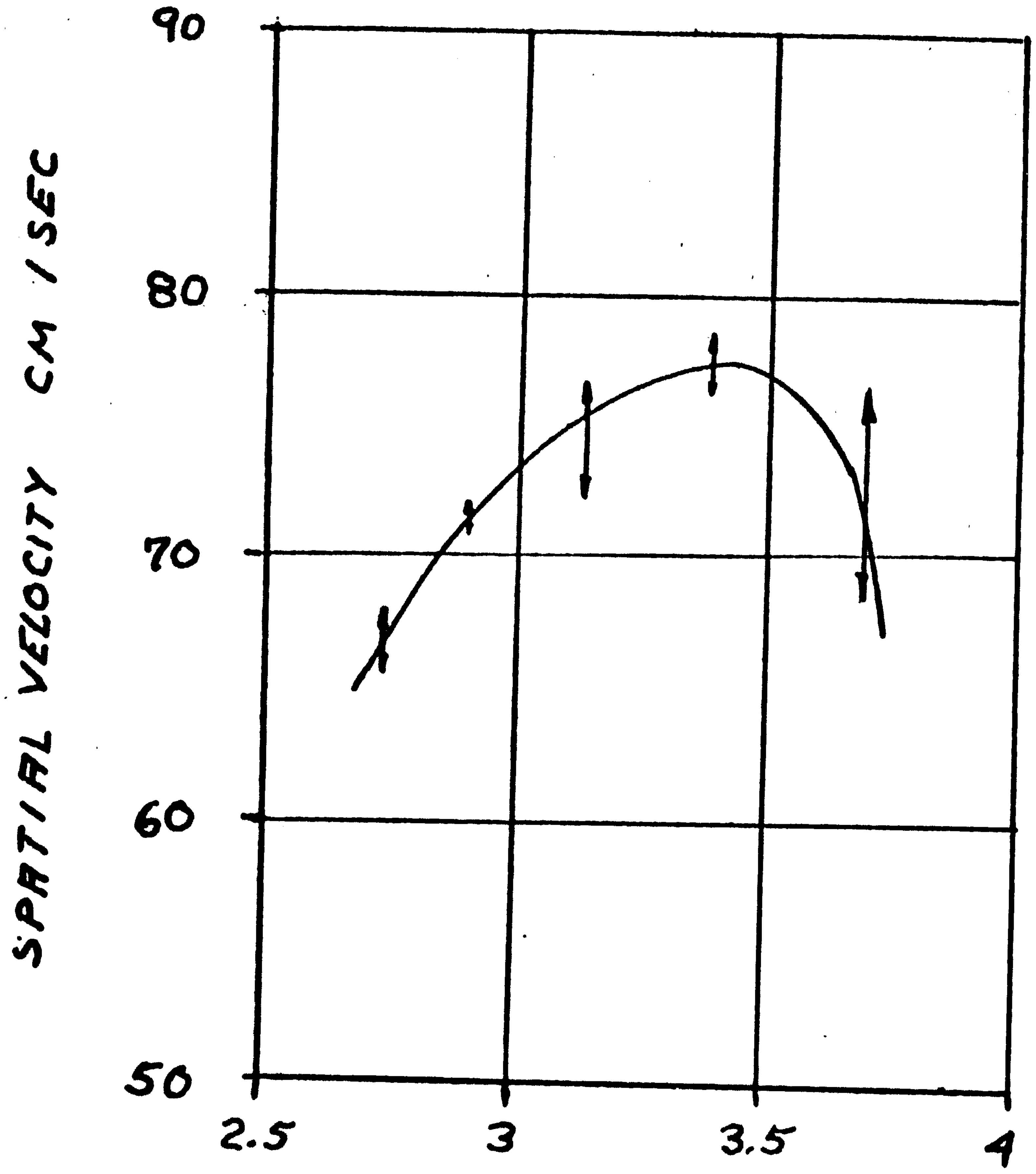


DEPENDENCE OF SPATIAL VELOCITY OF FLAMES OF PROPANE-AIR MIXTURES ON TUBE DIAMETER

CURVE A-3.4 CM ID TUBE

CURVE B-2.42 CM ID TUBE

FIG. E - 8

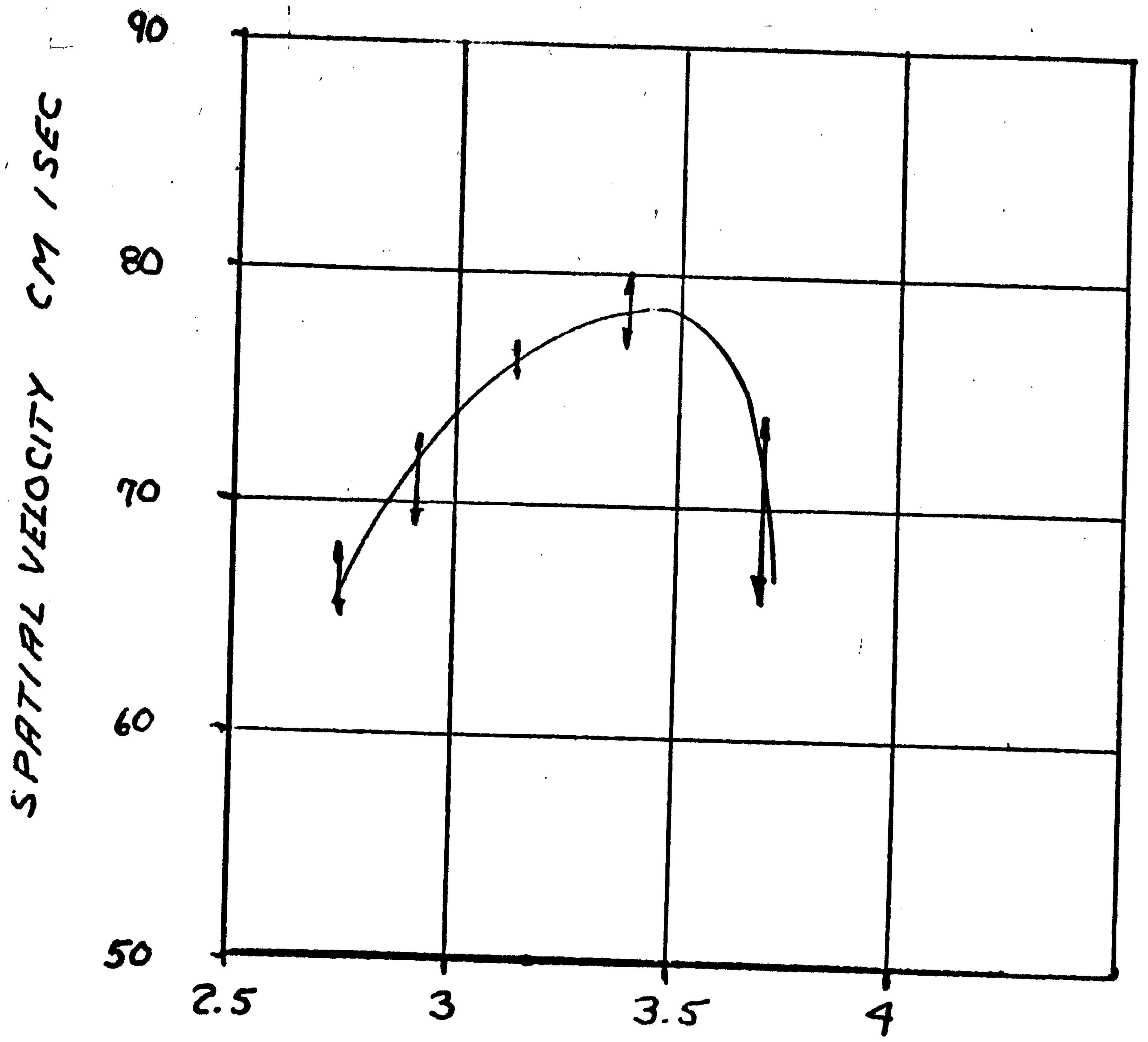


% N - BUTANE

OPEN IGNITION END (NO ORIFICE USED)
CLOSED UPSTREAM END
OBSERVATION POINT AT 1/4 TUBE
LENGTH FROM IGNITION POINT

2.42 CM ID TUBE

FIG. E - 9

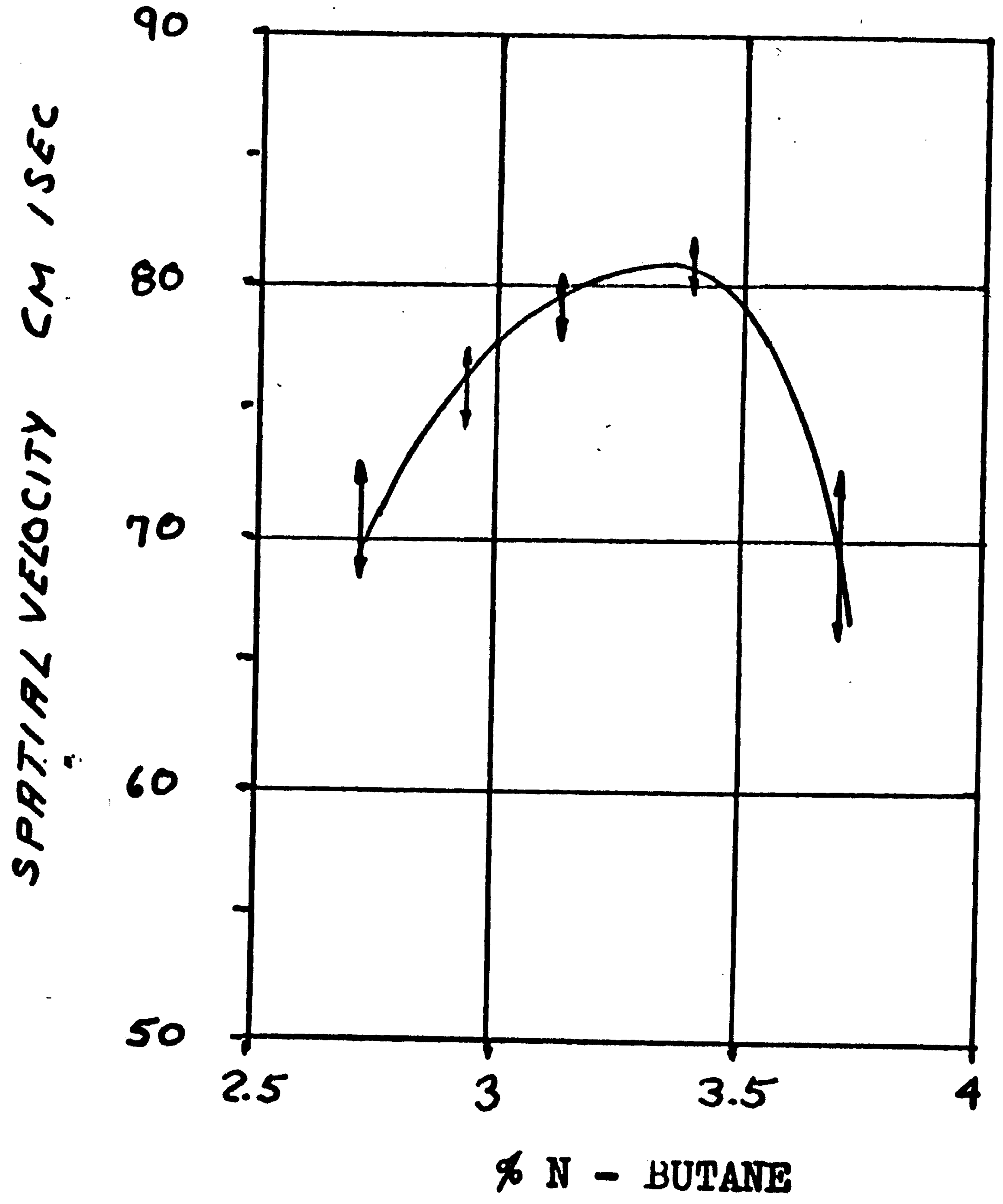


% N - BUTANE

.795 CM ORIFICE IGNITION END
CLOSED UPSTREAM END
OBSERVATION POINT AT 1/4 TUBE
LENGTH FROM IGNITION POINT

2.42 CM ID TUBE

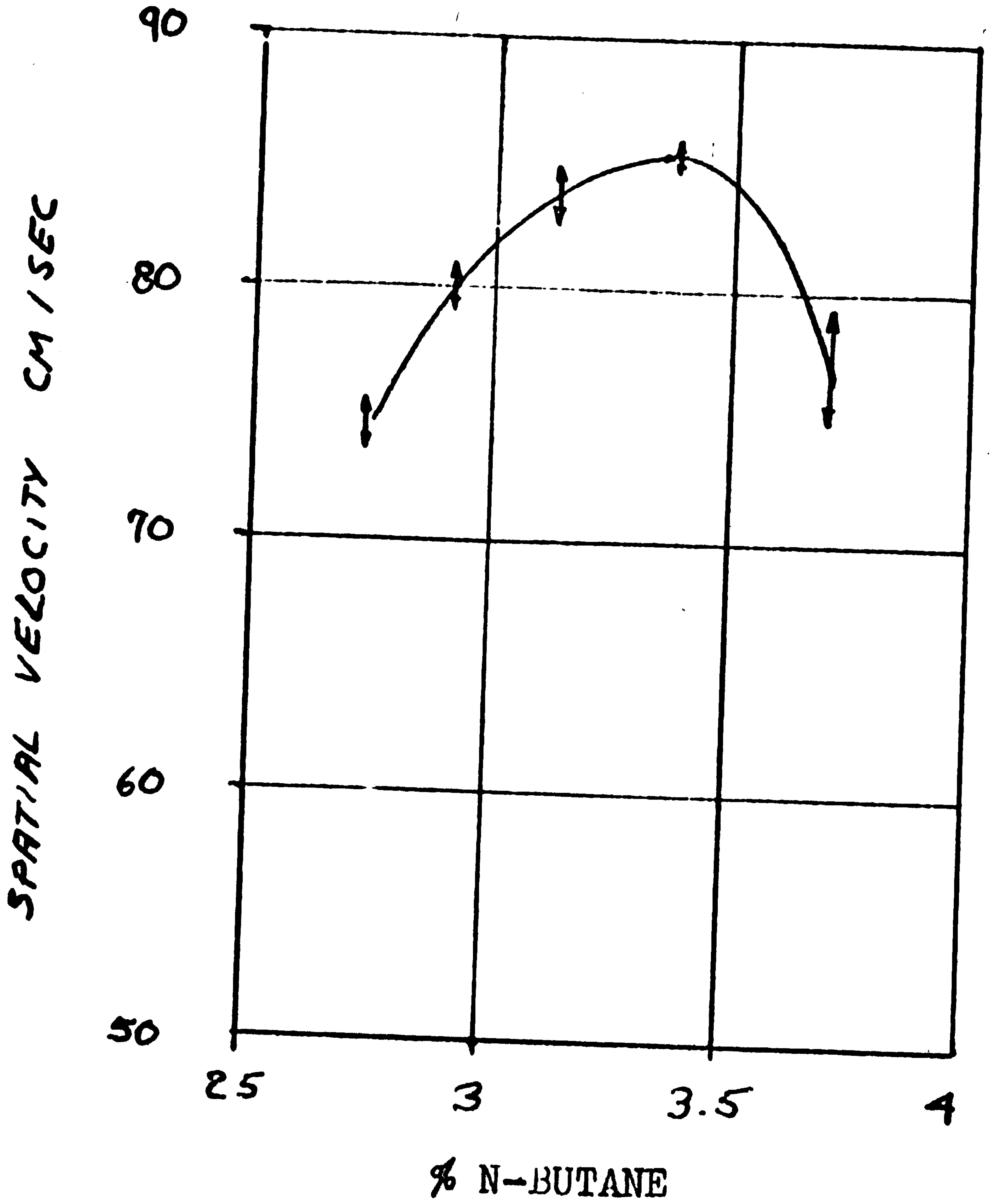
FIG. E - 10



OPEN IGNITION END (NO ORIFICE USED)
CLOSED UPSTREAM END
OBSERVATION POINT AT 1/4 TUBE LENGTH FROM IGNITION POINT

3.4 CM ID TUBE

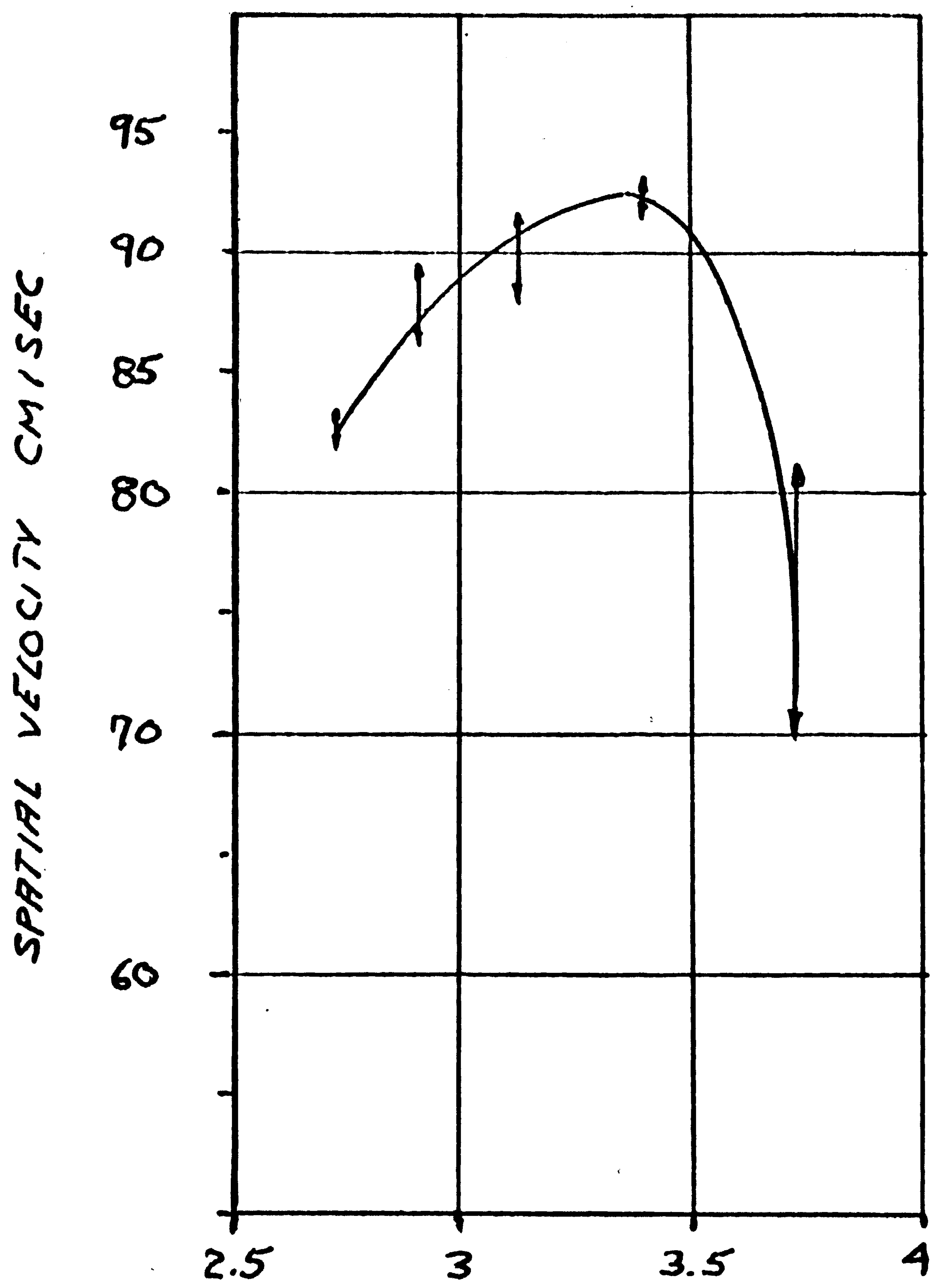
FIG. E - 11



1.27 CM ORIFICE IGNITION END
CLOSED UPSTREAM END
OBSERVATION POINT AT 1/4 TUBE
LENGTH FROM IGNITION POINT

3.4 CM ID TUBE

FIG. E - 12

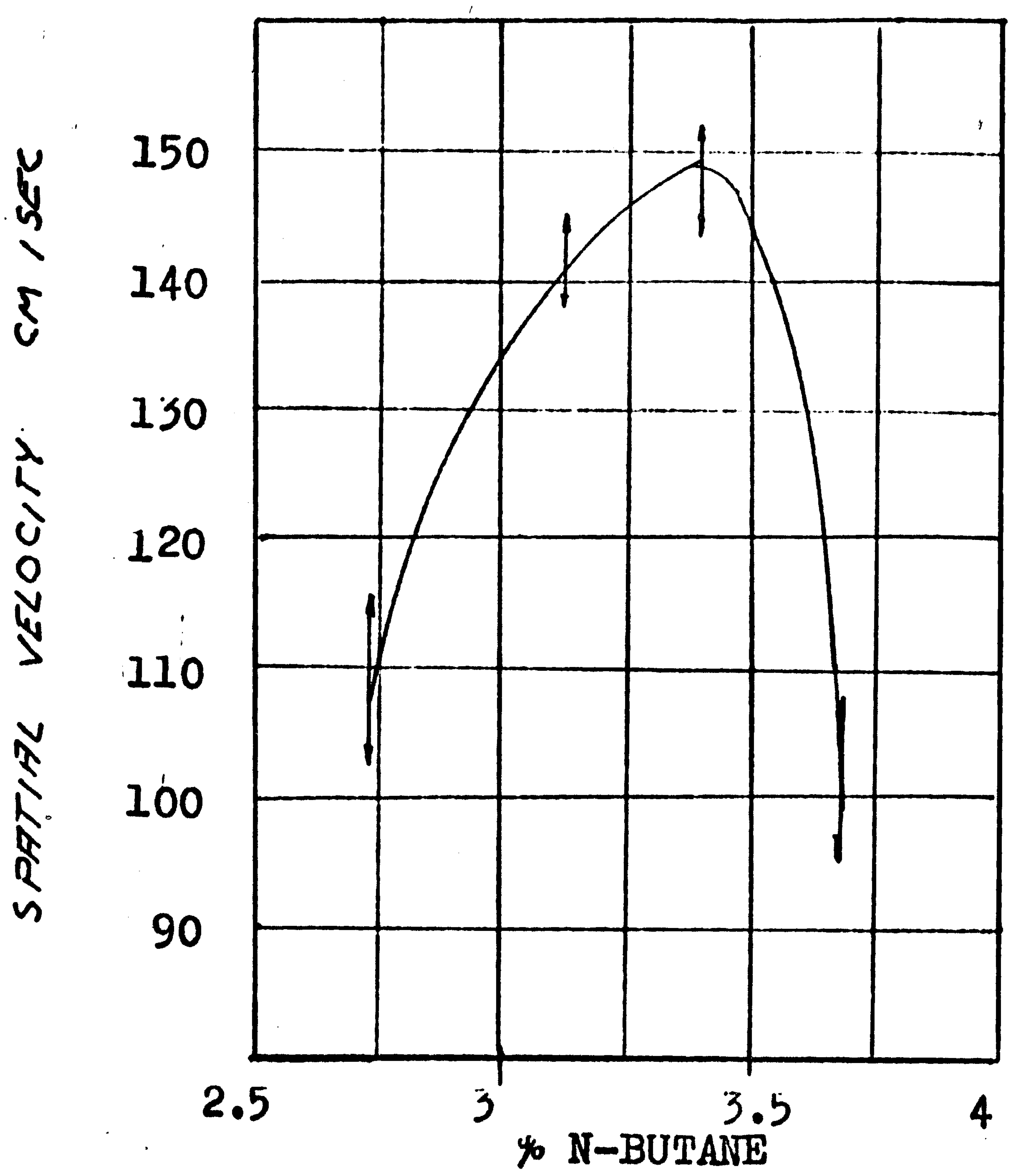


% N-BUTANE

1.27 CM ORIFICE IGNITION END
.238 CM ORIFICE UPSTREAM END
OBSERVATION POINT AT 1/4 TUBE
LENGTH FROM IGNITION POINT

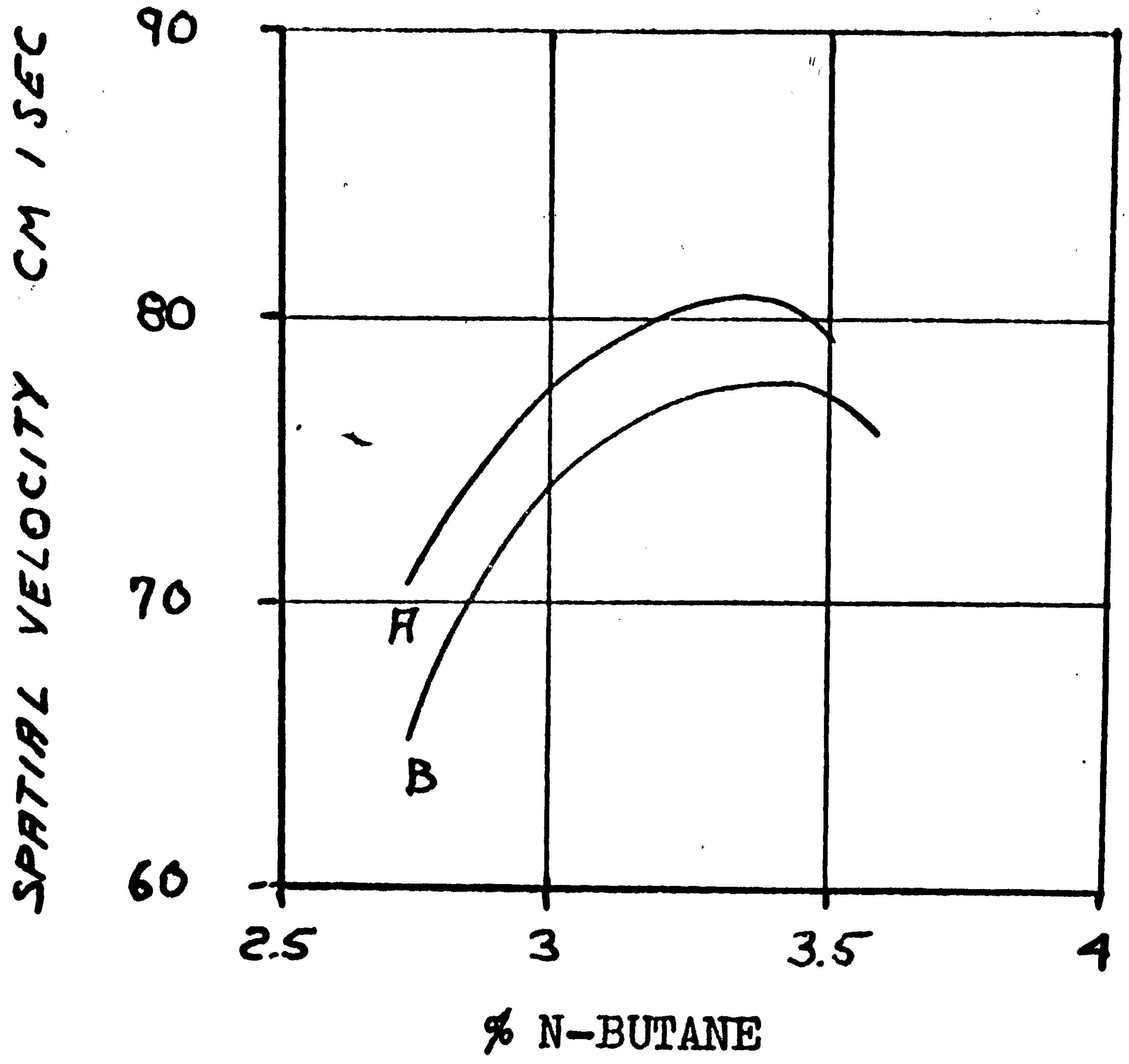
3.4 CM ID TUBE

FIG. E - 13 A



VARIATION VI TUBE METHOD

FIG E- 13 B

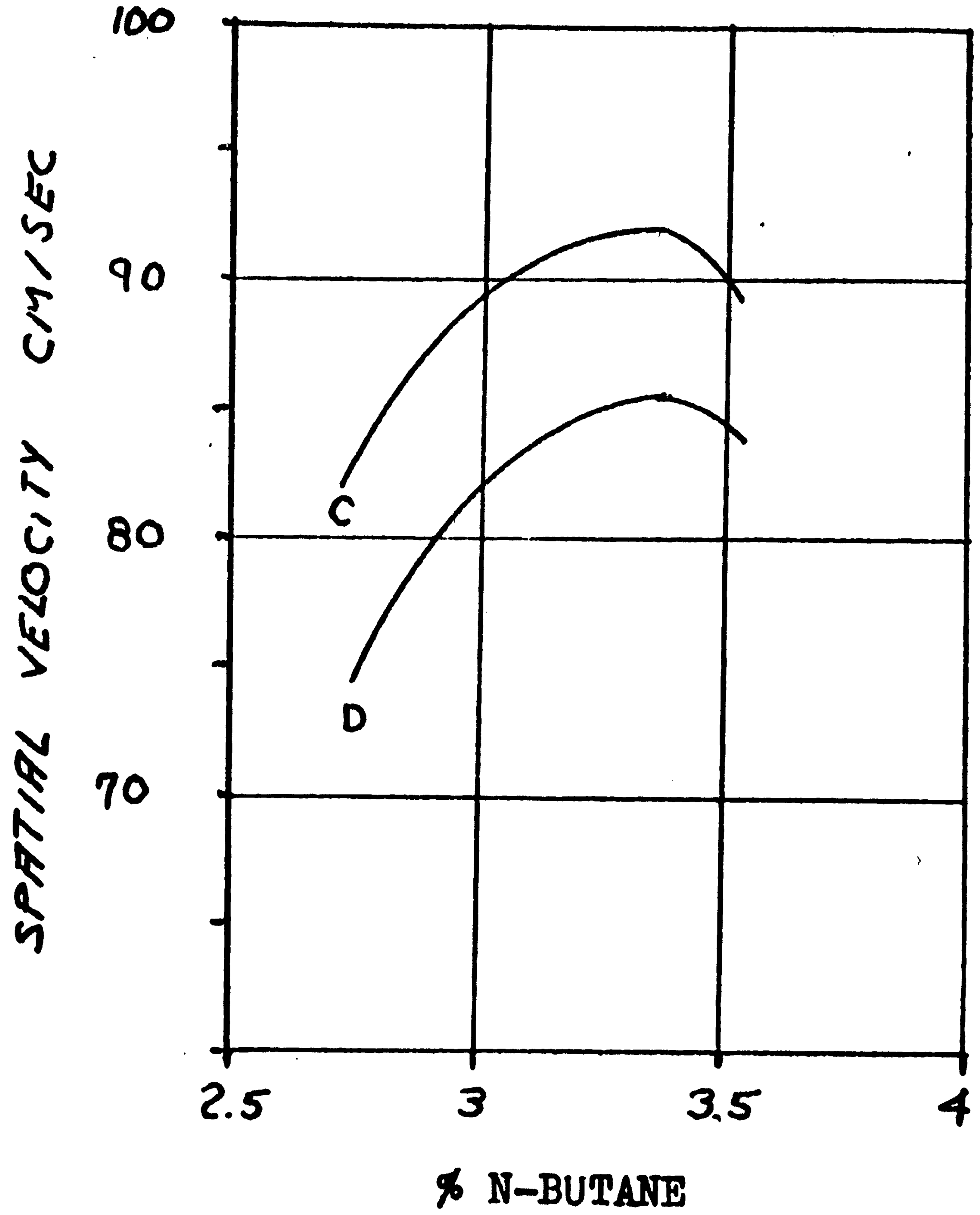


DEPENDENCE OF SPATIAL VELOCITY OF FLAMES OF BUTANE-AIR MIXTURES ON TUBE DIAMETER

CURVE A-3.4 CM ID TUBE

CURVE B-2.42 CM ID TUBE

FIG. E - 14



DEPENDENCE OF SPATIAL VELOCITY
OF FLAMES OF BUTANE-AIR MIXTURES
ON PRESENCE OF ORIFICE IN UPSTREAM
END OF TUBE

CURVE C -.238 CM ORIFICE UPSTREAM
END

CURVE D-CLOSED UPSTREAM END

3.4 CM ID TUBE

FIG. E - 15

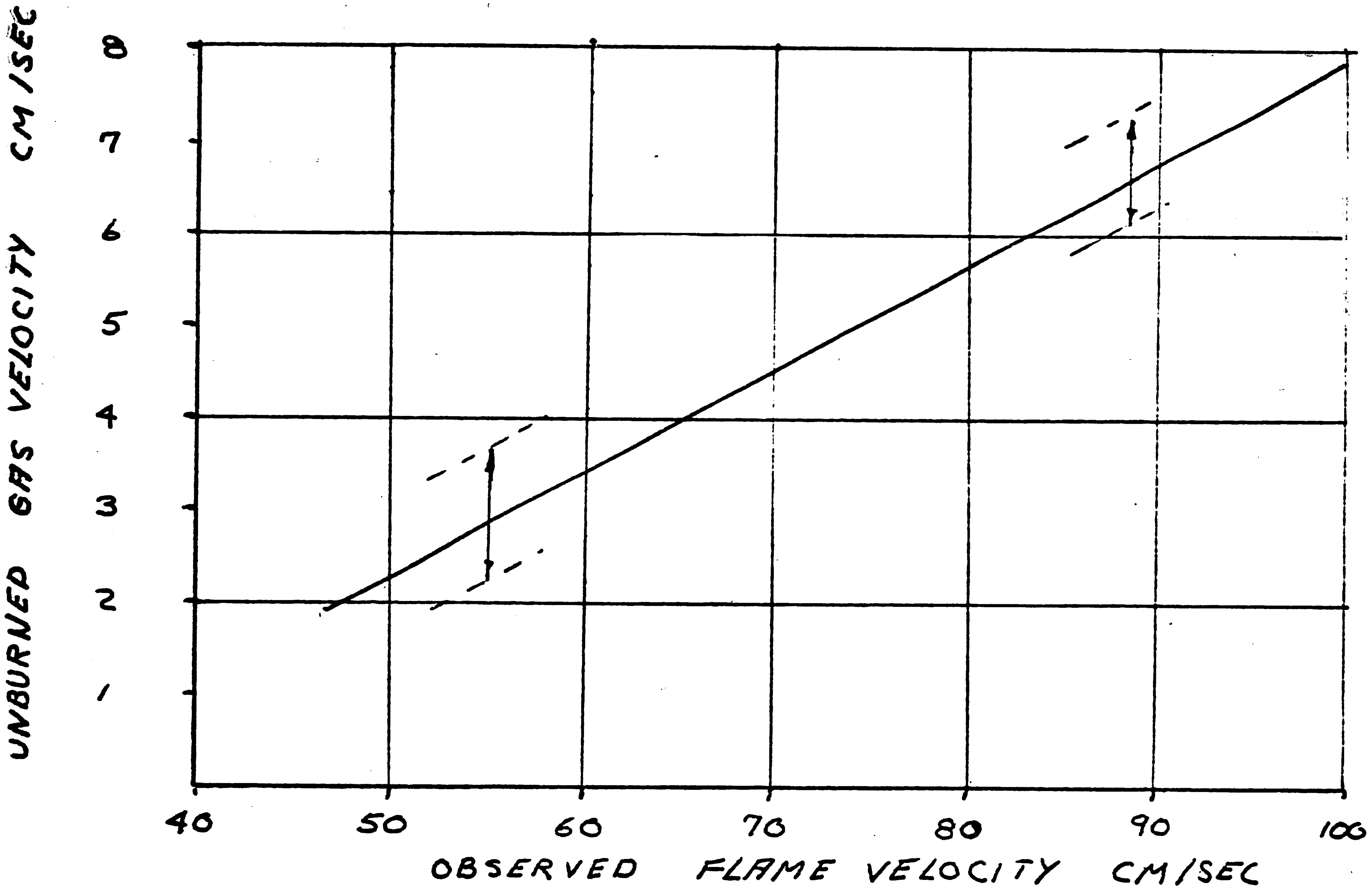
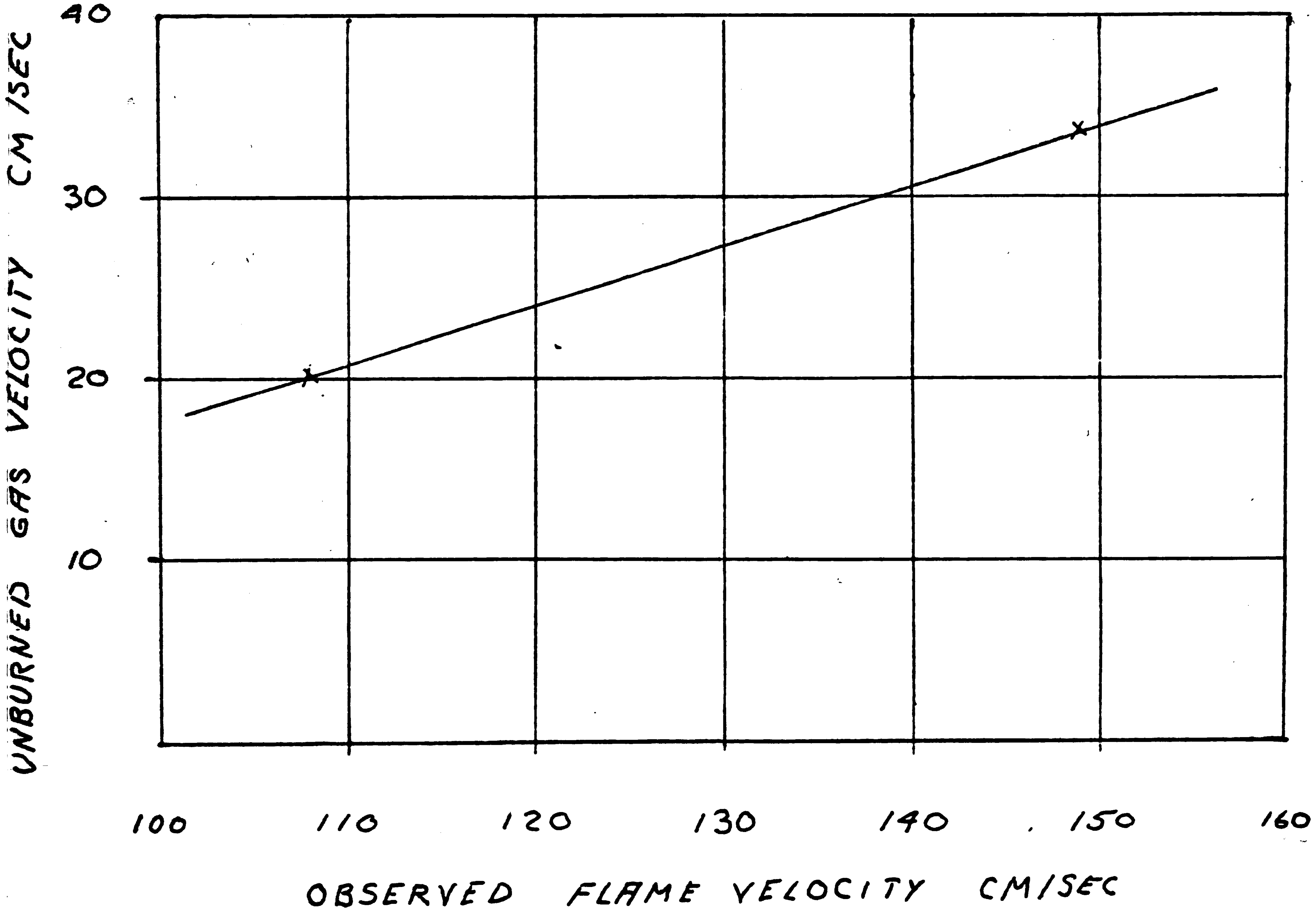
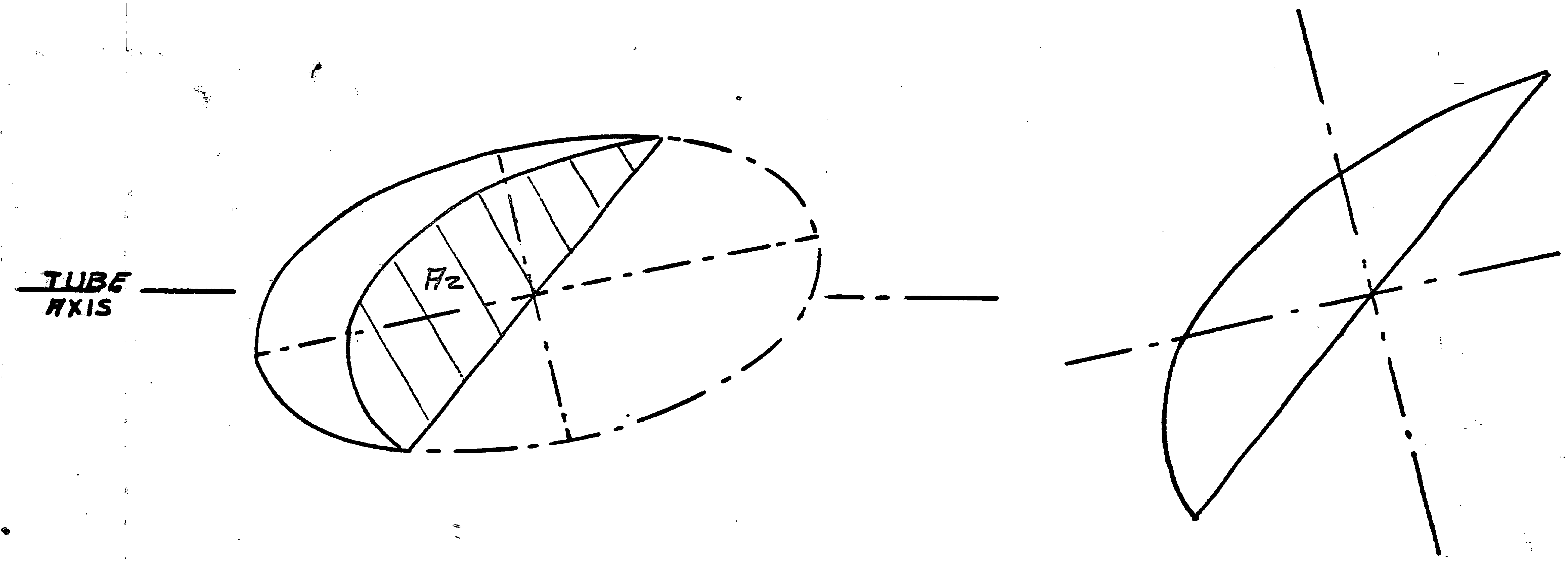

UNBURNED GAS VELOCITY CM/SEC
8
7
6
5
4
3
2
1
40
50
60
70
80
90
100
OBSERVED FLAME VELOCITY CM/SEC

FIG E-16 A

FIG E-16 B


40
30
20
10
UNBURNED GAS VELOCITY CM/SEC
100
110
120
130
140
150
160
OBSERVED FLAME VELOCITY CM/SEC

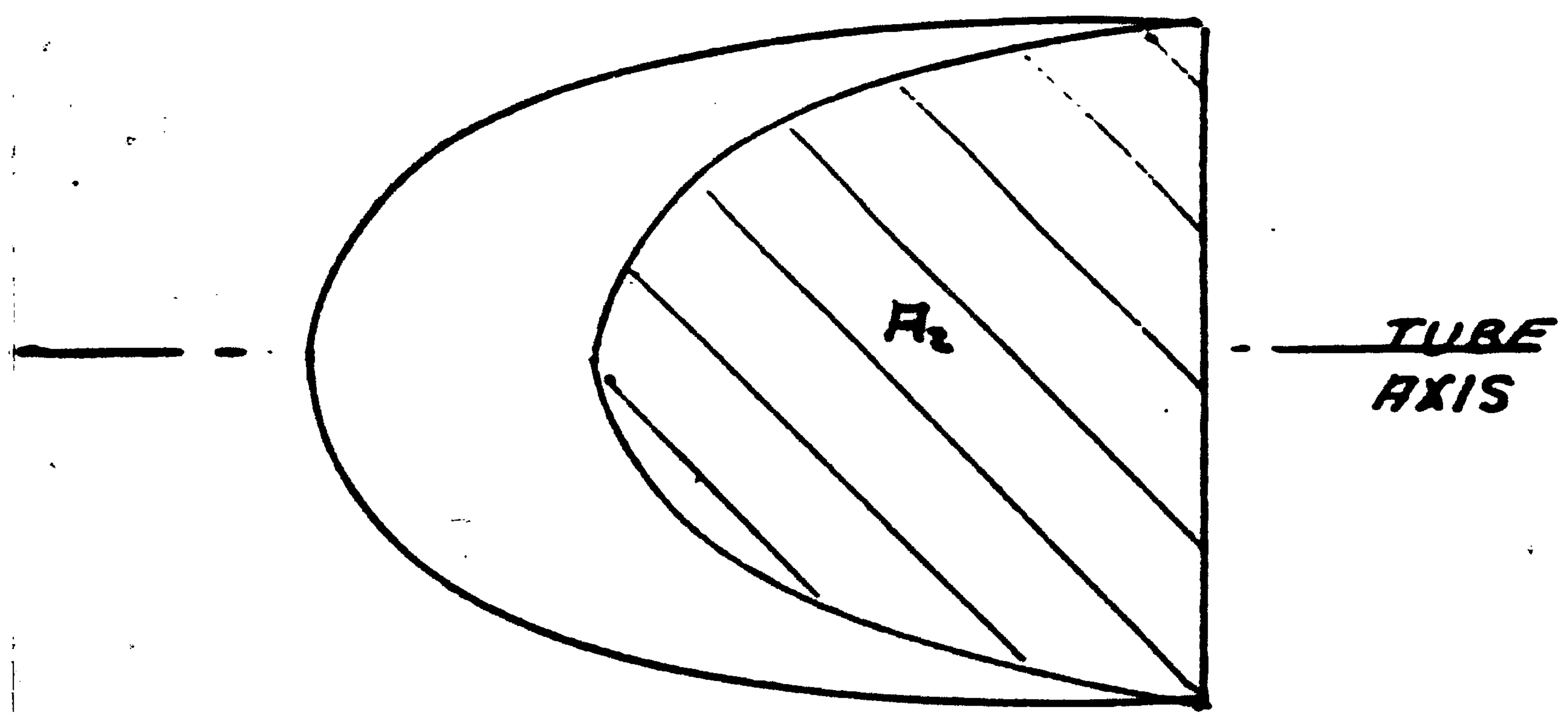
SCALE 2:1



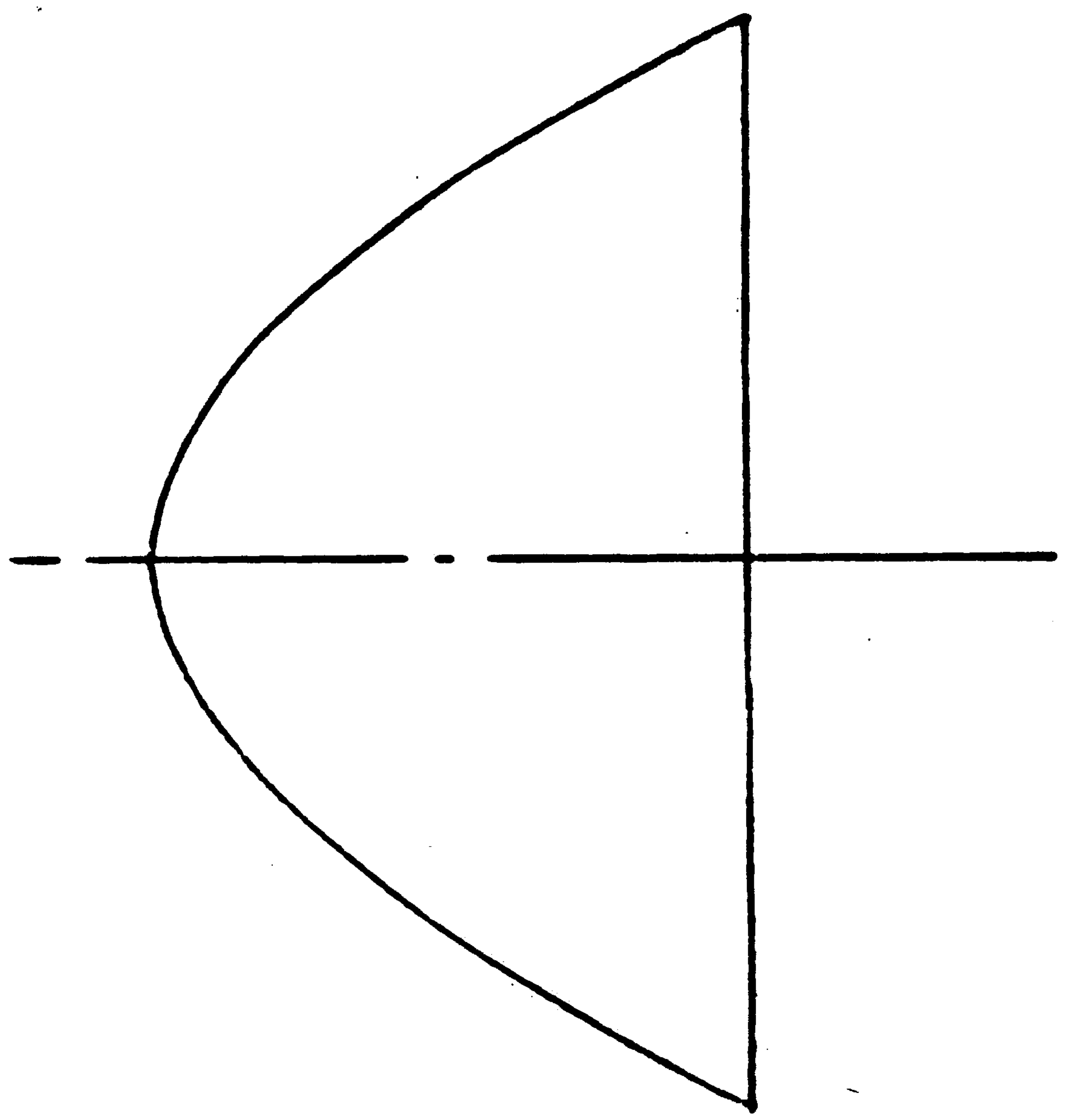
FLAME GEOMETRY
2.42 CM ID TUBE

AREA A_2

FIG E-17 A



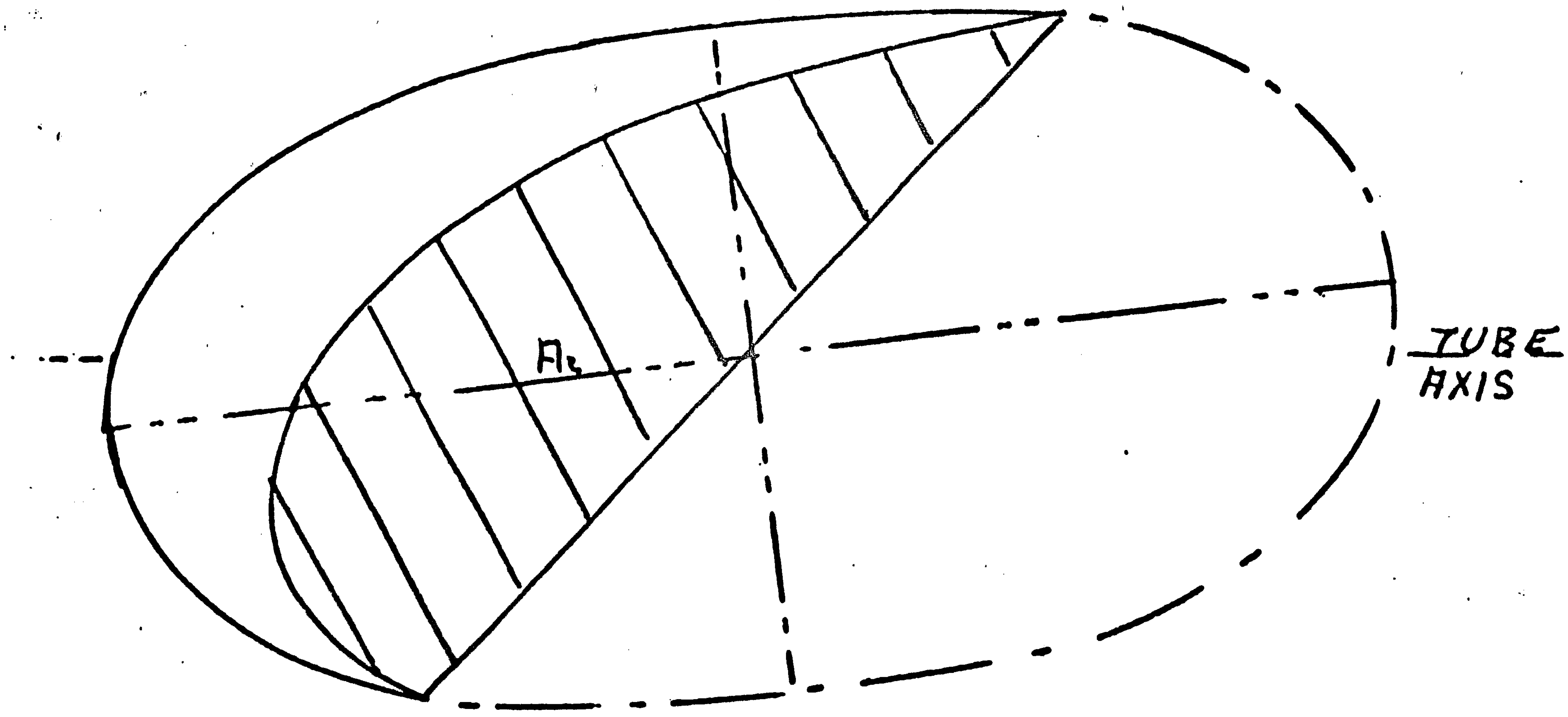
FLAME GEOMETRY
VARIATION VI



AREA A_2

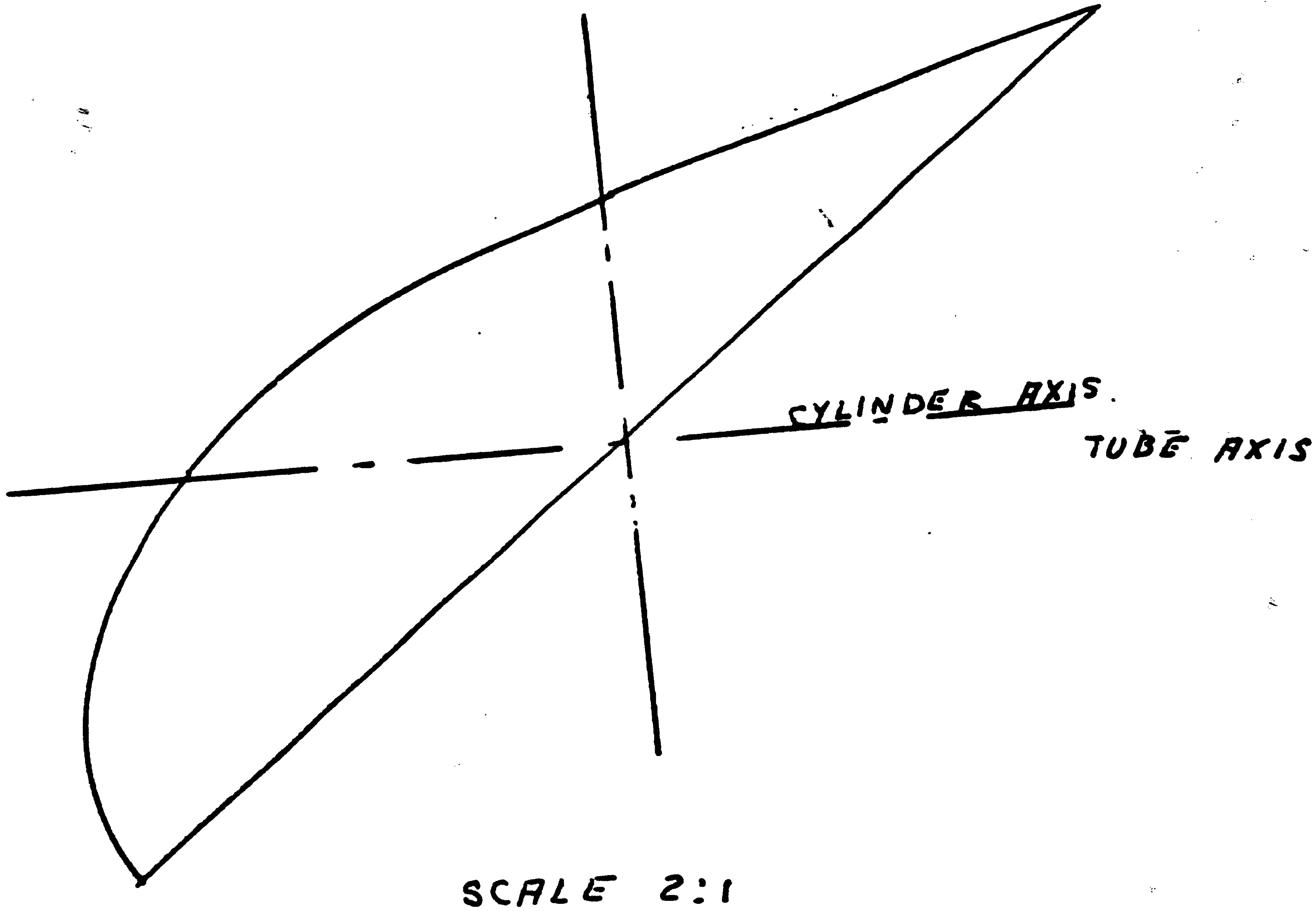
SCALE 2:1

FIG E-17B



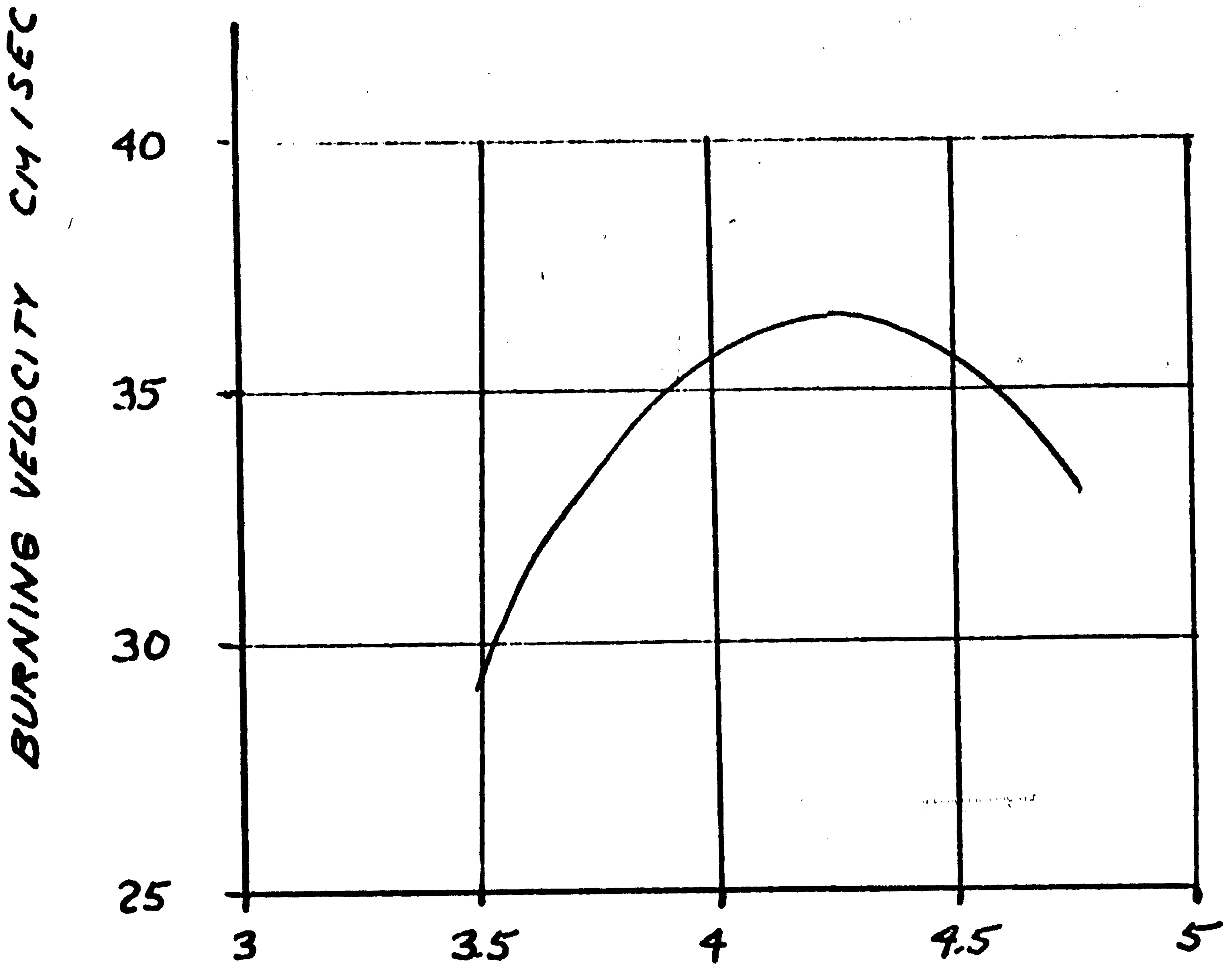
FLAME GEOMETRY
3.4 CM ID TUBE
(SCALE 2:1)

FIG E-18



SCALE 2:1

AREA A_2
3.4 CM ID TUBE
FIG E-19

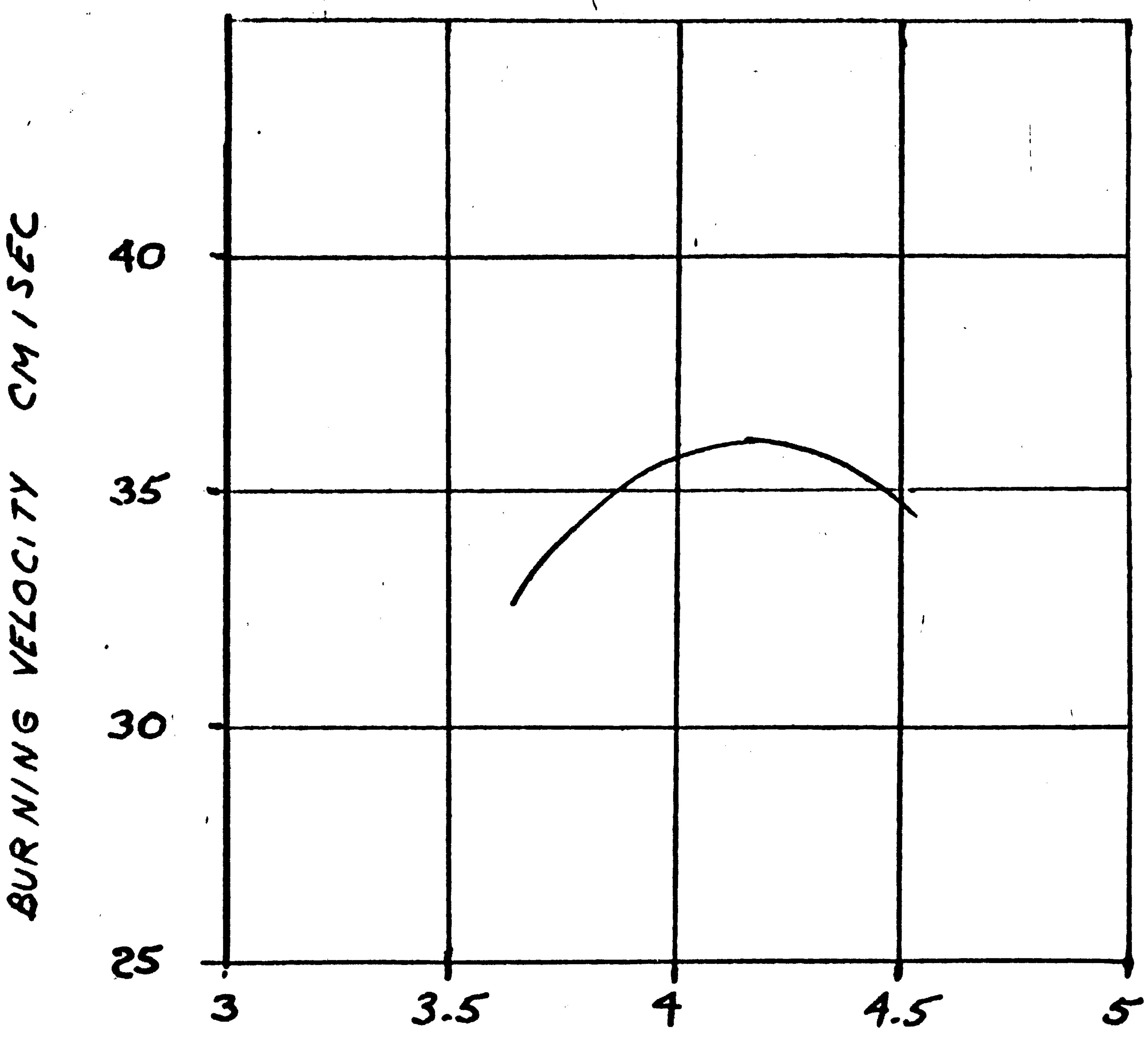


% PROPANE

TUBE METHOD

OPEN IGNITION END (NO ORIFICE USED)
CLOSED UPSTREAM END
2.42 CM ID TUBE

FIG. E - 20

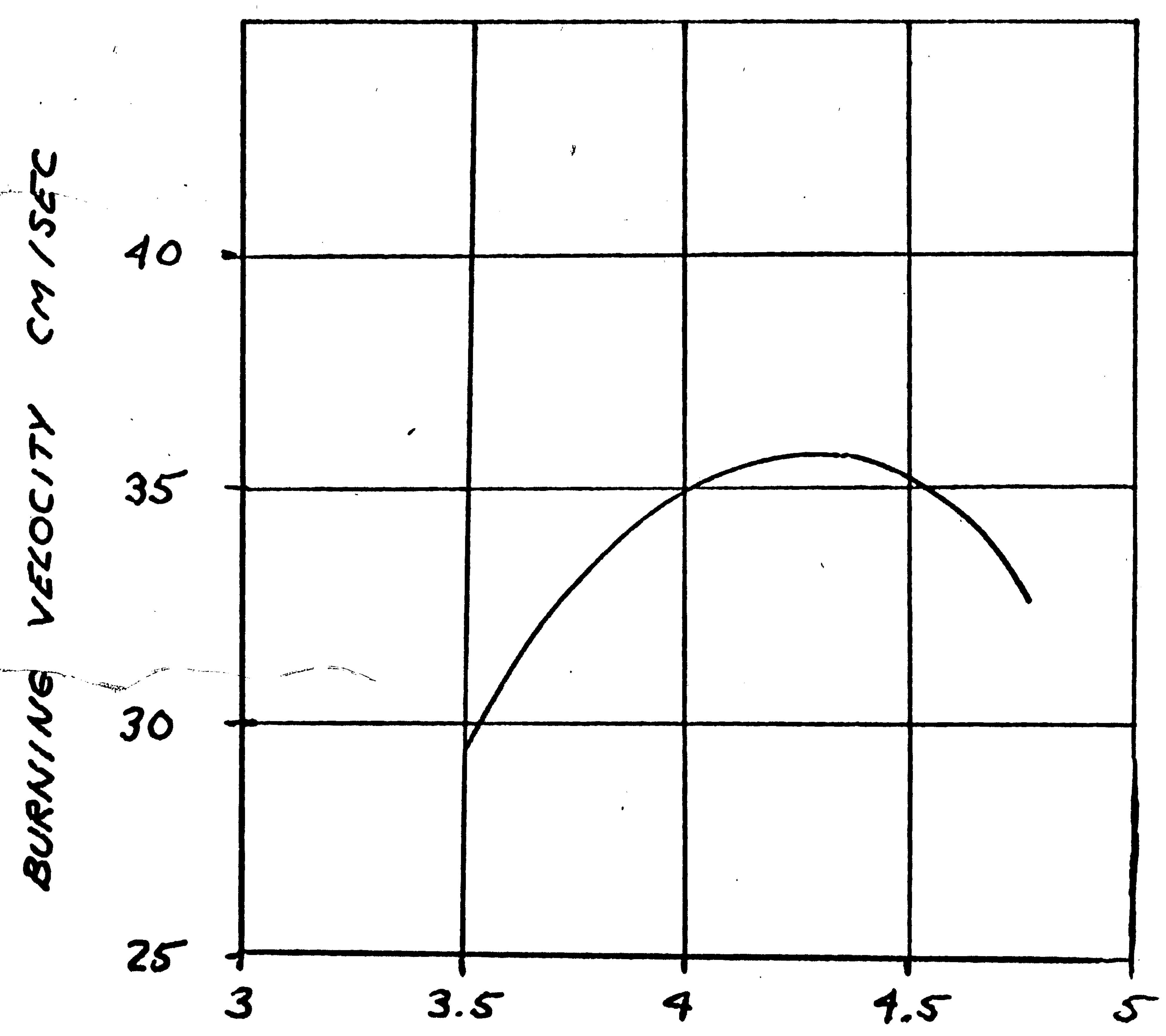


% PROPANE

TUBE METHOD

.795 CM ORIFICE IGNITION END
.198 CM ORIFICE UPSTREAM END
2.42 CM ID TUBE

FIG. E - 21

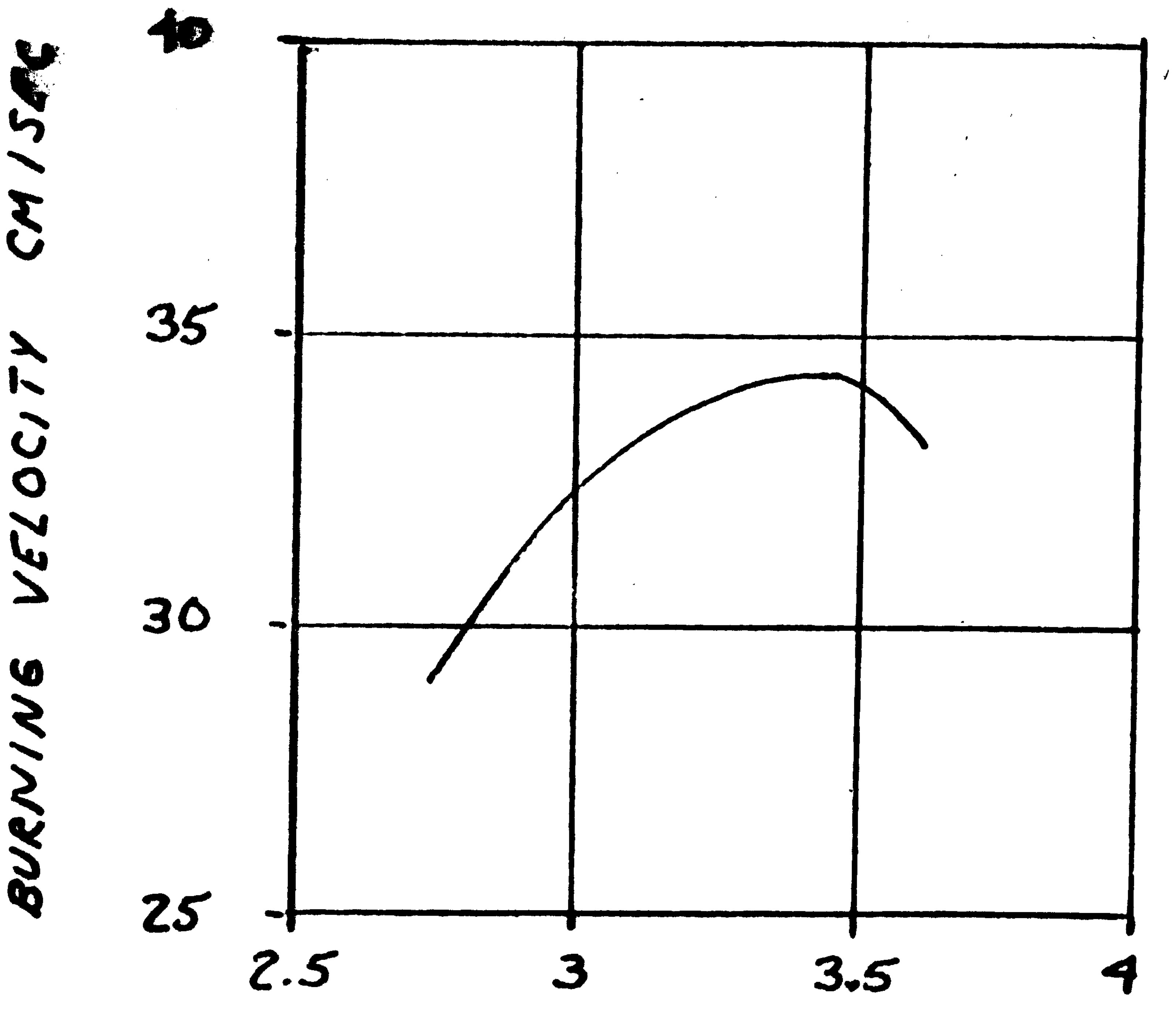


% PROPANE

TUBE METHOD

3.4 CM ID TUBE
OPEN IGNITION END (NO ORIFICE USED)
CLOSED UPSTREAM END

FIG. E - 22



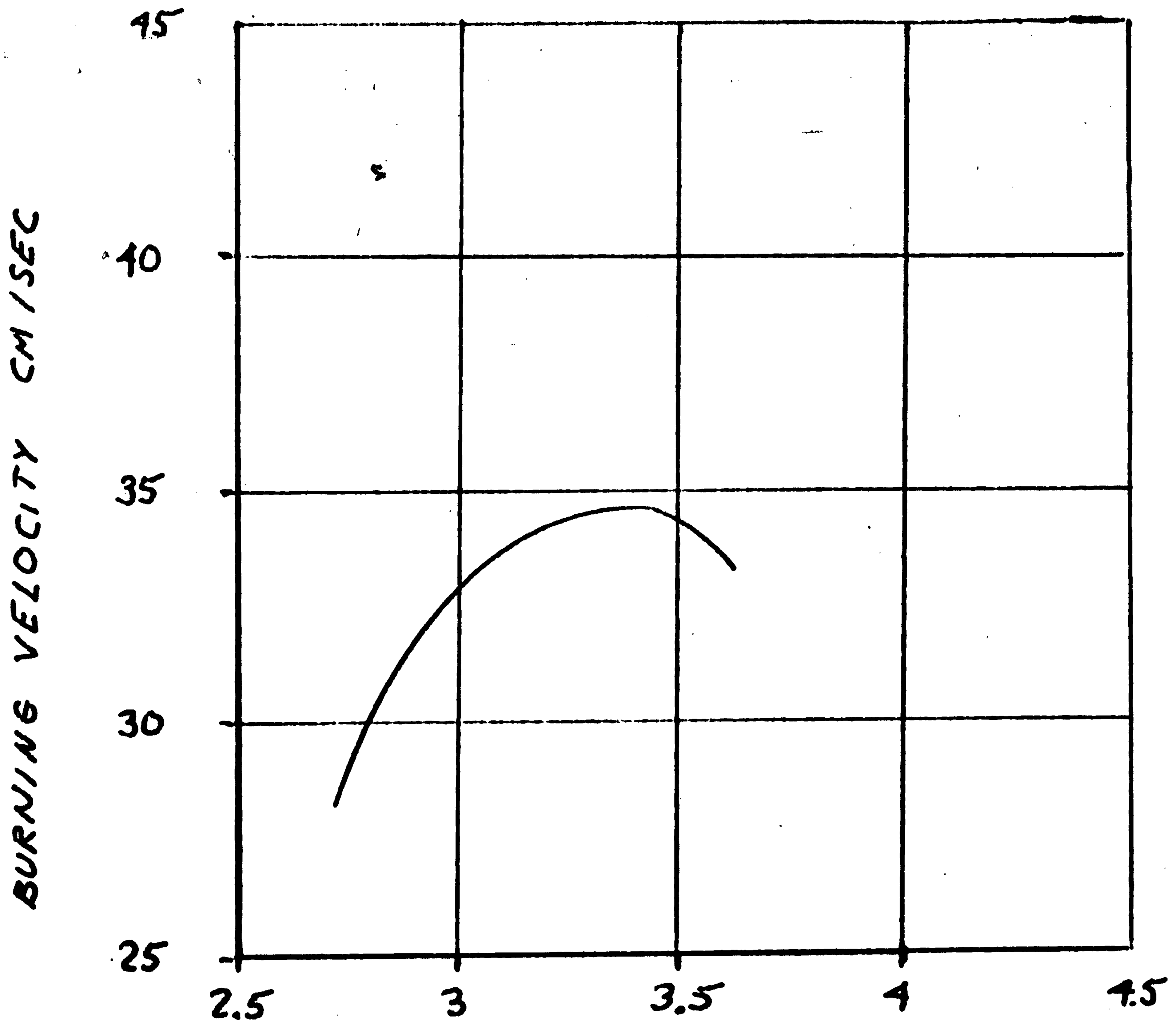
% N-BUTANE

TUBE METHOD

OPEN IGNITION END (NO ORIFICE USED)
CLOSED UPSTREAM END

2.42 CM ID TUBE

FIG. E - 23



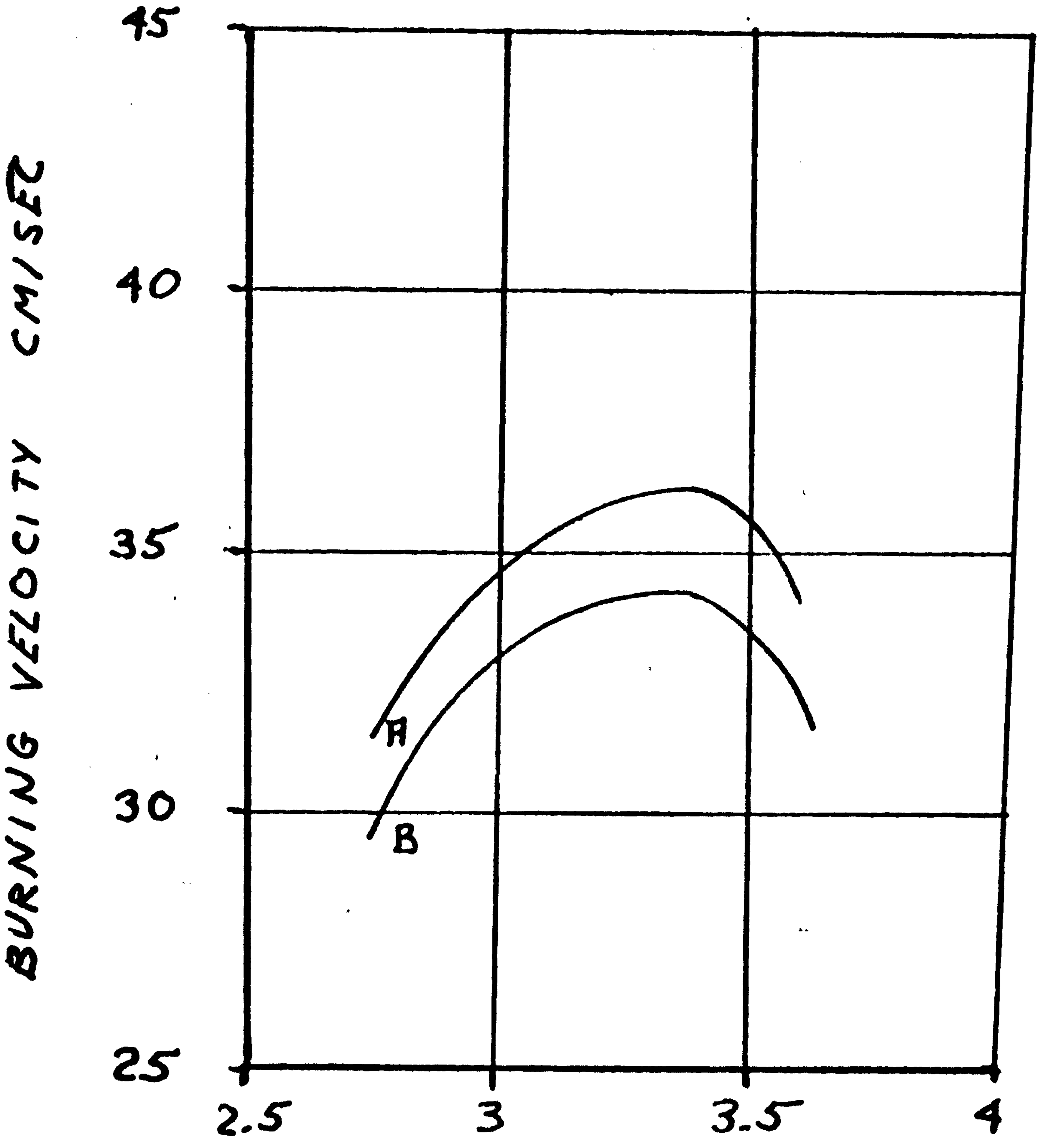
% N-BUTANE

TUBE METHOD

.795 CM ORIFICE IGNITION END
CLOSED UPSTREAM END

2.42 CM ID TUBE

FIG. E - 24



% N-BUTANE

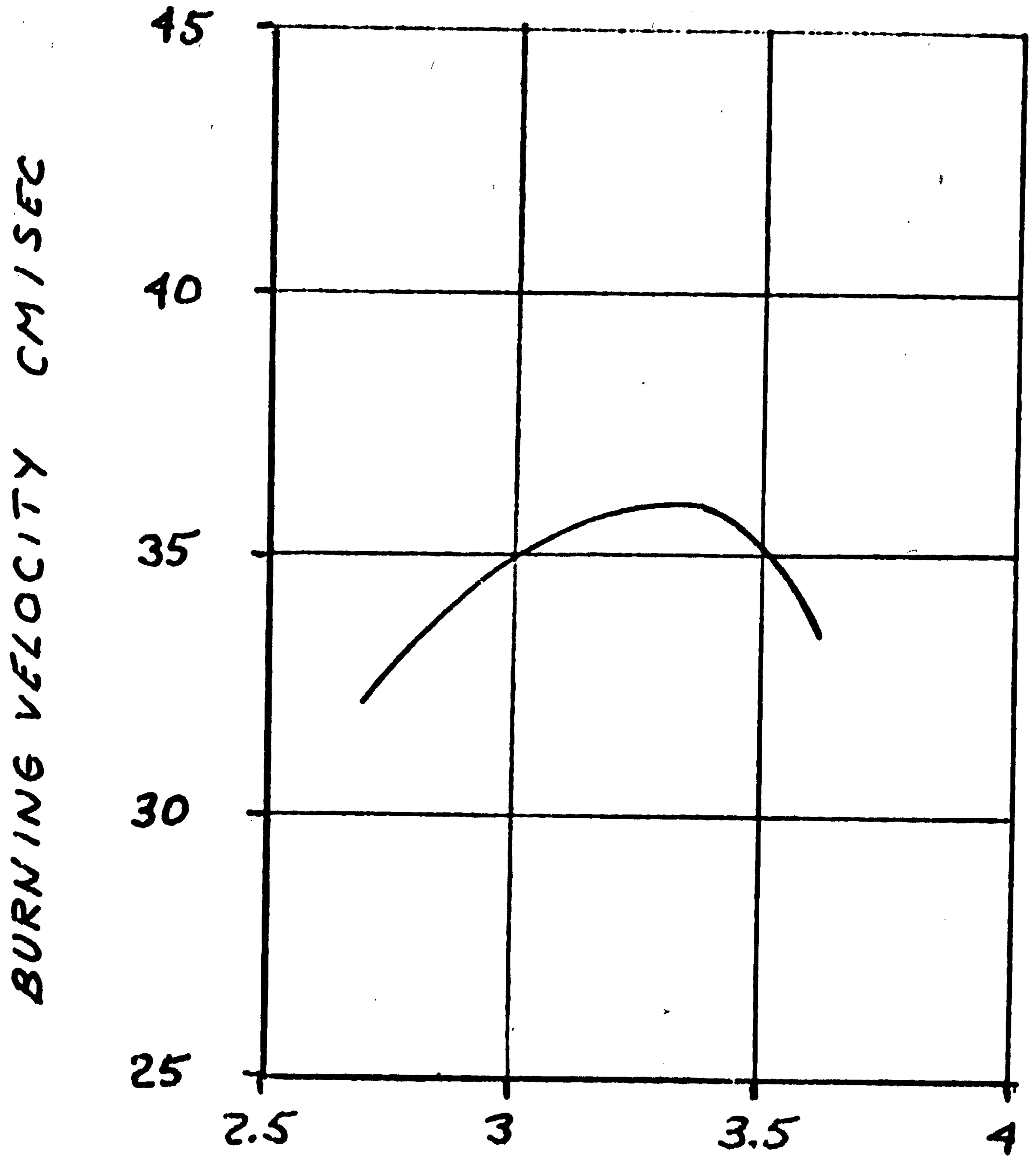
TUBE METHOD

3.4 CM ID TUBE
CLOSED UPSTREAM END

CURVE A - 1.27 CM ORIFICE
IGNITION END

CURVE B - OPEN IGNITION END
NO ORIFICE USED

FIG. E - 25

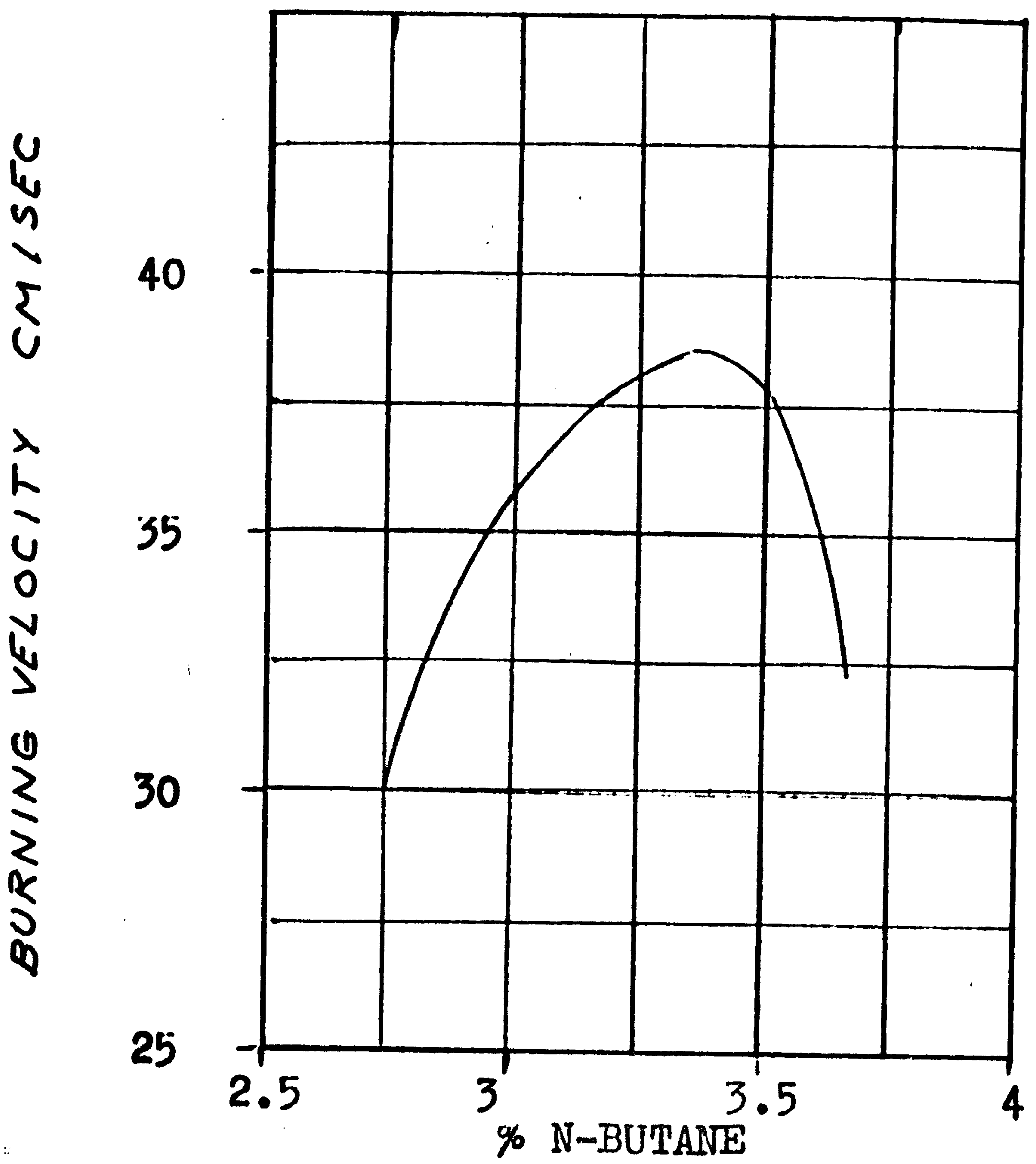


% N-BUTANE

TUBE METHOD

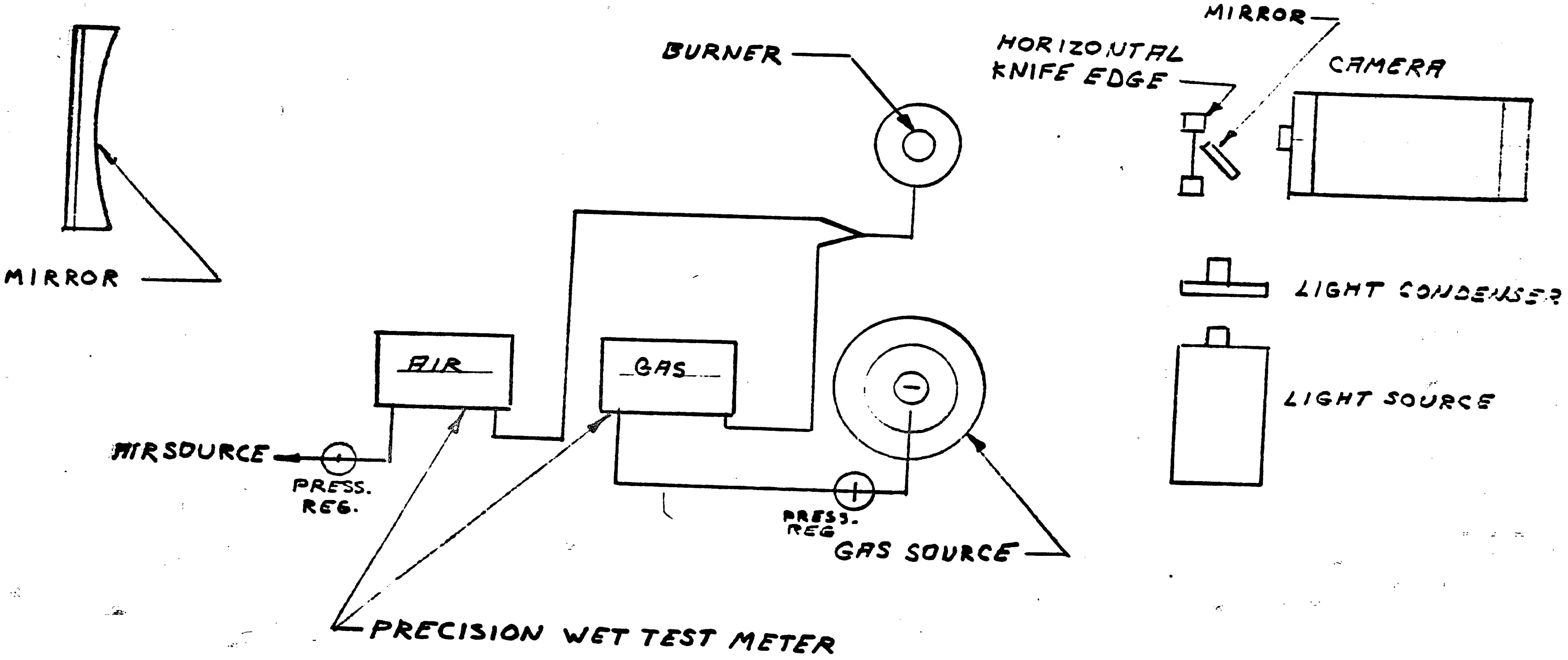
3.4 CM ID TUBE
1.27 CM ORIFICE IGNITION END
.238 CM ORIFICE UPSTREAM END

FIG. E - 26 A



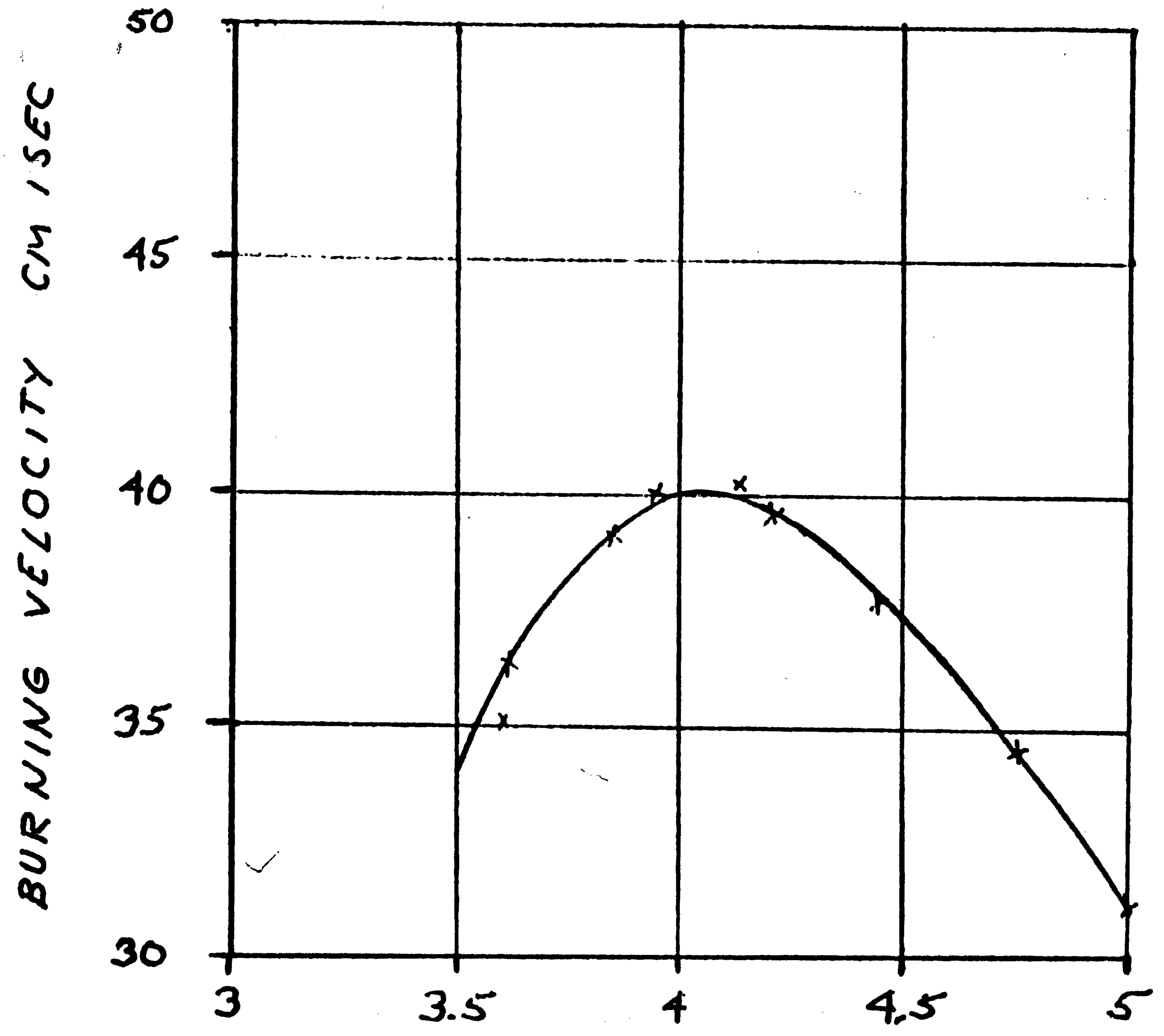
VARIATION VI TUBE METHOD

FIG E-26 B



APPARATUS - BURNER METHOD

FIG. E-27

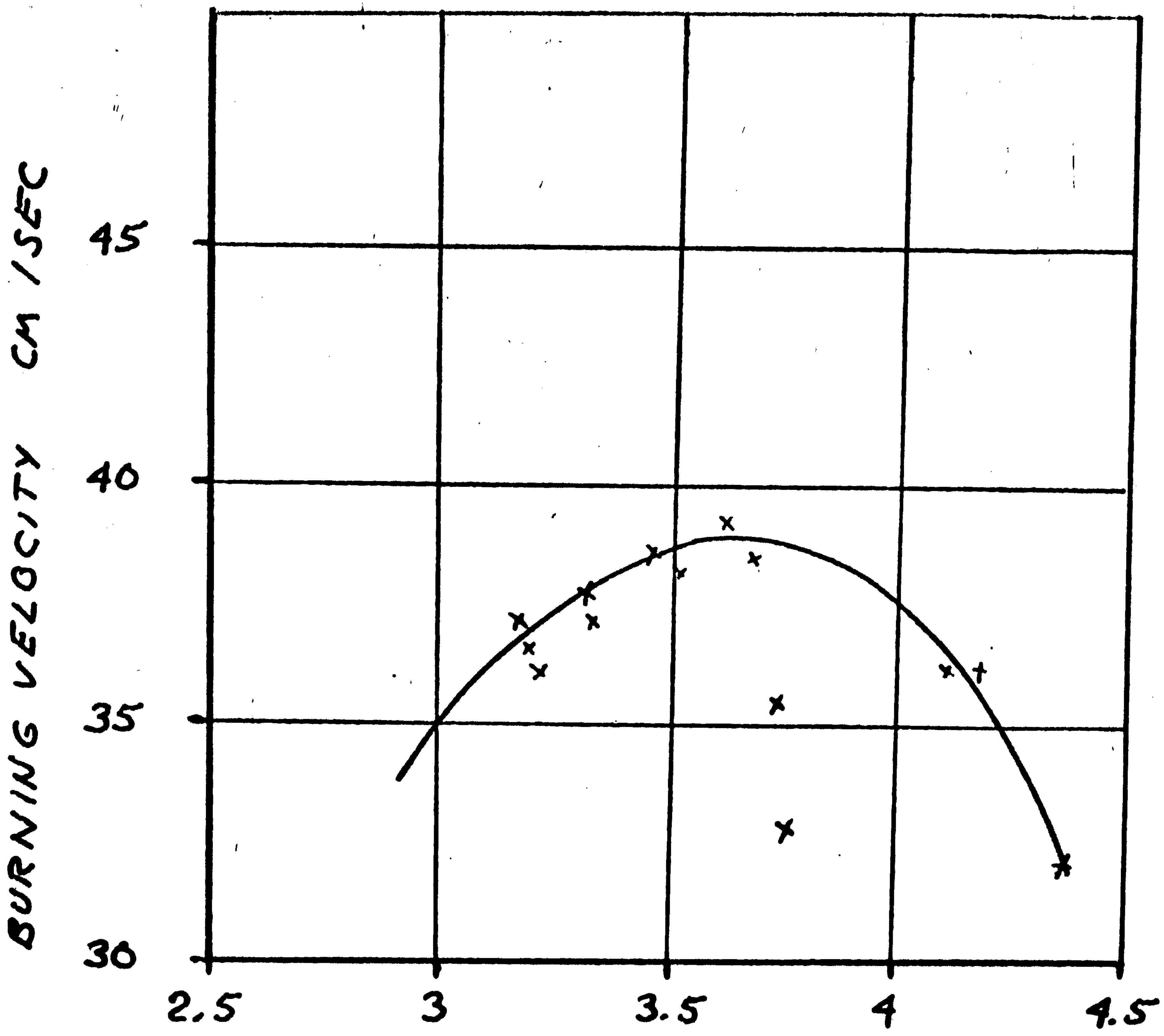


% PROPANE

BURNER METHOD

SCHLIEREN CONE

FIG. E - 28

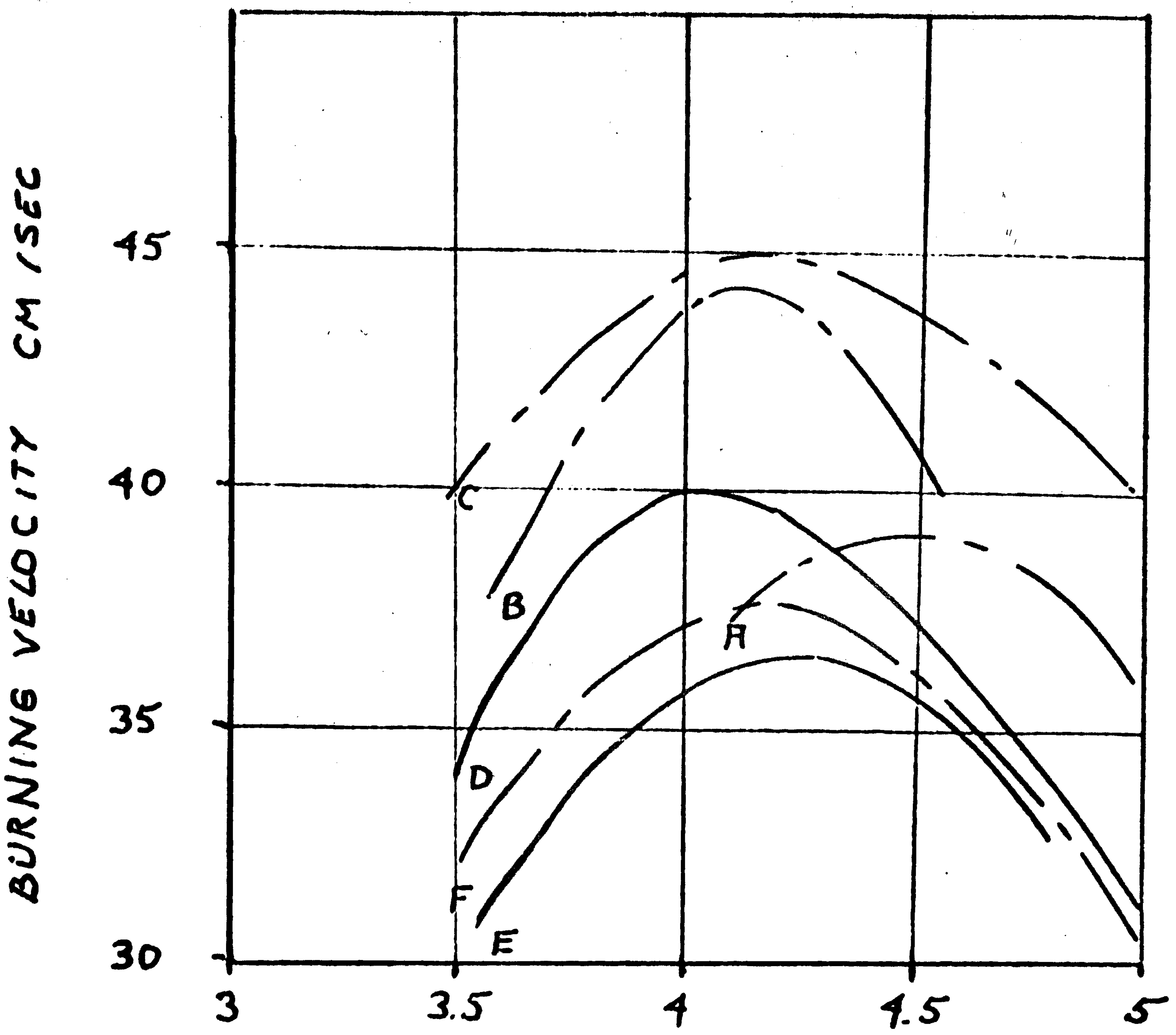


% N-BUTANE

BURNER METHOD

SCHLIEREN CONE

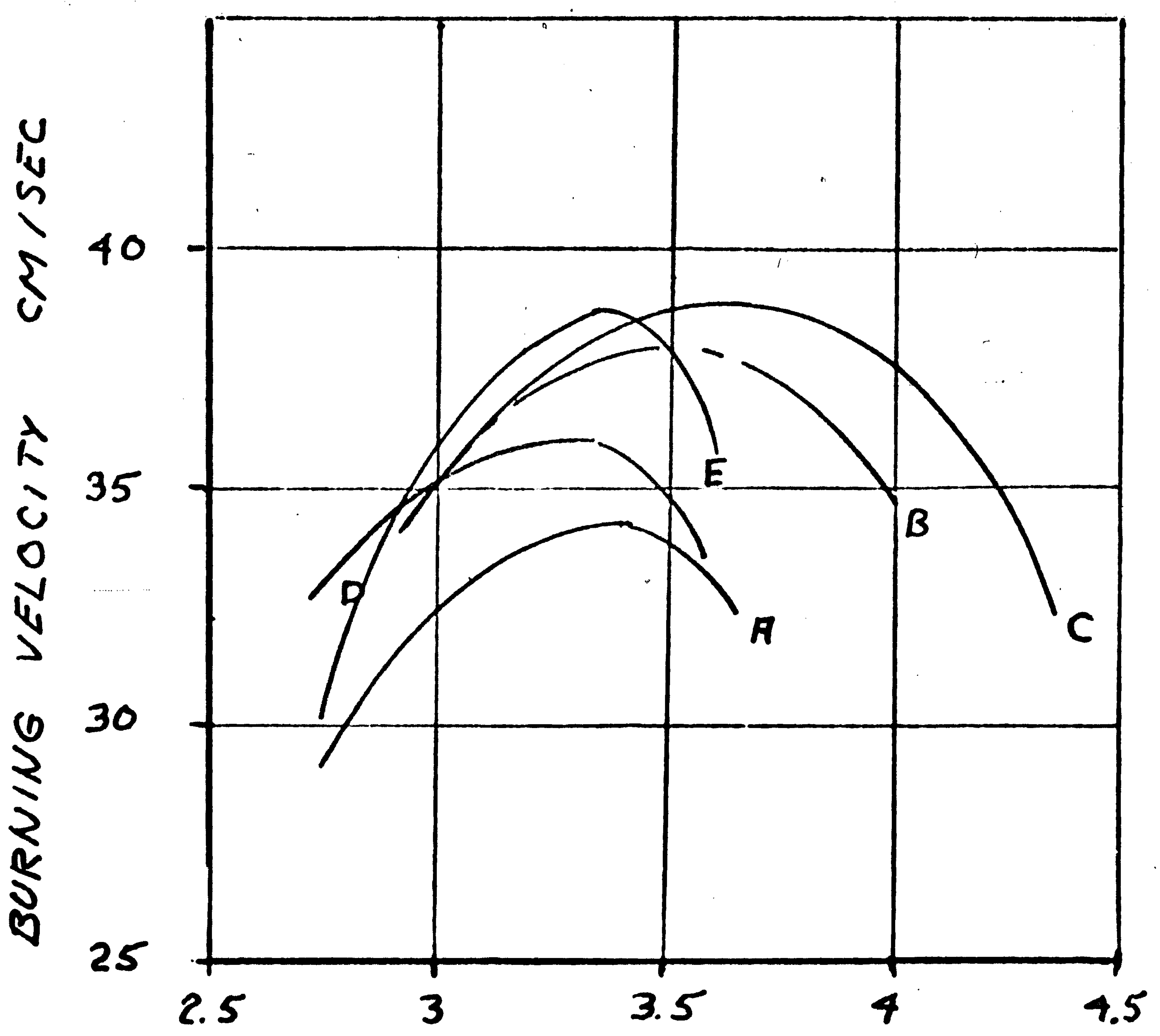
FIG. E - 29



% PROPANE

CURVE A	TUBE METHOD - GERSTEIN, LEVINE & WONG (27)
CURVE B	ANGLE METHOD AT ONE POINT OF VISIBLE CONE OF BUNSEN BURNER - SMITH & PICKERING (57)
CURVE C	BUNSEN BURNER - PARTICLE TRACK METHOD - ANDERSEN & FEIN (1)
CURVE D	BURNER METHOD - TOTAL SCHLIEREN CONE - DINICOLANTONIO
CURVE E	TUBE METHOD - DINICOLANTONIO
CURVE F	BURNER METHOD - SCHLIEREN CONE. BROEZE (5)

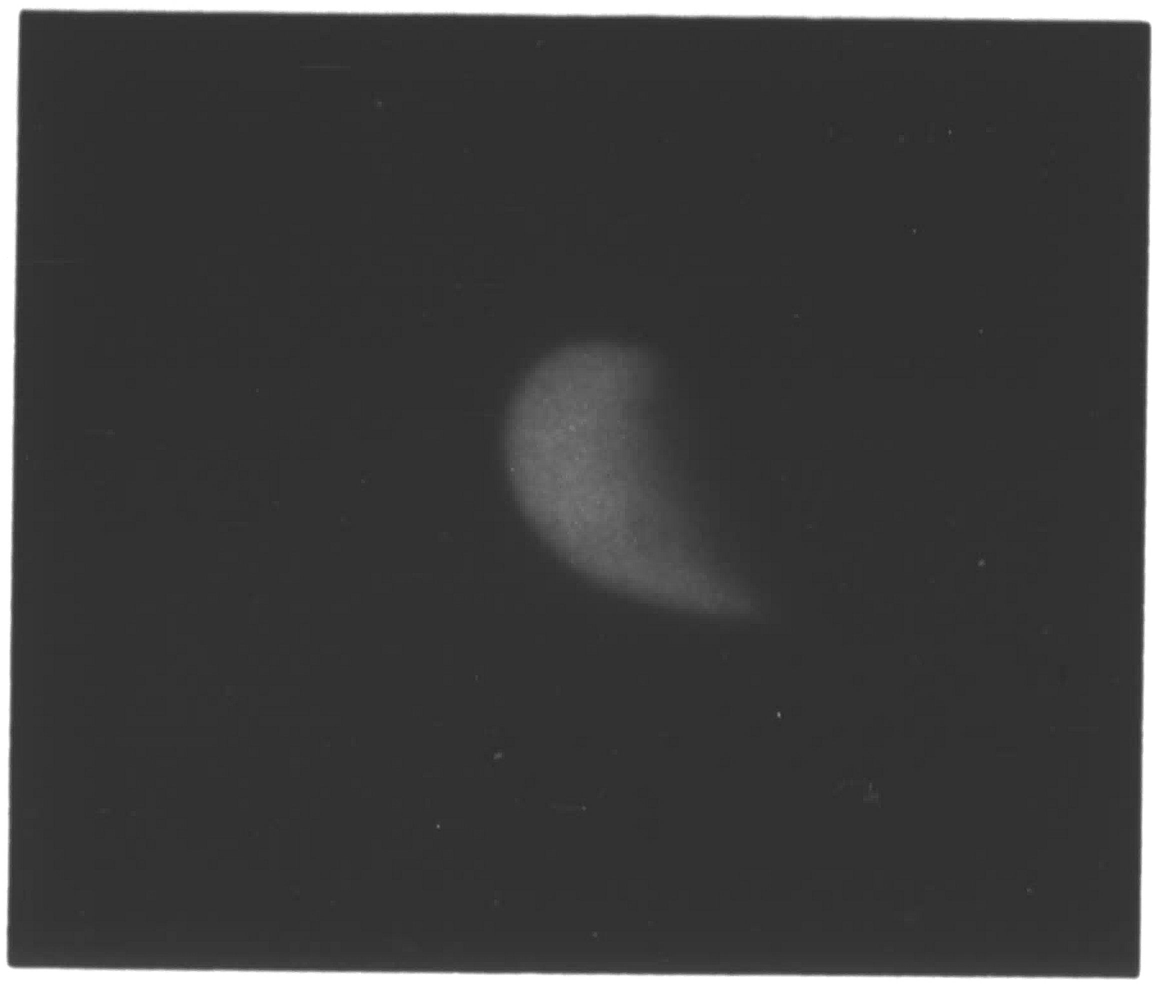
FIG. E - 30



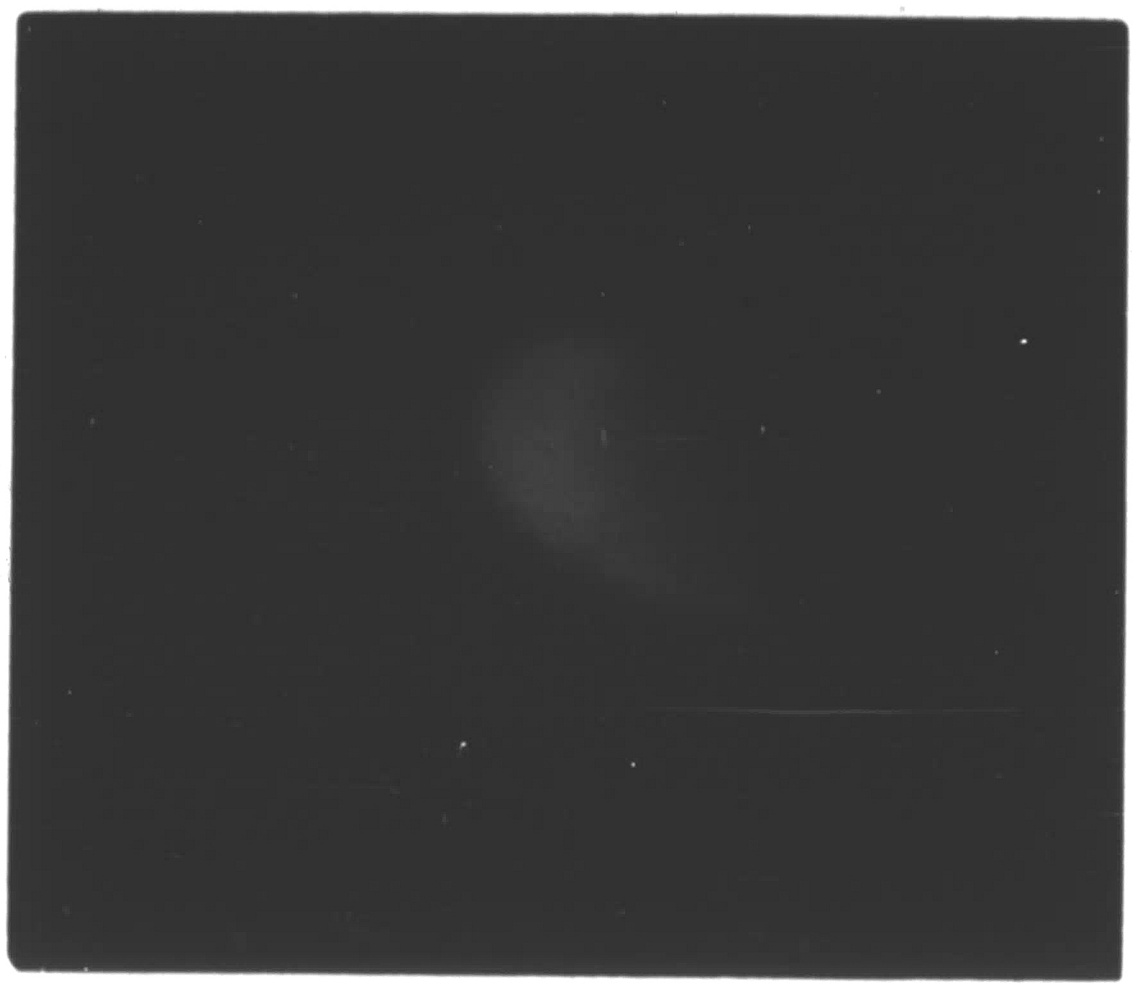
% N-BUTANE

CURVE A	TUBE METHOD -	VARIATION I DINICOLANTONIO
CURVE B	TUBE METHOD -	GERSTEIN, LEVINE, & WONG (27)
CURVE C	BURNER METHOD -	SCHLIEREN CONE DINICOLANTONIO
CURVE D	TUBE METHOD -	PROCEDURE OF GERSTEIN et al VARIATION V DINICOLANTONIO
CURVE E	**TUBE METHOD** -	VARIATION VI DINICOLANTONIO

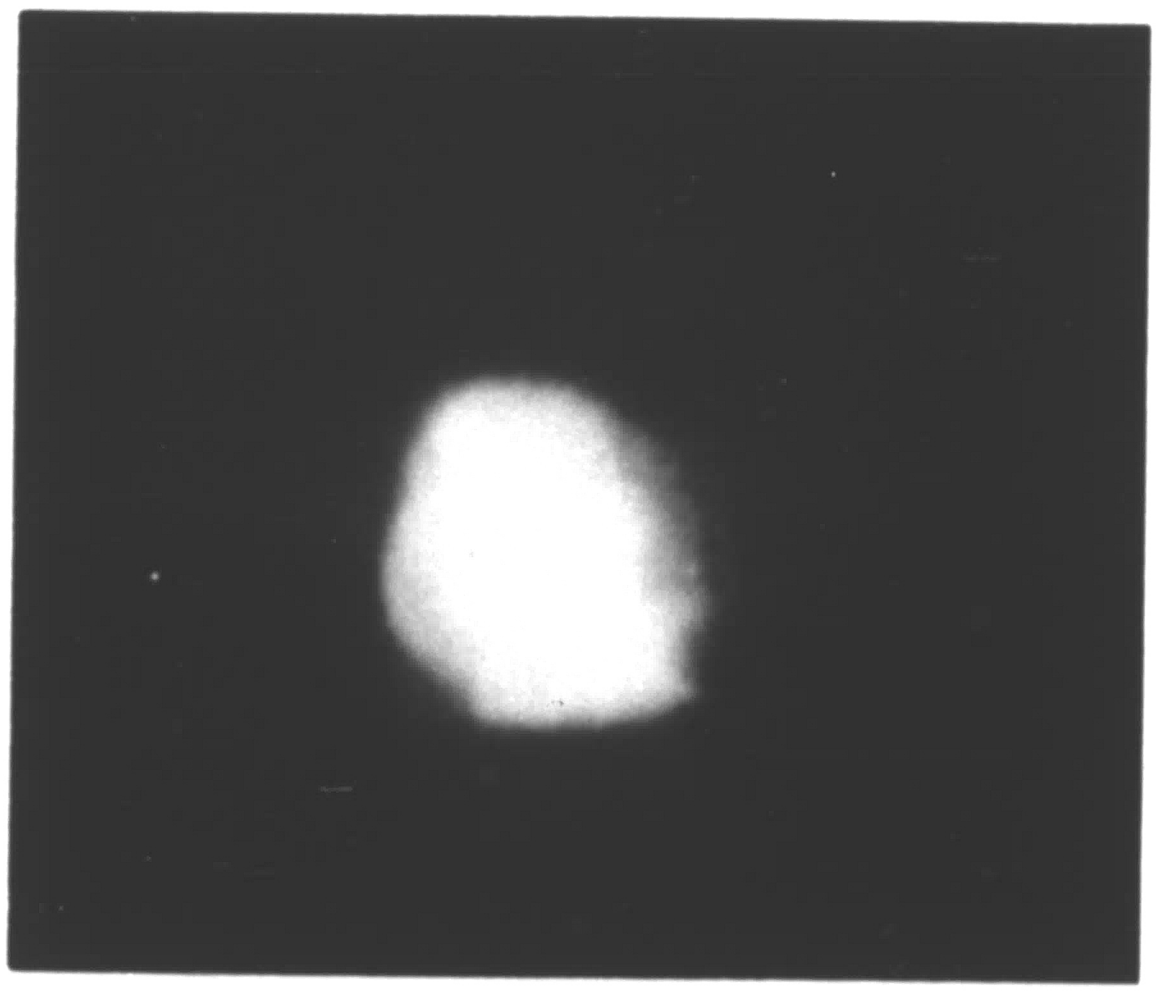
FIG E-31



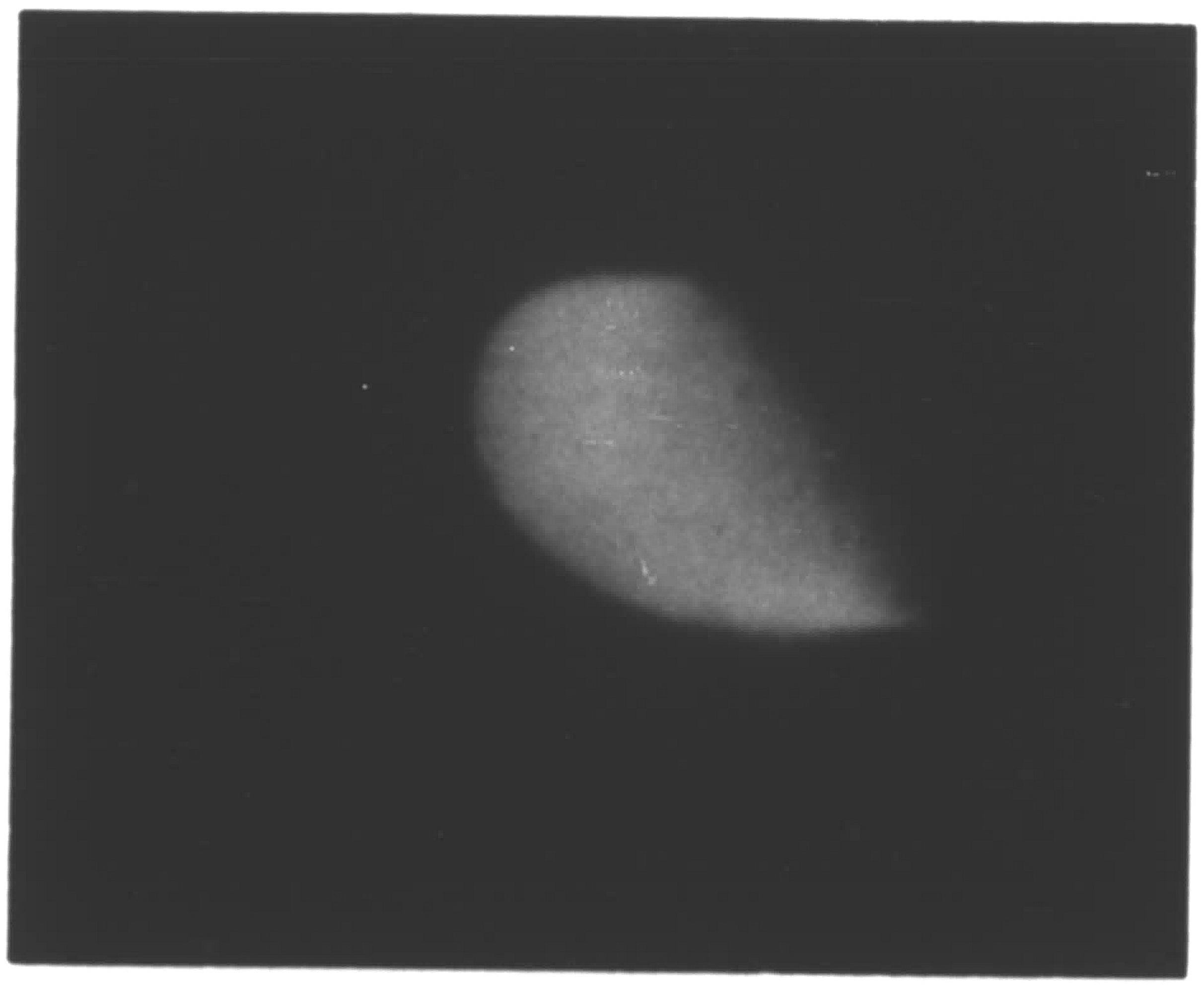
Laminar Propane Flame
2.42 cm ID Tube



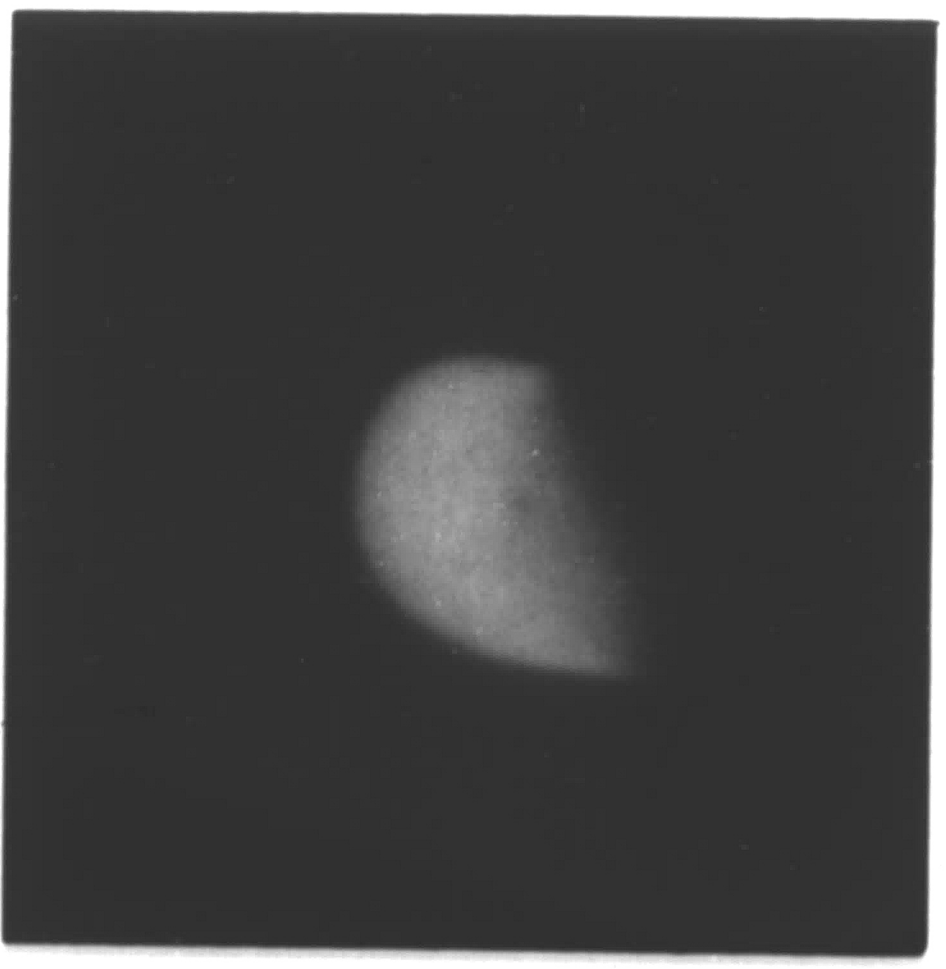
Laminar Butane Flame
2.42 cm ID Tube



Turbulent Propane Flame
3.4 cm ID Tube

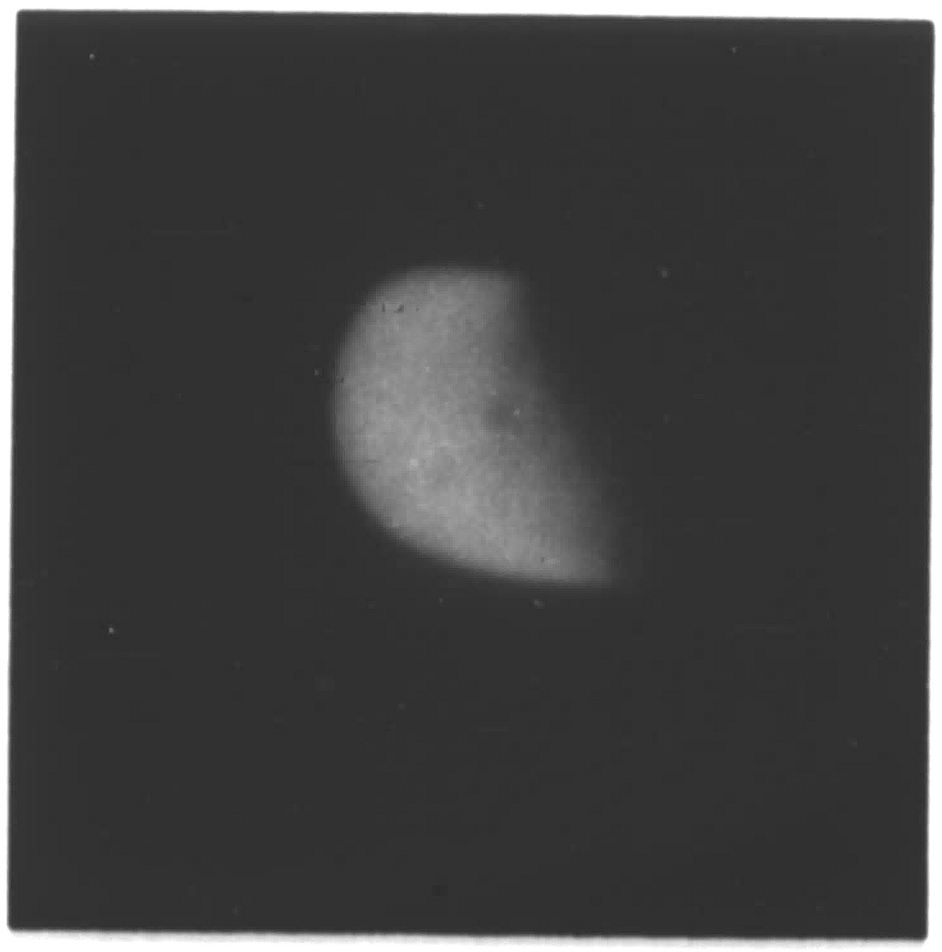


Laminar Propane Flame
3.4 cm ID Tube

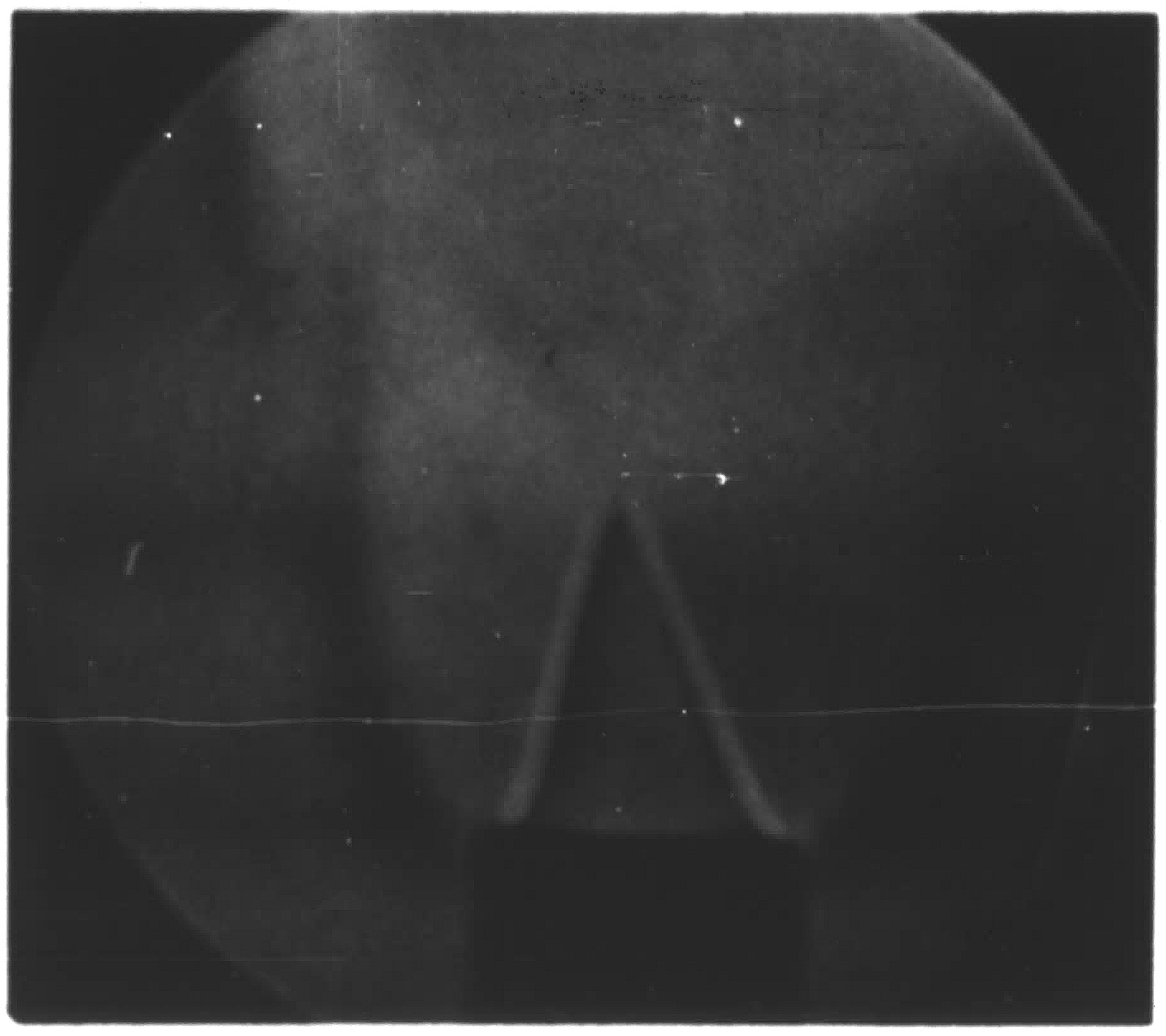


Laminar Propane Flame
3.4 cm ID Tube

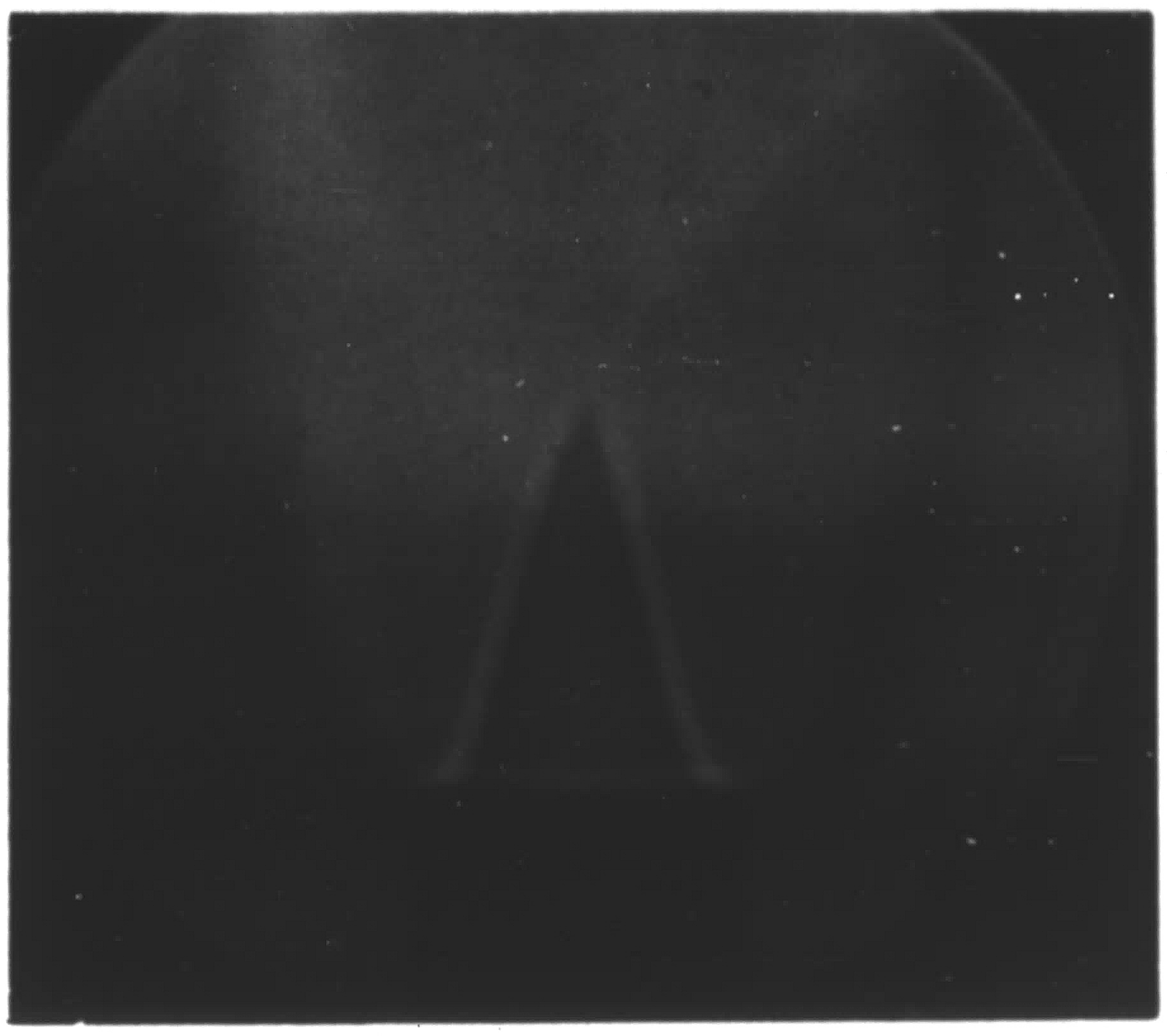
FIG F-32



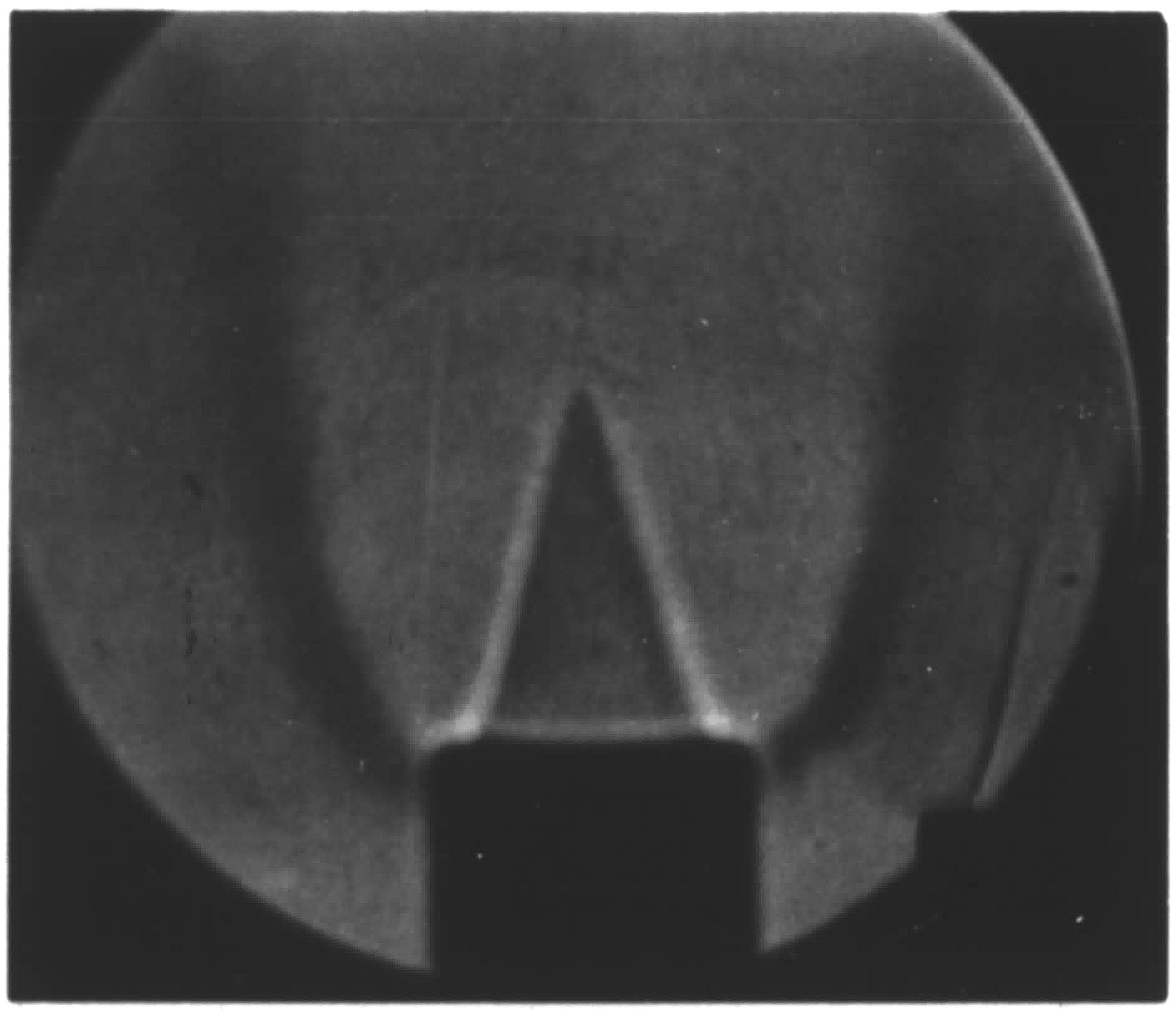
Laminar Butane Flame
3.4 cm ID Tube



3.58 % Propane
.0017525 ft^3. /sec.

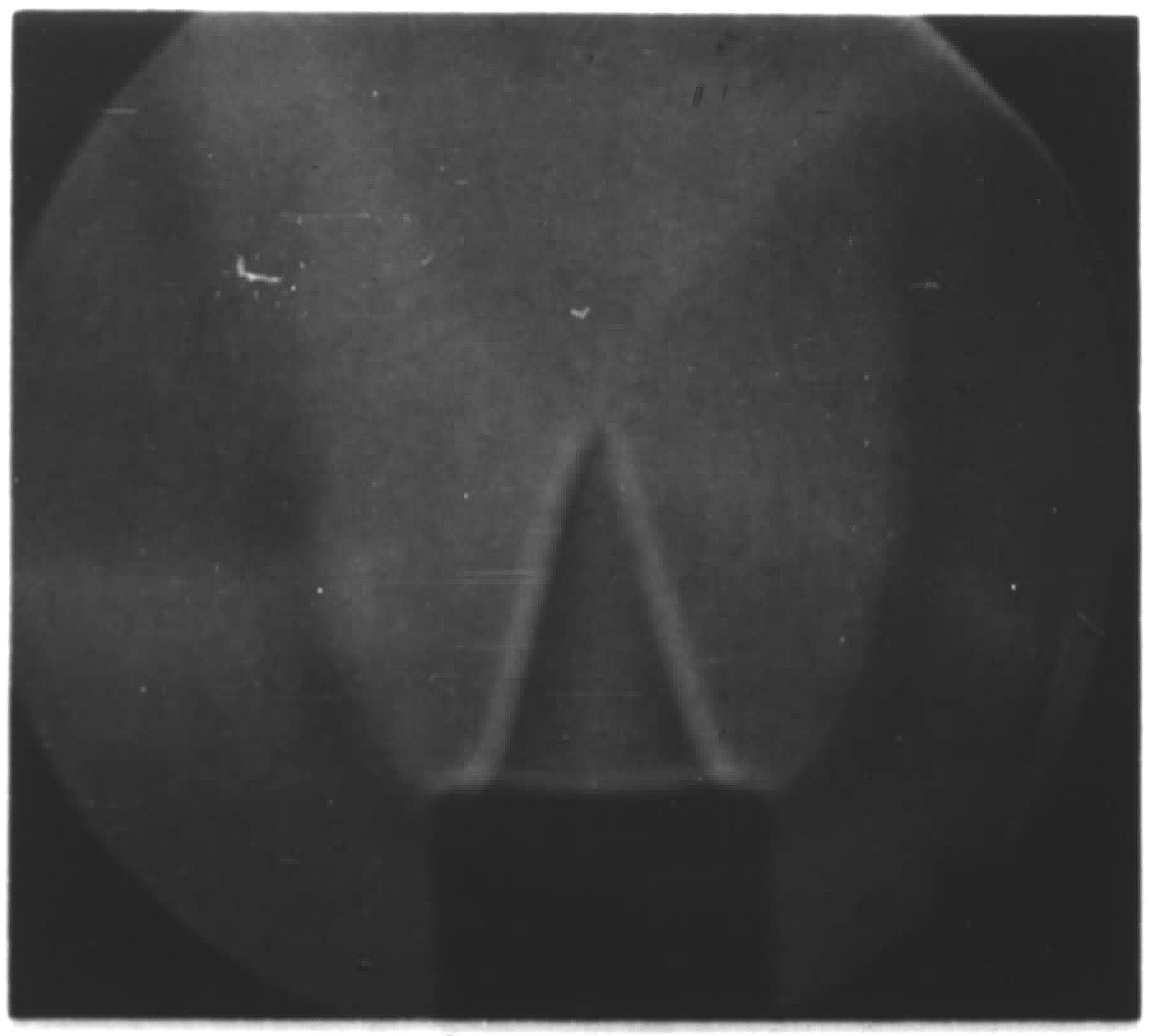


3.62 % Propane
.002158 ft^3. /sec.

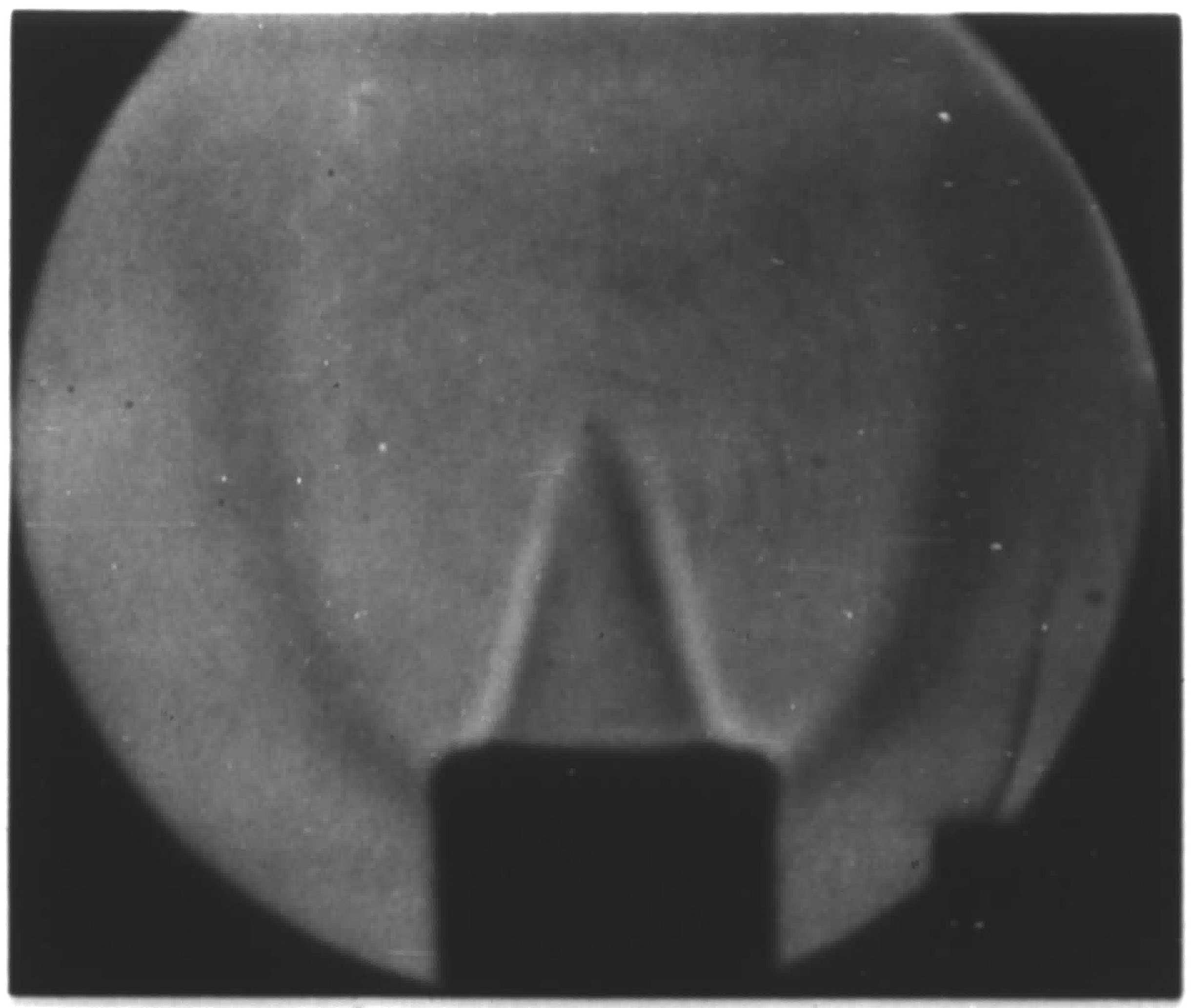


3.85 % Propane
.0021634 ft^3. /sec.

3.85 % Propane
.002007 ft^3. /sec.

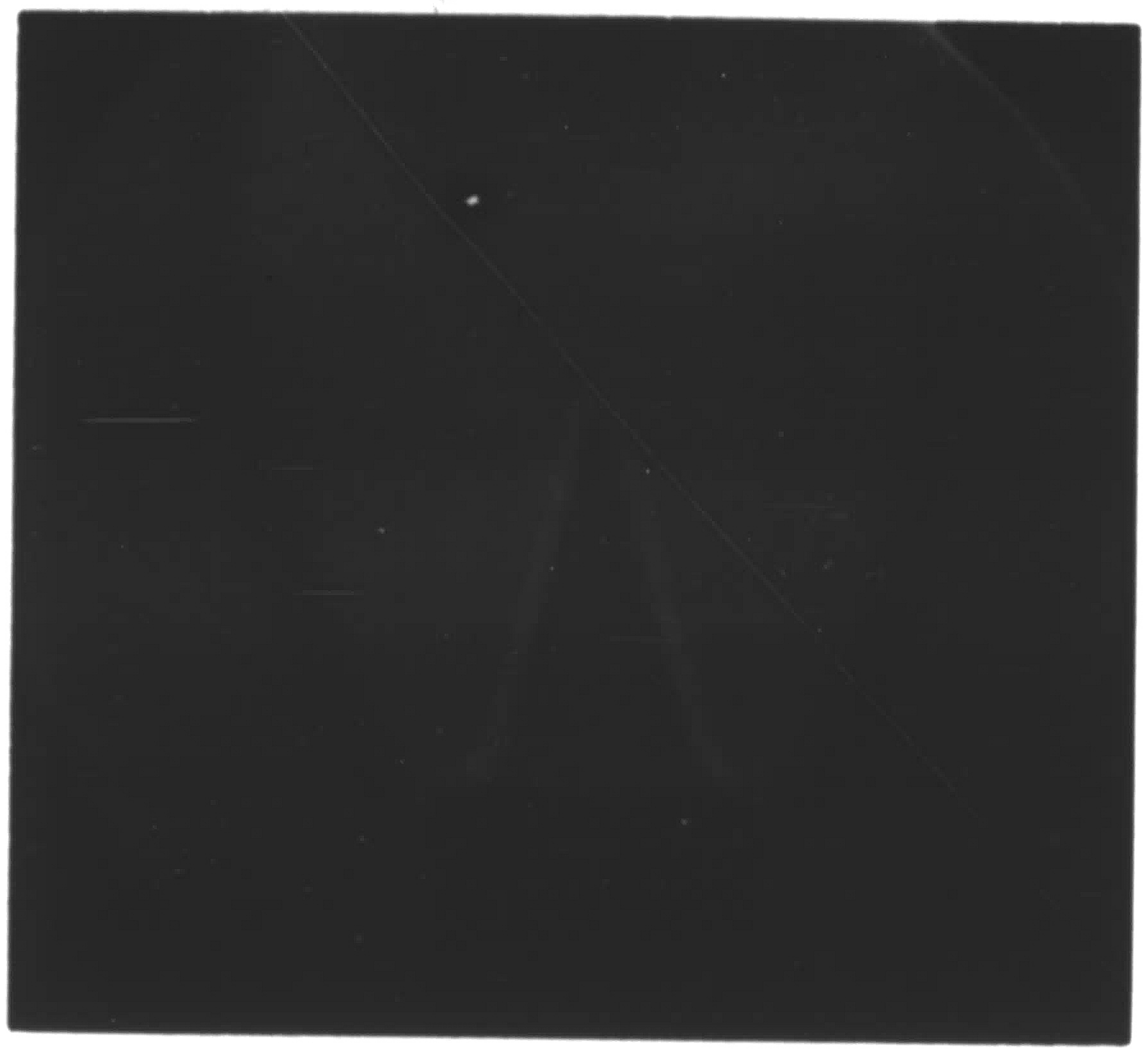


3.96 % Propane
.002218 ft^3. /sec.

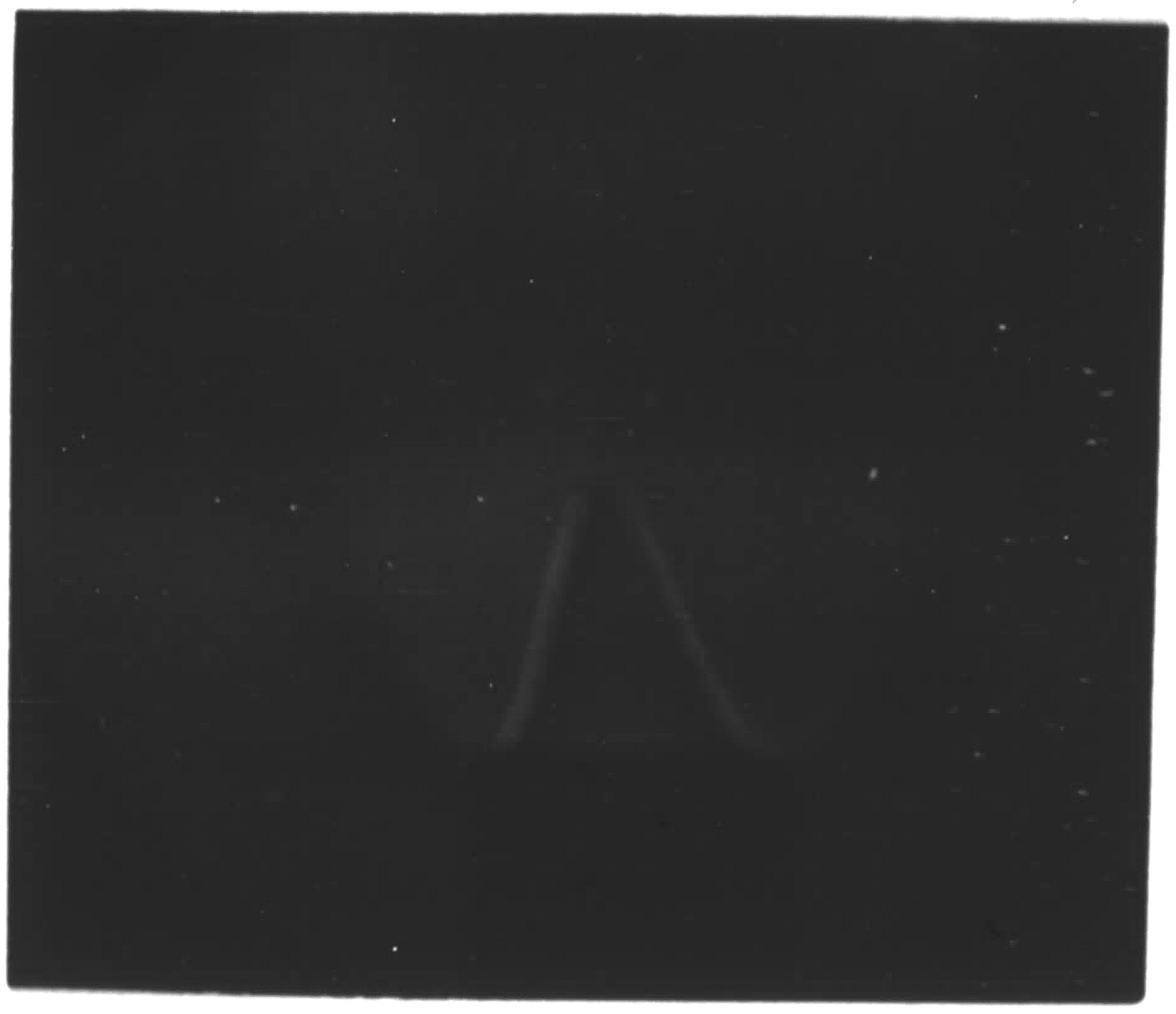


4.12 % Propane
.002128 ft^3. /sec.

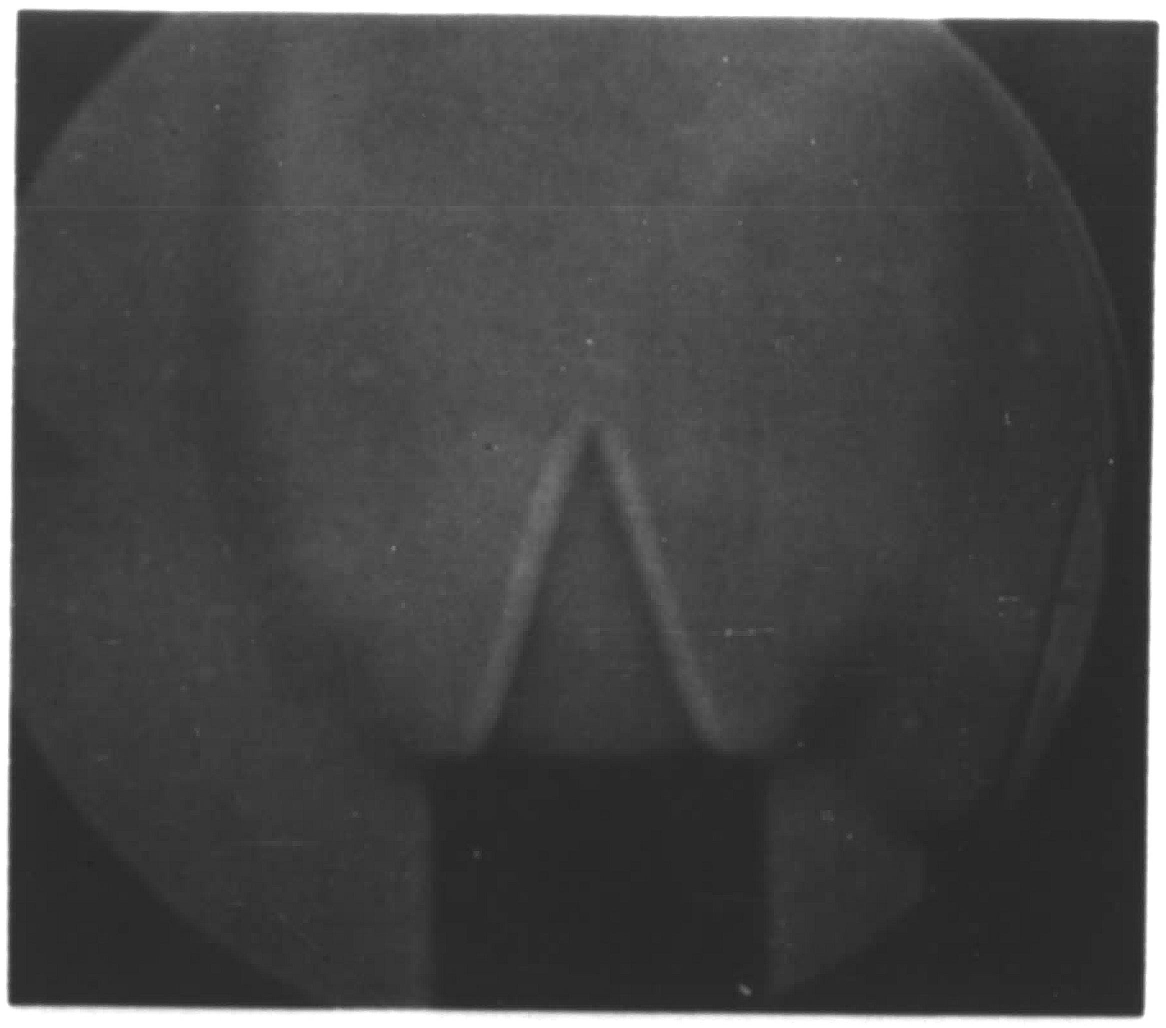
FIG. E-33



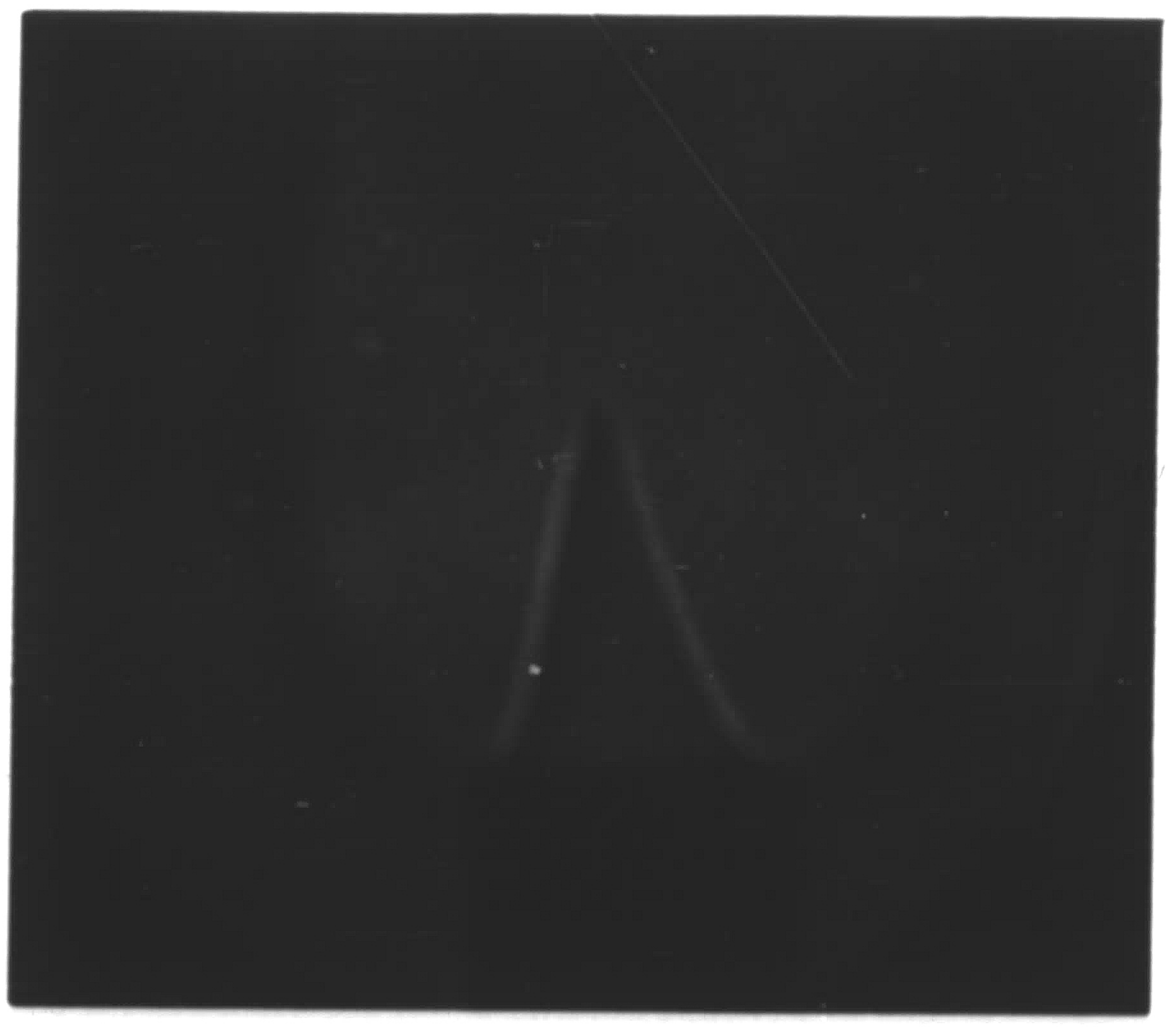
4.16 % Propane
.00222 ft^3. /sec.



4.42 % Propane
.001684 ft^3. /sec.

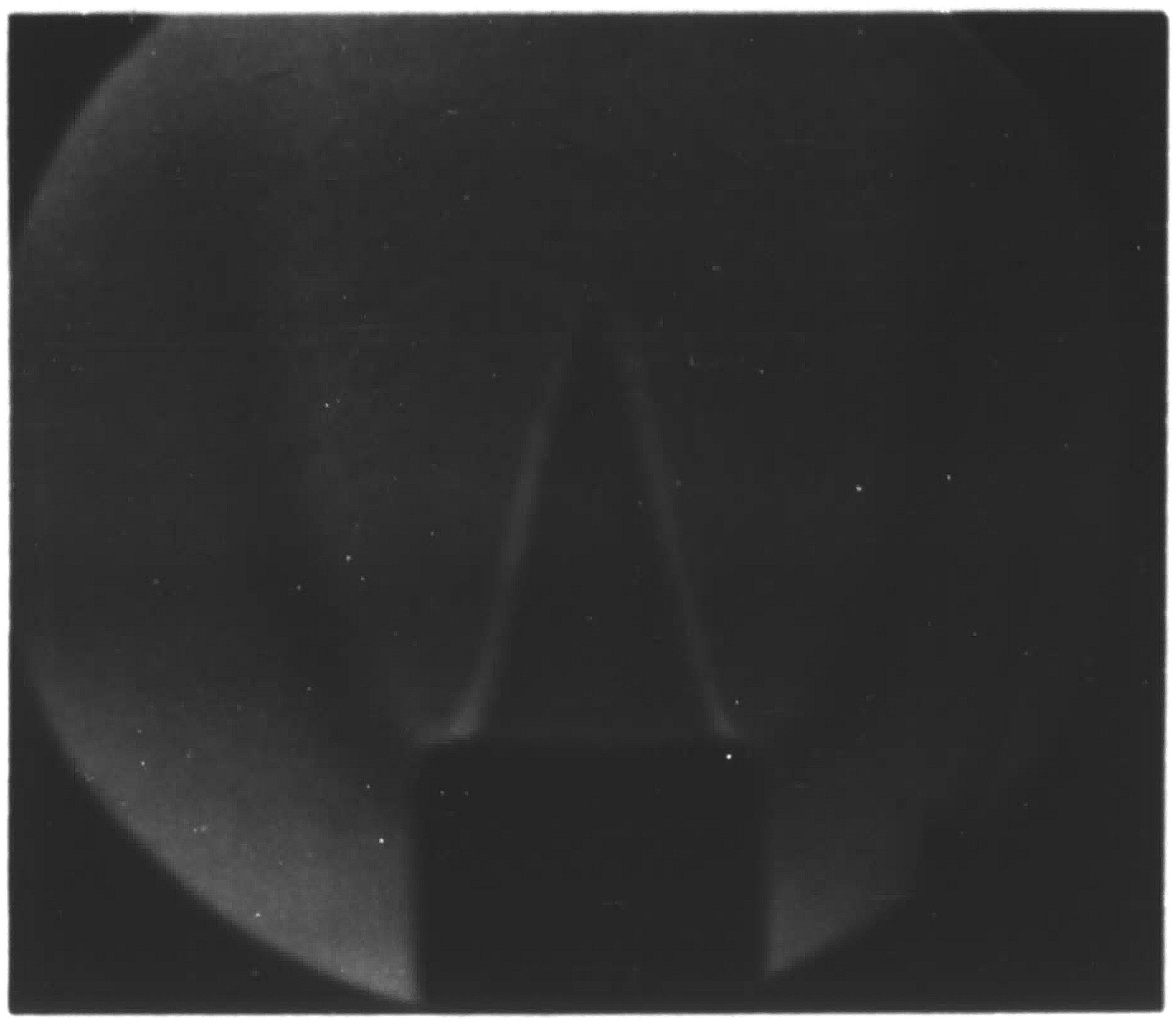


4.76 % Propane
.001617 ft^3. /sec.

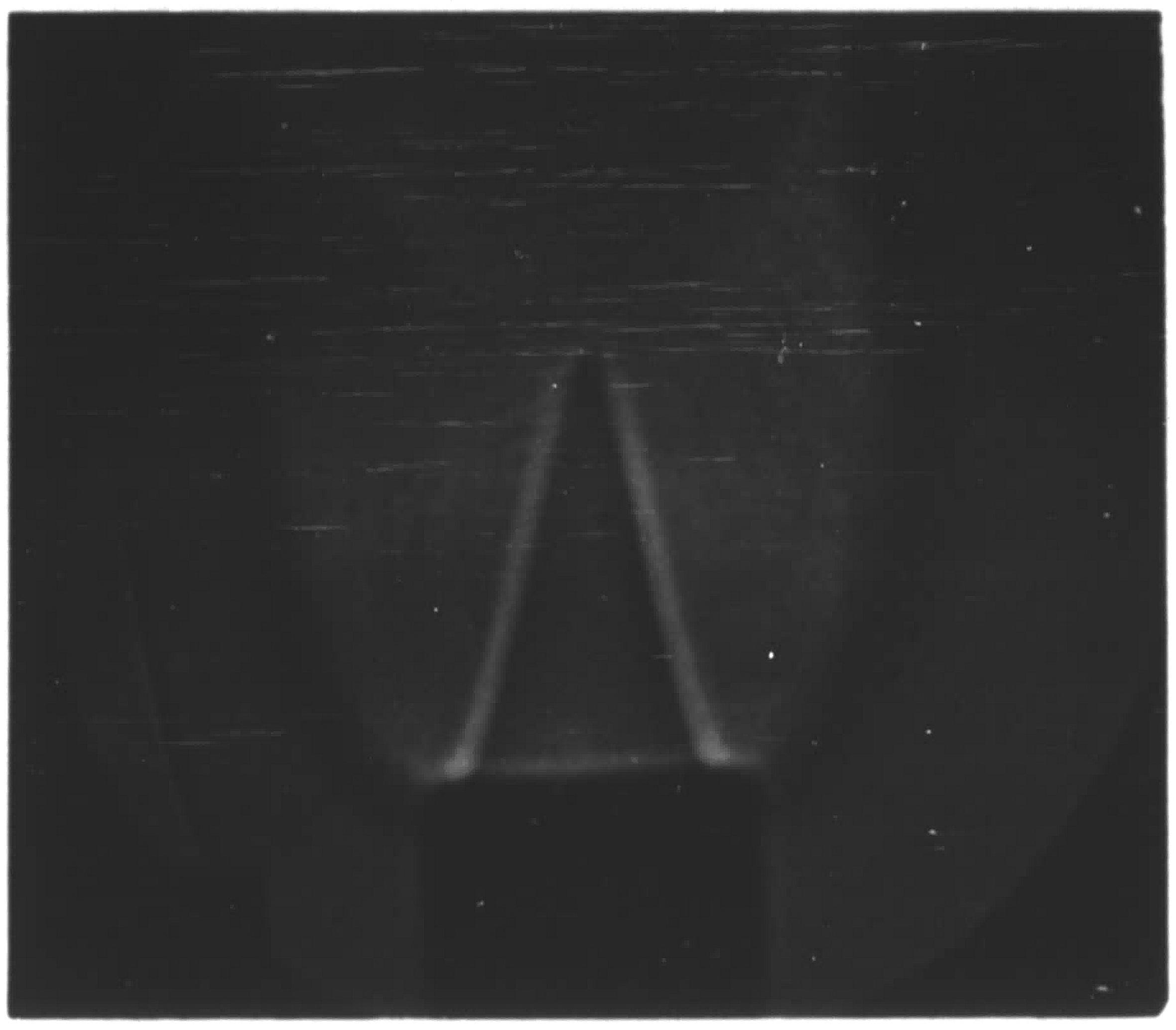


5.07 % Propane
.00164 ft^3. /sec.

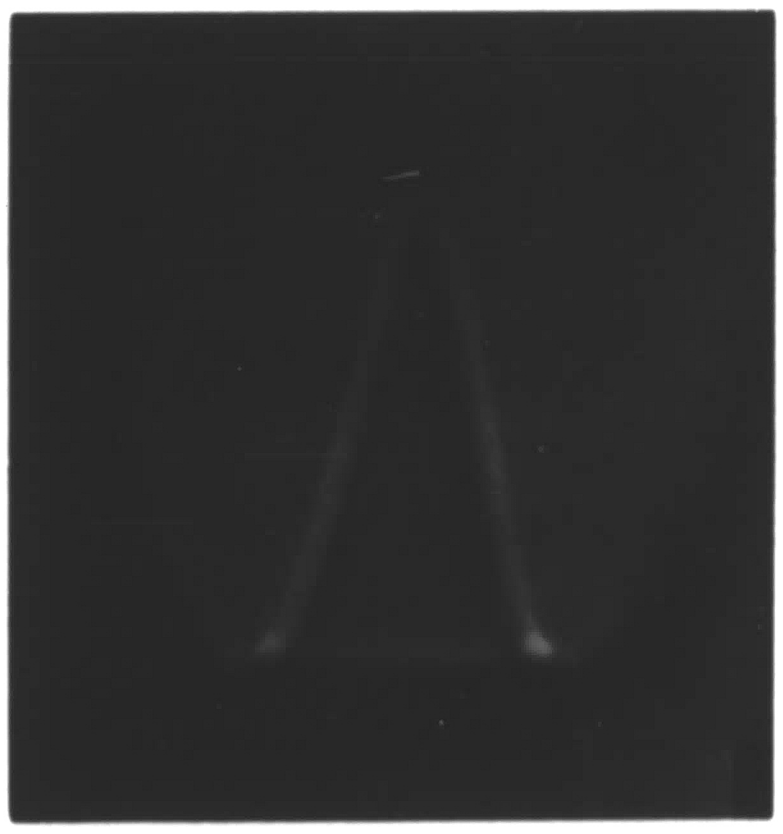
FIG. E-34



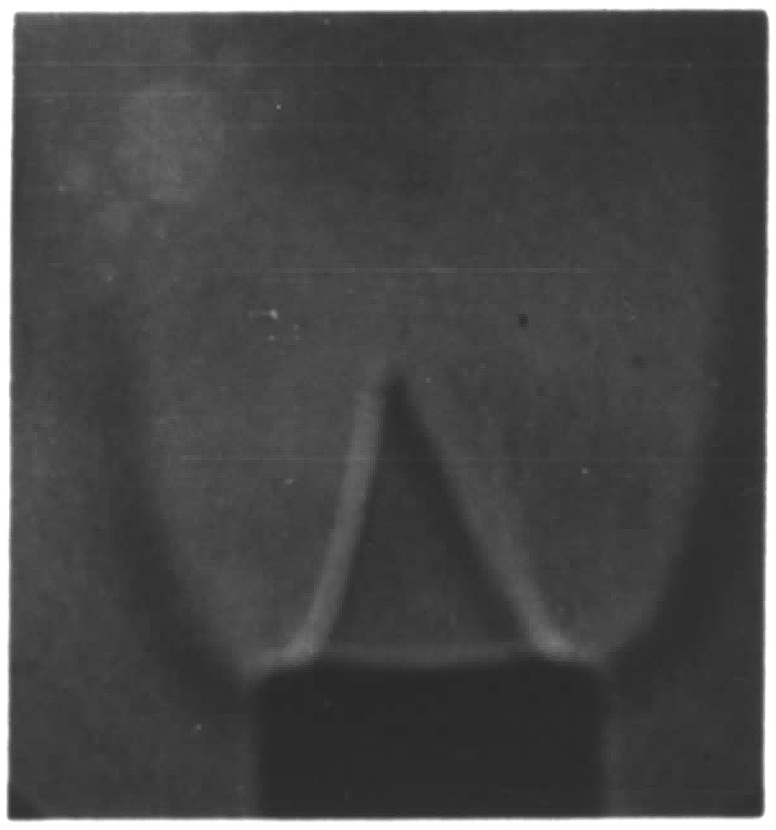
3.20 % Butane
.00240 ft^3. /sec.



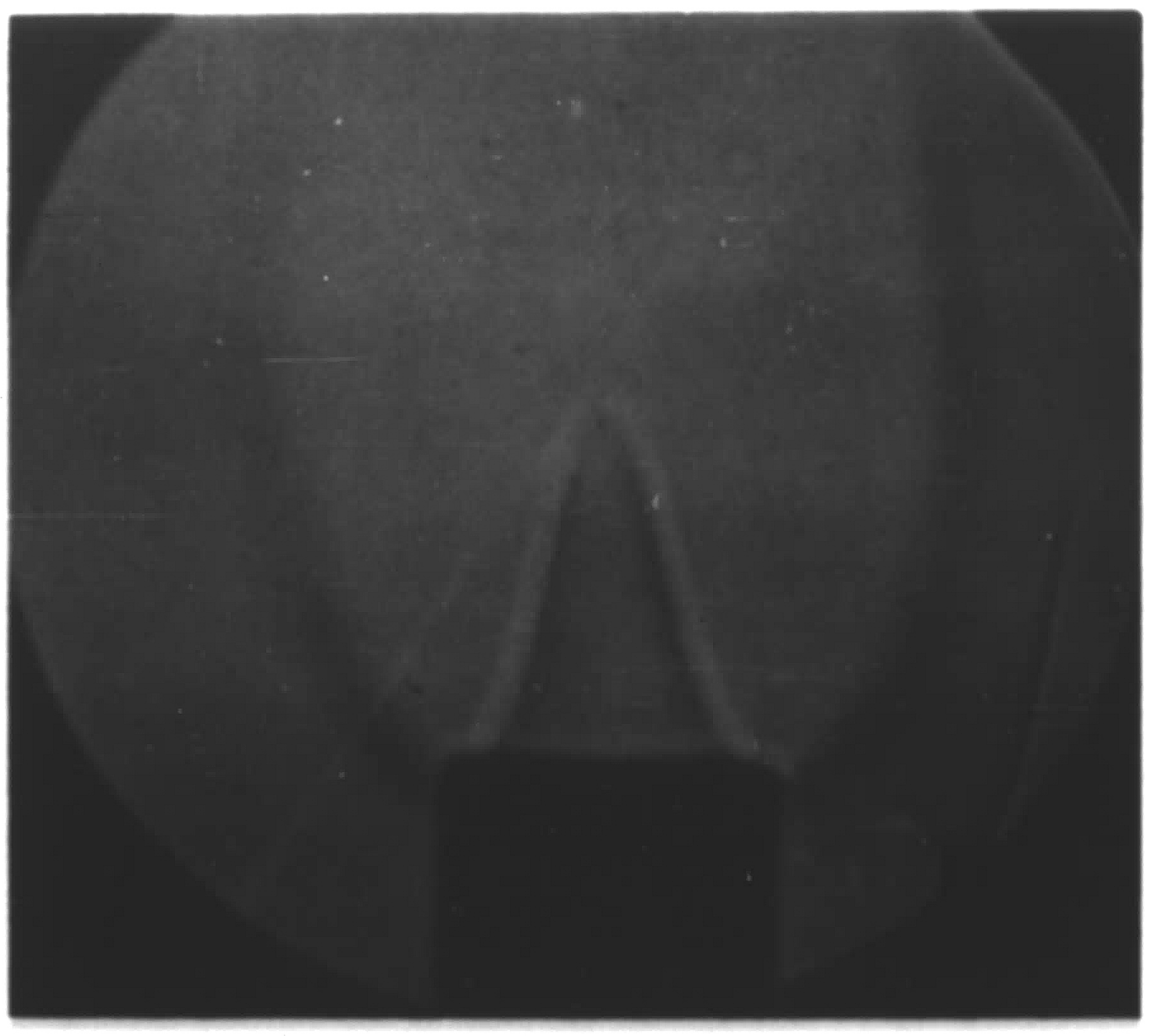
3.32 % Butane
.00234 ft^3. /sec.



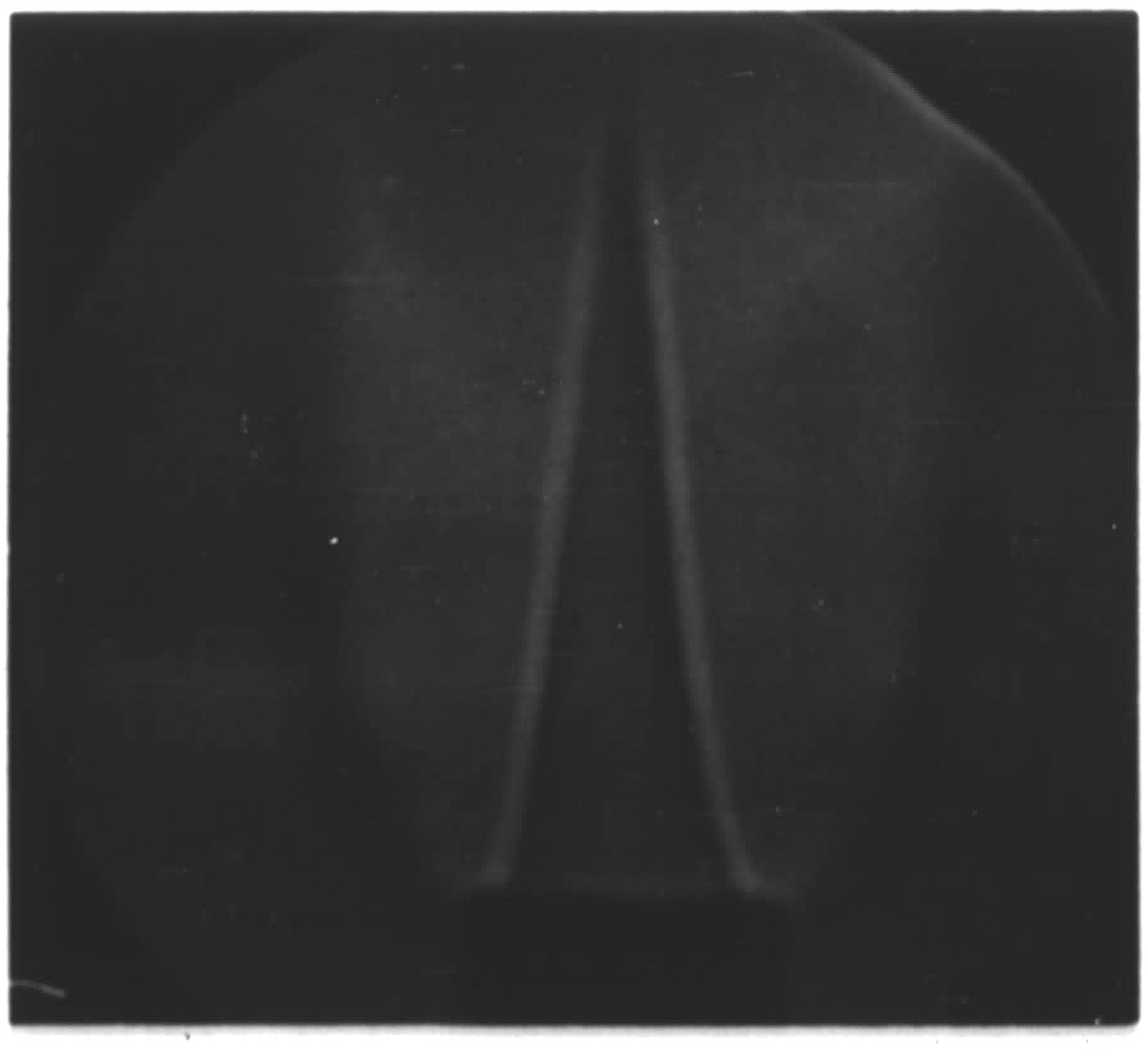
3.45 % Butane
.00259 ft^3. /sec.



4.1 % Butane
.001657 ft^3. /sec.



4.22 % Butane
.00193 ft^3. /sec.



5.26 % Butane
.00211 ft^3. /sec.

FIG. E-35

References:

1. Andersen, J.W., and Fein, R.S.: J. Chem. Phys. 17, 1268 (1949)

2. Ball: A study of a Two-Dimensional Flame. Combustion Project Report, Harvard University, July, (1951)

3. Bartholome, E.: Naturwissenschaften, 36, 171 (1949)

3a. Bartholome, E.: Naturwissenschaften, 36, 206 (1949)

3b. Bartholome, E., and Hermann, C.: Z Elektrochem., 54, 165 (1950)

4. Boys, S.F., and Corner, J.: Proc. Roy. Soc., A 197, 90 (1949)

5. Broeze, J.,: Third Symp. on Combustion, Williams & Wilkins, p. 146 (1949)

6. Conan, H.R., and Linnett, J.W.: Trans-Faraday Soc. 47, 981 (1951)

7. Corner, J.: Proc. Roy. Soc. (London) A 198, 388 (1949)

8. Coward, H.F., and Hartwell, F.J.: J. Chem. Soc. (London) 1996, 2676 (1932)

9. Coward, H.F., and Payman, W.: Chem. Revs. 21, 359 (1937)

10. Coward, H.F., and Guest, P.G.: J. Am. Chem. Soc., 49, 2479 (1927)

11. Coward, H.F., and Jones, G.W., U.S. Bureau Mines, Bul. 503 (1952)

12. Crussard, L. : Compt. Rend. 158, 125 (1914)

13. Damkohler, G.: Z Elecktrochem. 46, 601 (1940); Trans. in N.A.C.A Tech. Memo. 112

14. Daniell, P.J. : Proc. Roy. Soc. (London) A 126, 393 (1930)

References Cont.

15. **Dery**, R.J. : Third Symp. on Combustion and Flame explosion Phoenomena, Williams and Wilkins 30 (1949)

16. **Dugger**, G.L. : J. Amer. Chem. Soc. 72, 5271 (1950)

17. **Dugger**, G.L. : J. Amer. Chem. Soc. 73, 2398 (1951)

18. **Egerton**, A.C. and Badami, Proc. of Roy. Soc. A 228, 297 (1955)

19. **Egerton**, A.C., and Thabet, S. : Proc. Roy. Soc. A 211, 445, (1952)

20. **Egerton**, A.C., Sen, D.: Influence of Pressure on the Burning Velocities of Flat Flames, Fourth Symp. on Combustion, Williams & Wilkins 321, (1949)

21. **Evans**, M. "Current Theorectical Concepts of Steady -State Flame Prop." Chem. Reviews, Vol. 51, 365 (1952)

22. **Fiock**, E.F., andKing, H.K. : Natl. Advisory Comm. Areonaut. Repts. No. 531 (1935)

23. **Fiock**, E.F.and Marvin, C.F., Caldwell, F.R. and Roeder, C.H. : Natl. Advisory Comm. Aeronaut. Repts. No. 682 (1940)

24. **Friedman**, R. and Burke, E., Industrial & Engr. Chem. Vol. 43, 2772, Dec. (1951)

25. **Gayden**, A.G., and Wolfhard, H.G. : Fuel 29, 15 (1950)

26. **Gayden**, A.G., and Wolfhard, H.G. : Proc, Royl.Soc. (London) A 196, 105 (1949)

27. **Gerstein**, M., Levine, O., and Wong, E.L. :J. Amer. Chem. Soc. 73, 418 (1951)

References Cont.

28. Grove, J.R., Hoare, M.F. and Linnett, J.W.: Trans. Faraday Soc. 46, 745 (1950)

29. Guenoche, H., and Jouy, J. : Changes in the shape of Flames Propagating in Tubes, 403, Fourth Symp. (1952)

30. Guenoche, H. and Manson, N., and Mannot, G.: Compt. rend. 226, 163 (1948)

31. Guenoche, H. and Manson, N. Comptes. Rendus. Vol. 30, 726 Feb. (1950)

32. Gouy: Amer. Chem. Phys. 18, 27 (1879)

33. Johnston, W.C., Flame Propagation rates at reduced Pressures, SAE J. 62, Dec. (1947)

34. Jost, W., and Muffling, V., Z. Physic. Chem. A, 181 (1935)

35. Jouguet, E.: Compt. rend. 156, 872, 1058 (1913)

36. Jouguet, E. and Crussard, L.: Comprend. 168, 820 (1919)

37. Henkel, M.J. Hummel, H., and Spaulding, W.P.: Third Symp. on Combustion, Flame, and Explosion Phenomena, P. 135 Williams & Wilkins (1949)

38. Hirschfelder, J.O., and Curtiss, C.F.: Third symp. on Combustion, Flame and Explosion Phenomena, 121, Williams & Wilkins (1949)

39. Hirschfelder, J.O. and Curtiss, C.F.: J. Chem. Phys. 17, 1076 (1949)

40. Hirschfelder, J.O., and Curtiss, C.F.: Univ. of Wis. Naval Research Lab. Bul. CM 598, April, (1950)

References Cont.

41. **Hirschfelder**, J.O., Curtiss, C.F., Bird, R.B, and Spotz, E.L.: The Properties of Gases, Chap. IV John Wiley & Sons, (1953).

42. **Kamenetsky**, F., : Compt. rend. Acad. Sci., (URSS) 46, 232 (1945).

43. Lewis, B. Von Elbe, G., Fourth Symp. on Combustion and Flame and Explosion Phenomena, 358 (1953).

44. Lewis, B. Von Elbe, G., J. Chem. Phys. 2,537 (1934).

45. Lewis, B. Von Elbe, G., Combustion, Flames and Explosions of Gases, Acad. Press N.Y. (1961).

45a page 271
45b page 292
45c page 312
45d page 408
45e page 298

46. Lichty: Ind. and Engr. Chem. 44, 1359 (1952).

47. Markstein, G.H.: J. Chem. Phys. 17, 428 (1949).

48. Michaelson: Annalen Phys. u. Chem. (Wiedman) 37, 1 (1889).

49. Mallard, E., and LeChatelier, H.L.: Ann. Mines 4, 274 (1883).

50. Pickering and Linnett: Trans. Faraday Soc. 47, 9, 989 (1951).

51. Powling J. : Fuel, 28, 25 (1949).

52. Sachasse, H. and Bartholome, E.: Z. Elektrochem. 53, 183 (1949).

53. Schmidt, H.W., Steincke, H., and Newbert, U., "Flame and Schlieren Photographs of Comb. Waves in Tubes", Fourth Int'l symp. on Comb. Williams & Wilkins, 658 (1953).

References Cont.

54. Semenov, N., N.A.C.A. Tech. Memo. No. 1026 (1942).

55. Sherratt, S., and Linnett, J.W.: Trans. Faraday Soc. 44, 596 (1948).

56. Simon, D.M.: J. Amer. Chem. Soc. 73, 422 (1951).

57. Smith, F.A. and Pickering, S.F.: Natl. Bureau of Stand., J. Research, 17, 7 (1936).

58. Smith and Stinson: Fuels & Comb., 154 (1952).

59. Stevens, F.W., J. Amer. Chem. Soc. 48, 1896 (1926) 50, 3244 (1928).

60. Tanford, C., and Pease, R.N:J Amer. Chem. Phys. 15, 431, 861 (1947).

61. Tanford, C.: J. Chem. Phys. 15, 433 (1947).

62. Tanford, C.: Third symp. on Combustion, 140 (1949)

63. Ubbelohde, L., and Koelliker: J. Fur Gasbel, 49 (1916).

64. Van de Poll & Westerdjk: Z. Tech. Phyik, 22, 29 (1941).

65. Wheatley, P.J. and Linnett, J.W. Trans. Faraday Soc., 45, 1152 (1949).

66. Zeldovich, Ya. B., and Frank-Kamenetsky, D.A.: Compt. rend. acad. sci. (URSS) 19, 693 (1938).

67. Zeldovich, Ya.B. and Semenov, N.: J. Exptl. Theor. Phys. (URSS) 10, 1116 (1940); translated in N.A.C.A. Tech. Memo. 1084

68. Zeldovich, Ya.B.: J. Phys. Chem. (URSS) 22, No.1 (1948).

Biography

Arthur R. DiNicolantonio was born May 21, 1941, to Katherine and Pasquale DiNicolantonio in Atlantic City, New Jersey. He attended Holy Spirit High School in Atlantic City. He graduated high school in 1959 as Valedictorian of his class. While in high school he received many science awards, among these were, the Medical Society award, Roundtable of Science awards, Bausch and Lomb Science award and the American Chemical Society award.

He attended Villanova University from 1959 to 1963. In his Junior year he was awarded a Boeing Scholarship. He graduated first in his class of Mechanical Engineers. While at Villanova, he was elected to Tau Beta Pi Honor Fraternity in his Junior year. Upon graduation, he worked for DuPont at the Engineering Development Laboratory as an engineer. While working at DuPont, he took graduate courses in the evening at Drexel Institute of Technology. In 1964 he attended Lehigh University on a National Science Foundation Traineeship to work toward his Masters' Degree.