

THE UNIVERSITY OF MICHIGAN
INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

INFLUENCE OF α -RADIATION ON SOME ASPECTS
OF CONSTANT VOLUME COMBUSTION

by

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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT.....	ii
LIST OF TABLES.....	iv
LIST OF ILLUSTRATIONS.....	v
I. INTRODUCTION AND OBJECTIVE.....	1
II. SURVEY OF PAST WORK.....	3
III. ANALYSIS OF THE PROBLEM.....	13
IV. DESCRIPTION OF APPARATUS AND EXPERIMENTAL PROCEDURE.....	35
V. RESULTS.....	48
VI. DISCUSSION OF RESULTS.....	74
VII. CONCLUSIONS AND RECOMMENDATIONS.....	81
BIBLIOGRAPHY.....	82

LIST OF TABLES

<u>Table</u>		<u>Page</u>
(3-1)	Ionization Potential & Energy Per Ion Pair For Some Gases.	30
(5-1)	Summary Of The Results.....	49
(5-2)	Critical Gaps For Acetylene.....	50
(5-3)	Critical Gaps For Ethylene.....	51
(5-4)	Critical Gaps For Ethane (10" Initial Pressure).....	52
(5-5)	Critical Gaps For Ethane (20" Initial Pressure).....	53

LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1-1	Distribution Curve for the Reactants.....	1
3-1	Variation of Temperature with Time.....	18
3-2	Variation of q_1 and q_2 with Temperature.....	18
3-3	Variation of q_1 and q_2 with Temperature.....	19
3-4	Branching Chain.....	24
3-5	Flame Propagation from a Slab of Burned Gas.....	25
3-6	Minimum Igniting Energy as a Function of Electrode Distance.....	28
4-1	General Layout of Equipment.....	36
4-2	Construction of Constant-Volume "Bomb".....	37
4-3a	Explosion Bomb Assembly.....	38
4-3b	Explosion Bomb Dismantled.....	38
4-4	Electrode Assembly.....	39
4-5	Sparking Circuit.....	42
4-6	Timing Circuit.....	42
4-7	Construction of Polonium Source.....	45
5-1	Pressure Time Curves for Acetylene.....	54
5-2	Pressure Time Curves for Ethylene.....	54
5-3	Pressure Time Curves for Ethane.....	55
5-4	Primary Voltage versus Critical Gap.....	56
5-5	Primary Voltage versus Critical Gap.....	57
5-6	Evaluation of Spark Energy for Ethane.....	58
5-7	Evaluation of Spark Energy for Ethane.....	58
5-8	Evaluation of Spark Energy for Ethane.....	58

LIST OF ILLUSTRATIONS (CONT'D)

<u>Figure</u>		<u>Page</u>
5-9	Minimum Igniting Energy versus Critical Gap for Ethane.....	59
5-10	Minimum Igniting Energy versus Critical Gap for Ethylene.....	60
5-11	Minimum Igniting Energy versus Critical Gap for Acetylene.....	61
5-12	Instantaneous Voltage versus Time for C ₂ H ₆ (cold run).....	62
5-13	Instantaneous Current versus Time for C ₂ H ₆ (cold run).....	63
5-14	Instantaneous Voltage versus Time for C ₂ H ₆ (hot run).....	64
5-15	Instantaneous Current versus Time for C ₂ H ₆ (hot run).....	65
5-16	Instantaneous Voltage versus Time for C ₂ H ₄ (cold run).....	66
5-17	Instantaneous Current versus Time for C ₂ H ₄ (cold run).....	67
5-18	Instantaneous Voltage versus Time for C ₂ H ₄ (hot run).....	68
5-19	Instantaneous Current versus Time for C ₂ H ₄ (hot run).....	69
5-20	Instantaneous Voltage versus Time for C ₂ H ₂ (cold run).....	70
5-21	Instantaneous Current versus Time for C ₂ H ₂ (cold run).....	71
5-22	Instantaneous Voltage versus Time for C ₂ H ₂ (hot run).....	72
5-23	Instantaneous Current versus Time for C ₂ H ₂ (hot run).....	73
6-1	Activation Energy of the Chemical Reaction.....	77

CHAPTER I

INTRODUCTION AND OBJECTIVE

Introduction

It is generally assumed that a certain minimum of energy must be possessed by or supplied to a molecule or a group of molecules before they can react. Figure (1-1) shows that only a certain fraction of molecules possess an amount of energy equal to or larger than the activation energy of the reaction. The rate of chemical reaction due to thermal activation varies exponentially with the temperature.

Nuclear energy may be substituted for thermal activation. The main effect would be primary and secondary ionization and excitation of the molecules. These ion pairs and excited species that are formed might possess sufficient energy to react. This directs our thinking to the possibility of the use of such energy to induce chemical reactions at temperatures too low for these reactions to take place to any considerable extent by thermal activation.

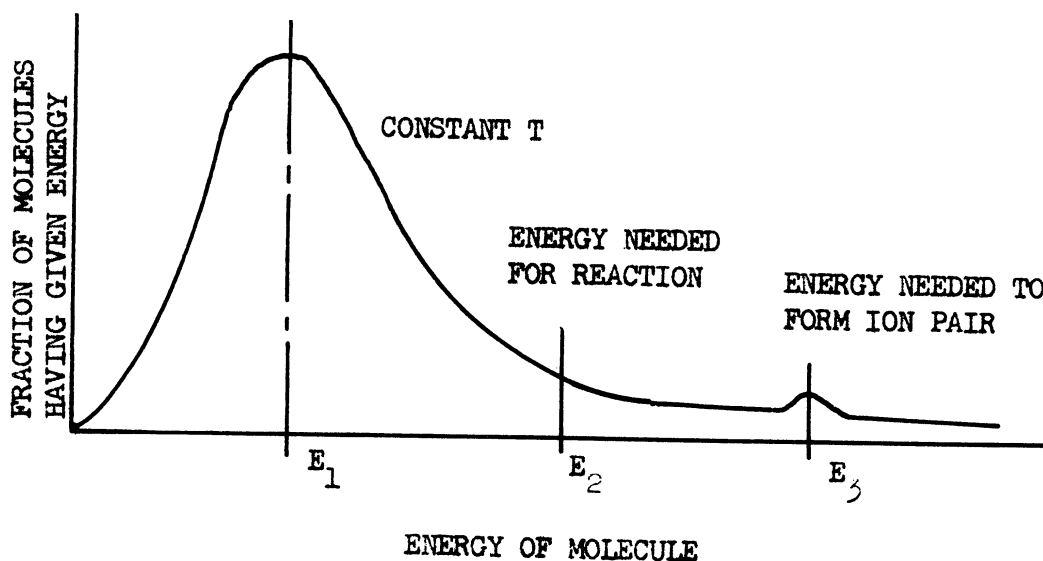


FIGURE (1-1) ENERGY DISTRIBUTION CURVE AMONG THE REACTANTS AT TEMPERATURE T° .

Objective

The purpose of this study was to compare the process of combustion of three hydrocarbons, namely, acetylene, ethylene, and ethane, when the spark gap was subjected to an alpha emitter, polonium-210, with the combustion of the same three fuels when normally burned. The comparison was confined to the following:

1. Delay period: The delay period in a combustion process is the time that elapses between application of the energy required to initiate combustion and the actual measurable rise in pressure. This quantity is mainly a function of a chain of chemical processes that take place immediately after the supply of such energy.

2. The time rate of pressure rise: It is an indication of the rapidity of combustion and hence of the time rate of chemical reaction.

3. The critical spark gap: It is defined as the narrowest spark gap that will give self sustaining combustion. This depends upon the rate at which energy is released within the gap and immediate vicinity as compared to the loss of energy due to conduction, convection and radiation to the surrounding media.

4. The spark energy: It is the energy expended in the gas when the spark crosses the critical spark gap. This depends among other things upon the breakdown voltage of the gap which in turn depends upon the ionization within the gap. It also depends upon the activation energy of the reactants.

CHAPTER II
SURVEY OF PAST WORK

Vincent and Van Wylen^{21,22} studied the effect of beta radiation on the combustion process by running two series of tests in a Waukesha CFR Diesel Test Engine. In the first series, cold (non-radioactive) palladium was placed in the engine and in the second series identical tests were run after the palladium had been made radioactive. The observed changes as a result of the beta particle radiation were in the direction of improved combustion. The minimum firing compression ratio was reduced. Pressure time measurements showed a reduction in the delay period and the fuel consumption tests showed a slight reduction in specific fuel consumption due to the beta particle radiation. However, later tests²³ performed by the same group under a more intensive source showed no effect of beta radiation. The same experiment was repeated²⁴ using a different shape for the source to avoid interference in the fuel injection pattern. The results obtained were still not conclusive as to the actual behavior of the combustion. The same paper²⁴ discusses preliminary tests on a spark ignition engine. The author's conclusions listed the following:

1. The effects of beta radiation on the combustion of fuel in a diesel engine are, if any, very small and were not detected with the apparatus used.
2. An analysis of the material filtered out of the exhaust gases showed an appreciable amount of contamination.

3. Since the performance of an internal combustion engine is subject to many variation, it would seem best to carry out future experiments in a manner which permits closer control of combustion processes.

The reports by Morrison, Cullen and Weir^{21,22,23,24} also included investigations of the steady flow combustion process under the effect of beta radiation. The results showed no measurable increase in the normal flame propagation velocities, under the influence of sources whose activities ranged between 6.6 and 36 curies at any of the pressures at which the flame was studied. These experiments were repeated using a radiation source surrounding the reaction zone so that any significant effect on the combustion process can be ascertained. The results showed that high levels of radiation of the order of 2000 curies increased the air specific impulse, the magnitude of the effect depending upon mass velocity, fuel air ratio and source activity. The tests also showed that the rich and lean limits of blow-off were slightly increased.

Experiments by Wolf and Tobey^{21,22,23} on the effect of beta radiation on slow oxidation of hydrocarbons showed an accelerating effect when palladium-109 was used as a source of radiation. However this accelerating affect was of the same order of magnitude as the observed experimental error. Further experiments by the same authors²⁴ to determine the effect of radiation on explosion thresholds showed a small but definite depression of the explosion limit of hydrogen, oxygen and nitrogen mixtures.

Combustion studies using a 12,000 curie gold source were carried on by Churchill, et al.²⁵ The influence of nuclear radiation from Au-198 and Au-199 on propane air flames at low pressures can be summarized as follows:

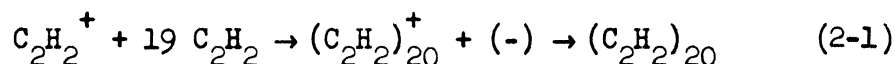
1. Rate of flame propagation determined from photographs of bunsen flames was increased up to 50 percent by nuclear radiation from the 12,000 curie source.
2. The intensity of radiation at 4315 \AA due to CH was increased by 14 percent at a pressure of 6 inches mercury absolute and up to 33 percent at 14 inches absolute by nuclear radiation at a level of 1500 curies.
3. The intensity of radiation at 5165 \AA due to C_2 was increased up to 150 percent by nuclear radiation at a level of 1500 curies.
4. The intensity of radiation at 3063 \AA due to OH was not affected significantly by nuclear radiation at levels up to 1500 curies.
5. Increase in the CH rotational temperature ranging from 50 to 100 percent at source strength up to 1500 curies.
6. Under the influence of radiation the maxima in the emission due to C_2 and OH were observed to occur at an earlier stage of the flame than the maximum of emission due to CH.

Since the turn of the century extensive work has been done on the effect of alpha particles on chemical reactions. However, this author has found nothing in the literature dealing with explosive combustion. When gaseous hydrocarbons are radiated with alpha particles ionization, decomposition, polymerization and oxidation have been observed.^{15,16} The relative ionization probabilities of ten hydrocarbons

have been determined by Otvos²⁶ for beta particles from C_2^{14} . For a hydrocarbon series the ionization probabilities increase linearly with the number of valence electrons.

Polymerization of Pure Acetylene

Lind, Bardwell and Perry¹⁵ found that under the influence of alpha radiation acetylene at ordinary temperature deposits a yellow powder known as cuprene. The number of molecules transformed, M, per ion pair, N, produced by alpha particles is given by $\frac{M}{N} = 20$, the highest value yet obtained in the alpha radiation of a single substance. Their assumption is that a cluster containing at least 19 neutral molecules of acetylene is formed around each acetylene ion and that the free electron which has no affinity for neutral acetylene molecules finally neutralizes the cluster, which, owing to the number of unsaturated valences, then becomes stabilized as a polymer which precipitates as a solid.



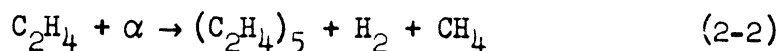
Owing to failure to find a solvent for the polymer the molecular weight is unknown. Also X-ray examination showed no lines.

Mund and Koch²⁸ reported that in the radiochemical polymerization of acetylene the influence of temperature is small between 0 and 100°C. The decrease in the ionic yield did not exceed 1 to 2 percent in this temperature range. Later Brehain and Storms¹⁸ found that polymerization depends upon the temperature, pressure and intensity of radiation. In some cases the change in $\frac{M}{N}$, that is, the number of molecules transformed, M, per ion pair, N, amounted to 10 percent between 0 and 100°C.

Mund and Koch²⁸ showed that at pressures exceeding 15 to 20 cm of mercury the radiochemical polymerization of acetylene is very slightly influenced by pressure variation. On the other hand Brehain and Storms¹⁸ reported that at low pressure the $\frac{M}{N}$ yield decreased.

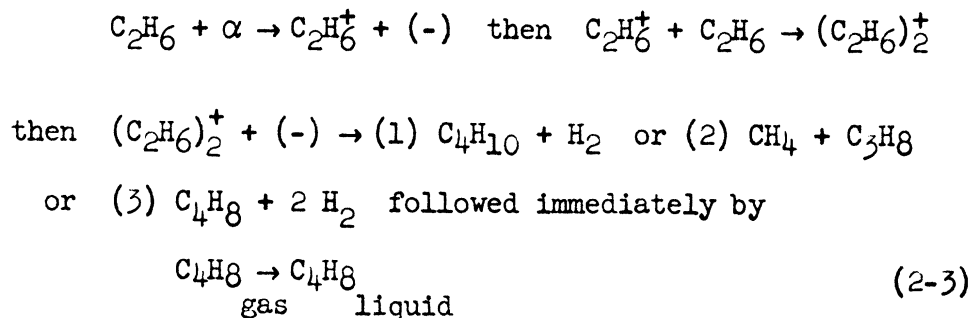
Polymerization of Ethylene

Mund and Koch²⁸ first studied the reaction under the influence of radon which is an alpha emitter. They described the appearance of liquid droplets which fell vertically to the bottom of their vessel. The evolution of permanent hydrogen and methane amounted to 10 percent of the disappearance of ethylene. Lind, et al.¹⁵ studied this reaction in a reaction vessel 1.855 cm in diameter at an initial temperature of 25°C and initial pressure of 996.4 millimeters and initial activity of 0.0542 curie. They described the reaction as follows:



Polymerization of Pure Ethane

Lind and Bardwell²⁰ studied the effect of alpha particles in a reaction sphere 3.977 centimeters in diameter at a temperature of 25°C. The activity of the source was .0922 curie. According to their results, they suggested the following mechanism for the reaction:



The mechanism is based upon the assumption of a singly charged two molecule cluster preceding elimination of hydrogen. To explain the immediate condensation of the unsaturated hydrocarbon, the assumption

is made that at least two of the four valences left free by the simultaneous removal of 2 H_2 from a two molecule cluster do not immediately satisfy each other and close up but remain open and act as centers of attraction for other similar open pairs until a large chain is condensed out as liquid, thus preventing the accumulation in the gas phase.

Oxidation of Acetylene Oxygen Mixtures

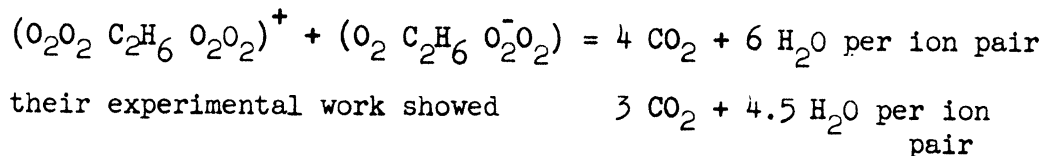
In the first attempt Lind, Bardwell and Perry¹⁵ used a mixture of $1 \text{ C}_2\text{H}_2 : 2 \text{ O}_2$. No solid polymer appeared and a colorless liquid phase with vapor pressure less than one millimeter was produced. Final analysis showed the presence of large amounts of CO_2 and CO in the gaseous phase.

Another series of measurements were made on a mixture of $1 \text{ C}_2\text{H}_2 : 1 \text{ O}_2$. This reaction was interrupted after about 30 percent of the C_2H_2 had reacted. Of the O_2 initially present, initial pressure 498 mm, 373.6 mm were found still free while 95.8 mm of CO_2 and 38.4 mm of CO had been generated thus accounting for all the original oxygen except 9.2 mm. Water vapor pressure of about 12 mm was measured which would account for 6 mm of O_2 yet unaccounted for, leaving not more than 3.2 mm as possibly present in the liquid phase. However, this difference is so small as to raise doubt to whether any oxygen was really combined with it. The one outstanding feature of the reaction is that no trace of cuprene appears in the presence of oxygen.

Oxidation of Ethane Oxygen Mixtures

Lind and Bardwell²⁰ irradiated a stoichiometric mixture of ethane and oxygen in a reaction sphere 1.985 cm in diameter. The initial temperature was 25°C and the initial activity was 0.1551 curie.

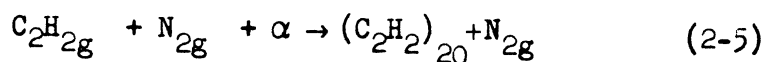
The result was complete oxidation to water and carbon dioxide. No liquid phase except water appeared. They assumed the following mechanism.



(2-4)

The Catalytic Influence of Ions of Inert Gas

Lind and Bardwell¹⁶ reported that ions of inert gas contribute as much to the reaction of acetylene with alphas as do the ions of the reactants. They used a reaction sphere 1.938 cm in diameter at an initial temperature of 25°C and initial activity .01907 curie. They found that under the ionizing influence of alpha radiation N₂ did not react but nevertheless exerted a large accelerating influence on the rate of polymerization to form solid cuprene.



$$\frac{M C_2H_2}{N (C_2H_2 + N)} = 20 \quad (2-6)$$

Comparison Between Unsaturated and Saturated Hydrocarbons under the Influence of Alpha Radiation

The most important characteristic of unsaturated hydrocarbons compared with saturated hydrocarbons is the larger number of molecules reacting per ion pair. The following empirical rules were reported²⁰ for saturated hydrocarbons: When only one component is $\frac{M}{N} = 2$ indicating that the positive ion collects one neutral molecule to form a cluster of two which reacts when an electron returns to neutralize the charge. If oxygen is added as a second reactant the first being oxidizable,

then $\frac{M}{N}$ = twice the number in the simplest stoichiometric formula. To explain the two-fold factor the following argument is adopted. Since the oxygen has high affinity for free electrons, the oxygen ions formed will cause as much clustering as the positive ones and hence double the amount of reaction. For the unsaturated hydrocarbons, the same rule does not apply. For a single component $\frac{M}{N}$ = 5 for ethylene and 20 for acetylene. This appears to be due to the prevalence of unsaturated valence enhancing either the ionic clustering or the subsequent stability of the neutral cluster or both. In the oxidation of unsaturated compounds the exclusivity of oxidation is still most clearly exemplified but the rule of doubling the amount of reaction no longer holds. In the case of acetylene $\frac{M}{N}$ amounts to about 27. This makes it appear that there is some specific stability attached to a given size of cluster for multiple bond compounds no matter what other molecules make up the cluster.

Also, when hydrocarbons are irradiated both the C-C and C-H bonds can be broken. The preference of one process to the other depends on the bond strength. The highly reactive fragments are capable of a variety of reactions. Aside from reacting with one another, they react with any foreign substance, especially when it is a good acceptor.

Summary

The previous experiments show that irradiation of hydrocarbons by alpha particles causes a chemical reaction to take place. The rate of this chemical reaction varies from one fuel to the other. It is enhanced by the presence of inert gases and also by the presence of oxygen. The reaction was in the direction of more stable compounds.

Cullen and Gluckstein modified the Arrhenius equation

$$\omega = Ke^{-E_a/RT} \quad (2-7)$$

where

- ω = speed of the reaction
- E_a = activation energy
- T = temperature
- K = constant of the reaction

to

$$\omega = K [e^{-E/RT} + y(\beta)] \quad (2-8)$$

to take into account the additional fraction of molecules possessing an energy greater than the activation energy. The value of $y(\beta)$ depends on the energy of the emitted particles, source activity, the average life of specie formed absorption factors and geometry. To calculate $y(\beta)$ it is necessary to calculate the number of ion pairs formed, then:

$$N = \frac{E\beta}{33R} \times 3.7 \times 10^{16} \text{ ion pair/sec/cm} \quad (2-9)$$

where

- E = Energy of the particles in MeV
- β = activity in curies
- R = range of electrons in centimeter.

For a system of principal dimension L , less than R , equation (2-9) is modified to read

$$N = \frac{EBL}{33R} \times 3.7 \times 10^{16}$$

If F is the fraction of electrons reradiated

$$N_T = 3.7 \times 10^6 \frac{EBL}{33R} S_n$$

where $S_n = 1 + F + F^2 + \dots + F^n$ $F < 1$

and n is the nearest integer less than R/L

$$\therefore y(\beta) = \frac{2\theta N_T}{AM} \quad (2-10)$$

where

M = molal flow rate (moles/sec.)

θ = the ratio of the average life of an ion to the residence time in the system

A = the Avogadro number

The authors indicated that these equations serve as a guide for the experimental design and are correct only to order of magnitude. They measured flame speeds in the bunsenburner, blow off velocities from a spherical flameholder and pressure drop due to combustion in the constant area combustor,

Their results showed that comparison of the flame speed and the blow off velocities from a spherical flame holder for propane air flames showed no significant change due to beta radiation at low source intensity. High intensity of β radiation tended to increase the pressure drop due to burning as a function of fuel air ratio above the pressure drop when no radiation was present.

Closure

The previous literature survey gives the various reactions that take place due to irradiation of hydrocarbons. It shows their dependence upon the type of irradiation, on the pressure, the temperature and foreign substances that might constitute part of the reactants.

CHAPTER III

ANALYSIS OF THE PROBLEM

Fundamental Considerations

Combustion Theories

The combustion of a gaseous fuel can be considered as a combined problem of the physical processes of diffusion, heat transfer, ionization, and chemical reaction during which the main part of dormant energy is released as heat of reaction. Various theories have been suggested.

The Thermal Theory

The thermal theory assumes that ignition is due to the heat imparted by the igniting source to the inflammable gas mixture with which it is surrounded. If the entire gas is to be ignited, the volume surrounding the igniting source must necessarily explode but it does not at all follow that this condition is sufficient. It has been found that when a spark insufficient to cause ignition is passed through a gas it is surrounded by a small aureole of flame. By sufficiently increasing the energy, dissipated in the spark, or by changing the discharge characteristics and consequently the size of the aureole, ignition may be caused to take place. This fact is the basis for the hypothesis that "ignition depends on the heating of a sufficient volume of the gas to a sufficient temperature."¹ Taylor and associates² studied the form of the temperature wave spreading by conduction from spherical and point sources. Their conclusions showed that if a source of ignition is regarded solely as a source of heat, the effectiveness of a given quantity of heat in raising a sufficient volume of a

combustible mixture to a given temperature (by conduction alone) depends upon the method by which heat is transferred to the mixture. Figure (3-1) illustrates this statement. Let curve (A) represent the variation of temperature with respect to time at a distance r from a point source. Curves (B) and (C) represent the temperature profile when the same quantity of heat is supplied in two equal portions within a finite interval. It can be seen that the maximum of the resultant curve (D) occurs shortly before the maximum of the second component. It is evident that the resultant maximum is smaller than the sum of the maxima of the two components and therefore smaller than the maximum of the original curve (A). The resultant maximum also evidently diminishes as the interval of time between the two components increases. It is thus concluded that the result of dividing the heat supplied into two equal installments separated by any finite interval of time is to lower the maximum temperature at any given point in the neighborhood. Similar considerations show that the same result holds if the two installments are unequal. If the heat is divided into three or more installments, equal or unequal, supplied at equal or unequal intervals of time, the same conclusion is warranted.

Hence if a given quantity of heat is supplied at a point of a uniform conducting medium in any manner during a finite interval of time, the maximum temperature at any neighboring point is lower than it would have been if all the heat had been supplied at the same instant. Also, if a given quantity of heat is supplied at a point in a uniform conducting medium in any manner during a finite interval of time, the volume of the medium that can be raised to any given

temperature is smaller than its volume if the heat had been supplied all at the same instant.

It follows that an instantaneous point source of heat is more effective in ignition than a point source in which heat is supplied in any manner (continuous or discontinuous) over a finite interval of time.

Experiments by Coward and Metier⁴ on the minimum volume required for a spark of minimum igniting energy to start combustion give support to what is known as thermal ignition of gases by electric discharge. Nothing in their results suggests the intervention of any electric effect as the foundation and origin of ignition other than the thermal effect of the degradation of electrical energy.

Mathematical formulation of the thermal theory:³¹ In a reaction in the gaseous phase with velocity, ω , the amount of heat given off per second by the volume undergoing reaction is

$$q_1 = V Q' \omega \quad (3-1)$$

where

V = volume of reaction vessel

$Q' = \frac{Q''}{N}$ = heat liberated per molecule reacting

Q'' = heat of reaction for one gram mol of the products

N = Avogadro number = 6×10^{23}

ω = number of molecules of the product appearing per second per unit volume

The velocity of the reaction is represented by the Arrhenius equation

$$\omega = K a^n e^{-E_a/RT}$$

where

a = number of molecules of reactants per unit volume

n = degree of the reaction

E_a = activation energy

K = proportionality factor

q_2 the amount of heat conducted away by the walls of the vessel, is given by

$$q_2 = X (T - T_0) S \quad (3-2)$$

where

X = coefficient of heat conductivity

T = temperature of the reacting gas

T_0 = vessel wall temperature

S = the area of the walls

Figures (3-2) and (3-3) show q_1 and q_2 as a function of the temperature T. Figure (3-2) corresponds to where the vessel wall is subject to a temperature T_0 and the pressure of the reacting gas changes, that is, the magnitude of a. Curve (1) corresponds to the smallest value of a, namely a_1 ; curve (2) to a medium value a_2 ; and curve (3) to the largest value a_3 . For $a = a_1$ the gain in heat q_1 is at first larger than the heat loss q_2 . As a result the gas will be heated to a higher temperature than that of the walls of the vessel. This situation continues, however, only up to the instant that the temperature of the gas reaches a certain value T_1' (intersection of the curves q_1 and q_2) where $q_1 = q_2$. Beyond this point the gas will not further heat up because for $T > T_1'$ the heat conducted away, q_2 , will be greater than

the heat gain, q_1 , and if for some reason, the gas temperature was to become greater than T_1' it will again cool down to the same temperature T_1' . Thus for the case considered the reaction does not lead to ignition. In curve (3), auto-ignition would certainly take place since more heat is constantly produced than is lost by conduction. Curve (2) represents the borderline case in which the curve and the straight line are tangent and in which at the point of contact at T_1 an unstable equilibrium would exist between heat production and heat loss; by a small addition of energy from the outside, the unstable condition must change into explosion. If V is the volume of the vessel, then:

$$V Q''K a^n e^{-E/RT_1} = X (T_1 - T_0) S \quad (3-3)$$

also

$$\left(\frac{dq_1}{dT}\right)_{T=T_1} = \left(\frac{dq_2}{dT}\right)_{T=T_1}$$

then

$$\frac{V Q''K a^n E e^{-E/RT_1}}{N RT_1} = X S \quad (3-4)$$

Eliminating $X S$ from both equations we get

$$T_1 = \frac{1 + \sqrt{1 - \frac{4 RT_0}{E}}}{2 \frac{R}{E}} \quad (3-5)$$

The positive sign gives a ridiculously high temperature so that:

$$T_1 = \frac{1 - \sqrt{1 - \frac{4 RT_0}{E}}}{2 \frac{R}{E}}$$

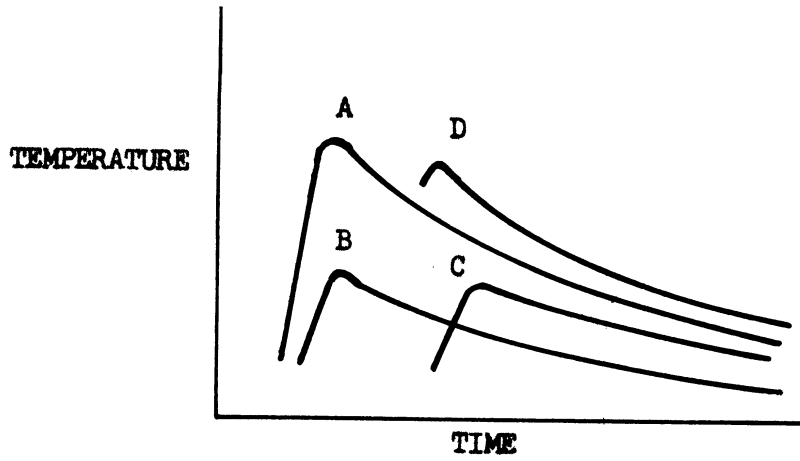


FIGURE (3-1) VARIATION OF TEMPERATURE WITH TIME

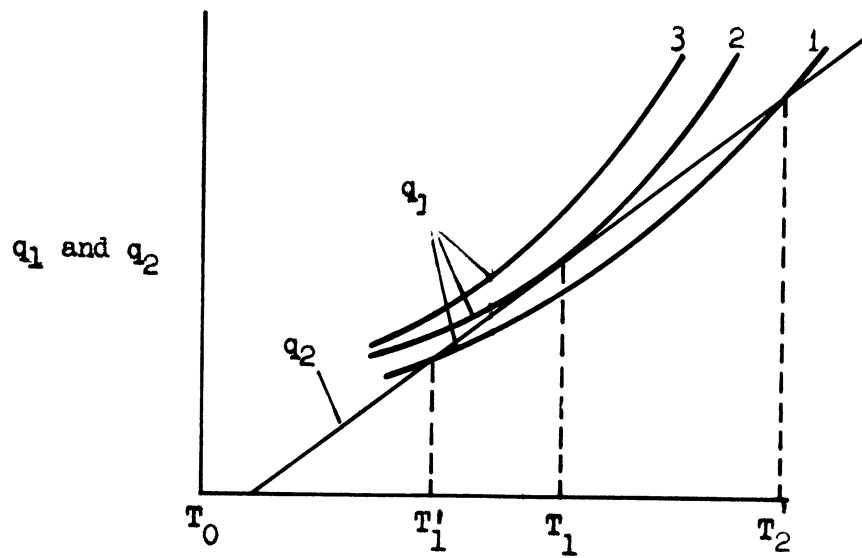


FIGURE (3-2) VARIATION OF q_1 AND q_2 WITH TEMPERATURE

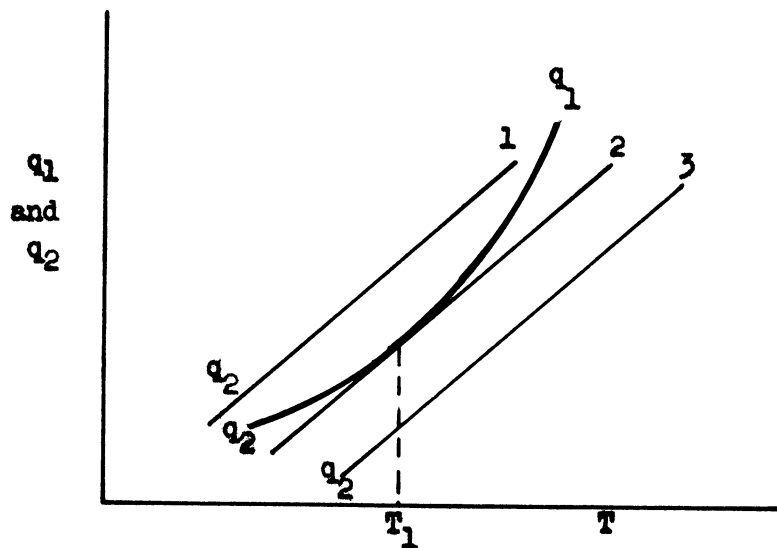


FIGURE (3-3) VARIATION OF q_1 AND q_2 WITH TEMPERATURE

$$T_1 = \frac{2\left(\frac{RT_0}{E}\right) + 2\left(\frac{RT_0}{E}\right)^2 + 4\left(\frac{RT_0}{E}\right)^3 + \dots}{2\frac{R}{E}} \quad (3-6)$$

For $\frac{RT_0}{E} < .05$ which is the usual value encountered in such reactions we may disregard the terms of the series starting with $4\left(\frac{RT_0}{E}\right)^3$

$$\therefore T_1 = T_0 + \frac{RT_0^2}{E}$$

$$\therefore \Delta T = T_1 - T_0 = \frac{RT_0^2}{E} \quad (3-7)$$

$$\therefore \text{if } \Delta T < \frac{RT_0^2}{E} \text{ explosion is impossible.}$$

Ionization Theory

Hot wires begin to give off electrons at about the temperature at which they are capable of starting ignition of a combustible gas mixture. This led many investigators³ to think that ignition by sparks and flames as well as hot wires may be due in some way to the ions and not to the heat associated with them. The theory claims that some kind of ionization precedes combustion. This is possibly due to the violent collisions which occur in the gas in contact with the sparks. That a gas has a particular ignition temperature may mean that ionization by collision begins at that temperature with absorption of energy from the source or later from that liberated by recombining atoms. Accordingly, when the chemical energy set free by combustion of a molecule exceeds that required for initial ionization of an adjoining molecule there is true explosion.

The conversely related phenomenon of chemical action produced by gaseous ionization has been theoretically treated by Thomson.³² The experimental data were collected and reviewed by Lind.³³ The two phenomena referred to:

- a. Chemical action → gas ions,
- b. Gas ions → chemical action,

suggested a cycle by which a reaction such as gaseous explosion or a flame may become self propagating. Lind suggested that if ionization plays a role it must be in assisting energy transfer at the flame front. Since gaseous ions have dimensions of the same order of magnitude as the surrounding molecules they will offer no advantage from the standpoint of mobility, but electrons on account of their smaller mass are moving with much higher velocities than the surrounding molecules even at thermal equilibrium and conceivably they may be ejected with still higher velocities from hot molecules. Wendt and Grimm⁴⁰ together had proposed an electronic theory of flame propagation and believed that they had found support in the suppression of ionization by "anti-knock" compounds. Their method consisted in passing air which had been ionized in an arc over a pool of benzene either with or without tetraethyllead into an electroscope. In the presence of the anti-knock compound the discharge of the electrodes is slower indicating more rapid recombination of the ions after passing the pool of benzene and before reaching the electroscope. From this, they concluded that gaseous ionization is much more reduced by the presence of an "anti-knock" and since flame propagation is slower when knocking is absent, the theory of a causal relation between ionization and flame propagation appeared to receive support. However, Lind and Bardwell⁴¹ studied

the slow oxidation of methane by oxygen under the influence of alpha radiation from radon with selenium diethyl as the anti-knock, no retardation of the reaction was observed. Whether the further conclusion is justified, that, since selenium has no effect on the slow rate of oxidation of methane under ionizing conditions, and since it does have an effect on the rapid oxidation in the cylinder hence the latter cannot be connected with ionization and that therefore ionization plays no role in flame propagation is still open to question.

Calcote³⁶ studied the electrical properties of flames. He determined the actual path taken by the flow lines in the inner cone of a bunsen flame. This was accomplished by introducing particles into the input flow stream. The flame was subjected to a transverse electric field. The inner as well as the outer cones were always deflected towards the negative electrode. Also, the flame stability was decreased. He estimated the ion concentration to be about 10^{12} ions/cc. His conclusion was that the observed effect of electric field on n-butane-air can almost be completely explained by a mechanical interpretation. Calcote and Pease³⁷ studied the effect of longitudinal electric fields on the bunsen flame and concluded that the electric field has a strong influence on the flame stability, the direction depending upon the field polarity. A mechanical model in which momentum is transferred from positive ions to the gas explains most of the results.

The large number of ions which must be present to produce these effects cannot be accounted for thermodynamically and are probably due to chemi-ionization, that is, ionization due to chemical reaction.

The Chain Theory

The chain theory is divided into

1. The theory of non-branching chains
2. The theory of branching chains.

The theory of non-branching chains states that a given active center disappears in the reaction but is replaced by a new center with the same properties which continues the chain.

The theory of branching chains assumes that the active center of a chain entering the reaction can give rise to two new centers. Thus, if one of the latter prolongs the chain, as it were, the second begins a secondary (branched) chain. These secondary chains, owing to further branching, can generate tertiary chains, and so on. Figure (3-4) gives a schematical representation of such branching chains.

Mathematical representation of the chain theory: If we consider a first order reaction, i.e., at each step a chain carrier reacts with one of the major components of the gas mixture, then if:

$\frac{dn}{dt}$ = rate of change in the concentration of active particles

I = rate of initiation of chain carriers

αn = rate of generation by chain branching

βn = rate of loss by chain breaking

then

$$\frac{dn}{dt} = I + \alpha n - \beta n \quad (3-8)$$

when a steady state is reached

$$\frac{dn}{dt} = 0$$

and

$$n_0 = \frac{I}{\beta - \alpha} \quad (3-9)$$

and the explosion limit is defined by $\alpha = \beta$.

If the branching reaction is of the second order, that is, if each one of the steps involves the interaction of two chain carriers, then:

$$\gamma n^2 = \text{rate of branching}$$

and

$$\frac{dn}{dt} = I + \gamma n^2 - \beta n = 0 \quad (3-10)$$

$$n_0 = \frac{\beta \pm \sqrt{\beta^2 - 4 \gamma I}}{2 \gamma} \quad (3-11)$$

For $4 \gamma I > \beta^2$, n becomes imaginary and therefore no steady state condition exists. The explosion limit is then defined by

$$\beta^2 = 4 \gamma I \quad (3-12)$$

The different factors that led to the development of the chain theory are:

1. A retardation of the chemical change when the dimensions of the vessel in which the reaction is taking place was decreased and thus allowing a smaller path for chains to traverse before reaching the wall.

2. Acceleration of the reaction in some instances by the presence of an inert gas.

3. Sensitivity of the reaction to inhibitors.

4. A rate of reaction being considerably greater than might be expected from a knowledge of the heat of activation and frequency of collision.

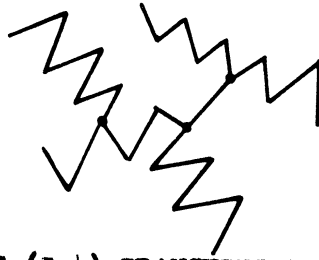


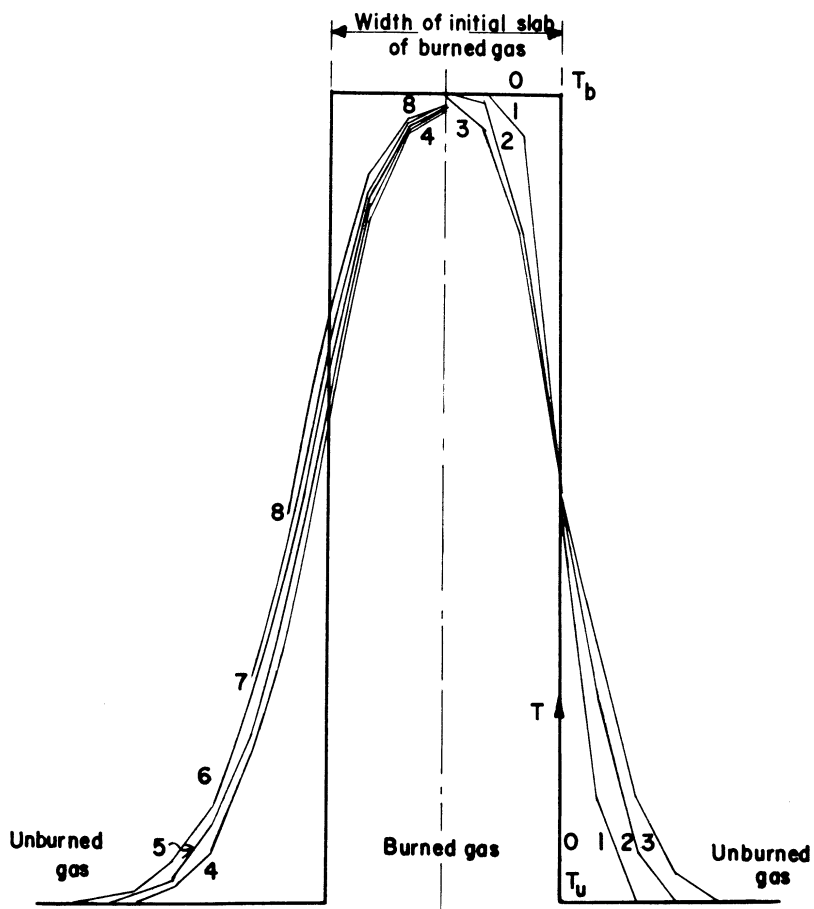
FIGURE (3-4) BRANCHING CHAIN

Critical Increment of Chemical Reaction

The following is a study of the development of a steadily propagating flame from an initial state in which a large reservoir of burned gas is in contact along a plane surface with a large reservoir of unburnt gas.

A combustible mixture is usually ignited by causing reaction to occur in a small part of the gas from which a flame then propagates by thrusting out small islets of hot gases into the unburnt gas. To examine the propagation from this small pocket of burnt gas consider an initial distribution of temperature of the rectangular form 0, Figure (3-5). This corresponds to a finite plane slab of burnt gas in an infinite sea of unburnt gas. Successive temperature distribution after the first instant are marked 1, 2, 3, etc. We observe that at first the temperature within the burnt gas pocket begins to fall by mixing with adjacent cold gas. However, this same mixing means that reactants diffuse inwards. They can then begin reacting and evolving heat. After the fourth interval of time the heat evolved begins to exceed the heat lost by conduction and the temperature rises. The temperature profile then adjusts itself until a steady flame is propagated outward into the unburnt gas.

If the slab is too thin the loss of heat by conduction will be too rapid for reaction to keep pace with it, the reaction is



FLAME PROPAGATION FROM A SLAB OF BURNED GAS

Figure (3-5)

extinguished and no flame is propagated. For propagation to occur the thickness of the burnt pocket must exceed a certain critical size known as the critical increment.

Spark Ignition

Ignition will be successful in causing a propagating flame if the spark provides sufficient energy to heat, to about the adiabatic temperature, T_b , a sphere of gas of diameter greater than the critical increment. Such a spark gap will be called the critical spark gap, d_c . If the minimum energy input is Q , we therefore can deduce

$$Q \approx c \rho \frac{\pi d_c^3}{6} (T_b - T_u) \quad (3-13)$$

where

c = specific heat of gas at constant pressure assumed constant for both reactants and products

ρ = density of gases, assumed constant.

According to Spalding⁹ the critical size of extinction is of the same order as twice the thickness of the steadily propagating flame. Consideration of energy conservation indicates that the maximum slope, assumed to occur near the mean temperature is related to the flame speed by the relation

$$k \left(\frac{dT}{dx} \right)_{\max} \approx \frac{1}{2} c \rho S (T_b - T_u) \quad (3-14)$$

where

S = laminar flame speed measured relative to the unburnt gas

$T_b - T_u$ = the whole temperature rise across the flame

k = conductivity

The flame thickness δ is therefore found from

$$\delta = \frac{T_b - T_u}{\left(\frac{dT}{dx}\right)_{\max}} \approx \frac{2\alpha}{S} \quad (3-15)$$

where

$$\alpha = \frac{k}{c_p} = \text{thermal diffusivity}$$

Then the approximate relation giving d_c will be

$$\frac{S d_c}{\alpha} = 4 \quad (3-16)$$

Substituting in equation (3-13), we get

$$Q \approx \frac{2 \pi k d_c^2 (T_b - T_u)}{S_u} \quad (3-17)$$

For the common range of combustible mixtures $\frac{K (T_b - T_u)}{S_u}$ does not vary rapidly, then:

$$Q \approx k_1 d_c^2 \quad (3-18)$$

This equation holds good for the right branch of the minimum igniting energy versus critical gap curve (see next paragraph). As we enter the quenching distance it no longer applies. The following equation was found to fit the experimental results.

$$Q = k_2 d_c^n \quad (3-19)$$

where n is negative.

The Minimum Igniting Energy Curve

Figure (3-6) represents the variation of the minimum igniting energy with the gap width. It takes a U-shape, staying approximately constant over a certain gap width and increasing as we proceed to the

right toward wider gaps and to the left within the quenching distance.

The parameters that affect the shape of the curve are:

1. Electrode distance
2. Size of the electrodes
3. Heat conductivity of the gas
4. The molecular structure of the fuel.
5. Diffusion

The influence of radiation on these parameters will be discussed in Chapter VI.

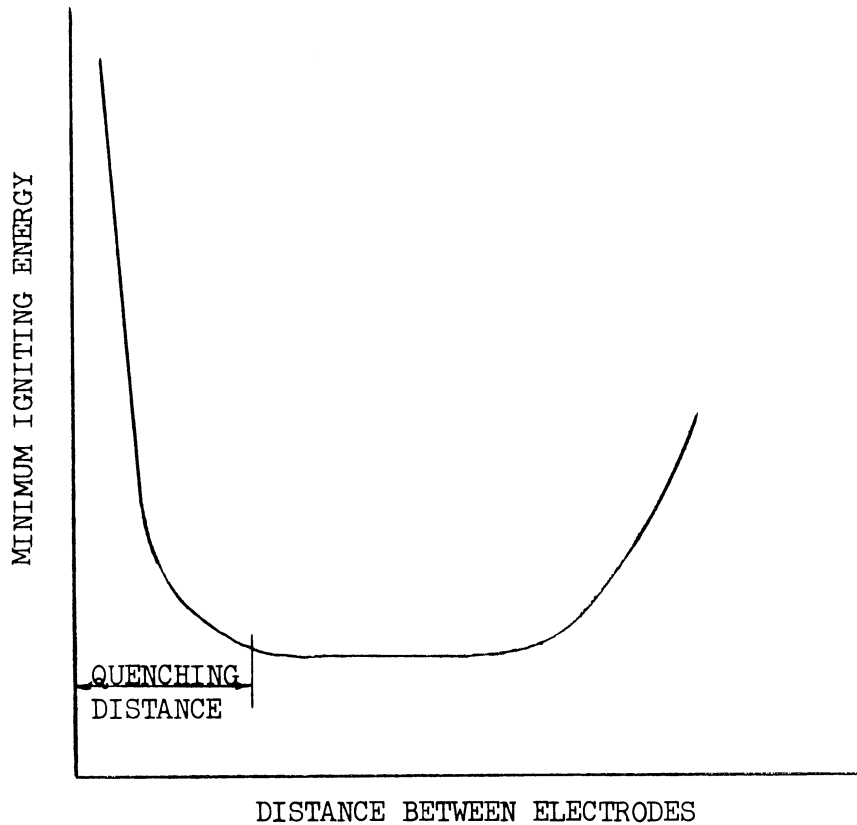


FIG. (3-6) MINIMUM IGNITING ENERGY AS A FUNCTION OF ELECTRODE DISTANCE

A simplified quantitative calculation by Jost⁶ and by Spalding⁹ gives the minimum diameter that will cause ignition. The simplified differential equation for heat conduction is given by

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2}$$

where

α = thermal diffusivity

T = temperature

t = time

x = distance from the conducting surface

Spalding solved this equation by the Dusenberre method. The value for x can be estimated by assuming values for the flame speed and thickness from existing experimental data.

Primary and Secondary Ionization

In the passage of alpha particles through a gas both primary and secondary ionization results. The primary ionization is due to collisions of alpha particles with molecules and the liberated electrons may have velocities between zero and $2V$ where "V" is the velocity of the alpha particle. If the velocity of the ejected electrons is sufficiently high they may in turn produce a number of ions before they come to rest. The number of ions produced by secondary ionization is approximately four-fifths of the total ionization.⁷ However, the total energy of the alpha particle is frequently more than twice the energy used in ionization and it is known that some of this energy produced some excited or metastable molecules. It may also split the molecules into radicals or atoms. The excitation of the molecules may be followed by spontaneous dissociation.⁸ The total energy of an alpha particle consumed during its passage in a gaseous media is about twice the energy corresponding to the ionization produced. In the following

table¹⁸ the second column represents the ionization potential of the gases listed in the first column, while the third column indicates the total energy of the alpha particle in e.v. divided by the number of ion pairs produced by this particle.

TABLE (3-1) IONIZATION POTENTIAL AND ENERGY
PER ION PAIR FOR SOME GASES

Gas	Ionization Potential e.v.	Energy Per Ion Pair e.v./ion
H ₂	16.5	33.0
N ₂	17.0	35.0
O ₂	15.5	32.3
He	24.6	27.8
A	15.3	25.4

Wourtz¹⁰ showed that in many reactions which appear to be simple the precise determination of the ionic yield $\frac{M}{N}$, that is, the ratio of the molecules undergoing reaction to the number of ions formed during the same time in the gas have given values different than unity. Experiments^{11,12} have shown that the ionic yield is a strong function of the intensity of radiation. Mund¹³ confirmed the more general hypothesis that the ions whose attractive force affects a large number of neutral molecules possessing induced and sometimes permanent polarity favors molecular collision and increases the energy contributed in the shocks. It is also feasible to add that the electrostatic field surrounding an ion is capable of disturbing the system formed by two molecules momentarily in contact. It could be stated that alpha particles scrape electrons from the same molecules, thus ionizing them, and leave others in an excited state. These molecules could serve as centers for the starting of chemical reaction.

Radiochemical Reaction Provocated by Alpha Rays¹⁸

In 1927, Mund and Koch¹³ attracted attention to the fundamental role which appears to take place in radiochemical phenomena due to the electrostatic attraction between the ions and the neutral molecules possessing permanent and induced polarity.

Considering every neutral molecule as possessing a dipole of electric moment

$$\mu = e l \quad (3-20)$$

Then the attractive force of an ionic charge, e , at a distance, R , is

$$F = \frac{e^2}{R^2} - \frac{e^2}{(R + l)^2} = \frac{2 e \mu}{R^3} \text{ approximately } (3-21)$$

One can see that as soon as a molecule possessing average kinetic energy comes within a critical distance ρ it will be captured by the ion. Consequently, every ion will be surrounded by a small region where the gas density will be larger than the average density and where the different concentrations in the case of a mixture of gases depends on the average concentration on one hand and on the electric moment of the different molecular species present in the mixture on the other hand. We, therefore, have a "planetary" system of extreme density. Consequently, the collision between the molecules of all species present will be extremely probable and violent and the conditions will be ripe for a chemical reaction to take place.

The ion recombination obeys the bimolecular law

$$\frac{dn}{dt} = - K n^2 \quad (3-22)$$

where n = number of ions per unit volume. Then around every alpha trajectory one can imagine a cylinder containing all the ion pairs of primary or secondary origin which are formed during its path. It is understandable that within these cylinders the initial concentration of the ions will vary from one point to the other and that diffusion varies the ionic concentration at any given point. However, if the recombination between the ions is sufficiently rapid one can neglect the effect of diffusion and assumes that the ionic concentration in an element of volume dV around a given point P depends solely upon the rate of recombination. If n_0 = ionic concentration in an element of volume dV at the instant $t = 0$ immediately after the passage of an alpha particle. Then, integrating equation (3-22)

$$K t = \frac{1}{n} - \frac{1}{n_0} \quad (3-23)$$

$$\therefore n = \frac{n_0}{1 + K t n_0} \quad (3-24)$$

Considering the method of forming an ion complex, the ion captures a dipolar molecule every time it comes with a distance ρ . It is thus clear that the number v of the captured molecules per unit time will be proportional to ρ^2 and to the number, C , of dipolar molecules in unit volume or

$$v = a \rho^2 C \quad (3-25)$$

If τ designates the time required to form an ion complex containing x molecules, then

$$\tau = \frac{x}{v} = \frac{x k'}{\rho^2 C} \quad (3-26)$$

where

$$k' = \frac{1}{a}$$

Substituting equation (3-26) into equation (3-24) then

$$n = \frac{n_0}{1 + x K K' \frac{n_0}{C \rho^2}} \quad (3-25)$$

This is the expression for the number of ions that will exist until they capture a minimum of x molecules.

It is obvious that the initial concentration, n_0 , is proportional to the energy of irradiation absorbed per unit volume and unit time in the element of volume dV . This energy is proportional to the total number of molecules in dV . It is thus proportional to C . If we designate by K'' the constant $\frac{n_0}{C}$ equation (3-25) becomes

$$n = \frac{n_0}{1 + \frac{x}{\rho^2} K K' K''} \quad (3-26)$$

This formula shows that for a given value of x , n is independent of pressure but directly proportional to the energy absorbed per unit volume at point P by the gas under consideration.

Now if the ions are the cause of chemical change reaction then the total number of molecules that will react per unit time in the irradiated gas will be

$$\int n_x dV = \int \frac{n_0}{1 + \frac{x}{\rho^2} K K' K''} dV$$

For any one gas the fraction $\frac{n_o}{1 + \frac{x}{\rho^2} K K' K''}$ is constant such that

$$\int n_x dV = \mu \lambda V = \lambda_o d^3 \quad (3-27)$$

where

d = diameter of irradiated volume

λ_o = constant

Equation (3-27) shows that the chemical reaction due to irradiation is proportional to the cubic diameter of the irradiated volume.

Closure

The foregoing chapter listed the different factors that influence the combustion process. It explained it on the basis of thermal, ionization and chain reaction theories. The ignition of a combustible mixture by means of an electric spark is also treated and the expression for the minimum igniting energy derived. The last section dealt with the chemical reaction provoked by the alpha rays.

Irradiation provides some of the conditions that exist in the combustion process. The ionization produced by the alpha particles has about the same order of magnitude as the number of ions that normally exist in the flames. The alpha particles help the initiation of a series of chain reactions. Also, due to the presence of the reaction products within the irradiated volume, the conductivity of the gases is reduced. It can, therefore, be expected that irradiation will affect the ignition and combustion of hydrocarbons.

CHAPTER IV

DESCRIPTION OF APPARATUS AND EXPERIMENTAL PROCEDURE

Description of Apparatus

Figure (4-1) shows the general layout of the equipment.

(1) is the spherical bomb while (2) is the pressure pickup screwed into the bomb. (3) is the bridge amplifier, (4) represents the oscilloscope and (5) represents the square wave generator. The bomb is connected to the mixing tanks (6) by means of $3/8$ inch copper tubing. (7) and (8) are the fuel and air tanks. (9) is the vacuum pump, while (10) is the pressure measuring devices used to measure pressures at various points in the system.

The Spherical Bomb

The bomb,¹⁹ Figures (4-2), (4-3a) and (4-3b), consisted of two identical spherical segments of stainless steel (internal radius of 12.243 cm.) between which the window assembly was clamped. The window, a short cylindrical window of pyrex glass, was supported in recesses in two stainless steel rings sealed with O-rings. The inner surface of the glass window was flush with the walls of the bomb so that the combustion chamber is spherical except for a $1/2$ inch cylindrical segment of glass. The supporting rings for the window were cut away in front to make the full vertical diameter of the bomb visible. Heavy bolts held the parts of the bomb together except in the region through which the flame was observed where a heavy clamp served this purpose without obscuring the view of the flame. Two diametrically opposite holes were drilled and threaded on the surface of the bomb. Two teflon pieces were screwed in these holes to serve as insulators for the

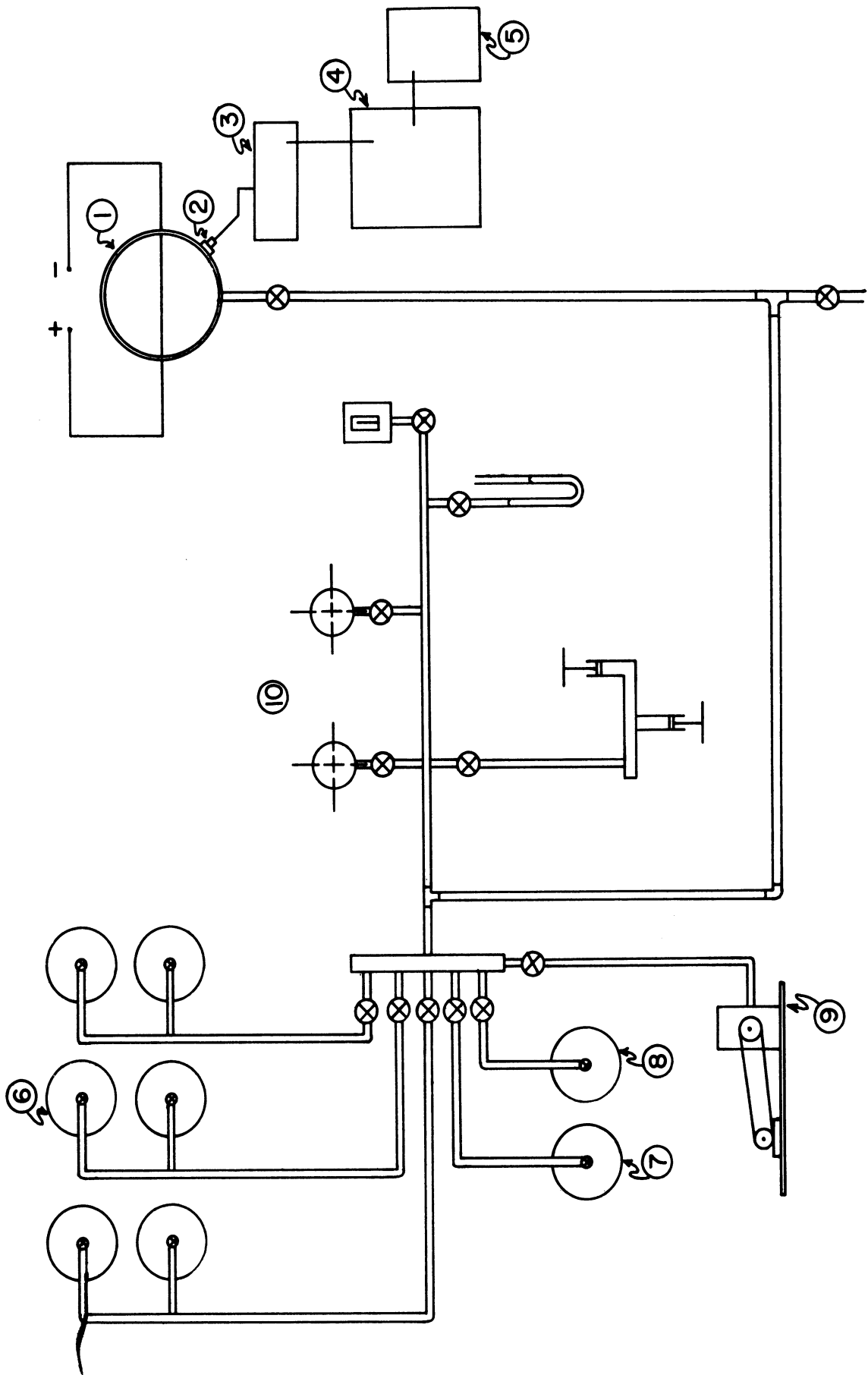


Figure (4-1) General Layout of Equipment

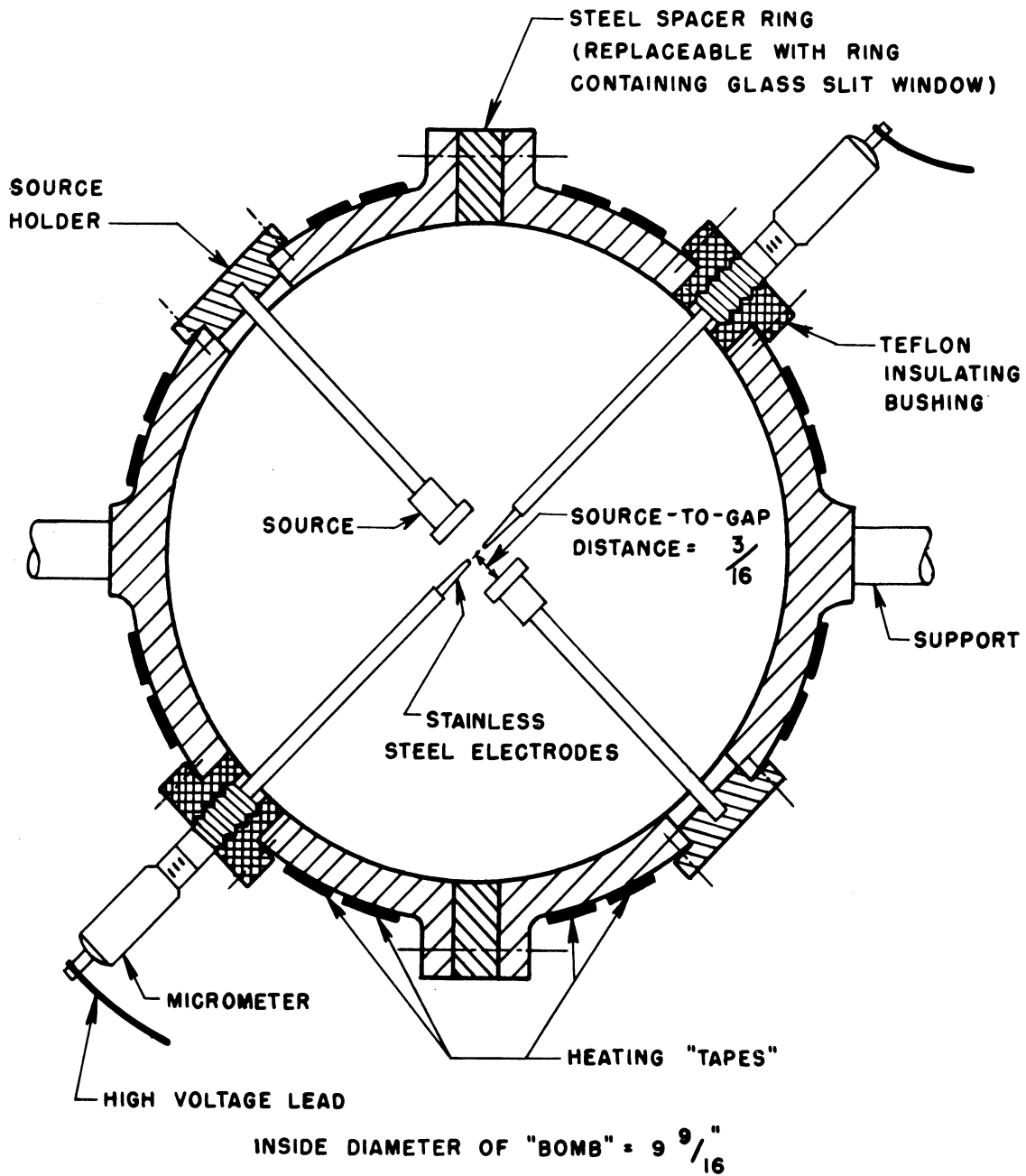


Figure (4-2) Construction of Constant-Volume "Bomb"

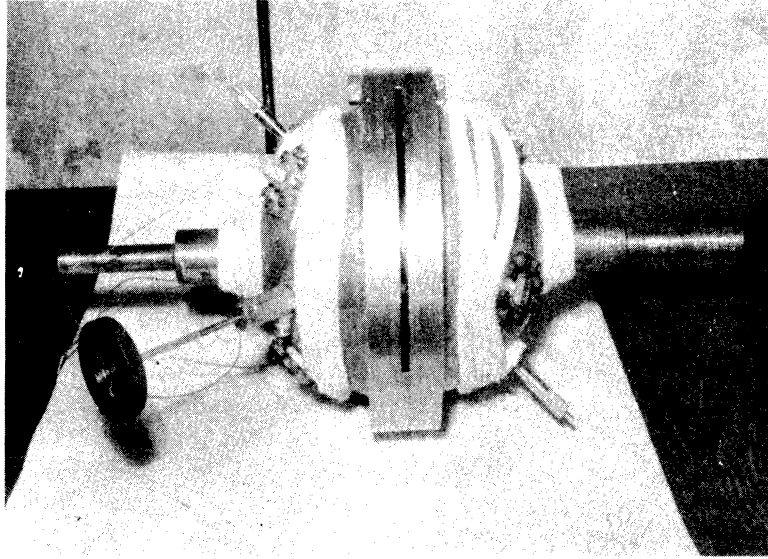


Figure (4-3a) Explosion Bomb Assembly

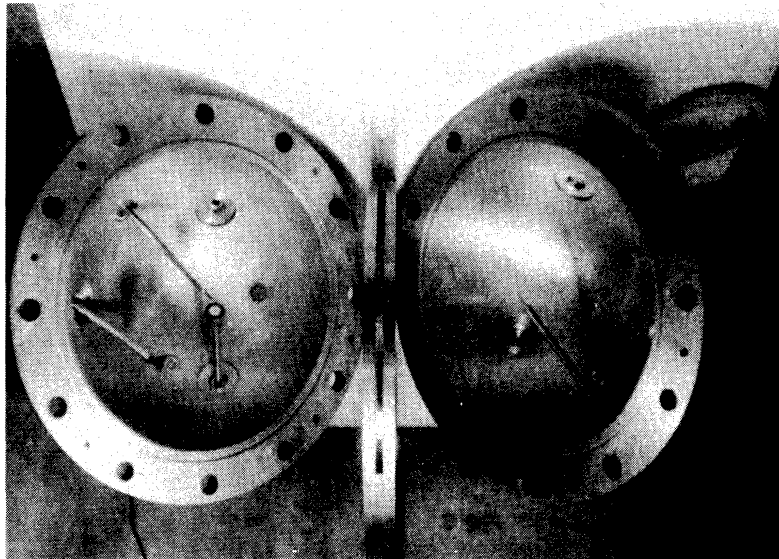
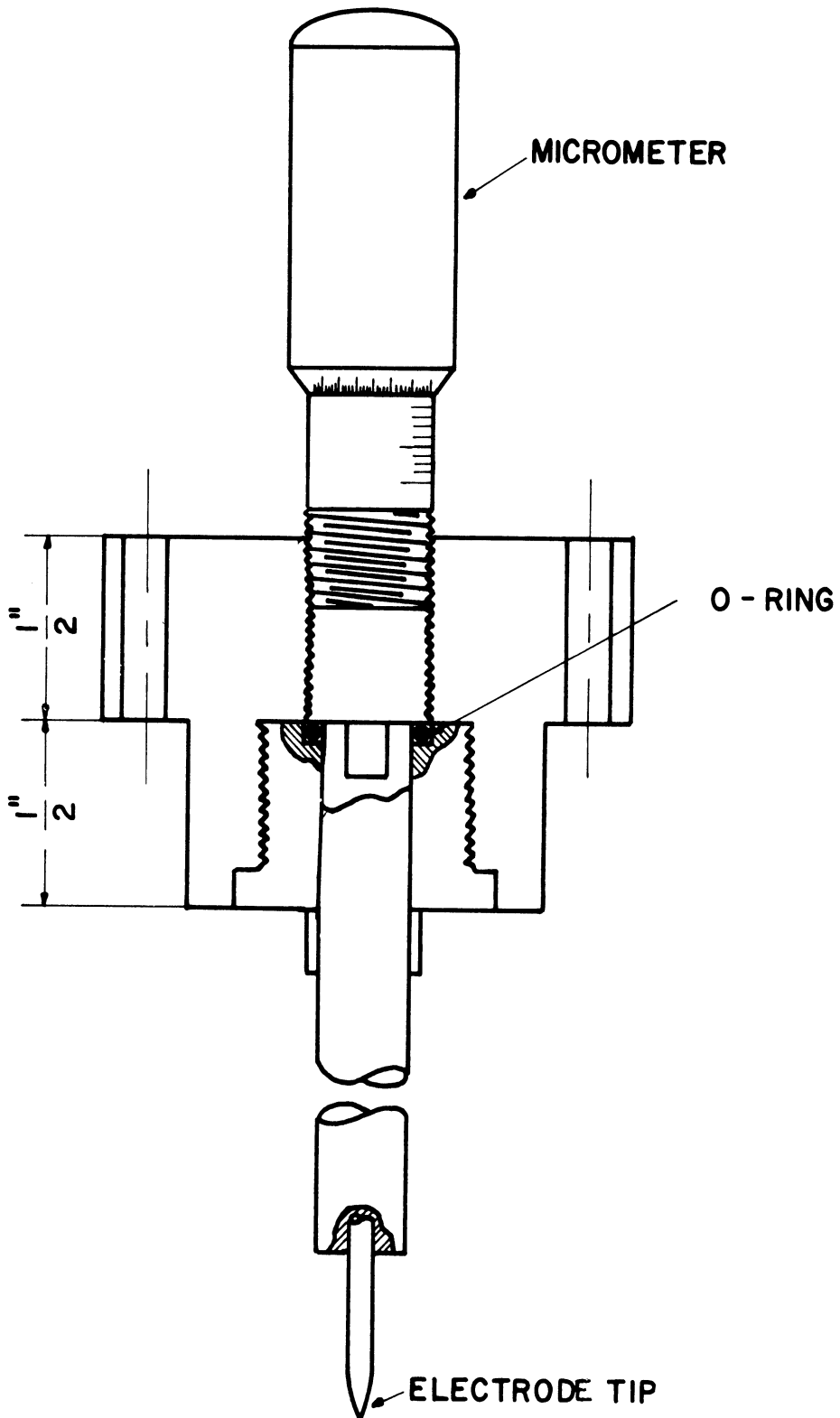


Figure (4-3b) Explosion Bomb Dismantled



ELECTRODE ASSEMBLY

FIGURE (4-4)

sparkling electrodes which were actually the rods of two micrometer gages, thus making possible accurate adjustment of the spark gap without dismantling the bomb assembly. A needle valve screwed in a 5/8 inch hole on the surface controlled both filling and exhausting of the bomb. Six 1-1/2 inch holes, which were needed for a prior experiment for which the bomb was used, were plugged by stainless steel plugs. A strain gage pressure pickup was screwed into one of these plugs while two others served as holders for two stainless steel rods going radially inwards. These rods served as holders for the real and dummy radiation sources. A heating strap was wound around the outside surface of the bomb in order to control its temperature. The temperature of the gas in the bomb was measured by means of a copper constantan thermocouple.

The Mixing Tanks

In order to be certain that the composition of the mixture was the same for all the runs thus providing a solid basis for comparison, premixed stoichiometric mixtures of air and fuel were prepared using the tanks labeled (6), (7), and (8). Tank number (8) contained air at 2400 pounds per square inch pressure while tank number (7) contained the fuel to be used. Tanks number (6) were the mixing tanks. To avoid explosion hazards the mixing tanks were placed in a shed fifty feet outside the building. They were connected to the bomb by three 1/4 inch copper tubing segments protected by a steel pipe. Controls for filling and evacuating the tanks were inside the building.

The Vacuum Pump

Two Cenco vacuum pumps capable of pulling down the pressure of the system to 100 microns or lower were used in parallel. Their

exhaust was directed to a filtering system which constituted one of the permanent facilities of the Phoenix Laboratory. This was a precautionary measure to avoid any contamination due to polonium leaving the surface of the radiation source.

Pressure Measuring Apparatus

Pressure measurements ranged from about 100 microns to above 100 pounds per square inch. Different pressure measuring devices were needed. The following is a listing of such equipment.

1. For measurement of pressures slightly above or below atmospheric a U-tube mercury manometer was used.
2. For higher static pressures measurement a bourdon type pressure gage calibrated against a dead weight tester was used.
3. For dynamic pressure measurement in the bomb an EP series strain gage pressure pickup made by Control Engineering was used. This utilizes a strain gage that gives an electrical signal corresponding to the instantaneous pressure inside the bomb. This signal was relayed to a BA-2 bridge amplifier made by Ellis Associates. The amplified signal was fed to the oscilloscope.
4. For the measurement of pressures of less than one mm a McLeod gage was used.

The Sparking Circuit

In order to produce sparks capable of igniting the fuel air mixtures under study a d-c power supply that produced up to 500 V was used. Figure (4-5) shows the ignition circuit. The power supply was connected to a 1 μ F condenser. The latter was connected in parallel to the primary of a 130:1 step up transformer. The secondary of the transformer was connected to the sparking electrodes through the

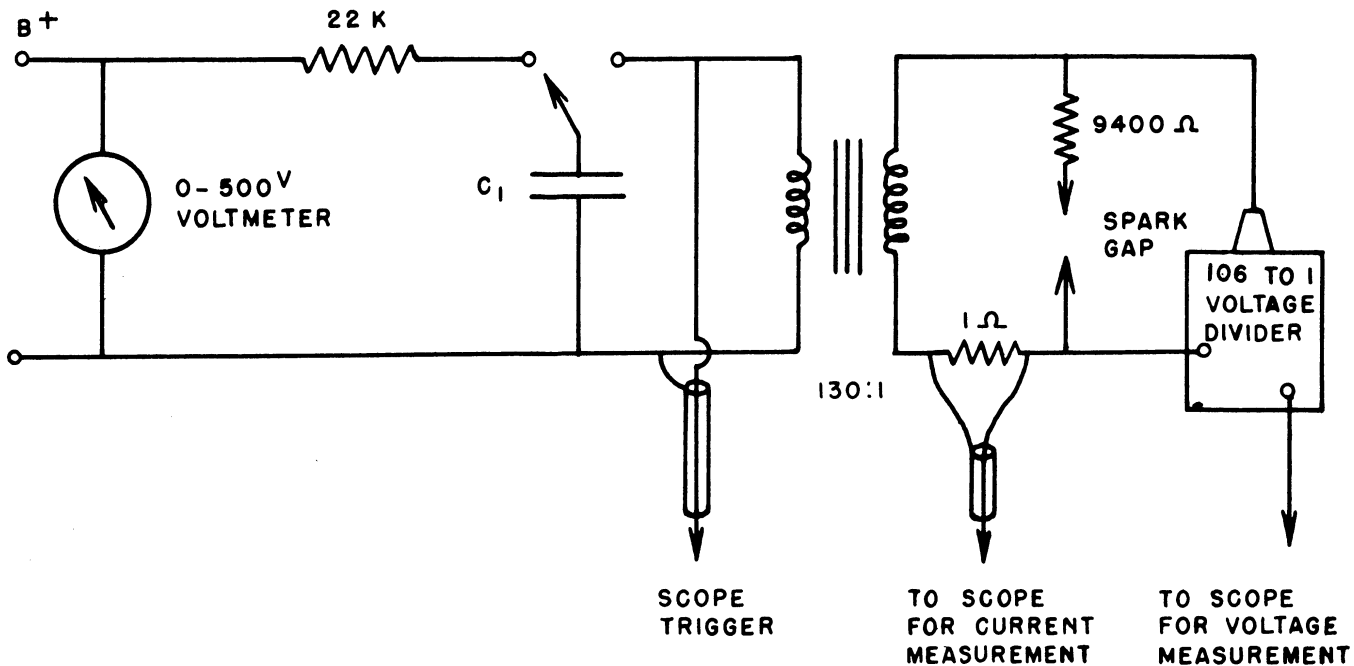


FIGURE (4-5) SPARKING CIRCUIT

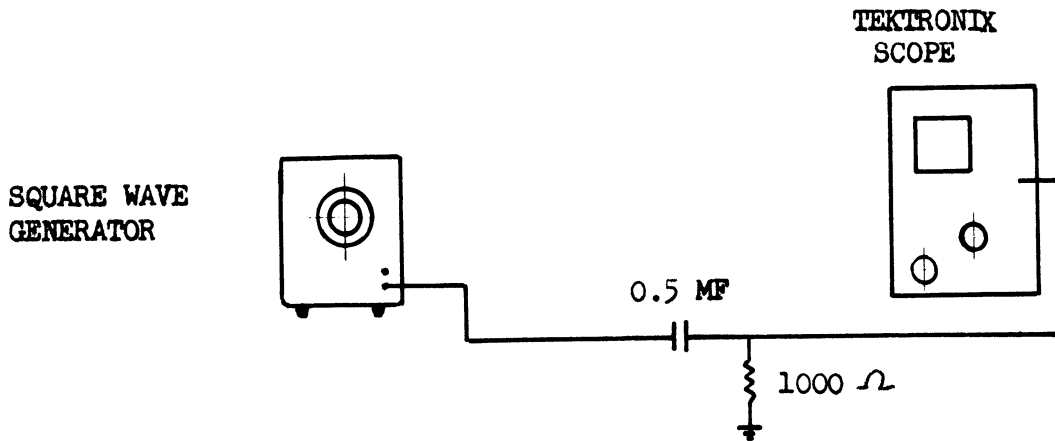


FIGURE (4-6) TIMING CIRCUIT

resistance $R_1 = 9400 \Omega$ A resistance $R_2 = 1 \Omega$ was included in the secondary. The procedure for producing a spark can be summarized as follows: The power supply was used to charge the condenser to a prefixed voltage. The condenser was then discharged into the primary of the transformer and a voltage capable of producing a spark appeared in the secondary circuit. For spark energy computation both the instantaneous current and voltage across the spark were recorded. Spark current measurements were obtained by photographing the trace on the oscilloscope which represents the variation of voltage across R_2 with respect to time. Similar measurements were made of the variation of voltage with respect to time across the spark gap. This was achieved through the use of a 106:1 voltage divider. The trigger circuit was connected to the primary of the transformer in order to give the scope sweep an earlier start.

The Oscilloscope

The signal from the strain gage pressure pickup was amplified and was fed to the y-component of a 512 Tektronix scope. The trace which appeared on the screen was photographed by means of a polaroid camera which was fitted to the scope by means of a special adapter. This oscilloscope was not suitable for current and voltage measurement of the spark, hence a 517 Tektronix scope with an accelerating voltage of 24 KV served this purpose. Pictures of the voltage time and current time traces were taken using a highly sensitive polaroid film.

The Timing Signal

The output of a square wave generator, manufactured by Hewlett Packard Company was fed to the scope after being reduced to a

pulse by passing through a differentiating circuit. This consisted of a .05 microfarad capacitor and a 1000 ohm resistance introduced into the circuit as shown in Figure (4-6). The pulses were placed at equal intervals of one-hundredth of a second.

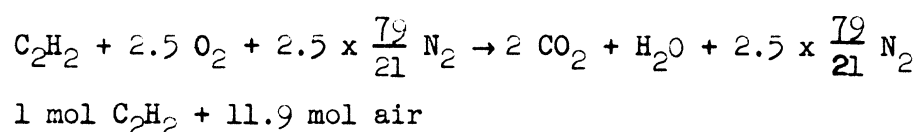
The Source

The source of irradiation was polonium-210 which has a half-life of 138 days. The sources were manufactured by the Mound Laboratories, Miamisburg, Ohio, by electro-depositing polonium on the surface of a stainless steel piece, Figure (4-7). This piece was then covered by a stainless steel window .00027 inch thick. Nickel was electro-plated on the edges for sealing purposes. The activity of the sources on February 24, 1956 was A-36, 1.20 curie; A-37, 1.06 curie; and A-34, 5 curie. The distance of the source from the spark gap was fixed at 3/16 inch. The range of alpha particles after penetrating through the window was approximately 1/2 inch in air at atmospheric pressure.

Experimental Procedure

The mixing tanks were evacuated to a pressure of 100 microns or less. Fuel was then introduced until the pressure necessary to give a stoichiometric mixture was reached. The mixing tanks were then charged with air until the total pressure equaled the predetermined mixture pressure. This was limited to 50 pounds per square inch gage to meet safety measures.

The following calculations give the ratio of partial pressures for air and the different fuels used.



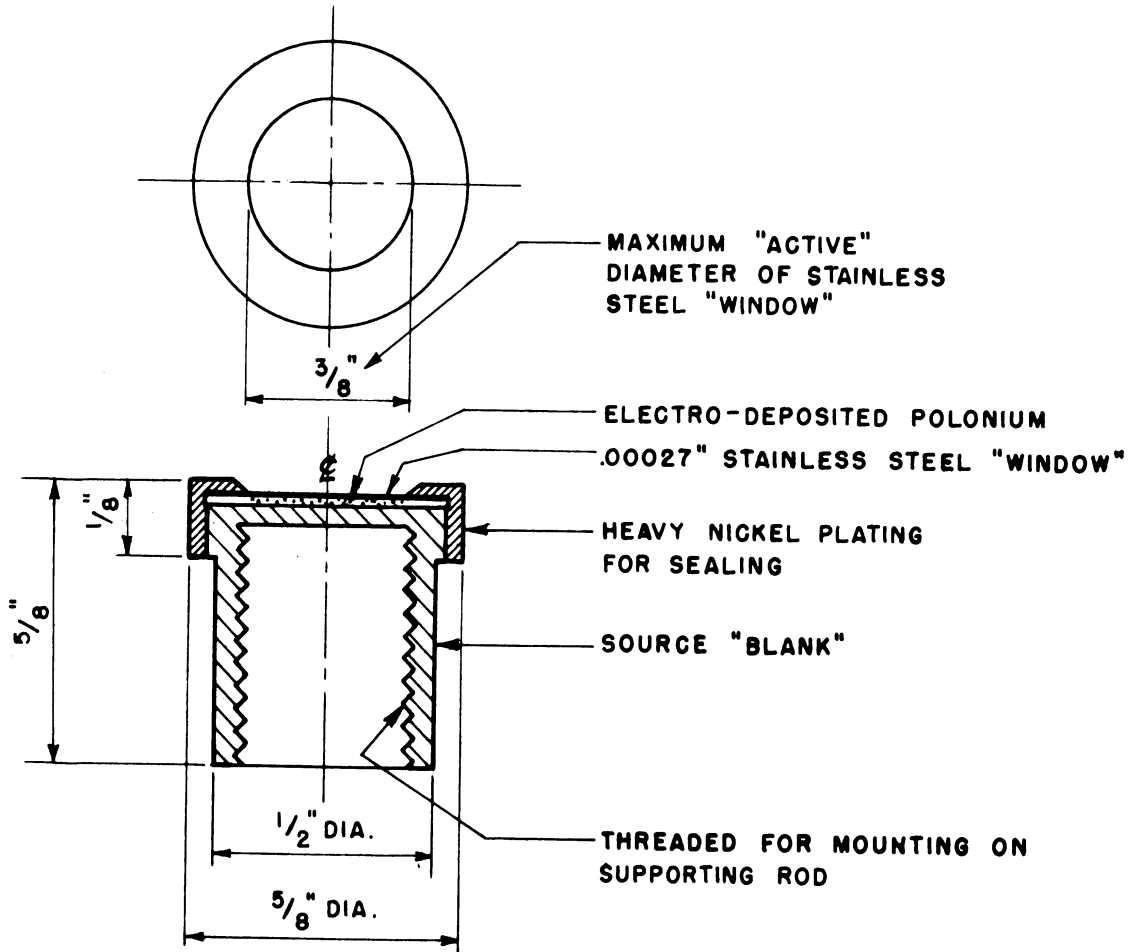
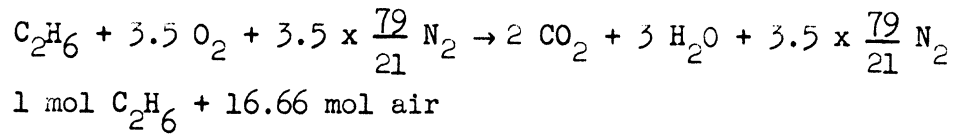
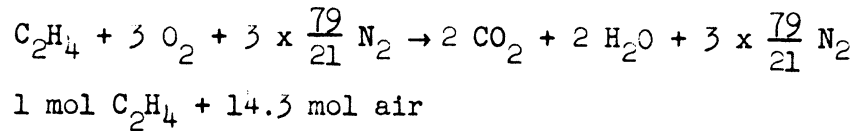


Figure (4-7) Construction of Polonium Sources



Calculations to reveal possible deviation from the ideal case due to compressibility of the gases showed that no correction for such effect was needed.

Calibration of the Pressure Pickup

The BA-2 Bridge Amplifier had two settings, static and dynamic. The static setting is used for calibration purposes. With the amplifier set to static, air under pressure was introduced inside the bomb and its pressure measured by the dead weight tester shown in Figure (4-1) and the pressure pickup. The latter caused a vertical displacement, proportional to the pressure, of the electron beam that appeared on the screen. The air pressure was then changed in small increments over the range of pressure encountered.

Actual Runs

The test is essentially a comparison test consisting of performing consecutive runs for which the names "cold" and "hot" were given. The first indicates that the bomb has been charged with the fuel air mixtures while the dummy sources are in position inside the bomb. The second one indicates the exact repetition of the previous test with the sole replacement of the dummy sources by the hot sources. To insure accuracy of measurements, calibration runs were performed before and after every series of runs.

Measurement of Delay Period and Rate of Pressure Rise

The procedure adopted in obtaining the pressure time curve was as follows:

1. The bomb was allowed to heat up until the thermocouple recorded a temperature of 120°F.
2. The bomb was evacuated to a pressure of 100 microns or less.
3. The stoichiometric air fuel mixture was introduced into the bomb until the predetermined initial pressure was reached.
4. With all the valves shut, a spark capable of burning the mixture was allowed to cross between the electrodes.
5. At the same instant the camera shutter was opened to take a picture of the trace that appeared on the scope screen which indicated the variation of pressure with time in the bomb.
6. This procedure was repeated to insure reproducibility.

Measurements for the Determination of the Critical Spark Energy

The minimum igniting energy was obtained as follows:

1. The primary voltage was fixed to the previously chosen value.
2. The gap was narrowed to get sparks without causing ignition.
3. The gap was then increased in small increments and a spark made to cross the gap after each step, until a gap was reached which gave the first igniting spark.
4. The variation of current and voltage with time was photographed for every spark obtained in item (3).

CHAPTER V

RESULTS

Delay Period and Rate of Pressure Rise

Figures (5-1) and (5-2) show that in the case of acetylene and ethylene no change was detected in the delay period when the spark gap was irradiated. Figure (5-3) shows that in the case of ethane a decrease in the delay period occurs under irradiation.

Figures (5-1), (5-2), and (5-3) also show that there was no measurable change in the rate of pressure rise with any of the fuels irradiated as compared to the rate of pressure rise with no radiation.

Critical Spark Gap

Figures (5-4) and (5-5) show that with radiation the critical gap was increased in the case of acetylene and ethylene while it was reduced in the case of ethane.

Figure (5-5) shows that with radiation present it was possible to ignite ethane air mixtures using a primary voltage of 80 V. Without radiation, the minimum possible primary voltage that produced a spark sufficient for ignition was 100 V.

The data from which Figures (5-4) and (5-5) were plotted are listed in Tables (5-2), (5-3), (5-4), and (5-5).

Spark Energy

Figures (5-6) and (5-7) show the variation of current and voltage with time plotted on graph paper. A curve representing power versus time was deduced from these two curves, Figure (5-8). The area under this curve represents the spark energy.

Figure (5-9) shows that under irradiation ethane required less energy to ignite.

Figure (5-10) shows that under irradiation ethylene showed no change in the energy requirement with narrow gaps and an increase in its value with wider gaps.

Figure (5-11) indicates that acetylene showed an increase in the energy required with narrow gaps and a decrease in its value with wider gaps.

The following is a table summarizing the results; it lists the changes that take place, due to irradiation, in the different parameters that were measured.

TABLE (5-1). SUMMARY OF THE RESULTS

	Acetylene	Ethylene	Ethane
Gap	increases	increases	decreases
Energy	increases	increases	decreases
Rate of Pressure Rise	no change	no change	no change
Delay Period	no change	no change	decreases slightly

TABLE (5-2) CRITICAL GAPS FOR ACETYLENE

Fuel	Type of Run	Initial Pressure		Primary Voltage	Gap Width
		In.	Hg Abs.	Volts	Inches
C ₂ H ₂	Hot	10		100	.04
	Hot	10		150	.033
	Hot	10		200	.028
	Hot	10		250	.026
	Hot	10		300	.023
	Hot	10		350	.022
	Cold	10		100	.037
	Cold	10		150	.030
	Cold	10		200	.025
	Cold	10		250	.023
	Cold	10		300	.021
	Cold	10		350	.020

TABLE (5-3) CRITICAL GAPS FOR ETHYLENE

Fuel	Type of Run	Initial Pressure		Primary Voltage		Gap Width	
		In.	Hg Abs.	Volts		Inches	
C ₂ H ₄	Hot	10		100		.095	
	Hot	10		150		.082	
	Hot	10		200		.079	
	Hot	10		250		.072	
	Hot	10		300		.066	
	Hot	10		350		.062	
	Cold	10		100		.090	
	Cold	10		150		.077	
	Cold	10		200		.073	
	Cold	10		250		.070	
	Cold	10		300		.065	
	Cold	10		350		.063	

TABLE (5-4) CRITICAL GAPS FOR ETHANE

Fuel	Type of Run	Initial Pressure		Primary Voltage	Gap Width
		In.	Hg Abs.	Volts	Inches
C ₂ H ₆	Hot	10		200	.124
	Hot	10		250	.120
	Hot	10		300	.116
	Hot	10		350	.114
	Hot	10		400	.114
	Hot	10		450	.113
	Cold	10		200	.145
	Cold	10		250	.140
	Cold	10		300	.130
	Cold	10		350	.122
	Cold	10		400	.121
	Cold	10		450	.118

TABLE (5-5) CRITICAL GAPS FOR ETHANE

Fuel	Type of Run	Initial Pressure In. Hg Abs.	Primary Voltage Volts	Gap Width Inches
C ₂ H ₆	Hot	20	80	.063
	Hot	20	100	.053
	Hot	20	200	.039
	Hot	20	300	.037
	Hot	20	400	.035
	Hot	20	500	.033
	Cold	20	100	.060
	Cold	20	200	.048
	Cold	20	300	.040
	Cold	20	400	.039
	Cold	20	500	.038

Sample of Calculation

Divider Ratio

This ratio was determined experimentally by comparing the magnitude of a square wave fed to the scope directly and through the divider.

$$D. R. = \frac{36}{0.34} = 106$$

Voltage Scale Cold Runs 1 cm = 15 x 10⁶ volts

Hot Runs 1 cm = 25 x 10⁶ volts

Current Scale Cold and hot runs 1 cm = 0.25 amp

Polaroid Picture Scale 1 cm = 2.5 cm

Sweep Speed 20 μ per cm

The area under the energy time curve was measured by means of a planimeter.

Figure (5-1)

Pressure Time
Curve for
Acetylene

I.P. 30"
I. Temp. 120° F

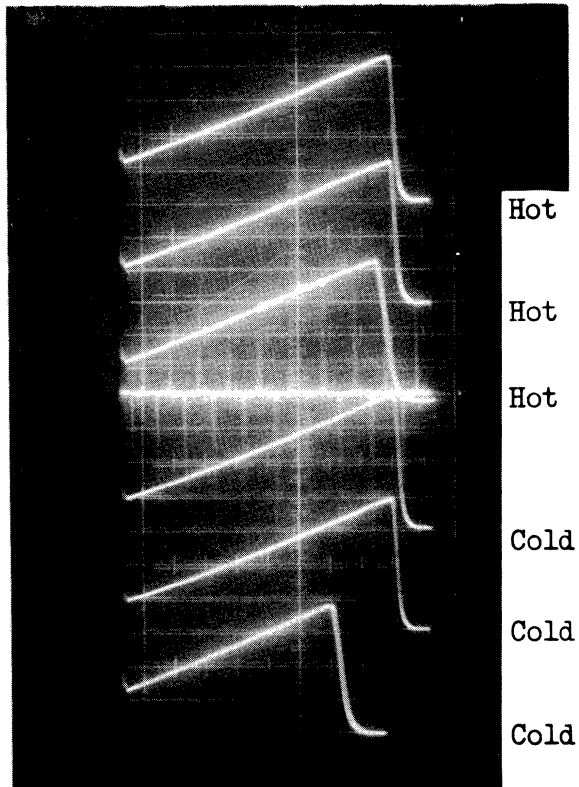
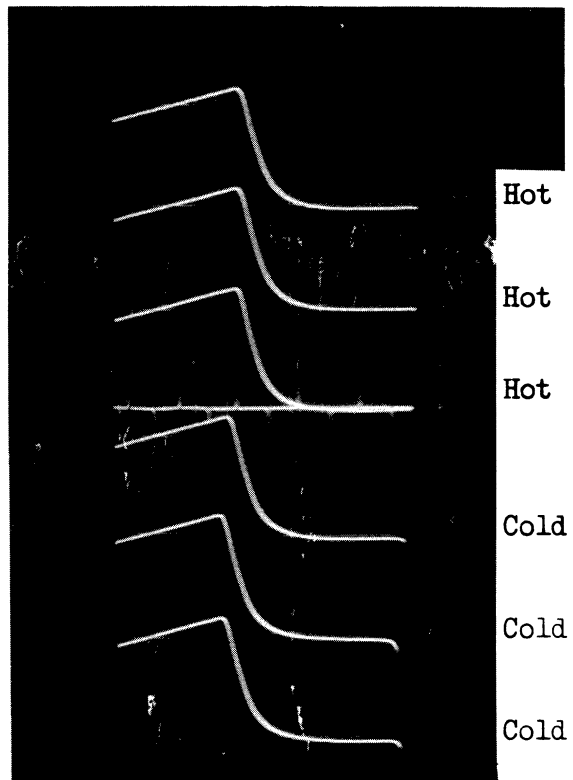


Figure (5-2)

Pressure Time
Curves for
Ethylene

I. P. 30"
I. Temp. 120° F



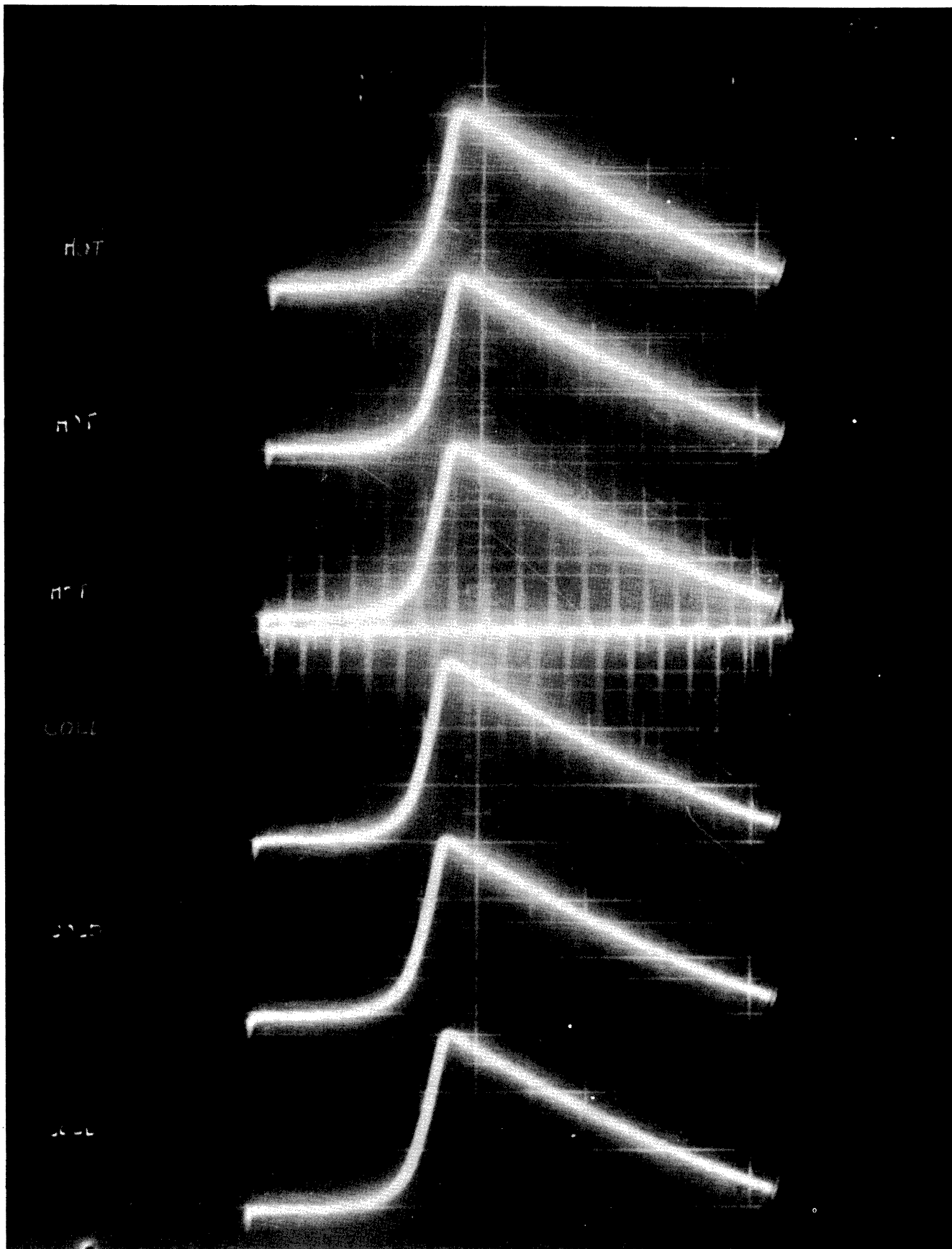


Figure (5-3) Pressure Time Curve For Ethane

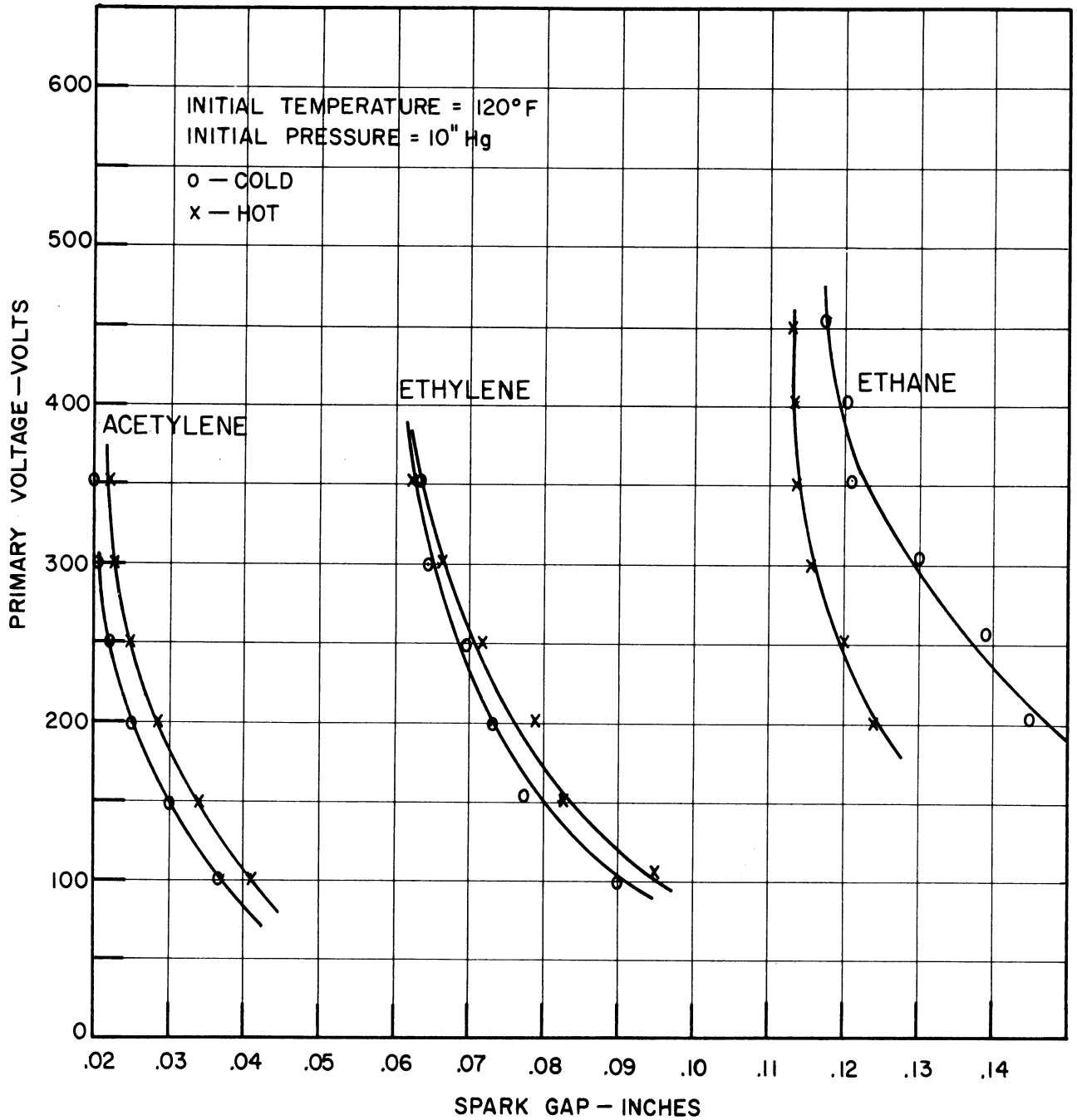


FIGURE (5-4). PRIMARY VOLTAGE VERSUS CRITICAL GAP

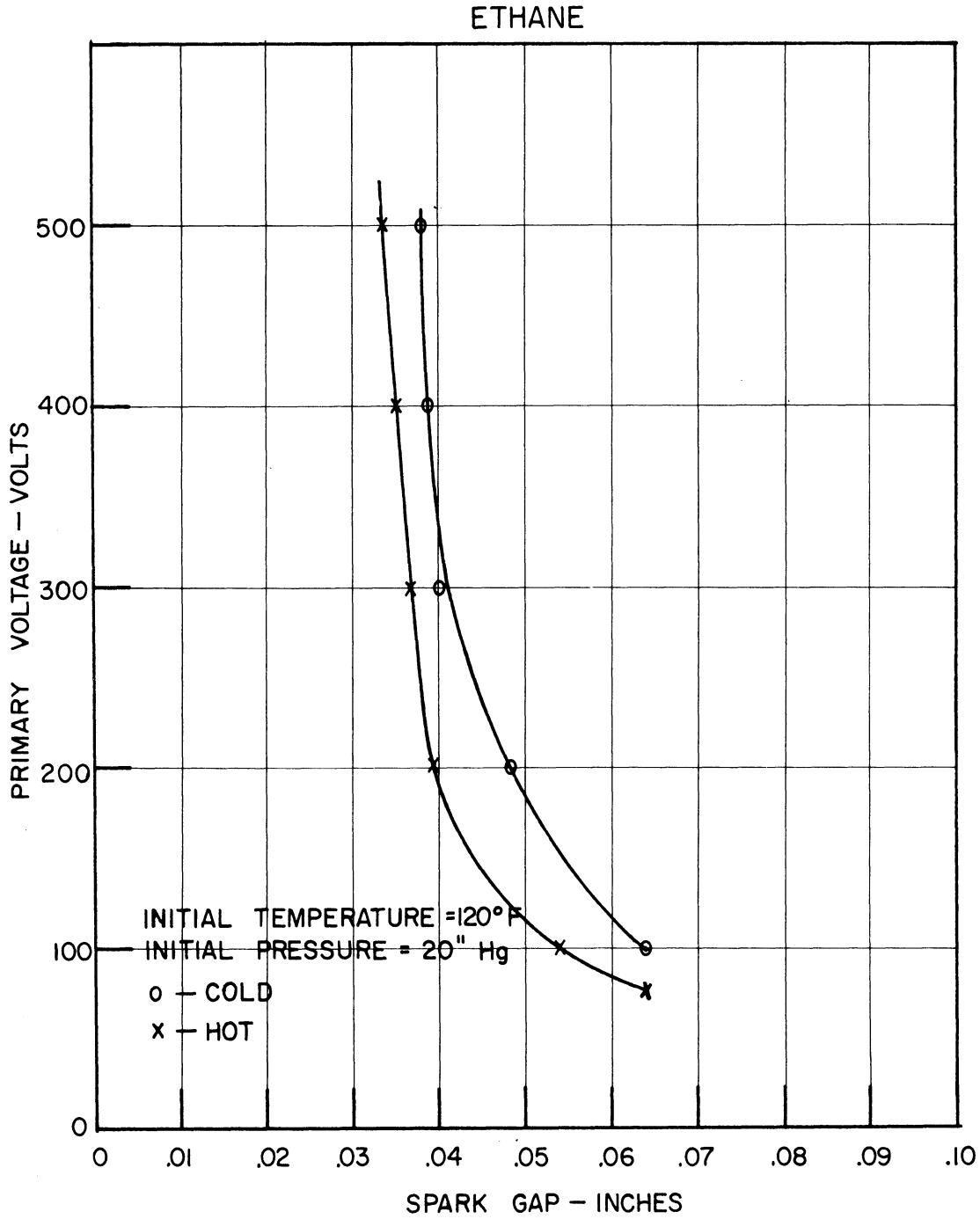


FIGURE (5-5). PRIMARY VOLTAGE VERSUS CRITICAL GAP

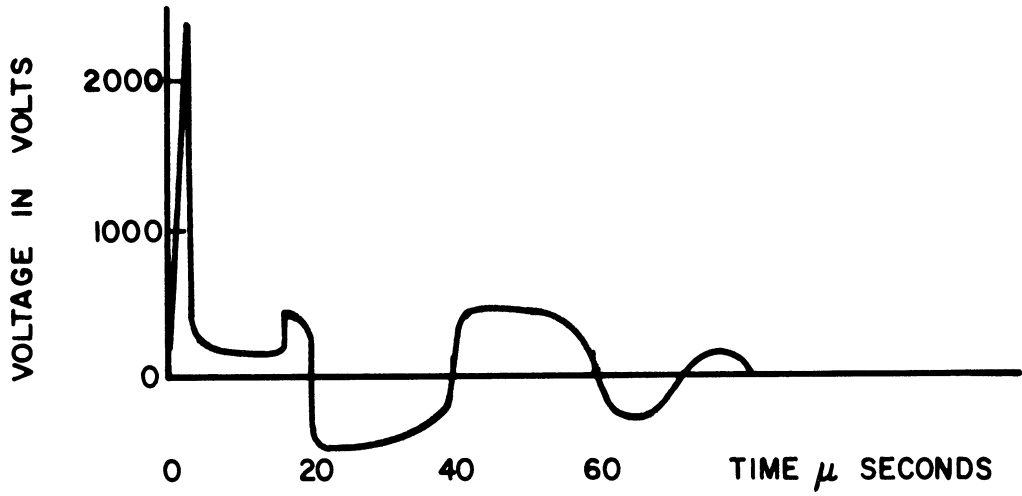


FIG. 5 - 6

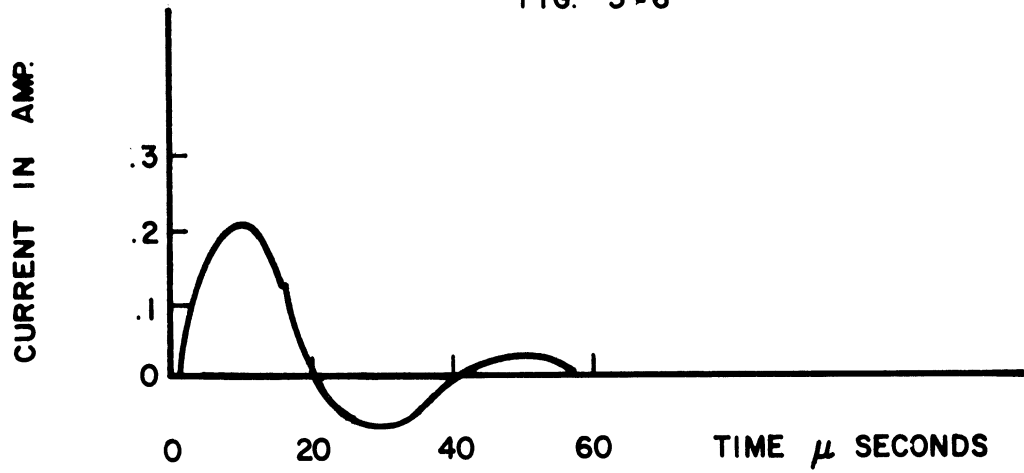


FIG. 5 - 7

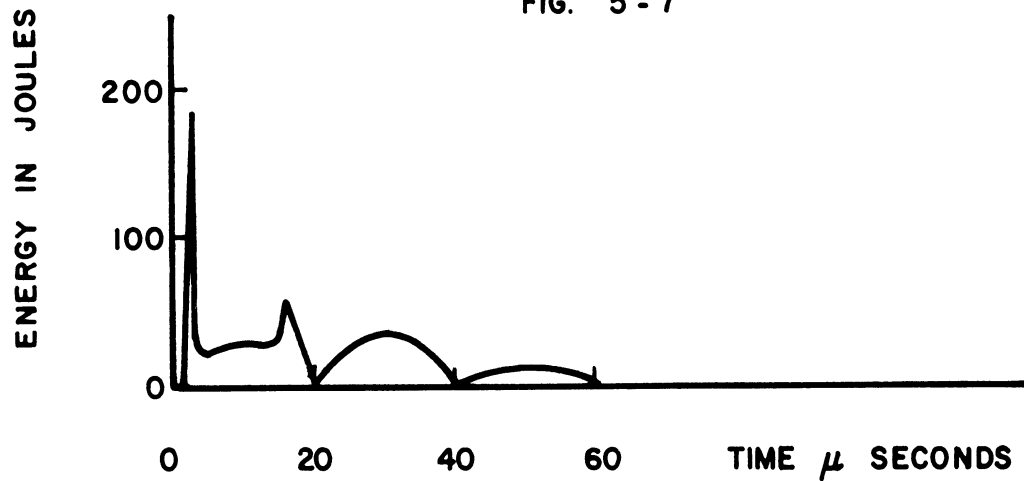


FIG. 5 - 8

FIGURES (5 - 6,7,8) EVALUATION OF SPARK ENERGY FOR ETHANE

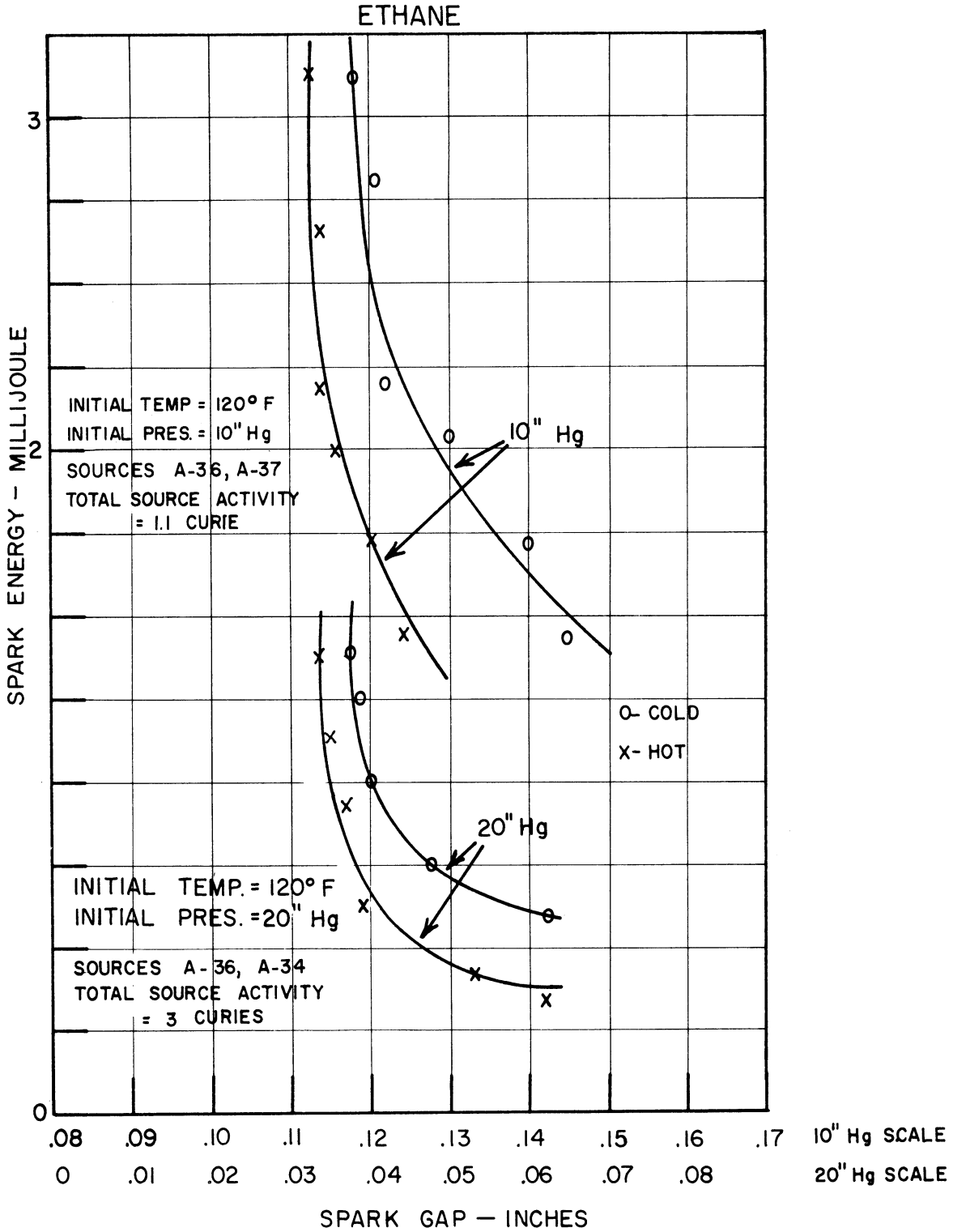


FIGURE (5-9). MINIMUM IGNITING ENERGY VERSUS CRITICAL GAP

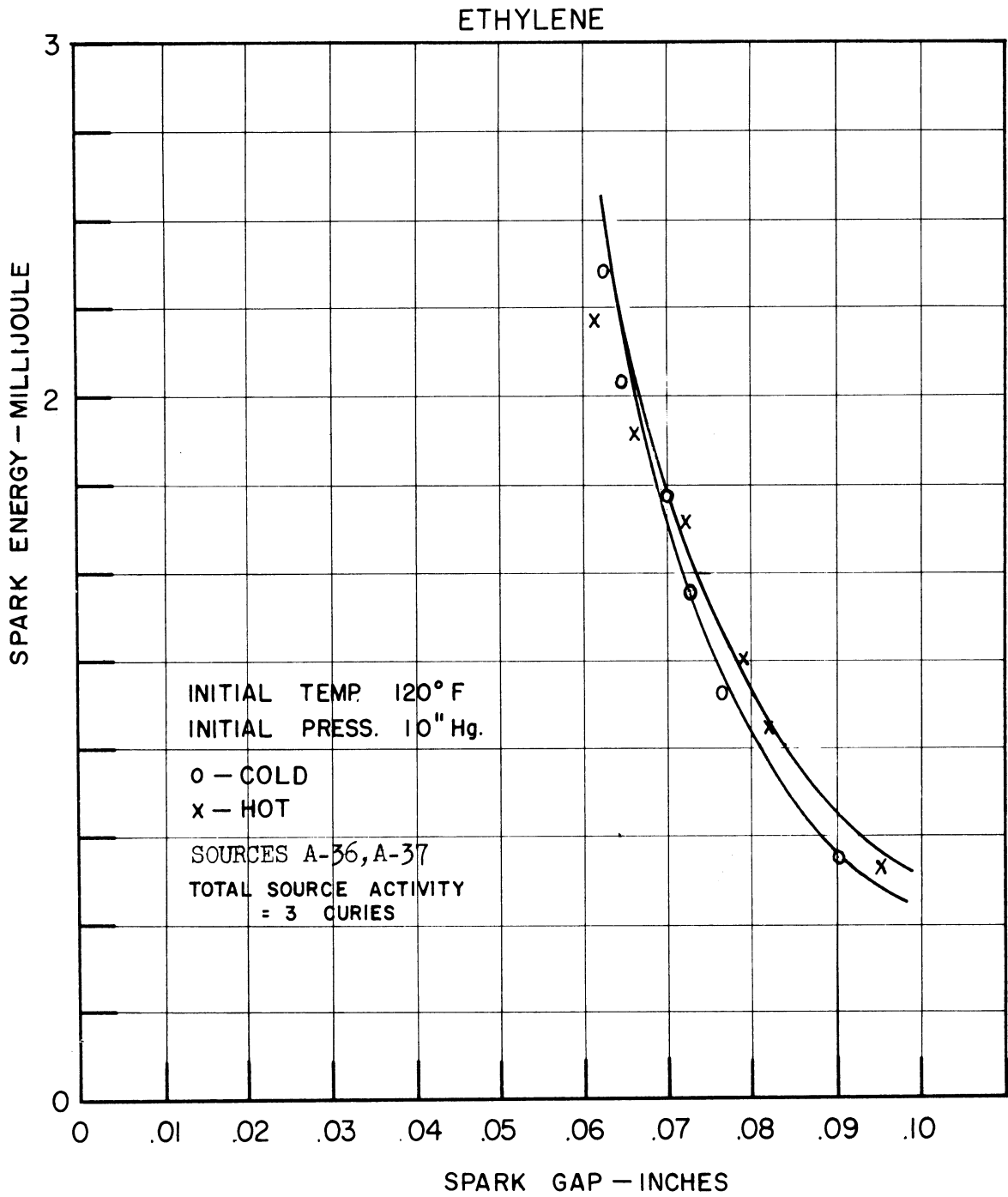


FIGURE (5-10). MINIMUM IGNITING ENERGY VERSUS CRITICAL GAP

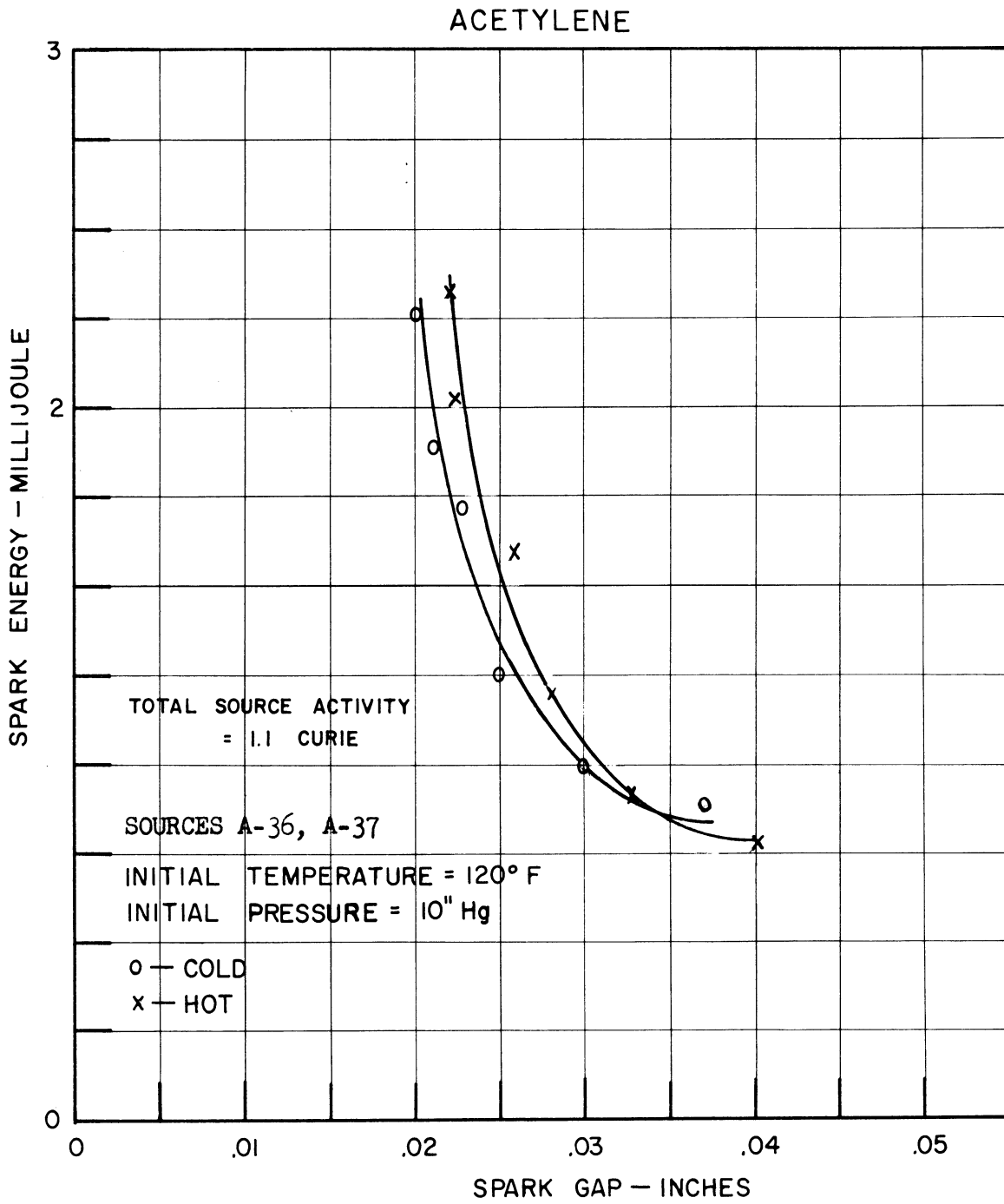


FIGURE (5-11) MINIMUM IGNITING ENERGY VERSUS CRITICAL GAP

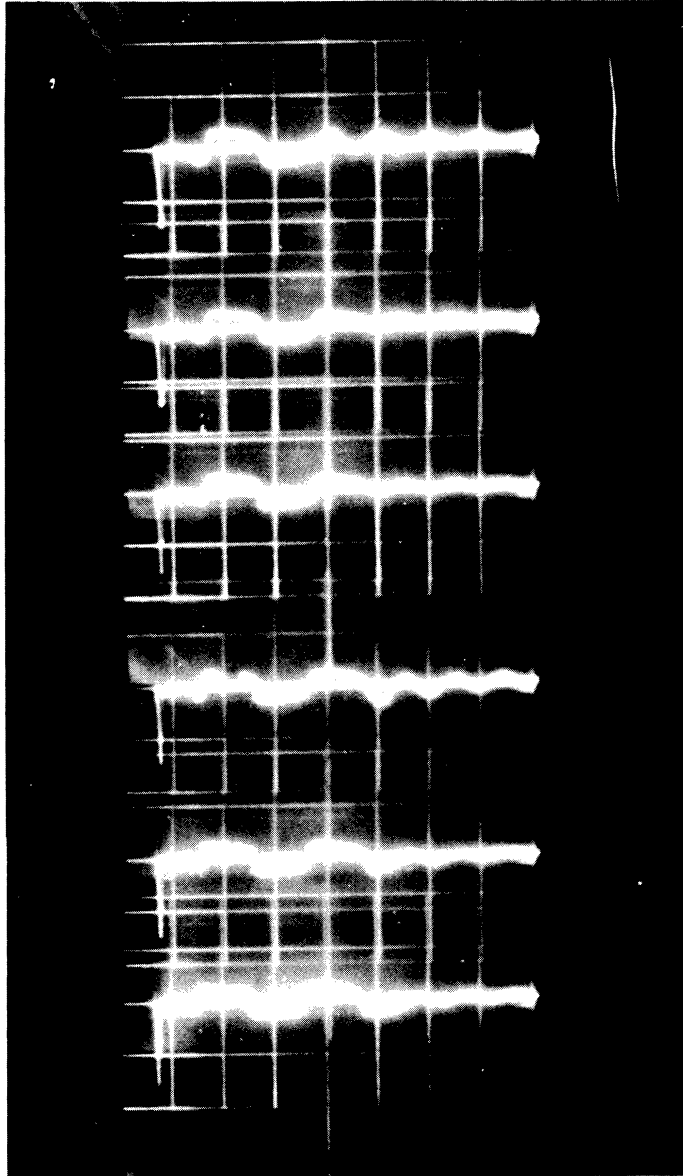


Figure (5-12) Spark Gap Instantaneous Voltage Versus Time For Ethane (Cold Runs).

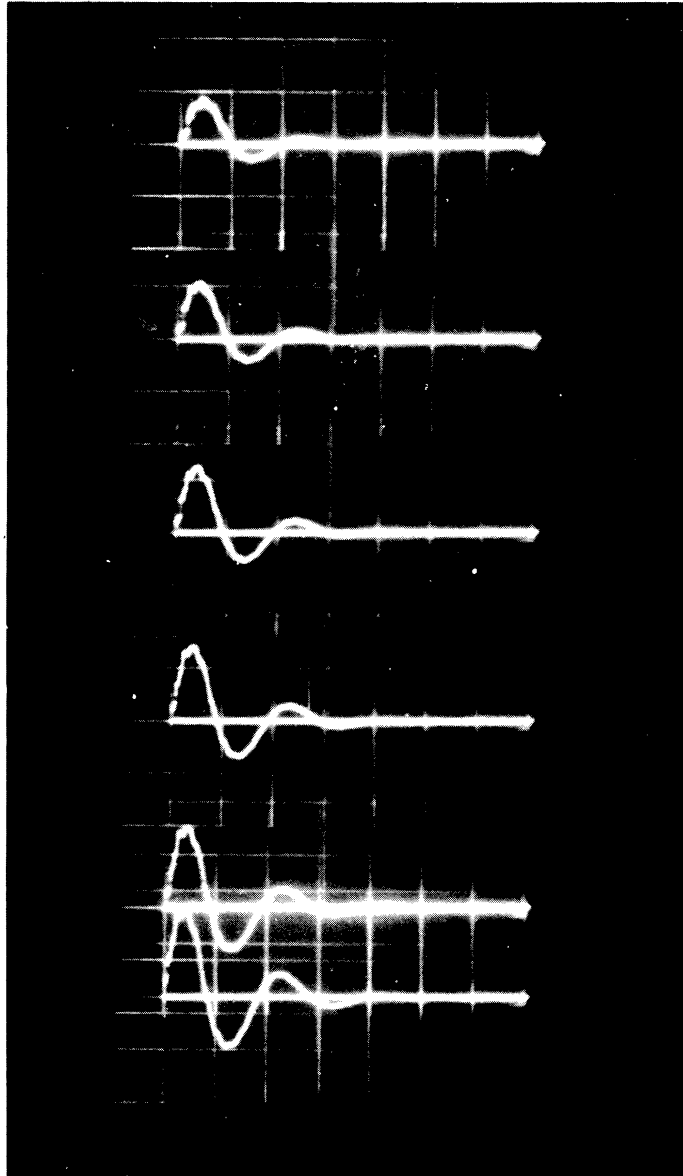


Figure (5-13) Spark Gap Instantaneous Current Versus Time For Ethane (Cold Runs)

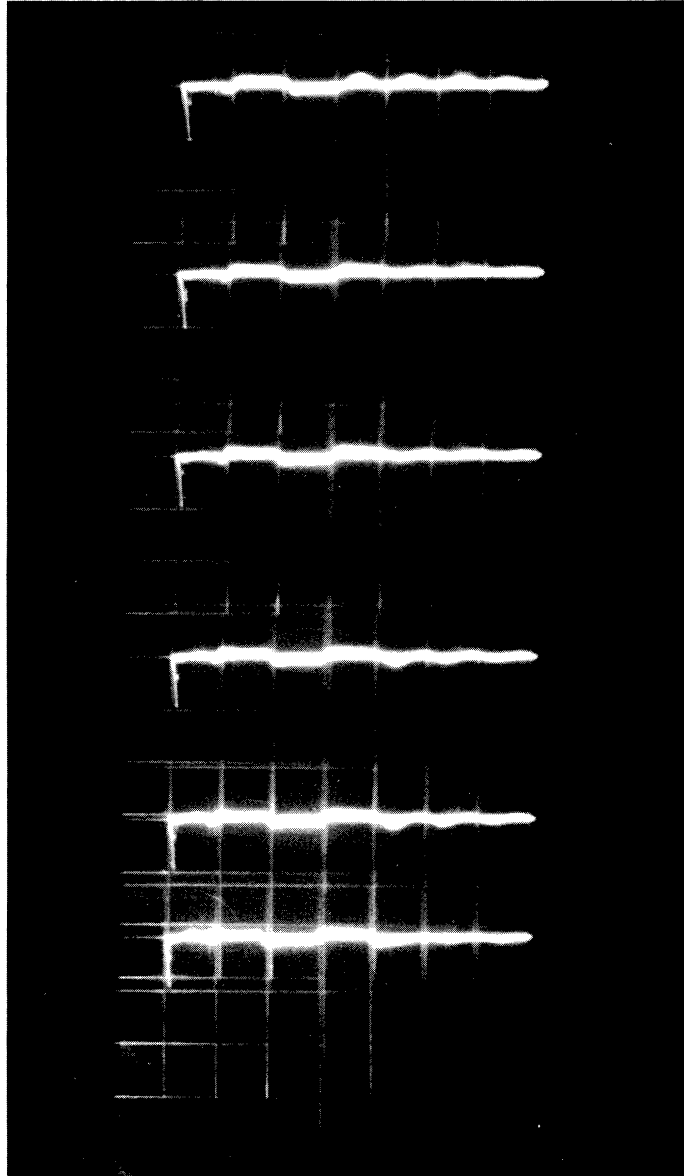


Figure (5-14) Spark Gap Instantaneous Voltage Versus Time For Ethane (Hot Runs)

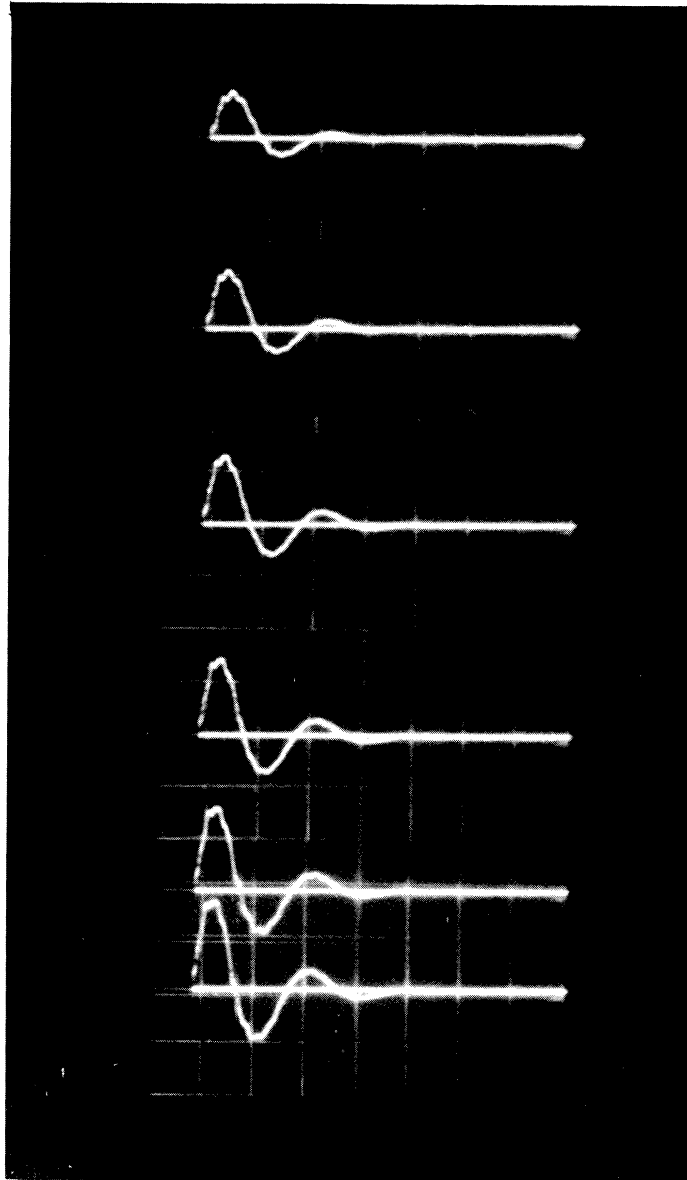


Figure (5-15) Spark Gap Instantaneous Current Versus Time For Ethane (Hot Runs)

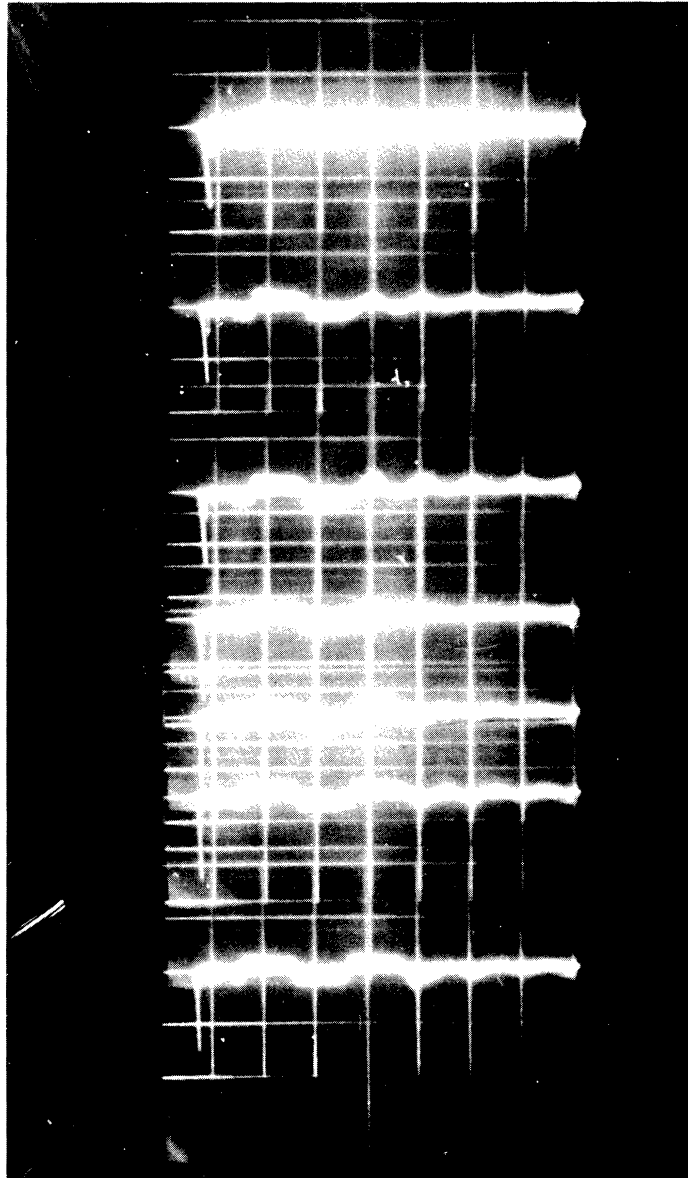


Figure (5-16) Spark Gap Instantaneous Voltage Versus Time For Ethylene (Cold Runs)

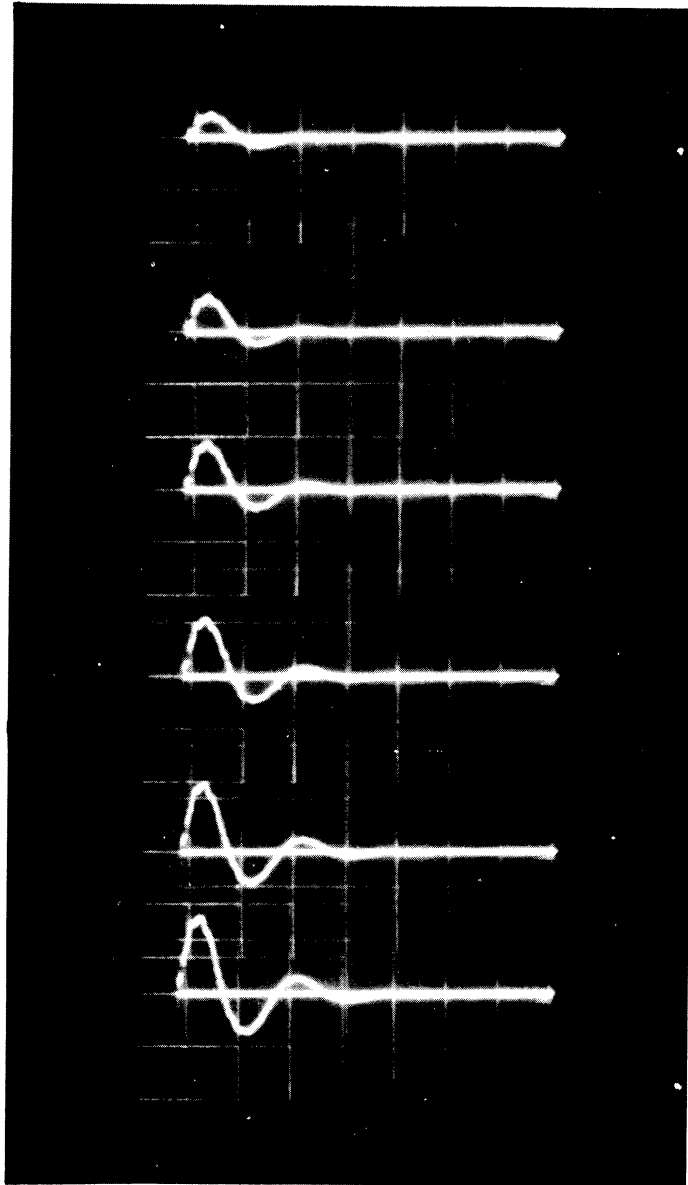


Figure (5-17) Spark Gap Instantaneous Current Versus Time For Ethylene (Cold Runs)

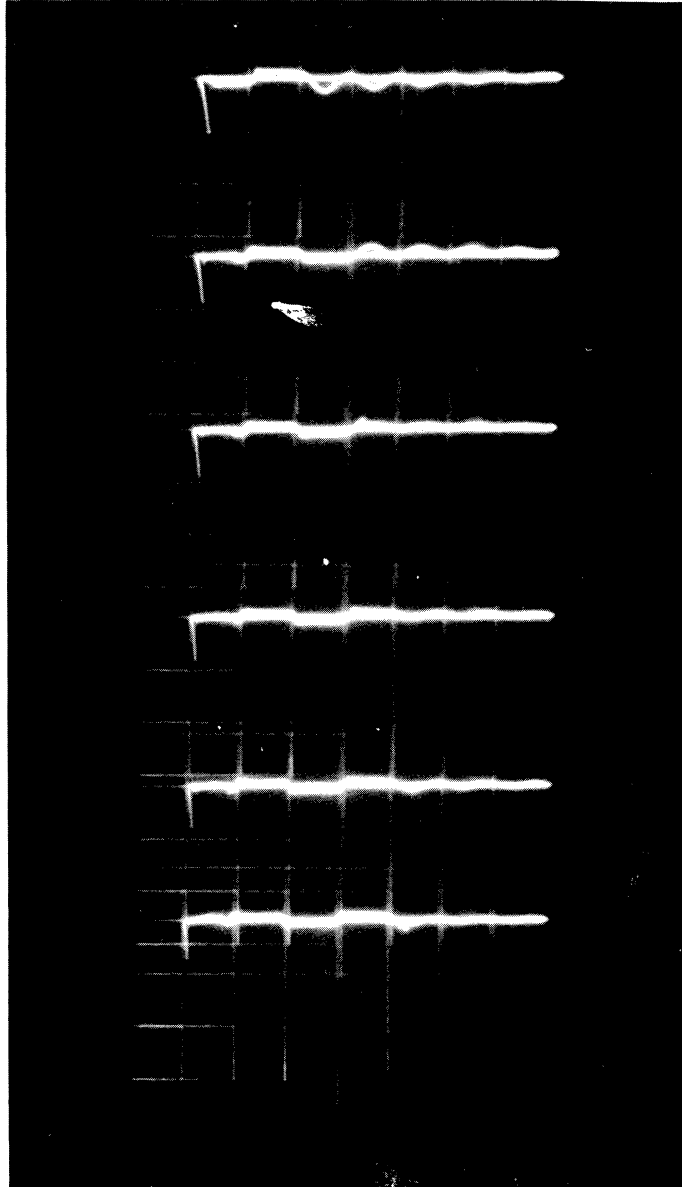


Figure (5-18) Spark Gap Instantaneous Voltage Versus Time For Ethylene (Hot Runs)

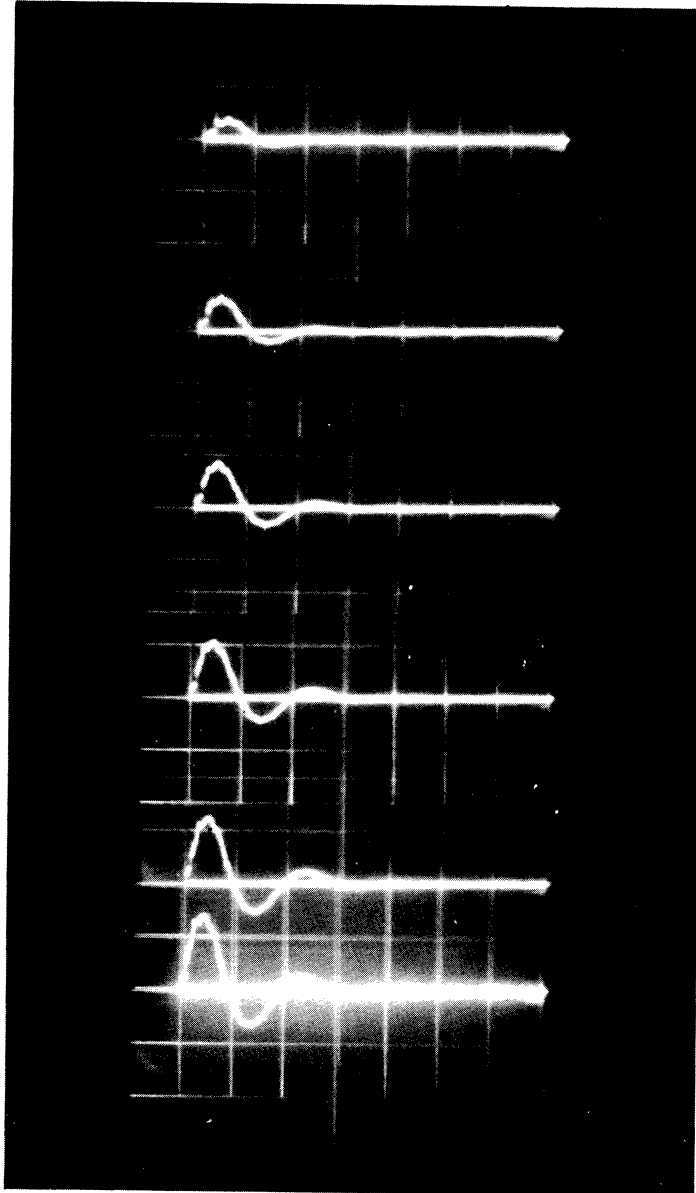


Figure (5-19) Spark Gap Instantaneous Current Versus Time For Ethylene (Hot Runs)

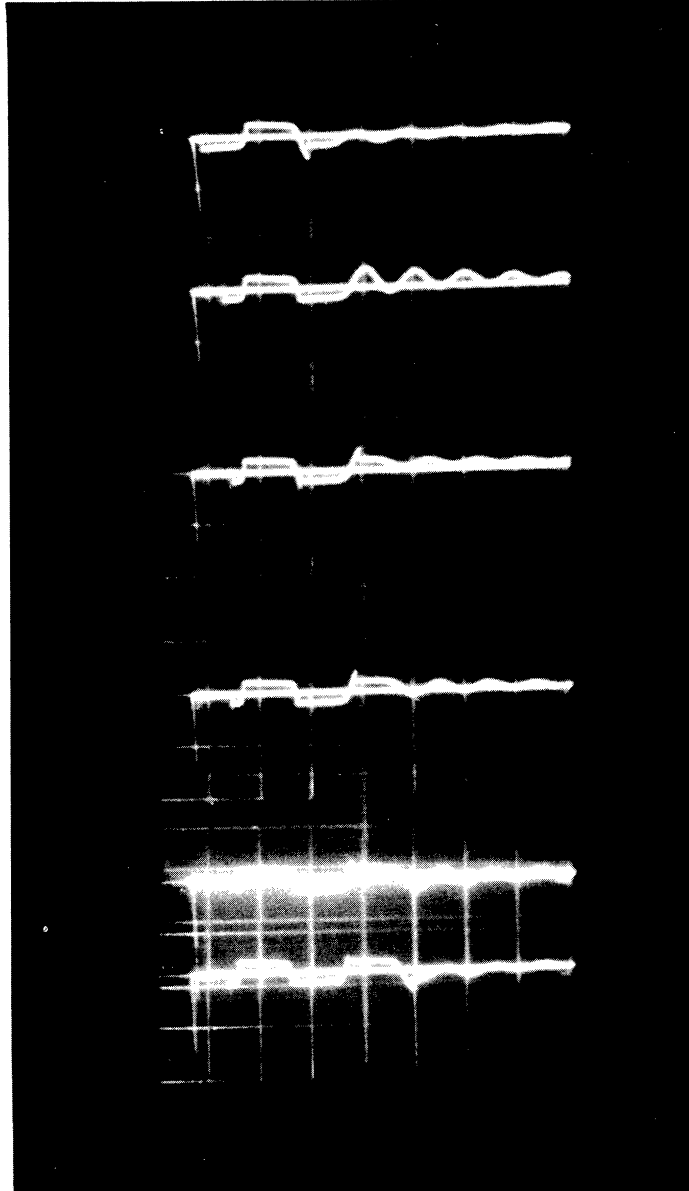


Figure (5-20) Spark Gap Instantaneous Voltage Versus Time For Acetylene (Cold Runs)

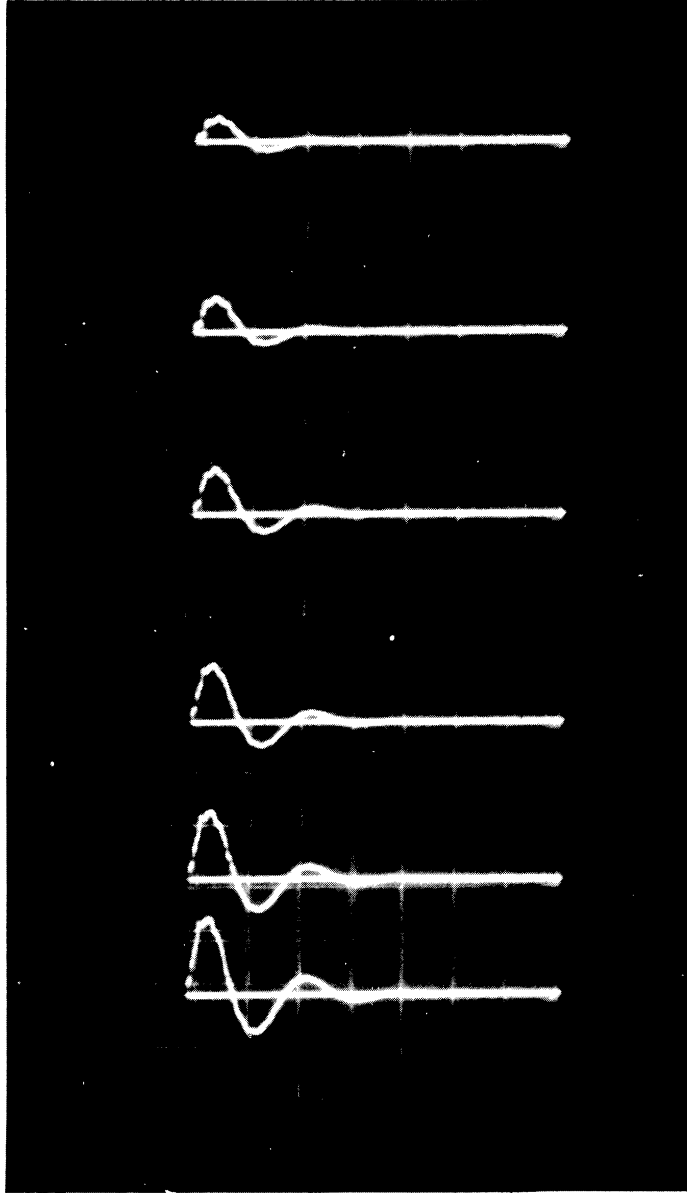


Figure (5-21) Spark Gap Instantaneous Current Versus Time For Acetylene (Cold Runs)

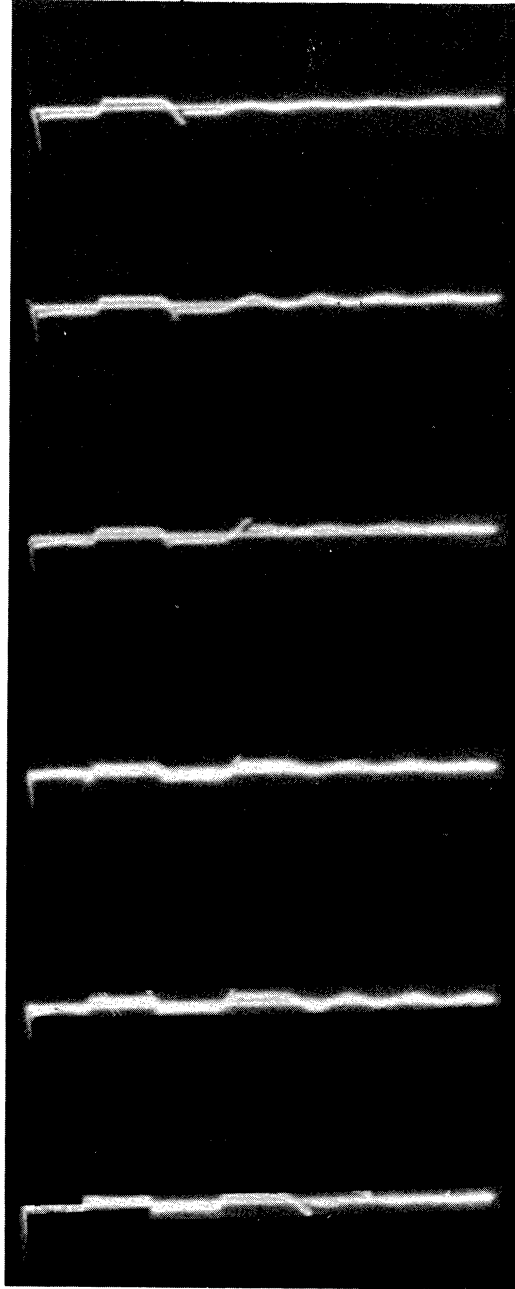


Figure (5-22) Spark Gap Instantaneous Voltage Versus Time For Acetylene (Hot Runs)

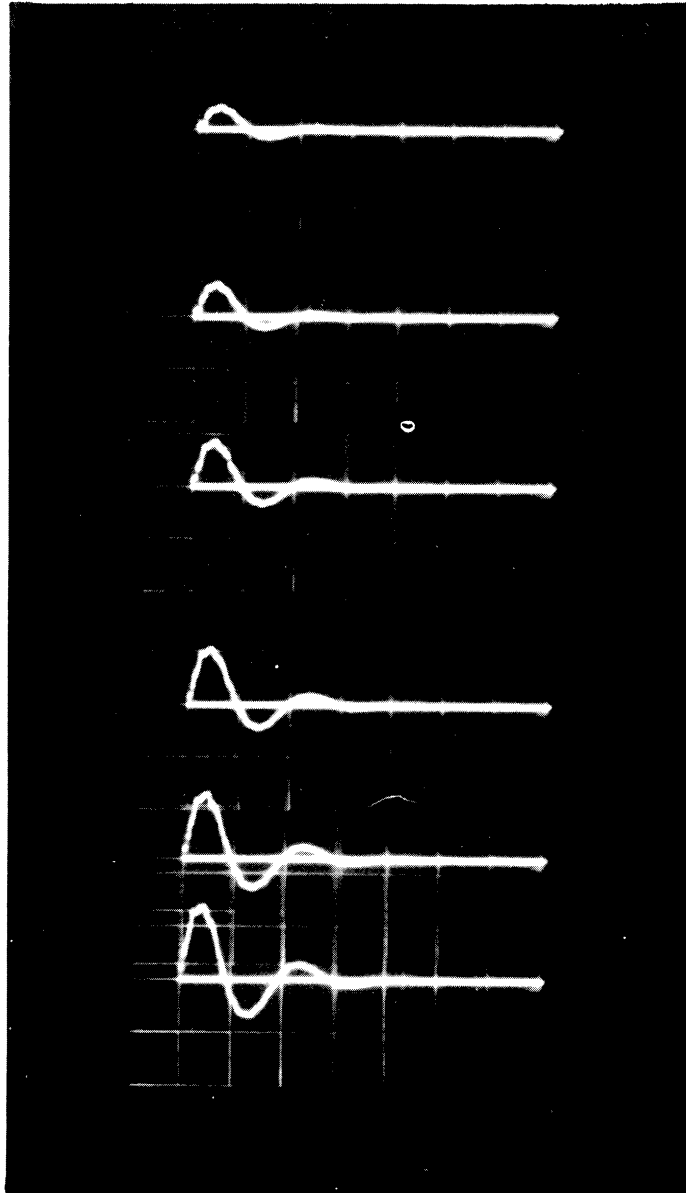


Figure (5-23) Spark Gap Instantaneous Current Versus Time For Acetylene (Hot Runs)

CHAPTER VI

DISCUSSION OF RESULTS

Estimate of the Number of Ions Formed Per Cubic Centimeter Per Second

Since the ionizing effect of the alpha particles will frequently be mentioned in the following discussion, the following is an order of magnitude calculation that gives the number of ions formed per cubic centimeter per second due to alpha particles. The media is assumed to be air at atmospheric pressure.

$$\begin{aligned} \text{Number of ions formed per cm path of alpha particles at N.T.P.} \\ = 25,000 \end{aligned}$$

If the effective power of the source is 5 curies then:

$$\text{Number of particles emitted per second} = 5 \times 3.7 \times 10^{10} = 18.5 \times 10^{10}.$$

Number of ions formed per cubic centimeter per second =

$$\frac{18.5 \times 10^{10} \times 25,000}{6} = 7.7 \times 10^{14}$$

where the irradiated volume = 6 cm^3 . Therefore 7.7×10^{14} molecules are ionized per cm^3 per second; such molecules are potential centers for starting chain branching reactions.

Discussion of Experimental Data

The discussion will be divided into two sections:

(a) The first section will cover the events that take place prior, during and after the passage of the spark.

(b) The second section will deal with the influence of such events on the combustion process.

a.1 Influence of radiation on the breakdown voltage

Ions are continuously formed in the spark gap and its vicinity; this causes a reduction in the breakdown voltage, Figure to (5-23). This breakdown voltage is, in effect, the driving force that determines the rate at which the energy stored in the circuit will be transferred to the gases in the first portion of the discharge.

a.2 Influence of radiation on the reaction

These ions, due to their electrostatic field, attract neutral molecules. As a result, the density of the gas increases and thus the probability of collision among the molecules is increased. The result is a chemical reaction with carbon dioxide, carbon monoxide and water as main products.^{15,16,20,29} Other active intermediate products are aldehydes, peroxides, alcohols and acids.^{35,36,37} These active species introduced may alter the course of the reaction or introduce other reactions. The energy released is used at least partially in the heating of the fresh gas molecules that continuously diffuse into the gap. Also, the presence of the reaction products within the gap may result in the starvation of the gap from the reactants. The degree of such an effect will depend upon the diffusion rate on one hand and upon the reaction rate on the other hand.

a.3 Influence of radiation on the thermal conductivity of the gases within the gap

The reaction products have coefficients of thermal conductivity 0.0000307, 0.0000499, and 0.000038 cal/sec cm² °C for CO₂, CO and H₂O respectively while that of the reactants, which is essentially equal to that of air, is 0.0000568. Therefore the coefficient of thermal conductivity of the products is lower than the value for the reactants.

Effect of Molecular Structure on the Minimum Igniting Energy

Since the intermediate products of the chemical reaction greatly influence the course of such reaction, the following section lists the different products of the oxidation of the fuels under study and their effect on the minimum igniting energy.

Bone and Hill³⁵ studied the reaction of ethane with oxygen; the intermediate reaction products consisted of acetaldehyde, formaldehyde, peroxide, formic acid, carbon monoxide, hydrogen, and water.

Kistiakousky and Lenher³⁶ studied acetylene oxidation with oxygen; the analysis of the products showed the formation of glyoxal and formadehyde in the early stages of the reaction.

Lenher³⁷ examined the oxidation of ethylene under atmospheric pressure. The products consisted mainly of carbon monoxide and water. A certain amount of peroxides and other more complex organic compounds, namely, ethylene oxide, glyoxal, formaldehyde, and formic acid, were also detected.

Calcote, et al.³⁴ studied the effect of molecular structure on the minimum igniting energy. The effect of structural changes in hydrocarbons showed that the ignition energy increases continuously with increasing linear chain length above ethane. He showed that chain branching generally increases the minimum ignition energy while unsaturation generally decreases it, alkynes being more effective than alkenes. Hence, hydrocarbon ignition energies decrease in the order **alkanes, alkenes, alkynes**. He also found that the peroxide group is very effective in lowering the ignition energy of normal alkane and that esters, ketones and aldehydes raise the ignition energy.

b. Influence of the (a) events on the combustion process

In considering part (b) it is beneficial to ask this question: What is necessary to cause ignition? In order for the molecules of the reactants at an energy level E_1 , to reach the more stable energy state of the products designated by E_2 , they will have to cross over what is known as the potential energy barrier, Figure (6-1). In other words a certain amount of energy will have to be supplied from an outside source to a certain number of molecules at a certain rate to get the reaction started. However, there are more than one combination for these quantities.

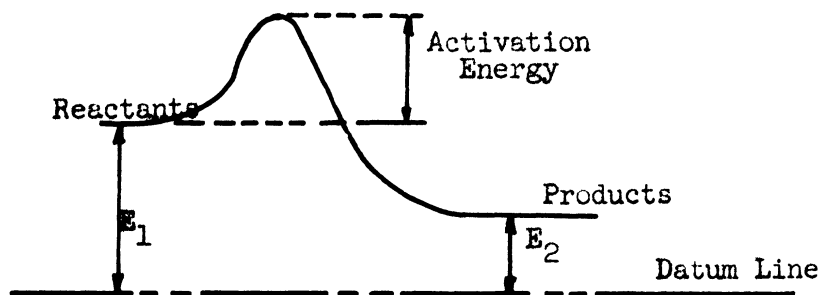


FIG. (6-1) ACTIVATION ENERGY OF THE CHEMICAL REACTION

Acetylene

The critical gap was increased when acetylene air mixtures were irradiated. As has been discussed before, the $\frac{M}{N}$ ratio is 20 for pure acetylene and higher for mixtures with air indicating that there has been a chemical reaction taking place within the gap. The average concentration of the reaction products is inversely proportional to the gap width. Acetylene air mixtures require a small gap to ignite and consequently the starvation effect is quite significant. A smaller number

of reactant molecules is thus available within the gap which necessitates an increase in the gap width to accommodate a large number of reactants molecules that compensates for the starvation effect.

The results also showed an increase in the energy required to initiate combustion under irradiation, Figure (5-11). This can be explained by referring to Colcote's work³⁴ which indicates that aldehydes existing in the spark volume causes an increase in the minimum energy. Another feasible explanation is the fact that the spark energy is distributed over the gaseous molecules within the spark gap. Such molecules, in the case of hot runs, consist of reactant molecules, intermediate products molecules, and products molecules. Therefore it is clear that some of the spark energy will go to molecules that are already in their most stable state and consequently will not greatly contribute to the initiation of combustion. However, the fresh gases that continuously diffuse into the spark gap are heated due to thermal energy released by the chemical reaction. Wider gaps showed the energy curve for the hot runs crossing under that for the cold runs indicating less energy requirement. However, due to the limited number of points this conclusion cannot be warranted.

Ethylene

The $\frac{M}{N}$ ratio for pure ethylene is 5, less than that of acetylene. The critical gap is about twice that of acetylene. The results showed an increase in the critical spark gap under irradiation. This indicates that the starvation effect is still predominant and offsets other factors that promotes ignition.

The minimum igniting energy curves showed no change when narrow gaps were irradiated. Wider gaps showed an increase in this quantity with

hot runs. This is in agreement with Calcote who states that the presence of aldehydes raises the minimum igniting energy; such aldehydes constitute one of the intermediate reaction products of ethylene with oxygen.

Ethane

The critical gap was decreased when ethane air mixtures were irradiated contrary to acetylene and ethylene. The starvation effect has been overshadowed by other factors that promote ignition. The same trend was observed in the energy calculations; irradiation resulted in a decrease in the minimum energy required to start ignition. This agrees with the previously mentioned work of Calcote,³⁴ et al. It is conceivable that during the course of the reaction, due to irradiation, peroxides were formed. Such peroxides were effective in lowering the minimum ignition energy of the mixture. The decrease in the energy is also reflected in the decrease in the critical gap size.

Relation Between Minimum Energy and Critical Gap

The experimental values of all three fuels satisfied equation (3-19); namely $Q = k_2 d^n$. The values of n were determined by the method of least squares and ranged between -2.38 to -5.2.

The energy of the polonium source was small as compared to the minimum igniting energy as can be seen from the following calculation.

Energy of alpha particles = 5.3 MEV per particle

If the source effective strength is about two curies, then:

$$2 \times 3.7 \times 10^{10} \frac{\text{disintegration}}{\text{sec curie}} \times 5.3 \frac{\text{MEV}}{\text{disintegration}}$$
$$\times 1.6 \times 10^{-10} \frac{\text{milliwatt} \cdot \text{sec}}{\text{MEV}} = 62.7 \text{ milliwatts}$$

The Delay Period

The slight decrease in the delay period under irradiation with ethane as a fuel, Figure (5-3), was consistent but too small to be conclusive. It may be due to peroxides formed in the course of the reaction.

The Rate of Pressure Rise

The fact that there was no detectable change in the rate of pressure rise may be attributed to the fact that the irradiated area was only that of the spark volume which is small in comparison to the volume of the whole bomb.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

The Following Conclusions Can Be Drawn From the Experimental Work

There is a definite influence of alpha particles on the spark ignition of hydrocarbon mixtures. This influence, however, does not follow the same trend. It promotes ignition in the case of ethane and hinders it in the case of ethylene and acetylene. It is feasible to state that the intermediate and final products that pre-exist in the spark gap before the passage of the spark, due to the chemical reaction caused by the alpha particles, are the main factors which affect the trend of the reaction during and immediately after the passage of the spark.

The Following Recommendations Can Be Drawn From the Experimental Work

1. A spectrographic study of the action of alpha particles on the gases existing in the spark gap would give an insight about the nature of the chemical reaction taking place.
2. The use of a wider range of hydrocarbons will give more information about the influence of intermediate products.
3. It is also desirable to repeat the previous experiment under the influence of strong beta and gamma sources. Flame speed measurements are recommended.
4. Due to the limited range of alpha particles, the study of their effect on the rate of pressure rise would be best conducted in a reaction vessel that has dimensions comparable to such range.
5. The right branch of the minimum igniting energy curve can be obtained by running the test at higher initial pressures to avoid sparking to the source surface.

BIBLIOGRAPHY

1. Wheeler, R. V. Trans. Chemical Society, Volume 117, 1920
2. Taylor-Jones, E., Morgan, J. D., and Wheeler, R. V., Phil. Mag., Volume 43, 1922.
3. Morgan, J. D., Principles of Ignition, Sir Isaac Pitman and Sons, Ltd. 1942.
4. Coward, H. F., and Metier, F. G., Journal American Chem. Soc., Volume 49, 1927.
5. Hinshelwood, C. N., "Kinetics of Chemical Changes in Gaseous Systems," Oxford, Clarendon Press, 1929.
6. Jost, W., "Explosion and Combustion Processes in Gases." McGraw-Hill Book Company Inc., 1946.
7. Lewis, B. and Von Elbe, "Combustion, Flames and Explosions in Gases." Academic Press Inc., 1951.
8. Rutherford E., et al, "Radiation and Radioactive Substances," 1951, Cambridge at the University Press.
9. Spalding D. Some Fundamentals of Combustions. New York Academic Press, 1955.
10. Wourtsel, J. Phip. et Rad., Volume 6, p. 77 (1920)
11. Mund, Schouwenaars and Devriendt, Bull. Soc. Chim. Belg., Volume 43, p. 49, (1934).
12. Luyckx, Bull. Soc. Chim. Belg., Volume 43, p. 117 (1934).
13. Mund W., Bull Soc. Chim. Belg., Volume 36, p. 19 (1927).
14. Stein, Trans. Faraday Soc., Volume 29, p. 583 (1933).
15. Lind, Bardwell and Perry, J., Am. Chem. Society, Volume 48, p. 1556 (1926).
16. Lind, and Bardwell, J., Am. Chem. Society, Volume 48, p. 1575 (1926).
17. Mund and Jungers, Bull. Soc. Chim. Belg., Volume 40, p. 158 (1931).
18. W. Mund, L'action Chimique des rayons alpha en phase gazeuse. Paris, Hermann and c^{ie}, Editeurs

19. E. Flock et. al NACA Report No. 682. Flame Speed and Energy Consideration for Explosion in a Spherical Bomb.
20. Lind and Bardwell, J. Am. Chem. Society, Volume 48, p. 2335 (1926).
21. Brownell, L. E., et al., Utilization of the Gross Fission Products, Progress Report 2 (COO-90) Eng. Res. Inst., Univ. of Mich., Ann Arbor, Mich. January 31, 1952.
22. Ibid Progress Report 3 (COO-91), June 30, 1952.
23. Ibid Progress Report 4 (COO-124), March, 1953.
24. Ibid Progress Report 6 (COO-198), April, 1954.
25. Churchill, S. W., et al., Combustion Studies with a 12,000 Curie Gold Source. University of Michigan, ERI., December 1955, 2288-6-T.
26. Otvos, "Ionization by C¹⁴ in the Ionization Chamber," Phys. Rev. 73, 537 (1948).
27. Egerton, Nature 121, 10 (1928).
28. W. Mund and W. Koch J. Physical Chemistry, Volume 30, p. 289 (1926).
29. Mund and Koch, Bull. Soc. Chim. Belg., Volume 34, 125, 241 (1925).
30. Cullen R. and Glukstein, Effect of Atomic Radiation on the Combustion of Hydrocarbon Air Mixtures. Fifth Symposium (International) on Combustion, 1955. p. 569.
31. N. N. Semenov, NACA Tech. Memo. No. 1024. "Thermal Theory of Combustion and Explosion." 1924.
32. Thomson, J. J., Phil. Mag., 47, 337-79 (1924).
33. S. C. Lind, "The Chemical Effect of α -particles and Electrons" A.C.S. Monographs, N. Y., 1921.
34. Calcote, H. F., et al. Spark Ignition, Effect on Molecular Structure. Ind. & Eng. Chem., 2656, 1952.
35. Bone, W. A., & Hill, S. G., Proc. Roy. Soc. London, A, 129, 434 (1930).
36. Kistiakowsky, G. B., and S. Lenker. J. Am. Chem. Society, 52, 3785 (1930).



37. Lenher, S., J. Am. Chem. Soc., 53, 3737, 3752 (1931).
38. Calcote, H. F. Third Symposium on Combustion Flame and Explosion Phenomena, p. 245. Baltimore, The Williams & Wilkins Company, 1949.
39. Calcote & Pease; Ind. Eng. Chem., 43, 2726 (1951).
40. Wendt, G. L., and Grimm, F. V., A Suggested Mechanism for Anti-knock Action. Ind. Eng. Chem. 16,890-3 (1924).
41. Lind, S. C., and Bardwell, Influence of an Anti-knock Compound in a Gas Ion Oxidation. (CA-21-1346).