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Author

Cheng, R.K.

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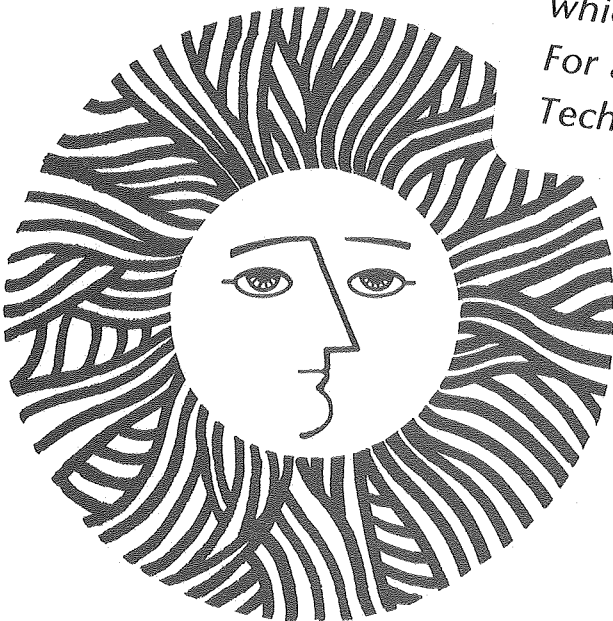
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R.K. Cheng and A.K. Oppenheim

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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R. K. Cheng and A. K. Oppenheim

Lawrence Berkeley Laboratory
University of California, Berkeley 94720

INTRODUCTION

Combustion in a homogeneous gas mixture initiated by a shock wave is characterized by the occurrence of two distinct ignition modes: strong ignition, occurring over a high temperature threshold and generating a blast wave, and weak ignition initiating a flame kernel devoid of gasdynamic effects. The strong ignition limit is a line of demarcation between the two cases. It is usually delineated on the plane of pressure and temperature of states at which the induction process takes place.

The basic concept of the strong ignition limit, introduced into the literature in the 1960's, was first pointed out and explored by Soloukhin and his associates.¹⁻³ At the same time it was employed by Strehlow and his students to study the initiation of detonation.⁴⁻⁶ The reflected shock technique used in these studies became one of the principal means for chemical kinetic studies of combustion in premixed gases.⁷⁻¹⁴ In the 1970's gasdynamic properties of exothermic processes associated with strong ignition have been explored in a program of studies conducted at Berkeley.¹⁵⁻²²

The distinction between weak and strong ignition behind reflected shock is exhibited in Figs. 1a and 1b by trajectories of wave fronts in time-space domain starting from the instance of shock reflection deduced from laser schlieren cinematographic records.¹⁴ The corresponding pressure records are provided in the inserts. For strong ignition, as shown in Fig 1a, the trajectory of the exothermic front is quite straight. Detailed analysis of its development^{19,21} confirms that it is essentially a blast wave. On the other hand, weak ignition (Fig. 1b) is characterized by a continuously accelerating front of the zone where the exothermic process takes place. Initiation of combustion in this case takes place at isolated spots creating flame kernels which eventually interact forming a flame-like structure.

In early publications of Soloukhin¹⁻³ involving stoichiometric H₂-O₂, strong ignition was interpreted as the onset of chain branching--the same criterion as that governing the classical second explosion limit. This theory was supported by the fact that a fair approximation of the strong ignition limit can be obtained by extrapolating the classical second explosion limit into the explosion region. Later, in a study by Meyer and Oppenheim¹⁵ also involving H₂-O₂, the strong ignition limit was shown to be associated with the sensitivity of induction time, τ , to change in temperature, T. The strong ignition limit was then expressed in terms of the partial derivative of induction time with respect to temperature at constant pressure,

$$\kappa = (\partial\tau/\partial T)_p \quad (1)$$

Subsequent work of Meyer and Oppenheim¹⁶ introduced a theory rationalizing the use of this criterion. The onset of strong ignition was attributed to a coherence in time and space of power pulses of exothermic centers arising in the medium in the course of the ignition process. It was shown specifically to occur when the variation in the induction times of the exothermic centers became sufficiently small throughout the medium, so that the exothermic process of most of the reaction centers coincided with each other in time. As a result of this coherence, the specific exothermic power per unit mass reached a relatively high value leading to the generation of a blast wave. Weak ignition corresponded to the case when the variation in the induction time from point to point was so erratic that the exothermic processes occurred at various centers separately, annihilating the generation of significant gas dynamic effects. Based on this argument, the maximum specific exothermic power was shown to be quite sensitive to the standard deviation in induction time--a product of the standard deviation in temperature and the sensitivity of induction time to change in temperature. Thus the criterion for strong ignition limit was identified with a specific value of κ deduced from experimental data. This criterion was applied to the H₂-O₂ and the CH₄-O₂ mixtures. For other hydrocarbon fuels such as i - C₈ H₁₈ and n - C₇ H₁₆ strong ignition limits were found to be independent of pressure, indicating that instead of κ , the proper criterion in this case is $(\partial \ln \tau / \partial T)_p$.¹⁷ This was rationalized as due to the fact that the half width of the exothermic power pulse was proportional to the induction time, while in previous cases it was virtually insensitive to the temperature.

In the past, flow visualization was the only means to determine strong ignition limit. However, on the basis of the experience we acquired, a simple and less time-consuming experimental technique was developed,²² it involved the use of pressure transducers as time-of-arrival meters delineating wave front trajectories. Vector polar solutions of wave-interaction processes accompanying the onset of strong ignition indicated that the front of the exothermic zone propagates at a velocity equal to the local speed of sound.

The objective of the study reported here was to carry out a systematic investigation of the induction time and strong ignition limit in a methane-hydrogen-oxygen system. Although the most interesting feature of this study was the determination of hydrogen as a reaction-promoting additive in the combustion of methane, the scope of the experimental program covers a full range of composition to investigate the interrelationship of mixture parameters with strong ignition limit. As a by-product the experiments provided data on induction times for various compositions of the mixture as functions of pressure and temperature.

EXPERIMENTS

All experiments were performed on a rectangular cross-section 3.8 cm x 4.45cm, aluminum shock tube. A bar-type barium-titanite pressure transducer is fitted at the end wall and two Kistler Type

601 gauges were mounted on the side wall at distances of 2 cm and 12 cm from the end. Pressure transducer signals were recorded on an oscilloscope and the incident shock velocity was measured with the use of a digital clock. Detailed description of the experimental and optical diagnostic systems can be found in Refs. 15 and 22.

Eleven mixtures were used, two of methane and oxygen, two of hydrogen and oxygen, and seven of various combinations of methane, hydrogen, and oxygen all in 90 percent argon dilution. Mixture compositions were specified in terms of two parameters ζ and ϕ .

$$\zeta \equiv X_{\text{H}_2} / (X_{\text{H}_2} + X_{\text{CH}_4})$$

and

$$\phi = [(X_{\text{H}_2} + X_{\text{CH}_4}) / X_{\text{O}_2}] / [(X_{\text{H}_2} + X_{\text{CH}_4}) / X_{\text{O}_2}]_{\text{stoich}}$$

where X_i ($i = \text{H}_2, \text{CH}_4, \text{O}_2$) is the mole fraction and ϕ is the equivalence ratio. The stoichiometric equation for the methane-hydrogen-oxygen system can be written as:



Figure 2 is a three-component composition diagram of the methane-hydrogen-oxygen system with 90 percent dilution showing the compositions of mixtures used in this study. The corresponding values of the mixture parameters are listed in Table I. In all, some 800 viable experimental runs were carried out. Initial conditions behind the reflected shock were determined by the use of normal shock relationships and the JANAF thermochemical data based on the measured incident shock velocity.

RESULTS AND DISCUSSIONS

Induction time

Induction time was measured at the end wall as shown in Fig. 1a. In order to evaluate κ , the induction time data were correlated in the form of an Arrhenius relation,

$$\tau = A[\text{fuel}]^x [\text{O}_2]^y \exp(E/RT) \quad (3)$$

as commonly done for a single fuel system. The quantities in square brackets denote concentrations in moles/cc, R is the universal gas constant; A , x , and y appear as correlation parameters, and E is the activation energy.

One of the most significant results we thus obtained was that the induction time for the $\text{CH}_4\text{-H}_2\text{-O}_2$ system could be correlated simply as follows:

$$\tau = \tau_{\text{CH}_4}^{(1-\epsilon)} \tau_{\text{H}_2}^{\epsilon} \quad (4)$$

where

$$\tau_{\text{CH}_4} = A_1 [\text{CH}_4]^{x_1} [\text{O}_2]^{y_1} \exp(E_1/RT) \quad (4a)$$

$$\tau_{\text{H}_2} = A_2 [\text{H}_2]^{x_2} [\text{O}_2]^{y_2} \exp(E_2/RT) \quad (4b)$$

τ_{CH_4} and τ_{H_2} are the induction time correlation equations for methane and hydrogen, while ϵ is a correlation parameter satisfying the conditions: $\epsilon \rightarrow 1$ for $X_{\text{CH}_4} = 0$ and $\epsilon \rightarrow 0$ for $X_{\text{H}_2} = 0$.

Equation 4 was based on the observation that the Arrhenius plots of induction times for the ternary mixtures of CH_4 , H_2 , and O_2 were consistent with those for the binary mixtures CH_4 - O_2 and H_2 - O_2 all yielding straight lines with activation energies for the CH_4 - H_2 - O_2 mixtures being higher than that of hydrogen and lower than for methane in a form expressed by this equation with good approximation.

The correlation parameters of Eqs. 4a and 4b were determined by using a nonlinear regression program of Marks.^{2,3} Table 2 lists these results in comparison to those reported in the literature.^{8, 11-14} In general our correlation parameters are in good agreement with the others.

Values of ϵ for other mixtures were determined by the same nonlinear regression program, and are listed in Table 1. It can be seen that all of the values of ϵ are approximately equal to ζ , falling, except for one, within the 95% confidence limit of ϵ . Equation (4) therefore could be used for the correlation of all the induction time data so that the induction time for the CH_4 - H_2 - O_2 mixtures could be predicted for a given mixture composition from the correlation parameters of CH_4 - O_2 and H_2 - O_2 mixtures. The CH_4 - H_2 - O_2 data for mixtures 5 and 6 of Table 1 are presented in Fig. 3.

The induction time data we obtained, including those for methane-hydrogen-oxygen mixtures, were confirmed within a factor of two by the results of computations based on recently compiled chemical kinetic data for the oxidation of methane²⁴ and hydrogen.¹⁸

Strong Ignition Limits

To determine strong ignition limits trajectories of the wave fronts for each experimental run were constructed. Strong ignition could be identified by two characteristic features of the trajectory of the exothermic front: (1) it is quite straight, and (2) it travels at a speed close to the sonic velocity of the states behind the reflected shock. The criterion used for the second condition was that the blast wave travels within ± 40 m/sec of the sonic velocity. This criterion was based on the error associated with each time-of arrival measurement of about 2 μsec , corresponding to an uncertainty of 40 m/sec in the velocity evaluated on this basis.

The results were plotted on the pressure-temperature plane forming an "auto-ignition" diagram for each of the eleven mixtures, an example is shown in Fig. 4. Boundary between the initial conditions of the two ignition modes is the strong ignition limit; it is indicated by the shaded area. Using Eq. 4, the curve of constant κ , giving the best fit through the center of the shaded region was evaluated, thus obtaining the critical value of κ for the strong ignition limit. In general, all the strong ignition limits could be expressed quite well by these lines. The ability of the curves of $\kappa = \text{const.}$ to describe all the strong ignition limits of the CH_4 - H_2 - O_2 mixtures suggests that their exothermic power pulses are independent of the induction time.

In Fig. 5 all the curves of $\kappa = \text{const.}$ we determined are plotted on a single "auto ignition" plane. Shown by the chain dotted lines are the classical explosion limit of Lewis and Von Elbe. Strong ignition limits for the methane-oxygen mixtures are at the highest temperature level, approximately 1000°K higher than for the

hydrogen-oxygen mixtures. Strong ignition limits for all the other mixtures lie in-between.

The temperature level at which strong ignition takes place is in general proportional to ζ and, to ϕ . Strong ignition in lean mixtures occurs at lower temperatures (e.g., for mixtures 7, 8, and 9, $\zeta = 0.667$). For mixtures with constant ϕ , increasing the amount of hydrogen, i.e., decreasing ζ , lowers the temperatures at which strong ignition occurs. (For example, in mixture 3, $\phi = 0.5$ and $\zeta = 1/3$; in mixture 5, $\phi = 0.56$ and $\zeta = 1/2$.)

Critical values of κ for the mixtures we used for our study are listed in Table 1. Variation in these values corresponding to the ± 25 K for the strong ignition limit regions are about ± 0.1 $\mu\text{sec}/\text{K}$. As can be seen, all the values of κ are grouped around -0.5 $\mu\text{sec}/\text{K}$ with a high of -0.69 for mixture 9 and a low of -0.19 for mixture 3. They appear to be independent of the equivalence ratio for mixtures of $\text{CH}_4\text{-O}_2$ and $\text{H}_2\text{-O}_2$, but show a slight increase with equivalence ratio for the $\text{CH}_4\text{-H}_2\text{-O}_2$ mixtures with constant ζ . As discussed earlier, strong ignition limit is affected by the shape of the exothermic power pulse which is fixed by (1) the heat of reaction, reaction rate and initial conditions for a given chemical system, (2) the standard deviation of temperature resulting from the interaction between the boundary layer and the reflected shock, and (3) the critical value of κ .

In view of this, it is of interest to note that, for the range of initial conditions and mixture compositions covered in our study, all the criteria for strong ignition limits fall within quite a narrow band. This leads to the conclusion that the sensitivity of the induction time to temperature is the most dominating factor in establishing conditions favorable for strong ignition. A slight variation in the values of κ for mixtures of $\text{CH}_4\text{-H}_2\text{-O}_2$ could have been caused by differences in the shape of exothermic power pulses. However, without further investigation this is just a tentative hypothesis.

The amount of diluent in the test mixture should also be of importance to the strong ignition limit, for it affects the specific exothermic power per unit mass of the reacting medium. Since all the test mixtures are diluted in 90% A, this effect can only be inferred by comparing the strong ignition limit of mixture 10 with that of an undiluted stoichiometric $\text{H}_2\text{-O}_2$ mixture obtained by Meyer and Oppenheim¹⁵ deduced from laser schlieren cinematographic records. The strong ignition limit in the undiluted case is at a temperature level 200K lower than that of mixture 10. The criterion of the strong ignition limit κ , deduced then on the basis of a less precise correlation of induction time data than done here was -2 $\mu\text{sec}/\text{K}$. To establish a rational comparison with the present result we evaluated κ for the undiluted case from the correlation formula of Eq. (4b). This was done by first comparing the predicted induction times at the strong ignition limit with measured values, and then computing κ on this basis. In general, the correlation formula predicted the induction time at 2 atm within 10 μsec of the measurement, while the corresponding value of κ in the middle of the zone of the strong ignition limit was -1.5 $\mu\text{sec}/\text{K}$. Since the value of -2 $\mu\text{sec}/\text{K}$ obtained by Meyer and Oppenheim corresponded to a lower temperature of the strong ignition limit, the above value of κ

should be considered as quite consistent. The effect of diluent appears as an inhibitor, for it imposes the requirement of a higher value of κ in order to generate a specific exothermic power pulse necessary for strong ignition to occur.

CONCLUSIONS

A study of the auto-ignition behind reflected shock in eleven mixtures of $\text{CH}_4\text{-O}_2$, $\text{H}_2\text{-O}_2$, and $\text{CH}_4\text{-H}_2\text{-O}_2$ covering a temperature range of 900-2400K and pressure range of 1-3 atm was carried out. The induction times were correlated with an equation of the Arrhenius form that was found to be quite satisfactory. All the strong ignition limits we determined could be expressed in terms of a constant value of $\kappa \equiv (\partial\tau/\partial T)_p$ deduced for each mixture from the correlation equation being quite insensitive to variations in initial mixture compositions for the induction time. The values of κ for all test mixtures we used were grouped around $-0.5 \mu\text{sec/K}$ and thermodynamic conditions. This leads to the conclusion that the dominating factor in establishing the actual level of the strong ignition limit is the sensitivity of the induction time to temperature. Comparison of the strong ignition limit of the present $\text{H}_2\text{-O}_2$ mixture with 90% A dilution to that of the undiluted mixture measured in an earlier study of Meyer and Oppenheim¹⁵ showed that the addition of diluent caused the value of κ to decrease from $-1.5 \mu\text{sec/K}$ to $-0.5 \mu\text{sec/K}$.

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Table 1. Mixture Parameters

NO.	CH ₄ :H ₂ :O ₂ :A	ζ	ϕ	ϵ	κ ($\mu\text{sec/K}$)
1	1:0:2:27	0.	1.0	0.	-0.44
2	1:0:4:45	0.	0.5	0.	-0.45
3	2:1:4:63	0.33	1.125	0.312	-0.19
4	2:1:8:99	0.33	0.562	0.326	-0.36
5	1:1:2:36	0.5	1.25	0.453	-0.23
6	1:1:4:54	0.5	0.625	0.514	-0.49
7	1:2:2:45	0.67	1.5	0.689	-0.34
8	1:2:3:54	0.67	1.1	0.712	-0.57
9	1:2:4:63	0.67	0.75	0.718	-0.69
10	0:2:1:27	1.0	1.0	1.0	-0.49
11	0:1:1:18	1.0	0.5	1.0	-0.51

Table 2. Induction Time Correlation Formulae For CH₄-O₂ & H₂-O₂

$$\tau_{\text{CH}_4} = A_1 [\text{CH}_4]^{x_1} [\text{O}_2]^{y_1} \exp(E_1/RT)$$

Source	x_1	y_1	A_1 (cc/mole) ^{x_1+y_1} μsec	E_1 kcal/mole
Serry & Bowman ¹²	0.4	-1.6	7.65×10^{-18}	50.6
Lifshitz et al ¹³	0.33	-1.03	3.62×10^{-14}	46.5
Tsuboi & Wagner ¹⁴	0.32	-1.03	2.5×10^{-18}	53.0
Present Result	0.48	-1.94	1.19×10^{-12}	46.4

$$\tau_{\text{H}_2} = A_2 [\text{H}_2]^{x_2} [\text{O}_2]^{y_2} \exp(E_2/RT)$$

Source	x_2	y_2	A_2 (cc/mole) ^{x_2+y_2} μsec	E_2 kcal/mole
Asaba et al ⁸	0.4→0.8	-0.5→-0.8	constant	0.
White & Moore ¹¹	-0.33	-0.66	1.58×10^{-11}	17.19
Present Result	0.145	-0.56	1.54×10^{-4}	17.20

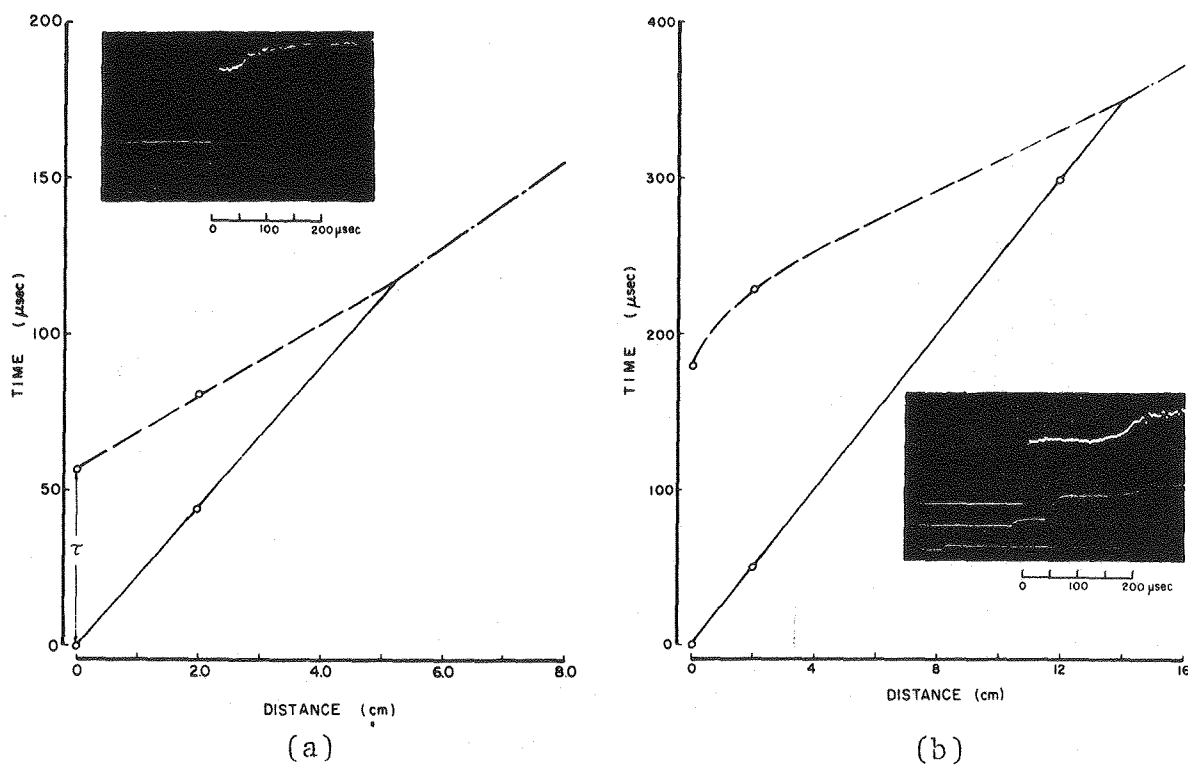


Fig. 1 Trajectories of wave fronts associated with (a) strong ignition and (b) weak ignition, ——— shock, - - - exothermic front, - · - · - transmitted front.

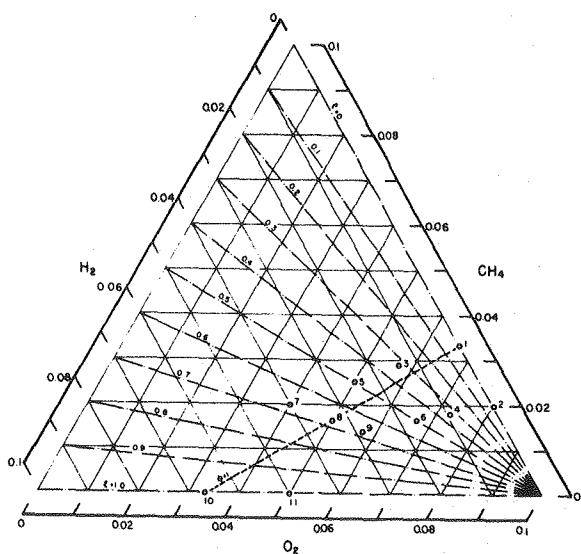


Fig. 2 Three-component composition diagram for $\text{CH}_4\text{-H}_2\text{-O}_2$, with 90% dilution.

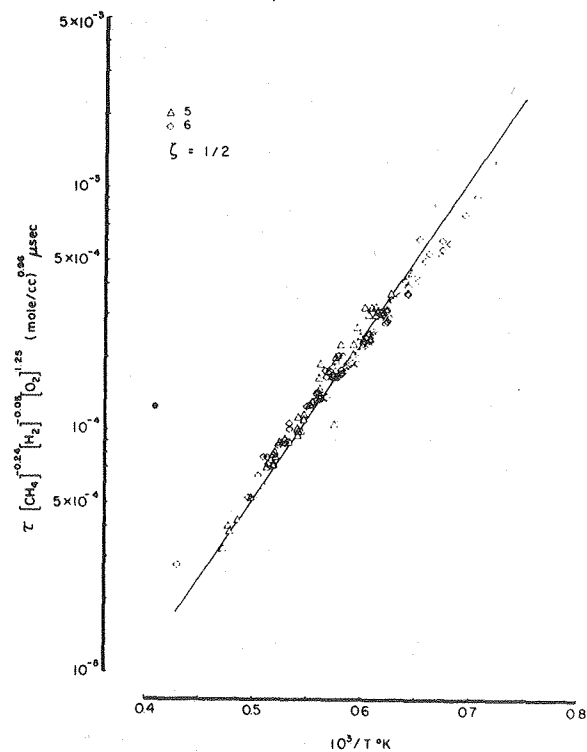


Fig. 3 Induction time data for mixture 5 and 6.

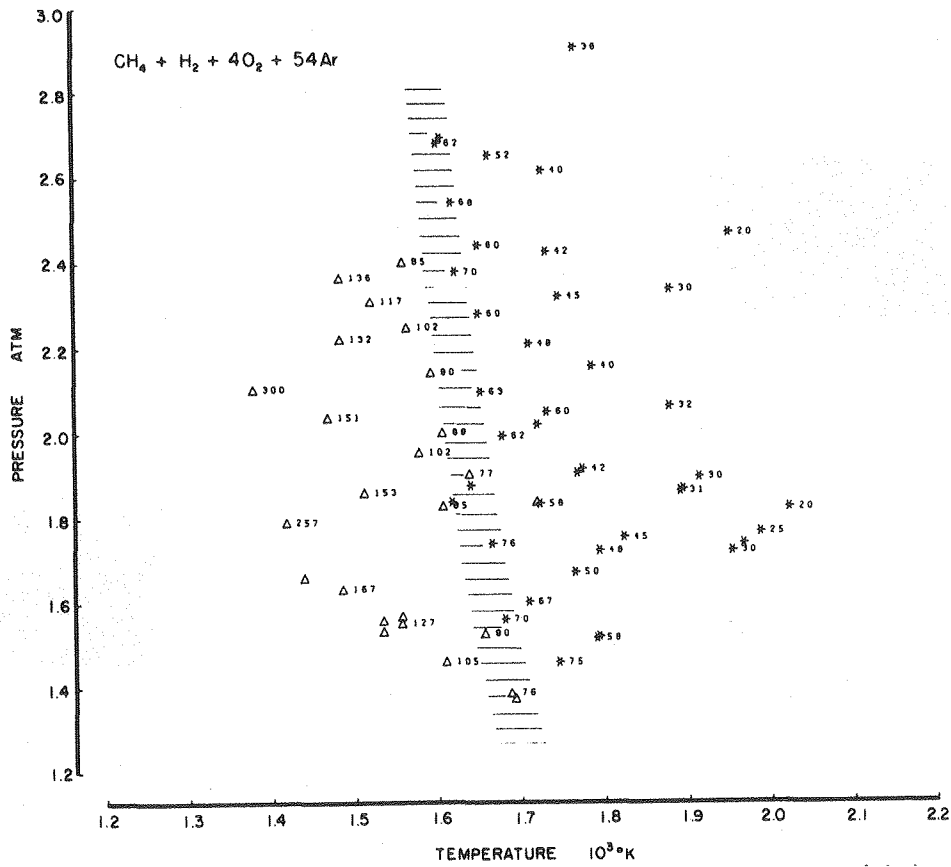


Fig. 4 Auto-ignition and strong ignition limit for mixture 6, * strong ignition, Δ weak ignition with corresponding induction time in μsec.

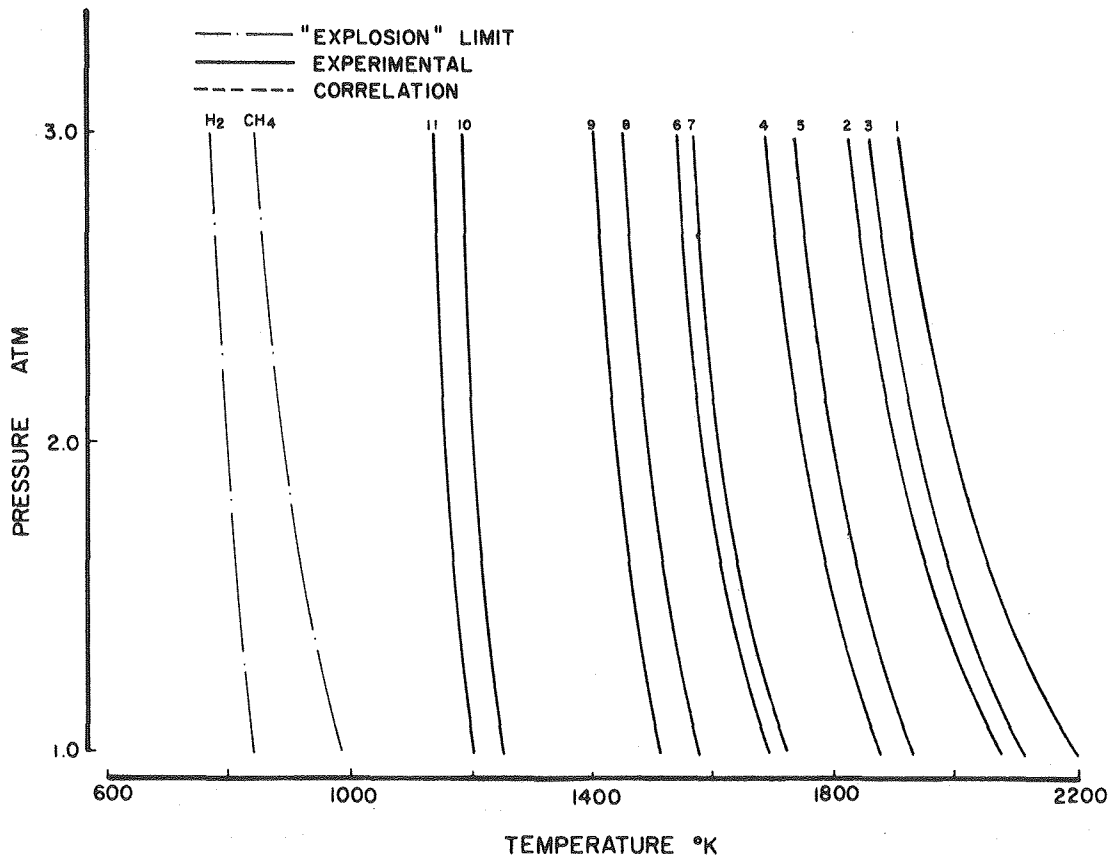


Fig. 5 Auto-ignition and strong ignition limits for all mixtures included in present study.