

SOME ASPECTS OF THE SLOW PROPAGATION OF FLAME IN GASES

with particular reference to

The Displacements of the Mixtures Giving Maximum Flame Velocities
in the Combustion of Methane

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Dedication to Lloyd Logan, Dr. Eng.

The high ideals and example of the late
Dr. Lloyd Logan were perhaps outstanding
among his many fine qualities and achieve-
ments that remain as sources of courage
for all who fortunately knew him.

To

Wilbert J. Huff, Ph.D, D. Sc. (Hon.),

Professor and Chairman of the Department of Chemical Engineering
in the University of Maryland, the writer desires to acknowledge
his very considerable indebtedness and to express his sincere
appreciation for much helpful counsel and for many kindnesses
and generous aids in his work.

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Considerations of the combustion of gases are essential to progress in varied scientific and technical fields. The development of the chemistry and kinetics of oxidation is inextricably associated in certain of its most active phases with gaseous combustion; a major branch of Chemical Engineering is based on the utilization of gaseous fuels; certain extensive considerations of safety in industries also have common fundamentals in the phenomena of the combustion of gases. The multiplicity and importance of the pertinent problems scarcely need be mentioned.

Great advances have been recorded in the literature reporting investigations of gaseous combustion, but the initiation and the propagation of flame have proved extremely complex. Some aspects of the propagation of flame in gases will be considered in this writing. Although the many studies of this topic form a catenulate whole, three fields of general endeavor may be distinguished: (1) the development of an adequate theoretical background; (2) the experimental study of the movement of flame; and (3) the application of the results of the two foregoing topics to scientific and technical problems.

Some new regularities in the characteristics of the slow propagation of flame in gases were suggested by a critical study of published data; contradictions of some of these inferred regularities were also disclosed. It was thought, therefore, that experimental investigation of an apparently fundamental characteristic of the propagation of flame might prove useful by establishing whether or not such regularities exist. Further, it seemed possible that on the basis of the data thus developed,

some contribution might be made to the theory, to the basic data for flame velocities, and to the advance of the application of these data. The investigation described in the following pages was therefore undertaken.

II - HISTORICAL

CHAPTER I - INTRODUCTORY

The formulation of a background for this investigation necessitated a critical examination of the literature in addition to extensive survey. Recent writings 1/ have dealt generally with various phases of the vast field of gaseous combustion so that an account only of the former of these studies will be given.

Although important practical results had been produced by studies of gaseous combustion as early as 1815 2/, it was not until about 1880 that the classic discoveries of Berthelot and Vieille 3/ and of Mallard and Le Chatelier 4/ disclosed the existence of several distinct modes of propagation of combustion in gaseous mixtures. The propagation of flame in the initial phases of gaseous explosions takes place in general with low uniform velocities not exceeding a few meters per second, and this propagation is distinct from subsequent phases involving irregular movements and detonating processes with velocities up to several thousands of meters per second.

The present treatment will be confined to the initial phases of the propagation of flame in gaseous mixtures; this field is of particular interest because of the extensive application of this mode of combustion in

1/ - See references B1, C1, L1, T1, and B2, C2, and F1 (Symposia) for examples. A more recent symposium appeared in Chaleur et Industrie in January 1938; although certain of the thirty papers presented are of interest, the most recent work and more advanced views seem absent in several instances. Of possible general interest is reference P4.

2/ - See reference B1, page 24, for an account of Davy's early work.

3/ - See References B3, B4, B5, B6, B7, and B8.

4/ - See references M1, M2, M3, M4.

chemical engineering. The effects of several factors on the rate of the slow propagation of flame, the existence of a maximum in this rate, the coordinates of this maximum and the effects of important variables on these coordinates will be considered, together with a treatment of the practical aspects of the data developed.

General:

Analyses of the slow propagation of flame in mixtures of combustible gases may be divided into two types according to whether they are based on a simple thermal theory or on more modern concepts. This section will review these theories in some detail, and summarize the present outlook in this field.

Classical Developments:

The thermal theory represents the classical approach and has been widely accepted and elaborated. This theory, in its early qualitative form, was the basis of the reasoning that led Davy to develop his renowned safety lamp. The fundamental concepts were more clearly indicated much later by Vicaire in a work (V1) relating to the temperatures of flames. This author considered the temperature developed in the combustion of a gaseous mixture and assumed for an initial treatment that the mixture burned simultaneously throughout; in modifying his equations for the actual phenomenon involving the spread of combustion at a finite rate, he made the following observations 5/ that epitomize adequately the fundamental tenets of the theory and indicate its state in 1870:

"En réalité les choses se passent autrement: la combustion commence dans une étendue limitée, portée à l'incandescence par une cause extérieure, et se propage successivement dans la masse suivant une sorte d'onde; elle ne commence en chaque point que lorsque, par le voisinage des points en combustion, la température y est devenue suffisamment élevée."

5/ Page 126 of reference V1.

The initial systematic analysis of the slow propagation of flame in combustible gases was published by Mallard (M5) in 1875. This author assumed that the controlling factor in this phenomenon was the transfer of heat by conduction from the burned to the unburned gases; he also assumed a linear relationship between the temperature and distance coordinates in this process. His derivation may be summarized briefly as follows:

--

Nomenclature:

θ = initial temperature of the mixture.
 t = temperature of inflammation.
 dt = variation in temperature.
 T = temperature after combustion.
 v = velocity of inflammation.
 l = distance.
 u = rate of cooling of a layer of burned gas by the neighboring unburned gas.
 τ = time.
 P = perimeter of tube.
 S = cross-section of tube.
 $\left. \begin{matrix} \alpha \\ a \\ c \\ \gamma \end{matrix} \right\}$ = coefficients of thermal transfer
 k = a constant.

Development:

$$dt = kdl \text{-----} (a)$$

$$dt = u d\tau \text{-----} (b)$$

$$\frac{dl}{d\tau} = v = \frac{u}{k} \text{-----} (1)$$

$$u = \alpha(T-t) \text{-----} (c)$$

$$k = \frac{dt}{dl} = a(t-\theta) \text{-----} (d)$$

$$a = \sqrt{\frac{\gamma p}{cs}} \text{-----} (e)$$

Final equation:

From substitution of the values from equations (c), (d), and (e) in (1), $v = \frac{\alpha(T-t)}{a(t-\theta)} = \alpha \sqrt{\frac{c}{\gamma}} \sqrt{\frac{p}{s}} \times \frac{T-t}{t-\theta} \text{-----} (2)$

Mallard stated that in this equation the coefficient $\sqrt{\frac{p}{s}}$ depends only on the shape of the tube, that γ depends on the nature of the gas and of the tube, that $\alpha\sqrt{c}$ depends uniquely on the nature of the gas, and that these values for most gases, excepting hydrogen, are nearly the same. Equation (2) therefore reduced to an expression of the approximate proportionality of the velocity of propagation to the ratio of temperatures, i. e.,

$$V \sim \frac{T - t}{t - \theta} \quad \text{-----} \quad (3)$$

This author noted the indication that flame propagates in a gaseous mixture exposed to the action of a local electric spark or of an ignited body only if the temperature of the combustion is greater than the temperature of inflammation. Also, he suggested that the loss of energy in free expansion of flames in open systems explained the observation of Bunsen that certain mixtures which are non-explosive in free air may be exploded in a closed vessel.

A somewhat more detailed treatment, essentially similar to that just discussed, was given by Mallard and Le Chatelier (ML) in 1883. These authors considered the possibilities of the transmission of heat energy by radiation, by a compression wave, and by conduction. They concluded that the last is uniquely applicable to the slow propagation of flame because of (1) the limited quantity of radiation, (2) the very low absorptive power of the cold gas for this energy, and (3) the patently unique applicability of propagation by compression to movements with velocities of the order of the velocity of sound. A brief summary of their development follows:

-- Nomenclature:

- θ = initial temperature of the mixture.
- t = temperature of inflammation.
- T' = temperature at the instant of combustion.
- T = temperature after combustion.
- C = mean specific heat of the burned gas between temperatures θ and T .
- C' = mean specific heat of the burned gas between temperatures t and T' .

Nomenclature: (Cont.)

s = distance

 τ = time.

$F(T,t)$ = a function representing the quantity of heat lost in unit time by the burned gas, which is proportional to L and vanishes only when $T = t$.

L = conductivity of the unburned gas.

 $f(T,t)$ = a constant.Development:

$$Q = c(T-\theta), \quad T = \frac{Q}{\lambda c} \quad \text{--- (f)}$$

$$T^1 = t + \frac{Q}{c^1} \quad \text{--- (g)}$$

If $c^1 = c$ and $\theta = 0$, then $T^1 = T + t$ --- (h)

$$c^1(t-\theta)ds = d\tau F(T,t) \quad \text{--- (i)}$$

$$\frac{ds}{d\tau} = v = \frac{F(T,t)}{c^1(t-\theta)} \quad \text{--- (4)}$$

Final Equation:

$$v = \frac{L(T-t)}{c^1(t-\theta)} \times f(T,t) \quad \text{--- (5)}$$

in which $f(T,t)$ is a constant.

These authors recognized the incompleteness of this analysis but noted six deductions of particular interest:

- (1) The zone of reaction is at a temperature higher than that of the hot burned gases. (Compare with Vicaire on page 126 of reference V1.)
- (2) Two limits of inflammability exist corresponding to $T = t$ in Equation (5) for lean and for rich mixtures.
- (3) The velocity of propagation is inversely proportional to $(t-\theta)$ in Equation 5, so that it increases with increase in initial temperature θ .
- (4) Effect of the diameter of the tube: an equation

$$T = \theta + \frac{Q}{c + \frac{k}{rV}} \quad \text{--- (6)}$$

was developed in which k is a constant coefficient of conductivity and r the radius of the tube, the other symbols having the significance previously noted. If r and V are large, k/rV is small compared to C, and T is unchanged. The meniscus-like shape of the flame surface was also explained

on the basis of the distribution of temperature caused by the cooling action of the walls.

- (5) Agitation increases the velocity of propagation by facilitating the transfer of heat.
- (6) The effectiveness of the igniting source increases with its temperature and volume.

This classical treatment was thus shown to be capable of explaining certain observed phenomena.

The inadequacies recognized in this treatment related chiefly to the temperature gradient and to the role of the reaction rate and elaborations were made by several workers ^{6/}. A review of these rather involved mathematical treatments indicates that they are fundamentally identical and that they retain the essential tenets of the theory as proposed by Mallard and Le Chatelier. Their inadequacy is now recognized, and they represent only a more nearly completed mathematical treatment of the classical theory. ^{7/} Therefore, a detailed review of all of these elaborations will not be made here. The development of Nusselt (N1), continued by Jahn (J1), will be discussed in some detail because this alone has led to numerical results.

Nusselt (N1) attempted to relate the slow propagation of flame to fundamental physical and chemical laws in a derivation which may be epitomized as follows:

Nomenclature:

λ - mean thermal conductivity of the mixture
 P_0 - initial pressure
 T_0 - initial temperature
 T_c - ignition temperature
 T_v - temperature after combustion
 T - temperature at any time
 H_2^0 - partial volume of hydrogen before combustion.
 O_2^0 - partial volume of oxygen before combustion.

^{6/} See reference D1, J2, J3, J4, N1, M6, and #1.

^{7/} See appendix of reference L2 for discussion.

- C_p - mean specific heat per unit volume between temperatures T_c and T_v
- R - gas constant
- w - ignition velocity
- x - distance coordinate in direction of flow.
- C₁ - a constant
- X - partial volume of any species X
- [X] - concentration of any species X
- i_x - heat content (enthalpy)
- Q, q - quantity of heat.
- h - net heating value of hydrogen per cu. m. at 15°C, 1 atm.

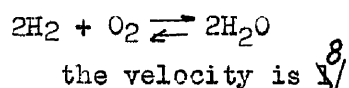
Development:

It was assumed that the maintenance of a stationary surface of combustion at constant pressure was conditioned by heat flow by conduction from the burned to the unburned gas, and this was expressed by

$$Q = w C_p (T_c - T_o) \frac{288 P_o \cdot 3600}{T_o \cdot 10000} = \lambda \frac{dt}{dx} \quad (j)$$

which would allow calculation of w if the distribution of temperature were known.

From the equation



$$\frac{dH_2O}{dt} = k_1 \frac{P_o^2}{R^2 T^2} (H_2^o - H_2O)^2 (O_2^o - \frac{1}{2}H_2O) + H_2O \times \frac{dP/T}{dt} \quad (k)$$

Transformation of this by $\frac{dx}{dt} = w \frac{T}{T_o} (1 - \frac{1}{2}H_2O)$ gave

$$\frac{dH_2O}{dx} = \frac{k_1 P_o^2 T_o}{w R^2 T^2 (1 - \frac{1}{2}H_2O)} \times (H_2^o - \frac{1}{2}H_2O)^2 (O_2^o - \frac{1}{2}H_2O) + H_2O \frac{dP/T}{dx} \quad (7)$$

which contains the temperature and the concentration of steam as dependent variables.

$$\frac{dH_2O}{dt} = \frac{dH_2O}{dt} = K_1 [H_2]^2 [O_2] - K_2 [H_2O]^2 \approx K_1 [H_2]^2 [O_2]; \text{ since } [H_2] = \frac{P}{RT} \times H_2$$

since $[X] = \frac{P}{RT} \times X$, and $H_2O + H_2 + O_2 + N_2 = 1$, $\frac{dH_2O}{dt} = K_1 \frac{P^2}{R^2 T^2} H_2^2 O_2 - H_2O \frac{dP/T}{dt}$;

but $H_2 = H_2^o - H_2O$, $O_2 = O_2^o - \frac{1}{2}H_2O$, and therefore

$$\frac{dH_2O}{dt} = K_1 \frac{P^2}{R^2 T^2} (H_2^o - H_2O)^2 (O_2^o - \frac{1}{2}H_2O) - H_2O \frac{dP/T}{dt}, \text{ which is}$$

identical with equation (K) when P is constant.

The increase in enthalpy i in a volume element of thickness dx , 9/

$$di = \frac{w \cdot P_0 \cdot 288 \cdot 3600}{10000 T_0} d \left[c_p T \left(1 - \frac{1}{2} H_2O \right) \right], \quad (1)$$

is accompanied by a heat flow

$$\frac{d}{dx} \left(\lambda \frac{dT}{dx} \right) dx \quad (m)$$

and by heat of combustion

$$dq = \frac{w P_0 \cdot 288 \cdot 3600}{10000 T_0} \left(1 - \frac{1}{2} H_2O \right) h d H_2O \quad (n)$$

These three quantities are related by the law of conservation of energy so that

$$dq + \frac{d}{dx} \left(\lambda \frac{dT}{dx} \right) dx = di \quad (8)$$

$$\text{or } \frac{d}{dx} \left(\lambda \frac{dT}{dx} \right) - \frac{w P_0 \cdot 288 \cdot 3600}{10000 \cdot T_0} \frac{d}{dx} \left[c_p T \left(1 - \frac{1}{2} H_2O \right) \right] + \frac{w P_0 \cdot 288 \cdot 3600}{T_0 \cdot 10000} \cdot h \left(1 - \frac{1}{2} H_2O \right) \frac{dH_2O}{dx} = 0 \quad (9)$$

To enable an approximate solution of this equation which will give the course of temperature and of the concentration of steam, Nusselt assumed (1) that the conductivity and specific heat remain constant, (2) that the contraction accompanying the reaction may be neglected, and (3) that the heat developed from unit length (i.e., unit of distance coordinate x) is constant and equal to the value at $x = 0$.

Then

$$\begin{aligned} \frac{dq}{dx} = b &= \frac{k_1 P_0^3 \cdot 288 \cdot 3600 \cdot h}{R^2 T_0^3 \cdot 10000} \left(H_2^0 - \frac{1}{2} H_2O \right)^2 \left(O_2^0 - \frac{1}{2} H_2O \right) + \\ &\quad \frac{w P_0 \cdot 288 \cdot 3600 \cdot h \left(1 - \frac{H_2O}{2} \right)}{10000 T_0} H_2O \frac{dT}{dx} \quad (o) \\ &= \frac{P_0^3 \cdot 288 \cdot 3600 \cdot h}{R^2 \cdot 10000} C_1 \left(H_2^0 \right)^2 O_2 \quad (p) \end{aligned}$$

9/ From: $i = \frac{w \cdot 3600 \cdot 288 P_0}{T_0 \cdot 10000} \left(1 - \frac{H_2O}{2} \right) c_p T$

$$i + di = \frac{w \cdot 3600 \cdot 288 P_0}{T_0 \cdot 10000} \left[T c_p \left(1 - \frac{H_2O}{2} \right) + d \left[T c_p \left(1 - \frac{1}{2} H_2O \right) \right] \right]$$

If $a = \frac{wP_0 \cdot 288 \cdot 3600 c_p}{10\,000 T_0}$, the equation for the temperature becomes

$$\lambda \frac{d^2T}{dx^2} - a \frac{dT}{dx} + b = 0, \quad (10)$$

the solution of which is

$$T = A_1 + A_2 e^{\frac{ax}{\lambda}} + \frac{b}{a} x. \quad (11)$$

The constants A_1 and A_2 are found 10/ to be $A_1 = T_c - A_2$ and

$$A_2 = \frac{T_v - T_c - \frac{b}{a} \chi_1}{e^{\frac{a\chi_1}{\lambda}} - 1}, \text{ and when } \chi = \chi_1, \frac{dT}{dx} \text{ must equal zero for a}$$

continuous curve so that

$$\left[\frac{a}{\lambda} (T_v - T_c) - \frac{b}{\lambda} \chi_1 + \frac{b}{a} \right] e^{\frac{a\chi_1}{\lambda}} - \frac{b}{a} = 0 \quad (q)$$

When $\chi = 0$, $\lambda \frac{dT}{dx} = a(T_c - T_0)$, so that the equation may be solved for w .

Final equation:

$$\text{Using } e^{\frac{a\chi_1}{\lambda}} = 1 + \frac{a\chi_1}{\lambda} \text{ and } \lambda b(T_v - T_c) = a^2(T_v - T_0)(T_c - T_0),$$

and remembering that $(T_v - T_0) c_p = hH_2^0$ as well as the values given for a and b , the final equation for the ignition velocity becomes:

$$w = \sqrt{\frac{C_1 \lambda P_0 T_0^2 (T_v - T_c) H_2^0 O_2^0}{103.7 R^2 c_p (T_c - T_0)}} \text{ m/sec} \quad (12)$$

Nusselt made numerical calculations with this formula and found that if C_1 were chosen to make a calculated value agree with some experimental value the accord between observed and calculated values of w for mixtures of hydrogen and air was rather good over the entire explosive range. He also gave equations for the combustion of carbon monoxide, producer gas,

10/ From conditions $\chi = 0, T = T_c$
 $\chi = \chi_1, T = T_v$

and mixtures containing inert gases. He noted some indications from these equations which are representative of the elaborated thermal theory:

- (1) A maximum ignition velocity is demanded by the formula with a mixture containing an excess of combustible, at a value agreeing with that from tests with mixtures of hydrogen and air.
- (2) The thickness of the reaction zone, computed from $\chi_1 = \frac{a}{b}(T_V - T_0)$ is shown to be of the order of 10^{-2} cm.
- (3) Two inflammable limits exist for $T_V = T_c$ and $w = 0$. These limits should be independent of the pressure P_0 .
- (4) Preheating the gases should extend the explosive region.
- (5) Preheating the gases should produce a large increase in the ignition velocity.
- (6) The ignition velocity should increase in proportion to the square root of the pressure.
- (7) Substitution of oxygen for air in the mixture should increase the ignition velocities in proportion to $1: \frac{1}{\sqrt{0.21}}$ or 2.18:1

While some of these observations are supported by experimental evidence, others are not; this suggests inadequacy in the basic assumptions of this type of analysis.

Jahn (J1) has pointed out that Nusselt's use of the equation $(T_V - T_c) C_p = h \times H_2$ is admissible only when there is no more hydrogen present in the mixture than corresponds to the theoretical proportions for complete combustion; as soon as the mixture contains an excess of hydrogen only as much hydrogen can burn in the reaction zone as corresponds to the oxygen present, so that equation (12) applies only when combustible is in defect. Accordingly, Jahn deleted this simplification and obtained an equation valid for the entire explosive range,

$$u_s = \sqrt{\frac{C_1 H_2^2 O_2 \lambda (T_V - t_c) h_1 T_c^2 P_0}{C_p^2 (T_V - T_0) (T_V - T_c) 103.7 R^2}} \quad (13)$$

This author further designated the volume-fraction of oxygen in the atmosphere as a and the volume-fraction of inert in the atmosphere as b so that

$$H_2 + (1 - H_2) (a + b) = 1$$

and

$$O_2 = (1 - H_2)a .$$

A final generalized equation, grouped advantageously, was given by Jahn as

$$u = \sqrt{C_1 H_2^2 (1 - H_2)^a} \cdot \sqrt{\frac{\lambda (T_V - T_C) h_1}{C_p^2 T_C (T_V - T_0) (T_C - T_0)}} \cdot \sqrt{\frac{T_0^2}{103.7 P_0}} \quad (14)$$

in which $C_1 = \frac{k_1 P_0^2}{R^2 T_C^2}$.

The first two radicals represent the effects of the reaction velocity and of thermal factors, respectively; the value of the last radical is constant for given initial conditions of temperature and pressure.

Recent advances:

There have been many recent developments that have stressed the necessity for revision of this classical approach to the problem of the slow propagation of flame. The inadequacy of this approach has become obvious from various experimental studies, and the importance of factors such as the reaction rate, or of chain carriers or active particles in this process has become evident.

For example, the qualitative effects of the thermal conductivity and specific heat as predicted by formulas based on the thermal theory are verified experimentally, but the results are not at all in quantitative accord with these predictions. Tests of this have been made by substituting argon or helium, of widely different thermal conductivities but identical low heat capacities, for nitrogen in the air or "atmosphere" from which combustible mixtures were prepared. The measurements first recorded (C3) were for spacial speeds of flame in tubes, but nevertheless indicated the conclusion noted above. Subsequent series of measurements in tubes of flame velocities referred correctly to the unburned gas (H1) showed a ratio of 1.67:1 for these velocities in mixtures containing helium or argon, respect-

ively, while the ratio of the thermal conductivities of these mixtures is several times this figure. 11/ Other measurements of flame velocities in initial stages of combustion in bombs of constant volume (L3) and in soap bubbles 12/ have led to the same conclusion. Lewis and von Elbe 13/ have made the interesting observation that reasonable postulates of changes in other quantities in the equation of Mallard and Le Chatelier could be made that would account for these effects, which postulates stress the importance of diffusion phenomena in the flame front.

The importance of considerations of other than purely thermal factors has been emphasized adequately in the literature 14/.

Recent developments have shown the importance of reaction velocity, chain reactions, and diffusion in this problem and have suggested that the propagation of flame may be as influenced by the diffusion of active particles as by the transfer of heat. A further weakness of the thermal theory, recently stressed by Lewis and von Elbe (L4), lies in uncertainty as to the concept of ignition temperature. It has been recognized ever since measurements of this quantity were attempted that it is not a true property of gaseous mixtures but is affected by the properties of the system as a whole and by time. 15/ Perhaps the most cogent results showing the inadequacy of purely thermal concepts have been obtained from studies of the electrical ignition of gases, in which this ignition temperature figures as a fundamental in the thermal theory. These studies, reviewed recently by Bradford and Finch (B13), have furnished additional evidence that indicates the minor

11/ This ratio is roughly 10 at ordinary temperatures.

12/ See references F2 and page 374 of reference F3.

13/ See P. 350 of reference L4.

14/ For examples see references B9, B10, B11, B12, B13, B16, C4, H2, J5, J6, and L4.

15/ For example see reference B1, pages 59 and 80, and reference C1, page 88.

importance of temperature and shows that it may be considered only as a measure of collision frequency 16/.

The first analysis of the slow propagation of flame from this modern viewpoint was made by Lewis and von Elbe (L2) for explosions of ozone. This analysis, while relatively simple in essentials, involved a mathematical treatment that was extremely difficult and possible only through rather vigorous approximations and assumptions. Only the general tenets of the development will be mentioned here; a helpful abridgement was given by the same authors in a recent review (L4) and the original paper should be consulted for further details. Lewis and von Elbe recognized that the slow propagation of flame might be controlled by diffusion of active species rather than by the flow of heat and that the concept of ignition temperature was uncertain. They based their analysis on the concept that the rate of change of concentration of the various constituents in an elementary layer due to mass flow, diffusion, and chemical reaction is zero, and they avoided reference to the ignition temperature. Equations were supplied by relationships of continuity, by the gas law, and by the plausible postulate that the total energy per unit mass of mixture remains

16/ A convincing experimental test (B13) of the purely thermal theory of the electrical ignition of gases proved the necessity for other considerations by showing that the igniting power of a spark is not a function of peak current but is more uniquely stipulated by frequency. The thermal theory implies that the igniting power of a given quantity of energy lies dormant until conversion into heat is effected, and thus igniting power increases with increasing entropy. The ratio of entropy to energy would then be at a maximum for ignition by a source of least igniting energy. However, the results reported by these authors indicate that despite possible decrease in igniting power from decrease in either the amount or the rate of energy dissipation, a suitable decrease in frequency may overbalance this effect. Entropy being an extensive property, these results indicate that igniting power increases with decreasing entropy (decreasing peak current and frequency); this obviously contradicts the thermal theory. The authors advance an "excitation theory of electrical ignition" which stipulates that the condition for ignition is the production of a suitable concentration of specifically activated species.

constant throughout the process 17/. The six equations obtained were formally insoluble because of uncertainties of the reaction mechanism and lack of knowledge of processes of multiple diffusion. Reasonable simplifying assumptions and approximations were therefore made, and these authors were successful in obtaining an equation which allowed calculations of burning velocities. These calculated values agreed roughly with experimental values (i.e. within about five-fold). The agreement was viewed as satisfactory because of the approximations and assumptions made. The theory also furnished interesting information relative to the structure of the flame front.

A recent application of these modern concepts to the results of a study of the propagation of flame in mixtures of hydrogen and oxygen at low pressures (G2) has produced interesting evidence showing the importance of various factors in the propagation of flame.

A recent paper (Z1) has considered the general mathematical treatment of this problem in detail, and has raised numerous objections to the work of Lewis and von Elbe. Some of these objections are apparently urged as basic in character. However, this treatment is of interest chiefly from a mathematical standpoint. The paper apparently contributes little to the basic concepts noted above and exemplified by the work of Lewis and von-Elbe, and is admittedly incapable of producing any general solution of the problem. While forthcoming publications by the authors of this recent treatment (Z1) may be of more pointed interest, this paper will not be given detailed consideration in this place for reasons noted and because such review would add nothing to a perspective of the problem in view of rapid developments in this rather highly controversial field.

17/ The thermal theory requires an excess of energy in the unburned gas immediately ahead of the flame; in the present theory this excess may be rendered vanishingly small by the possibility of a few active particles initiating reaction in the unburned gas at a rate much greater than that of initiation by thermal means.

Summary:

The sum of the experimental evidence has indicated that purely thermal considerations are definitely inadequate for the complete analysis of the slow propagation of flame in gaseous mixtures. A recent treatment based on modern concepts involving chain reactions and the diffusion of active particles and avoiding reference to the uncertain ignition temperature has shown for the particular case of ozone-oxygen flames a rough agreement between theoretical and actual burning velocities; this adds weight to the aptness of these revised considerations.

However, the success of the elaborated thermal theory in explaining a number of observations and in fitting experimental results places a fundamental question as to the degree of its applicability to the gross features of the propagation of flame. It has apparently been widely held abroad that the classical theory has been so strengthened by experimental data that its interest is indisputable. The view has been expressed ^{18/} that the chemistry of the intermediate reactions in the combustion of gases and the multiple mutual effects in reactions in mixtures may be assembled as a constant in an expression derived from the law of mass action involving only the initial concentrations of the reacting gases. The further examination of this question represents broadly the interest of the present investigation.

^{18/} See reference J1, page 69.

CHAPTER 3 - ON THE MEASUREMENT OF THE PROPAGATION OF FLAME

General:

Recent literature^{19/} has treated in detail the various methods for determining flame velocities, so that an extensive review would seem out of order in this place. However, a concise report of a critical examination of certain of the fundamental literature may be given.

Terminology:

Considerable confusion has been caused by lack of explicitness in the terminology used to describe the slow propagation of flame. In English, terms such as "normal velocity of flame movement," "velocity, or speed of propagation," "velocity, or speed of combustion," "speed of uniform movement," "fundamental speed," "flame speed," "flame velocity," "ignition velocity," "transformation velocity," and "burning velocity" have been used, and the equivalents of these in French and German have appeared, as well as other expressions. There is an evident need for consideration of these terms. This situation has apparently led some recent writers to coin new phrases which only add to the extant confusion.

A scrutiny of the meanings intended for the various terms shows that despite the numerous expressions only two basic concepts are involved and that of these only one is of interest in the present work. These concepts are (1) the linear rate of movement of flame in space and (2) the velocity of flame movement perpendicular to the surface of the flame and relative to the unburned gas. The first quantity, of which outstanding common examples are the "speed of uniform movement of flame" and "flame speeds", is of interest but is not a fundamental tool for study of the transformation of

^{19/} General treatments may be found in references B1, C5, F3, L1, S1, and S2.

gaseous mixtures. This is a consequence of the geometry of the propagation of flame: this propagation is in a direction normal to the flame front, and a fundamental necessity is reference of the movement to the unburned gas in order to measure the rate of transformation of the unburned mixture.

There seems little reason for preference among the various terms. The term "flame velocity" will be used herein to express the rate of transformation mentioned, i.e. the rate of movement of flame in a direction normal to the flame surface and relative to the unburned gas. This quantity is not a property of combustible mixtures in the strict sense, since it is affected by the properties of the system in which the flame movement takes place.

Burner methods:

In a classical work on the temperature of the flames of carbon monoxide and hydrogen, Bunsen (B14) had occasion to measure the pressures produced by the explosions of these gases, and recognized that measurements in a closed system of any size might be completely invalidated by a slow propagation of flame through the mixture. In order to determine the magnitude of the velocity of this propagation and thus the suitability of his apparatus, he devised an original method which consisted essentially of producing a Bunsen flame by passing a homogeneous stream of a combustible mixture through a small orifice in a plate and then reducing the pressure behind this stream until flashback occurred. Calibrations established the relationship between the velocity of efflux from the orifice and the pressure, and Bunsen stated ²⁰ §/ that the velocity

²⁰ §/- Referring to this, Bunsen stated: "Dieser Rückschlag musst nämlich eintreten, wenn die Geschwindigkeit mit der das Gasgemisch die Ausströmungsöffnung passirt, unendlich wenig geringer ist, als die Geschwindigkeit, mit der sich die Entzündung von den Oberen brennenden Gasschichten nach der unteren noch nicht brennenden hin fortpflanzt. Man hat dann nur die Ausflussgeschwindigkeit des nicht brennenden Gasgemisches bei dem Drucke, unter welchem die Flamme zurückschlug, direct zu messen, um die Fortpflanzungsgeschwindigkeit der Entzündung, welche dieser Ausflussgeschwindigkeit gleich ist, mit annähernder Genauigkeit zu erhalten."

of the flame was essentially equal to the velocity of efflux at the instant of flashback, thus introducing the fundamental concept of the dynamic equilibrium in Bunsen flames. His measurements were basically in error because of the implicit assumption that the velocity of the unburned gas was uniform across the section of the orifice and because of influences of the apparatus; the method nevertheless was in itself a useful tool and laid the foundation for the burner methods.

Gouy (G1) improved and modified this method in connection with studies of the photometric properties of colored flames. The innovation of his work rested in recognition of the aptness of the dynamic equilibrium described by Bunsen for every point of the surface of the inner cone of the Bunsen flame 21/; this fundamental advance is termed the "Gouy postulate". Gouy derived a fundamental equation expressing this equilibrium by considering a filament of unburned gas of cross-section a and vertical velocity v striking under an angle α an element of the cone surface of area w to which the flame velocity V was perpendicular; velocities were related by

$$V = v \sin \alpha \quad \text{-----} \quad (16)$$

and areas by

$$a = w \sin \alpha$$

so that

$$w = \frac{av}{V}$$

and

$$\sum w = \frac{\sum av}{V} ; \quad \text{-----} \quad (17)$$

this last equation states that the surface of the inner cone ($\sum w$) is equal

21/- Gouy stated: "...l'inflammation se propagerait à partir de chaque point de la surface du noyau et normalement à cette surface avec une vitesse V. Puisque, dans l'état de régime, la surface du noyau demeure immobile, il y a, en chaque point de cette surface, égalité entre cette vitesse V et la composante normale à la surface de la vitesse v du filet gazeux qui y arrive sous un angle α : $V = v \times \sin \alpha$."

to the discharge (Σav) divided by the flame velocity (V). To test this relationship Gouy made the experiments listed in Table I, translated from the original, by varying the orifice while maintaining constant the flow and the composition of the mixture. He considered the results proof of the validity of the equation. The small variations noted are of doubtful significance, because no details of the procedures employed are available. It should be observed that Gouy's work suffered from the same misconception as that of Bunsen, i.e., that the velocity of the stream of unburned gas was uniform across its section.

TESTS OF VALIDITY OF EQUATION FOR BUNSEN CONE;
FROM GOUY, ANN. CHIM. PHYS. (5) 18, 27(1879). 3/

<u>First Condition</u>		<u>Second Condition</u>	
Diameter of orifice, meters	Surface	Diameter of orifice, meters	Surface
<u>A - Excess of gas in mixture.</u>			
0.019	16.96	0.030	16.73
0.019	15.25	0.030	15.19
0.019	22.20	0.030	22.60
0.019	33.85	0.030	30.81
0.030	13.80	0.030 ^{1/}	13.18
0.019	9.24	0.030 ^{1/}	9.89
0.030	17.24	0.030 ^{2/}	18.20
<u>B - Neutral mixture.</u>			
0.006	3.42	0.009	3.21
0.006	1.89	0.009	1.92
0.006	0.93	0.009	0.86

1/ A wire was placed in the center of the orifice.

2/ A disc 0.012 m. diameter was placed in the center of the orifice.

3/ Tests made with discharge and mixture constant, orifice varied; flame projected on screen and area of inner cone obtained from trace by considering it a solid of revolution.

Many later workers have used the burner method for studies of combustion phenomena, and while the Gouy postulate has been retained there have appeared various methods for obtaining the area of the surface of combustion or, of treating the results. Thus, while Michelson (M7), Corsiglia (C6), Khitrin (K1), and Tammann and Thiele (T2) have retained Guoy's original method of obtaining the area mentioned from the projections either of the flames or of photographic negatives of these, Bunte and Semlanizin 22/ weighed cut-out figures prepared from photographs of the flames, several workers at Karlsruhe 23/ have measured only the height of the inner cone, or determined its actual area by probing with thermocouples (U4), and Stevens (53) measured the slant heights of cones on photographs. Smith and Pickering (S2) measured the slope of the flame surface at the diameter corresponding to the mean velocity of the unburned gas and calculated flame velocities directly from the equation for velocities in the Gouy postulate. All of these methods would yield identical results if the inner cone of the Bunsen flame were a true right cone; the differences in the results of the several methods originate in deviations of the shape of the inner cone from a right cone. The detailed discussion of these deviations is beyond the scope of this treatment; the field was summarized recently by the writer (D2) 24/. These deviations consist of a rounding at the apex of the inner cone and of a flare at the base of this cone, with

22/ See reference U1, footnote on page 1227.

23/ Examples are references B11, B12, J1, H3, U2, U3, U4, and U5.

24/ A complete review was made in 1937 (D2) and a subsequent pertinent paper (K2) was discussed in a brief review in 1938 (page 6 of reference D3); a general treatment may be found on pages 193-205 of reference L1.

an accompanying elevation of the flame above the port of the burner. The effects have been considered in detail by various workers, and it has been found that their sum passes through a minimum for mixtures in nearly stoichiometric proportions for various gases when burned with air. Thus, Ubbelohde and Hofsass (U1) stated that the original work of Ubbelohde and de Castro established that if too great an excess of combustible gas were avoided, maximum variations of 5 percent existed between results for flame velocities based on measurements of the heights of the inner cones or of the surfaces of these cones by the method of Gouy and Michelson; errors with large excess of combustible were many times this figure. These authors also stated that the u_{GW} methods agree for mixtures in the neighborhood of the maximum of flame velocity. They also mentioned the error introduced in readings of the height of the cone by the diffraction of light by the outer flame, and considered it negligible. Ubbelohde and Dommer (U4) verified the conclusion of Ubbelohde and de Castro for mixtures of methane and of carbon monoxide with air by comparing the results for flame velocities obtained from simple measurements of the cone height with the results based on the actual area of the surface of combustion as determined by probing with thermocouples. They found that for mixtures containing up to approximately 13 percent methane or 65 percent carbon monoxide the difference between the results by the two methods was never more than 4 percent and passed through zero in this range; richer mixtures gave much greater deviations. Khitrin (K1) made similar studies for mixtures with air of benzene and of ether and obtained somewhat greater differences that passed through a minimum near the stoichiometric mixture; this minimum was of the order of 8 percent in tests with benzene at atmospheric pressure.

It has apparently been accepted abroad, and particularly in Germany, that the burner method is on the whole independent of effects produced by the apparatus used. Thus, Bunte and Litterscheidt (B11) in an important work

involving measurements of flame velocities in complex mixtures of the chief constituents of technical gases considered the accuracy of the method in some detail and came to this conclusion. These authors advanced experimental evidence in support of the uniqueness of the dependence of the flame velocities obtained on the composition of the mixtures, including (1) excellent agreement between measurements of flame velocities using normal and divided Bunsen flames for mixtures giving flame velocities near the maximum, (2) independence of the results for flame velocity of the velocity of flow of the unburned gas for large reductions of this (two- to three-fold) below the limiting critical velocity, (3) independence of results of the diameter of the burner for values between about 4 and 7 mm., and (4) independence of the results of the nature of common materials used in constructing the burners. The more recent detailed work of Smith and Pickering (S2) has advanced the measurement of flame velocities by burner methods and has defined more clearly the limitations of the methods and the degree of admissible acceptance of the general conclusion noted. This work was reviewed recently (S1). It has been found that the most consistent results may be obtained with the widest range of variations in experimental conditions through measurements of the slope of the flame surface at the diameter corresponding to the mean velocity of the unburned gas by application of a fundamental equation of the Gouy postulate.

In sum, it has been found that the shape of the flame surface must not differ markedly from that of a true right cone for the successful application of any method of computation for measurements by the burner method. So long as the flow of the unburned gas is laminar, the flame velocities obtained by these methods are independent of this flow over the extreme range giving stable ~~flames~~^{flames}; secondary combustion has no effects on the results when the flame velocity is near its maximum; the results are independent of

the diameter of the burner port if this is not much less than 4 mm.; on the whole, the effects of extraneous variables and apparatus as reflected in distortions of the inner cone are minimized or eliminated by the use of mixtures giving flame velocities near the maximum.

Bomb Methods:

These methods are of two types that utilize either the propagation of flame under conditions of constant pressure or of constant volume. Only the principles and general aspects of the methods will be mentioned here. The spherical propagation of flame forms the basis for measurements of this type, generally, and this may be analyzed somewhat more rigorously than the propagation of flame in stationary Bunsen flames or in tubes, despite complications introduced. It has been shown by various workers 25/ that the propagation of flame may be quite accurately spherical.

A first method was developed by Stevens (S4) for investigation of flame propagation under constant pressures and was used by this author in several studies, 26/. Subsequent detailed studies of the method by Fiock and Roeder (F4) resulted in improvements and in recognition of its limitations. In essence, the measurements are made by recording photographically the movement of flame in a mixture of combustible gas in a soap-bubble, the mixture being ignited at the center by an electric spark. A relatively simple analysis of the data allows deduction of the flame velocities. However, it has been found that certain of the earlier results must be questioned because of the rapid rate of interchange of water vapor between the mixture and the atmosphere surrounding the bubble. This effect is of ^{critical} ~~initial~~

25/ For example see references F3, K3, and E1.

26/ See references S4, S5, S6, S7, and S8.

importance in studies with mixtures containing carbon monoxide, as is well known.

The constant-volume method has been discussed recently by several authors, 27/. It involves the measurement of pressure as well as the photographic recording of the movement of the flame and possesses certain advantages over the method just mentioned, as will be indicated in the following discussion. Both methods require that the explosions emit sufficient light for photographic purposes. Extreme flame velocities may not be measured because of convective effects in mixtures with low flame velocities and of pressure effects and vibrations in mixtures with extremely high flame velocities. Further, the constant-pressure method suffers from the limitations that only moist, non-corrosive gases may be used, that water vapor is always present at a partial pressure which is determined not only by temperature but by the composition of the soap film as well, and that relatively restricted ranges of temperature and pressure are available for study; it possesses the advantages of high accuracy and relatively simple analysis, together with freedom from vibrations in the gas and from the necessity, common in the constant-volume method, of restricting the studies to a limited part of the process. The constant-volume method suffers from inaccuracies inherent in the difficult problem of measuring pressures which vary rapidly and over a wide range, but is capable of ready adaptation to studies of the effects of variables such as temperature and pressure. Lewis and von Elbe have indicated 28/ that a combination of procedures involving the simultaneous records of pressure and of flame travel by photographic means leads to an optimum procedure which

27/ See references F3, L1, and L6.

28/ See pages 180-183 of reference L1.

should give very useful results. Work in this field is now active.

Tube Methods:

The propagation of flame in tubes used in classical experiments by Davy and by Mallard and ~~Le~~^{de} Chatelier and was employed extensively by Dixon and followers in the British school in studies of combustion phenomena. These early results, which have been adequately summarized by Bone and Townsend 29/, were only for spacial speeds of flame and hence are of limited interest. More recent developments (C5, C8) have led to interesting fundamental results through modified procedures including provisions for obtaining instantaneous photographs of the flame front during its travel through the tube. These photographs allow the deduction of the area of the flame front and with the spacial rate of movement allow deduction of the flame velocity. Data obtained by this new method have been published for mixtures with air of ^mMethane (C5), carbon monoxide and benzene (K4).

Correlations:

At present the exact correlation of the results obtained for the flame velocity by these various methods is not possible because of the lack of data. However, there are cogent indications that these methods are capable of giving values for flame velocities which are in substantial agreement. Until comparatively recently the true relationship between the spacial speed of flame and the flame velocity as herein defined was not generally appreciated, and it appeared that the burner method gave much lower values than the tube or bomb methods. The recognition of the distinction noted above has essentially removed this divergence.

The burner method was originally compared with the constant-pressure

29/ See pages 103-133, of reference B1.

bomb method by Stevens (S3) whose data show very good agreement between the two methods for mixtures of carbon monoxide with air. Other agreements have been noted between these two methods for mixtures with air of benzene and of carbon monoxide (K4, K5). Further comparisons for other gases are not possible because of limited data. However, it may be observed that while it was first believed (B11) that an agreement also existed for mixtures of methane and oxygen between the data of Stevens (S3) and of Ubbelohde and Dommer (U3), more recent values (J1) have introduced a discrepancy which has not as yet been explained or verified by other data.

Results have been attained in initial stages of explosion in bombs of constant volume that agree with those obtained in bombs of constant pressure,
30/.

The modified tube method was originally compared with the results of other workers using the burner method by Coward and Hartwell (C5) and their results indicate an agreement in order of magnitude between the two methods for mixtures of methane and air. The results from the modified tube method seem somewhat lower than the most reliable data from the burner method, however, which may be due to the role of the walls in the case of propagation in a tube. A similar correspondence has been reported (K4) for mixtures with air of benzene and of carbon monoxide.

In general, therefore, it seems admissible to accept, in the absence of further data, the equivalence of these methods for measurements of the same fundamental quantity.

Conclusions:

The choice of a method for a particular study of flame velocities involves detailed consideration of the nature of the data desired and of the effects to be studied. Thus, for fundamental data involving the effects of

30/ See reference S8, p375 of reference F3, and page 7 of reference F4, and page 3 of reference F2.

wide variations in experimental variables such as temperature or pressure, which are of particular interest in connection with studies of the combustion process in internal combustion engines, the new methods of Flock and Marvin (F3) or of Lewis and von Elbe (L1) are undoubtedly of unique interest. In contrast, the studies of the propagation of flame in cases in which a constant pressure obtains may be made most simply, perhaps, by one of the other methods described. Simplicity is highly desirable because of the consequent minimization of errors.

The burner method seems simplest of those available and is applicable with certainty to the measurement of the flame velocities in mixtures producing flames that approximate closely a geometrical cone. Also, this method would seem of particular interest in applications of gaseous combustion because of the patent close relationship of the results to problems of the utilization of gases in Bunsen burners.

CHAPTER 4 - ON PERTINENT RESEARCHES ON THE COMBUSTION PROCESS IN GASES

The Nature of the Relationship of the Flame Velocity and Mixture Composition:

Perhaps the first systematic series of measurements showing the effect of the composition of the mixture on the flame velocity were made in 1875 by Mallard (M5) with mixtures of methane and air using the original method of Bunsen. The data are summarized in Table II and Mallard's original curve is reproduced in Figure 1. The curve of Figure 1, although questionable because of the method employed in its derivation, shows the general nature of the relationship between the flame velocity and the proportion of combustible in the mixture burned. The outstanding characteristics of this relationship are the existence of a maximum in the flame velocity and the apparent indications of zero flame velocities in two mixtures corresponding roughly to the two limits of inflammability. The maximum flame velocity is seen to be attained with a mixture containing approximately 11 percent methane, while the mixture in stoichiometric proportions contains only 9.47 percent methane; maximum flame velocity is attained therefore in a mixture containing an excess of combustible. This divergence 31/ was noted by Mallard 32/.

The subsequent work of Mallard and Le Chatelier (M1) introduced a basic question regarding the nature of the dependence of the flame velocity

31/ This divergence of the mixture giving maximum flame velocity from the mixture in combining proportions will be referred to as the "displacement D_v " or simply as the "displacement."

32/ Mallard stated:

"Il est à remarquer que la proportion qui donne la vitesse maximale correspond point exactement à celle pour laquelle le grisou trouve, dans l'oxygène de l'air, la quantité nécessaire pour se combuster. En effet 1 volume d'air contient la quantité d'oxygène nécessaire pour brûler théoriquement 0.148 vol. de grisou, tandis que la vitesse maximale est obtenue avec 0.122 vol. de grisou seulement.

Ce fait singulier tient sans doute à cet équilibre chimique si remarquable et encore si mal connu que M. Deville a signalé sous le nom de tension de dissociation, et qui pose une limite aux combinaisons qui peuvent s'effectuer entre les gaz mélangés."

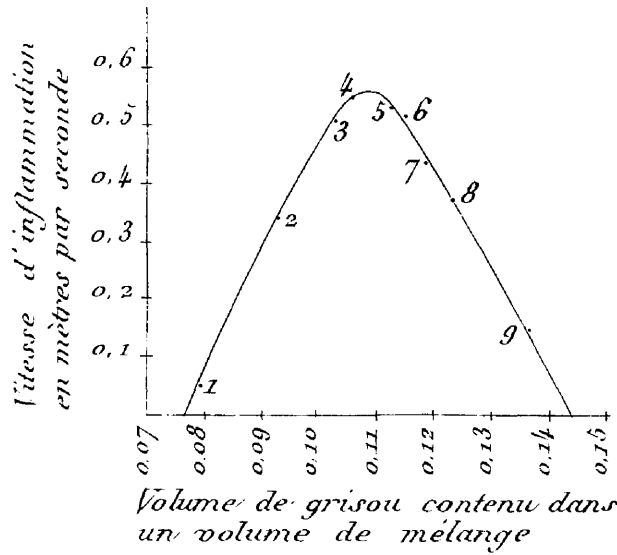
TABLE II

FLAME VELOCITIES IN MIXTURES OF METHANE AND AIR AS DETERMINED BY
MALLARD, ANN. CHIM. PHYS. (7) 7, 355 (1875) BY BUNSEN'S METHOD^{1/}

Volume percent methane in the mixture	Flame velocity, meters per sec.
7.9	0.041
9.3	.325
10.3	.505
10.6	.550
11.3	.524
11.5	.515
11.8	.440
12.3	.375
13.8	.139

^{1/} Values based on flashback of a Bunsen flame through
an orifice.

Fig. 1. *Air et grisou.*



Relation between Flame Velocity in Mixtures of Methane and Air and the Composition of these Mixtures, as given by Mallard, Ann. Chim. Phys. (7) 7, 355 (1875); see Table II.

on the composition of the mixture by indicating that this relationship could be represented by two oblique straight lines intersecting at an apex corresponding to the maximum flame velocity. Early cogent indications that this was not the case are to be found in the work of Michelson (M7) who derived curves from measurements of flame velocities by the improved burner method that showed the pronounced curvature indicated originally by Mallard. This type of curve is now accepted as a true representation of the relationship.

A feature of these curves that is of incidental interest here is the nature of the lower extremes and the velocity of propagation in the "limit" mixtures. Observing the difficulties of the direct measurement of these limits, Mallard and Le Chatelier suggested that they could be obtained by extrapolation of each branch of curves for the flame velocities to the axis of abscissas where the speed would be zero. This question was the subject of further work by the later school of English investigators 33/, who concluded that the speed in a limit mixture is finite and far from zero. However, as these latter deductions were based on measurements of the spacial "speeds of uniform movement" in tubes they are not acceptable. It now seems generally agreed 34/ that the extrapolation of the curves relating flame velocities and mixture compositions, with suitable allowances for the effects produced by secondary air in normal Bunsen flames, may furnish useful indications of the limits of inflammability 35/. This subject has recently been considered in detail by Bunte and Jahn (B15). The direct measurement of these

33/-See page 109 of Report B1.

34/-See references J1 for example.

35/-For example, ^extension of the curves given by Coward and Hartwell (C5) for flame velocities in mixtures of methane with air from the modified tube method to the axis ^{shows} ~~then~~ limits of inflammability of 5 to 15 percent methane, in close agreement with results of direct measurements (C7).

limits may be accomplished accurately and conveniently by other means 36/.

The General Existence of the Displacement D_V : 37/

Returning to the other outstanding feature of the relationship of flame velocity and mixture composition, many investigations of the combustion process in gases have led to a general recognition of the displacement D_V as a general, outstanding characteristic of the slow propagation of flame. This has been expressed by many writers, and the few data listed in Table III, taken at random from recent measurements of flame velocities, emphasize this for several types of combustible gases and vapors burned with air or with oxygen. Although this conclusion has been widely recognized and was indicated even by the results of measurements of spacial flame speeds in tubes, it is emphasized here because of the existence of some misstatements in recent reference works 38/. The divergences among individual results noted in Table III probably originate in large measure in scattering and sparsity of the data, and in estimations of the positions of the curves and of their maxima.

36/-See references C7 and J7 for examples.

37/-See footnote 31, page 32 for definition.

38/-Thus, on page 268 of reference H4 there appears the following statement: "The maximum flame speed in tubes is usually obtained in mixtures containing about 15 percent more combustible gas than is required for complete combustion. With methane, however, maximum speed occurs when the methane and the oxygen are in their combining proportions." This statement, aside from being based on spacial speeds of flame rather than on flame velocities, is not supported by experimental evidence. Further, while the general existence of the displacement D_V is recognized by specific reference on p.89 of reference C1, the following inaccurate statement appears on p.92 of the same reference: "It will be noted that the maximum speed mixtures do not correspond with perfect air-gas mixtures. The small vertical cross line on the charts marks the perfect air-gas mixture, and it will be seen that this does not coincide with the maximum speed mixture exactly, but may be either on the air-rich or gas-rich side of the perfect mixture."

TABLE III

SOME DATA SHOWING THE GENERAL EXISTENCE OF THE DISPLACEMENT OF THE MIXTURE
GIVING MAXIMUM FLAME VELOCITY FROM THE EQUIVALENT MIXTURE^{1/}

Combustible Mixture:	Volume Percent for Equivalence	Combustible: Maximum Flame Velocity	Displacement, D _v	Reference and Method of Measurement ^{2/}
Hydrogen - air	29.5	42.5	13.0	(1), Burner
" "	"	45	15	(2), "
" "	"	43	13	(3), "
" "	"	43.0	13.5	(4), "
" "	"	43 ^{3/}	13.2	(5), "
Hydrogen - oxygen	66.7	71.0	4.3	(4), "
" "	"	71	4	(3), "
Carbon monoxide - air	29.5	42 ^{3/}	12.3	(5), "
" "	"	53	23	(6), "
" "	"	53	23	(1), "
" "	"	45	15	(2), "
" "	"	51	21	(3), "
" "	"	52.5	23	(4), "
" "	"	47	17	(7), "
" "	"	49	19	(8), Tube
Carbon monoxide - oxygen	66.7	77.5	10.8	(4), Burner
" "	"	74	7	(9), "
" "	"	67	0	(10), Soap bubble
" "	"	67	0	(10), Burner
" "	64.9	69	4.1	(11), Soap bubble
Methane - air	9.47	9.7	0.2	(5), Burner
" "	"	10	0.5	(6), "
" "	"	10.5	1.0	(1), "
" "	"	10	0.5	(2), "
" "	"	10	0.5	(3), "
" "	"	10.4	0.9	(4), "
" "	"	9.9	0.4	(12), Tube
Methane - oxygen	33.3	33	0	(9), Burner
" "	"	33	0	(3), "
" "	"	33.3	0	(4), "
" "	"	34	1	(10), Soap bubble
Ethane - air	5.6	5.8 ^{3/}	0.2	(5), Burner
Propane - air	3.9	4.3 ^{3/}	0.4	(5), "
Butane - air	3.1	3.5 ^{3/}	0.4	(5), "
Butane - oxygen	13.3	13	0	(13), Soap bubble
Pentane - air	2.6	3	0.4	(6), Burner
Hexane - air	2.2	2.4	0.2	(6), "
Cyclohexane - air	2.3	2.3	0	(6), "
Ethylene - air	6.5	7	0.5	(6), Burner
" "	6.5	6.8	0.3	(2), "
Acetylene - air	7.7	9.8	2.1	(6), "
" "	7.7	8.8	1.1	(2), "
Acetylene - oxygen	28.6	28	0	(9), "
" "	28.6	28	0	(3), "
Propylene - air	4.4	4.8	0.4	(6), "
Diethlether - air	3.4	4.8	1.4	(6), "
" "	3.4	3.6	0.2	(14), "
Benzene - air	2.7	3.0	0.3	(6), "
" "	2.7	2.8	0.1	(8), Tube
" "	2.7	2.7	0	(14), Burner

^{1/} Approximate values given in many cases, based on estimates of coordinates of maxima of curves for flame velocities.

^{2/} Methods: "burner" - based on the Bunsen cone; "soap bubble" - the constant pressure bomb of Stevens; "tube" - the modified tube method of Coward and Hartwell; for details see previous chapter. References listed:

- (1) Bunte and Litterscheidt, Das Gas u. Wasserfach, 73, 837 (1930)
- (2) Passauer, Das Gas u. Wasserfach, 73, 313 (1930)
- (3) Brückner, Gastafeln: R. Oldenbourg, Berlin (1937)
- (4) Jahn, Der Zündvorgang in Gasgemischen, R. Oldenbourg, Berlin (1934)
- (5) Morgan, American Gas Practice, II, 615 (1930)
- (6) Bunte, Das Gas u. Wasserfach, 72, 213 (1932)
- (7) Kolodstew and Khitrin, Tech. Phys. USSR, 2, 1034 (1936)
- (8) Khitrin, Tech. Phys. USSR, 4, 110 (1937)
- (9) Brückner and others, Z. Autogene Metalbearbeitung, 23, 257 (1936)
- (10) Stevens, N. A. C. A. Rept. 305
- (11) Flock and Roeder, N. A. C. A. Rept. 532
- (12) Coward and Hartwell, J. Chem. Soc., p. 2676 (1932)
- (13) Stevens, N. A. C. A. Rept. 317
- (14) Khitrin, Tech. Phys. USSR, 2, 926 (1936)

^{3/} Computed from data given in terms of percent of theoretical air.

Pertinent Data for the Displacement D_V :

The definition of the maximum of flame velocity in the usual curves is a matter of considerable difficulty because many of the data published include very few points for mixtures giving close to maximum flame velocities. However, the data listed in Table III illustrate several widely recognized general points: displacements are largest for mixtures of carbon monoxide with air, mixtures containing hydrogen also give large displacements, and hydrocarbon and combustion with oxygen in general give low displacements.

Within limits warranted by the data, several investigations have indicated that pressure has no marked effect on the displacement. Thus, Ubbelohde and Koelliker (U2) measured flame velocities by the burner method for mixtures of carbon monoxide and air under pressures of from 1 to 4 atmospheres in 8 steps; although their curves show maxima which disclose an irregular relationship between the displacement and the pressure, the data are badly scattered and these authors concluded (page 84 of ref. U2) that the maximum is not noticeably shifted in the direction of the abscissa. Measurements were also made by Ubbelohde and Andwandter (U5) for these same mixtures under pressures of from approximately $\frac{1}{4}$ to 1 atmosphere in 6 steps; these also showed the absence of any effect on the displacement (p.231 of ref. V5). More recent works studying the effect of pressure on the flame velocity by various methods have shown no effects on the displacements for pressures from 1 to 3.5 atmospheres for mixtures with air of benzene and ethyl ether (K1) 39/

Other measurements have indicated that the character of an inert in the mixture has no marked effect on the displacement 40/.

39/-A reserve is required in some cases because of sparsity of the data. It should also be noted that measurements in soap bubbles, see references S10 and K5, are not cited because, as noted by Fiock and Roeder (F4, pages 11 and 12), the results of such tests show combined effects of changes in partial pressure of water vapor and total pressure rather than unique effects of the latter factor alone.

40/ For example see reference B1, pages 116-118, and reference C3.

The effects produced by preheating the gases before combustion seem to be somewhat irregular. Thus, the measurements of Ubbelohde and Dommer (U3) indicated a progressive increase in the displacement D_v as a consequence of increasing the temperature of preheating up to over 400 deg. C for mixtures with air of carbon monoxide and of methane. This is indicated by the data of Table IV, A, which show a progressive increase in the amount of combustible required for maximum flame velocity with increase in the temperature of preheat. (The equivalent mixture is not affected by preheat, of course.) The later measurements of Passauer (P1) were made with a variety of gases and disclose a variety of effects. The data of Table IV, B, suggest rather definite and regular increases of the displacement with increasing temperature of preheat for mixtures with air of dry and moist carbon monoxide, of methane and of Weiner city gas, while the data for the mixtures of hydrogen and ethylene show relative independence of these two factors. The irregularities in certain of the data may originate in scattering in the neighborhood of the maxima. Other corroborative evidence is given by Tammann and Thiele (T2).

TABLE IV

EFFECT OF PREHEAT ON THE DISPLACEMENT OF THE MIXTURE GIVING MAXIMUM
FLAME VELOCITY; PREPARED FROM UBBELOHDE AND DOMMER, J. F. GASSEL, 57, 757 (1914)
AND PASSAUER, GAS U. WASSERFACH, 73, 313 (1930)^{1/}

Preheat, °C.	Volume Percent Combustible for Maximum Flame Velocity	Equivalent Mixture	Displacement ^{2/} D _v
A - From Ubbelohde and Dommer:			
1. <u>Mixtures of carbon monoxide and air</u>			
20	48	29.5	18.5
150	50	"	20.5
350	51	"	21.5
460	53	"	23.5
2. <u>Mixtures of methane and air</u>			
20	9.4	9.48	0
185	9.7	"	0.2
430	10.2	"	0.7
B - From Passauer:			
1. <u>Dry mixtures of carbon monoxide and air</u>			
20	40	29.5	10.5
85	40	"	10.5
180	40	"	10.5
305	43	"	13.5
435	45	"	15.5
540	50	"	20.5
2. <u>Moist mixtures of carbon monoxide and air</u>			
20	46	29.5	16.5
100	49	"	19.5
230	49	"	19.5
350	47	"	17.5
460	49	"	19.5
550	52	"	22.5
3. <u>Mixtures of methane and air</u>			
20	10.5	9.5	1.0
95	10.7	"	1.2
200	10.8	"	1.3
350	11.0	"	1.5
470	11.0	"	1.5
520	11.2	"	1.7
610	11.0	"	1.5
680	10.8	"	1.3
4. <u>Mixtures of hydrogen and air</u>			
20	46	23.5	16.5
190	46	"	"
310	46	"	"
430	46	"	"
5. <u>Mixtures of ethylene and air</u>			
20	6.9	6.5	0.4
110	7.0	"	0.5
160	7.0	"	0.5
290	7.0	"	0.5
435	7.0	"	0.5
515	6.6	"	0.1
6. <u>Mixtures of Weiner city gas and air</u>			
20	22.0	21.6	0.4
120	23.0	"	1.4
280	23.6	"	2.0
510	23.7	"	2.1
645	23.0	"	1.4
720	23.6	"	2.0

^{1/} All measurements of flame velocities by the burner method.

^{2/} Displacement of mixture giving maximum flame velocity from the equivalent mixture.

Some interesting effects were developed by further scrutiny of available data. Thus, tabulations such as Table V were prepared from published studies of the combustion of binary mixtures of various combustible gases, and the results plotted as in Figure 2. The volume-percents of combustible giving maximum flame velocity for these mixtures when burned with air were judged from the published data and curves. The displacement D_v thus found was reduced to a "percent displacement" by division of the actual displacement by the volume-percent of combustible in the equivalent mixture; this placed the results on a better basis for comparisons. The similarity of the curves representing this percent displacement as a function of the composition of the binary combustible mixture was striking. In general, the curves of Figure 2 indicate three distinct phases in the effects produced on the percent displacement by progressive addition to the binary mixture of combustible gases of the constituent with the smaller displacement: (1) rapid decrease, (2) relative constancy, and finally (3) slow decrease of the percent displacement for the mixture. Only the curve for mixtures of carbon monoxide and acetylene with air shows marked divergence from this general nature. Another regularity suggested by Bunte (S12) that has apparently been given credence abroad 41/ states that for hydrocarbons the displacement decreases as the size of the molecule increases.

41/ - See page 123 of reference B16.

TABLE V

DISPLACEMENTS OF MIXTURES GIVING MAXIMUM FLAME VELOCITIES

FOR SOME BINARY SERIES^{1/}

Volume Fraction of A	Mols per Mol	air req'd. for Fraction	Volume Fraction of B	Mols per Mol	air req'd. for Fraction	Total Air Req'd. Mols	% Gas in Theoret. Mixt.	Gas of q_1 Maximum Flame Velocity	Displacement D_v	Percent Displacement ^{2/}
Series 1 ^{3/} A=CO, B=H ₂ :										
1.0	2.39	2.39	0.0	2.39	0.00	2.39	29.5	53.0	23.5	79.7
0.9	2.39	2.15	0.1	2.39	0.24	2.39	29.5	49.0	19.5	66.2
0.8	2.39	1.91	0.2	2.39	0.48	2.39	29.5	47.0	17.5	59.3
0.7	2.39	1.67	0.3	2.39	0.72	2.39	29.5	45.5	16.0	54.3
0.6	2.39	1.43	0.4	2.39	0.97	2.39	29.5	44.5	15.0	50.9
0.5	2.39	1.20	0.5	2.39	1.20	2.39	29.5	44.0	14.5	49.1
0.4	2.39	0.97	0.6	2.39	1.43	2.39	29.5	44.0	14.5	49.1
0.3	2.39	0.72	0.7	2.39	1.67	2.39	29.5	44.0	14.5	49.1
0.2	2.39	0.48	0.8	2.39	1.91	2.39	29.5	43.3	13.8	46.8
0.1	2.39	0.24	0.9	2.39	2.15	2.39	29.5	43.0	13.5	45.7
0.0	2.39	0.00	1.0	2.39	2.39	2.39	29.5	42.5	13.0	44.1
Series 2 ^{4/} A=CO, B=C ₂ S ₂ :										
1.0	2.39	2.39	0.0	14.34	0.0	2.39	29.5	53	23.5	79.7
0.985	2.39	2.35	0.015	14.34	0.22	2.57	28.0	41.5	13.5	48.2
0.95	2.39	2.27	0.05	14.34	0.72	2.99	25.1	34	8.9	35.5
0.9	2.39	2.15	0.10	14.34	1.43	3.58	21.8	30	8.2	37.6
0.8	2.39	1.91	0.2	14.34	2.87	4.78	17.3	23	5.7	32.3
0.5	2.39	1.20	0.5	14.34	7.17	8.37	10.7	14	3.3	30.8
0.0	2.39	0.00	1.0	14.34	14.34	14.34	6.5	8.5	2.0	30.6
Series 3 ^{4/} A=CO, B=C ₂ H ₂ :										
1.0	2.39	2.39	0	11.95	0	2.39	29.5	53	23.5	79.7
0.9	2.39	2.15	0.1	11.95	1.2	3.35	23.0	36	13.0	56.5
0.8	2.39	1.91	0.2	11.95	2.39	4.30	18.9	27	8.1	42.9
0.5	2.39	1.20	0.5	11.95	5.98	7.18	12.2	15	2.8	22.9
0.3	2.39	0.72	0.7	11.95	8.37	9.09	9.18	12.5	3.3	36.2
0.0	2.39	0.00	1.0	11.95	11.95	11.95	7.72	10.0	2.3	29.5
Series 4 ^{3/} A=CO, B=CH ₄ :										
1.0	2.39	2.39	0.0	9.56	0.00	2.39	29.5	53.0	23.5	79.7
0.9	2.39	2.15	0.1	9.56	0.96	3.11	24.3	37.0	12.7	52.3
0.8	2.39	1.91	0.2	9.56	1.91	3.82	20.7	28.5	7.8	37.7
0.7	2.39	1.67	0.3	9.56	2.87	4.54	18.1	23.2	5.1	28.2
0.6	2.39	1.43	0.4	9.56	3.82	5.25	16.0	20.5	4.5	28.1
0.5	2.39	1.20	0.5	9.56	4.78	5.98	14.3	18.0	3.7	25.9
0.3	2.39	0.72	0.7	9.56	6.69	7.41	11.9	14.8	2.9	24.4
0.0	2.39	0.00	1.0	9.56	9.56	9.56	9.47	10.5	1.03	10.9
Series 5 ^{3/} A=H ₂ , B=CH ₄ :										
1.0	2.39	2.39	0.0	9.56	0.00	2.39	29.5	42.5	13	44
0.9	2.39	2.15	0.1	9.56	0.96	3.11	24.3	32.0	7.7	31.6
0.8	2.39	1.91	0.2	9.56	1.91	3.82	20.8	25.5	4.7	22.6
0.7	2.39	1.67	0.3	9.56	2.87	4.54	18.1	21.5	3.4	18.8
0.6	2.39	1.43	0.4	9.56	3.82	5.25	16.0	19.0	3.0	18.7
0.5	2.39	1.20	0.5	9.56	4.78	5.98	14.3	17.0	2.7	18.9
0.3	2.39	0.72	0.7	9.56	6.69	7.41	11.9	14.0	2.1	17.6
0.0	2.39	0.00	1.0	9.56	9.56	9.56	9.47	10.5	1.0	10.9
Series 6 ^{4/} A=CO, B=C ₆ H ₁₄ :										
1.0	2.39	2.39	0.00	45.4	0.0	2.39	29.5	53	23.5	79.7
0.99	2.39	2.37	0.01	45.4	0.45	2.82	26.2	40.6	14.4	54.9
0.975	2.39	2.33	0.025	45.4	1.14	3.47	22.4	30.6	3.2	36.6
0.95	2.39	2.27	0.05	45.4	2.27	4.64	13.1	22.0	3.9	21.6
0.9	2.39	2.15	0.1	45.4	4.54	6.69	13.0	16	3.0	23.1
0.8	2.39	1.91	0.2	45.4	9.08	10.99	8.34	10	1.66	19.9
0.5	2.39	1.20	0.5	45.4	22.7	23.9	4.02	4.5	0.48	11.9
0.0	2.39	0.00	1.0	45.4	45.4	45.4	2.16	2.5	0.34	15.7

1/ Computed from data given by Bunte and Litterscheidt and by Bunte in Das Gas und Wasserfach, 73, 837 (1930) and 75, 213 (1932), and listed in columns 1, 4, and 9.

2/ Displacement D_v divided by % gas in theoretical mixture and multiplied by 100.

3/ Data for % gas at maximum flame velocity from Bunte and Litterscheidt, footnote 1.

4/ Data for % gas at maximum flame velocity from Bunte, footnote 1.

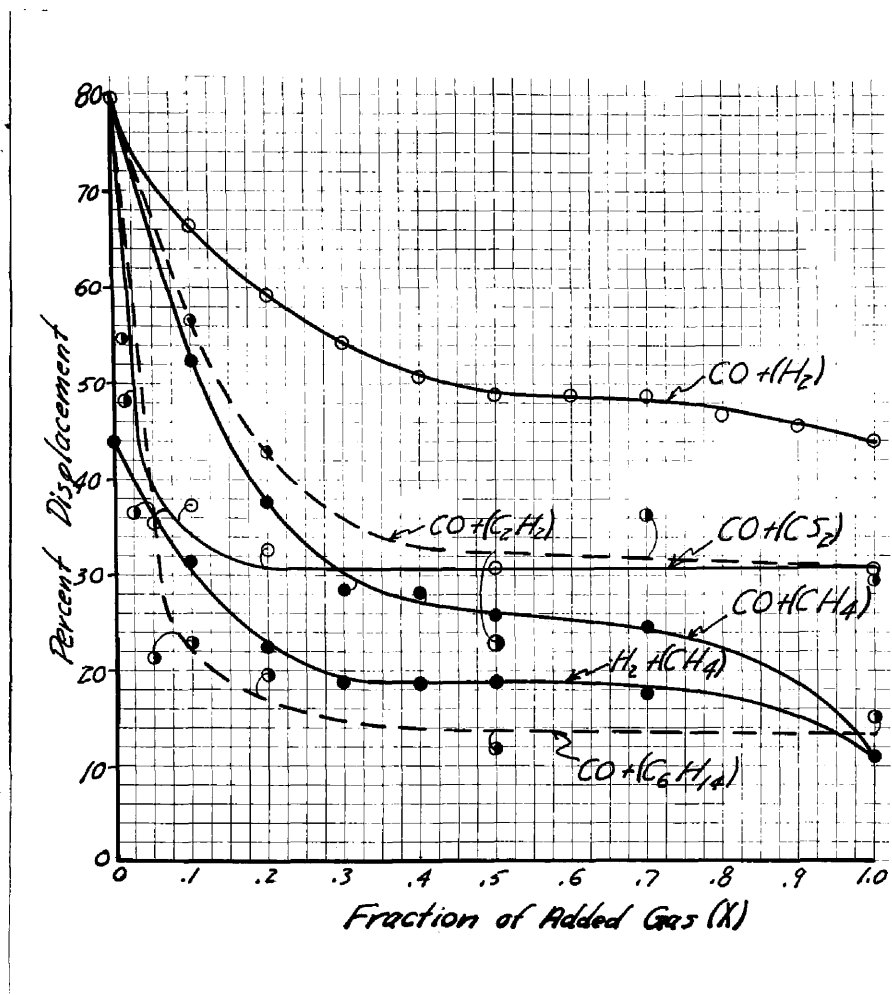


Figure 2. Relations between the Displacements of Mixtures giving Maximum Flame Velocities and the Composition of some Binary Mixtures; Deduced from Published Data; see Table V.

Finally, a striking situation was found to exist that has apparently escaped the attention of investigators and that seemed to demand intensive study in the light of the foregoing. This relates to the effects produced by the oxygen content of the atmosphere used for combustion on the displacement D_V for various gases. The first works designed to disclose in a systematic way the effects of the concentration of oxygen in the atmosphere used for combustion on the flame velocity characteristics were carried out by Mason and Wheeler (M6) and by Payman(P2) and were discussed more recently by Payman and Wheeler(P3). These data were obtained by the early tube method 42/ for mixtures of methane with atmospheres composed of oxygen and nitrogen in various proportions. Figures listed in Table VI were derived as most representative of the published results, and the actual and percent displacement are represented in Figure 3 as functions of the composition of the atmosphere used for combustion. Apparently regular increases in the displacements are disclosed as a result of increase of the oxygen content of the atmosphere up to 33 percent oxygen, following which an irregular period occurs with displacements of practically zero for atmospheres containing 50 and 100 percent oxygen. In a more recent work, Jahn (J1) has investigated by the burner method these same effects (of concentration of oxygen in the atmosphere used for combustion on the flame velocity) for mixtures of hydrogen, carbon monoxide and methane with atmospheres composed of various proportions of oxygen and either nitrogen or carbon dioxide. Although detailed consideration was given the displacement D_V in this investigation, as noted in the next chapter, no general attention was apparently given the interesting relations indicated between the concentration of oxygen in the atmosphere and the displacement.

42/ Although the measurements of the special speeds of flame have been criticized, there is reason to believe in the utility of ^Vbasic indications derived from such measurements. *certain*

TABLE VI

EFFECTS OF CONCENTRATION OF OXYGEN IN THE ATMOSPHERE USED
FOR COMBUSTION ON THE DISPLACEMENTS OF THE MIXTURE GIVING MAXIMUM
SPECIAL FLAME SPEEDS^{1/}

Volume-percent Oxygen in Atmosphere	Volume-percent in Theoretical Mixture	of Methane for Maximum Flame Speed ^{6/}	Displacement D _v ^{2/}	Percent Displacement ^{3/}
<u>A - Data of columns 1 and 3 deduced from results of Mason and Wheeler:^{4/}</u>				
15.05	7.02	7.2	0.2	2.8
17.60	8.08	8.4	0.3	3.7
18.85	8.61	9.0	0.4	4.6
20.6	9.34	9.9	0.6	6.4
20.9	9.47	10.0	0.5	5.3
<u>B - Data of columns 1 and 3 deduced from results of Payman:^{5/}</u>				
21	9.47	10.0	0.5	5.3
33	14.58	15.8	1.2	8.2
50	19.84	20.0	0.2	1.0
66	25.08	25.8	0.7	2.8
100	33.00	33.2	0.2	0.61

^{1/} For combustion of methane based on published measurements obtained by tube method of special speeds of flame.

^{2/} Column 3 - Column 2.

^{3/} (Column 4 x 100) ÷ column 2.

^{4/} From Trans. Chem. Soc., 111, 1044 (1917).

^{5/} From J. Chem. Soc., 117, 48 (1920).

^{6/} Obtained by scaling published curves.

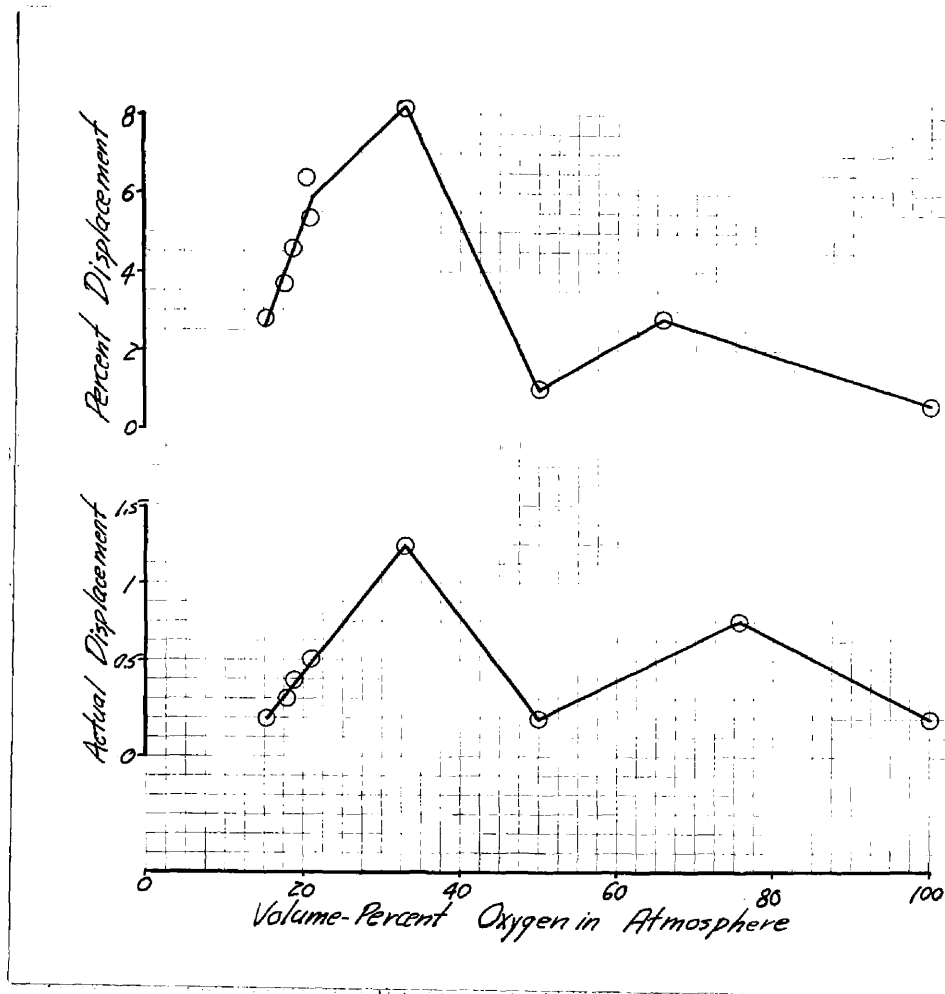


Figure 3. Relations between the Displacements of Mixtures of Methane giving Maximum Flame Speed and the Concentration of Oxygen in the Atmosphere Used for Combustion; Deduced from Published Data; see Table VI.

Thus, for discussion of the effect of the concentration of the oxygen in the atmosphere on the content of combustible giving maximum flame velocity, Jahn constructed the graph reproduced in Figure 4 but apparently overlooked the indication of a regular type of relationship between the displacement D_V and the oxygen content of the atmosphere. The vertical distances between the curves for the maximum flame velocities and those for the equivalent mixtures in Figure 4 indicate at once that at least for mixtures containing hydrogen and carbon monoxide there is a striking regularity. The computations of Table VII are based on Jahn's data; the results are plotted in Figure 5 43/. In marked contrast to the irregularities shown in Figure 3 for similar values deduced from the results of the English workers, regular relationships are disclosed in general in Figure 5 between the displacements and the concentration of oxygen in the atmosphere used for combustion. For methane, the lower curve of Figure 5 suggests a relative constancy of the displacement despite changes in the concentration of oxygen in the atmosphere, and some irregularities are suggested in the curve for percent displacements for mixtures containing methane. Further, the curves of Figure 5 for the actual displacements for hydrogen and carbon monoxide exhibit definite coincident maxima that seem absent in the case of methane. Although the data as listed in Table 7 suggest some regular variation in the displacements for mixtures containing this gas, the differences indicated are of the order of 0.2 percent methane on the figure and seem of questionable significance in the absence of details of experimental procedures or of precision measures for the results.

In sum, evidence exists of regularities in several respects that suggest that the displacement D_V is a fundamental characteristic of the slow propagation of flame in gases that is suitable for investigation. Regular

43/-Jahn (J1) also gives data for atmospheres containing CO_2 instead of N_2 as inert that show similar effects.

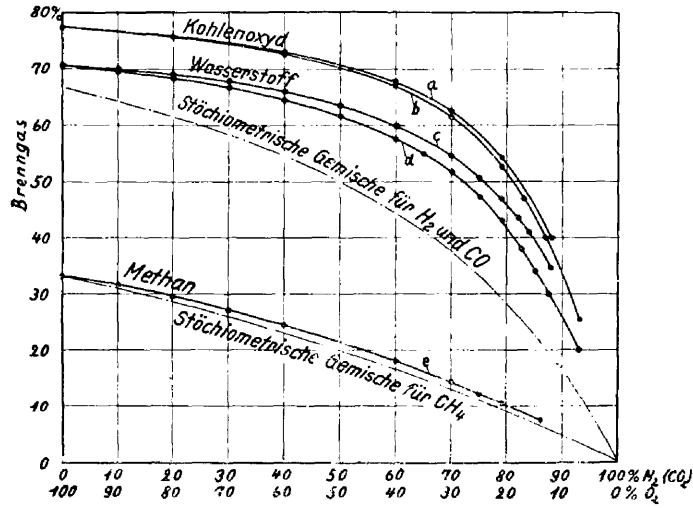


Abb. 9.

Gemische maximaler Zündgeschwindigkeit.

- Kurve d, H₂ im Gemisch mit (N₂ + O₂).
 " c, H₂ " " " (CO₂ + O₂).
 " b, CO " " " (N₂ + O₂).
 " a, CO " " " (CO₂ + O₂).
 " e, CH₄ " " " (N₂ + O₂) und (CO₂ + O₂).

Figure 4: Relations between the Compositions of the Mixture giving Maximum Flame Velocity and the Composition of the Atmosphere Used for the Combustion, from Jahn's "Zündvorgang", reference J1.

EFFECTS OF CONCENTRATION OF OXYGEN IN THE ATMOSPHERE USED FOR
COMBUSTION ON THE DISPLACEMENT OF THE MIXTURE GIVING MAXIMUM FLAME

VELOCITIES^{1/}

Composition of Atmosphere, Volume Percent Oxygen	Content of Combustible for Equivalence Maximum Flame Velocity	Displacement D _v	Percent Displacement		
<u>Series 1 - Hydrogen:</u>					
100	0	66.7	71.0	4.3	6.4
98.5	1.5	66.5	71.0	4.5	6.8
90	10	64.3	70.0	5.7	8.9
80	20	61.6	68.5	6.9	11.2
70	30	58.4	67.0	8.6	14.7
60	40	54.6	64.5	9.9	18.1
50	50	50.0	61.5	11.5	23.0
40	60	44.5	57.5	13.0	29.2
35	65	41.2	55.0	13.8	33.5
30	70	37.5	51.5	14.0	37.3
25	75	33.3	47.5	14.2	42.6
21	79	29.6	43.0	13.4	45.3
17.5	82.5	26.0	38.5	12.5	48.0
15	85	23.1	35.0	11.9	51.5
12.5	87.5	20.0	31.0	11.0	55.0
7	93	12.3	20.0	7.7	62.6
<u>Series 2 - Carbon Monoxide:</u>					
100	0	66.7	77.5	10.8	16.2
98.5	1.5	66.5	77.5	11.0	16.5
80	20	61.6	75.5	13.9	22.6
60	40	54.6	72.5	17.9	32.8
40	60	44.5	67.0	22.5	50.5
30	70	37.5	61.5	24.0	64.0
21	79	29.6	52.5	22.9	77.3
17	83	25.4	47.0	21.6	85.0
13	87	20.7	40.0	19.3	93.2
7	93	12.3	25.5	13.2	107.3
<u>Series 3 - Methane:</u>					
100	0	33.3	33.3	0	0
98.5	1.5	33.0	33.0	0	0
80	20	28.6	29.5	0.9	3.15
60	40	23.1	24.2	1.1	4.76
40	60	16.7	18.0	1.3	7.78
30	70	13.0	14.2	1.2	9.23
25	75	11.1	12.2	1.1	9.91
21	79	9.5	10.4	0.9	9.43
14	86	6.5	7.3	0.8	12.3

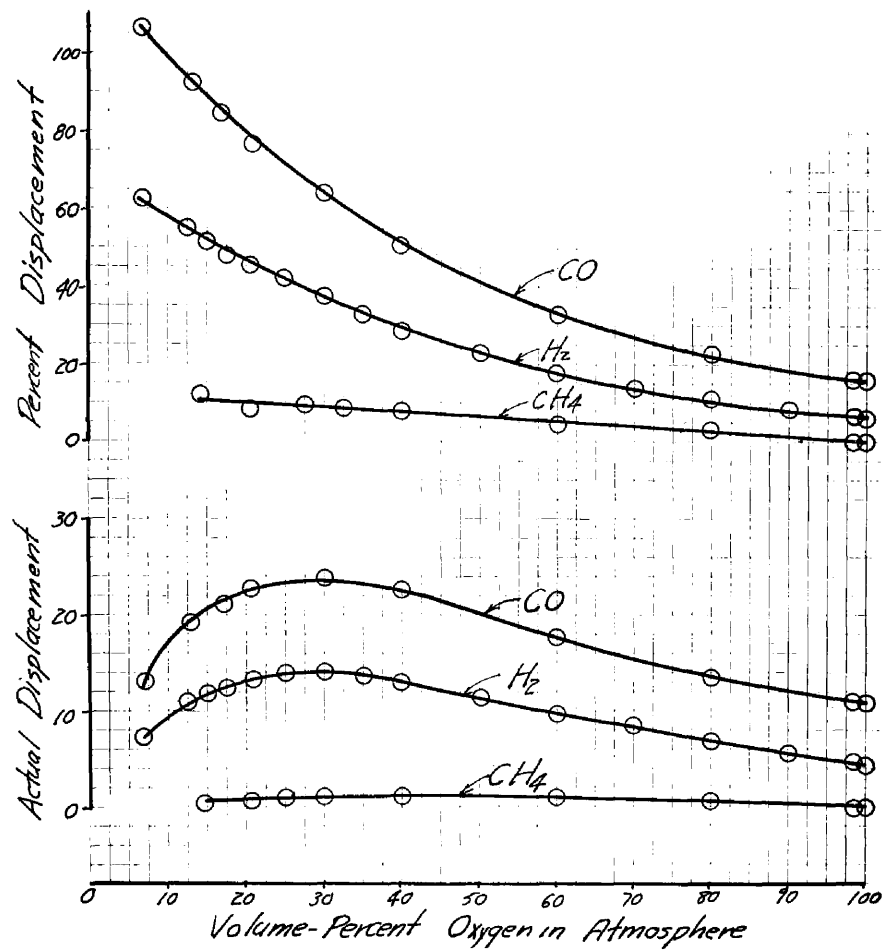


Figure 5. Relations between the Displacements of Mixtures of H₂, CO, and CH₄ giving Maximum Flame Velocity and the Composition of the Atmosphere Used for Combustion; Deduced from Published Results of Jahn (J1) as in Table VII.

relationships have been deduced particularly from published data for mixtures containing hydrogen and carbon monoxide between the displacements and the concentration of oxygen in the atmosphere used for combustion. In contrast, such regularities are not suggested by available data for methane; conflicting indications exist in this connection, and include suggestions of relative independence and of irregular relationships between these two factors.

Prior Analyses of the Displacement D_V :

An early observation of this displacement was interpreted by Mallard (see footnote 32 of p. 32) as a consequence of dissociation. Mallard and Le Chatelier (M1), on the other hand, suggested that the marked effect they observed for mixtures of hydrogen and air was due to opposing effects of the temperature of combustion and of the high thermal conductivity of hydrogen. Although this latter proposal seems plausible for this particular case, it must be concluded that no such simple explanation may account adequately for the phenomenon observed: This phenomenon proves entirely general for many types of gases, and the displacement is greatest for carbon monoxide and of considerable magnitude for other gases for which the thermal conductivities are less than or of the same order as that of air.

A first systematic treatment of this displacement was given by Payman (P2) and was later reviewed by Payman and Wheeler (P3); these considerations were based on measurements of the spacial speeds of flame in tubes but are nevertheless of pointed interest. The analysis is based on concepts of the thermal theory of the slow propagation of flame, previously reviewed. These authors concluded that the spacial speed of flame depends on the temperature and on the rate of reaction. A major factor in determining the temperature and the amount of the displacement was given as the specific heat of the gas added to an equivalent mixture. The rate of reaction was considered to depend on temperature and on the composition of the mixture

in accordance with the law of mass action expressed in terms of the initial concentrations of the reactants. From the law of mass action, Payman noted that 44/ for the combustion of methane or of hydrogen with any given atmosphere the maximum effect of the mass action factor is obtained with an excess of combustible in the mixture except for combustion with pure oxygen when this maximum coincides with the equivalent mixture. This displacement demanded by the effect of mass action was opposed in Payman's argument by the effect of temperature in increasing the reaction rate, and this effect was assumed to be greatest for the mixture in combining proportions. The cooling effect of the excess combustible gas was viewed as determinative of the amount of the displacement.

Several experimental verifications of this reasoning were made by Payman and by Payman and Wheeler, and included (1) the establishment of excess oxygen in the mixture giving maximum flame velocity in a series studying the inverse combustion of oxygen in an atmosphere composed of nitrogen and either hydrogen or methane, (2) the absence of any displacement in the combustion with pure oxygen of methane or of hydrogen, and (3) the absence of the displacement in the combustion with air of a gas such as producer gas which contains a high proportion of inerts.

44/-Payman's deduction involved the implicit assumption of termolecular processes, and may be seen as follows: designate as C_X the concentration of any species X, as x and a the percentages of combustible in the mixture and of oxygen in the atmosphere, respectively, and as y and z the effects of mass action for the combustion of methane and of hydrogen, respectively, we have

$$y = C_{CH_4} \times C_{O_2}^2 = x \left[\frac{(100-x)a}{100} \right]^2 = x(100-x) \left(\frac{a}{100} \right)^2$$

$$\frac{dy}{dx} = 0 = 100 - 3x, \quad x = 33\frac{1}{3} \text{ for methane.}$$

$$z = C_{H_2}^2 \times C_{O_2}^2 = x^2 \left[\frac{(100-x)a}{100} \right]^2$$

$$\frac{dz}{dx} = 0 = 200 - 3x; \quad x = 66\frac{2}{3} \text{ for hydrogen.}$$

Coward and Jones suggested (C3) that the influence of mass action on the rate of reaction in mixtures of methane and air would be obscured by the influence of the widely different temperatures obtaining in mixtures near equivalence. These authors felt that Payman's argument was strengthened however by the data they obtained (mentioned on p. 14 and indicating the absence of any effect on the displacement of widely differing flame temperatures and thermal capacities and conductivities) and noted that this argument if correct implied a low temperature coefficient for the combustion reaction at flame temperatures. There is theoretical support for this last view from the Arrhenius equation.

It has been noted that the lucid explanation of Payman is not without difficulties, particularly in connection with the effect of the specific heat of the combustible gas on the amount of the displacement. For example, Jones and others (J8), studying the flame temperatures of hydrocarbon gases, noted the slight displacement of the mixture giving maximum flame temperature toward excess gas, which displacement is evidently due to the dissociation of the products of combustion 45/; they also noted the lack of agreement between the mixtures giving maximum flame temperatures and maximum flame velocities. These authors observed 46/ that the displacement for propane, butane, and ethylene should be less than that for methane, while in fact those for propane and ethylene are larger and that for butane of the same order as that for methane. The data on which these conclusions are based are not cited; comparisons from Table III do not lead to the same specific conclusions but fail to disclose any regularity between the displacement and the specific heat of the combustible gas.

45/-The effect of the dissociation on the flame temperature is calculable, and Jones et al noted good agreement between the computed contents of combustible corresponding to the maxima and those found experimentally.

46/-See p. 879 of reference J8.

A more recent and extensive examination of this question 47/ has been made by Jahn (VI) on the basis of measurements of flame velocities by the burner method, mentioned previously. Although a perusal of this paper and of the work of Payman and of Payman and Wheeler indicates substantial parallels in important fundamentals, Jahn's work will be epitomized here. The analysis is made from the generalized form of Nusselt's equation for the flame velocity as developed by Jahn, equation 14 of page 14 in which the several factors in this equation have been grouped into separate expressions representing the effects of the reaction velocity and of thermal factors. Jahn showed, as did Payman, that with the exception of combustion with pure oxygen the maximum of reaction velocity is attained with a mixture containing an excess of combustible gas. Likewise, it was observed that the effect of the group of thermal factors was at a maximum at equivalence. The general basis for the observed displacements was then given, in common with the earlier statements of Payman, as the result of an interaction between these two effects. Jahn noted from the curves reproduced in Figure 4 that in contrast to the theoretical requirement of zero displacement for combustion with pure oxygen, the displacements established for both hydrogen and carbon monoxide were still large in this limiting case, and vanished only for methane; for the first two gases the displacement was noted to decrease with decreasing inert content in the atmospheres. Substitution of carbon dioxide for the nitrogen as the inert in the atmosphere was found to cause a regular increase in the displacements for both hydrogen and carbon monoxide, but did not affect those for methane. Jahn suggested that high thermal conductivity of

47/-A not very cogent suggestion, pages 73 and 74 of reference T2, is based on radiation losses from flames and a proposed shielding effect by the gases of secondary combustion.

hydrogen resulted in attainment of the maximum effect of the thermal factors with an excess of hydrogen. For carbon monoxide, this difference in conductivities does not exist, and it is supposed that the form used for expression of the reaction velocity through the mass action law requires revision in this case (i.e. the "constant" C of equation 14 varies and may increase with increasing content of carbon monoxide) because of the well-known effects of the intermediate chemism of the reaction. For methane, any excess combustible is assumed to participate in the reaction, at least in part, by an endothermic pyrolysis which decreases the development of heat immediately as an excess of methane is present, thus lowering the reaction velocity and accounting for the very small displacements observed. Difficulties existed in connection with the ignition temperatures; values calculated from the formula for the limits of inflammability, i.e. for zero flame velocity in the limit mixtures, agreed fairly well for calculations based on either limit (i.e. within about 12% on the average) but were from about 450 to 900 degrees C higher than measured values. Also, while equation 14 demands an infinite flame velocity for an initial temperature equal to the ignition temperature, Passauer (P1) and Tammann and Thiele (T2) were successful in obtaining measurements of flame velocities with temperatures of preheat approximating accepted ignition temperatures. These difficulties introduce questions relating to the adequacy of basic assumptions. Jahn next gave detailed consideration to the mutual effects of the two factors of reaction velocity and thermal effects. It seems unnecessary to discuss these developments minutely as they are well expressed in the original paper, but it may be noted that this author evolved an interesting graphical scheme involving the construction of curves of equal flame velocities using as coordinates the content of combustible for maximum velocity and the concentration of oxygen in the atmosphere; a triangular construction allows consideration of several series of mixtures representing inverse combustions, (an extension of the type of considerations previously noted

by Payman), and leads to verification of several predictions based on the argument set forth above. Jahn's consideration of the reaction velocity showed such accord between equation 14 and the experimental results that the adequacy of the expression of the complex processes of the combustion in terms of a constant and of the law of mass action involving only initial concentrations of the reactants was considered proven.

CHAPTER 5 - THE PRESENT INVESTIGATION

The displacement of the mixture giving maximum flame velocity from the mixture in combining proportions has been noted as a general characteristic of the slow propagation of flame in gases that exhibits regularities suggesting its fundamental character. In contrast to these regularities there exist some discrepancies in the literature and irregularities that raise basic questions. An outstanding question relates to the effects produced by changes in the composition of the atmosphere used for combustion. Thus for some gases, regular changes are produced in the displacement and in the percent displacement by this factor; for methane, such regularities are apparently absent and indications of marked irregularities also exist.

As noted previously, the present investigation was undertaken because it seemed possible that experimental development of the points mentioned might establish whether or not such regularities are general, might lead to a critical discussion of the importance of various views of the process of the slow movement of flame, and produce collaterally data of practical importance.

III - EXPERIMENTAL

CHAPTER I - INTRODUCTORY

The investigation of the propositions noted in the last chapter of the preceding section necessitated determinations of the flame velocities in mixtures of methane with atmospheres composed of oxygen and nitrogen in various proportions. A review of the methods available for such determinations, as summarized in Chapter 3 of Section II, led to adoption of the burner method for these experiments. This method is based on the dynamic equilibrium in the inner cone of the Bunsen flame between the flame velocity and the velocity of flow of the unburned gases. It suffers certain limitations but seemed suitable for this work because the range of maximum validity of the results obtained through its use coincides with the range of interest of the experiments contemplated. Further, the results of this comparatively simple method are closely related to problems involved in the utilization of gases through combustion.

Plans were formulated and apparatus constructed for these measurements using atmospheres containing oxygen and nitrogen in various proportions representing the extreme range possible, i.e., from one containing substantially pure oxygen to another containing a high proportion of nitrogen that was near the limit that prevents the propagation of flame. It was found, however, that the characteristic nature of the effects under investigation was established adequately by tests made with atmospheres containing between 20 and 80 percent oxygen. Troublesome experimental difficulties developed in attempted measurements using the atmospheres representing the extremes in composition; measurements under these extreme conditions were not made because a great amount of labor and expense would have been involved which would have made no essential contribution to the results.

From the nature of the proposed investigation it will be seen that measurements of an essentially relative character should suffice in answer to the questions raised.

The purity of the gases was not therefore a question of paramount importance, provided it remained constant throughout the tests. Consequently, commercial compressed oxygen and nitrogen which contained 99.5 percent of their principal constituents, 48/ and a large cylinder of compressed commercial methane were used without treatment other than drying and filtering. The specifications supplied for the methane by the manufacturer were as follows:

<u>Constituent</u>	<u>Volume percent</u>
Methane	Not less than 92
Air	Not more than 4.5
Ethane	Not more than 2
Nitrogen	Not more than 2.

Preliminary analyses of this material with an Elliott apparatus indicated that it contained practically no carbon dioxide, unsaturated hydrocarbons, oxygen or carbon monoxide, and that about 98 percent of hydrocarbon combustible was present which seemed to be substantially pure methane. Subsequent analyses with a Bureau of Mines Orsat apparatus 49/ confirmed the absence of unsaturates, carbon monoxide and hydrogen, and showed 0.7 percent oxygen and 98.6 percent methane when the latter was calculated from the carbon dioxide produced by slow combustion over platinum. However, a discrepancy existed between the contraction observed in this combustion and the carbon dioxide produced that indicated the presence of a small amount of a higher

48/-Purity within 0.1 percent on the figure, according to the manufacturer.

49/-Grateful acknowledgment is made to Dr. S. Karrer and staff of the Research Department of the Consolidated Gas Electric Light and Power Company of Baltimore for making these analyses.

paraffin hydrocarbon. The analysis used for calculations in the work recorded in the following pages was therefore based on the amount of air corresponding to the oxygen observed, as this oxygen was in all probability from air, and the hydrocarbon will be written as methane. The very small amount of ethane which was probably present should have no effect on the basic trends disclosed by the data. The computed analysis is:

<u>Constituent</u>	<u>Volume percent</u>
Methane	96.7
Oxygen	0.7
Nitrogen	2.6

CHAPTER 2 - APPARATUS

The measurement^f of the flame velocity of gases by the burner method requires two chief arrangements, namely (1) means for measuring the flows of gases and for proportioning these gases and (2) means for producing and for measuring a suitable flame. Detailed descriptions of such apparatus have appeared in the literature 50/, and that used in the present investigation is essentially similar to these. A diagram of this apparatus is given in Figure 6, and a snapshot showing a general view is reproduced in Figure 7.

The gases were taken from pressure cylinders, air being drawn from a small holder in cases, and their flows were controlled by two needle valves in each gas line. The gases were filtered through glass wool and were dried by passage through two tubes 1-1/8 inches in diameter and at least 7 inches long which were filled with a granular calcium chloride.

In order that the results might be independent of changes in the temperature of the laboratory, all gases were preheated to a standard temperature of 40 degrees Centigrade (104 degrees Fahrenheit). This heating was accomplished by passing the gases through coils of copper tubing which were immersed in a bath of water the temperature of which was controlled automatically. The internal diameter of the copper coils ranged from 1/8 to 3/8 inches and their length from 6 to 13 feet, according to the flow required and to the pressure drop that could be tolerated. Attempted calculations, for purposes of design, of the thermal transfers obtained were unsuccessful; the substantial establishment of equilibrium between the temperatures of the water in the bath and of the gases was verified experimentally by immersing a thermometer in the stream of gases as it issued from the port of the burner. The water in the

50/ See reference S2 for example

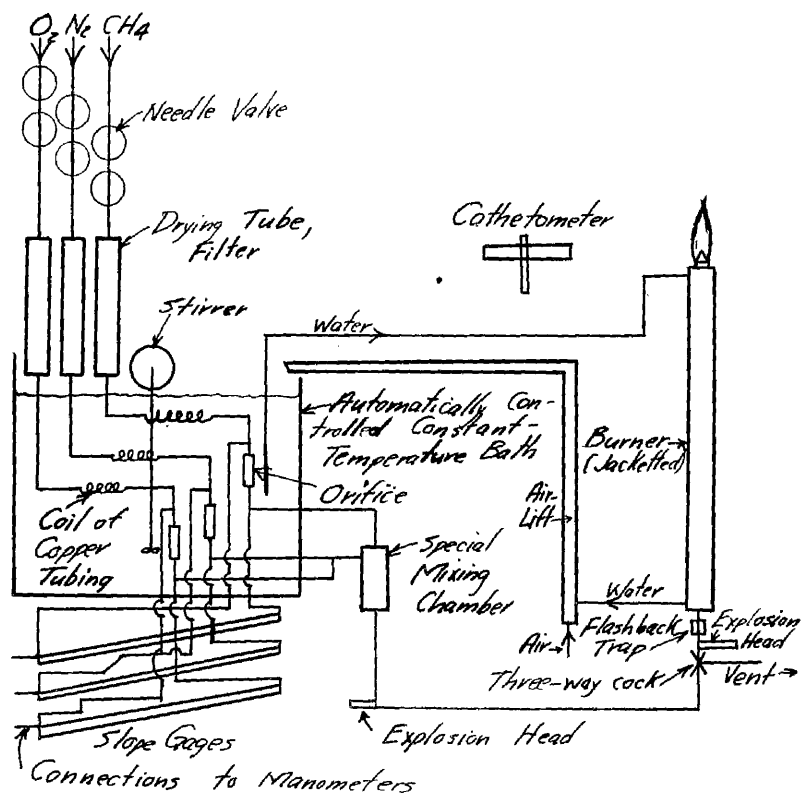
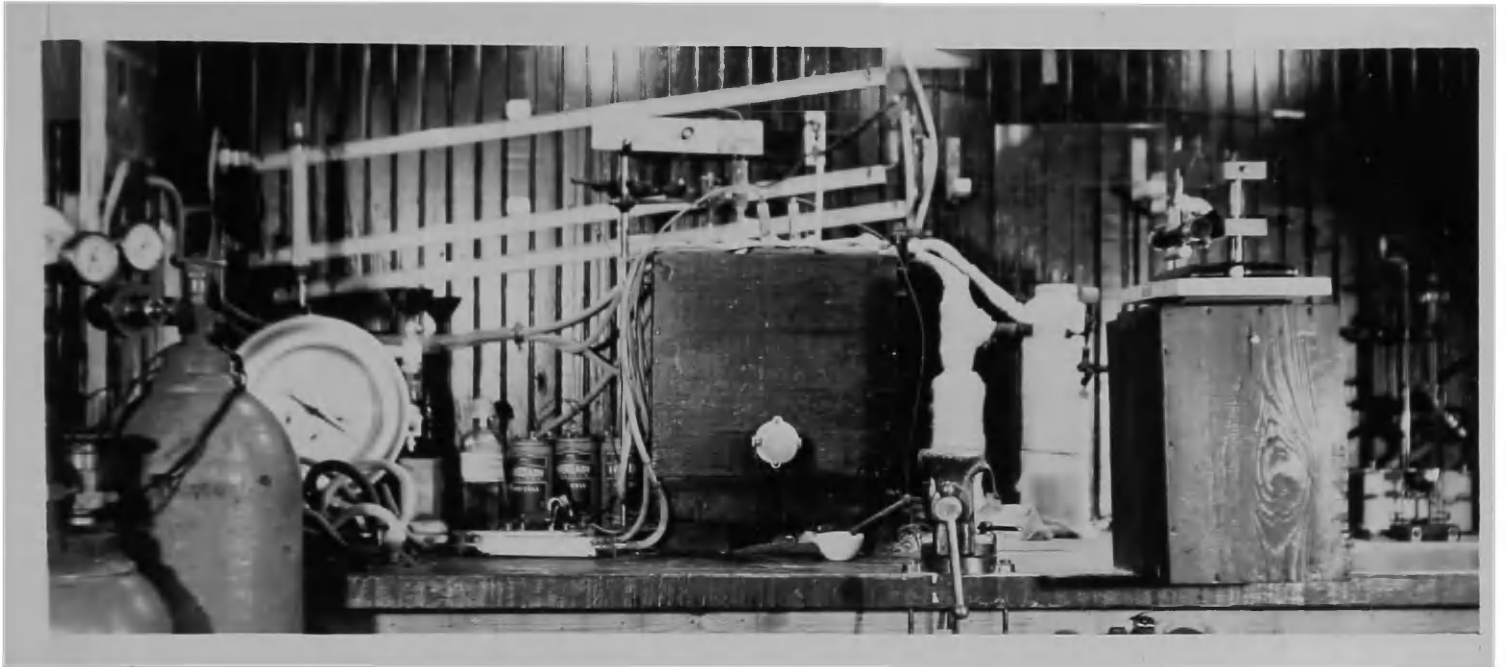


Figure 6. Schematic Diagram of Apparatus Used for Determining Flame Velocities by the Burner Method.

bath was heated by immersed carbon-filament electric bulbs; the temperature was regulated by a simple bulb-type mercury-toluene regulator activating a relay which controlled the flow of current to the heating lamps. Agitation from a stirrer and from other circulation produced by an air pump used to pass the water through the jacket of the burner, as described later, made possible the control of temperature within 0.2 degree Centigrade. A small amount of potassium dichromate was added to the water to prevent the corrosion of metallic parts of the apparatus.

The flows of the gases were determined as volume-rates by orifice-type flowmeters. The orifices, prepared from capillary tubing of Pyrex glass, were immersed in the heated bath to avoid the effects of variations in temperature on their cross-section and resistance to flow. Differential pressures were measured across these orifices by means of slope-gages one meter long with a rise of approximately 10 cm. These gages were provided with enlargements at either end of the "U" to prevent the passage of the liquid into the gas lines in the event of any sudden irregularities in the flow or pressure. Dibutyl phthalate was used in these gages to avoid contamination of the gases by a volatile liquid. Standard meter sticks served as scales.

In addition to the differential flow meters, manometers were provided to measure the pressure of each gas before it entered the orifice. Care was taken to keep this pressure at all times within reasonable limits of the pressure which obtained in the calibration of the orifices, so that errors might be avoided and the necessity of a pressure correction eliminated. As an additional precaution the effects involved were established quantitatively for a critical case in which the rates of flow were near the maximum employed. Some orienting tests, summarized in Table VIII, indicated the mutual reactances between the gas stream as reflected in the pressures before the orifices and defined limits for the variations which might be expected in an extreme case.



**Figure 7. General View of Laboratory Apparatus Used
for Determining Flame Velocities.**

TABLE VIII

SUMMARY OF ORIENTING TESTS SHOWING MUTUAL EFFECTS OF THE
FLOWS IN THE GAS STREAMS ON THE PRESSURES AT THE SEVERAL ORIFICES^{1/}

Test No.	Oxygen		Nitrogen		Methane	
	Flowmeter Reading	Pressure on orifice, cm H ₂ O	Flowmeter Reading	Pressure on orifice, cm H ₂ O	Flowmeter Reading	Pressure on orifice, cm H ₂ O
1	-	-	27.8	8.0	-	-
2	60.0	23.9	27.7	16.2	-	-
3	60.0	26.1	27.7	18.5	10	16.7
4	60.0	27.1	27.7	19.5	30	21.0
5	60.0	28.0	27.7	20.5	55	26.7
6	60.0	29.4	27.7	21.6	80	33.4

<u>1/</u>	<u>Gas</u>	<u>Orifice Number</u>
	Oxygen	19
	Nitrogen	12
	Methane	8

Other tests, Table IX, established the flows for the several conditions of pressure by means of procedures described subsequently. In these tests the pressures on the orifices were arbitrarily varied over the ranges established in Table VIII, and the results show the absence of serious effects of these differences of pressure on the volume-rates through each orifice. The data obtained in these tests agree well among themselves and with the results of routine calibrations, reported later, as indicated in Table IX. The agreement between individual measurements of the present series and also between these results and those reported subsequently average approximately 5 parts in 1000 except for the last tests with orifice number 8. These last tests agree among themselves but differ from the results of routine calibrations by approximately 3 percent; this divergence is due presumably to the short period of flow used in this particular test which magnifies the errors both in measurements of volume and of time.

TABLE IX

EFFECT OF PRESSURE ON THE VOLUME - RATES OF FLOW THROUGH SEVERAL TYPICAL ORIFICES

Setting of Flowmeter ^{1/}	Pressure on orifice ^{1/}	Conditions of Metering			Volume ^{2/} through meter, cu.ft.	Time for flow, sec.	Volume-rate of flow, ^{3/} c.c. dry gas at 40°C. (104°F.) and 30" Hg per second, from	
		Pressure: cm. H ₂ O	Temperature: °F.	Barometer "Hg			<u>Present Measurements</u>	<u>Routine Calibrations</u> ^{4/}
<u>Orifice No. 19, Oxygen:</u>								
60.0	17.6	0.9	81.0	29.93	0.300	94.8	90.2	
60.0	17.6	0.9	81.0	29.93	0.300	95.1	89.9	
60.0	20.7	0.9	81.0	29.93	0.300	94.6	90.4	
60.0	22.5	0.9	81.0	29.93	0.300	94.7	90.3	90.0
60.0	25.9	1.0	81.0	29.93	0.300	94.5	90.5	
60.0	38.7	1.0	81.0	29.93	0.300	94.5	90.5	
<u>Orifice No. 12, Nitrogen:</u>								
27.8	7.4	0.4	80.7	29.93	0.100	127.4	22.3	
27.8	13.6	0.4	80.7	29.93	0.100	127.1	22.4	
27.8	18.0	0.4	80.7	29.93	0.100	126.9	22.4	22.3
27.8	20.0	0.4	80.7	29.93	0.100	126.8	22.5	
27.8	23.1	0.4	80.7	29.93	0.100	126.5	22.5	
<u>Orifice No. 8, Methane:</u>								
10.0	5.3	0.5	80.4	29.91	0.100	98.2	29.0	
10.0	17.1	0.5	80.4	29.91	0.100	97.6	29.2	29.0
80.0	20.6	0.6	80.4	29.91	0.100	43.4	65.5	
80.0	35.0	0.6	80.4	29.91	0.100	43.5	65.4	63.6

^{1/} The settings for the meters for oxygen and nitrogen were chosen from typical conditions for a test at higher rates of flow; the settings for the meter for methane were chosen to cover the extreme range of values which might be encountered in such a test.

^{2/} Volume by meter, under temperature and pressure indicated.

^{3/} In computing these flows it was assumed that the gas was substantially saturated with water vapor during its passage through the meter.

^{4/} Values read from curves plotted from data recorded subsequently in Table X.

The orifices were calibrated by determining the times required for the passage of a definite volume of the gas to be used, as measured by a wet-type displacement meter, for various settings of the slope gages. The gas was metered either before or after passage through the heating coils and orifices, and was either dried carefully after metering and before passing into the orifices in the first case or cooled before metering by passage through coils immersed in a bath of water at the temperature of the room in the second case; the latter procedure was used exclusively when the resistance of the heating coils to flow required an initial pressure higher than a safe value for a wet-type meter. In every set of calibrations it was established by suitable tests for leaks before and after each run that the gas passing through the meter passed through the orifices. Care was taken to assure a steady state in every set of tests. It was assumed that at the relatively low rates of flow encountered the gas was completely saturated with water vapor during its passage through the wet meter.

The two meters used were standard laboratory wet meters which passed 0.1 cubic feet of gas per revolution; the dials were graduated into 100 equal parts. The accuracy of these meters was checked by displacing through them air from a standard gasometer. Further routine checks were made at times simply by running them in series. These tests indicated for both meters very close agreements with the gasometer, i.e., within 2 parts in 1000. In general, integral numbers of revolutions of the meters were used for all calibrations except those at the lowest rates of flow in order to avoid errors from possible differences in the volumes of the separate compartments of the rotor. For tests at the lowest rates of flow, i.e., of the order of 3 cc per sec., fractions of a revolution were used and some duplicate tests indicated that the procedure used was admissible; also, a general lack of dispersion of the data indicated that the volume passed in a fraction of a revolution was practically independent of the position of the rotor for the meters used.

The results of the calibrations of the orifices used in the final tests reported here are listed in Table X, and a typical curve representing the data for the first of these, orifice No. 3 when calibrated with methane, is given in Figure 8.

The gases issuing from the orifices were conveyed through carefully insulated lines into a specially designed mixing chamber where intimate contact and mixing of the constituents for the gas mixture were provided. The uniformity of the mixture was favored further by the subsequent flow of the gases through approximately two feet of 1/2 inch pipe, three ells, a cock, and, in most tests, through a flashback trap.

The flames were produced from this homogeneous mixture on burners prepared from polished seamless brass tubing and conditions were controlled so that laminar flow obtained in all tests. In order to assure knowledge of the volume of gas flowing from the burner it was necessary to assure a standard temperature for this gas; this was done simply by circulating water from the constant-temperature bath through a jacket surrounding the burner. Three burners were used, with internal diameters of 7.92, 4.76 and 3.07 mm. The length of the seamless tube in these burners was approximately 60 cm to favor a perfected condition of flow in the gases issuing from the port. Two of the burners are included in the photograph of Figure 9. They were designed especially for this work. Suitable shields were provided to protect the flames from drafts.

SUMMARY OF CALIBRATIONS OF ORIFICE - TYPE FLOWMETER^{1/}

Setting of slope gage	Volume through meter ^{2/} cu. ft.	Time for flow, sec.	Metering Conditions			Rate of Flow, cc. of dry gas at 104°F., 30" Hg, per second.
			Pressure: 3/ cm H ₂ O	Temperature: 4/ °F.	Barometer "Hg	
<u>Orifice No. 3, Methane:</u>						
15.0	0.020	346.1	11.7	72.2	29.76	1.70
31.2	0.030	353.2	18.0	71.5	29.76	2.52
45.0	0.030	279.5	22.9	71.2	29.76	3.18
63.5	0.050	384.8	28.8	71.0	29.76	3.90
76.3	0.050	336.6	32.8	70.3	29.76	4.47
86.4	0.050	321.6	35.9	70.0	29.76	4.70
<u>Orifice No. 7, Methane:</u>						
19.0	0.100	482.9	7.1	78.0	30.09	6.01
34.4	0.100	376.4	10.3	78.0	30.09	7.74
49.8	0.100	318.7	13.3	77.8	30.09	9.17
63.1	0.100	283.8	15.9	77.8	30.08	10.33
78.1	0.100	255.7	18.7	77.7	30.06	11.49
92.3	0.110	245.3	23.8	77.4	30.06	13.25
<u>Orifice No. 8, Methane:</u>						
9.9	0.100	98.0	0.4	79.0	30.12	28.3
10.0	0.100	96.5	0.4	79.6	30.12	29.8
10.0	0.100	99.1	0.4	79.8	30.12	29.0
24.9	0.100	76.9	0.4	79.8	30.12	37.4
40.0	0.100	63.9	0.4	80.0	30.12	45.0
55.0	0.200	111.3	0.4	80.0	30.12	51.7
65.0	0.150	76.9	0.4	80.0	30.12	56.1
79.9	0.150	67.7	0.5	80.0	30.12	63.7
87.8	0.175	67.6	0.6	80.0	30.12	74.4
<u>Orifice No. 14, Methane:</u>						
17.1	0.100	123.2	11.6	76.8	29.70	23.4
17.3	0.100	123.9	11.6	76.8	29.69	23.4
23.9	0.100	99.7	13.6	76.8	29.69	26.4
30.1	0.100	101.4	15.4	76.8	29.70	28.6
30.2	0.100	101.4	15.4	76.8	29.69	28.6
45.2	0.100	86.1	19.9	76.8	29.70	33.8
59.8	0.100	76.1	24.0	76.8	29.70	38.4
73.5	0.100	69.2	27.8	76.8	29.70	42.4
73.6	0.100	69.1	27.8	76.8	29.69	42.4
87.8	0.100	69.6	34.1	76.8	29.70	47.9
87.8	0.100	61.2	34.1	76.8	29.69	48.2
87.9	0.100	61.2	34.1	76.8	29.70	48.2
<u>Orifice No. 8, Air:</u>						
10.0	0.150	294.9	8.9	76.2	29.95	14.8
20.0	0.210	296.8	13.8	76.3	29.96	20.7
20.1	0.210	295.8	14.0	76.0	29.95	20.8
30.0	0.200	229.8	18.7	75.8	29.96	25.7
40.1	0.200	197.6	23.2	75.8	29.96	29.9
50.1	0.200	173.2	27.1	75.7	29.96	34.3
57.9	0.200	160.6	30.3	75.6	29.97	37.1
<u>Orifice No. 6, Oxygen:</u>						
10.2	0.100	319.2	6.4	79.4	29.98	9.0
21.3	0.100	244.4	9.7	79.4	29.98	11.8
35.4	0.150	294.8	13.8	79.4	29.98	14.8
50.5	0.200	332.7	18.1	79.4	29.98	17.5
50.7	0.200	331.8	18.1	79.4	29.98	17.6
64.8	0.200	269.4	22.1	79.4	29.98	19.9
78.0	0.200	266.3	26.1	79.4	29.98	22.1
<u>Orifice No. 19, Oxygen:</u>						
10	0.200	122.6	0.7	76.0	29.87	47.0
10	0.100	60.5	0.7	76.0	29.87	47.6
10	0.200	122.8	0.6	81.0	29.98	46.4
10	0.200	122.1	0.6	81.0	29.98	46.7
20	0.210	105.1	0.7	76.0	29.87	57.5
30	0.200	86.2	0.8	76.0	29.87	66.8
30	0.300	128.6	0.6	81.0	29.98	66.5
40	0.200	76.5	0.8	76.0	29.87	75.2
50	0.200	69.6	0.9	76.0	29.87	82.7
60	0.200	64.0	1.0	76.0	29.87	90.0
60	0.400	127.3	0.8	81.0	29.98	89.6
<u>Orifice No. 8, Nitrogen:</u>						
10.1	0.200	332.5	10.0	79.3	30.00	17.4
19.9	0.200	256.0	15.2	79.6	30.02	22.7
20.0	0.200	255.8	15.2	79.6	30.00	22.7
30.0	0.250	266.4	20.6	79.2	30.00	27.4
40.0	0.300	271.3	26.8	79.2	30.00	32.5
49.9	0.300	243.1	32.6	79.6	30.02	36.5
49.9	0.300	243.4	32.6	79.6	30.00	36.5
<u>Orifice No. 11, Nitrogen:</u>						
13.8	0.200	184.2	22.7	77.0	29.72	31.7
23.9	0.200	145.3	34.0	77.0	29.73	40.6
33.0	0.200	125.6	43.9	77.0	29.73	47.4
40.7	0.210	119.6	52.8	77.0	29.73	52.8
47.7	0.200	103.0	63.5	77.0	29.73	58.9
47.7	0.200	103.1	63.5	77.0	29.72	58.9
<u>Orifice No. 12, Nitrogen:</u>						
15.0	0.055	92.0	0.4	78.6	30.11	17.2
15.0	0.050	84.0	0.3	78.0	30.11	17.1
15.0	0.050	83.5	0.3	79.0	30.11	17.2
22.4	0.100	142.0	0.4	78.6	30.11	20.3
22.5	0.100	142.0	0.4	78.0	30.11	20.3
30.0	0.100	142.4	0.4	78.6	30.11	23.1
30.0	0.100	144.3	0.4	78.6	30.11	23.2
37.5	0.100	109.5	0.5	78.6	30.11	26.3
37.5	0.100	109.5	0.4	78.7	30.11	26.3
45.0	0.100	90.7	0.5	78.6	30.11	31.7
45.0	0.100	90.0	0.5	78.9	30.11	32.0
45.1	0.100	89.3	0.5	78.6	30.11	32.2

^{1/} Iterative calibrations made as described in text using calibrated wet-type displacement meters.

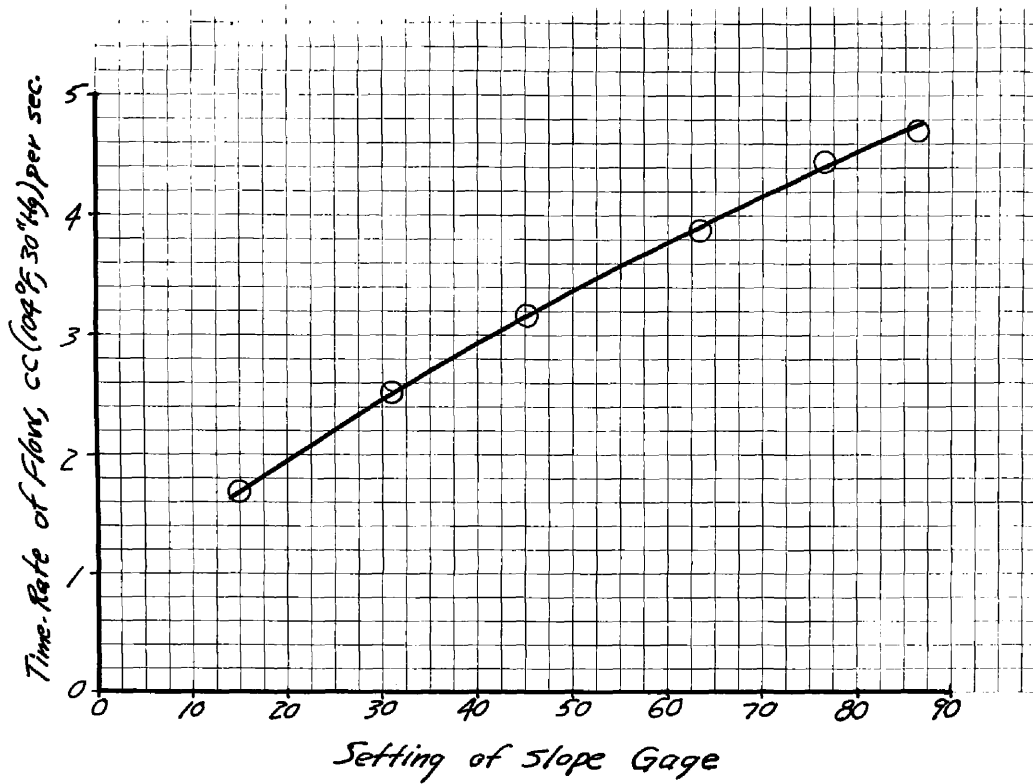


Figure 8. Typical Calibration Curve for Orifice-Type Flowmeter;
Data for Orifice #3, Passing Methane, from Table X.

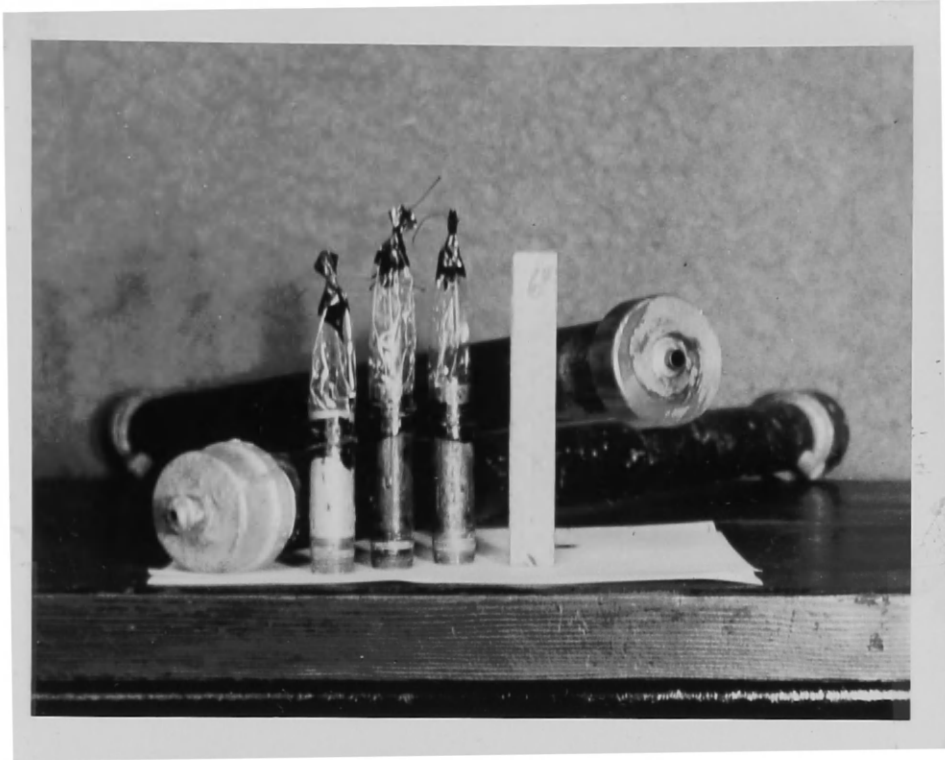


Figure 9. Burners and Explosion-Heads Used in Experimental Work.

Traps were placed at the bases of the burners in attempts to arrest explosions originating in flashback. These were made of fine-mesh brass screens or of fine copper wool packed in a short length of pipe and were provided with a T-cock to divert the gas stream to a flue. However, it was found impractical to arrest by these means certain of the explosions initiated in mixtures containing atmospheres with high concentrations of oxygen, so that provisions were made for the release of pressure developed in the event such an explosion occurred. Explosion heads were made of tubular Cellophane, as shown in Figure 9, and were effective in preventing the destruction of important parts of the apparatus in nearly all cases.

The measurements of the height of the inner cone of the flame were made with an improvised cathetometer illustrated in Figure 10. This device consisted of a mounted telescope, containing cross-hairs, which was fitted with a level. Its vertical movement was regulated by a screw and measured by micrometer-calipers graduated to 0.001 inches. Judging from the data listed in Table XI which were selected at random from iterative routine settings of the device, the reproducibility of the readings was of the order of .001 inches; as routine readings of the heights of the flame were always greater than 0.300 inches, this is reflected in the results as a maximum deviation of 3 parts in 1000.

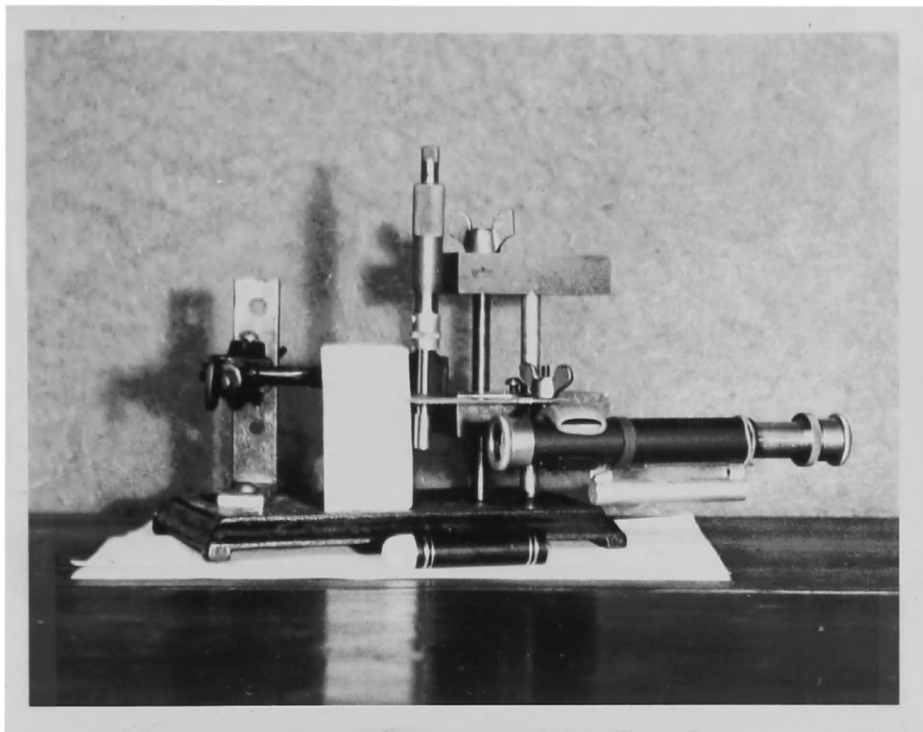


Figure 10. Cathetometer Used for Measuring Heights
of the Flames.

TABLE XIREPRODUCIBILITY OF SETTINGS OF CATHETOMETER^{1/}

(1) Settings	<u>d^{2/}</u>	(2) Settings	<u>d</u>
0.1063	- .0007	0.0900	- .0013
.1025	+ .0031	.0887	0.0000
.1066	-.0010	<u>.0874</u>	<u>+0.0013</u>
<u>.1070</u>	<u>- .0014</u>		
Av. 0.1056	a.d. ^{3/} = 0.0016	Av. 0.0887	a.d. 0.0009
(3) Settings	<u>d</u>	(4) Settings	<u>d</u>
0.1061	-0.0018	0.0816	-0.0003
.1043	.0000	.0813	.0000
<u>.1024</u>	<u>+ .0019</u>	<u>.0810</u>	<u>+ .0003</u>
Av. 0.1043	a.d. 0.0012	Av. 0.0813	a.d. .0002

Average of the a.d.'s \approx 0.001 in.

1/ From routine data, chosen at random.

2/ Deviation d = (Mean - observation).

3/ Average deviation a.d. = $\frac{\sum |d|}{n}$ where n = the number of observations.

CHAPTER 3 - PROCEDURE

The general procedure consisted of the following steps: (1) estimation of the probable flows to produce suitable flames for each set of experiments contemplated, (2) preparation and rough calibration of orifices to obtain these flows, (3) selection and final calibration of orifices, (4) initial tests to determine the suitability of the experimental conditions, and finally (5) the conduct of the tests for flame velocities. Of these steps, only the first and the last two require treatment here.

In estimating the probable flows required to produce suitable flames, the maximum flame velocity to be encountered was judged from values in the literature. ^{51/} A burner was then selected that would permit dynamic equilibrium in a Bunsen flame by producing a linear velocity of efflux approximately five times as great as this maximum flame velocity but still sufficiently low so that the critical value of the Reynolds criterion was not exceeded. From the flows of gases thus derived, a combination of roughly calibrated orifices was selected which would produce the conditions detailed, and these were carefully calibrated as described in the last chapter.

The compositions of the mixtures produced were computed from the flows of the individual gases. This simple procedure made unnecessary innumerable analyses of the gases; it has been found capable of accuracies of the order of 0.1 percent (S2). Experimental verification of the validity of the total flows thus obtained was derived from several tests; in these, the mixed gases were metered in the displacement meter and very good agreement found be-

^{51/} Although widely divergent values appear in the literature for these flame velocities, by suitable (graphical) means a rough estimate could be made of the value to be expected, particularly after the first tests of the present investigation.

tween the observed rates of flow and the rate computed from the settings of the slope gages and from the calibration curves for the orifices. It may be noted that the presence of the small amount of nitrogen in the combustible gas caused a slight variation in the net content of oxygen in the atmosphere in each series of tests with a constant initial ratio of oxygen to nitrogen and with varying amounts of the combustible gas. Computations showed such variations to be beyond the limits of experimental error except in extreme cases in which the atmospheres were very rich in oxygen; in such cases some significant change was introduced. However, the changes could be neglected in general in any single series of mixtures because of the relatively small amount of combustible used. For simplicity, such small effects on the net oxygen content of the atmosphere have been neglected in the calculations.

Initial tests of the suitability of the combination of orifices and burner were made as follows: It was first determined that no leaks existed in the apparatus, as this was essential both to knowledge of the flows from the burner port and to knowledge of the flows of the individual gases from which were computed the compositions of the mixtures. Such tests were usually made by closing the system and by determining whether or not a static pressure of 10 to 20 cm. of water could be retained for approximately four minutes without appreciable decrease, or for approximately one minute when the rates of flow to be used were high. If these tests proved satisfactory, the flow of the atmosphere was then adjusted by introducing the oxygen and nitrogen at the desired rates, and the combustible was admitted. The flame was lighted immediately as the mixture reached its lower limit of inflammability, to avoid dangerous explosions from delayed ignitions. The flow of the combustible was then increased, and if the flame resulting was a Bunsen flame which seated on the port of the burner and which had desirable physical characteristics, the flow of the methane was increased further to the maximum value required to give the richest mixture assigned in preliminary calculations. If

this series of changes gave evidence of producing the range of mixtures desired with flames that remained stable on the burner and possessed the desired characteristics, namely a shape approximating closely a geometrical cone and heights convenient for measurement, the final determinations of flame velocity could be made. In the event of an instability of the flame, such as lifting or flashback (which resulted in explosions), or if the cones were of undesirable characteristics, it was necessary to repeat these initial tests using new conditions.

The appearance of the flames produced in these tests formed a basis for reasonable alterations in the conditions of experiment if suitable flames were not obtained at first. The oxidizing or reducing character of the mixture was of course readily deduced from the appearance of the flame. Further, these tests gave a useful qualitative index of the composition of the mixture producing maximum flame velocity. Thus, on progressive increase of the flow of methane, the height of the inner cone decreased progressively and then increased; since the flow of the methane was in most cases a relatively small fraction of the total flow, the point of minimum height in this series was readily indicative of the position of the maximum flame velocity.

As a consequence of the estimates involved in the initial calculations, several tests of the type described above were usually required before suitable flames were obtained with all mixtures desired. As the work progressed, better estimates were possible and experimental arrangements were developed which were applicable over a wide range of conditions.

In making each observation in the final determinations of flame velocities, all gas-flows were carefully adjusted, the setting of the cathetometer made, the readings of the flowmeters checked, the cathetometer setting checked, and the results then recorded. The time required for this routine eliminated the possibility of inclusion of unobserved errors originating in change in the composition of the gas. Such a change might be due (1) to the allowance of an

insufficient time for the composition of the mixture to attain its proper equilibrium value after having been changed from a previous test, (2) to poor regulation, or (3) to other effects such as dirt in the needle valves. In each series of tests the rate of flow of the methane was increased while the rate of flow and composition of the atmosphere were maintained substantially constant. 52/ After reaching the maximum flow of methane, this flow was reduced to a value near that used for the initial observation, and a reading taken. This procedure furnished a further check on the constancy of conditions throughout the tests; extraneous effects, such as the preheating due to flames of high intensity of combustion which burned close to the port of the burner, were thus placed in evidence. In addition, details such as the establishment of the absence of leaks in the apparatus, precision of the regulation of the temperature, and observations of the pressures on the orifices to assure the applicability of their calibrations without a correction factor for pressures were carefully executed.

52/-In some instances it was possible to extend the scope of the tests by advantageous adjustments of the relations of the flows of atmosphere and of combustible.

CHAPTER 4 - PRECISION OF THE MEASUREMENTS

The results for the concentration of the combustible in the mixtures burned, and for the flame velocities are of primary interest.

Composition of the Mixtures:

It was noted in the preceding chapter that the procedure of producing the mixtures by proportioning them with flowmeters is capable of accuracies of the order of 0.1 percent. In the present work the proportion \underline{x} of methane in the mixtures was computed from the flows of combustible, oxygen and nitrogen designated \underline{C} , \underline{O} , and \underline{N} , respectively, by a simple equation of the form

$$x = \frac{fC}{C + O + N} \quad (18)$$

in which f is the fraction of methane in the combustible, 0.967 as previously noted. This expression may be treated best by setting the total flow $C+O+N$ equal to \underline{Q} so that

$$x = \frac{fC}{Q} \quad (19)$$

Now if \underline{dC} and \underline{dQ} are the absolute precision measures of \underline{C} and of \underline{Q} , the relative error in \underline{x} , written as $\underline{dx}/\underline{x}$, is given by

$$\frac{dx}{x} = \sqrt{\left(\frac{dC}{C}\right)^2 + \left(\frac{-dQ}{Q}\right)^2} \quad (20)$$

The values for the solution of this equation follow from the accuracies of the several measurements of flow. These measurements depend on measurements of volume by a wet-type displacement meter and of time. Other factors such as the reproducibility and the regulation of the settings of slope gages, and the precision of other observations used in computing correction factors also enter. It was indicated in Chapter 2 of this Section that the meters used were found to be in excellent agreement (i.e., within 2 parts in 1000) with a standard gasometer. Routine checks of these meters in-

indicated that this accuracy was in general maintained. Scrutiny of the other errors involved in the measurement of flow and of the data from the routine checks of the meters makes it seem probable that a constant relative error of 0.5 percent is an adequate allowance for the total error in any single measurement of flow 53/. The relative error in the total flow Q is then $\sqrt{3} \times 0.005$ or 0.0087 in the general case in which three separate gases were used. In view of the approximations made this may be written as 0.009.

Substitution of relative errors of 0.005 and 0.009 in equation (20) gives the relative error in x:

$$\frac{dx}{x} = 0.01$$

The values of x in these experiments ranged approximately from 0.10 to 0.30 so that with the lowest values of x recorded, in which the error above would have maximum effect on the absolute error in x, the figures are apparently significant to three decimal places.

The values for the displacement D of the maximum of flame velocity, being derived from two values of x, are thus significant to three decimal places. The precision measure applicable from the foregoing considerations would be $\sqrt{2} \times 0.01$ or 0.014, but this must be amended as will be indicated in the next section after the results have been reviewed.

Values of Flame Velocity:

Errors of the method were considered in Chapter 3 of Section III.
 The basic equation expressing the dynamic equilibrium in the inner cone of the Bunsen flame, which equilibrium forms the basis for the results II herein reported, states that if a quantity of gas Q cm³ per sec. flows from a port and forms thereon a Bunsen cone with an area of S cm², the flame velocity is

53/-The accuracy of these meters is discussed in references B17 and W1.

given by

$$U = \frac{Q}{S} \quad (21)$$

Now if dQ and dS are the precision measures of Q and of S , then the relative error in U , written as du/u , is given most simply by

$$\frac{du}{U} = \sqrt{\left(\frac{dQ}{Q}\right)^2 + \left(\frac{dS}{S}\right)^2} \quad (22)$$

Expression of $\frac{dU}{U}$ as a relative error despite the constant absolute magnitude of the errors contributing to dS is a convenient simplifying assumption which will be justified subsequently.

Of the values needed for the solution of equation (22), the relative error in Q was given previously as 0.009.

S was derived from measurements of the diameter of the burners and of the heights of the inner cones. The relationship between these quantities is

$$S = \pi r \sqrt{r^2 + h^2} \quad (23)$$

The diameters of the burners were measured to 0.001 inches using micrometer calipers, so that the precision measure of r is

$$dr = 0.0013 \text{ cm.}$$

The heights of the cones were also measured to 0.001 inches or 0.0025 cm; since h was derived from two such observations the precision measure of h is $\sqrt{2} \times 0.0025$,

or

$$dh = 0.0035 \text{ cm.}$$

The average deviation derived previously (Table XI, page 65) from repeated settings of the cathetometer is approximately one-third of this value. The errors dr and dh are reflected in dS according to the equation

$$ds = \sqrt{\left(\frac{\partial S}{\partial r} dr\right)^2 + \left(\frac{\partial S}{\partial h} dh\right)^2} \quad (24)$$

Differentiation of equation 23 gives

$$\frac{\partial S}{\partial r} = \frac{\pi(2r^2 + h^2)}{\sqrt{r^2 + h^2}}$$

and

$$\frac{\partial S}{\partial h} = \frac{\pi rh}{\sqrt{r^2 + h^2}}$$

so that

$$dS = \sqrt{\left[\frac{\pi(2r^2 + h^2)}{\sqrt{r^2 + h^2}} dr \right]^2 + \left[\frac{\pi rh}{\sqrt{r^2 + h^2}} dh \right]^2} \quad (25)$$

The factors dr and dh were, as noted, of constant absolute magnitude in the experiments, and it was necessary to consider the effect of the magnitude of r and h on the relative importance and contributions of these factors to the total error in S , since it was desired to express the final error in U as a relative error. Three sets of data representing the extremes of the ranges for r and h were selected for calculations of dS in equation (25). The results of these calculations are listed in Table XII and show that in the extreme the value of dS is of the order of 0.9 percent, and that this value is not increased by the variations in r and h over the ranges encountered. A series of approximate calculations based on average values of the heights of the cones rather than on the extreme (minimum) values listed in Table XII gave a weighted average for the relative error in S of 0.8 percent.

The maximum determinate error in U is now obtained by substitution of these data in equation (22):

$$\begin{aligned} \frac{dU}{U} &= \sqrt{0.009^2 + .009^2} \\ &= 0.009 \end{aligned}$$

In view of the nature of these computations it seems admissible to modify this

to

$$\frac{dU}{U} = 0.01.$$

TABLE XII

ANALYSIS OF EFFECTS OF ERRORS IN MEASUREMENT OF THE FLAME^{1/}

Data		Calculated Results			Number of Series of tests to which the data are Applicable
Radius of burner, cm.	Height of cone, cm.	Surface of cone, cm. ²	Absolute Error in Surface of cone, ^{2/} cm ²	Percent Relative Error in Surface of cone ^{3/}	
0.154	1.000	0.490	0.0045	0.92	6
0.238	0.630	0.503	0.0040	0.80	1
0.396	0.500	0.794	0.0050	0.63	1

Weighted average percent relative error in surface of cone = 0.87

-
- ^{1/} Data selected to show maximum effects of errors of constant magnitude in radius r and height h on the precision measure of the surface s.
- ^{2/} From equation (6).
- ^{3/} Values in preceding column divided by the surface of the cone and multiplied by 100.

Conclusions:

The foregoing considerations indicate a maximum determinate relative error of the order of 1 percent in the value of \underline{x} , the fraction of methane in the mixtures, and of 1 percent in the values of \underline{U} , the flame velocity. Other considerations relating to the error of the method of measuring flame velocities, as discussed in Chapter ³/₂ of Section II, indicate that the latter figure should be increased somewhat. It is believed, however, that maximum flame velocities as measured in this work should be accurate within 1 to 2 percent. It will be seen that the reproducibility of the data to be recorded in the next chapter is in harmony with such a degree of precision in nearly all cases, and it may be noted that particular precautions were exercised in choosing procedures and in making measurements to eliminate so far as possible the effects of any extraneous variables or of other indeterminate errors.

CHAPTER 5 - DATA AND RESULTS

The essential data from the experimental measurements of the flame velocities in mixtures of methane with atmospheres composed of oxygen and nitrogen and containing between 20 and 80 percent oxygen are summarized in Table XIII. The data for each series of tests are listed approximately in the order in which they were obtained.

Deductions of the maximum flame velocities and of the corresponding concentrations of methane were made from large-scale graphs prepared from the data of Table XIII. Rectification of representative curves was attempted and it developed that no simple form of equation would represent the data accurately. Combinations of equations were found which would fit the data satisfactorily, but as these were purely empirical, disclosed nothing fundamental relating to the nature of the curves, and required a laborious series of computations for determination of the constants involved, a more direct approach was made which should result in reliable deductions.

TABLE XIII

SUMMARY DATA OF DETERMINATIONS OF FLAME VELOCITIES IN MIXTURES OF METHANE WITH ATMOSPHERES CONTAINING OXYGEN AND NITROGEN IN VARIOUS PROPORTIONS 1, 2/

Data						Results			
Combustible Meter Setting	Flows of the Gases 5/		Nitrogen		Height of Inner Cone of Flame, 6/ cm.	Volume Fraction of Oxygen in Atmosphere, a	Volume Fraction of Methane in Mixture, 7/ X	Flame Velocity, U, cm/sec.	
	Meter Flow cc/sec.	Oxygen Meter Setting	Meter Flow cc/sec.	Meter Flow cc/sec.					
Series 1 - A: Approximately 21 volume-percent oxygen in atmosphere; burner 0.792 cm. in diameter. 2/ Orifices used: Methane, No. 3; Air, No. 2. 3/									
		Air Meter Flow							
28.9	2.40	35.8	28.1	0.809	0.209	.076	27.2		
28.3	2.37	33.1	27.0	0.710	0.209	.078	29.0		
33.8	2.67	35.2	27.9	0.532	0.209	.084	32.9		
37.3	2.83	34.8	27.7	0.552	0.209	.089	36.1		
43.8	3.13	39.2	29.6	0.564	0.209	.092	38.2		
41.3	3.00	34.8	27.7	0.522	0.209	.094	37.6		
48.4	3.31	39.2	29.6	0.569	0.209	.097	38.1		
52.9	3.50	39.1	29.5	0.596	0.209	.102	37.1		
57.3	3.69	39.1	29.5	0.692	0.209	.107	33.4		
63.2	3.93	38.9	29.4	0.831	0.209	.114	29.1		
69.2	4.18	38.8	29.4	1.077	0.209	.120	23.5		
68.8	4.16	37.3	28.3	1.143	0.209	.122	21.9		
68.7	4.15	33.3	27.1	1.355	0.209	.128	18.0		
68.6	4.15	30.9	25.0	1.477	0.209	.133	15.8		
68.7	4.15	26.8	24.1	1.688	0.209	.142	13.1		
62.4	3.90	37.3	28.8	0.857	0.209	.115	27.8		
50.8	3.43	37.5	28.9	0.591	0.209	.102	36.4		
37.5	2.83	37.7	28.9	0.626	0.209	.086	34.4		
Series 1 - B: Conditions same as in Series 1 - A.									
		Air Meter Flow							
35.9	2.75	38.5	29.3	0.664	0.209	.083	33.3		
37.5	2.83	38.6	29.3	0.657	0.209	.085	33.7		
40.2	2.96	38.2	29.1	0.629	0.209	.089	34.6		
42.4	3.06	38.5	29.3	0.606	0.209	.091	35.9		
45.3	3.20	38.7	29.4	0.590	0.209	.095	36.9		
47.9	3.30	38.8	29.4	0.613	0.209	.097	35.8		
49.3	3.35	38.7	29.4	0.607	0.209	.099	36.3		
52.3	3.48	38.9	29.5	0.628	0.209	.102	35.7		
53.9	3.55	39.0	29.5	0.637	0.209	.104	35.4		
56.6	3.65	39.4	29.7	0.668	0.209	.106	34.5		
61.1	3.85	39.6	29.8	0.787	0.209	.110	30.7		
50.6	3.41	39.7	29.8	0.620	0.209	.099	36.2		
41.0	3.00	39.7	29.8	0.636	0.209	.088	35.2		
36.3	2.73	39.8	29.9	0.689	0.209	.082	33.0		
Series 1 - C: Conditions same as in Series 1 - A.									
		Air Meter Flow							
39.4	2.92	41.0	30.4	0.722	0.209	.085	32.5		
42.4	3.06	41.1	30.4	0.662	0.209	.088	34.8		
45.1	3.10	41.2	30.4	0.669	0.209	.089	34.6		
44.4	3.20	41.2	30.4	0.658	0.209	.092	35.2		
45.9	3.22	41.3	30.5	0.635	0.209	.092	36.2		
47.3	3.27	41.3	30.5	0.636	0.209	.093	36.1		
48.2	3.32	41.4	30.5	0.638	0.209	.095	36.2		
49.4	3.36	41.3	30.5	0.632	0.209	.096	36.4		
49.4	3.36	41.3	30.5	0.635	0.209	.096	36.3		
50.6	3.41	41.3	30.5	0.640	0.209	.097	36.2		
51.8	3.47	41.4	30.5	0.628	0.209	.099	36.7		
53.0	3.50	41.5	30.6	0.640	0.209	.099	36.4		
54.3	3.57	41.5	30.5	0.648	0.209	.101	36.0		
56.1	3.64	41.4	30.5	0.656	0.209	.103	35.8		
58.0	3.72	41.5	30.6	0.701	0.209	.105	34.2		
48.0	3.31	41.5	30.6	0.626	0.209	.094	36.8		
39.2	2.91	41.0	30.4	0.719	0.209	.084	32.6		
Series 2 - A: Approximately 32 volume-percent oxygen in atmosphere; burner 0.476 cm. in diameter. 2/ Orifices used: Methane, No. 1; Oxygen, No. 6; Nitrogen, No. 3. 3/									
20.0	6.16	78.0	22.1	44.8	34.6	1.329	0.390	.095	62.2
27.7	7.08	78.0	22.1	44.7	34.5	1.035	0.390	.107	80.2
34.6	7.73	78.0	22.1	44.8	34.6	0.905	0.390	.116	92.2
43.1	8.52	78.0	22.1	44.9	34.7	0.765	0.389	.126	109
50.2	9.19	78.0	22.1	44.9	34.7	0.710	0.390	.134	114
57.1	9.80	78.0	22.1	44.9	34.7	0.687	0.389	.142	119
61.9	10.2	78.0	22.1	44.9	34.6	0.647	0.389	.147	123
69.9	11.0	78.0	22.1	44.8	34.7	0.643	0.390	.156	131
76.7	11.6	78.1	22.1	45.0	34.7	0.634	0.389	.164	134
85.1	12.4	78.0	22.1	44.7	34.5	0.634	0.390	.173	136
89.1	12.7	78.0	22.1	44.7	34.5	0.655	0.390	.177	133
92.0	13.0	78.0	22.1	44.9	34.7	0.699	0.389	.180	128
95.0	13.3	78.0	22.1	44.8	34.6	0.744	0.390	.183	120
97.2	13.5	78.0	22.1	44.7	34.5	0.771	0.390	.186	116
97.0	13.5	69.8	20.7	39.9	32.4	0.819	0.391	.195	104
79.9	11.9	77.8	22.1	44.7	34.5	0.628	0.390	.167	136
79.7	11.9	78.0	22.1	44.9	34.7	0.639	0.389	.167	134
20.0	6.16	78.0	22.1	44.8	34.6	1.321	0.390	.095	62.5
Series 2 - B: Conditions same as in Series 2 - A.									
65.9	10.6	78.0	22.1	44.8	34.6	0.644	0.390	.152	131
73.0	11.3	78.0	22.1	44.9	34.7	0.634	0.389	.160	134
79.0	11.8	78.0	22.1	44.8	34.6	0.626	0.390	.166	137
85.1	12.4	78.0	22.1	44.8	34.6	0.631	0.390	.173	137
91.1	12.9	78.0	22.1	44.8	34.6	0.664	0.390	.179	132
66.0	10.6	77.9	22.1	44.7	34.5	0.640	0.390	.152	131
Series 3 - A: Approximately 50 volume-percent oxygen in atmosphere; burner 0.307 cm. in diameter. 2/ Orifices used: Methane, No. 14; Oxygen, No. 19; Nitrogen, No. 11. 3/									
17.5	23.5	15.6	52.7	40.0	52.9	1.305	0.499	.176	204
27.5	27.7	15.6	52.7	39.9	52.8	1.319	0.499	.201	208
33.0	29.7	15.7	52.8	39.9	52.8	1.319	0.500	.212	211
37.8	31.3	15.6	52.7	39.9	52.8	1.338	0.500	.221	210
45.1	33.8	15.5	52.6	39.8	52.7	1.368	0.500	.235	209
60.3	38.7	15.6	52.7	40.0	52.9	1.419	0.499	.259	209
17.5	23.5	15.5	52.6	39.8	52.7	1.274	0.500	.176	208
Series 3 - B: Conditions same as in Series 3 - A:									
20.2	24.8	15.5	52.7	39.9	52.8	1.282	0.500	.184	209
27.6	27.8	15.6	52.8	39.9	52.8	1.274	0.500	.201	215
33.1	29.8	15.8	52.9	39.9	52.8	1.265	0.501	.213	220
37.5	31.2	15.5	52.7	39.9	52.8	1.275	0.500	.221	221
45.1	33.8	15.8	52.9	39.8	52.7	1.308	0.501	.234	219
55.1	37.0	15.9	53.0	39.8	52.7	1.399	0.501	.251	210
19.8	24.5	15.7	52.7	39.8	52.7	1.274	0.500	.182	210
Series 4 - A: Approximately 55 volume-percent oxygen in atmosphere; burner 0.307 cm. in diameter. 2/ Orifices used: Methane, No. 14; Oxygen, No. 19; Nitrogen, No. 11. 3/									
25.5	27.0	20.3	57.7	32.2	46.9	1.170	0.551	.198	231
32.5	29.6	20.4	57.8	32.3	47.0	1.144	0.551	.212	241
40.3	32.2	20.6	58.0	32.1	46.8	1.147	0.553	.227	245
45.2	33.8	20.7	58.1	32.4	47.1	1.186	0.552	.235	241
49.9	35.3	20.1	57.5	31.9	46.6	1.198	0.552	.244	239
59.7	38.5	20.5	57.9	32.3	47.0	1.279	0.552	.259	230
25.4	26.9	20.0	57.4	32.1	46.8	1.151	0.551	.198	234
Series 4 - B: Conditions same as in Series 4 - A.									
26.4	27.2	20.5	57.8	32.0	46.8	1.148	0.553	.200	236
32.4	29.5	20.5	57.8	32.3	47.0	1.156	0.551	.212	239
37.4	31.2	20.3	57.6	32.3	47.0	1.162	0.551	.222	240
42.6	32.9	20.3	57.6	31.9	46.8	1.172	0.551	.232	240
47.4	34.4	20.7	58.0	32.2	46.9	1.183	0.553	.239	242
57.6	37.8	20.7	58.0	32.2	46.9	1.290	0.552	.256	228
25.9	27.1	20.3	57.6	32.0	46.8	1.146	0.551	.199	236

TABLE XIII (Continued)

SUMMARY DATA OF DETERMINATIONS OF FLAME VELOCITIES IN MIXTURES OF METHANE WITH ATMOSPHERES CONTAINING OXYGEN AND NITROGEN IN VARIOUS PROPORTIONS 1/2/

Data						Results			
Combustible Meter Setting	Flows of the Gases 5/		Nitrogen		Height of Inner Cone of Flame, 6/ cm.	Volume Fraction of Oxygen in Atmosphere, 7/	Volume Fraction of Methane in Mixture, 1/	Flame Velocity, U, cm/sec.	
	Flow Meter Setting	Oxygen Flow cc/sec.	Meter Setting	Flow cc/sec.					
Series 5 - A: Approximately 60 volume-percent oxygen in atmosphere; burner 0.307 cm. in diameter. 4/ Orifices used: Methane, No. 11; Oxygen, No. 19; Nitrogen, No. 11. 3/									
14.9	22.3	24.6	61.9	23.1	40.0	1.149	0.608	.173	222
25.0	26.8	24.5	61.8	22.9	39.9	1.079	0.608	.201	244
34.8	30.3	24.5	61.8	22.9	39.9	1.051	0.608	.221	258
45.0	33.8	24.7	62.0	22.9	39.9	1.065	0.609	.240	261
55.0	37.0	24.5	61.8	22.9	39.9	1.105	0.608	.257	258
64.9	40.2	24.2	61.5	22.9	39.9	1.149	0.607	.273	253
75.0	43.6	24.3	61.5	23.0	40.0	1.233	0.606	.290	242
83.5	46.5	24.1	61.4	23.0	40.0	1.374	0.605	.303	222
14.7	22.2	24.5	61.8	23.0	40.0	1.132	0.607	.173	225
Series 5 - B: Conditions same as in Series 5 - A.									
30.0	28.7	24.5	61.8	23.0	40.0	1.053	0.607	.212	254
37.5	31.3	24.2	61.6	23.0	40.0	1.038	0.606	.227	262
45.0	33.8	24.2	61.6	23.0	40.0	1.055	0.606	.240	263
52.5	36.2	24.2	61.6	22.9	39.9	1.101	0.607	.253	257
60.0	38.6	24.3	61.7	23.0	40.0	1.126	0.606	.265	256
30.0	28.7	24.3	61.7	23.1	40.0	1.030	0.607	.212	259
Series 6 - A: Approximately 65 volume-percent oxygen in atmosphere; burner 0.307 cm. in diameter. 4/ Orifices used: Methane, No. 11; Oxygen, No. 19; Nitrogen, No. 11. 3/									
40.0	32.0	35.0	71.3	21.1	38.4	1.133	0.650	.218	257
47.4	34.4	35.0	71.3	21.2	38.5	1.138	0.649	.231	261
55.0	36.9	35.0	71.3	21.0	38.3	1.143	0.651	.244	263
59.9	38.6	35.0	71.3	21.1	38.4	1.152	0.650	.252	264
64.9	40.2	35.1	71.4	20.9	38.2	1.152	0.651	.259	267
75.0	43.6	35.0	71.3	21.0	38.3	1.320	0.651	.275	239
40.0	32.0	35.0	71.3	21.2	38.5	1.130	0.649	.218	257
Series 6 - B: Conditions same as in Series 6 - A:									
39.9	32.0	35.0	71.3	21.0	38.3	1.135	0.651	.218	256
47.5	34.4	35.2	71.5	21.2	38.5	1.129	0.650	.230	263
53.9	36.5	35.1	71.4	21.1	38.4	1.138	0.650	.241	264
59.3	38.4	35.0	71.3	20.9	38.2	1.150	0.651	.251	264
65.1	40.3	35.2	71.5	21.3	38.6	1.156	0.649	.259	267
69.9	41.9	35.0	71.3	21.0	38.3	1.228	0.651	.267	253
75.0	43.6	35.0	71.3	20.9	38.2	1.326	0.651	.275	238
39.9	32.0	35.0	71.3	20.9	38.2	1.135	0.651	.219	256
Series 7 - A: Approximately 70 volume-percent oxygen in atmosphere; burner 0.307 cm. in diameter. 4/ Orifices used: Methane, No. 5; Oxygen, No. 19; Nitrogen, No. 11. 3/									
15.1	32.2	42.0	76.8	15.1	33.0	1.098	0.700	.219	265
24.9	37.4	42.0	76.8	15.2	33.0	1.107	0.700	.246	273
30.1	40.1	42.1	76.9	15.1	32.9	1.107	0.700	.258	273
35.1	42.8	42.0	76.8	15.0	32.9	1.112	0.700	.271	273
40.2	45.3	42.0	76.8	15.0	32.9	1.142	0.700	.283	279
50.2	48.5	42.0	76.8	15.0	32.9	1.255	0.700	.301	261
14.9	32.0	42.0	76.8	15.0	32.9	1.093	0.700	.218	266
Series 7 - B: Conditions same as in Series 7 - A.									
15.1	32.2	42.0	76.9	15.0	32.9	1.086	0.701	.219	268
25.1	37.6	42.0	76.9	15.0	32.9	1.085	0.701	.247	276
30.1	40.1	42.0	76.9	15.0	32.9	1.110	0.701	.259	277
35.4	42.8	42.3	77.0	15.1	33.0	1.133	0.700	.271	277
40.5	45.3	42.3	77.0	15.1	33.0	1.157	0.700	.282	276
49.9	49.3	42.0	76.9	15.0	32.9	1.266	0.701	.300	259
15.0	32.1	42.2	77.0	15.1	33.0	1.088	0.700	.219	268
Series 8 - A: Approximately 80 volume-percent oxygen in atmosphere; burner 0.307 cm. in diameter. 4/ Orifices used: Methane, No. 5; Oxygen, No. 19; Nitrogen, No. 11. 3/									
20.0	34.8	60.0	90.0	27.8	22.3	1.026	0.800	.228	294
30.0	40.1	60.0	90.0	27.8	22.3	1.026	0.801	.270	311
37.0	43.6	59.8	90.0	27.5	22.2	1.026	0.801	.284	310
44.0	46.7	59.6	89.6	27.6	22.3	1.050	0.801	.300	310
52.5	50.7	60.0	90.0	27.6	22.3	1.080	0.799	.312	303
60.0	53.7	59.7	89.7	27.8	22.4	1.124	0.800	.337	285
72.5	60.0	59.4	89.6	27.5	22.2	1.236	0.801	.229	299
20.0	34.8	59.7	89.7	27.5	22.2	1.005	0.801	.229	299
Series 8 - B: Conditions same as in Series 8 - A.									
30.0	40.0	59.6	89.3	28.0	22.4	1.046	0.799	.254	298
38.1	44.1	59.7	89.4	27.7	22.3	1.060	0.800	.273	302
45.8	47.5	58.9	89.2	27.9	22.3	1.082	0.800	.288	301

1/ Determinations by the burner method; purity of gases: oxygen and nitrogen 99.5 volume percent, methane, 96.7 percent.
 2/ All gases dried with calcium chloride and preheated to 40 degrees, C. Quiescent flames produced by a perfected laminar flow in all cases.
 3/ Data obtained in the calibration of these orifices were given in Table I.
 4/ Special burners jacketted with water at 40 degrees, C. prepared from seamless brass tubing polished internally.
 5/ Flows recorded as cm³ of dry gas per sec. at 40 degrees, C., 30 in. Hg.
 6/ Only flames closely approximating geometrical cones were used; heights given above the port of the burner.
 7/ Corrected for fraction of methane (0.967) in the combustible gas.

By suitable relation of scales for the coordinates U and x , previously defined as the flame velocity and the volume-fraction of methane in the mixture burned, respectively, a smooth curve which represented closely the experimental data could be drawn. These curves were placed so that the sum of the residuals for the experimental points was zero; this sum was determined graphically. 54/ The values of the maximum flame velocity were read from these curves, and the compositions of the corresponding mixtures were likewise estimated from the points of tangency of horizontal lines drawn across the maxima of the curves. The latter values, (designated x_m), were then computed from values read from the curves for equal increments in composition with the help of the differentiated form of Newton's formula for interpolation 55/. An example of this process is given by computations detailed in Table XIV which are based on the sample curve represented in Figure 11, prepared from the data for series 2-A in Table XIII. The detailed results of these calculations are listed in Table XV. In Table XVI is presented a final summary of the experimental results. It will be noted in these tables that in general the agreement between duplicate tests is quite satisfactory. Excellent agreement will also be noted between the computed and estimated values of the concentration of methane in the mixture of maximum flame velocity.

54/-Divergences (scattering) in the data indicated that the method of averages furnished an adequate criterion of the correctness of the representation of the data.

55/-See pp. 214-217 and 234-237 of reference L5.

TABLE XIV

SAMPLE CALCULATION OF RESULTS FROM DATA IN TABLE XIII

1. Data plotted in Figure 11 and a smooth curve drawn so that the sum of the residuals for the experimental points is zero.
2. Estimated coordinates of the maximum of this curve are

$$u = 136 \text{ cm/sec.}, \chi_m = 0.170.$$

3. Computation of χ_m ^{1/}:

χ	<u>u, Values from Curve</u>	<u>Successive Differences</u>		
		Δ_1	Δ_2	Δ_3
0.160	133	-	-	-
0.165	135	+2	-	-
0.170	136	+1	-1	-
0.175	134	-2	-3	-2
0.180	126	-8	-6	-3

$$\frac{dy}{dx} = 0 = \frac{1}{h} \left[a_0 + (2n-1) \frac{b_0}{2!} + (3n^2 - 6n + 2) \frac{c_0}{3!} \right]$$

$$h = .005, a_0 = 2, b_0 = -1, c_0 = -2$$

$$0 = \frac{1}{0.5} \left[2 + (n - 0.5)(-1) + \left(\frac{3n^2 - 6n + 2}{6} \right) (-2) \right]$$

$$6n^2 - 6n - 11 = 0, n = 1.96, \text{ or } 2.0$$

$$\text{So } \chi_m = .160 + .005 \times 2.0 = .170$$

4. Displacement of the maximum:

$$\text{Stoichiometric mixture: } \text{CH}_4 + 2\text{O}_2 + 2 \frac{(1 - 0.389)}{0.389} \text{N}_2$$

$$\chi_s = .164 = \frac{1}{3 + 2 \left(\frac{0.611}{0.389} \right)}$$

$$\chi_m = .170$$

$$\underline{\underline{D = .006}}$$

^{1/} From the differentiated form^s of Newton's formula for interpolation.

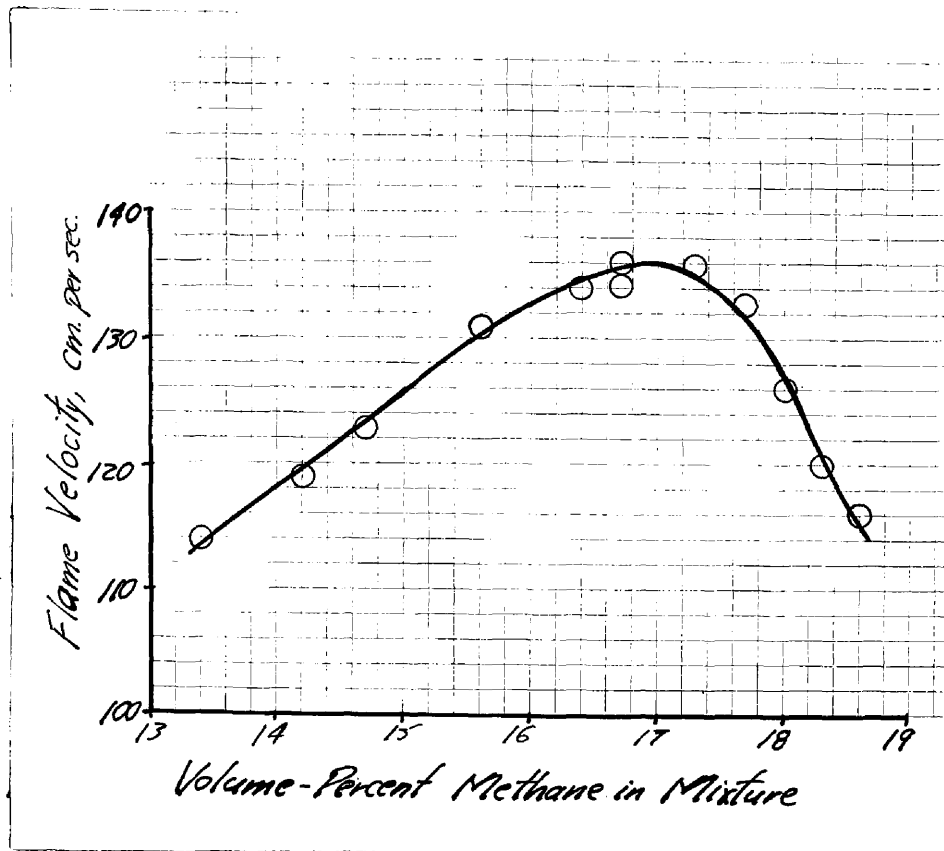


Figure 11. Representation of Large-Scale Plot Used in
Deducing Coordinates of the Maximum of Flame
Velocity; Data from Series 2 - A of Table XIII.

The values for the displacements of the mixtures producing maximum flame velocity from the stoichiometric mixture as listed in Table XVI suggest a relationship between this displacement and the fraction of oxygen in the atmosphere used. The relationships are indicated by the curves of Figure 12. These relationships are qualitative chiefly as a consequence of uncertainties in the estimates of the values for x_m , but they establish definitely that for atmospheres approaching the extremes 56/ in composition the values of the displacement D_v or of the percent displacement are low, whereas with an atmosphere containing approximately equal fractions of oxygen and nitrogen the values are much higher and pass through maxima.

The primary interest of this investigation is thus answered positively by data showing for mixtures containing methane a regular relationship between the displacement D_v or the percent displacement and the fraction of oxygen in the atmosphere used for combustion, in contrast to inconsistencies noted in the literature previously cited, and paralleling indications for gases other than methane, as cited.

56/-i.e., approaching pure oxygen or an atmosphere high in nitrogen and barely capable of propagating flame.

TABLE XV

DETAILED COMPILATION OF RESULTS FROM TABLE XIII

Number of Series	Volume Fraction of Oxygen in Atmosphere, a	Volume - Fraction of Methane in the Stoichiometric Mixture, $s+$	Fraction of Methane in Mixture of Maximum Flame Velocity, χ_m			Displacement of the Mixture of Maximum Flame Velocity, D	Maximum Flame Velocity, U_m cm/sec.	Notes
			From Curve	Computed	Best Values			
1-A	0.209	.095	0.096	.097	.097	0.002	38.1	Approximate values; initial series of tests.
1-B	0.209	.095	0.097	.097	.097	0.002	36.4	—
1-C	0.209	.095	(0.097)	.097	.097	(0.002)	36.4	Data somewhat scattered; χ_m approximate, U_m definite.
2-A	0.390	.163	0.170	.170	.170	0.007	136	—
2-B	0.390	.163	(0.170)	.170	.170	0.007	137	—
3-A	0.500	.200	(0.215)	-	-	(0.015)	211	Data do not establish χ_m .
3-B	0.500	.200	0.216	.215	0.215	0.015	221	—
4-A	0.552	0.216	(0.225)	.225	.225	(0.009)	243	Scant data in range of χ_m ; value for this approximate.
4-B	0.552	0.216	0.230	.228	.228	(0.012)	242	Data somewhat inconclusive as to χ_m .
5-A	0.607	0.233	0.242	0.243	0.243	0.010	261	—
5-B	0.607	0.233	(0.240)	-	-	-	263	Data do not establish χ_m accurately.
6-A	0.650	0.245	(0.254)	-	-	(0.009)	(265)	χ_m not conclusively established.
6-B	0.651	0.246	(0.254)	-	-	-	(265)	—
7-A	0.700	0.259	(0.265)	0.265	0.265	0.005	278	Rather flat maximum.
7-B	0.701	0.260	(0.265)	0.265	0.265	0.005	277	—
8-A	.800	0.286	0.288	.287	.287	0.001	311	—
8-B	.800	-	-	-	-	-	302	Incomplete data.

TABLE XVI

FINAL SUMMARY OF RESULTS FROM TABLES XIII AND XV

Number of Series	Volume Fraction of Oxygen in Atmosphere	Volume - Fraction of Methane		Displacement of the Mix- ture of Maximum Flame Velocity D_v	Percent Displacement, $\frac{D_v}{\chi_{st}} \times 100$	Maximum Flame Velocity, cm/sec	Remarks
		in Stoichiometric Mixture χ_{st}	in Mixture of Maximum Flame Velocity χ_m				
1	0.209	0.095	0.097	0.002	2.1	36.4	Series 1-A omitted
2	0.390	0.163	0.170	0.007	4.3	137	--
3	0.500	0.200	0.215	0.015	7.5	216	--
4	0.552	0.216	(0.227)	(0.011)	5.1	243	χ_m approximate.
5	0.607	0.233	0.243	0.010	4.3	262	--
6	0.651	0.246	(0.254)	(0.008)	3.3	265	χ_m approximate.
7	0.701	0.260	0.265	0.005	1.9	278	--
8	0.800	0.286	0.287	0.001	0.4	307	--

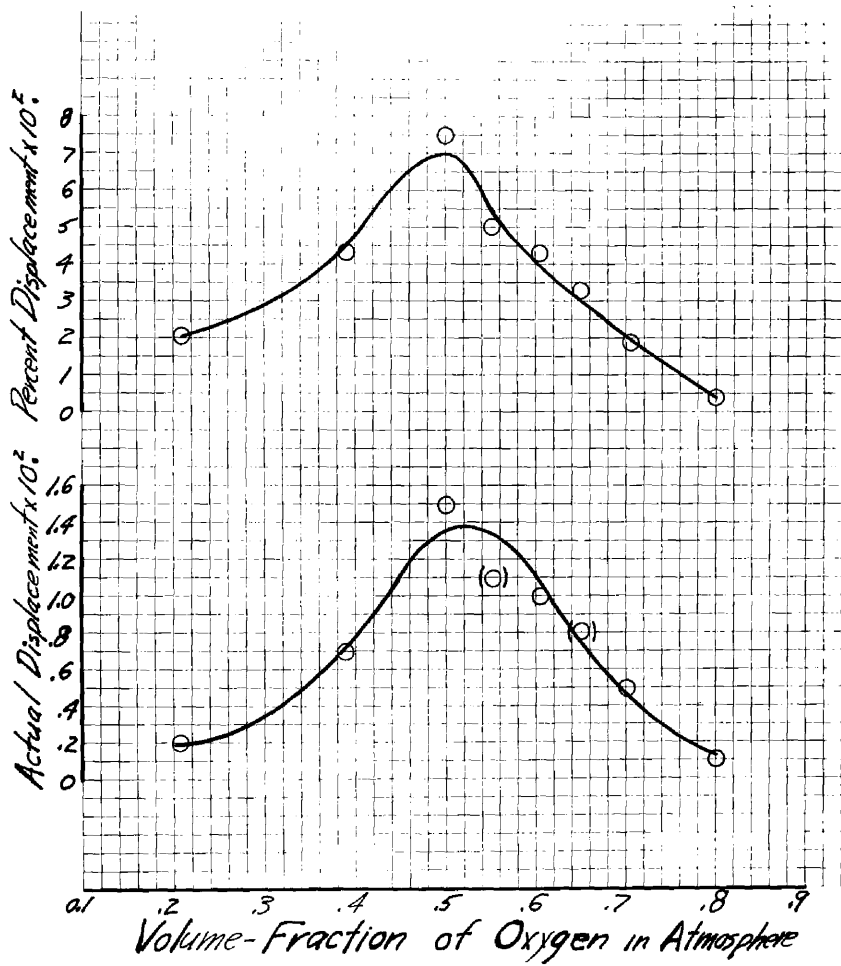


Figure 12. Relation between the Displacements of the Mixtures giving Maximum Flame Velocities for the Combustion of Methane and the Composition of the Atmosphere Used for the Combustion; see Table XVI.

Interesting data for the effect of the concentration of oxygen in the atmosphere on the flame velocities are also evident from Tables XIII and XVI. A common plot of these data, Figure 13, shows the nature of the family of curves and discloses the general relationships between the three variables represented (a being treated as a parameter). The values of the maxima of flame velocity are represented in Figure 14 as functions of the composition of the atmosphere. 57/

57/ For the range $0.2 \leq a \leq .8$ this relationship may be represented approximately by an equation of the type $y = ax^b - c$.

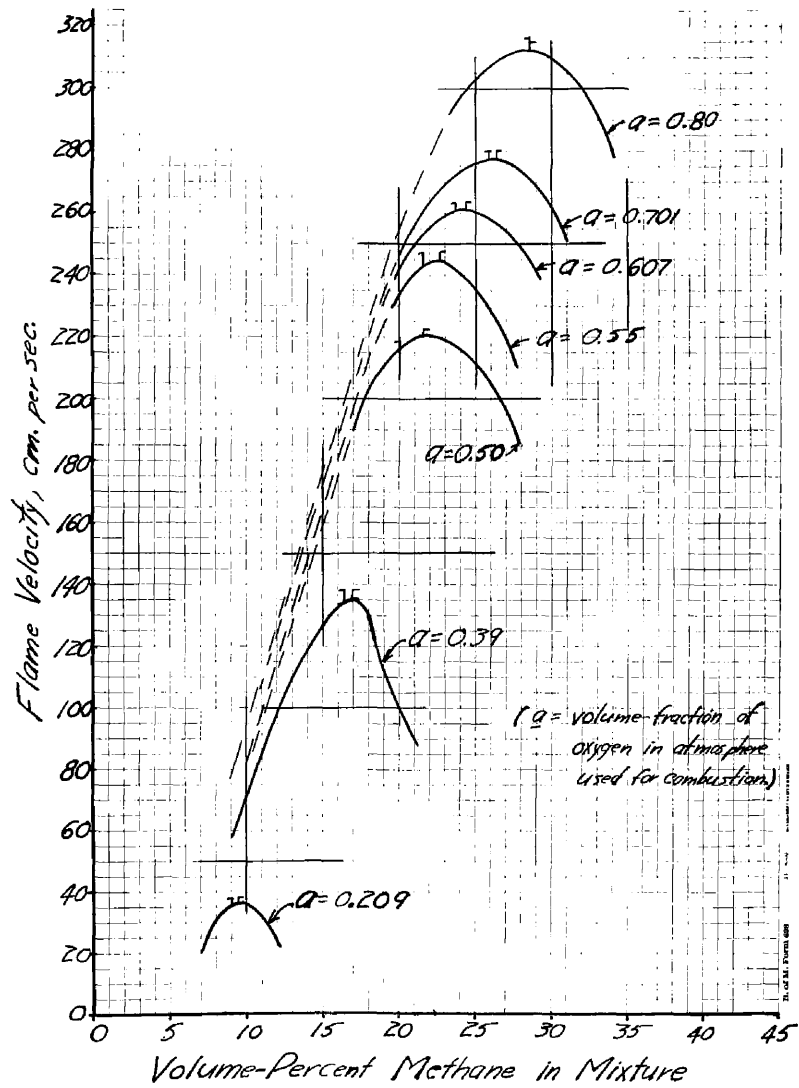


Figure 13. Relations between the Flame Velocity in the Combustion of Methane and the Content of Methane in the Mixture, for Combustion with Various Atmospheres.

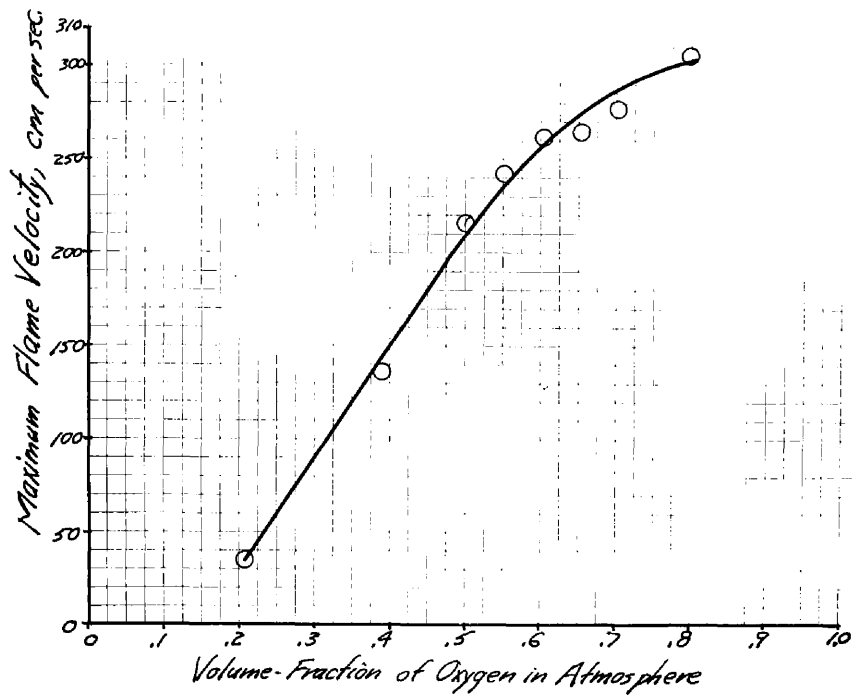


Figure 14. Relation between the Maximum Flame Velocity in the Combustion of Methane and the Content of Oxygen in the Atmosphere used for the Combustion.

IV - CONCLUSION

CHAPTER 1 - COMPARISONS OF RESULTS WITH VALUES IN THE LITERATURE

Values for the Displacements:

In common with many previous measurements of flame velocities for methane, those presented in the last chapter show in general relatively small values for the displacement of the mixture giving maximum flame velocity from the equivalent mixture. However, the relationships established between the displacements and the concentration of oxygen in the atmosphere stand in marked contrast to results deduced from previous measurements. Thus, while irregularities are shown for the percent displacement for methane when this is represented as a function of the composition of the atmosphere both in Figures 3 and 5 derived from previous measurements, the curve in Figure 12 established by the present work suggests a continuous relationship exhibiting a maximum. Further, in contrast to the irregularities shown in Figure 3 and to the relative constancy in the displacement D_{γ} except for combustion with pure oxygen as shown in Figure 5, the corresponding curve in Figure 12 deduced from the present measurements again shows a continuous relationship that also exhibits a maximum.

The curves for the displacement D_{γ} represented as a function of the composition of the atmosphere as deduced from the data of Jahn (J1), Figure 5, show for hydrogen and carbon monoxide substantially the same type of regularity as suggested for methane by the results of the present investigation. In view of the emphasis placed in the present series of measurements on the range of mixtures giving close to maximum flame velocity, it seems that acceptance of the characteristic relationship as shown in Figure 12 is compelled. This relationship is common then to both types of combustible gases.

The other relationships for the percent displacements are of collateral interest; a significant point is the establishment of a continuous relationship for methane in Figure 12, complementing the continuous relationships for hydrogen and carbon monoxide in Figure 5. The existence of a maximum in the curve deduced from the present measurements and the absence of such a maximum for hydrogen and carbon monoxide in Figure 5 is only a consequence of the relative magnitudes of the displacements and contents of combustible for equivalence for the various gases and of differences in the rates of change of these factors with the composition of the atmosphere.

Values for the Flame Velocities:

The value for the maximum flame velocity for combustion of methane with air and the relationship of the flame velocity to the composition of the mixtures for this case agree well with previous measurements by similar methods. The maximum value of 36.4 cm per second recorded in Table XVI is in substantial agreement with values recently reported, such as 35 (B18), 37 (B11), (B12) and about 39 (S2) cm. per second.

Other data with which comparisons may be made are those of Jahn (J1), and as indicated in Table XVII there is agreement in order of magnitude between these measurements and those of the present investigation. For this comparison, values of the maximum flame velocities were read from Figure 14 for convenient values of concentration of oxygen in the atmosphere and from a similar curve prepared from data given by Jahn. The divergences between the two sets of data, Table XVII, are of variable magnitude and average about 15 percent. This agreement seems satisfactory in view of the probable differences in the compositions of the gases used in the two sets of tests, of the different initial temperatures of the mixtures (which would make the present values somewhat greater than those of Jahn), and of the absence of available details of the apparatus used by Jahn.

TABLE XVII

COMPARISON OF MAXIMUM FLAME VELOCITIES FOR METHANE BURNED
WITH VARIOUS ATMOSPHERES

Volume-Fraction of Oxygen in Atmosphere	Maximum Flame Velocity, cm. per sec.	
	From Jahn ^{1/}	From Present Measure- ments
0.2	30	30
0.3	78	95
0.4	127	156
0.5	170	213
0.6	212	255
0.7	250	285
0.8	282	305
1.0	333	320 ^{2/}

^{1/} Jahn, G., *Zündvorgang in Gasgemischen*, R. Oldenbourg, Berlin, 1934;
values read from a large-scale curve prepared from data given by Jahn
on page 19 of this paper.

^{2/} Extrapolated for comparison..

The data derived in the present work, although not extended to combustion with pure oxygen, produce interesting evidence in connection with the divergence in published results for the flame velocities of methane burned with oxygen. The original measurements of these flame velocities were made by Ubbelohde and Dommer (U3) by the burner method. These authors were not successful in obtaining data to define the complete curve for flame velocities because this velocity became so great with mixtures near equivalence that even in a 2 mm. burner turbulent effects were encountered that indicated that the limiting critical velocity had been exceeded. Nevertheless, flame velocities of 6 m. per second with 40 percent methane in the mixture and of 7.2 m. per second with 35.6 percent methane were obtained. Stevens' measurements were the next reported, and were obtained by the method originated by this author, using the propagation of flame in constant-pressure bombs. These data (S3) gave a complete curve for the flame velocities showing a maximum of about 620 cm. per sec. with a mixture close to equivalence. The rough correspondence between these data and those of Ubbelohde and Dommer has been cited as evidence of the equivalence of measurements by the burner method and the constant-pressure bomb (B11). However, the more recent measurements of Jahn (J1) gave in contrast a maximum flame velocity, of 333 cm. per sec. and hence introduced a discrepancy that has not as yet been explained. A comparison of the results of the present work with these others adds weight to the results obtained by Jahn; in addition to the general agreement of the present data with those of Jahn for the range $0.2 \leq a \leq 0.8$, extrapolation of the curve of Figure 14 gives a value of ca. 320 cm. per sec. for the flame velocity of methane burned with oxygen, agreeing well with the value reported by Jahn. The divergence noted between the results obtained by Jahn and those of Stevens and of Ubbelohde and Dommer is thus emphasized by the present results. This divergence has not been explained. It seems probable that the use of such a

small burner by Ubbelohde and Dommer might have introduced important errors, and the correspondence between the values of Ubbelohde and Dommer and of Stevens is only rough and may be fortuitous. 58/ More data are needed to reconcile the divergence but in the absence of this it would seem admissable to accept tentatively a value of approximately 330 cm. per sec. for the flame velocity of methane burned with oxygen.

58/-The recent work on the method developed by Stevens mentioned on page 27 has indicated the necessity for revision of much of the earlier data chiefly because of the effects of water vapor on the flame velocities; this factor is of minor importance in the combustion of methane, and would not per se cast doubt on the results of Stevens.

General:

It was noted in section II that there exist fundamental questions of the aptness of various considerations in connection with the details of the slow propagation of flame. Crucial experiments are not needed, however, to decide between purely thermal considerations and others involving the role of activated particles; it is generally recognized that the former considerations are definitely inadequate in this connection, and that despite the complexities introduced by the latter factors, future advances must take account of their effects.

Although this conclusion may be viewed as definite in connection with the detailed mechanism and inner chemism of the propagation of flame, there still exists a basic question of the practical utility of results obtained from considerations based solely on thermal concepts. The data developed in the present investigation prove rather crucial in this connection.

Discussion of Previous Relationships:

Some interesting facts have been noted in connection with the adequacy of purely thermal considerations for practical problems involving the gross features of the propagation of flame. As noted in Section II, many experimental observations are in qualitative accord with predictions based on the thermal theory and ^{among these} predictions are some of greatest practical importance, such as the limits of inflammability, and the effects on the rates of flame propagation of preheating and of the diameters of tubes 59/. More recently, the work of Jahn

interesting

59/-An additional observation, noted previously, relates to the absence of the displacement in the case of the combustion of producer gas with air. This was advanced by Payman (P2) and elaborated by Payman and Wheeler (P3). The phenomenon is particularly striking when one considers that the displacement for carbon monoxide, the chief combustible constituent of the gas, is the greatest known for common combustibles. An explanation for this important practical fact followed considerations of both normal and inverse combustions: considering the burning of producer gas as an example of the combustion of an atmosphere of oxygen and nitrogen with an inflammable atmosphere of nitrogen and combustible, these authors point out that it is readily conceivable that the inert present in the producer gas might balance the nitrogen in the air so that a very small displacement would be noted. This deduction is, of course, in accord with experiment.

(J1) has indicated good agreement between the thermal theory and the effects produced on the flame velocity by changing the concentration of oxygen or the character of the inert in the atmosphere used for combustion. These agreements have in general been strictly qualitative; it should be noted that the application of the Nusselt equation for flame velocities is a semi-empirical process.

In contrast to these verifications, certain outstanding practical observations, noted previously, seem at variance with these considerations. The effects produced on the flame velocity by preheating and by change of pressure and the effects of these changes on the content of combustible required for maximum flame velocity are neither uniform nor in accord generally with predictions based on an expression of the type of equation 14 which represents the elaborated thermal theory, as noted in section II. For example, an increase in the displacement D_v would seem required by equation 14 as a result of increased initial temperature, but while such an increase was noted in section II for some gases it was conspicuously absent for others; the indication derived seems of little utility.

Dependence of the Displacement D_v on the Oxygen Content of the Atmosphere:

The outstanding observations made in the past of the effect of the concentration of oxygen in the atmosphere used for combustion on the displacement D_v were confined principally to indication that this displacement should disappear when the atmosphere is pure oxygen. Payman and Wheeler (P3) advanced measurements of spacial flame speeds in tubes for mixtures with oxygen of methane and of hydrogen as proof of this; subsequent experiments made by other methods have verified this conclusion for methane (J1), (S3) but have not been in accord with this in the case of hydrogen (J1).

Other observations of effects on the displacement related chiefly to the heat capacity of inerts, and it may be inferred from these arguments

that as the concentration of oxygen increases there should be a progressive decrease in the displacement D_V .

Jahn gave detailed consideration to the displacement D_V , as noted in section II. In common with Payman (P2) this author noted that the factor a representing the concentration of oxygen in the atmosphere appeared in the expression for the reaction velocity and that it influenced only the absolute amount of the effect of mass action or of reaction velocity. Payman stated (P2) that provided this factor a remains constant, the composition of the atmosphere does not affect the content of combustible required to produce the maximum effect of the factor of reaction velocity. Jahn also viewed this factor a as a parameter, but made a statement 60/ for which there seems no a priori reason; it seems that this author appends to the statement above an observation that the composition of the atmosphere can have no effect on the content of combustible required for maximum flame velocity. This author noted, however, that as the inert content of the atmosphere decreased the mixture giving maximum flame velocity approached more nearly the equivalent mixture for each of the three gases studied; only in the case of methane did these two mixtures coincide.

Some original considerations based on the generalized Nusselt equation (Equation 14 of page 14) may be adduced to illustrate a mechanism by which the effect established in this investigation might possibly have been foreseen from the thermal theory. It should be understood that there are assumptions involved in such reasoning that seem questionable and hence detract from its cogency; examples are the assumption of the applicability of the law of mass action with the use of initial concentrations of reactants in the expression for the reaction velocity, and the assumption of the adequacy of the fundamental tenets of

60/-From page 12 of ref. J1: "Die Zusammensetzung der Atmosphäre hätte demnach nur Einfluss auf den Absoluten Betrag des Massenwirkungseffektes und damit der Reaktionsgeschwindigkeit, nicht aber auf den für das Maximum geforderten Brenngasgehalt."

the purely thermal theory, as discussed previously. Before presenting a detailed analysis it may be noted generally that an approach may be made through consideration of the mutual effects of the factors of thermal effects and of reaction velocity as they appear in the generalized Nusselt equation; this consideration must of necessity rest on the evaluation of the respective weights of these factors. For purposes of this analysis the effects of the first factor (i.e. of thermal effects) may be summarily stated to be of minor importance: this is admissible because systematic consideration of the effects of variations in the quantity \underline{a} on the several elements contributing to the factor of thermal effects indicates that such variations should have no marked effect on the weight of this factor. It might be expected that the magnitude of the displacement D_V would be least for smallest values of \underline{a} in view of the variable importance of dissociation in contributing indirectly to the displacement. However, in any case the mixture giving maximum weight to the thermal factor would be close to the equivalent mixture. Coming to the other factor, of reaction velocity, it may be noted in common with the conclusion reached by several investigators that when \underline{a} is unity, i.e. when the atmosphere is pure oxygen, the weight of the effect of reaction velocity in demanding a displacement D_V vanishes, while in general as \underline{a} decreases from unity this weight increases. It seems conceivable that although the apparent absolute magnitude of the displacement demanded by the factor of reaction velocity patently would increase as \underline{a} decreases because of the indications from the law of mass action, the concurrent operation of the variable \underline{a} might cause the weight of this effect and hence the displacement to pass through a maximum and eventually to decrease when \underline{a} becomes very small. This then would account for the characteristic relationship developed in the present investigation. A more detailed analysis follows:

It will be recalled that the displacement is a consequence, according to this theory, of a competition between the factors representing the reaction velocity and the thermal effects in an expression such as that given by Jahn in equation 14. As noted, it seems that it is admissible for simplicity to concede that the weight of the factor representing thermal effects may be substantially constant, and that the maximum for this factor is attained in a mixture near equivalence, regardless of the composition of the atmosphere. Now, following the general reasoning of the proponents of the theory, it seems that the magnitude of the displacement will depend largely on the weight of the factor of reaction velocity, as noted in the last paragraph. Specifically, for the combustion of carbon monoxide or of hydrogen, the mass action product calls for a maximum of reaction velocity with a mixture containing $2/3$ combustible, while for methane this mixture would contain $1/3$ combustible. The contents of combustible required for equivalence for these gases decrease, of course, with decrease in \underline{a} . These relationships are indicated in Figure 15,A, and the divergence of the curves for maximum mass action product and equivalent mixtures, indicated as \underline{d} in the figure, is seen to increase for all three gases as \underline{a} decreases, contributing a progressively greater measure to the weight of the mass action factor. The figure also indicates a greater absolute divergence for carbon monoxide and for hydrogen than for methane, suggesting, in the absence of complicating factors, larger displacements for the first two gases, as observed experimentally. The other factor contributing to the weight of the total factor for reaction velocity is given in equation 14 simply as proportional to the square root of \underline{a} in the cases of carbon monoxide and hydrogen, and to \underline{a} for methane. The variations of this constituent with \underline{a} are obvious, but are represented in Figure 15, B, to facilitate discussion. Now the total weight of the factor of reaction velocity will be given by the product of these two effects; it at once becomes evident that as a consequence of the competition

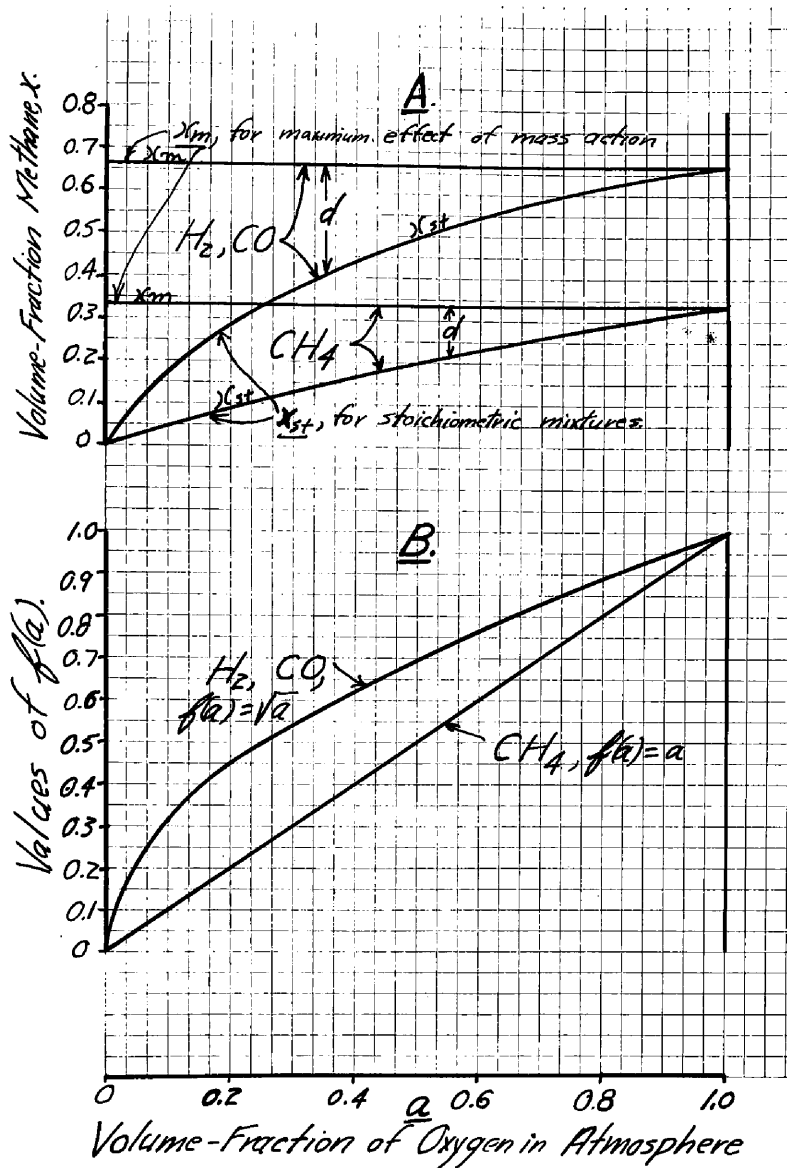


Figure 15. Curves for Discussion of Adduced Explanation of the Relationship Established in this Investigation; see Text, from Page 91.

between the values \underline{d} and the effects of \underline{a} in this product, this weight and with it the displacement D_V increase to a maximum as \underline{a} decreases from unity and then decrease when \underline{a} becomes very small. This is the effect observed experimentally (Figure 12).

In figure 5, the maxima for the displacements for carbon monoxide and for hydrogen, when represented as dependents of the factor \underline{a} , are exhibited concurrently for these gases at a noticeably lower value of \underline{a} than in the case of methane as shown in the relation developed in the present work, Figure 12. That this effect would be expected from the above qualitative reasoning may be seen from Figure 15. Qualitatively, the contribution of the portion involving \underline{a} to the total weight of the factor for the reaction velocity decreases much more slowly at first, i. e., following initial decreases in \underline{a} from unity, in the case of hydrogen and carbon monoxide than for methane, but more rapidly at later stages when \underline{a} is very small. This would result in a slower decrease in the contribution to the weight of the factor of reaction velocity from this source, and would account for the attainment of the maxima of the displacements for hydrogen and for carbon monoxide at a lower value of \underline{a} than for methane. The same conclusion would be indicated by the relatively greater divergence of the curves for the first two gases as shown in Figure 15, A. This conclusion is supported by the following analysis: (A)-For the combustion of hydrogen or of carbon monoxide the content of combustible for stoichiometric equivalence in mixtures with atmospheres containing a volume-fraction \underline{a} of oxygen may be given as $x_{st} = \frac{2a}{2a+1}$ so that the difference \underline{d} in Figure 15-A is $\frac{2}{3} - \frac{2a}{2a+1}$ or $\frac{2-2a}{6a+3}$; since the other contributing factor is proportional to \sqrt{a} , the weight \underline{W} of the mass action factor demanding a displacement will be of the form $\frac{2\sqrt{a-2a^{3/2}}}{6a+3}$ which has a maximum for $12a^{5/2} + 18a^2 - 15a + 3 = 0$ or for a value of \underline{a} near 0.17 (checked by change of sign of first derivative from + to - and by

a negative second derivative). (B)-For the combustion of methane, \underline{d} is similarly related to \underline{a} through $\frac{2-2a}{3a+6}$, \underline{W} is given by $\frac{2a-2a^2}{3a+6}$, and a maximum exists for $a^2+4a-2=0$ or for $\underline{a} = 0.45$ (second derivative negative). These values check the qualitative conclusions noted, and the numerical correspondence of the results for the values of \underline{a} corresponding to the maximum values of D_V in Figures 5 and 12 is striking.

Conclusions:

In the absence of experimental evidence one might have predicted qualitatively the effect established in this investigation of the concentration of oxygen in the atmosphere on the displacement D_V from thermal considerations that are admittedly inadequate in connection with the detailed mechanism of the propagation of flame. It is suggested on these grounds that despite the inadequacies noted in the thermal theory, and despite the necessity for inclusion of other considerations in the detailed study of the propagation of flame, the thermal theory is a valuable practical tool and indeed the best available on which to base predictions, in the absence of experimental data, of important practical effects in gaseous combustion.

CHAPTER 3 - ON TECHNICAL ASPECTS OF THE RESULTS

The importance of data for flame velocities in the problems of the utilization of gases is now rather generally recognized. However, general appreciation is apparently lacking of certain of the applied fundamental concepts in the rating of gases and in the control of combustion. Some outstanding points pertinent to these matters were summarized recently by the writer (D2, D3). Examples of this lack are undue stress on maximum flame-outputs, and lack of thorough exploitation of control of combustion through control of the composition of the mixtures burned. Maximum flame-outputs are of unquestioned importance but an emphasis on ranges of values attainable would seem proper in view of operations such as the heating of coke-ovens in which it is extremely important to maintain uniformly low flame-outputs to assure even heating of large surfaces of refractories. Further, it has been common practice to pre-mix gases in industrial firing in nearly combining proportions with the atmosphere used; this practice is neither logical nor generally productive of any optimum condition.

A fundamental approach to the general rating of gases and to the control of combustion is afforded by the flame-output function. In view of the extensive treatment of this concept by Brückner and collaborators and others 61/, and of a recent consideration of essential applied aspects by the writer (D3), details need not be given here. The form of the expression for the specific flame-output 62/ offers a guide to important effects produced by the composition of the mixture burned. Thus, the slope of the branches of

61/-For examples see reference B19, B20, B18, B21, B22, and G3.

62/- $J_s = \frac{u \times W}{k}$, in which J_s is the specific flame-output, or rate of release of k energy per unit of port area, u is the flame velocity, W is the lower heating value either of the primary mixture or of the total combustible fed to the burner, and k is a constant for standard flames, usually taken as 0.5, that expresses the ratio of areas of port and inner cone, or of flame velocity and velocity of flow of unburned gas from the burner.

curves representing flame-outputs as functions of the composition of the primary mixture and the positions of the maxima of primary and total flame-outputs are determined by similar functional relationships for the flame velocity and the heating value. These factors determine, then, the range of control available; scrutiny of published data discloses very extensive possible variations in flame-outputs as a direct consequence of variation in the composition of the mixture burned.

The results herein recorded for the combustion of methane are substantially applicable to common natural gases that are of great technical importance. Although enrichment with oxygen of atmospheres for use in large-scale technical combustion operations is not yet feasible economically, the data of the present investigation place emphasis on an important phenomenon that is now cognizable as common to both types of technical gaseous fuels, namely the characteristic relationship between the displacement D_V and the concentration of oxygen in the atmosphere used for combustion. Since the displacement D_V is a function of the composition of the atmosphere, it would be expected that the displacements from the equivalent mixture of the mixtures giving maximum flame-outputs 63/ would also vary with the composition of the atmosphere. This is of evident importance in technical problems involving the attainment of high intensities of combustion. The relationship between the displacement D_V for mixtures giving maximum flame velocities and the displacements D_J for mixtures giving maximum flame-outputs may be seen from the form of the flame-output function. The displacements D_J will obviously be determined by the position of the maximum of the flame velocity and by the relative rates of change of the flame velocity and heating values with change in the composition of the mixture burned. The maximum for primary flame output will correspond in general to

^{These}
63/ - ~~This~~ displacements of mixtures giving maximum flame-outputs will be referred to as the "displacements D_J ."

a content of combustible between that for equivalence and for maximum flame velocity, and that for the total flame output will obtain with an excess of combustible greater than that in the mixture giving maximum flame velocity.

These effects are not as evident or striking in the case of the combustion of methane as with other gases giving larger values for the displacements D_v , but values for flame outputs for methane are nevertheless of pointed interest. The determination of these values was not a primary object of this work, but sufficient data were developed to allow good estimates of the coordinates of the maxima attainable. Thus, the sample calculation for the combustion of methane with air, summarized in Table XVIII and represented graphically in Figure 16, illustrates the points noted and discloses extensive ranges of flame-outputs available as a result of variation of the composition of the mixture burned.

A summary of similar calculations based on all of the data for flame velocities obtained in the present work is given in Table XIX and in Figure 17. In making certain of these calculations and of those in Table XVIII, more figures have been retained to indicate trends than are justified from considerations of precision. A striking increase of maximum flame-outputs is immediately evident from these data, and a summary of interesting results is given in Table XX. These show that the maximum specific primary flame-output increases very rapidly and approximately linearly with increase in a and that a range of maximum values of about 25-fold is made available by enrichment of the atmosphere up to 80 per cent oxygen. Since values are attainable that are much lower than the maxima, the overall available range is of the order of approximately 45-fold. Similarly, total flame-outputs increase greatly with increase in a and the range of intensities of combustion made available in the region $0.2 \leq a \leq 0.8$ is seen to be of the order of 50-fold. The displacements of the maxima of flame-outputs are also seen to vary with the composition of the atmosphere used for combustion; for the

TABLE XVIII

SAMPLE CALCULATIONS OF SPECIFIC FLAME-OUTPUTS: MIXTURES OF
METHANE AND AIR^{1/}

Volume Percent Combustible in Mixture	Flame Velocity ^{2/}		Lower Heating Values, Btu per cu. ft. ^{3/}		Specific Flame Output	
	cm. per ft. per sec.	sec.	Primary Mixture ^{4/}	Total Combustible	Btu per sq. ft. per sec Primary	Total
7.5	26.8	.879	68.6	68.6	121	121
8.0	30.3	.995	73.1	73.1	145	145
8.5	33.7	1.11	77.7	77.7	173	173
9.0	36.9	1.21	82.2	82.2	199	199
9.5	38.1	1.25	86.3	86.8	216	217
10.0	37.7	1.24	85.9	91.4	213	227
10.5	34.7	1.14	85.4	95.9	195	219
11.0	31.2	1.02	85.0	101	173	206
11.5	27.8	.912	84.5	105	154	192
12.0	23.6	.774	84.1	110	130	170
12.5	20.0	.656	83.6	114	110	150
13.0	17.0	.558	83.2	119	92.8	133

^{1/} Based on a constant k of 0.5 in $\frac{J_s}{V_s} = \frac{u \times w}{k}$ in which $\frac{J_s}{V_s}$ = specific flame output, u = flame velocity, w = lower heating value, and k = constant for standard flame, \cong ratio of areas of port and inner cone or of velocities of flow and flame.

^{2/} Taken from smooth curve for data of series 1A of Table 13.

^{3/} Based on 913.8 Btu per cu. ft. at 60°F., 30 in. mercury, dry gas, from A. G. A. Combustion, p. 38 (1932).

^{4/} i.e., lower heating value corresponding to combustion of primary mixture.

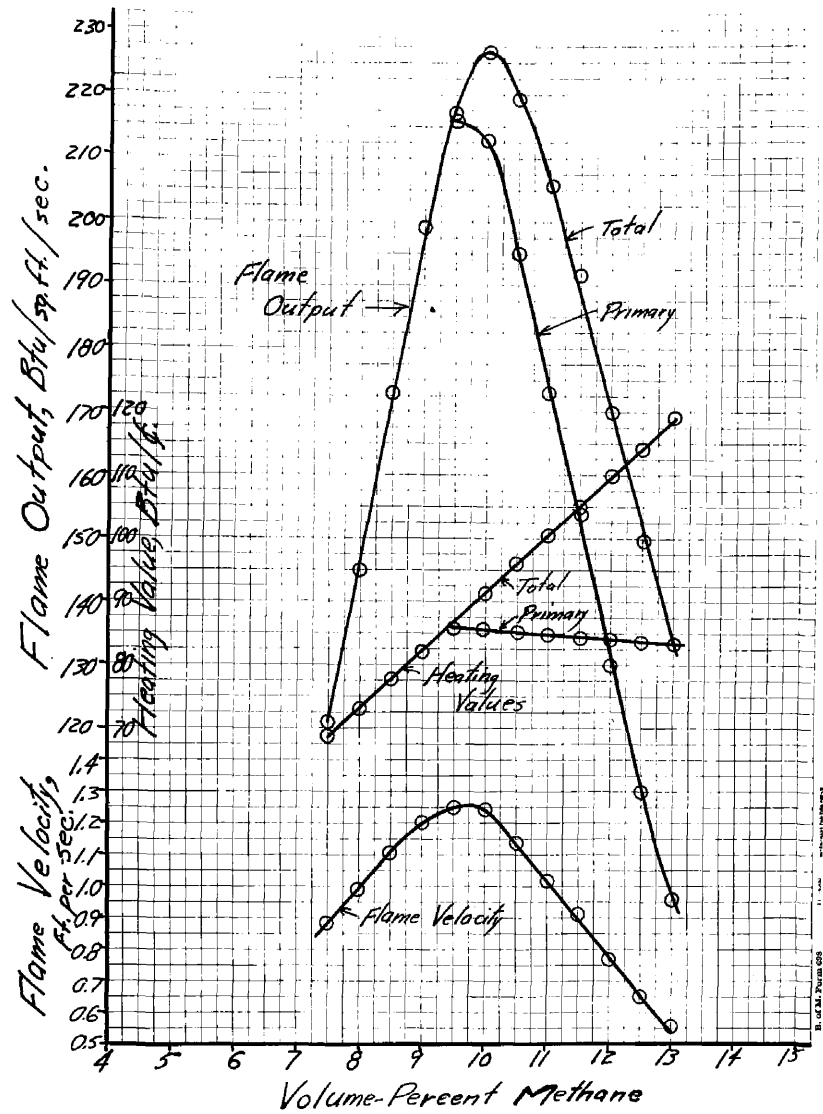


Figure 16. Sample Curves Showing Relationships between Flame Velocity, Heating Values, and Specific Flame-Outputs and the Content of Methane in Mixture with Air; see Table XVIII.

TABLE XIX

SUMMARY OF CALCULATIONS OF SPECIFIC FLAME OUTPUTS FOR COMBUSTION

OF METHANE WITH VARIOUS ATMOSPHERES

Volume Percent Combustible	Specific Flame Outputs		Volume Percent Combustible	Specific Flame Outputs	
	Btu per sq. ft. Primary	per sec. Total		Btu per sq. ft. Primary	per sec. Total
(1) $a = 0.209, \chi_{st} = 9.47$			(2) $a = 0.39, \chi_{st} = 16.3$		
7.5	121	121	10.0	421	421
8.0	125	145	11.0	563	563
8.5	173	173	12.0	708	708
9.0	199	199	13.0	866	866
9.5	216	217	14.0	984	984
10.0	213	227	15.0	1130	1130
10.5	195	219	15.5	1250	1250
11.0	173	206	16.0	1270	1270
11.5	154	192	16.5	1320	1270 1340
12.0	130	170	17.0	1320	1380
12.5	110	150	17.5	1290	1410
13.0	92.8	133	18.0	1220	1380
			18.5	1120	1310
			19.0	1040	1260
			19.5	990	1230
			20.0	938	1200
			21.0	832	1130
(3) $a = 0.50, \chi_{st} = 20.0$			(4) $a = 0.552, \chi_{st} = 21.6$		
18.0	2200	2200	20.0	2800	2800
19.0	2400	2400	20.5	2920	2920
19.5	2490	2490	21.0	3030	3030
20.0	2580	2580	21.5	3140	3140
20.5	2600	2670	22.0	3140	3220
21.0	2614	2770	22.5	3135	3310
21.5	2610	2860	23.0	3110	3360
22.0	2580	2920	23.5	3060	3430
22.5	2560	2980	24.0	3020	3470
23.0	2530	3020	24.5	2970	3500
24.0	2460	3100	25.0	2920	3530
25.0	2380	3170	25.5	2830	3530
26.0	2280	3200	26.0	2760	3550
26.5	2200	3180	26.5	2710	3540
27.0	2140	3160	27.0	2630	3530
27.5	2070	3130			
28.0	1990	3090			
(5) $a = 0.607, \chi_{st} = 23.3$			(6) $a = 0.701, \chi_{st} = 26.0$		
20.0	2910	2910	22.0	3490	3490
21.0	3150	3150	23.0	3720	3720
22.0	3360	3360	24.0	3930	3930
22.5	3490	3490	25.0	4130	4130
23.0	3580	3580	25.5	4240	4240
23.5	3630	3680	26.0	4330	4330
24.0	3620	3750	26.5	4270	4400
24.5	3600	3840	27.0	4240	4470
25.0	3560	3900	27.5	4190	4530
25.5	3530	3980	28.0	4140	4590
26.0	3470	4030	29.0	4010	4660
27.0	3370	4100	29.5	3930	4690
28.0	3270	4180	30.0	3840	4690
28.5	3190	4180	30.5	3750	4690
29.0	3120	4190	31.0	3630	4640
29.5	3020	4160			
30.0	2930	4140			
(7) $a = 0.800, \chi_{st} = 28.6$					
25.0	4530	4530			
26.0	4810	4810			
27.0	5040	5040			
27.5	5120	5120			
28.0	5270	5270			
28.5	5360	5360			
29.0	5300	5410			
29.5	5270	5510			
30.0	5170	5530			
30.5	5130	5640			
31.0	5040	5660			
32.0	4900	5750			
32.5	4800	5770			
33.0	4700	5780			
33.5	4560	5750			
34.0	4430	5720			

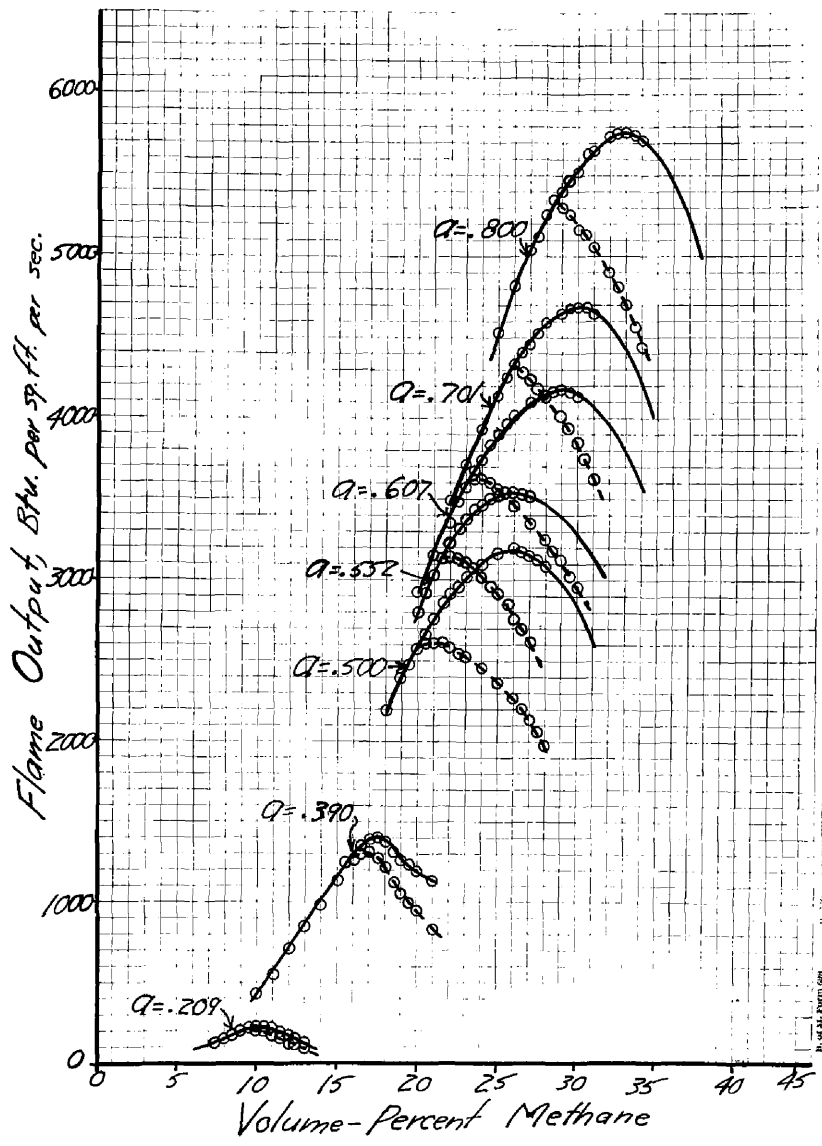


Figure 17. Relations between the Flame Outputs in the Combustion of Methane and the Content of Methane in the Mixture, for Combustion with Various Atmospheres; see Table XIX.

TABLE XX

SUMMARY OF RESULTS FOR FLAME - OUTPUTS OF METHANE

BURNED WITH VARIOUS ATMOSPHERES

Volume-Fraction of Oxygen in Atmos- phere	Volume- Percent Combustible for Equiv- alence	Maximum Primary Flame - Output			Maximum Total Flame - Output		
		Btu per sq. ft. per Second	Volume Percent Combustible	Displace- ment D _{Jp}	Btu per sq. ft. per Second	Volume Percent Combustible	Displace- ment D _{JT}
0.209	9.5	216	9.5	0	227	10.0	0.5
0.390	16.3	1320	16.5	0.2	1410	17.5	1.2
0.500	20.0	2615	21.0	1.0	3200	26.0	6.0
0.552	21.6	3140	22.0	0.4	3550	26.0	4.4
0.607	23.3	3630	23.5	0.2	4190	29.0	5.7
0.701	26.0	4330	26.0	0	4690	30.0	4.0
0.800	28.6	5360	28.5	0	5780	33.0	4.4

primary flame-output the relationship suggested by the approximate values in Table XX is regular and exhibits a maximum, while that for the total flame-outputs is somewhat irregular but much greater displacements are shown.

These considerations indicate very marked possibilities of variation of intensities of combustion by the simple device of enrichment with oxygen of the atmosphere used for combustion.

V--EPITOME

The literature relating generally to gaseous combustion has been reviewed and a critical examination of publications relating to the theory, to the measurement and to certain of the characteristics of the slow propagation of flame has been recorded. This examination showed some regularities in the behavior of the displacement of the mixture giving maximum flame velocity from the equivalent mixture that suggested this characteristic as an interesting topic for study, from both scientific and technical viewpoints. The effects produced on this displacement by important variables were found from published data to be regular in some respects but irregular in others. A rather crucial divergence was developed for the effects of the composition of the atmosphere used for combustion on the displacements for mixtures containing methane as the combustible.

Examination of this divergence was rendered difficult by the relatively small displacements for methane. However, measurements of flame velocities in mixtures of methane with various atmospheres composed of nitrogen and of 20 to 80 volume-percent oxygen were made with particular reference to the range of mixtures giving close to maximum flame velocity. These measurements established qualitatively in contrast to previous measurements for this gas a regular relationship between the displacement referred to and the composition of the atmosphere with a maximum displacement near 50 volume-percent oxygen in the atmosphere. The flame velocities obtained agreed in order of magnitude with comparable previous measurements. Similar relationships deduced from reliable previous measurements with other gases, hitherto unemphasized, led to the conclusion that this relationship is common to both types of combustible gases of technical importance.

This primary conclusion was shown to be rather crucial in connection with considerations of the gross features of the slow propagation of flame. An original development based on the thermal theory proved capable of explaining

semi-quantitatively the effect established. This and other considerations emphasized the utility of predictions of the gross features of the slow propagation of flame that are based on the thermal theory, even though this theory is recognized as inapplicable to problems involving the details and inner chemism of combustion.

The data developed emphasize the importance of the displacement referred to in the technical utilization of gaseous fuels in general. Calculations of intensities of releases of energy based on these data demonstrated fundamental points in the technical aspects of gaseous combustion for methane or qualitatively for common natural gases. They disclosed a range of specific flame-outputs of about 50-fold that may be made available in the combustion of methane by enrichment with oxygen of the atmosphere used for combustion and by suitable control of the composition of the mixture burned. Quantitative estimates of these effects were given. Finally, the results produced collateral evidence indicating that despite unexplained divergences in the literature a maximum flame velocity of approximately 330 cm. per sec. obtains for the combustion of methane with oxygen.

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0.552	21.6	3140	22.0	0.4	3550	26.0	4.4
0.607	23.3	3630	23.5	0.2	4190	29.0	5.7
0.701	26.0	4330	26.0	0	4690	30.0	4.0
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