

SECTION

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FLAME PROPAGATION— A CRITICAL REVIEW OF EXISTING THEORIES

by

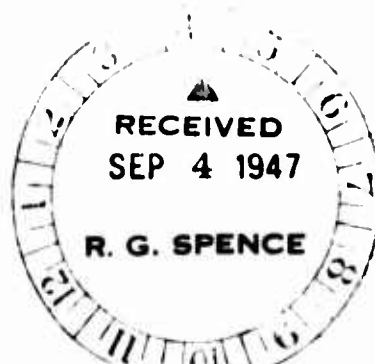
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FLAME PROPAGATION
CRITICAL REVIEW OF EXISTING THEORIES

A. Introduction

This report is intended as a comprehensive review of the present state of the theory of flame propagation in gases. The case of detonation will not be included, the discussion being limited to slow combustion (deflagration).

The main purpose of the theory of flame propagation is to relate the velocity of the flame front relative to the unburnt gas to fundamental physical and chemical properties of the combustible mixture.

Though the first attempts to carry out this proposition were made more than fifty years ago, this problem is still far from being solved, and what has been achieved is of little value for practical application.

The main reason for this failure became apparent when research on the kinetics of combustion reactions revealed their complicated nature. It is now common knowledge that combustion reactions take place by chain mechanisms, involving unstable intermediate products. However, it has not been possible yet to obtain a conclusive knowledge of the details of combustion reactions. Without this knowledge the theory of flame propagation has to be based on hypothetical reaction mechanisms; this fact is primarily responsible for the discrepancies between theory and experiment.

This does not mean that the theory in its present form does not have considerable value. Apart from forming a basis for future development, it

shows that the importance of studying flame propagation goes beyond the original purpose of calculating flame speeds. Once a definite knowledge of reaction mechanisms is available, the theory of flame propagation will give an insight into the complicated interaction of chemical reactions, diffusion and heat conduction taking place in the combustion zone. Therefore, the importance of further research in the field of kinetics of combustion reactions cannot be overemphasized.

A theory based on the effects of heat conduction, diffusion and chemical kinetics, if successful, would enable the calculation of flame speeds under simple flow conditions, e.g. those in the well-known soap-bubble and Bunsen burner methods. A more complete theory would have to include also the modifications introduced by more complicated flow conditions, particularly by turbulence. The attempts to include these effects in the theory are only at their beginning; the experimental evaluation of this aspect of flame propagation likewise presents difficulties not yet overcome.

Another complication arises in many technical applications because the assumption of a homogeneous mixture of fuel and air, on which the usual theories of flame propagation are based, is not fulfilled. A special case, namely, combustion in the mixing zone of fuel and air, with mixing taking place exclusively by diffusion, has been treated theoretically with remarkable success. Future development will have to include the cases of convective mixing and of partially premixed gases and should establish thus the connection with the theory of propagation in homogeneous mixtures.

B. Definition of Transformation Velocity

Before discussion the theory of flame propagation, it is necessary to find a definition of the velocity of flame motion which is unique and independent of the motion and local state of the unburnt gas.

One commonly encountered definition is:

"Flame velocity is the velocity of the flame front in a direction perpendicular to its surface, relative to the unburnt gas where it is at initial conditions."

A more satisfactory definition is the following:

"The flame velocity is equal to the mass flow of unburnt gas through unit area of the flame front, divided by the initial density."

Under stationary conditions of one-dimensional flow, the second definition is equivalent to the first one.

This can be demonstrated by the relations in the Bunsen burner cone, which is shown in the idealized diagram Figure 1. V is the flow velocity of the unburnt gas, V_n it's component perpendicular to the cone surface, $d\omega$ an element of cone surface and $d\omega$ its projection on the base. The mass flow through $d\omega$ is given by $dq = \rho_0 v d\omega = \rho_0 v d\omega \sin \alpha$ where ρ_0 is the initial density. Because of the relation $V_n = v \sin \alpha$ there follows $V_n = \frac{1}{\rho_0} \frac{dq}{d\omega}$

As V_n corresponds to the first definition, and $\frac{1}{\rho_0} \frac{dq}{d\omega}$ to the second definition of propagation velocity, the equivalence of the two is thus proven.

It is impossible to observe this velocity directly, as conditions where the unburnt gas is at rest cannot be realized experimentally. The velocity of propagation must be calculated either as the vector difference of the observed velocity of flame movement and velocity of flow of the unburnt gas, or more conveniently as total mass flow through the flame front, divided by the surface of the flame front and by the initial density.

It should be mentioned that unfortunately a confusing variety of terms is used in the literature on flame propagation. In this report the term "transformation velocity"^{*}, S_f , will be adopted for the quantity defined above, in accordance with the National Bureau of Standards and the NACA¹.

C. The Thermal Theories

(1) The Older Thermal Theories

The thermal theories are based on the equation of balance of thermal energy in the combustion zone. The objections raised by various authors^{2,3,6,7,8,9,9a,19,29} against the purely thermal point of view in treating flame propagation will be discussed in later chapters.

* Other terms frequently used for the same quantity are: burning velocity², fundamental flame speed³, flame speed⁴, ignition velocity⁵, and normal velocity^{9a}.

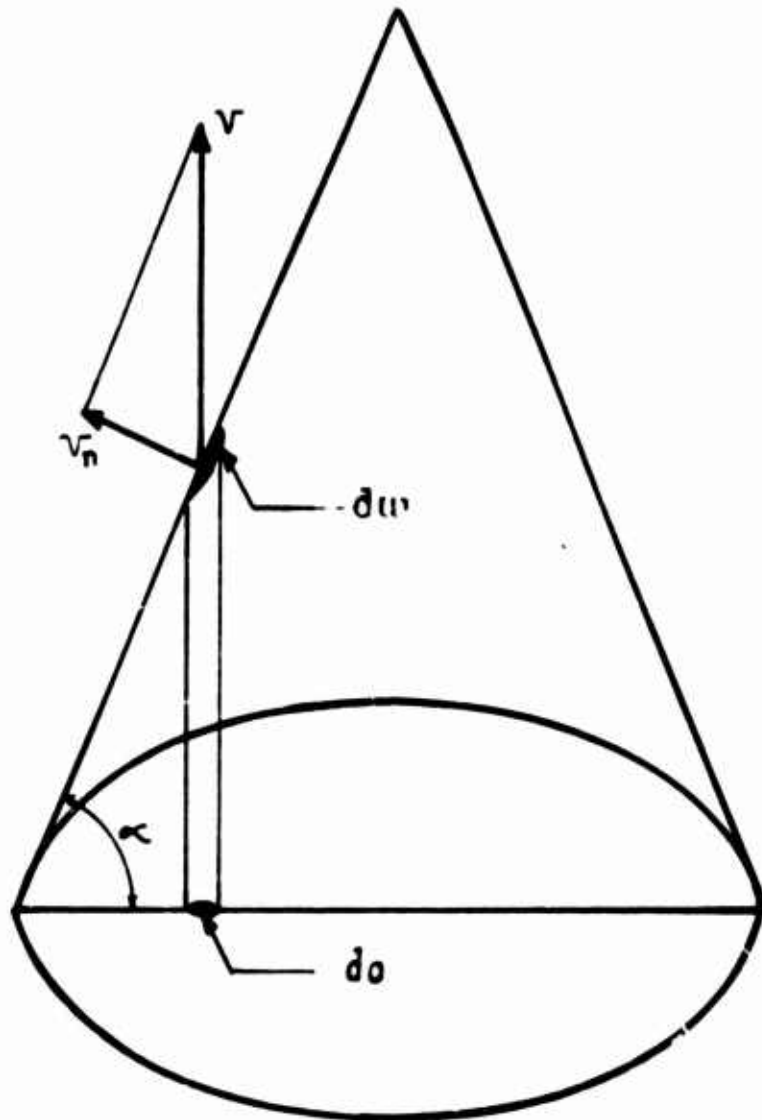


FIG. 1
BUNSEN BURNER CONE (IDEALIZED)

The equation of heat balance can be derived as follows⁶: denoting by H the heat content of unit mass, by ρ the density of the gas, by $\vec{\Omega}$ the vector of heat flow, by W the reaction rate and by Q the heat of reaction, referred to unit mass of combustible, the rate of change of heat content per unit volume is given by

$$\frac{\partial(\rho H)}{\partial t} = -\text{div } \vec{\Omega} + w Q \quad (1)$$

The heat flow vector is given by

$$\vec{\Omega} = -\lambda \text{ grad } T + \rho H v \quad (2)$$

where λ is the heat conduction coefficient, T the absolute temperature, and v the velocity of gas motion. Combining equations (1) and (2) with the continuity equation

$$-\frac{\partial \rho}{\partial t} = \text{div}(\rho v) \quad (3)$$

there results (taking in account that

$$\text{div}(\rho H v) = H \text{div}(\rho v) + \rho v \text{ grad } H)$$

$$\rho \frac{\partial H}{\partial t} = \text{div}(\lambda \text{ grad } T) - \rho v \text{ grad } H + w Q \quad (4)$$

As the treatment is concerned with flame propagation in uniform medium under stationary conditions, the coordinate system can be fixed in the flame front. This causes all time derivatives to vanish. By disregarding the curvature of the flame front, the equations can be specialized further to the case of one-dimensional flow. The continuity equation under these conditions becomes $\frac{\partial}{\partial x}(\rho v) = 0$

where X is the direction of flow, which leads to

$$\rho v = q = \rho_0 v_0 = \text{Const.} \quad (5)$$

where q is the mass flow, ρ_0 the initial density, and v_0 the velocity of the unburnt gas at initial conditions relative to the flame front, which by definition is identical with the transformation velocity S_t . Assuming in addition λ to be independent of temperature, and replacing $\frac{dH}{dx}$ by $c_p \frac{dT}{dx}$ * where c_p is the specific heat at constant pressure, equation (4) becomes finally

$$\frac{d^2 T}{dx^2} - \frac{R c_p}{\lambda} S_t \frac{dT}{dx} + \frac{w Q}{\lambda} = 0 \quad (6)$$

The problem consists in finding that value of S_t which is compatible with a solution $T(x)$ of equation (6) which fulfills the boundary conditions:

$$T = T_0 \quad \text{for } x = -\infty$$

$$T = T_f \quad \text{for } x = +\infty$$

where T_0 and T_f are the initial and final temperatures respectively.

* This approximation can be shown to be reasonably valid (ref. 6, footnote p. 20); with the same degree of approximation, Q can be assumed to be independent of temperature.

The main complication lies in the dependence of the reaction rate ω on the temperature and concentrations of, in general, a number of substances participating in the reaction. These concentrations, as functions of x are determined by diffusion, generation and destruction of particles according to the particular reaction mechanism. The lack of knowledge of the reaction mechanisms of the most important combustion processes precludes at present an exact treatment of the problem, as will be discussed more in detail in Chapter G. Only by introducing rather radically simplifying assumptions can an approximate solution be found.

The older attempts of solution are based on the assumptions, that:

- (a) Up to a certain ignition temperature, T_i which is taken to be a unique function of composition and pressure, no reaction takes place.
- (b) Once this temperature has been reached the reaction proceeds at a constant rate, determined only by the initial conditions. Assumptions of this nature led to the following expressions for the transformation velocity

$$S_t = \kappa \frac{\lambda}{c_p} \frac{T_f - T_i}{T_i - T_0} \quad (\text{Mallard and Le Chatelier}^{10})$$

$$S_t = \sqrt{\frac{\lambda f}{\rho_0 c_p} \frac{T_0}{T_i} \frac{T_f - T_i}{T_i - T_0}} \quad (\text{Jouget, Crussard}^{11})$$

$$S_t = \sqrt{\frac{\lambda f}{\rho_0 \bar{c}_p} \frac{T_0}{T_m} \frac{T_f - T_0}{T_i - T_0}} \quad (\text{Daniell}^{12})$$

$$S_t = \sqrt{\frac{K \lambda \bar{w}}{\rho_0 \bar{c}_p a_0} \frac{T_f - T_i}{T_i - T_0}} \quad (\text{Dancköhler}^{13})$$

Here K denotes a constant, f a quantity proportional to the reaction rate, \bar{c}_p the average specific heat at constant pressure, λ the heat conductivity, ρ_0 and T_0 the initial density and absolute temperature, T_i the ignition temperature, T_f the final temperature (absolute) and T_m a harmonic mean temperature nearer to T_f than to T_i , \bar{w} the mean reaction rate and a_0 the initial concentration of combustible. By further specializing the formulas for $H_2 - O_2$ and $H_2 - O_2 - N_2$ or $H_2 - O_2 - CO_2$ mixtures, the following expressions were derived:

$$S_t = \sqrt{K \frac{\lambda \rho_0 T_0^2}{\bar{c}_p} \frac{T_f - T_i}{T_i - T_0} [H_2] [O_2]} \quad (\text{Nusselt}^{14})$$

$$S_t = \underbrace{\sqrt{K \cdot H_2^2 (1 - H_2) \alpha}}_{\text{"reaction-kinetic" term}} \underbrace{\sqrt{\frac{\lambda (T_f - T_i) h_1}{\bar{c}_p^2 T_c (T_f - T_0) (T_i - T_0)}}}_{\text{"thermic effect" term}} \underbrace{\sqrt{\frac{T_0^2}{\rho_0}}}_{\text{"initial condition" term}} \quad (\text{Jahn}^{15})$$

where $[H_2]$ and $[O_2]$ are molar concentrations, H_2 the mol fraction of hydrogen, α the mol fraction of oxygen in the atmosphere $O_2 + N_2$ or $O_2 + CO_2$, h_1 the heat of combustion of unit volume of hydrogen, p_0 initial total pressure. It will now be outlined briefly how an expression similar to those cited is derived⁶. The origin of the coordinate system is placed at the boundary between heating and reaction zone, the positive x -axis pointing towards the reaction zone (Figure 2).

Thus, for $x < 0$, equation (6) reduces to

$$\frac{d^2 T}{dx^2} - \alpha \frac{dT}{dx} = 0 \quad \alpha = \frac{\rho_e c_p}{\lambda} S_t \quad (7)$$

With the appropriate boundary conditions, the solution is

$$T - T_0 = (T_i - T_0) \cdot e^{\alpha x} \quad \text{for } -\infty < x < 0 \quad (8)$$

In the reaction zone of thickness d_r the reaction rate w is assumed to be constant. Thus, there can be written

$$w = -\frac{da}{dt} = -\frac{da}{dx} \frac{dx}{dt} = \frac{a_e}{d_r} S_t \quad (9)$$

where a is the concentration of combustible, with the initial value a_0 . Furthermore, the heat of reaction can be expressed through the total temperature rise:

$$Q \frac{d_0}{\rho_0} = L = c_p (T_f - T_0) \quad (10)$$

where L is the heat of reaction referred to unit mass of the whole mixture. Introducing expressions (9) and (10), the solution of the fundamental equation

$$\frac{d^2 T}{dx^2} - \alpha \frac{dT}{dx} + \frac{WQ}{\lambda} = 0 \quad (6)$$

for the reaction zone, $0 < x < d_r$ becomes

$$T - T_0 = (T_f - T_0) \frac{x}{d_r} + (T_i - T_0) \frac{e^{\alpha x} - e^{\alpha d_r}}{1 - e^{\alpha d_r}} \quad (11)$$

In order to determine S_1 (which is contained in α), an additional boundary condition must be introduced, namely, the continuity of $\frac{dT}{dx}$ at the boundary of heating and reaction zone. Equating $\left(\frac{dT}{dx}\right)_{x=0}$ from equation (8) to $\left(\frac{dT}{dx}\right)_{x=0}$ from equation (11), the transcendental equation for α

$$\frac{T_i - T_0}{T_f - T_0} = \frac{1 - e^{-\alpha d_r}}{\alpha d_r} \quad (12)$$

is obtained.

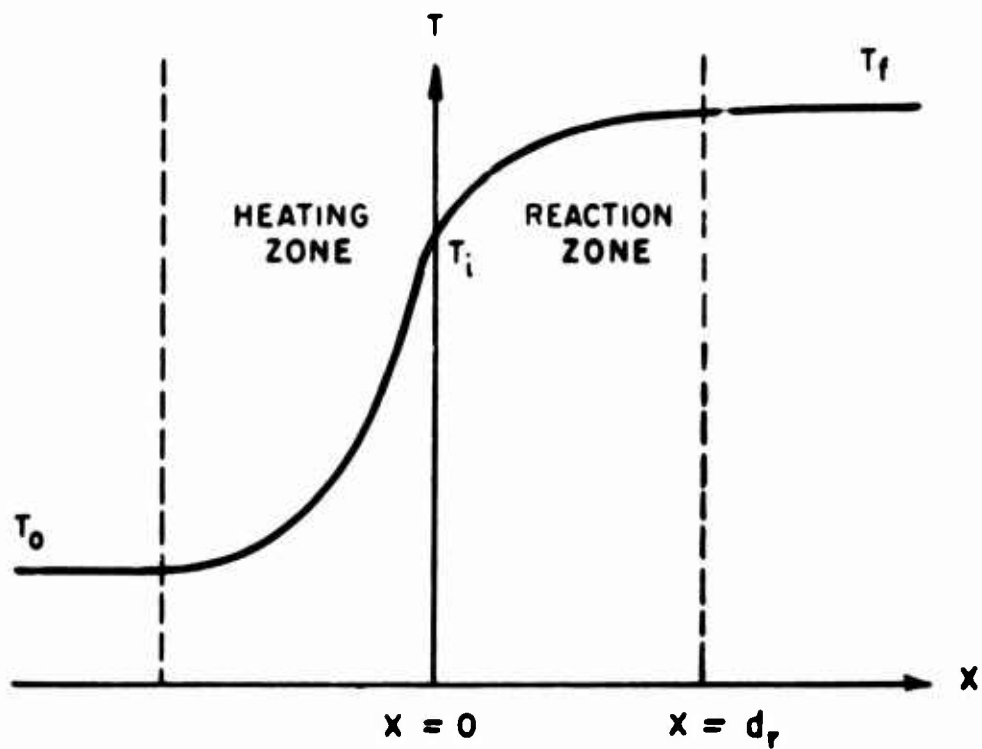


FIG. 2

TEMPERATURE DISTRIBUTION IN THE FLAME FRONT

In the older theories the ignition temperature T_i was identified with the one determined by "static" ignition tests, in which it was found to be much lower than T_f . Therefore, $\frac{T_i - T_0}{T_f - T_0}$ was assumed to be small, or $\propto d_r$ large.

This led to the approximation

$$\frac{T_f - T_0}{T_i - T_0} \cong \propto d_r = \frac{\rho_0 c_p}{\lambda} \cdot d_r \cdot S_f \quad (13)$$

Substituting d_r from equation (9) leads to the final result

$$S_f = \sqrt{\frac{\lambda w}{\rho_0 c_p a_0} \frac{T_f - T_0}{T_i - T_0}} \quad (14)$$

This is essentially identical with the expressions given on pages 7 & 8. The various forms of the expressions result from special assumptions about the dependence of the reaction rate on the initial conditions.

(2) The Theory of Zeldovich and Frank-Kamenetsky^{6,7,18,19}

The older thermal theories have been criticized by various authors on the ground that they are based on assumptions which cannot be justified by the current theory of reaction kinetics. Theoretical considerations and a great amount of experimental evidence^{9,16,17} have established that the temperature of ignition of an explosive gaseous mixture

depends on other variables beside initial composition and pressure. Most important for the theory of flame propagation is the relation between the ignition temperature and the time lag (induction period) of ignition. Whereas in the usual experimental determinations of ignition temperatures this time lag is of the order of 0.1 to several seconds, in a flame travelling at only 1 m/sec. and having a thickness of the heating zone of 0.1 mm the induction period is only 10^{-3} sec. From this consideration the authors of the newer thermal theory^{6,7,18,19} conclude that the ignition temperature in a flame must be taken very high, approaching the final temperature T_f . More explicitly, it is stated^{7,25}, that it can be lower than T_f only by an amount of the order of $\frac{RT_f^2}{E}$, where E is the activation energy of the reaction and R the gas constant. This conclusion is in agreement with the experimental fact, that the transformation velocity does not reach infinity on raising the initial temperature to values as high as, or even higher than, the "static" ignition temperature, as would follow from the expressions derived according to the older theories. In accordance with these considerations which show that the ignition temperature T_i is not a well-defined physical quantity, Zeldovich and Frank-Kamenetsky introduce it merely for convenience of computation; no particular significance is attributed to it and it is eliminated from the final expressions. The reaction rate is introduced now as a function of temperature and concentration. The derivation as given by Semenov⁶ will be followed here.

As a first step, an approximate solution of equation (6) for the reaction zone, $(0 < x < d, T_i < T < T_f)$ is derived by neglecting the term $\frac{\rho_o c_p}{\lambda} S_f \frac{dT}{dx}$. (Semenov justifies this simplification by taking into account equations (9) and (10); since equation (9) is based on the assumption of a constant reaction rate, Semenov's proof cannot be considered correct.) Neglecting the term with $\frac{dT}{dx}$ replacing $\frac{d}{dx}$ by $\frac{dT}{dx} \cdot \frac{d}{dT}$ and integrating equation (6) over the reaction zone $(0 < x < d_r)$ there results

$$\left(\frac{dT}{dx}\right)_{x=0} = \sqrt{\frac{2Q}{\lambda} \int_{T_i}^{T_f} w dT} \quad (15)$$

(as $\frac{dT}{dx}$ vanishes for $x = d_r$)

For $-\infty < x < 0$, solution (8) is carried over into the new theory. This gives

$$\left(\frac{dT}{dx}\right)_{x=0} = \propto (T_i - T_o) \cong \propto (T_f - T_o) \quad (16)$$

The last approximation is justified since T_i is now assumed to be close to T_f . Substituting for $(T_f - T_o)$ from equation (10), and equating (15) with (16), the general expression for the transformation velocity is obtained:

$$S_f = \frac{1}{\rho_o L} \sqrt{2\lambda Q \int_{T_i}^{T_f} w dT} = \sqrt{\frac{2\lambda}{\rho_o \alpha_o L}} \cdot I, \quad I = \int_{T_i}^{T_f} w dT \quad (17)$$

A suitable law for the reaction rate must now be introduced into this expression. Here the main difficulty arises, due to the complex character of practically all the important combustion reactions. Zeldovich and Frank-Kamenetsky have applied the new theory only where a "classical" (Arrhenius) kinetic law can be assumed*. (For comprehensive discussions of chemical kinetics in gases, see refs. 20, 21)

Thus, there is introduced:

$$\begin{aligned}
 W &= S \cdot e^{-\frac{E}{RT}} && \text{for a zero order reaction} \\
 W &= K \cdot a \cdot e^{-\frac{E}{RT}} && \text{for a 1st order reaction} \\
 W &= K a^2 e^{-\frac{E}{RT}} && \text{for a 2nd order reaction}
 \end{aligned}
 \tag{18}$$

Here, E is the activation energy, a the concentration of combustible, and the factors S and K depend essentially only on the collision frequency of the molecules, which can be calculated by the methods of statistical mechanics^{20,21}.

The factor $e^{-\frac{E}{RT}}$ increases very rapidly with temperature for the usual values of the activation energy (25,000 to 80,000 cal/mol)

* This does not mean that the mechanism of the reaction is assumed to be simple and, respectively, of zero order, mono- or bimolecular. Compare ref. 21 for this essential distinction between order and mechanism of a reaction.

Therefore, the temperature dependence of S or K is neglected, their value being taken at the highest temperature T_f . Since the difference $\Theta = T_f - T$ is small compared with T , the following approximation can be made:

$$e^{-\frac{E}{RT}} \cong e^{-\frac{E}{RT_f}} \cdot e^{-\frac{E}{RT_f^2} \cdot \Theta} \quad (19)$$

In the case of zero order reaction, the integral I in equation (17) can now be evaluated immediately:

$$I = \int_{T_i}^{T_f} S e^{-\frac{E}{RT_f}} \cdot e^{-\frac{E}{RT_f^2} \cdot \Theta} dT = S e^{-\frac{E}{RT_f}} \cdot \frac{RT_f^2}{E} \int_0^{\beta_i} e^{-\beta} d\beta$$

with $\beta = \frac{E}{RT_f^2} \cdot \Theta$, $\beta_i = \frac{E}{RT_f^2} (T_f - T_i)$

It is seen that the integral

$$j = \int_0^{\beta_i} e^{-\beta} d\beta = 1 - e^{-\beta_i}$$

converges towards the value one very rapidly for increasing β_i .

The authors of this theory set the integral equal to one, on the assumption that the term $\frac{E}{RT_f}$ is always large enough to justify both conditions:

$$j \cong 1 \quad \text{equivalent to } \beta_i \geq 2, \quad \text{and}$$

$T_f - T_i \ll T_f$, which has been previously assumed to be valid (p. 12). The remarkable result of this assumption is the elimination of the ignition temperature from the final expression.

The formula for the transformation velocity for zero order reaction becomes thus

$$S_f = \sqrt{\frac{2\lambda}{\rho_0 a_0 L}} S e^{-\frac{E}{RT_f}} \frac{RT_f^2}{E} = \sqrt{2 \frac{\lambda}{\rho_0 c_p} \frac{S e^{-\frac{E}{RT_f}}}{a_0} \frac{RT_f^2}{E(T_f - T_d)}} \quad (20)$$

A new problem arises in the treatment of first- and second-order reactions, because the concentration a has to be brought into a functional relation to the temperature. By transforming equation (6) suitably, and introducing the diffusion equation for a it can be shown⁶ that the variables

$$\alpha = \frac{a_0}{\rho_0} - \frac{a}{\rho} \quad \text{and} \quad \theta = \frac{c_p}{Q} (T - T_d)$$

obey the differential equations

$$\begin{aligned} \frac{\lambda}{c_p} \frac{d^2 \theta}{dx^2} - S_f \frac{d\theta}{dx} + w &= 0 \\ D \rho \frac{d^2 \alpha}{dx^2} - S_f \frac{d\alpha}{dx} + w &= 0 \end{aligned} \quad (21)$$

where D is the coefficient of diffusion.

Both variables have, in addition, to fulfill the same boundary conditions:

$$\begin{aligned} (\alpha)_{-\infty} &= (\theta)_{-\infty} = 0 \\ (\alpha)_{+\infty} &= \frac{a_0}{\rho_0} = \frac{L}{Q} = \frac{c_p}{Q} (T_f - T_d) = (\theta)_{+\infty} \end{aligned} \quad (21')$$

If the following condition is satisfied:

$$D = \frac{\lambda}{\rho c_p} = \chi \quad (22)$$

where χ is the coefficient of temperature conduction, α must be identical with θ throughout the whole range $-\infty < x < +\infty$.

Condition (22) is never exactly fulfilled; however, the elementary kinetic theory of gases gives us a first approximation

$$\lambda = \rho c_v D, \text{ and a better approximation leads to } \lambda = K \rho c_v D, \\ \text{with } K c_v \cong c_p \quad (\text{ref. 22})$$

This result can be written

$$c_p T + \frac{aQ}{\rho} = c_p T_o + \frac{a_o Q}{\rho_o} = c_p T_f = \text{Const.} \quad (23)$$

Since $c_p T$ is the enthalpy and $\frac{aQ}{\rho}$ the chemical energy available per unit volume, (23) expresses the constancy of the sum of thermal and chemical energies during the whole combustion process. This relation had already been postulated without proof by Lewis and von Elbe², in their theory, which will be discussed later. It is very important to note that it holds only if condition (22) is fulfilled.

Equation (23) can be transformed by means of (10) to

$$a = a_o \cdot \frac{\rho}{\rho_o} \cdot \frac{T_f - T}{T_f - T_o} = a_o \cdot \frac{T_o}{T} \cdot \frac{T_f - T}{T_f - T_o} \quad (23')$$

On evaluating the integral I in (17), the approximations (19) are again introduced, and T in the denominator of (23') is approximately put equal to T_f . T_i is eliminated again in an analogous way as in the case of zero order reactions. The expressions for the transformation velocity S_f become thus:

$$S_t = \sqrt{\frac{2 \lambda c_p K}{\rho_0 L^2} \cdot \frac{T_0}{T_f} \left(\frac{RT_f^2}{E} \right)^2 e^{-\frac{E}{RT_f}}} =$$

$$= \sqrt{2 \frac{\lambda}{\rho_0 c_p} \frac{T_0}{T_f} \left(\frac{RT_f^2}{E(T_f - T_0)} \right)^2 \cdot K e^{-\frac{E}{RT_f}}} \quad (24)$$

for first order reaction ($W = K a_0 e^{-\frac{E}{RT}}$)

and

$$S_t = \sqrt{4 \frac{\lambda K a_0 c_p^2}{\rho_0 L^3} \left(\frac{T_0}{T_f} \right)^2 \left(\frac{RT_f^2}{E} \right)^3 e^{-\frac{E}{RT_f}}} =$$

$$= \sqrt{4 \frac{\lambda}{\rho_0 c_p} \left(\frac{T_0}{T_f} \right)^2 \left(\frac{RT_f^2}{E(T_f - T_0)} \right)^3 K a_0 e^{-\frac{E}{RT_f}}} \quad (25)$$

for second order reaction ($W = K a_0^2 e^{-\frac{E}{RT}}$)

In one of their papers¹⁹ Zeldovich and Frank-Kamenetsky give a general expression for reactions of order p :

$$S_t = \sqrt{2 p! \frac{\chi}{\tau_f} \frac{1}{\theta_f^{p+1}}} \quad (26)$$

where χ is the temperature conductivity ($= \frac{\lambda}{\rho c_p}$), τ_f the time during which the reaction would proceed isothermally at the temperature T_f and at the initial concentration a_0 .

$$\left(\frac{1}{\tau_f} = K a_0^{p-1} e^{\frac{E}{RT_f}} \right) \quad \text{and}$$

Θ_f is equal to $\frac{E}{RT_f^2} (T_f - T_0)$. Equations (20), (24) and (25) are seen to agree with (26), except for the factors $\frac{T_0}{T_f}$ and $\left(\frac{T_0}{T_f}\right)^2$, respectively, which enter the expressions due to a correction on the diffusion equation applied by Semenov (See ref. 6, foot notes pp. 35 and 41).

It is evident that the effects of temperature and concentration on the reaction rate on passing through the combustion zone oppose each other. Semenov⁶ therefore investigates the validity of the assumption previously made (see p. 12 that practically no reaction takes place until the temperature approaches the final temperature T_f . For the case of second-order reaction, he shows that the assumption $T_f - T_i \leq 0.25 T_f$ is valid only for values of $\gamma = \frac{RT_f}{E} \leq 0.1$ or, with $T_f = 2000^\circ$, for $E \geq 40,000$ cal/mol.*

Obviously, for the case of first-order reaction, a less rigorous restriction applies.

Formulas (24) and (25) can be formally obtained by introducing into the expression for zero-order reaction, (20), an effective concentration

$$a_{\text{eff}} = \frac{a_0 c_p}{L} \left(\frac{RT_f^2}{E} \right) \frac{T_0}{T_f} = \frac{\rho c_p}{Q} \frac{RT_f^2}{E} \frac{T_0}{T_f} \quad (27)$$

and setting $S = K a_{\text{eff}}$ for first-order and $S = K a_{\text{eff}}^2$ for second-order

* He points out, in this connection, that a factor of 2 instead of 4 under the square root in equation (25) is more nearly correct.

reactions. This allows the extension of the theory to cases where the reaction rate depends on the concentrations of more than one chemical species. For instance, if the kinetic law $W = K \cdot a \cdot b \cdot e^{-\frac{E}{RT}}$ can be applied, and there is a deficiency of a and an excess of b , b_{eff} may be set equal to its concentration in the combustion products and a_{eff} calculated according to (27). Semenov⁶ calls attention to the second form of equation (27), which shows that a_{eff} does not depend directly on the initial concentration a_0 ; this circumstance imposes considerable limitations on the possibility to draw conclusions on reaction kinetics from flame propagation data.

Finally, the theory is extended to cases where: (1) specific heat and heat conductivity vary with temperature; (2) the number of molecules changes during reaction, and (3) the diffusion coefficient is not equal to the coefficient of temperature conduction [condition (22)]. The final expressions given are:

$$S_t = \sqrt{\frac{2\lambda c_p K}{\rho_0 L^2} \left(\frac{T_0}{T_f}\right) \left(\frac{\lambda}{c_p \rho D}\right) \frac{n_1}{n_2} \left(\frac{RT_f}{E}\right)^2 e^{-\frac{E}{RT_f}}} \quad (24a)$$

for first-order reaction, and

$$S_t = \sqrt{\frac{2\lambda K a_0 c_p^2}{\rho_0 L^3} \left(\frac{T_0}{T_f}\right)^2 \left(\frac{\lambda}{c_p \rho D}\right)^2 \left(\frac{n_1}{n_2}\right)^2 \left(\frac{RT_f}{E}\right)^3 e^{-\frac{E}{RT_f}}} \quad (25a)$$

for second-order reaction,

Where the values of λ, c_p, ρ have to be taken for the reaction products at the final temperature T_f , D is the diffusion coefficient of the reacting substance in the reaction products at the temperature T_f , n_1 is the number of molecules before and n_2 the number of molecules after reaction.

D. Comparison of the thermal theories with experimental results

A large amount of experimental material on flame propagation velocities exists, and many attempts have been made to verify the predictions of the older thermal theories with these data. It should be remembered in this connection that the older theories do not allow the calculation of absolute values of the transformation velocity, as the expressions contain an unknown constant (K or f in the formulas on pages 7 & 8). For some particular initial condition in a series of experiments the theoretical value can thus be fitted to the experimental result. The incorrect assumptions of the older theories, namely, constant ignition temperature and constant rate of heat liberation throughout the combustion process, are largely responsible for the numerous discrepancies between experimental and theoretical values.

Formulas of the form

$$S_t = \sqrt{K \frac{\bar{w}}{a_0} \frac{\lambda}{c_p \rho_0} \frac{T_f - T_i}{T_i - T_0}} \quad (\text{ref. 13})$$

allow the prediction, in a qualitative way, of the existence of limits of inflammability, as for very lean or very rich mixtures T_f must become equal

to T_i and S_t must become zero. Qualitative predictions of the dependence of S_t on the composition of the gas mixture in fairly good agreement with experimental results were made by Jahn¹⁵.

Lewis and von Elbe⁴⁹ have recently emphasized that the formula of Mallard and Le Chatelier¹⁰ in the form

$$S_t = \frac{\lambda}{\rho c_p} \frac{T_f - T_i}{T_i - T_o} \frac{1}{d_r}$$

offers possibilities for the study of combustion which have not been fully appreciated in the past. They propose a semi-empirical approach, combining experimental values of S_t and d_r with the Mallard-LeChatelier treatment for deriving other useful information, such as the overall reaction rate. They assert also that the rather difficult measurement of d_r can be replaced by the determination of the more easily measurable quenching distance, that is the distance between the flame front and a solid heat-conducting surface. A theory linking the minimum spark energy for ignition with quenching distance and transformation velocity was also proposed by these authors. For a more detailed critical discussion of the older thermal theories, reference is made to the reviews by Lewis and von Elbe², Coward and Payman³ and Jost^{8,9}.

The new thermal theory has been applied so far only to the combustion of carbon monoxide, and of the liquid nitroglycol⁶. This restriction is due to the fact that the authors of this theory doubt its applicability to fast reactions of the branched chain type, particularly to the

combustion of hydrogen and the hydrocarbons. Though the actual reaction mechanism of the carbon monoxide oxidation is of a chain character and its details are not established conclusively, a kinetic law of the general form (18),

$$w = -\frac{d[\text{CO}]}{dt} = -2\frac{d[\text{O}_2]}{dt} = \frac{d[\text{CO}_2]}{dt} = Z e^{-\frac{E}{RT}} \cdot [\text{CO}] \cdot [\text{H}_2\text{O}] \quad (18')$$

with $E = 25000$ cal, is assumed by Semenov⁶ for this reaction.

This law takes care of the observation that moisture has a profound influence on the flame propagation in CO. (cf.ref.1) Two cases have to be distinguished, on introducing (18') into equation (17):

(1) Excess of CO in the initial mixture. Here the concentrations of CO and H_2O are both taken at the final temperature and in the burnt gas, by multiplying each with $\frac{T_o}{T_f}$ and setting $[\text{CO}]_f = [\text{CO}]_o = [\text{CO}_2]_f$

$$\text{Thus (18')} \text{ becomes } w = Z \cdot e^{-\frac{E}{RT_f}} \left(\frac{T_o}{T_f}\right)^2 \cdot [\text{H}_2\text{O}]_o [\text{CO}]_f$$

The transformation velocity is computed by applying equation (17), with the following substitutions:

$$Z = \frac{c}{\lambda n} \quad , \quad \lambda = \frac{1}{3} \lambda c \rho c_p \quad (28)$$

where λ is the mean free path, c the mean molecular velocity and n the number of molecules per unit volume of the gas at the temperature T_f . By furthermore setting

$$c = c_{300} \sqrt{\frac{T_f}{300}} \quad , \quad \frac{Q}{L \rho_o} = \frac{1}{[\text{CO}_2]_f} \quad , \quad \text{and} \quad \frac{1}{L} = \frac{\mu n_o}{Q [\text{CO}_2]_f} \quad ,$$

where μ is the molecular weight of CO and $n_0 = n \frac{T_f}{T_0}$ is the number of molecules per unit volume at the initial temperature T_0 , and by assuming the numerical values

$$Q = 7.10^4 \text{ cal/mol}, \quad \mu = 30, \quad c_{300} = 5.10^4 \text{ cm/sec}$$

the following expression for the transformation velocity is obtained:

$$S_f = \sqrt{1400 \frac{T_f T_0^2}{E} e^{-\frac{E}{RT_f}} \frac{[H_2O]_0 [CO]_f}{[CO_2]_f^2}} \quad (29)$$

(2) Excess of oxygen. According to what was said previously, equation (27) must be applied in this case to introduce the effective concentration of CO. To give the final formula,

$$[CO]_{\text{eff}} = \frac{c_p \rho_0}{Q} \frac{RT_f^2}{E}$$

has to be substituted for $[CO]_f$ in (29)

Without giving numerical results, Semenov⁶ states that the agreement of these expressions with the experimental data of Flock¹, Jahn¹⁵, Passauer²³ and unpublished observations by Barsky is satisfactory. Figure 3 shows a plot taken from Semenov's paper showing a comparison of his results with the data of Chitrin, Barski, and Jahn. In particular, Barsky's experiments are stated to confirm the following predictions of the theory:

(a) for excess oxygen the transformation velocity does not depend on either the initial CO or O₂ concentration, if by suitable inert admixtures the gas composition is adjusted in such a way that the final temperature T_f is held constant; (b) for excess CO, the transformation velocity varies with $\sqrt{[CO]_f}$ if again T_f is maintained constant. It is further stated

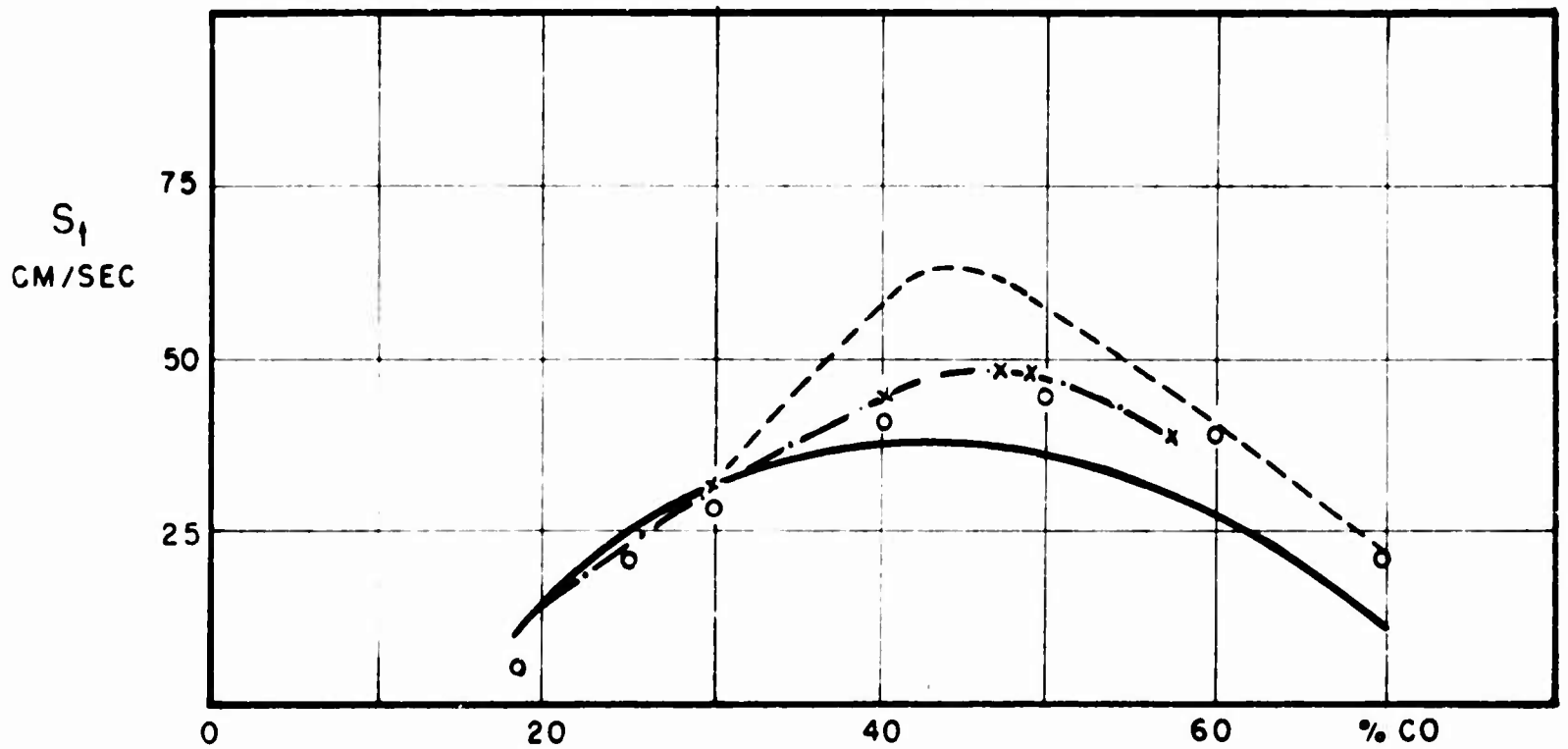


FIG. 3

TRANSFORMATION VELOCITY OF CARBON MONOXIDE-AIR MIXTURES

(AFTER SEMENOV REF. 6)

FULL CURVE : DATA OF PASSAUER

X : DATA OF CHITRIN

O : DATA OF BARSKY

DASHED CURVE : THEORETICAL VALUES

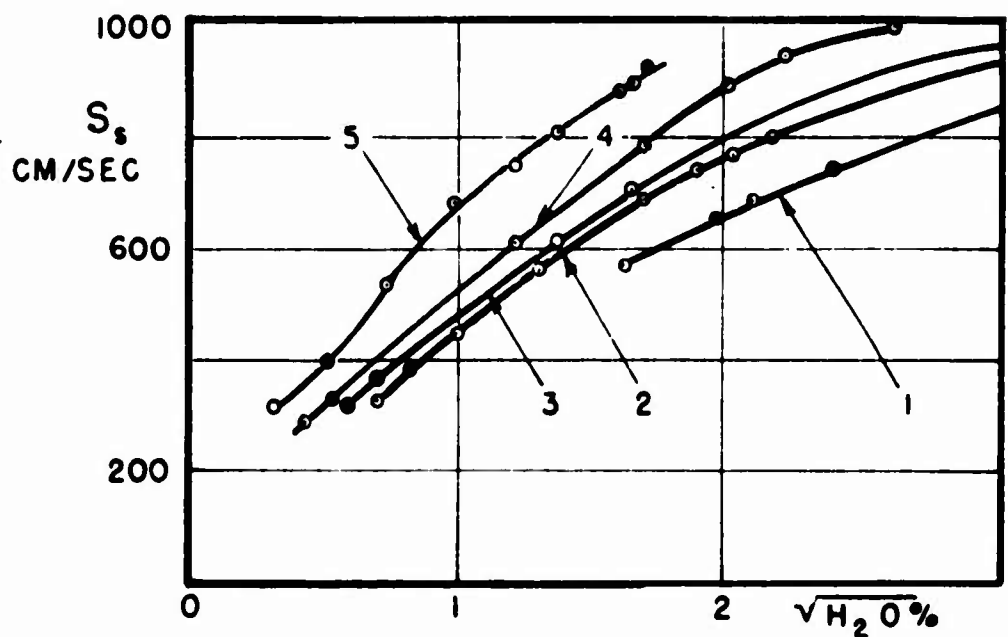


FIG. 4

SPATIAL FLAME VELOCITY VS. SQUARE-ROOT OF H_2O CONCENTRATION

(REPLOTTED OF DATA BY FIOCK AND MARVIN REF. 1 BY SEMENOV, REF. 6)

- 1: $P_{CO + O_2} = 100$ MM
- 2: $P_{CO + O_2} = 150$ MM
- 3: $P_{CO + O_2} = 200$ MM
- 4: $P_{CO + O_2} = 300$ MM
- 5: $P_{CO + O_2} = 760$ MM

that Flock's data (ref. 1, Fig. 9) give approximately straight lines, if replotted as S_s^* vs. $\sqrt{[H_2O]}$. Figure 4 in agreement with the theory. Finally, in the case of CO-air mixtures, the theory predicts independence of the transformation velocity from the total pressure for constant moisture percentage and inverse proportionality to \sqrt{p} for constant partial pressure of water. This is said to be in agreement with experiment. For CO-O₂ mixtures, temperatures around 3000° K are reached in the flame and therefore dissociation must be taken into account. Semenov indicates that the theory then predicts an increase of S_f with $p^{0.12}$, while experiments showed an increase with $p^{0.2}$.

The application of the thermal theory to the combustion of nitroglycerol will not be discussed here, as combustion on the surface of a liquid is beyond the scope of this report. A similar theory of flame propagation in a colloidal propellant⁵⁰ should also be mentioned here, without further discussion.

E. Thickness of the flame front and shape of flames near walls according to the newer thermal theory.

Once the transformation velocity is determined, it is possible to compute the thicknesses of the heating zone and reaction zone. From equations (7) and (8), it is seen that the temperature difference $T - T_0$ drops from

$$T_i - T_0 \quad \text{to} \quad \frac{1}{e} (T_i - T_0) \quad \text{in a distance}$$

$$d_t = \frac{\lambda}{c_p \rho} \frac{1}{S_t} = \frac{\chi}{S_t} \quad (30)$$

*Spatial flame velocity in soap-bubble experiments

This value is taken as a measure of the heating zone thickness. From equation (16), by putting the mean value of $\frac{dT}{dx}$ equal to $\frac{1}{2} \left(\frac{dT}{dx} \right)_0$ and by integrating, one obtains

$$d_r = 2 \frac{T_f - T_i}{T_f - T_0} d_t \sim 0.4 d_t \quad (31)$$

as thickness of the reaction zone. With the usual values of transformation velocity S_t and temperature conductivity χ , d_t is of the order of 0.2 to 0.3 mm, and d_r of the order of 0.1 mm. Semenov deduces further that the gas molecules stay about $3 \cdot 10^{-5}$ sec in the reaction zone and suffer during that time about 10^4 collisions. Direct experimental evidence for the existence of the heating zone is furnished by observations of Van de Poll and Westerdijk²⁴. Figure 5 shows a simultaneous striae- and normal photograph of a burner flame by these authors. It can be clearly seen that a constant distance is maintained over the whole flame surface between the striae image, (inner trace), which indicates the beginning of the heating zone, and the image of the luminous layer (outer trace), indicative of the reaction zone.

Equations (30) and (31) account for the observed dependence of the flame front thickness on pressure⁴². Since λ , c_p and S_t depend very little on pressure, d_t and d_r must be approximately inversely proportional to P in accordance with the experimental results.

In a recent paper²⁵, Frank-Kamenetsky draws conclusions from the thermal theory on the shape of a flame near walls of a tube. It has been mentioned on page 12 that according to the newer thermal theory, the

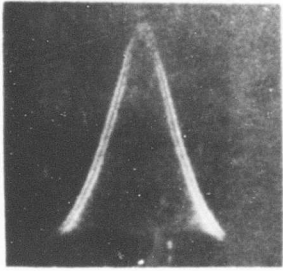


FIG. 5
SIMULTANEOUS NORMAL AND STRIAE
PHOTOGRAPH OF A BUNSEN FLAME.
(AFTER VAN DE POLL AND WESTERDIJK
REF.24)

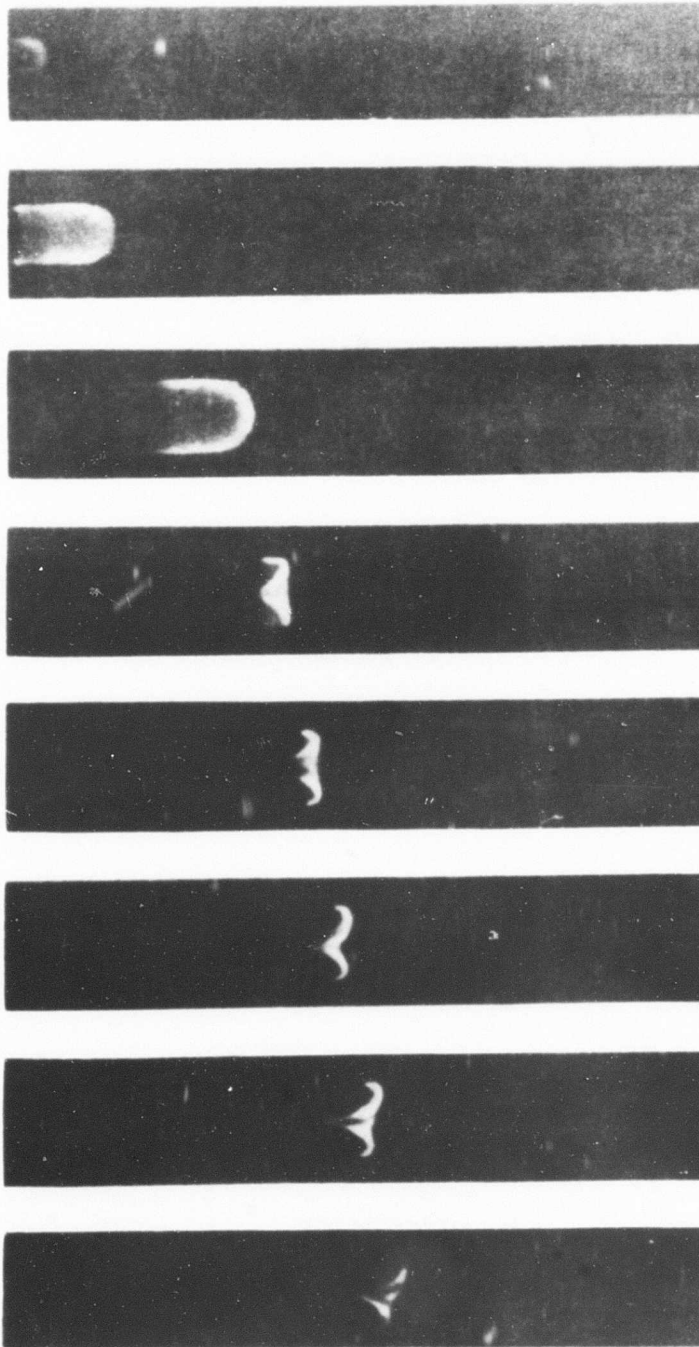


FIG. 8
FLAME PROPAGATING IN A CLOSED CYLINDER
(AFTER ELLIS AND WHEELER, REF 26)

temperature in the reaction zone can be lower than T_f only by the small amount $\frac{RT_f^2}{E}$. Frank-Kamenetsky concludes therefore that the flame front can reach the wall only with practically constant temperature T_f or break up before reaching it. A rigorous theory would have to be based on the two-dimensional heat conduction and flow problem at the wall. Instead, as a rough approximation, Frank-Kamenetsky concludes that no heat flow parallel to the flame front can take place in the reaction zone. The following cases are discussed in his paper:

1. The heat flow $\Omega_1 = c_p \cdot \rho_0 \cdot S_t (T_f - T_0)$ perpendicular to the flame front is greater than the heat flow through the wall

$$\Omega_2 = \beta (T_f - T_0),$$

where β is the heat transfer coefficient, and it is assumed that the outside of the tube is kept at the initial temperature T_0 . The flame will then reach the wall at such an angle that the component of Ω_1 perpendicular to the wall equals Ω_2 , Fig 6a. The angle φ must then fulfill the condition

$$\sin \varphi = - \frac{\beta}{c_p \rho_0 S_t} \quad (33)$$

where φ is taken positive if it contains the unburnt gas. It is seen that φ must always be negative if heat flows through the wall from inside to outside. Experimental evidence for this behavior of a flame is given, for instance in a series of flame photographs made by Ellis and Wheeler²⁶, Figure 8; it shows that the flame, propagating in a closed tube, curves always backwards at the wall, no matter how the gas flow distorts its shape during the travel.

2. If heat flows from the wall into the flame, e.g. due to catalytic reaction or by heating it sufficiently from outside, φ assumes positive values, Figure 6b.
3. The wall stays cold inside, ($\beta \gg c_p \rho_0 S_f$); then the flame cannot reach it but will assume a shape as in Figure 7a. The distance d will be roughly equal to the thickness of the heating zone d_f given by equation (30). In the case of a flame burning outside a tube, (Bunsen burner), the same distance must appear, Figure 7b. The views and experimental results reported in a paper by Garside, Forsyth and Townend⁵, particularly the analogous behavior of "dead space" and rounding of the flame tip in burner flames, and of limiting diameter in tube propagation, are in agreement with Frank-Kamenetsky's conclusions.

F. The theory of Lewis and von Elbe

It has been pointed out by various authors^{2,3,8,19} that the theory of flame propagation must be revised, taking into account the kinetics of chain reactions, and the presence of active centers (free atoms and radicals) in the reaction zone. The first attempt in this direction is due to Lewis and von Elbe^{2,27}, in their treatment of the decomposition of ozone. These authors recognized the importance of diffusion in flame propagation, and consequently based their theory on the diffusion equation

$$D \frac{d^2 N_{O_2}}{dx^2} - \frac{d}{dx} (N_{O_2} S_x) + w = 0 \quad (34)$$

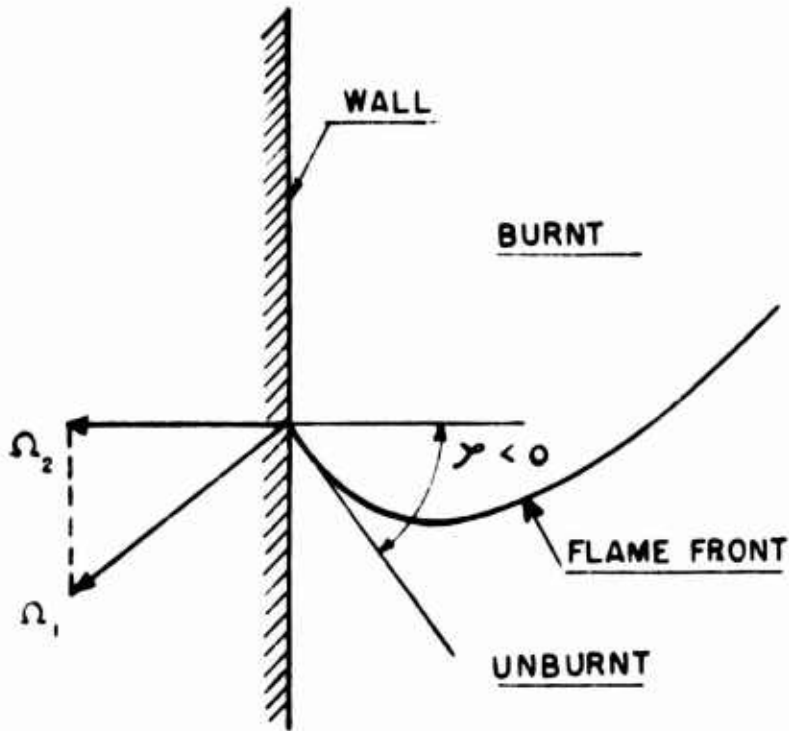


FIG. 6a

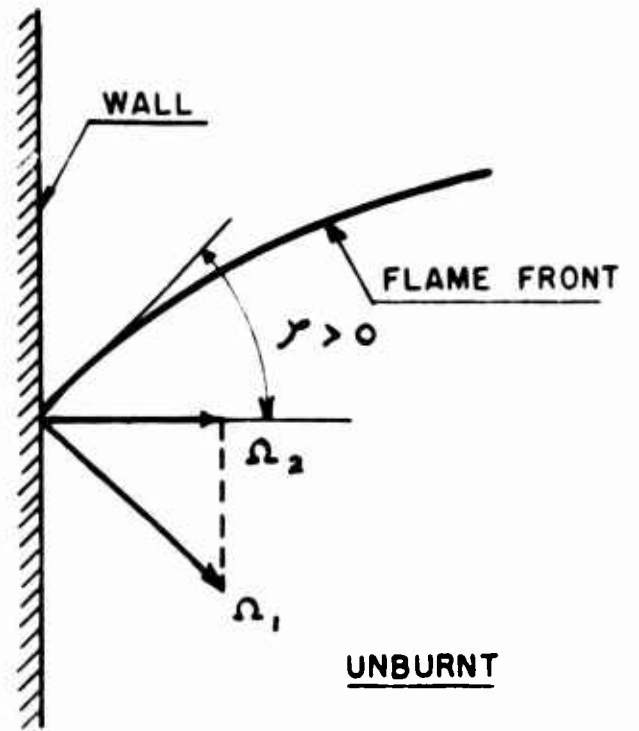


FIG. 6b

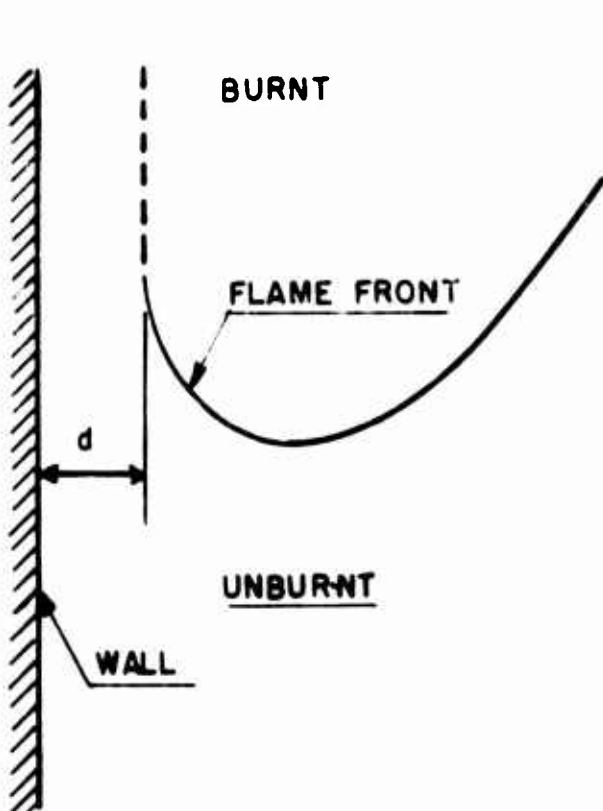


FIG. 7a

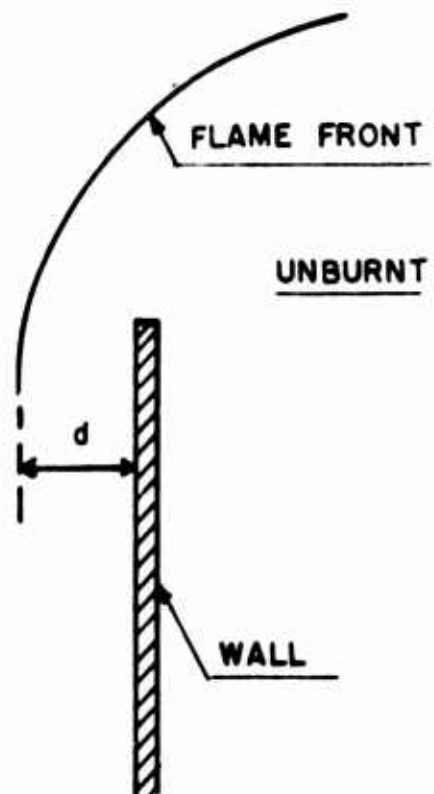


FIG. 7b

SHAPES OF A FLAME NEAR A WALL
(AFTER FRANK-KAMENETSKY REF. 25)

for the concentration N_{O_2} of oxygen. Here D is the diffusion coefficient, S_x the flow velocity at x given approximately by

$$S_x = S_t \frac{T}{T_0} \quad (35)$$

and W the reaction rate of the reaction $O + O_3 \rightarrow 2O_2$, (a)

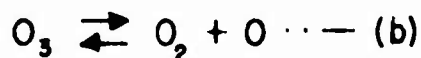
$$W = \frac{dN_{O_2}}{dt} = 2i \cdot e^{-\frac{E}{RT}} \quad (36)$$

Since O_2 is present in considerable excess, its concentration can be approximately written

$$N_{O_2} = N_{O_2}(f) \cdot \frac{T_f}{T} \quad (37)$$

The following additional assumptions are made:

(1) The reaction



is very fast in comparison to (a), so that the concentrations can be linked by an equilibrium equation:

$$\frac{N_O \cdot N_{O_2}}{N_{O_3}} = K = 3.03 \cdot 10^9 \cdot \frac{N_{O_2}(f)}{P} \cdot \frac{T_f}{T} e^{-12300/T} \quad (38)$$

The expression for the equilibrium constant was derived from data by Kassel.

(2) The sum of thermal and chemical energy is constant throughout the reaction zone. This assumption is introduced in the form

$$N_{O_3} E_{O_3} + N_O E_O = (N_{O_2} + 1.5 N_{O_3} + 0.5 N_O) \bar{c}_p (T_f - T) \quad (39)$$

where E_{O_3} is the molar heat of decomposition of ozone and E_O the

molar heat of recombination of oxygen atoms, both at the temperature T , and \bar{c}_p the mean molar heat capacity of oxygen between T and T_f .

(3) Finally, the following equation is introduced:

$$S_t N_{O_3(o)} = \frac{1}{1.5} \int_{T_0}^{T_f} w \cdot \frac{dx}{dT} \cdot dT \quad (40)$$

which expresses, that all the ozone entering the reaction zone in the unit of time must be decomposed after having passed through it.

For the collision number Z and the diffusion coefficient D expressions given by the kinetic theory of gases are introduced. The final result is given in the form:

$$S_t = 1.05 \times 10^{-8} c_p (1+m) T_0 p^{1/2} \times \left(\int_{T_0}^{T_f} \frac{\left(\frac{T_f}{T} - 1\right)^2 e^{-15300/T}}{\left(1.76 \times 10^{14} e^{-12300/T} + 3.4 \times 10^4 p\right)^2} dT \right)^{1/2} \quad (41)$$

m is the initial molar ratio of oxygen to ozone. A comparison of values obtained by graphical integration of (41) and of experimentally determined transformation velocities is given in Table 1.

TABLE 1 (after Lewis and von Elbe)

p	T_0	T_f	m	S_t calc.	S_t exper.
mm	°K	°K		cm/sec	cm/sec
624	300	1239	3.054	253	55
2560	427	1343	3.054	451	158
595	302	1922	1.016	333	160
3760	468	2044	1.016	664	747

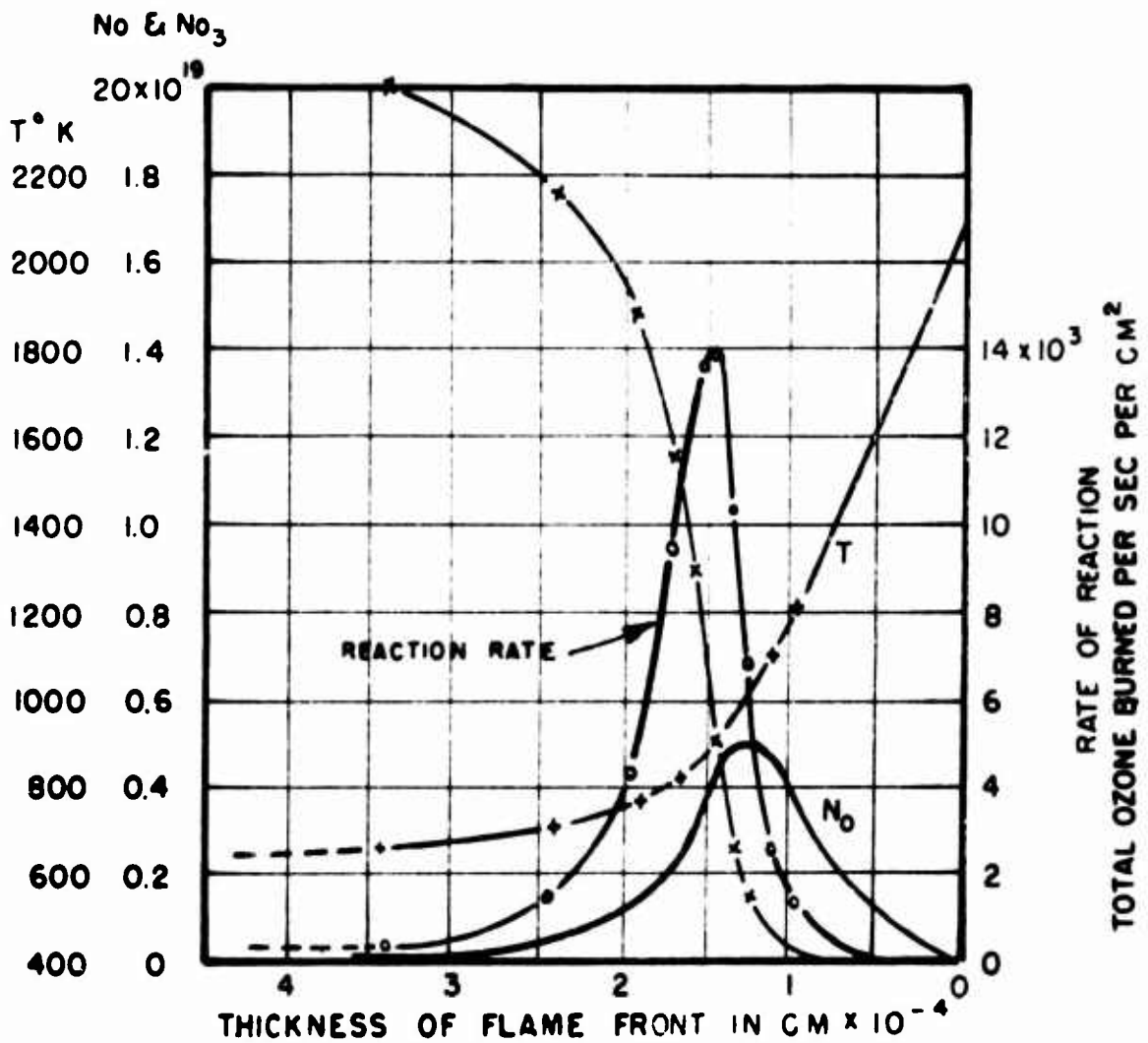


FIG. 9

STRUCTURE OF REACTION ZONE OF OZONE FLAME
 49.6% OZONE IN OXYGEN, $P = 3760\text{MM}$, $T_0 = 468^\circ\text{K}$,
 $T_f = 2044^\circ\text{K}$ (AFTER LEWIS AND V. ELBE, REF. 2 AND 27)

For the last experiment listed in the table, Lewis and von Elbe give a graphical representation of the structure of the reaction zone, Figure 9. It seems rather improbable, however, that the reaction rate should reach its maximum at so low a value of the temperature, as shown in this graph.

The theory of Lewis and von Elbe constitutes the first successful calculation of the absolute value of the transformation velocity S_t . The fair agreement between experimental and theoretical results could be achieved because the particular kind of reaction selected by the authors allowed the introduction of simplifying assumptions. The fundamental assumption of this theory, namely, the constancy of the sum of thermal and chemical energies, was later shown by Zeldovich and Frank-Kamenetsky⁶ to hold under the condition that the coefficients of temperature conduction and diffusion are equal (see p. 16). They showed further the equivalence of the equations of diffusion and of heat conduction under the same condition. Both the theory of Lewis and von Elbe and the thermal theory are based in addition on a kinetic law of the form $W = S \cdot e^{-\frac{E}{RT}}$. Therefore, the two theories should give similar results and the theory of Lewis and von Elbe constitutes a particular case of the more general thermal theory of Zeldovich.

G. Formulation of the thermal theory for more complex reaction mechanism

In a qualitative way, Zeldovich and Semenov⁷ have discussed the problem of dealing with chain reactions in flame propagation. They distinguish two main types of reactions:

Type 1: The life time of the active centers is short compared with the duration of the reaction. In this case, the instantaneous concentrations of the active centers can be determined with sufficient accuracy by equilibrium with the reacting substances and are uniquely connected with the concentrations of these substances. The reaction rate can be expressed in this case by a "classical" law of the form $W = S e^{-\frac{E}{RT}}$, in terms of the concentrations of the reacting substances alone. For this type of reaction, the theories of Lewis and von Elbe and of Zeldovich and Frank-Kamenetsky can be applied.

Type 2: The life time of the active centers is of the same order as the time of reaction or larger. This condition leads to the autocatalytic type of chain reaction. This class, with the combustion of hydrogen and the hydrocarbons as outstanding examples, presents difficulties for the theory of flame propagation which have not yet been overcome. The complications are due only in part to the purely mathematical side of the problem, to a greater part, however, to the lack of definite knowledge about the mechanisms of the reactions.

Formulated quite generally, as has been done for instance by Damköhler²⁸, (cf. ref. 9 pp. 115-117), the problem consists in finding a simultaneous solution of the differential equation of heat conduction, equation (6), and of as many diffusion equations as there are different kinds of particles taking part in the reactions. In these equations appear the terms which give the generation of heat and the creation or destruction of particles, which depend explicitly on the temperature and the concentrations, not on the independent variable x . This has led Zeldovich and Frank-Kamenetsky¹⁹ to eliminate x entirely from the equations, by introducing the following set of variables: as independent variables, the non-dimensional temperature θ and the non-dimensional concentration ν ; (for instance by setting $\theta = \frac{T - T_0}{T_f - T_0}$, $\nu = \frac{n - n_0}{n_f - n_0}$); as dependent variables, the expressions

$$\eta = \xi \frac{d\theta}{dx}, \quad \zeta = \xi \frac{d\nu}{dx} \quad (42)$$

where ξ is a constant of the dimension of a length (e.g. equal to the thickness of the heating zone $\xi = \frac{x}{S_t} = \frac{\lambda}{c_p \rho_0 S_t}$). In these variables, the differential equations of heat conduction and diffusion become*

$$\eta \frac{d\eta}{d\theta} - \eta + \lambda_1 f(\theta, \nu) - \mu \mathcal{F}(\theta) = 0 \quad (43)$$

$$\zeta \frac{d\zeta}{d\nu} - \zeta + \lambda_2 f(\theta, \nu) = 0 \quad (44)$$

* These equations lack generality, however, in that the factor of the second term cannot be unity in all equations if the condition $D = \mathcal{X}$ is not fulfilled, and in that the same function $f(\theta, \nu)$ need not apply for the generation of heat and of particles.

where λ_1, λ_2 and μ are non-dimensional parameters, containing among other constants the transformation velocity $S_{t,f}$ is a dimensionless function expressing the dependence of the reaction rate on temperature and concentration, and $\Psi(\theta)$ expressing the heat loss due to walls and radiation. In the general case, several equations (44) have to be set up. With the indicated choice of θ and ν the simple boundary conditions

$$\eta = 0, \quad \zeta = 0 \quad \text{for } \theta = \nu = 0 \text{ and } \theta = \nu = 1 \quad (45)$$

are obtained. The authors give explicit solutions only for the following cases:

For reactions characterized above under type 1, and neglecting heat loss, there results the thermal theory^{6,7,18}, leading to the general solution

$$S_t = \sqrt{2 p! \frac{\chi}{T_f} \frac{1}{\theta_f^{p+1}}} \quad (26)$$

which has been discussed on page 18.

For the other extreme, an isothermal autocatalytic reaction ("cool flame", diffusional propagation) only equation (44) in the form

$$\zeta \frac{d\zeta}{d\nu} - \zeta + \frac{D}{S_t^2} w = 0 \quad (44a)$$

has to be solved. The authors give the solutions

$$S_t = \frac{5}{\sqrt{6}} \sqrt{\varphi D} \approx 2 \sqrt{\varphi D} \quad (46)$$

for a kinetic law $w = \varphi \cdot \nu (1 - \nu)$ (46a)

where φ is the coefficient of auto-acceleration, and

$$S_t = (1 - 2\alpha) \sqrt{\frac{\varphi D}{2}} \quad (47)$$

for a kinetic law

$$w = \varphi \nu^2 (1 - \nu) - \alpha \varphi \nu (1 - \nu) \quad (47a)$$

corresponding to auto-acceleration of second order with destruction of active centers. α is the ratio of rate of destruction to rate of reaction. It is seen that in the latter case propagation is limited to the range $\alpha < \frac{1}{2}$. It is pointed out by the authors, that kinetic conditions in all real cases are too complicated to allow an analytical solution of equations (43), (44).

H. Hydrodynamic aspects of flame propagation

The theory as discussed up to here neglects the possible effects of motion in the gas. Gas flow, however, is always present, either due only to the combustion process itself, or in addition introduced by external conditions.

The hydrodynamical treatment of combustion under the assumption of strictly one-dimensional flow leads to the Hugoniot curve, Fig. 10, which

gives the locus of the final states for a given initial state, in terms of pressure p and specific volume V . A detailed review of this theory has been given in a recent report⁴³ so that the discussion here can be brief.

Slow combustion (deflagration) corresponds to the portion AB of the Hugoniot curve. The velocities V_1 of the unburnt and V_2 of the burnt gas relative to the flame front are both zero in point A. In going from A to B, both increase; in point B V_1 reaches a maximum but remains always smaller than the velocity of sound in the unburnt gas, c_1 and V_2 becomes equal to the velocity of sound in the burnt gas, c_2 . It can be shown that the flow states corresponding to points beyond B ($V_1 < c_1, V_2 > c_2$) cannot be realized. Which point between A and B will correspond to the actual combustion process is not determined by hydrodynamics. In the case of strictly one-dimensional flow with a plane flame front V_1 is identical with the transformation velocity S_t . From the point of view of the thermal theory of flame propagation it has been always assumed that $S_t = V_1$ and V_2 are so small that the combustion process can be represented by a point very near to A on the Hugoniot curve. In other words it has been assumed that $V_1 \ll c_1$ and $V_2 \ll c_2$. This assumption is not too restrictive in many cases, since the observed values of S_t are very small compared with the velocity of sound in the unburnt gas. As long as $V_1 \ll c_1$ and $V_2 \ll c_2$, the pressure gradient across the flame front will be very small (ref. 2, p. 163) and its effect on heat conduction, diffusion and chemical kinetics can be neglected.

For larger values of V_1 and V_2 an influence of the flow on the transformation velocity cannot be excluded any more. No theory on this effect exists yet. It appears reasonable to assume, however, that the rise of pressure and temperature due to the compression wave traveling ahead of the flame front will lead to an increased transformation velocity. This acceleration can take place only until point B is reached. Propagation processes with still higher velocities correspond to the portion CD and beyond D of the Hugoniot curve (detonation). It has been shown^{43b} that under the assumption that the detonation process consists of a shock wave followed by combustion, and assuming strictly one-dimensional flow, stable propagation corresponds only to point D, where V_1 is a minimum, and $V_1 > c_1$, $V_2 = c_2$. This state is reached only through unstable transition states. Detonation will not be discussed further in this report and reference is made to the texts of Lewis and von Elbe² and Jost^{9,9a} for reviews of this subject.

The assumption of one-dimensional flow is actually never fulfilled for a flame propagating in a pipe. Jost (ref. 9, p. 92-96) has stressed the fact that the unburnt gas must be in a vortex-like motion in order to enable the front of a flame propagating in a tube to assume the convex shape which is always observed. (This shape will be due, at least in part, to the condition imposed on the flame near the wall, p. 26). A hydrodynamical treatment of this complicated motion has not yet been attempted. The effect of this motion on the flame speed is accounted for theoretically only in an increase of flame surface without a change in transformation

velocity. However, the motion of the gas changes the shape of the flame front so profoundly that it becomes difficult or even impossible to calculate the transformation velocity from the observed propagation speed. This has precluded a check of the validity of the theory in this case.

A large effect of flow on flame propagation is finally to be expected where turbulent motion is present. That such turbulence may even originate in the flame itself, due to a peculiar instability, has been demonstrated by Landau²⁹. His treatment is based on the following assumptions:

- (a) The dimensions which characterize the hydrodynamical problem (such as tube diameter, dimensions of bodies in contact with the gas) are large compared with the thickness of the combustion layer, so that the latter can be treated as a surface of discontinuity.
- (b) The propagation velocity is small compared with the velocity of sound, allowing the gas to be treated as incompressible.
- (c) Viscosity is neglected, restricting the validity of the result to large values of the Reynolds numbers $\frac{\alpha V_1}{\nu_1}$, $\frac{\alpha V_2}{\nu_2}$ where α is a characteristic dimension, V_1 and V_2 are the velocities of the unburnt and burnt gas, and ν_1 and ν_2 are the kinematic viscosities of unburnt and burnt gas.

As is usual in the theory of flame propagation, the origin of the coordinate system is fixed in a small portion of the combustion layer, which is considered as a plane discontinuity surface; the X -axis points in the direction of the unperturbed gas movement, which is assumed to be

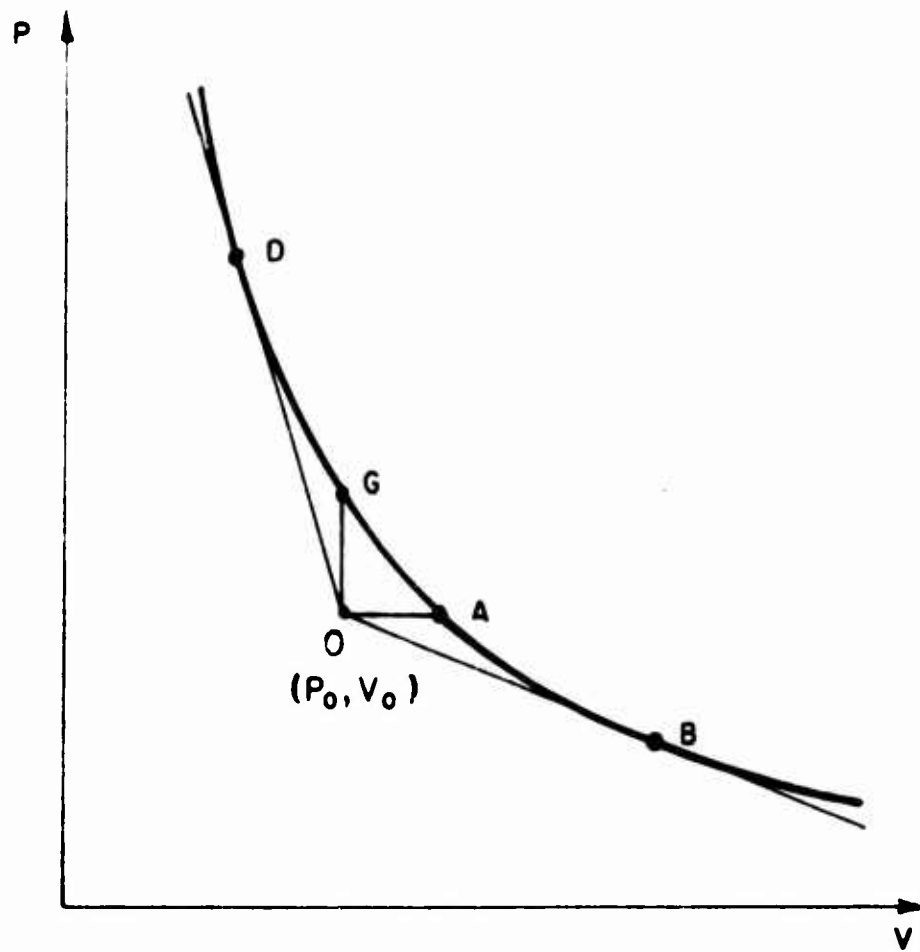


FIG. 10
HUGONIOT CURVE

velocity. However, the motion of the gas changes the shape of the flame front so profoundly that it becomes difficult or even impossible to calculate the transformation velocity from the observed propagation speed. This has precluded a check of the validity of the theory in this case.

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As is usual in the theory of flame propagation, the origin of the coordinate system is fixed in a small portion of the combustion layer, which is considered as a plane discontinuity surface; the X -axis points in the direction of the unperturbed gas movement, which is assumed to be

perpendicular to the combustion layer. The index 1 refers to the unburnt gas ($x < 0$), the index 2 to the burnt gas ($x > 0$). A small perturbation velocity V' is superposed over the unperturbed movement V . The components of V' must fulfill the differential equations (neglecting small terms of second order):

$$\text{(continuity)} \quad \frac{\partial v_x'}{\partial x} + \frac{\partial v_y'}{\partial y} = 0 \quad (48)$$

$$\frac{\partial v_x'}{\partial t} + v \frac{\partial v_x'}{\partial x} = - \frac{1}{\rho} \frac{\partial p'}{\partial x} \quad \text{(Euler)} \quad (49)$$

$$\frac{\partial v_y'}{\partial t} + v \frac{\partial v_y'}{\partial x} = - \frac{1}{\rho} \frac{\partial p'}{\partial y}$$

where ρ is the density and p' the perturbation pressure. Equations

(48) and (49) lead to

$$\frac{\partial^2 p'}{\partial x^2} + \frac{\partial^2 p'}{\partial y^2} = 0 \quad (50)$$

Solutions are sought which are periodic in time and in y , by setting them proportional to $e^{iky + \Omega t}$. Instability will then correspond to the case $\text{Re}(\Omega) > 0$. The solutions fulfilling equations (48), (49) and (50) are

$$v_{1x}' = A e^{iky + kx + \Omega t} \quad (51)$$

$$v_{1y}' = iA e^{iky + kx + \Omega t}$$

$$p_1' = A \rho_1 \left(\frac{\Omega}{k} + v_1 \right) e^{iky + kx + \Omega t}$$

in the unburnt gas, and

$$v_{2x}' = B e^{iky - kx + \Omega t} + C e^{iky + \Omega t - \frac{\Omega}{v_2} x}$$

$$v_{2y}' = iB e^{iky - kx + \Omega t} - C \frac{i\Omega}{kv_2} e^{iky + \Omega t - \frac{\Omega}{v_2} x} \quad (51a)$$

$$p_2' = -B \rho_2 \left(v_2 - \frac{\Omega}{k} \right) e^{iky - kt + \Omega t}$$

for the burnt gas. It will be seen that the solutions are set up so that they vanish for $|x| \rightarrow \infty$, if $\text{Re}(k) > 0$, and $\text{Re}(\Omega) > 0$.

This is of course necessary if they should indicate that a disturbance small everywhere else becomes large within the combustion zone. For this reason the particular solution with the factor C , obtained by setting $p' = 0$ cannot be used for the unburnt gas.

At the discontinuity ($x=0$) the following boundary conditions must be fulfilled: based on assumption (b) it is assumed that the propagation

velocity is not affected by the disturbance. The displacement of the discontinuity in the X -direction

$$\zeta(y,t) = D e^{iky + \Omega t} \quad (52)$$

is therefore connected with the disturbance velocities by

$$v_{1X}' = v_{2X}' = \frac{\partial \zeta}{\partial t} \quad \text{for } X = 0 \quad (53)$$

To the same approximation, the pressure is assumed to be continuous across the discontinuity:

$$p_1 = p_2 \quad \text{for } X = 0 \quad (54)$$

Finally, the tangential component of the velocity must be continuous at the discontinuity. The angle of inclination of the discontinuity,

assumed to be small in the initial stage of perturbation, is $\frac{\partial \zeta}{\partial y}$.

Thus, to a first approximation, the tangential velocity is composed of the projection of v' equal to v_Y' , and the projection of v equal to $v \frac{\partial \zeta}{\partial y}$.

This gives

$$v_{1Y}' + v_1 \frac{\partial \zeta}{\partial y} = v_{2Y}' + v_2 \frac{\partial \zeta}{\partial y} \quad \text{for } X = 0 \quad (55)$$

as last boundary condition.

The conditions (53), (54) and (55) lead to four linear homogeneous equations for the constants A, B, C, D , which have a non-trivial

solution only if the equation for Ω :

$$\Omega^2 (v_1 + v_2) + 2 \Omega v_1 v_2 k + k^2 v_1 v_2 (v_1 - v_2) = 0 \quad (56)$$

is fulfilled, (where the continuity condition, $\rho_1 v_1 = \rho_2 v_2$, has been taken into account). In the case of combustion, there is always

$\rho_1 > \rho_2$, $v_1 < v_2$. Equation (56) has then always solutions for which $Re(\Omega) > 0$ (considering $Re(k) > 0$). Unstability under

the assumed conditions is thus proved. Landau's conclusions from this result are as follows:

The "thermal" regime of combustion, on which the usual theories of flame propagation are based^{*}, is valid only under conditions which depend essentially on viscosity (small Reynolds number, contradictory to the assumptions made in the derivations of the instability). Under conditions of large Reynolds numbers, however^{**}, instability will lead to a diffuse combustion zone in which turbulence will cause heat transfer considerably in excess of that due to conduction. Since turbulent motion depends essentially on the characteristic dimensions of the

* this obviously includes "diffusional" propagation p. 34

** Though not stated clearly in Landau's paper, his implication is obviously that turbulence need not exist in the gas before the flame has passed. The unburnt gas may also be at rest relative to the tube. Turbulence will appear always in the flame zone if the Reynolds numbers $\frac{\rho v_1}{\mu}$, $\frac{\rho v_2}{\mu}$ are large, where v_1 , v_2 are the gas velocities relative to the combustion zone.

problem, Landau concludes that in this "convective" regime of combustion the width of the combustion zone and the propagation velocity will depend on the characteristic dimensions. More explicitly, for flame propagation in a tube, and under conditions where viscosity and heat conduction (or diffusion) cannot have influence, Landau concludes from dimensional considerations that the thickness d of the flame zone must be proportional to the tube diameter δ and the propagation velocity must be proportional to $\frac{\delta}{\tau}$, where τ is a reaction time dependent only on the chemical kinetics.

This result:

$$d \sim \delta, \quad v \sim \frac{\delta}{\tau} \quad (57)$$

is said to be valid for V small compared to the velocity of sound and for large Reynolds numbers.

Though this result will have to be accepted with some caution, experimental data confirm the increase of propagation velocity with tube diameter. Figure 11 shows the results of measurements by Coward and Hartwell³⁰ (ref. 9, p. 99). Two distinct regions can be observed in the graph: the increase of observed flame speed up to a diameter of about 10 cm could be explained by the authors by determining the surface of the flame front from flame photographs, Figure 12. Table 2 shows that the true transformation velocity, obtained by multiplying the observed speed with the ratio of tube cross section to flame surface, is constant.

TABLE 2

Flame speeds in 10% Methane-air mixture in tubes of various diameters

(Coward and Hartwell, ref. 30)

TUBE DIAMETER	FLAME MOVEMENT	OBSERVED FLAME SPEED	FLAME SURFACE	TRANSFORMATION VELOCITY
cm		cm/sec.	cm ²	cm/sec.
10	Horizontal	111	300	29
10	"	71	189	29
5	"	92	66	27
5	"	61.5	48.5	25
2.5	"	71.5	12.6	28
2.5	"	63	11.0	28
2.5	"	59	10.4	28
5	Upward	68	48	28
5	"	92.5	66.5	27
5	Downward	61	46	26
5	"	58	63.5	26

This range corresponds to the regime called "thermal" by Landau. For diameters between 10 and 20 cm, the graph Figure 11 indicates an unstable transition and for still larger diameters an approximately linear increase of propagation velocity. Coward and Hartwell point out that in this range

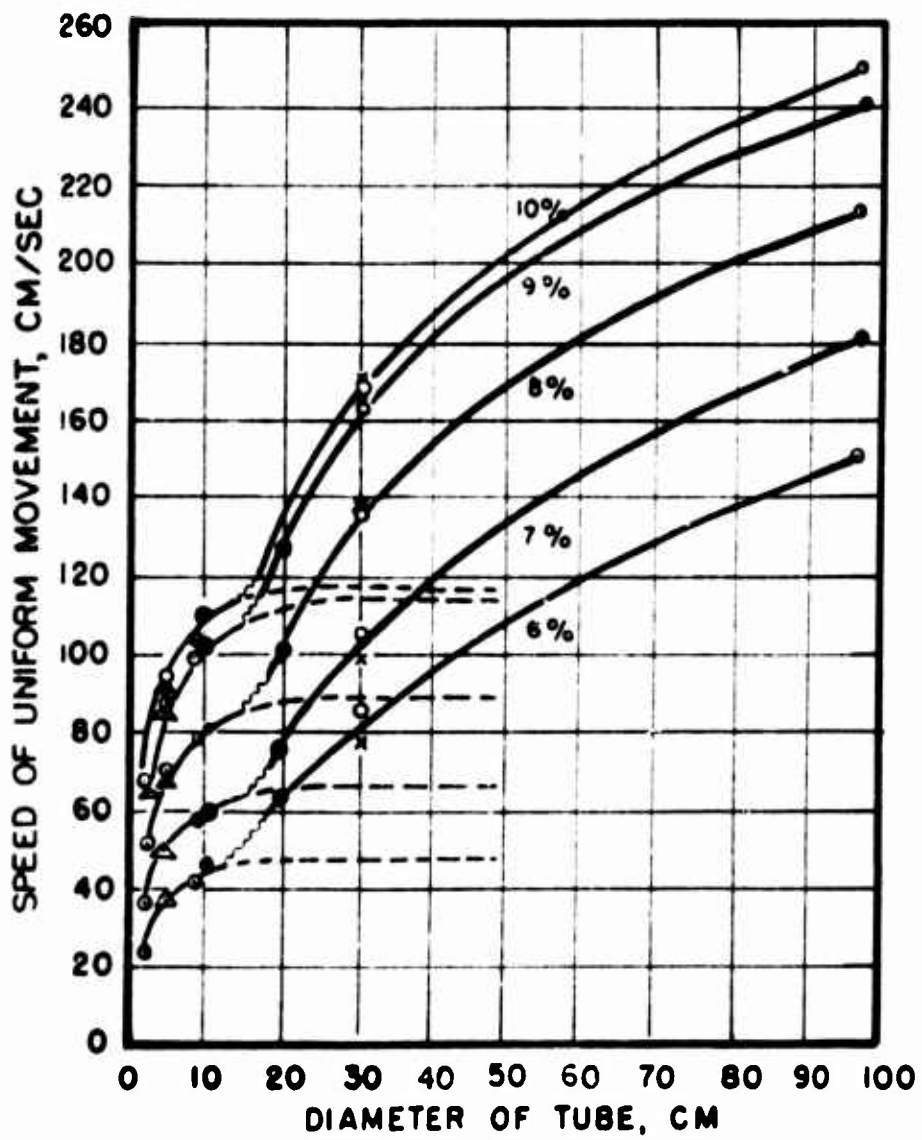
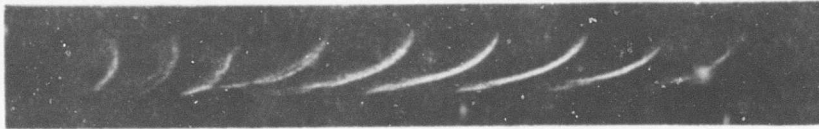


FIG. 11
 FLAME SPEEDS IN METHANE-AIR MIXTURES IN
 TUBES OF VARIOUS DIAMETERS (AFTER COWARD
 AND HARTWELL REF 30)



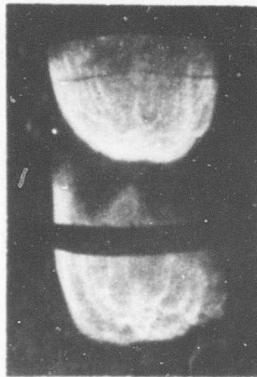
a



b



c



d

FIG. 12

PHOTOGRAPHS OF METHANE-AIR FLAMES PROPAGATING
IN TUBES OF VARIOUS DIAMETERS.

- a: D= 2.5 CM HORIZONTAL PROPAGATION
b: D= 5 CM " "
c: D= 10 CM " "
d: D= 24 CM DOWNWARD "

(AFTER COWARD AND HARTWELL, REF. 30)

it was impossible to estimate the flame surface, since it became irregular and diffuse. The beginning of this irregular appearance can already be observed in the photograph for diameter 10 cm, Figure 12. It seems reasonable to assume that this range is identical with Landau's "convective" regime.

Landau includes in his paper a discussion of the limitations imposed on the propagation velocity by the laws of gasdynamics (cf. p.35). His proof of the instability of processes corresponding to points beyond **B** on the Hugoniot curve (Figure 10) appears to be unnecessarily complicated. The subject is treated in a more satisfactory way in ref. 43 and 43a. It should be borne in mind that the limiting velocity corresponding to point **B** lies already outside the range of validity of the theory of Landau, as the velocity of the burnt gas V_2 relative to the flame front becomes equal to the velocity of sound at this limit. Therefore, deviations from the simple expressions (57) should be expected already for lower velocities. In a qualitative way Landau's theory explains many of the difficulties experienced by workers in the field of flame propagation in tubes (ref. 9, page 101), and the instability postulated by Landau may be responsible for the increase in flame velocity obtained by introducing constrictions³¹ or wire spirals³² into the tubes.

The influence of turbulence on the velocity of flame propagation has been investigated by Damköhler^{13,13a} and Shchelkin^{33,33a}. Both authors base their treatment on the description of turbulent flow by means of a

characteristic length l' , an average fluctuation velocity $\overline{v'}$, and an exchange quantity ϵ . Damköhler defines these quantities according to the phenomenological theory of Prandtl (cf. ref. 34): the mixing length l' is defined by

$$\overline{|v'|} = l' \left| \frac{\partial u}{\partial y} \right|, \quad (58)$$

where $\overline{|v'|}$ is the time average of the absolute value of the instantaneous fluctuation velocity v' , and $\left| \frac{\partial u}{\partial y} \right|$ the absolute value of the gradient of the flow velocity u in a direction y perpendicular to the flow. The exchange parameter ϵ was introduced by Prandtl in analogy to the kinetic theory of gases: in a quiescent gas kinematic viscosity ν , coefficient of diffusion D and coefficient of temperature conduction χ are, to a first approximation, equal and given by (cf. p. 16 and ref. 22)

$$\nu = D = \chi = \frac{1}{3} l c \quad (59)$$

where l is the mean free path and c the mean molecular velocity. Prandtl showed that in a turbulent medium these coefficients have to be replaced by the quantity ϵ , which is defined in an analogous way by ϵ

$$\epsilon = l' \overline{|v'|} \quad (60)$$

Shchelkin adopts definitions in accordance with the statistical theory of Taylor and Karman (cf. ref. 35): as characteristic length he introduces the scale, defined by

$$L = \int_0^{\infty} \overline{R(x)} dx \quad (61)$$

where $R(x)$ is the correlation coefficient

$$R = \frac{\overline{v' v_1'}}{\sqrt{\overline{v'^2}} \sqrt{\overline{v_1'^2}}} \quad (61a)$$

between the fluctuation velocities v' and v_1' at two points a distance x apart. The average fluctuation velocity is defined by Shchelkin as the R.M.S. value of v' . Unfortunately Shchelkin makes no distinction between scale L and mixing length l' in his treatment, using expression (60) in spite of the fact that in the statistical theory the coefficient of exchange ϵ is not related to the scale by this formula. Because both Damköhler's and Shchelkin's theories are of a rather crude and qualitative nature, these discrepancies of definitions will be disregarded in the following discussion.

The following cases are treated by Damköhler and by Shchelkin:

- (a) The mixing length l' is small compared with the thickness of the flame front d , $l' \ll d$.

In this case, the shape of the flame front will not be affected by turbulent motion. The only effect will be an increase of all transport processes, like heat conduction and diffusion. It follows from dimensional analysis that the transformation velocity is proportional to

$$\sqrt{\frac{x}{\tau}} \text{ or } \sqrt{\frac{D}{\tau}}, \text{ where } \tau \text{ is a characteristic time}^*$$

* The expressions for S_t of the older thermal theory, pages 7&8, as well as those of the new thermal theory, formula (26) and those for "diffusional" propagation, (46) and (47), have all this general form.

If $l' \ll d$, this time is the reaction time, depending only on the physicochemical properties of the gas mixture. Since χ or D has to be replaced by ϵ in a turbulent flow, Dancköler writes for the propagation velocity under turbulent conditions, if $l' \ll d$,

$$S_{\text{turb.}} = S_{\text{lam}} \sqrt{\frac{\epsilon}{\chi}} = S_{\text{lam}} \sqrt{\frac{\epsilon}{U}} \quad (62)$$

where S_{lam} is identical with the transformation velocity S_t in a laminar flow.

In order to account for the fact that the propagation velocity must become equal to S_{lam} for zero turbulence, Shchelkin assumes that the total coefficient of heat exchange is the sum of temperature conductivity χ and turbulent exchange quantity ϵ . This leads to the alternative expression

$$S_{\text{turb}} = S_{\text{lam}} \sqrt{\frac{\chi + \epsilon}{\chi}} = S_{\text{lam}} \sqrt{1 + \frac{\epsilon}{\chi}} \quad (63)$$

Shchelkin points out, however, that the case $l' \ll d$ is not likely to occur in practice, as the width of the flame front is normally of the order 0.1 mm and mixing lengths smaller than this are not encountered under the conditions of flow in practical applications. Only for slow-burning mixtures the thickness of the flame front can be considerably larger and in this case the condition $l' \ll d$ could be fulfilled more easily.

(b) The intermediate range, $l' < d$, is discussed only by Shchelkin.

In this case, heat conduction (and diffusion) will still be governed by the coefficient of turbulent exchange $\epsilon = l' \bar{v}$, but the time τ in the general expression for the transformation velocity $S \sim \sqrt{\frac{x}{\tau}}$ will no longer be equal to the reaction time under laminar flow conditions. Shchelkin asserts this to be so because in a certain plane parallel to the flame front and within the combustion zone turbulent mixing will bring together gas of the whole temperature range $T - l' \frac{dT}{dx}$ to $T + l' \frac{dT}{dx}$. If the temperature gradient $\frac{dT}{dx}$ is replaced approximately by $\frac{1}{d}(T_f - T_0)$, it is seen that the effect of turbulence on the reaction rate will become noticeable if $\frac{l'}{d}(T_f - T_0)$ cannot be neglected compared with T . Shchelkin points out that the time of reaction, proportional to $e^{E/RT}$ under laminar conditions, will increase by becoming proportional to $e^{R[T - l'/d(T_f - T_0)]}$. (This expression cannot be considered correct as it corresponds to the maximum reaction time, not to the average. However, considering the fact that the regions at higher temperature $T + \frac{l'}{d}(T_f - T_0)$ correspond to regions occupied by burnt gas, turbulence will cause some increase in average reaction time.) The author asserts that by increasing l' more and more, a point will be reached where the time of chemical reaction will become so large that the rate-determining factor will be the time of turbulent mixing, of the order $\frac{l'}{\bar{v}}$ instead.

In this way, Shchelkin believes that a continuous change from case (a) $l' \ll d$, to case (c), $l' \gg d$, can be established.

(c) Mixing length l' large compared with (laminar) thickness of flame front $d, l' \gg d$.

Both authors assert that in this case the effect of turbulent motion will consist essentially only in a distortion of the flame front and therefore in an increase of its surface and of the effective propagation velocity in the same proportion. (Semenov⁶ considers this to be the only possible effect of turbulence on flame propagation.)

For small values of \bar{v}' Shchelkin adopts the same simplified description of the flame front already used by Damköhler, Figure 13. The component of \bar{v}' in the direction of flame travel is assumed to create rapidly changing cone-shaped elevations and depressions in the flame front. The area of the base of these cones is of the order l'^2 , and the height of the order $\bar{v}' \frac{l}{S_{10m}}$, since $\frac{l}{S_{10m}}$ is the average time a uniform velocity \bar{v}' is operative to build up a cone. The ratio of the cone surface A_c to the base A_b is thus

$$\frac{A_c}{A_b} = \sqrt{1 + B \left(\frac{\bar{v}'}{S_{10m}} \right)^2}$$

where B is a constant. Assuming the true propagation velocity S_{10m} to remain unchanged by turbulence, the apparent propagation velocity S_{turb} will be increased by the ratio of the surfaces, that is

$$\left(\frac{S_{turb}}{S_{10m}} \right)^2 = 1 + B \left(\frac{\bar{v}'}{S_{10m}} \right)^2 \quad (64)$$

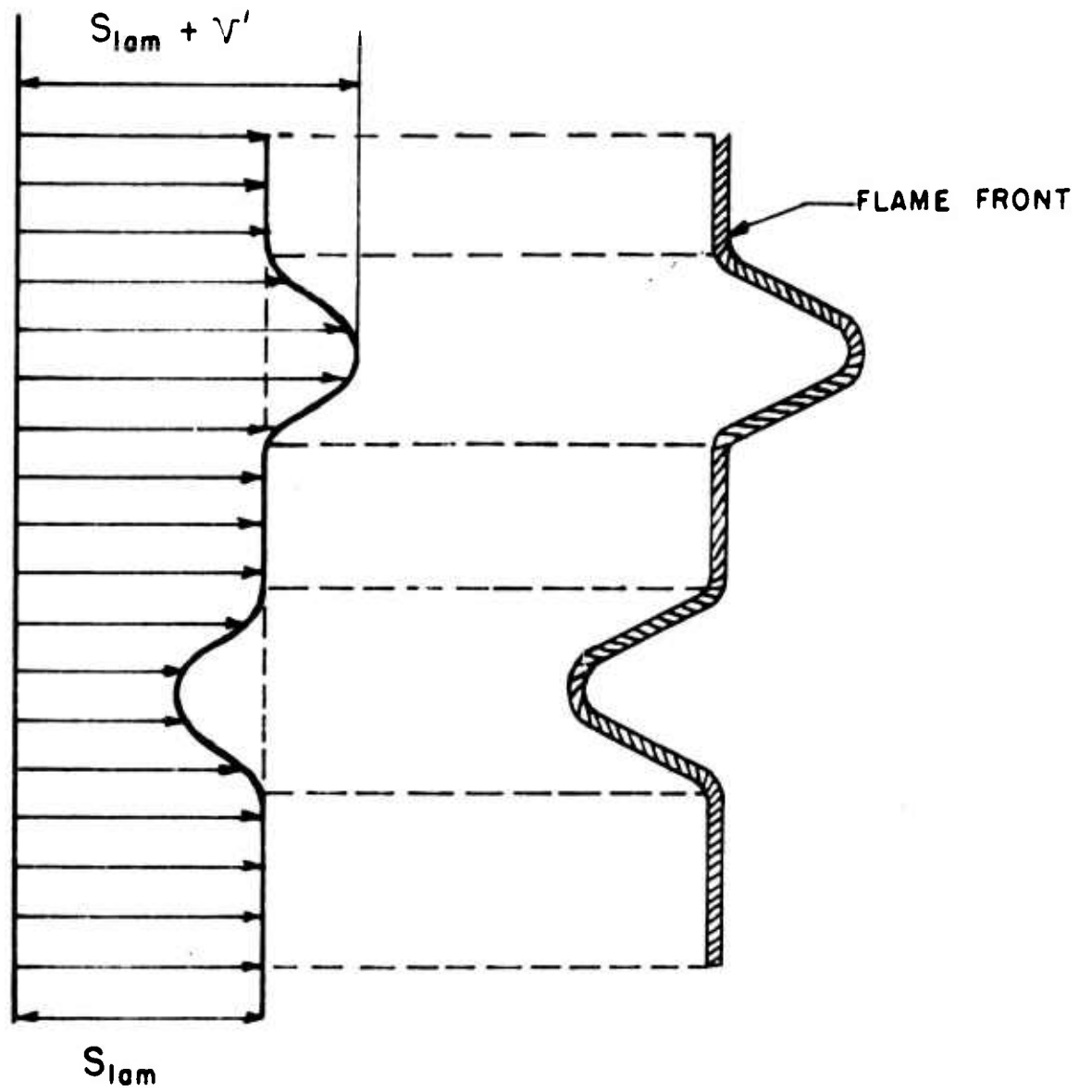


FIG. 13

FLAME FRONT IN A TURBULENT STREAM (AFTER
DAMKÖHLER, REF. 13 AND SHCHELKIN, REF. 33)

For large values of \bar{v} this hyperbolic law goes over asymptotically into a linear relation

$$S_{\text{turb}} \sim \bar{v} \quad (64a)$$

which had been already postulated by Damköhler. (An objection can be raised against this theory: for sufficiently large values of v' , the flame front will be disrupted and propagation will no longer be possible. This upper limit may depend not only on v' , but also on the mixing length l' .) Shchelkin discusses the case $\bar{v} \gg S_{\text{lam}}$ separately. He describes the combustion zone in this case as consisting of a number of islands of unburnt mixture surrounded by burnt gas and decreasing in size while passing through the combustion zone, Figure 14. (As indicated in this figure, there must be a continuous flame front toward the unburnt gas, otherwise combustion would cease, as mentioned above.) Shchelkin asserts that under these conditions heat exchange is determined entirely by the coefficient of turbulent exchange $\epsilon = l' \bar{v}$ and the rate of burning is determined only by the time of turbulent mixing, of the order $\frac{l'}{v'}$. Introduced into the general expression for the propagation velocity $S \sim \sqrt{\frac{\epsilon}{\tau}}$, this gives

$$S_{\text{turb}} \sim \sqrt{\frac{l' \bar{v}}{\frac{l'}{v'}}} = \bar{v}$$

that is the same linear law (64a) previously derived. This rather crude derivation can hardly be considered correct; a computation of the combustion time of a gas volume l'^3 introduced by Shchelkin to justify further the identification of τ with $\frac{l'}{v'}$, is evidently incorrect.

From expression (64) Shchelkin draws the following conclusions:

1. If the mixing length \mathcal{L}' is large compared with the thickness of the flame front, the turbulent propagation velocity S_{turb} depends only on \bar{V} , not on \mathcal{L}' .
2. For values of \bar{V} of the order of S_{lom} , the relative increase of propagation velocity $\frac{S_{\text{turb}}}{S_{\text{lom}}}$ is larger for slow-burning mixtures, for instance for mixtures near the limits of propagation.
3. For \bar{V} large compared with S_{lom} , S_{turb} depends on \bar{V} according to the linear relation (64a); the factor of proportionality (\sqrt{B}) depends probably on the "structure" of turbulence, that is it will depend for instance on the roughness of pipe walls; it will be independent, however, of the physicochemical properties of the gas mixture, and especially of the transformation velocity under laminar conditions S_{lom} .

Very few experimental data are available for comparison with this theory. Damkohler["] carried out observations on Bunsen burners, which indicate an increase of propagation velocity with increasing turbulence, but do not allow a conclusive quantitative evaluation. The diffuse character of the flame front under turbulent conditions is clearly visible in Damkohler's["] flame photographs. Shchelkin cites work on combustion in motors^{36,37}, as experimental evidence for his theory; the increase of propagation velocity with the number of revolutions and the small influence of the chemical nature of the fuel observed in these experiments

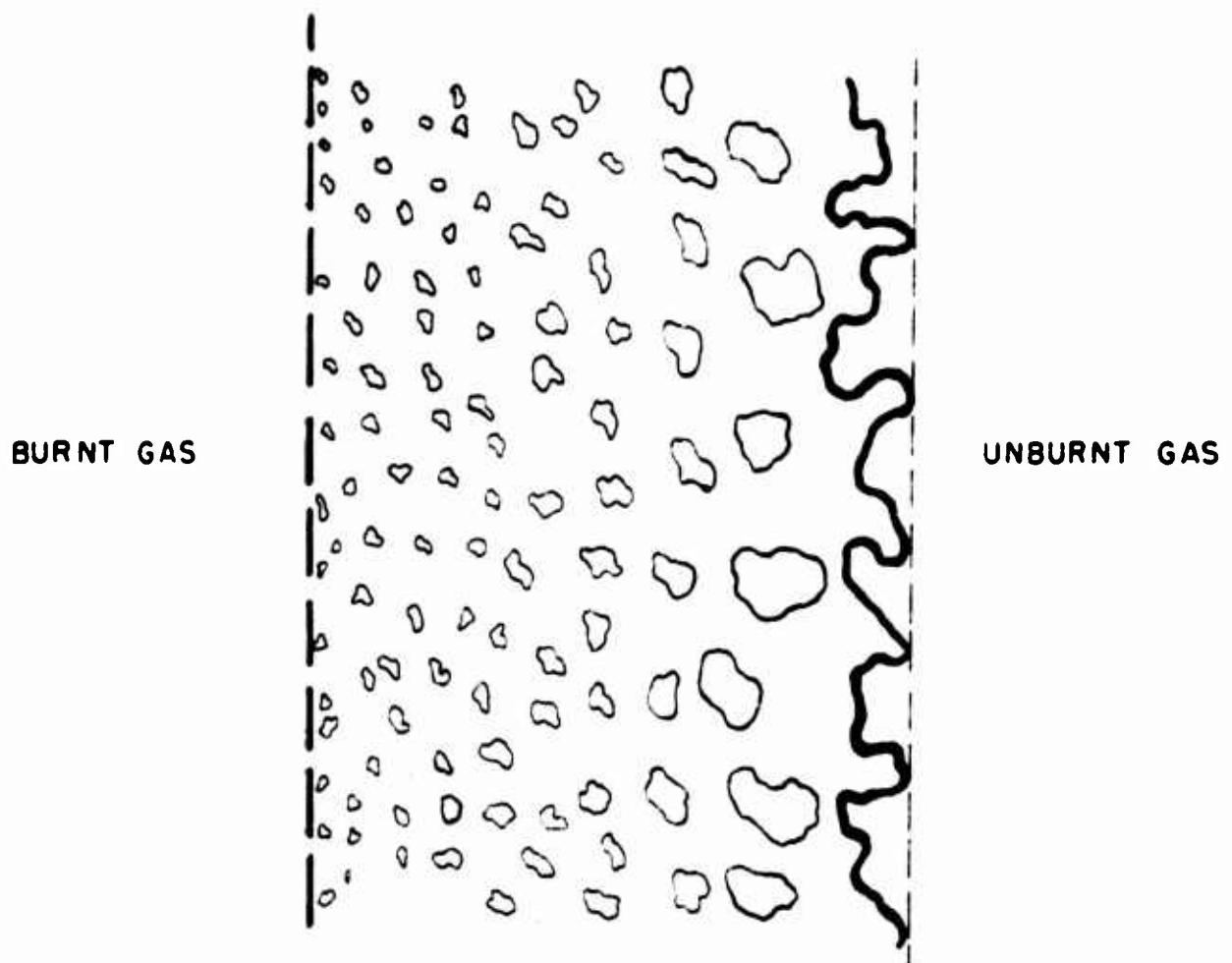


FIG. 14

COMBUSTION ZONE IN A HIGHLY TURBULENT GAS
(AFTER SHCHELKIN REF. 33)

confirm in a qualitative way the theoretical conclusions. Obviously, no quantitative results can be derived because of the lack of any information about turbulent conditions in engine combustion. Recent observations of Unger³⁸ on flame propagation in tubes show the increase of propagation velocity with increase of turbulence. These measurements were carried out in steel tubes in vertical position, the flame propagating downward against the gas stream. Figure 15 shows a plot of propagation velocity (calculated as the sum of observed flame velocity and average gas stream velocity) against Reynolds number for 3 tube diameters. Since \bar{V} is approximately proportional to the Reynolds number, the curves do not agree too well with Shchelkin's hyperbolic law, but they show the asymptotic linear relation for larger values of

Shchelkin's theory was criticized and a modified theory was proposed recently by Wohl⁴⁹. The expressions proposed by this author are:

(a) for $l' < d$:
$$S_{turb} = S_{lom} \sqrt{1 + \frac{\bar{V}}{S_{lom}}}$$

with the approximations

$$S_{turb} = S_{lom} + k \bar{V} \quad \text{for small } \bar{V}$$

and
$$S_{turb} = \sqrt{k \bar{V} S_{lom}} \quad \text{for large } \bar{V}$$

(k is a constant)

(b) for $l' > d$:
$$\frac{S_{turb}}{S_{lom}} = \frac{S_{turb} + k \bar{V}}{S_{turb}}$$

with $S_{turb} = \sqrt{k \bar{V} S_{lom}}$ as approximate solution for $\bar{V} > S_{lom}$

(c) for $l' > d, \bar{V} \gg S_{lom}$:
$$S_{turb} = k \bar{V}^{2/3} S_{lom}^{1/3}$$

In concluding this chapter, it seems hardly necessary to point out that the hydrodynamical aspects of flame propagation, and especially the influence of turbulence, are highly important for the applications of combustion. More experimental work under well-defined conditions of turbulence is needed to evaluate the existing theories. From the theoretical point of view, one possible effect of turbulence on flame propagation which had not been taken into account by Damköhler and by Shchelkin is a direct influence on the course of the chemical reaction; for instance the concentrations in the reaction zone could be changed by turbulence in such a way that the average life time of active particles would be modified. Only an experimental approach to this problem seems possible, however, because of the limited knowledge of the reaction mechanisms involved.

I. Theory of flames formed in the mixing zone of fuel and air (diffusion flames)

In the preceding chapters it had been assumed tacitly that a homogeneous combustible mixture of fuel and air (or oxygen) has been formed before flame propagation takes place. An entirely different situation exists when the mixing of fuel gas and air (or oxygen) and combustion take place at the same time and a stationary flame is formed in the mixing zone. In the important technical applications of this type of combustion, this mixing is always a result of turbulent convection and diffusion. However, only the case of true diffusional mixing has so far received theoretical

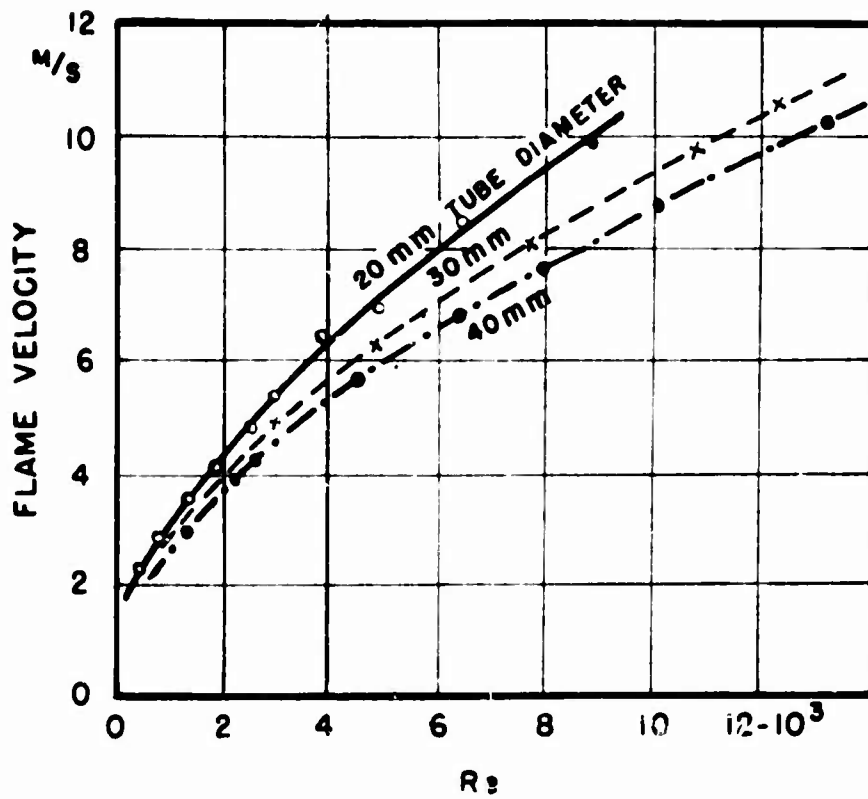


FIG. 15

FLAME VELOCITY AS A FUNCTION OF
 REYNOLDS NUMBER AND TUBE DIAMETER
 VERTICAL TUBE, 21% ILLUMINATING GAS IN AIR
 (AFTER UNGER, REF. 38)

treatment, and the term "diffusion flame" is customary in this case*. Since diffusional mixing occurs much more slowly than the chemical reaction could proceed at the usual temperatures and pressures, diffusion alone is the rate-determining factor and it is possible to treat this case without introducing any assumptions about reaction rates and mechanisms. On the other hand the treatment is limited to a determination of the shape of the flame and no information about the rate or mechanism of reaction can be expected. This problem has been treated by Burke and Schumann³⁹ (cf. ref. 2, pp. 220-234) for the cases of a cylindrical and of a flat flame.

Only the cylindrical case will be discussed here. Figure 16 shows the experimental arrangement on which the treatment is based. The following simplifying assumptions were introduced by Burke and Schumann:

- (a) The flame zone coincides with the locus of the points where inter-diffusion has produced a stoichiometric mixture.
- (b) Fuel gas and air flow with equal velocity v , constant over the cross section as well as along the flow.
- (c) The coefficient of diffusion is constant.
- (d) Diffusion occurs only radially.

Fortunately the effects of deviations from assumptions (b) and (c) tend to compensate each other, as the increase of temperature in the flame

* It is hardly necessary to point out that this case is entirely different from the "diffusional propagation" discussed on page 34.

brings about at the same time an increase of velocity along the flow, increasing the length of the flame, and an increase of the coefficient of diffusion, decreasing the flame length. In order to simplify the boundary conditions and treat the problem as the diffusion of a single gas, the initial concentration of oxygen C_2 is introduced as a negative concentration of fuel $-\frac{C_2}{i}$, where i is the number of oxygen molecules which combine with one molecule of fuel. By setting $Y = Vt$ the diffusion equation for the fuel concentration C is obtained in the form

$$\frac{\partial C}{\partial Y} = \frac{D}{v} \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right) \quad (65)$$

Denoting the initial fuel concentrations by C_1 the solution must fulfill the following conditions (Figure 16).

$$C = C_1 \text{ for } Y = 0, \quad 0 \leq r < L$$

$$C = -\frac{C_2}{i} \text{ for } Y = 0, \quad L \leq r \leq R$$

$$\frac{\partial C}{\partial r} = 0 \text{ for } r = 0 \text{ and } r = R$$

Reference is made to the original paper and to the text of Lewis and von Elbe for the details of the mathematical treatment. By setting $C = 0$, the solution gives the flame shape as a relation between r and Y . In the case of an underventilated flame, the flame front will curve outward (Figure 16) and the height is given by the value of Y for $r=R$; for an overventilated flame, the front terminates at the axis, and the height is the value of Y for $r = 0$.

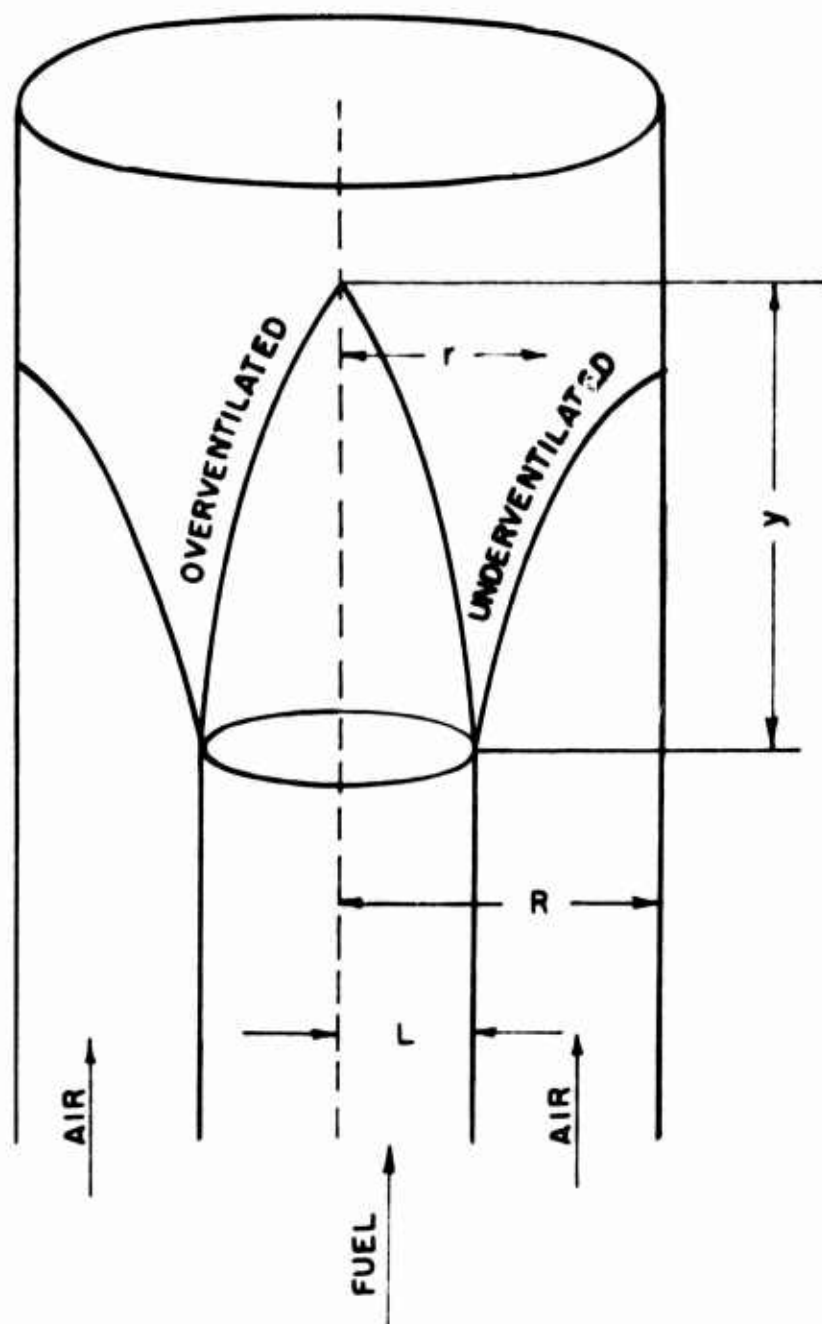


FIG. 16

DIFFUSION FLAME
(AFTER BURKE AND SCHUMANN, REF 39)

A number of the conclusions reached by Burke and Schumann are derived by Jost (ref. 9, pp. 207-216) through a much simpler treatment. He points out that the assumptions introduced by Burke and Schumann preclude a high degree of accuracy, so that his treatment, based on the same assumptions, should be adequate enough. The depth of penetration of the air into the fuel gas is approximated by Jost as being equal to the mean square displacement:

$$x^2 = 2Dt \quad (66)$$

By identifying x^2 with r^2 and t with $\frac{Y}{V}$ there results

$$Y = \frac{V r^2}{2D} \quad (67)$$

The following conclusions, agreeing with those of Burke and Schumann, can be drawn from this result:

- (a) Since the total gas flow is proportional to $V r^2$, the flame height Y will remain unaltered by changing the dimensions of the burner (r) without changing the total flow.
- (b) The height Y is proportional to the flow velocity V and inversely proportional to the coefficient of diffusion D .
- (c) For constant mass flow, a change in pressure will not affect the height, as V and D are then both inversely proportional to pressure.
- (d) Substitution of an inert gas for part of the combustible gas will shorten an overventilated flame and lengthen an underventilated one.

Jost's simple treatment allows even a quantitative estimation of the flame height, which agrees fairly well with the values obtained by Burke and Schumann theoretically and experimentally. As an example, with $L = \frac{1}{2}$ inch, $R = 1$ inch, $D = 0.0763$ sq. inch/sec. and $v = 0.610$ inch/sec. the rigorous treatment gives $\gamma = 1.31$ inch, while Jost's formula leads to

$$\gamma = \frac{0.61 \times 0.5^2}{2 \times 0.0763} = 1 \text{ inch}$$

Burke and Schumann show in their paper the good agreement with experimental results achieved by their theory. A still better agreement was reached by them by sampling the gas composition at various points along the axis and selecting a value of D in the calculation which reproduced the experimental distribution of concentrations as closely as possible.

The excellent agreement obtained by the diffusion theory is due, as mentioned before, to the fact that the rate of chemical reaction is large compared with the speed of the diffusion process. On the other hand, if the reaction rate is small compared with the rate of diffusion, a diffusion flame can serve as a means to investigate reaction rates (ref. 21, p. 283, ref. 40, p. 15).

Recently Damköhler and Sander⁴¹ proposed a method to investigate fast gas reactions under approximately isothermal conditions, based on the theory of diffusion flames of Burke and Schumann. The arrangement is

similar to the one shown in Figure 16 except that provision is made for heating the gas streams before entering the reaction chamber and for cooling at a short distance downstream, to stop the reaction and allow chemical analysis of the reaction products at intermediate stages. The relations derived by Burke and Schumann were found to hold well in model experiments with O_2 and CO_2 as interdiffusing gases. The authors point out that it should be possible, by merely changing the total pressure, and keeping the mass flows constant, to vary the reaction time without changing the temperature and concentration distributions in the reaction chamber, provided the heat of reaction can be neglected compared with the heat content of the gases. The length of the reaction chamber is chosen so small that diffusion to the wall of the gas entering through the center tube is negligible, precluding the possibility of a catalytic reaction on the wall surface. No actual reaction experiments are reported by Damköhler and Sander, so that the value of this application of diffusion flames for the field of combustion research remains to be proven.

Even with combustion in a homogeneous mixture diffusion processes of the kind discussed in this chapter may under certain circumstances play an important role. Goldmann⁴⁴ suggested that the fact that very lean hydrogen-air or hydrogen-oxygen mixtures can maintain an upward propagating flame could be explained by assuming that combustion takes place in one or several rising gas balls which receive a sufficient supply of hydrogen by diffusion. This accounts also for the fact that combustion is less complete for leaner H_2 mixtures. A modification of this theory has

been proposed by Clusius, Kölsch and Waldmann⁴⁵. In their combustion experiments with lean $H_2 - D_2 - O_2$ mixtures these authors obtained an excess of H in the products of combustion and an excess of D_2 in the remaining mixture, in accordance with the diffusion theory of Goldmann. Since they could not observe any macroscopical inhomogeneity of the flame front, they suggested that the combustion zone consists of small filaments perpendicular to the flame front. Combustion takes place only in these filaments, which occupy but a fraction of the flame surface, and hydrogen diffuses into the filaments and maintains thus a combustible mixture. While these authors did not actually observe this structure, some observations of a filamentous appearance of burner flames of lean hydrogen mixtures and of rich mixtures of higher hydrocarbons have been reported⁴⁶.

A simple explanation of the way in which the flame front disintegrates into these filaments has been given by Zeldovich⁴⁷. In mixtures not too far off from stoichiometric composition flame propagation is controlled by heat conduction. This tends to stabilize the flame front, because the regions which are convex toward the unburnt gas will propagate with a smaller velocity than those which are concave (ref. 9, p.125). In very lean or very rich mixtures, however, diffusion will be the controlling process. Since diffusion takes place in the direction opposite to the propagation, the effect will be contrary to that of heat conduction: the velocity will increase in the convex and decrease in the concave parts, leading ultimately to a disruption of the flame front (Figure 17).

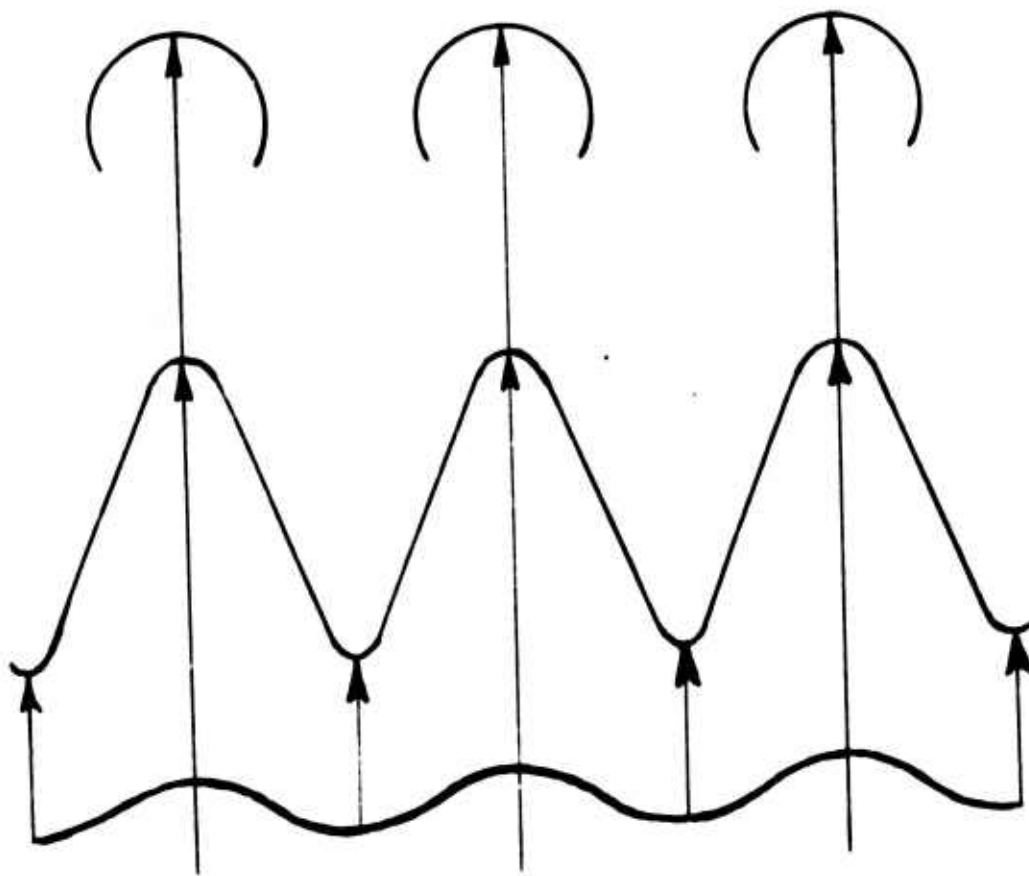


FIG 17
DISINTEGRATION OF FLAME FRONT
NEAR THE LIMIT OF PROPAGATION
(AFTER ZELDOVICH, REF. 47)

J. Conclusion and recommendations

The theory of flame propagation can be subdivided into two groups of problems:

- (a) study of the transformation velocity, and
- (b) hydrodynamical aspects of flame propagation.

The theory of the transformation velocity takes into account the simultaneous actions of heat conduction, diffusion and chemical kinetics in the flame, disregarding any effects of flow. At the present stage of limited knowledge of reaction kinetics the treatments are based on hypothetical assumptions about the reaction mechanisms. So far the theory has been developed mainly for reactions which can be approximately represented by a classical kinetic law, $w = S \cdot e^{-\frac{E}{RT}}$; even in this simplest case theoretical values do not agree too well with experimental results. Unfortunately, a major group of combustion reactions belongs to the auto-catalytic chain type, which does not allow such an approximation. In addition to this lack of definite knowledge about reaction kinetics, which constitutes the main obstacle for the success of the theory, considerable difficulties may also arise for the treatment due to the large deviations from thermal equilibrium likely to occur in the combustion zone. It is to be expected that new methods in research on reaction kinetics⁴⁸ will provide valuable information for the future development of the theory of the transformation velocity.

The hydrodynamical treatment of flame propagation has so far given a satisfactory result only in dealing with detonation, and with the simplest cases of slow combustion, namely, the spherically symmetrical flow under conditions of constant pressure (soap bubble) and constant volume (spherical bomb) (cf. ref. 1). More complicated flow conditions, particularly the important cases of Bunsen burner flames and of flame propagation in pipes, have been treated up to now only by empirical or semi-empirical methods.

The hydrodynamical theory of one-dimensional flow, which predicts an upper limit for the flame velocity in the case of slow combustion (deflagration), has not been able to account for the fact that the whole range from the transformation velocity up to the velocity of detonation can be observed under suitable experimental conditions. Several different flow effects can concur in producing an increase of the propagation velocity:

- (a) turbulence due to the flow in the unburnt gas.
- (b) turbulence due to the instability of the flame front postulated by L \ddot{e} ndau²⁹, and
- (c) pressure and temperature rise due to the compression wave generated in the unburnt gas by the combustion process.

The theoretical explanations of the influence of hydrodynamical parameters on flame propagation usually rest on the basic hypothesis that the transformation velocity is not affected by the flow conditions. Exceptions to this assumption are made only for the case of turbulence

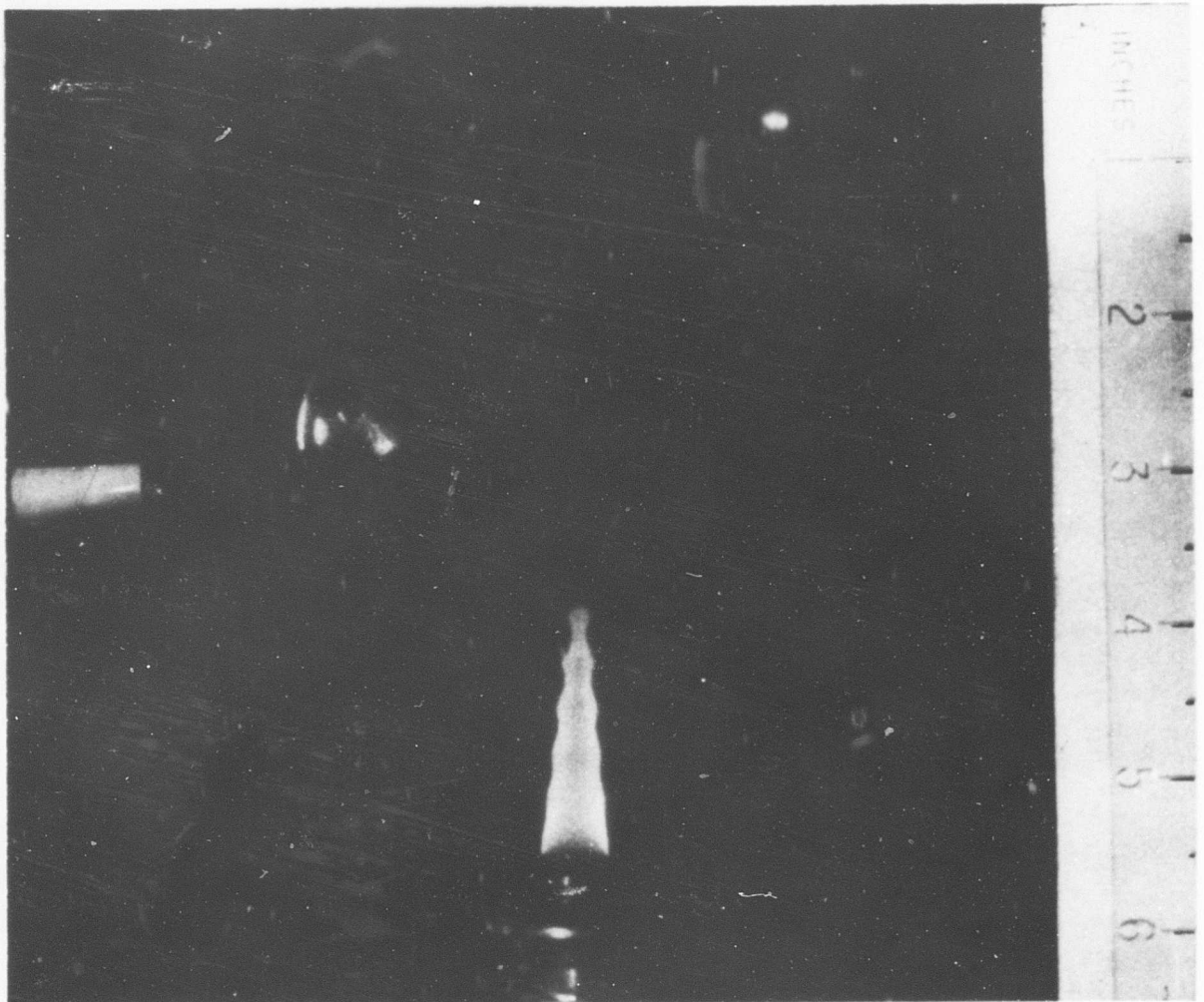


FIG. 18

STROBOSCOPIC PHOTOGRAPH OF A BUNSEN BURNER FLAME
DISTURBED BY AN ALTERNATING ELECTRICAL FIELD.

INNER DIAMETER OF NOZZLE 1.02 CM. AVERAGE FLOW
VELOCITY 376 CM/SEC 4.25% BY VOLUME NATURAL GAS
(NATOX) IN AIR.

2500 VOLT, 500 c.p.s. APPLIED BETWEEN NOZZLE AND
SPHERE.

with a mixing length small compared to the thickness of the flame front, and for cases in which the velocity of the unburnt gas relative to the flame front is not small compared with the velocity of sound. In all other cases the influence of the flow parameters is assumed to be limited to an increase of the surface of the reaction zone.

An experimental study of the details of the mechanism by which the surface of the flame is increased would furnish valuable information for a better understanding of the phenomena encountered in flames in a turbulent medium. It appears quite hopeless, however, to attempt such a study under conditions of actual turbulence. Preliminary experiments carried out in Cornell Aeronautical Laboratory⁵¹ indicate that one approach to this problem might be the stroboscopic observation of a flame front subjected to a periodic disturbance. As an example, Figure 18 shows the stroboscopic pattern of a Bunsen burner flame obtained under the influence of an electrical field of 500 c.p.s., applied between the nozzle and the spherical electrode visible to the left of the flame. This method should provide among other data an indication of the upper limit of propagation velocity attainable by turbulence.

K. Symbols

v, u	flow velocity
q	mass flow
ρ	density
ρ_0	initial density
S_t	transformation velocity
H	heat content
$\vec{\Omega}$	vector of heat flow
w	reaction rate
Q	heat of reaction per unit mass of combustible
λ	coefficient of heat conduction
T	absolute temperature
c_p	specific heat at constant pressure
T_0	initial temperature
T_i	ignition temperature
T_f	final temperature, temperature of combustion
α	concentration of combustible
α_0	initial concentration of combustible
p	pressure
p_0	initial pressure
L	heat of reaction per unit mass of total gas mixture
d_r	thickness of reaction zone
E	activation energy

R	gas constant
S, K	constants in expression for the reaction rate
D	coefficient of diffusion
χ	coefficient of temperature conduction
ν	kinematic viscosity
Z	collision coefficient
ℓ	mean free path
c	mean molecular velocity
d_t	thickness of heating zone
$Re()$	real part of ()
τ	characteristic time, reaction time
d	thickness of flame zone
ℓ'	turbulent mixing length
v'	instantaneous value of fluctuation velocity
$\overline{v'}$	time average of fluctuation velocity
ϵ	coefficient of turbulent exchange
Re	Reynolds number
S_{turb}	flame propagation velocity under turbulent conditions
S_{lamin}	flame propagation velocity under laminar conditions

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