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There has been concern as to whether an unconfined combustible cloud arising from the release of liquefied natural gas could detonate. Accordingly, a laboratory scale experimental program and accompanying theoretical treatment were initiated to evaluate this possibility. A sector of a cylindrical cloud was modeled by a special shock tube. Blast waves of variable strength were transmitted into the combustible mixture of interest. Since methane-air couldn't be detonated, the critical initiation energy requirements for various stoichiometric methane-oxygen-nitrogen mixtures were determined and then extrapolated to determine the value for methane-air. Extremely high values were indicated. Inasmuch as natural gas commonly contains ethane and/or propane, stoichiometric mixtures containing various percentages of these gases were tested. Small additions of either (but ethane moreso than propane) reduced the critical initiation energy appreciably, although the values were still quite high. The analytical study shed much light on the competing chemical kinetic and gas dynamic processes. The analysis allowed planar, cylindrical, and spherical geometries to be considered. Further, it independently predicted the characteristics observed experimentally, thus supporting the experimental results.

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INITIATION OF DETONATION IN UNCONFINED NATURAL GAS-AIR CLOUDS

FINAL REPORT

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FOR

GAS RESEARCH INSTITUTE

CONTRACT NO. 5014-363-0132

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RESEARCH SUMMARY

TITLE	Initiation of Detonation in Unconfined Natural Gas-Air Clouds GRI Code: GRI Contract Number: 5014-363-0132
CONTRACTOR	Gas Dynamics Laboratories, Department of Aerospace Engineering, The University of Michigan, Ann Arbor
PRINCIPAL INVESTIGATOR	Professor J.A. Nicholls
TIME SPAN	January 1, 1978 through December 31, 1979
MAJOR ACHIEVEMENTS	A unique experimental facility and a closely related theoretical model were developed in order to assess the danger of detonation in unconfined natural gas-air clouds. In this way much more accurate assessments of the danger can be made without the necessity of the extremely expensive, time consuming large scale field tests.
RECOMMENDATIONS	The experimental facility and associated analysis has been developed to a fairly high degree and should be used to advantage. Some further developments of both aspects should be undertaken as the technique is applied to other gaseous systems of interest (such as alternate gaseous fuels). Many details of the initiation process and the influence of cloud inhomogeneity are still not clearly understood.

DESCRIPTION OF WORK COMPLETED

There has been concern as to whether an unconfined combustible cloud arising from the release of liquified natural gas could detonate. Accordingly, a laboratory scale experimental program and accompanying theoretical treatment were initiated to evaluate this possibility. A sector of a cylindrical cloud was modeled by a special shock tube. Blast waves of variable strength were transmitted into the combustible mixture of interest. Since methane-air couldn't be detonated, the critical initiation energy requirements for various stoichiometric methane-oxygen-nitrogen mixtures were determined and then extrapolated to determine the value for methane-air. Extremely high values were indicated. Inasmuch as natural gas commonly contains ethane and/or propane, stoichiometric mixtures containing various percentages of these gases were tested. Small additions of either (but ethane moreso than propane) reduced the critical initiation energy appreciably, although the values were still quite high. The analytical study shed much light on the competing chemical kinetic and gas dynamic processes. The analysis allowed planar, cylindrical, and spherical geometries to be considered. Further, it independently predicted the characteristics observed experimentally, thus supporting the experimental results.

INTRODUCTION

The transportation and storage of large amounts of liquified natural gas (LNG), which is predominantly methane, presents the possibility of tank rupture and, hence, spillage or leakage. The resulting cloud that is formed may conceivably be ignited by hot chimney gases, an open flame, electrical equipment, etc. In these cases it is most likely that a deflagration wave will be initiated which, in itself, can cause extensive damage as it propagates throughout the cloud. However, the question arises as to whether the deflagration can accelerate and develop into a fully established detonation with the attendant high pressures and velocities. In the case of combustion of a mixture under confinement — as, for example, when ignition occurs near the closed end of a constant cross sectional area pipe — the dominant processes are as follows. The flame, in moving away from the closed end, generates lower density products which, by conservation of mass, causes the flame to accelerate and the unburned mixture to be set in motion ahead of the flame. That is, the flame acts like a piston. The accelerating wave transmits weak compression waves into the unburned mixture which raises the pressure and temperature and hence, usually, the rate of combustion. Further, the gas motion generates a boundary layer on the walls of the pipe and, along with this, turbulence. As a consequence, the flame shape is wrinkled and the piston effect is reinforced. If these dynamic interactions continue, the flame can go through transition to detonation. In the case of an unconfined cloud, ignited at a point, there will be a tendency for flame acceleration; however, with no enclosing walls, the boundary layers and high degrees of turbulence will not be generated. Thus it seems very unlikely that a flame would go through a transition to detonation in a completely unconfined cloud. Of course, if localized high turbulence levels existed because of other effects, the flame acceleration mechanism would be present. Or, if there were local confinements, such as pipes, walls, etc., flame acceleration could occur.

Another mode of ignition is that wherein a large amount of energy is released very rapidly in a localized region. In this case, strong blast waves (shock waves followed by an expansion zone) propagate into the unburned mixture. The Mach number, and hence strength of these waves, may be well above detonation Mach numbers. It is then of interest to know whether detonation will propagate throughout the cloud. It is this mode of ignition, namely by a blast wave, that has been used to assess the possibility that detonation can occur in unconfined clouds of natural gas and air.

Considerable uncertainty has surrounded the question of whether methane-air is capable of detonation; this being particularly true under conditions of no confinement. In 1954 Gerstein, Carlson, and Hill[1] reported on the detonation of a stoichiometric natural gas-air mixture in a very large pipe (61 cm x 91 m). However, the natural gas included about 8%, by volume, of ethane. Kogarko[2] reported on the attainment of detonation for a range of methane-air mixtures in a large diameter (30.5 cm) pipe. He used a large explosive charge as the initiator and there was about 2% of heavier hydrocarbons present. The authors of this report have reservations as to whether the pipe was long enough (11.2 m) to prove that detonation was established.

Vanta, Foster, and Parsons[3] investigated the detonability of natural gas-air mixtures under simulated unconfined conditions. They used a large plastic bag and an explosive igniter. They concluded that detonation was not observed except, possibly, for a stoichiometric mixture. Bull et al.[4] recently reported on a study of the detonability of $CH_4 + 2O_2 + XN_2$ mixtures wherein the gas was confined in a polyethylene bag and controlled amounts of the solid explosive, Tetryl were used. These experiments were restricted to $X \leq 5.53$ ($X = 7.52$ for air) but extrapolation of the results indicated that about 22 kg of Tetryl would be required to detonate methane-air. Boni, Chapman, and Cook[5] using a numerical approach, predicted the magnitude of explosive yield required to initiate detonation in mixtures of $CH_4 + 2O_2 + XN_2$. Their predictions agreed quite well with Bull's experimental results (limited in X and threshold energy) but their extrapolated value for air, 10^6 - 10^7 grams of Tetryl, is much higher than the extrapolation of experimental results by Bull et al.[4]

Recently some large scale experiments with rather high initiation energies have been conducted at the Naval Weapon Center. Detonation has not been observed and indications are that much higher energy levels would be required. Such experiments are very expensive, they lack complete control, and detailed measurements in sufficient number are not feasible. On the other hand, laboratory scale experiments suffer from limited size and the possibility of confinement effects. Accordingly, it was deemed imperative to conduct an integrated experimental-analytical approach to the problem. Both phases of this study are described in the following.

TECHNICAL SECTION

As indicated in the Introduction, the objective of this study was to assess the possibility that detonation could occur in an unconfined natural gas-air cloud. Further, it was pointed out that this would be done by examining the most severe case, i.e. blast wave initiation. In most actual cases, the problem would be one of energy release at a point and hence be a problem of spherical geometry. However, there is much similarity between the planar, cylindrical, and spherical systems and the same theory can be applied to any of them. The study of a spherical explosion in the laboratory suffers from the fact that a larger explosion is required and that it is difficult to make many detailed measurements. The cylindrical system is much better in this regard and yet has the advantage of more geometrical complexity than for the planar case. Hence a cylindrical geometry was adopted for the experimental phase.

Experimental Apparatus

The experimental setup used for this study was originally developed for heterogeneous mixtures. With some modifications, it was adapted to the homogeneous all-gaseous case. The idea underlying the apparatus was to be able to model a cylindrically shaped combustible cloud. In this way controlled experiments can be conducted, many measurements can be made, and it is possible to apply an analytical treatment. The development of the apparatus follows from Fig. 1. That is, it is assumed that there is a combustible cloud wherein there are no variations in the vertical or azimuthal direction and, at least for this work, none in the radial direction. At time t = 0, an amount of energy is released instantaneously along a line source (hence an axis of symmetry) which results in a cylindrical shock wave moving radially outwards. This shock wave may or may not lead to detonation. In view of the symmetry of the problem,

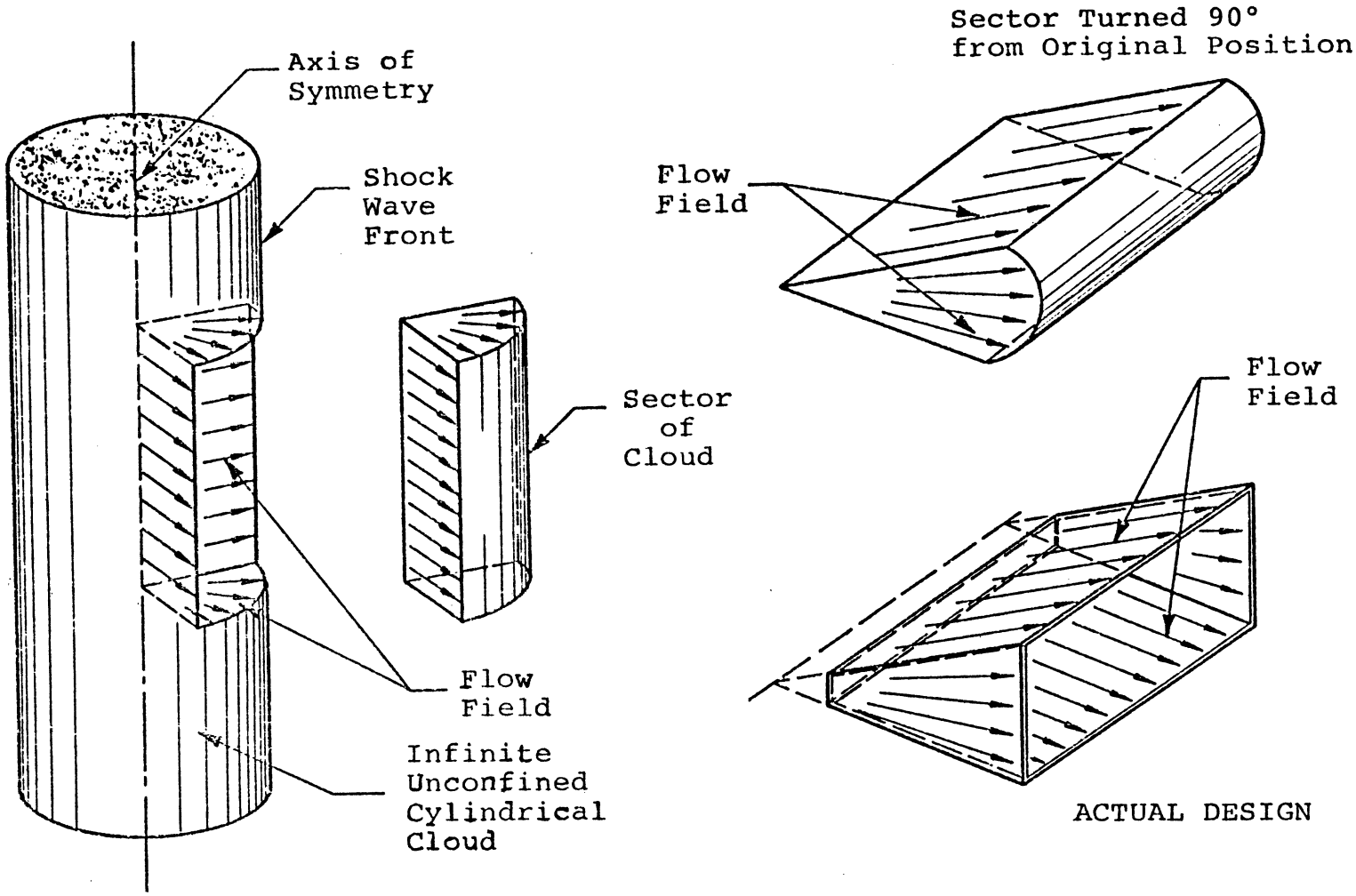

Figure 1. Development of the Experimental Facility

the apparatus developed is based on a limited height and angular sector of the cloud, as shown in Fig. 1. The chamber, as used, has a 20° included angle, a cloud height of 5.21 cm, and a radial size of 137.67 cm. A sketch of the chamber is shown in Fig. 2.

The experimental detonation facility consists of the following main components.

1. A sectored detonation test chamber into which the gaseous combustible cloud is introduced.
2. A gas mixing system.
3. An initiator energy source system.
4. Instrumentation for facility operation, measurements, recording, and data acquisition.
5. Special attachment equipment.
6. Hardware, support elements for the chamber, and other equipment.

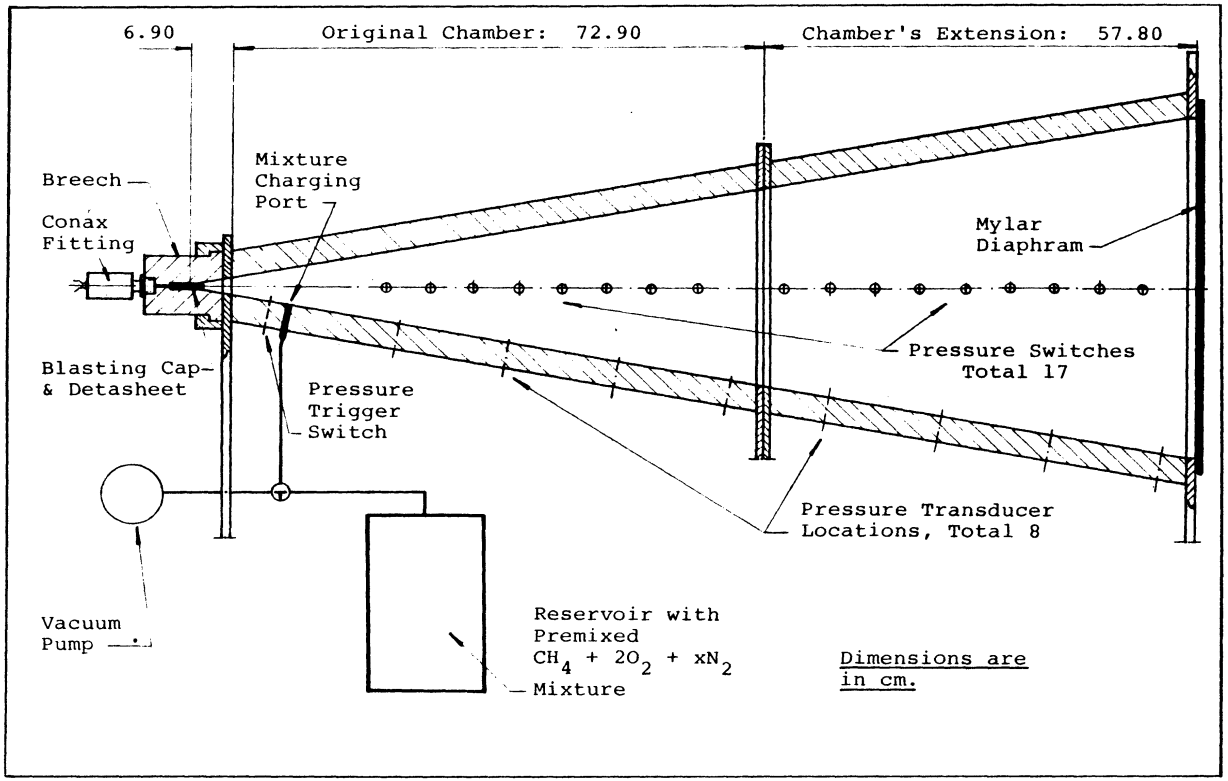

Figure 2. Schematic of Sectored Shock Tube

At the narrow end of the chamber, a breech-like holder for the electrically initiating blasting cap and controlled amounts of condensed explosive, DuPont Detasheet C, was mounted. The characteristics of the blasting caps and condensed explosive used in the experimental work are given in Table 1. In the course of the experimental work, different amounts of condensed explosive were used in combination with a blasting cap. This combination is termed "initiator" charge. The blasting cap E-106 was used in the majority of the runs but two other types were occasionally used. They were DuPont E-101-6 and DuPont ATLAS No. 6. In Table 2, the most common combinations of the initiator charge and the energy level used in the experimental work are given. The initiator energy level, E_{oi}, was calculated from knowledge of the energy release of the used combination. For cylindrical cloud studies, this result needs to be corrected for the geometry effect. Namely, the total energy release was along an axial length of 5.21 cm and into an angular sector of 20°, rather than along a unit length and into an angle of 360°.

The relation used for an initiator energy calculation is,

$$E_{oi} = K\,(E_{cap} + 3947.3\ W) \qquad (\text{joules cm}^{-1})$$

where

K - explosive amplification factor (see Ref. 6)

$$K = \frac{1}{5.21}\,\frac{360°}{20°} = 3.4577 \qquad (1/\text{cm})$$

E_{cap} - blasting cap energy, joules

W - amount of condensed explosive, grams

3947.3 - energy release of condensed explosive, DuPont Detasheet C, joules gm^{-1}

The calculated results are given in Table 2 to the first decimal place. A conversion,

$$1\ \text{ft-lbf ft}^{-1} = 22.472\ \text{joules cm}^{-1}$$

must be applied if English units are desired.

In operation, a mylar diaphragm covered the open end of the chamber and the air in the chamber was evacuated. The previously prepared gaseous

TABLE 1. PROPERTIES OF DUPONT BLASTING CAPS AND CONDENSED EXPLOSIVE, DUPONT DETASHEET C

Condensed Explosive Detasheet C	
Content	63% PETN - 8% NC
Detonation Velocity, (m/s)	7000
Density, (gms/cc)	1.5
Heat of Explosion, (cal/gm)	1100
Blasting Cap, Heat of Explosion (joules)	
E-106	977.3
E-101-6	500.60
ATLAS No. 6	1491.40

TABLE 2. INITIATOR ENERGY LEVELS

Blasting Cap plus Grams of Detasheet C	Initiator Blast Energy Content E_{oi} (joules/cm)
E-101-6	1,731.2
ATLAS No. 6	5,157.9
E-106	3,379.8
E-106 + 0.5	10,203.6
+ 1.0	17,027.8
+ 2.0	30,676.0
+ 3.0	44,324.3
+ 4.0	57,972.6
+ 5.0	71,620.9
+ 6.0	85,277.3

mixture was then introduced. Initiation of the condensed charge caused a cylindrical blast wave to be transmitted into the mixture. A pressure transducer sensed the wave and triggered an oscilloscope raster which was sensitive to the output of 17 pressure switches. Thus the wave position as a function of time was determined and the slope gave the local wave velocity. A continuously decreasing wave velocity indicated that detonation had not been achieved. On the other hand, establishment of a constant velocity wave indicated the attainment of Chapman-Jouguet (CJ) detonation. Various gaseous mixtures were tested, using a range of initiator energy levels, to determine whether detonation was established.

Experimental Results

The initial experimental work employed methane-air mixtures of equivalence ratio, ϕ, that varied from 0.7 to 1.06. The maximum initiator energy level used in this experimental work was E_{oi} = 78,445.0 joules cm^{-1}. It soon became evident that the experimental apparatus did not permit the extreme energy levels required to detonate methane-air. Accordingly, it was decided to go to stoichiometric methane-oxygen-nitrogen mixtures, starting with pure oxygen,and to determine the detonability characteristics as the nitrogen dilution was increased. The idea was to determine the critical or threshold initiator energy level that was required to establish a self-sustained detonation wave for each mixture and then to extrapolate the results to the "air" case. Bull[4] had used this technique in his plastic bag experiments.

Three different methane-oxygen mixtures namely, lean (ϕ = 0.790), near stoichiometric (ϕ= 0.950), and rich (ϕ = 1.150) were investigated. In all cases and for all initiator energy levels used, detonation was achieved. The representative experimental results, R versus T', for a near stoichiometric mixture and for two appreciably different initiator energy levels are shown in Fig. 3. The experimental results fit a straight line very well. This characteristic along with the fact that the slope is independent of E_{oi}, indicates a constant velocity CJ detonation has been realized. This measured velocity agreed very well with the theoretically predicted CJ velocity.

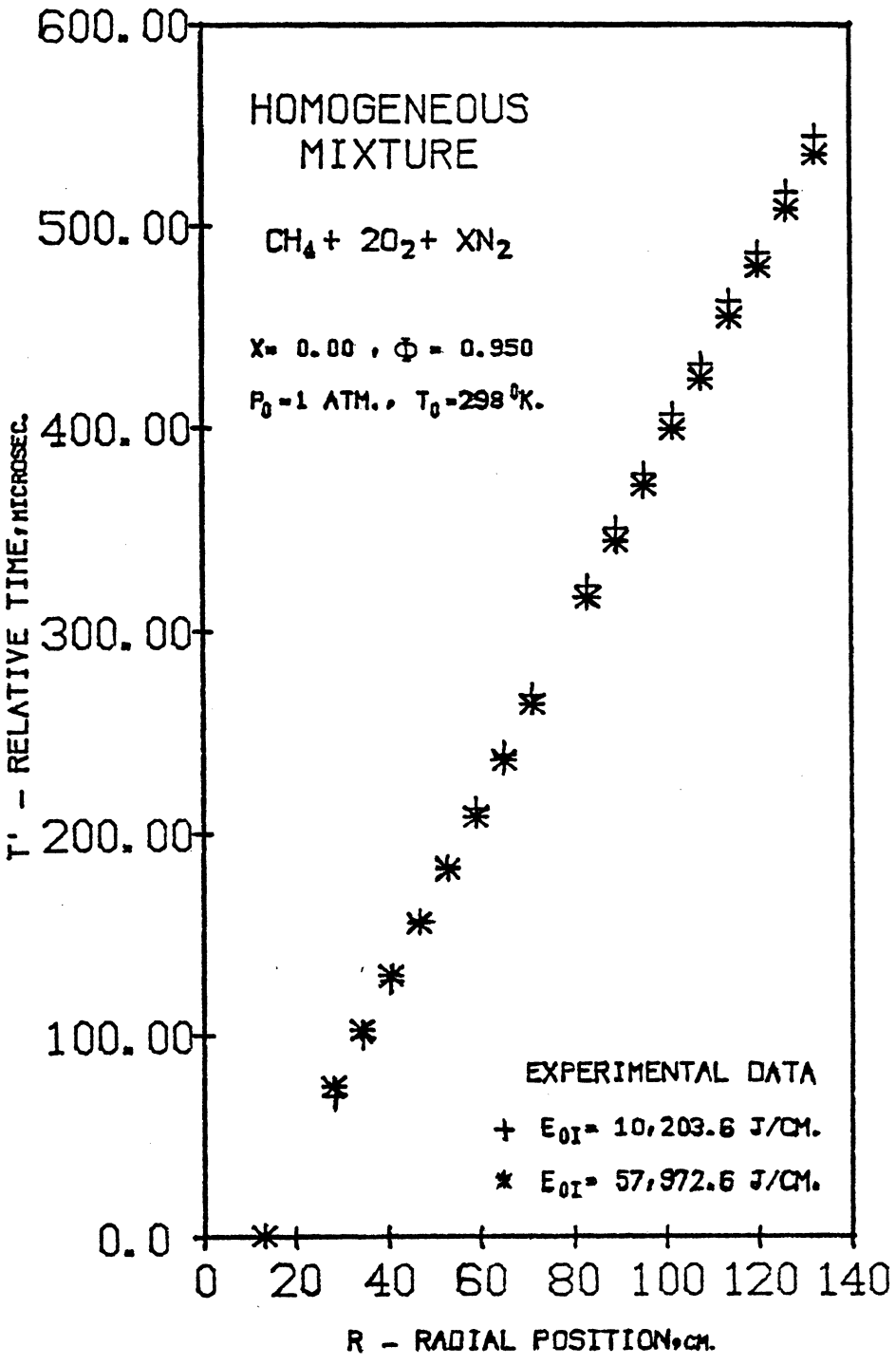

Figure 3 Experimental Homogeneous Data, R Versus T'

Experiments were then conducted wherein varying amounts of nitrogen were added to stoichiometric methane-oxygen mixtures, i.e. $CH_4 + 2O_2 + XN_2$ (X = 7.52 for air). For small amounts of nitrogen, detonation was easily achieved and the results were similar to those shown in Fig. 3. However, as more nitrogen was added the initiation energy required increased rapidly. An interesting case is shown in Fig. 4 where the nitrogen dilution is moderate (X = 3.728), and two initiator energies were tested. The local wave Mach number, regressed from the radius-time data, is plotted as a function of radius. While some of the oscillation which appears may be attributed to the method of numerical regression used, some of it represents the actual behavior of the detonation. It can be noted that the lower energy level run did not produce detonation. For the higher energy, the detonation Mach number is close to the theoretically predicted CJ value.

A great number of experiments were conducted and, where detonation could be achieved, the observed detonation Mach numbers compared to the theoretical values are shown in Fig. 5. It is to be observed that the excellent agreement begins to deviate at high nitrogen contents.

The results of many experiments employing various initiator energy levels and nitrogen dilution are shown in Fig. 6 in the log E_{oi} versus X plane with indication as to whether there was detonation, no detonation, or the result was uncertain. It appears to be appropriate to separate the detonation from no-detonation regions by a linear relation. This linear relation, $E_{oi} = f(X)$, represents the critical initiation energy as a function of nitrogen dilution. A similar linear relation for the spherical case was obtained by Bull et al[4]. Assuming that this linearity holds in the range above that investigated, an extrapolation to the "air" case as well as to the "no-nitrogen" case would indicate the following critical energy levels;

(i) For the "air case, i.e. methane-air

$$(E_{oi})_{crit} = 7.5 \times 10^6 \text{ joules cm}^{-1}$$

or

$$W_{crit} = 550 \text{ gm of Detasheet}$$

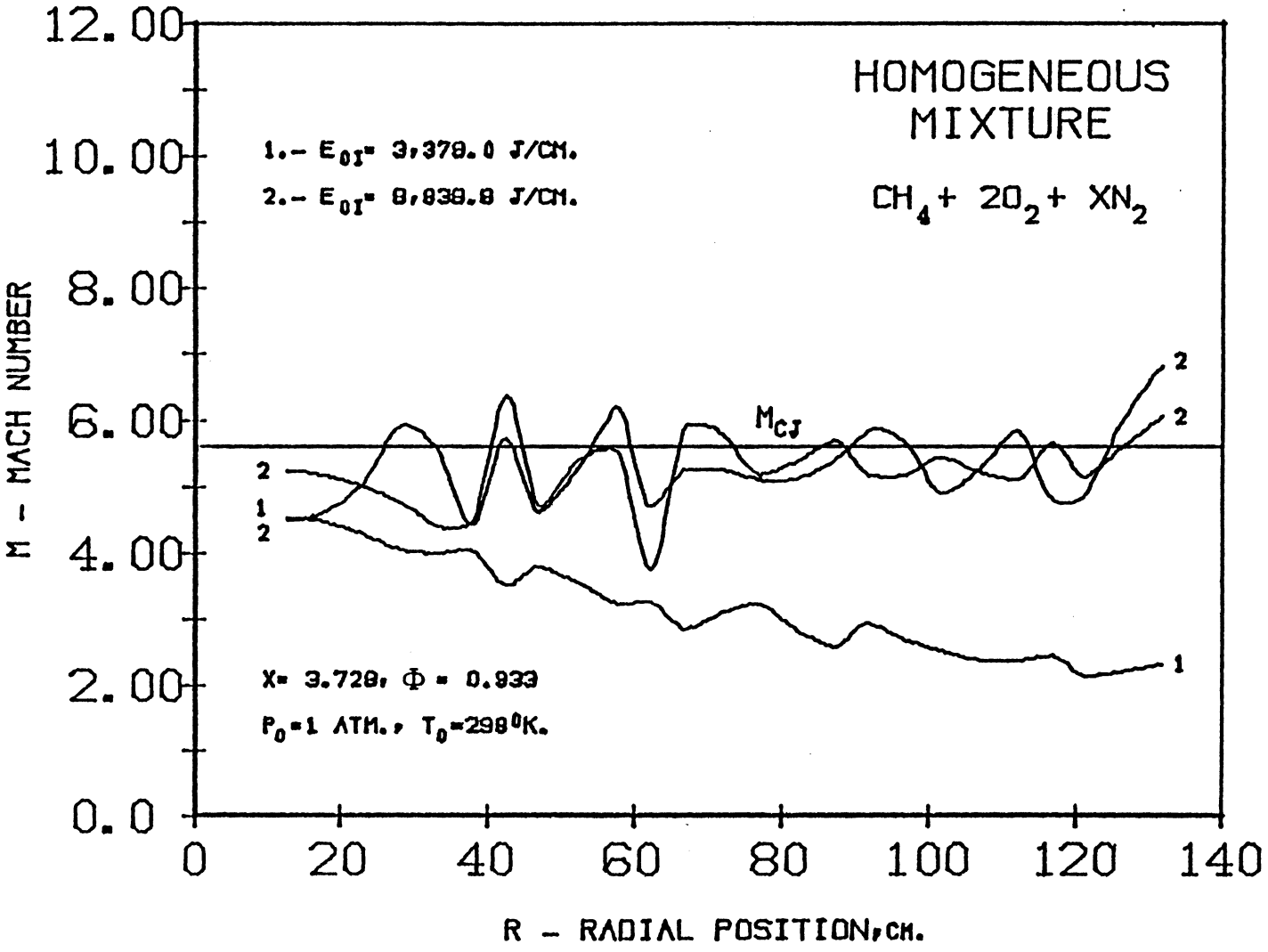

Figure 4. Mach Number versus Radius for Two Energy Levels

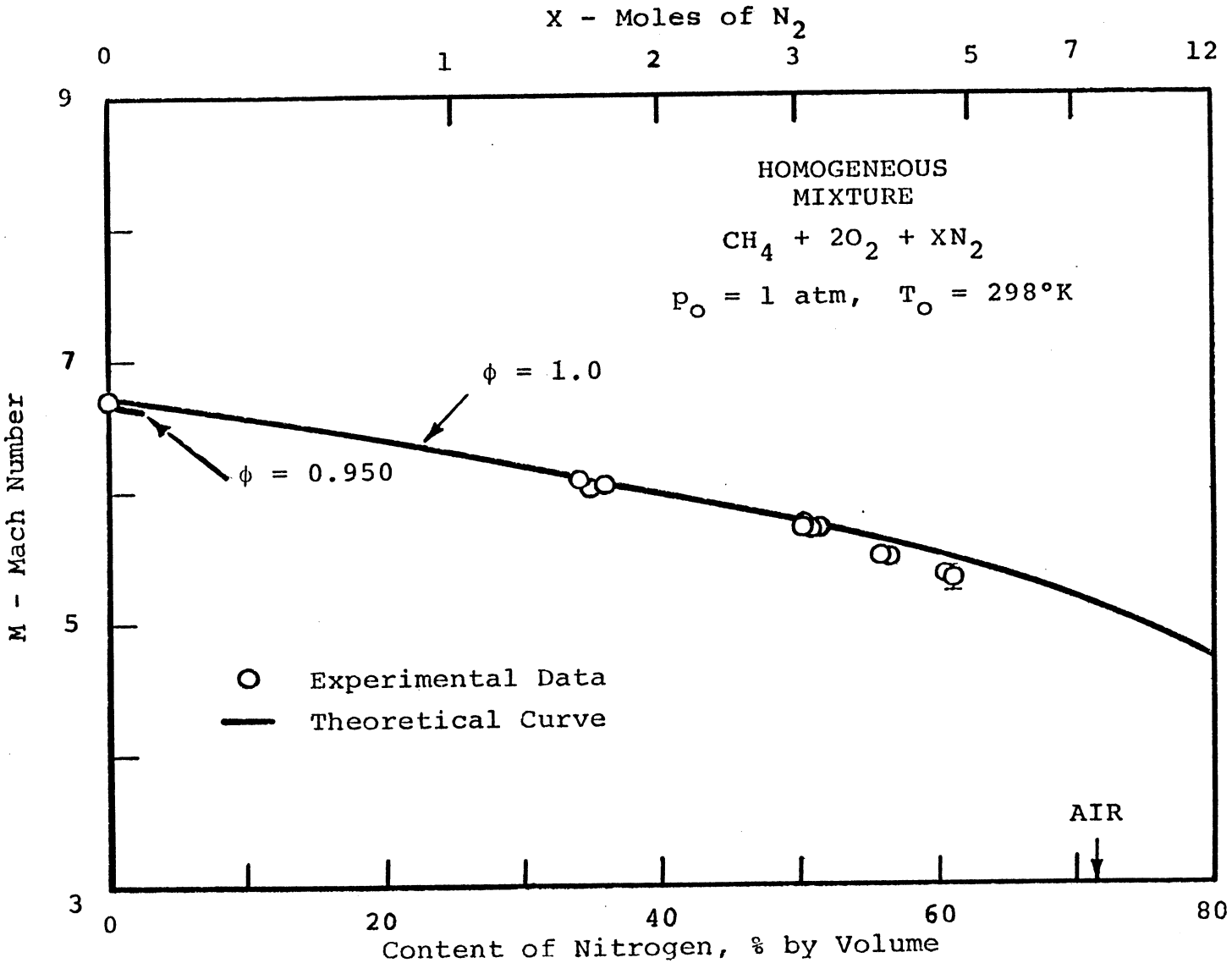

Figure 5. Comparison of Calculated and Measured Detonation Velocity

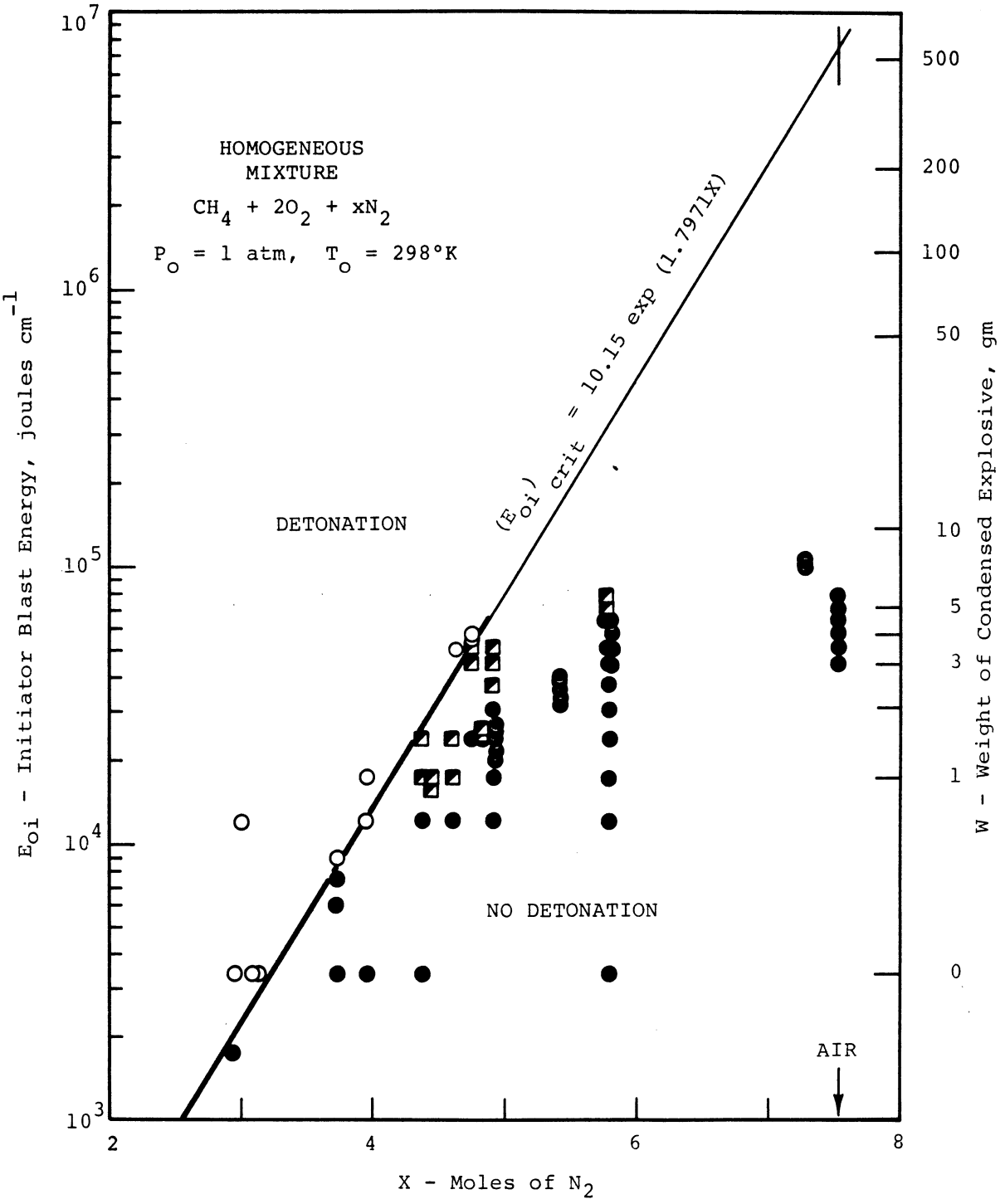

Figure 6. Correlation of Measured $(E_{oi})_{crit}$ with Molar Content of Nitrogen.

O - Detonation; ● - No Detonation; ◪ - Uncertain

(ii) For the "no-nitrogen" case, i.e. methane-oxygen

$$(E_{oi})_{crit} \sim 10 \text{ joules cm}^{-1}$$

These two cases indicate an extremely high energy level and a very low energy level, respectively.

The experimental results, shown in Fig. 6, lead to the following mathematical relation between $(E_{oi})_{crit}$ and X.

$$(E_{oi})_{crit} = 10.15 \exp (1.7971X)$$

where

$$0 \leq X \leq 7.52$$

This relation is comparable to Bull et al.'s[4] results for the spherical case as both are linear functions in the semi-log plane. However, there is a discrepancy (as X increases) between Boni's[5] predictions and Bull's[4] extrapolated results. Boni's calculations, which cover the range of X up to 7.52, are not represented by a single function in the semi-log plane but indicate that E_{oi} increases even faster for higher X. Unfortunately, the correct functional relation between $(E_{oi})_{crit}$ and X, could not be confirmed due to the lack of experimental results for methane-air. Since the predicted critical initiator energy level (for "air" case) was very high the limitations imposed on the experimental work due to safety requirements and excessive cost preclude experiments at higher nitrogen levels. There is the possibility that neither Bull et al.'s nor Boni et al.'s critical initiator energy level are correct but that even higher values are needed, or, for that matter, that stoichiometric methane-air mixtures at ambient conditions cannot be detonated at all.

The extrapolated critical initiator energy level for the "air" case is subject to appreciable uncertainty in that there is high sensitivity to the straight line extrapolation.

Further experiments were conducted in recognition of the fact that natural gas usually contains some ethane and/or propane. Using precisely the same techniques and operating with stoichiometric mixtures in every case, various methane-ethane-air mixtures were tested and the critical, or threshold, initiator energy was determined. The results were reported by

Vander Molen and Nicholls and are shown in Fig. 7. It is to be noted that small additions of ethane markedly reduce the energy level required. However, after the ethane concentration exceeds 15-20% of the total fuel, the change is relatively small. A very similar situation exists for the case of propane addition. A limited number of experiments are shown in Fig. 8 for a stoichiometric methane-propane-air mixture. In general, the initiation energies for this case are greater than for the ethane mixtures. This behavior is in agreement with the bag tests of Bull[8]. At higher propane concentrations the data indicate a continuing appreciable reduction in threshold energy as the amount of propane is increased. This characteristic is in contrast to the ethane case, where the variation was slight, and may possibly just reflect the fact that insufficient data is available.

Theoretical Analysis

The theoretical determination of the "critical initiation energy" has been the subject of a number of recent investigations as discussed in the review by Lee[9]. The finite difference calculations of Boni et al.[5] mentioned earlier is, perhaps, the most recent development. All these theories rest on the basis that initiation depends on the interaction between the decay of the initiating blast and the growth of the induction zone behind the shock front. Determination of a clear cut criterion for the onset of initiation is a key difficulty, and has required the introduction of various arbitrary or empirical assumptions. Thus Boni et al.[5] chose the initiation energy by inspecting Mach number-radius trajectories computed numerically for different values of the blast energy. The objective of the present theory is to simplify the computations and to establish a more precise criterion for the onset of detonation.

A two front detonation, such as discussed by Soloukhin[10], is used here. As shown in Fig. 9, the leading front of such an interface with finite thickness is a shock wave and the trailing front is a reaction front, separated from the shock by the induction distance ε_I. A second order single step irreversible reaction is assumed to occur instantaneously on the reaction front where the bulk of the heat release occurs.

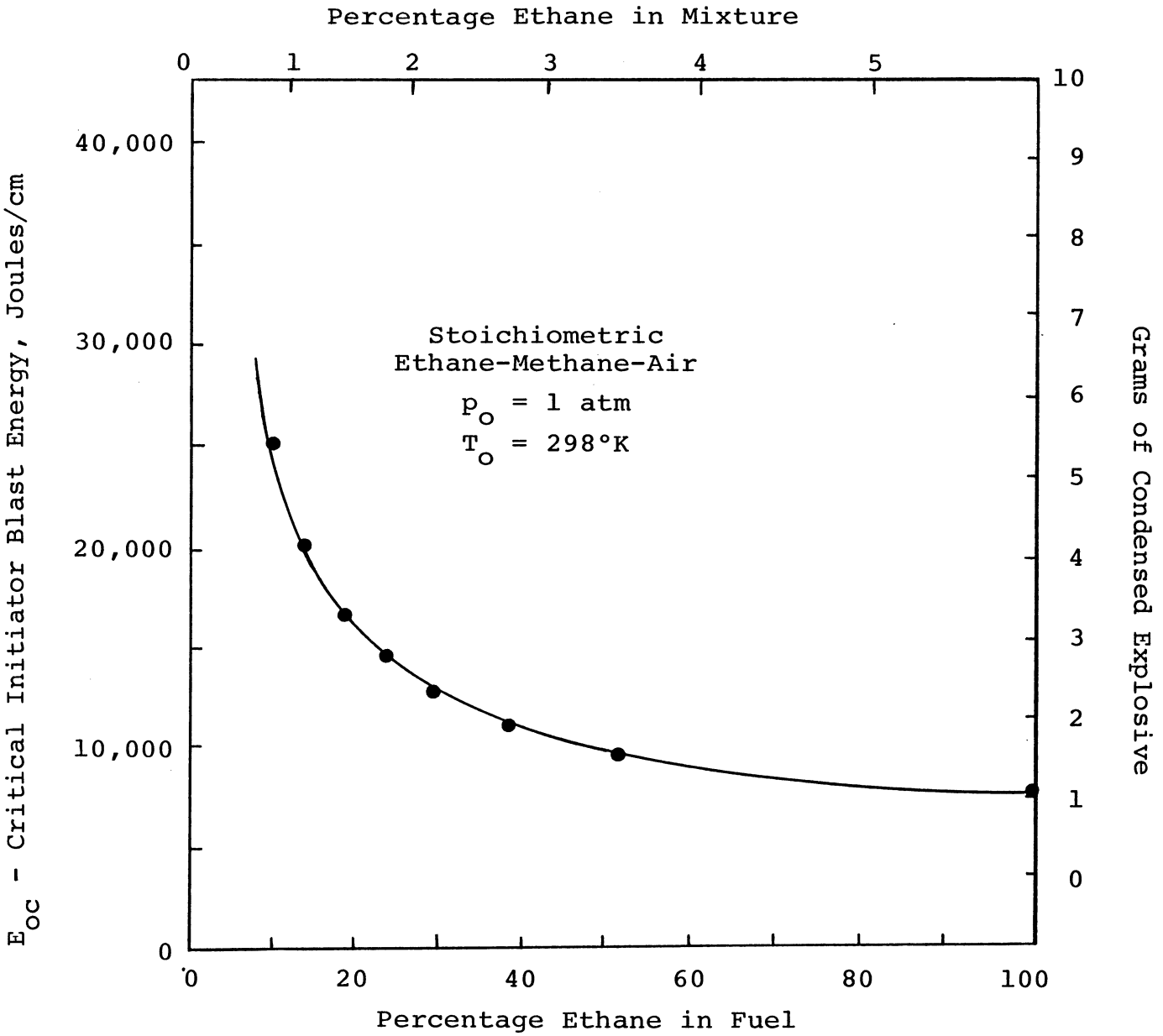

Figure 7. Initiation Energy for Various Stoichiometric Ethane-Methane-Air Mixtures.

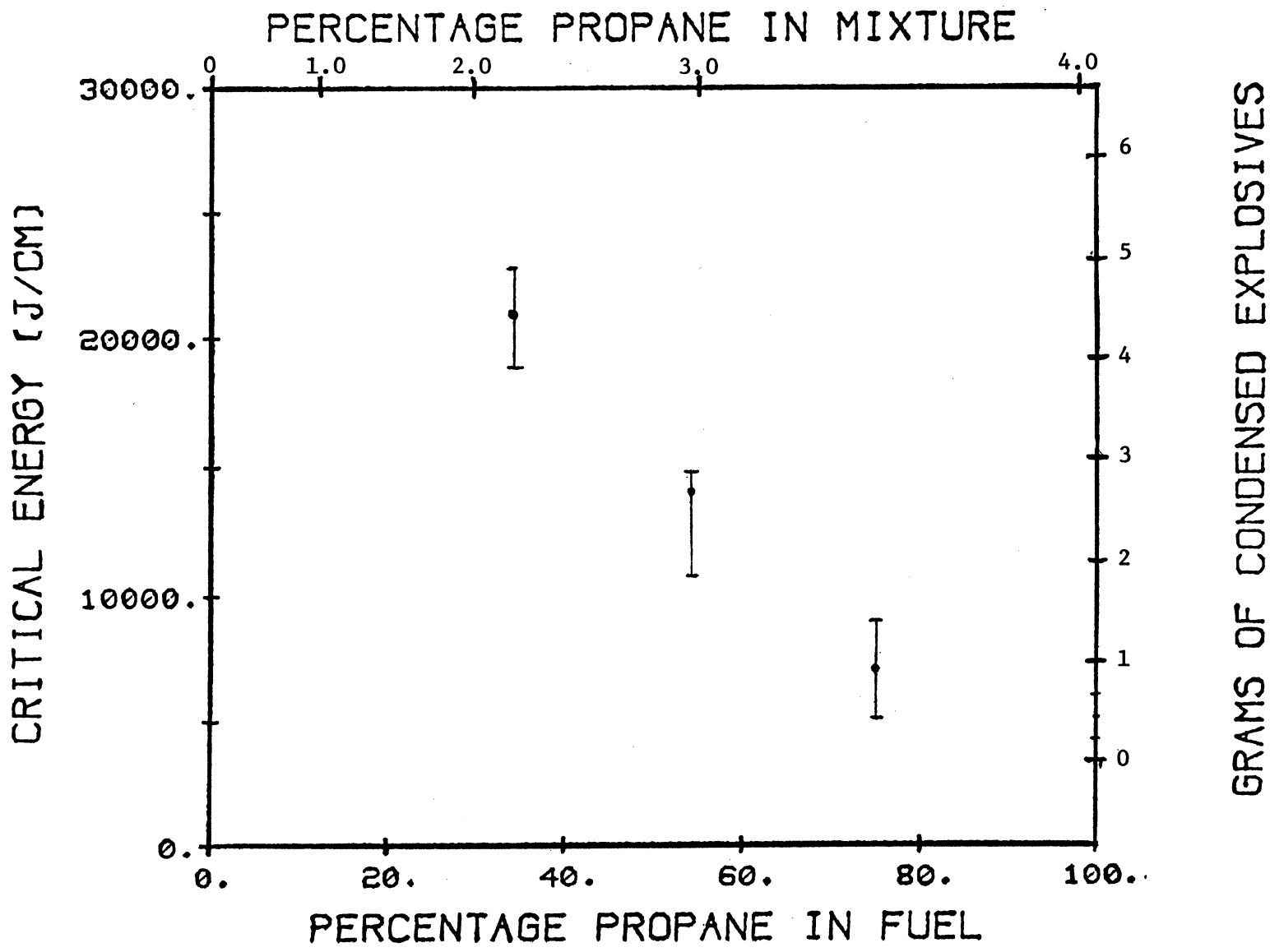

Figure 8. Initiation Energy for Various Stoichiometric Propane-Methane-Air Mixtures.

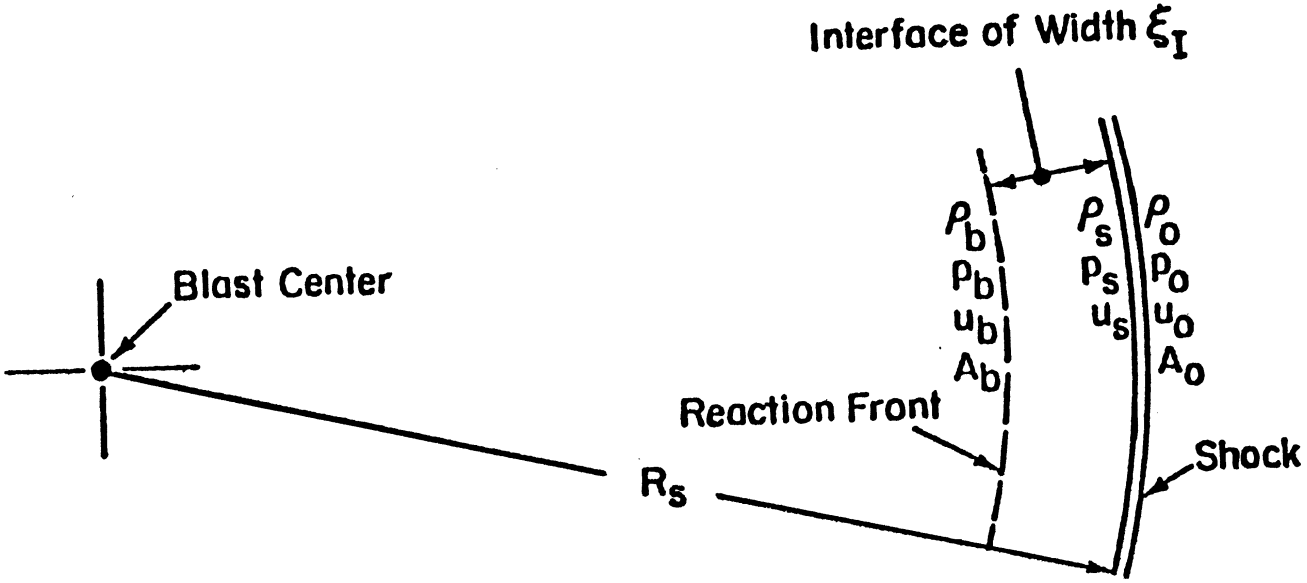

Figure 9. The Two Front Detonation

Two characteristic length scales representing chemical and hydrodynamic flow processes are present in this two front model. The chemical processes occur on the characteristic length scale ℓ_c of the order of the induction distance. Therefore, by using ℓ_c to stretch the radial coordinate r, it is possible to formulate simplified equations for the induction distance and the distribution of the flow properties within the induction zone. With this knowledge, the conservation equations across the interface with finite width can be solved to compute the conditions downstream of the reaction front.

The hydrodynamic processes occur on the characteristic length scale of the order of the shock radius R_s. Since $\ell_c/R_s \ll 1$, it follows that on this scale, the two front wave can be approximated by a discontinuity. The boundary conditions for the hydrodynamic flow are given by the conditions behind the reaction front. The distribution of the flow properties can then be calculted by using the technique developed by Bach et al.[11] for a discontinuous detonation wave.

The governing equations for a one dimensional nonsteady flow without transport effects and body forces are used. The induction kinetics are approximated by the following single second order irreversible reaction (A—fuel, B—oxidizer, C—combustion products).

$$aA + bB \rightarrow cC$$

Arrhenius kinetics are assumed for the mass rate of change of species A per unit volume, W_A, so that the species conservation equation for A is

$$\bar{\rho}\left\{\frac{\partial Y_A}{\partial \bar{t}} + \bar{u}\,\frac{\partial Y_A}{\partial \bar{r}}\right\} = \bar{W}_A = -B\bar{\rho}\, Y_A^{a} Y_B^{b} e^{-\bar{T}_a/\bar{T}} \qquad (1)$$

where Y_A and Y_B are the mass fractions of A and B, and barred quantities are dimensional.

A system with a high activation energy $\bar{E}_a$ is considered such that the post shock particle temperature $\bar{T}_s$ satisfies the conditions $\bar{E}_a \gg R\bar{T}_s$, or $\beta = R\bar{T}_s/\bar{E}_a = \bar{T}_s/\bar{T}_a \ll 1$. The end of the induction zone is then marked by the fact that a small change in the value of the flow properties [~O(β)] results in a large relative change [~O(1)] in the reaction rate. It can

then be shown from Eq. (1) that

$$\frac{l_c}{R_o} \cong t_r M_s e^{\bar{T}_a/\bar{T}_s} \tag{2}$$

where

R_o = explosion length = $[E_o/k_i \rho_o a_o^2]^{1/(i+1)}$

k_i = 1, 2π, 4π for i = 0, 1, 2
corresponding to plane, cylindrical or spherical symmetry

$t_r = t_c/t_b$

$t_c = [B Y_{A_o}^{a-1} Y_{B_o}^{b}]^{-1}$ = chemical time scale

$t_b = R_o/a_o$ = blast wave time scale

Equations describing the induction zone structure now can be derived by stretching the independent variables as follows:

$\tau_B = R_s/\dot{R}_s$ $\quad w = (\dot{R}_s - \bar{u})/\dot{R}_s$ $\quad \tau = \bar{t}/\tau_B$

$\rho = \bar{\rho}/\bar{\rho}_o$ $\quad p = \bar{p}/\bar{p}_o$ $\quad \eta = (R_s - \bar{r})/l_c$

$u = \bar{u}/\dot{R}_s$ $\quad h = \bar{h}/\bar{c}_{po}\bar{T}_o$ $\quad Y_i = Y_i/Y_{io}$

$T = \bar{T}/\bar{T}_o$ $\quad \theta = R_s\ddot{R}_s/\dot{R}_s^2$

where subscript 'o' is used to denote the undisturbed medium.

Two small parameters, l_c/R_s and β, appear in these equations, suggesting an expansion of the form

$$f = f_s + \beta f^{(1)} + (l_c/R_s) f_1 + \ldots$$

for the parameters of the flow. Since, usually, $\beta >> l_c/R_s$ it is found that to first order in β the conservation equations become

Continuity:

$$\rho^{(1)} w_s + w^{(1)} \rho_s = 0 \tag{3}$$

Momentum:

$$\rho^{(1)} w_s^2 + 2w^{(1)} w_s \rho_s + p^{(1)}/(\gamma_o M_s^2) = 0 \tag{4}$$

Energy:

$$T^{(1)} + [(\gamma_o - 1)/2]\, M_s^2 2w^{(1)} w_s - Q Y_A^{(1)} = 0 \qquad (5)$$

where

$$Q = \bar{Q}/\bar{c}_{po}\bar{T}_o$$

and $\bar{Q}$ is the heat release per unit mass of fuel-oxidizer mixture. The species equation becomes:

$$w_s[(dY_A^{(1)})/d\eta] = e^{T^{(1)}/T_s} \qquad (6)$$

The subscript s refers to conditions immediately behind the shock.

Solving Eqs. (3) to (6) for the temperature coefficient T_1 yields the result

$$T^{(1)} = -T_s \ln[1 - (\eta/w_s F)]$$

where

$$F = (T_s/Q)[(\gamma + 1)(M_s^2 - 1)] \Big/ \left[(\gamma + 1)(M_s^2 - 1) - 2(\gamma - 1)\left(1 + \frac{\gamma-1}{2} M_s^2\right)\right]$$

This solution diverges as $\eta \to w_s F$ and this value of η, denoted as η_I, is used as the induction distance so that

$$\eta_I = w_s F = \epsilon_I/l_c \qquad (7)$$

This definition of induction distance is similar to that introduced by Hermance[12]. Treatment of the end of the induction zone requires a detailed asymptotic analysis[13] which is not considered here.

Equations (3) to (6) further reveal that the structure of a diverging detonation wave is approximately like that of a quasisteady plane detonation to first order in β.

On the hydrodynamic scale, the approximation of a single front detonation wave is valid provided $l_c/R_s \ll 1$; however to determine the jump across this discontinuity the induction zone must be taken into account as indicated below. The distribution of flow properties between a single front detonation wave and blast center, has already been determined approximately by Bach et al.[11] using Sakurai's velocity distribution law and Porzel's power law for the density distribution:

$$x = r/R_s \tag{8}$$

$$u = u_b x \tag{9}$$

$$\rho = \rho_b(1 - x)^q \tag{10}$$

Substituting Eqs. (8)-(10) in the momentum equation yields the following expression for the pressure

$$p = p_b - \left[\frac{\rho_b}{q+2}\right](1 - x^{q+2}) \cdot \left[2\theta\delta \frac{du_b}{d\delta} + u_b(1 - u_b - \theta)\right] \tag{11}$$

$$q = (i + 1)(\rho_b - 1),\ \delta = 1/M_s^2$$

where u_b, ρ_b and p_b are the boundary conditions to be determined from the analysis of the interface with finite width as described below.

Using the control volume bounded by the two fronts as shown in Fig. 9 the conservation equations for the interface become

Mass:

$$\frac{d}{dt}\iiint_{V_I} \bar{\rho}\, dv - \rho_o \dot{R}_s \bar{A}_o + \bar{\rho}_b[(\dot{R}_s - \dot{\varepsilon}_I) - \bar{u}_b]\bar{A}_b = 0 \tag{12}$$

Momentum:

$$\frac{d}{dt}\iiint_{V_I} \bar{\rho}\,\bar{u}\, dv + \bar{\rho}_b\bar{u}_b[\dot{R}_s - \dot{\varepsilon} - \bar{u}_b]\bar{A}_b = \bar{p}_b\bar{A}_b - p_o\bar{A}_o \tag{13}$$

Energy:

$$\frac{d}{dt}\iiint_{V_I} \bar{\rho}\left(\bar{e} + \frac{\bar{u}^2}{2}\right)dv - \rho_o e_o \dot{R}_s \bar{A}_o + \bar{\rho}_b\left(\bar{e}_b + \frac{\bar{u}_b^2}{2}\right)$$

$$\cdot\,(\dot{R}_s - \dot{e}_I - \bar{u}_b)\bar{A}_b = \bar{p}_b\bar{A}_b\bar{u}_b \tag{14}$$

where V_I is the volume of the region between the two fronts.

Equation (12) can be expressed in the form

$$\rho_b w_b A_b = 1 - d_1$$

where d_1 is the volume integral in Eq. (12), made dimensionless with $\rho_o \dot{R}_s A_o$, and is computed by using Eq. (7) as follows,

$$d_1 = \frac{1}{\rho_o \dot{R}_s \bar{A}_o} \frac{d}{dt} \iint_{V_I} \int \bar{\rho}\, dv = \frac{1}{\rho_o \dot{R}_s \bar{A}_o} \frac{d}{dt} (\bar{\rho}_s V_I)$$

$$= \rho_s \frac{\varepsilon_I}{R_s} \left[M_s \left(\frac{1}{\rho_s} \frac{d\rho_s}{dM_s} + \frac{1}{\varepsilon_I} \frac{d\varepsilon_I}{dM_s} \right) + i \right]$$

In the above equation, the terms of order $\beta(\varepsilon_I/R_s)$ and $(\varepsilon_I/R_s)^2$ are neglected. The factor d_1 represents the effect of the finite thickness of the wave front and the nonsteady effects on the usual mass conservation relation for a discontinuous front.

Equations (13) and (14) can be treated similarly. Together with the equation of state (perfect gas), these equations can then be solved iteratively to obtain ρ_b, u_b, p_b, and T_b, the density, velocity, pressure, and temperature, immediately downstream of the two front wave.

Following Bach et al.[11], the integrated energy equation is used to determine the trajectory of the two front wave. After algebraic reduction the following equation is obtained for the trajectory

$$1 = Z^{i+1} \left[\frac{I}{\delta} - [\gamma_o(\gamma_o - 1)(i+1)]^{-1} - \frac{\bar{Q}}{a_o^2} \frac{\rho}{(q+i+1)} \times \{1 - [(\varepsilon_I/R_o)/Z]\}^{q+i+1} \right] \tag{15}$$

where $Z = R_s/R_o$ and I is given by

$$I = \frac{p_b}{(\gamma_o - 1)(i+1)}$$

$$- \frac{\rho_b \left[2\theta\delta \frac{du_b}{d\delta} + u_b(1 - u_b - \theta) \right]}{(\gamma_o - 1)(i+1)(q+i+3)} + \frac{\rho_b u_b^2}{2(q+i+3)}$$

The differential equation (15) is of second order in M_s through its dependence on θ.

Equation (15) is solved numerically for the wave trajectory in the M_s - Z plane. For each fuel-oxidizer mixture solutions are obtained for a decreasing sequence of trial values of E_o or, what is equivalent, of the explosion length R_o. The value of E_o for which transition to detonation first fails is then identified as the critical initiation energy.

Calculations of M_s - Z trajectories were made for stoichiometric methane-oxygen-nitrogen mixtures ($CH_4 + 2O_2 + XN_2$) for values of X up to 7.52 corresponding to air, and for both cylindrical and spherical symmetry.

The reaction rate data to be used in Eq. (1) was determined from the experiments by Tsuboi and Wagner,[14] and in terms of the variables used here, is as follows:

$$B = 3.177 \times 10^{12} \left(\frac{\rho_o}{M_a} \right)^{a-1} \left(\frac{\rho_o}{M_b} \right)^{b}$$

$$a = 0.68$$

$$b = 1.02$$

$$E_a = 222 \text{ KJ/mole}$$

where ρ_o is in gm/liter and M is molecular weight in gm/mole with $M_a = 16$ and $M_b = 32$.

In addition, the values of c_p, γ, and the molecular weight are assumed to be constant and identical for the reactants and products. An initial temperature T_o of 298°K was used.

A typical set of numerically calculated spherical wave trajectories in the M_s - Z plane for a $CH_4 + 2O_2 + 4.245\ N_2$ mixture is shown in Fig. 10 for different values of t_r, the ratio of the characteristic chemical to the characteristic blast time.

These curves indicate the typical subcritical wave behavior observed experimentally by Bull et al.[4] and Edwards et al.[15] That is, the Mach number M_s drops below the Chapman-Jouguet value prior to the final establishment of a detonation. Similar results were obtained by Bach et al.[11] and by Boni.[5]

From the numerical results shown in Fig. 10, it appears that the critical initiation energy, E_{oc}, is associated with a singularity in Eq. (15)

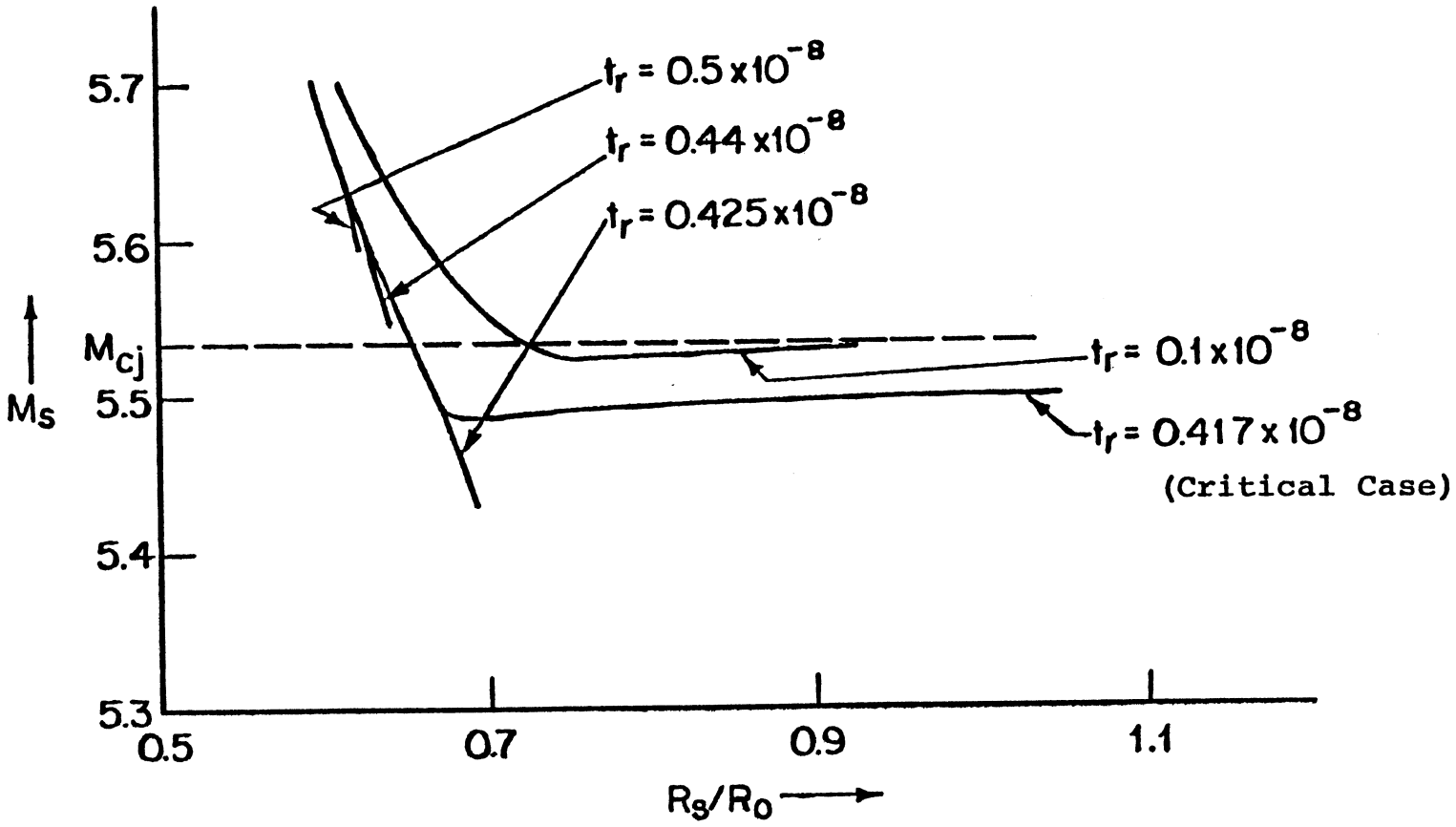

Figure 10. Wave Trajectories in the M_s - R_s/R_0 plane.

with a behavior similar to a saddle point. Thus, close to the critical value a very small change in E_o will cause the solution to diverge. In the case shown in Fig. 10, a 2% increase in t_r, which varies inversely with E_o, results in a transition from a convergent to a divergent detonating solution. In the present analysis, the critical value of t_r ($t_{r_{crit}}$) has been computed to within 1% of the value at transition.

As shown in Fig. 11 the values of E_{oc} predicted from the present theory for spherical symmetry (i = 2) and the experiments of Bull et al.[4] compare very well, suggesting that the present theory contains the essential features of the direct initiation process.

Lee[9] has suggested the interesting empirical relation that the critical explosion length, R_{oc}, is independent of geometry. With this relationship in mind, all the theoretical and experimental results are presented as plots of R_{oc} versus X in Fig. 12. The theoretical curves for cylindrical and spherical symmetry support the suggestion that R_{oc} is independent of geometry, and further are in good agreement with the measurements of Bull et al.[4] The experimental values of R_{oc} for cylindrical symmetry measured in the present investigation are significantly greater than either the theory or the spherical data of Bull et al.[4] From non-reacting blast wave experiments in the sectored chamber, it is known that appreciable energy losses are associated with the breech and chamber and that the energy fraction lost increases with energy level. However, some of this effect is gas dynamic in nature. A trustworthy correction factor is not known so the energy levels employed have been reported without correction. The experiments of Bull et al.[4] used a central high explosive charge so that such losses were not present.

Boni et al.[5] found that the linear extrapolation of experimental data used by Bull et al.[4] is not valid for values of X beyond about 4. Boni et al.[5] attributed the nonlinearity of their results to the two step reaction scheme used in the analysis. The present theory used a one step reaction and essentially reproduced the linear semi logarithmic plot of Bull et al.[4] for E_{oc} versus X. The question of whether the two reaction scheme is needed to compute the critical initiation energy of CH_4-air mixtures can only be resolved once experimental data for X close to the value for air becomes available.

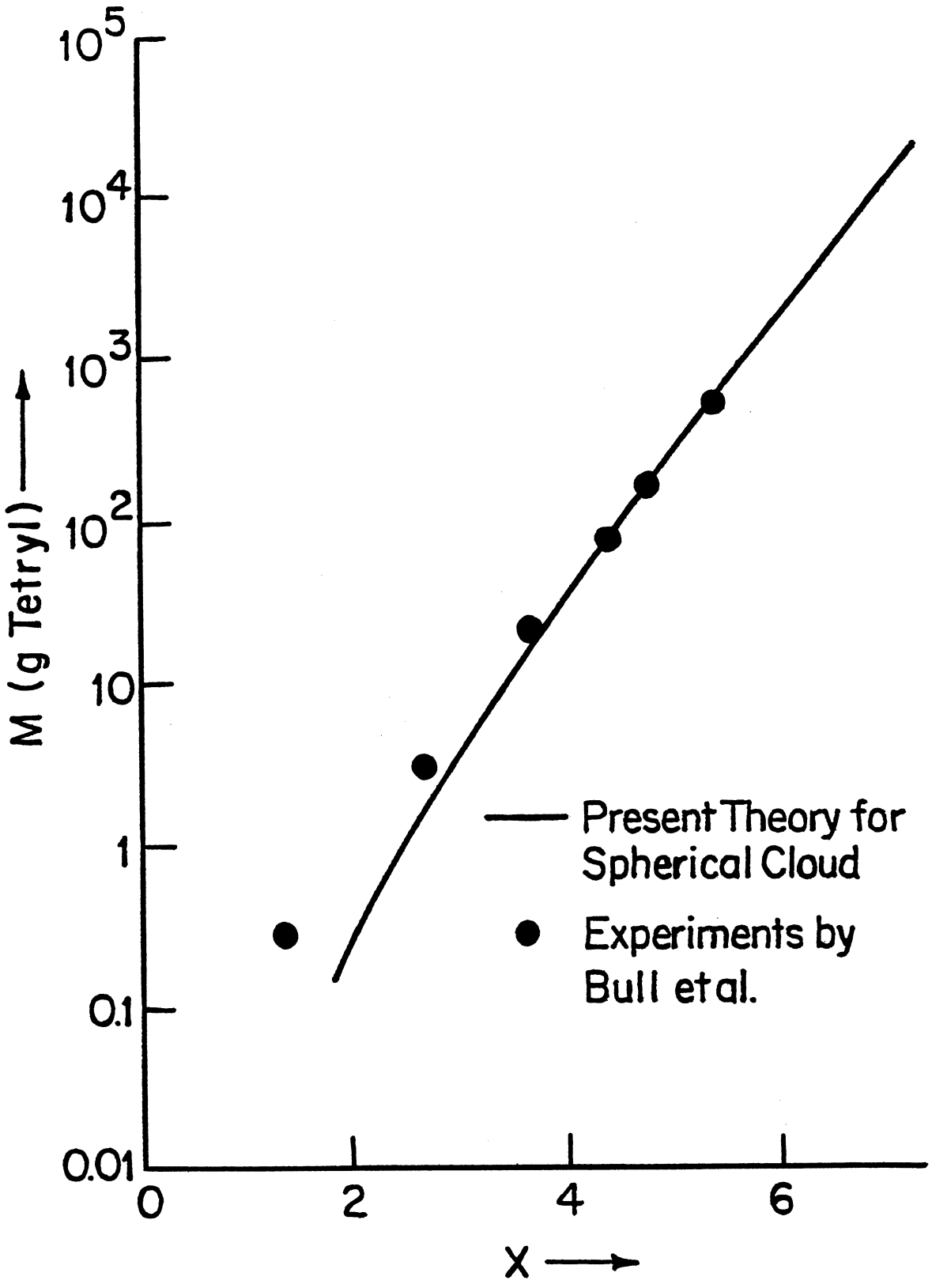

Figure 11. Comparison of Theory and the Experiments of Bull et al.[4]

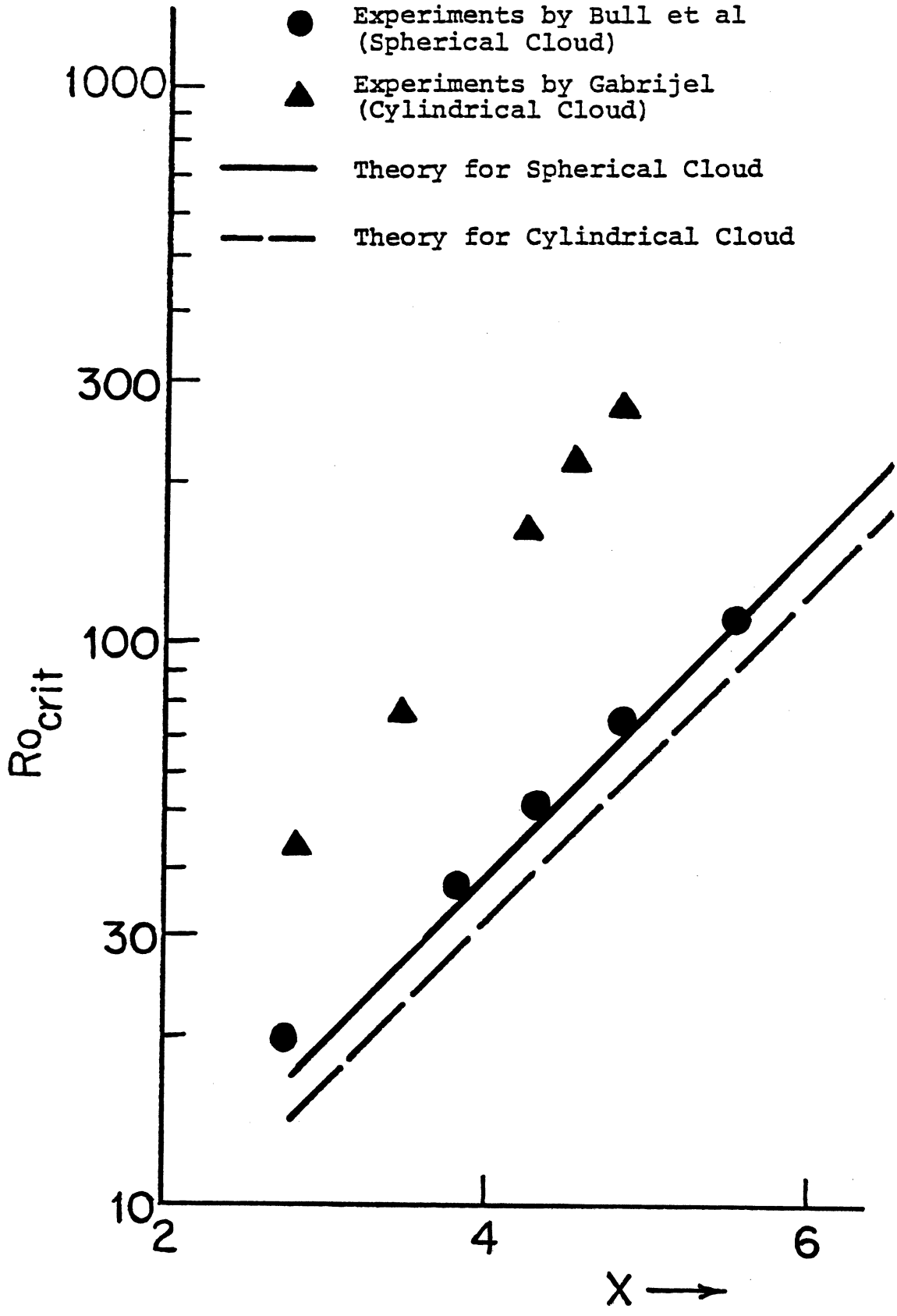

Figure 12. Theoretical and Experimental Variation of the Critical Explosion Length.

The predictions of the present theory are very encouraging in light of available experimental results. The cylindrical shock tube experiments provide values of R_{oc} of the proper order of magnitude and show the variation of R_{oc} with X, even without taking account of energy losses to the breech and the shock tube walls. It is also quite likely that the reduced initiation energies observed when small amounts of ethane are added to methane would be reflected in the theory provided appropriate values of the activation energy and pre-exponential factor are used in Eq. (1). However, such calculations have not yet been made.

MAJOR ACHIEVEMENTS OF THE PROJECT

A unique experimental facility and a closely related theoretical model were developed in order to assess the danger of detonation in unconfined natural gas-air clouds. In this way much more accurate assesments of the danger can be made without the necessity of the extremely expensive, time consuming large scale field tests.

MAJOR TECHNICAL PROBLEMS ENCOUNTERED

Because of the insensitivity of methane-air mixtures, it was impossible to use the extremely high energy levels required to attain detonation. Accordingly, it became necessary to determine the threshold initiation energy levels for a number of stoichiometric methane-oxygen-nitrogen mixtures and then to extrapolate to the "air" case. In this process, the higher nitrogen concentration mixtures required high energy levels and hence caution had to be exercised in order to determine whether the "initiating" process was still affecting the wave propagation. Certainly the theoretical analysis helped in this regard but it was strongly influenced by the uncertainty in the value of the constants for methane chemical kinetics.

CONCLUSIONS

The experimental portion of this program as well as the analytical portion indicate that detonation of pure methane-air clouds is unlikely, which is in agreement with the results of other investigators. The confidence in this statement is heightened by the good agreement between the theory and experiment. Other gases, such as ethane and propane, which are present in natural gas increase the likelihood of detonation although a very energetic source would still be required. In a real case, the presence of cloud inhomogeneities would make detonation all the less likely. Some concern must still be present in the event of confined spaces where possible ignition energy sources could lead to detonation. The present program has shown that laboratory scale experiments can be used to assess the effect of various parameters on the behavior of large natural gas-air clouds.

RECOMMENDATIONS

The experimental facility and associated analysis has been developed to a fairly high degree and should be used to advantage. Some further developments of both aspects should be undertaken as the technique is applied to other gaseous systems of interest (such as alternate gaseous fuels). Many details of the initiation process and the influence of cloud inhomogeneity are still not clearly understood.

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