CURRENT THEORETICAL CONCEPTS OF STEADY-STATE FLAME PROPAGATION[1]

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I. INTRODUCTION

In recent years the many physical and chemical processes involved in steady-state flame propagation have been recognized. This does not mean that the problem of describing a flame has been solved, for major difficulties still remain. The difficulties are of two kinds: (*1*) our ignorance of the details of the chemical processes and (*2*) our inability to handle satisfactorily the complex mathematical equations which are required to describe the system. A variety of methods of attack have been developed, and it is the purpose of this review to delineate the methods which are aimed at solving the mathematical problem.

A perspective of the field is possible only with recognition of the numerous assumptions and approximations found in the various theories. The plan of this review is to state in Section II the fundamental laws which should form the basis for flame propagation theory and then to outline the approximations used by various authors for the purpose of obtaining a mathematical solution. In Section III the problem is considered from the point of view of mathematics, in order to understand the mathematical problem involved. On the basis of the major assumptions the theories are divided into three groups—comprehensive, thermal, and diffusional—which are discussed in Sections IV, V, and VI. In these sections consideration is given to the theories from the first proposed in 1881 to those recently advanced.

When possible, the notation of the individual author has been followed. However, for the sake of clarity and because in some instances notation varies from paper to paper of a single author, certain changes in the original notation have been made. The following terms are used consistently throughout the review:

t = time coördinate,
x = space coördinate,
v = velocity of gases relative to the flame front (except in Section II),
ρ = density,
τ = specific volume,
p = pressure,
T = temperature,
M = mass rate of flow ($ml^{-2}t^{-1}$),
λ = heat conductivity (except in Sections IV,A and VI,B),
c_p = heat capacity at constant pressure,
c_v = heat capacity at constant volume,
μ = coefficient of viscosity (except in Section VI,E),
D = diffusion coefficient for a binary mixture, and
R = gas constant.

The subscripts 0 and 1 indicate conditions at the cold and hot boundaries of the flame, respectively. The subscript m indicates a mean value.

II. GENERAL EQUATIONS AND SIMPLIFYING ASSUMPTIONS

x, y, z = space coördinates,
u, v, w = components of velocity in x, y, z directions, respectively,
$q = \sqrt{u^2 + v^2 + w^2}$,
e = specific internal energy,
i = specific enthalpy,
I = total enthalpy, including heat of formation,
n_i = concentration of the ith component,
V_i = diffusion velocity of the ith component,
E = activation energy, and
R' = gas constant divided by effective molecular weight of gas.

The solution of the problem of steady-state flame propagation requires contributions from the fields of fluid dynamics, chemistry, and mathematics. Inas-

much as flame propagation may always be interpreted as chemical reaction in a flowing gas, the basic equations of fluid dynamics must be used for a description of the system. The problem differs from that of ordinary compressible flow, however, because of the reaction processes occurring in the system, and these processes must be investigated and described by the methods of chemistry. Finally, since the fluid dynamical and chemical processes require mathematical description, usually in terms of a system of differential equations, contributions from the field of mathematics are necessary for the solution.

A. The basic equations of fluid dynamics and the generalizations and simplifications required for their use in theories of one-dimensional, steady-state, non-viscous flame propagation

The analysis of the phenomenon of flame propagation is conveniently begun with a consideration of the fluid dynamical differential equations required for the description of the system (24, 73). Except at discontinuities the classical equations of fluid dynamics govern the behavior of the motion of a medium in which the gradients of velocity and temperature are small, so that the forces in the gas are due entirely to pressure and not at all to viscosity and thermal conduction. This means that there is no friction and the entropy of the element remains unchanged. External forces such as gravity are not taken into account, nor is energy loss by radiation. The equations express the principle of conservation of mass, Newton's law of conservation of momentum, the principle of conservation of energy, and the particular form of the equation of state. They are expressed in rectangular coördinates as follows, where $\rho_t = \partial\rho/\partial t$, $\mu_x = \partial u/\partial x$, etc.:

$$\rho_t + (\rho u)_x + (\rho v)_y + (\rho w)_z = 0 \qquad \text{(mass)} \quad (1.01)$$

$$u_t + uu_x + vu_y + wu_z + \frac{1}{\rho} p_x = 0 \quad \text{(momentum)} \quad (1.02)$$

$$v_t + uv_x + vv_y + wv_z + \frac{1}{\rho} p_y = 0$$

$$w_t + uw_x + vw_y + ww_z + \frac{1}{\rho} p_z = 0$$

$$[\rho(\tfrac{1}{2}q^2 + e)]_t + [\rho u(\tfrac{1}{2}q^2 + i)]_x + [\rho v(\tfrac{1}{2}q^2 + i)]_y + [\rho w(\tfrac{1}{2}q^2 + i)]_z = 0$$

$$\text{(energy)} \quad (1.03)$$

$$p\tau = R'T \quad \text{(equation of state for ideal gas)} \quad (1.04)$$

The theories of flame propagation require the following modifications and simplifications of equations 1.01–1.03. The modifications are necessary because of the character of burning; the simplifications are made to facilitate mathematical solution.

(*a*) The problem is assumed to be one-dimensional, so that all quantities depend, in addition to the time *t*, only on one space coördinate *x*, so that the com-

ponents v and w of the velocity vanish. This assumption enormously simplifies the mathematical problem.

(b) A steady-state flow is assumed, so that all quantities are independent of t, and the system of partial differential equations is reduced to a set of ordinary differential equations. This assumption eliminates the important class of problems of combustion occurring in non-steady flow.

(c) If velocity gradients exist, terms for the contribution from viscous friction must be included in equations 1.02–1.03 (27, 74). The theories of flame propagation generally assume that the velocity gradients are small and may be neglected, and the viscosity term which remains even in the one-dimensional equations of momentum and energy is ignored.

(d) The temperature gradient through the flame zone is large, so that a term providing for change in energy in an element of the gas because of heat conduction must be included in equation 1.03.

Equations 1.01–1.03 may now be modified according to modifications (a) to (d) above, giving the following one-dimensional steady-state equations which include the effects of viscosity and heat conduction:

$$(\rho u)_x = 0 \qquad \text{(conservation of mass)} \quad (1.05)$$

$$(\rho u^2 + p - \mu u_x)_x = 0 \qquad \text{(conservation of momentum)} \quad (1.06)$$

$$[\rho u(\tfrac{1}{2}u^2 + i) - \mu u u_x - \lambda T_x]_x = 0 \quad \text{(conservation of energy)} \quad (1.07)$$

(e) The chemical nature of the gas changes across the flame zone. The first consequence of this is that energy is liberated, and the rate of heat liberation must be included in the energy equation (equation 1.07).

The second consequence is that the concentration of each component of the gas becomes a variable of the problem and it is necessary to state equations of continuity for a certain number of the components. For the steady-state condition, the equation of continuity is the mathematical statement that the rate of accumulation of a component in an element of gas is equal to zero. Each equation of continuity contains three terms, which express the change in concentration of the component because of (i) mass flow, (ii) diffusion, and (iii) chemical reaction. For a system of n components, the n equations of continuity, taken with the fact that mass is neither created nor destroyed in chemical reactions, imply the conservation of mass (51). It is not necessary to state n equations of continuity for a gas mixture containing n components. Following Hirschfelder and Curtiss (51, 52, 53) in their analysis of the number of equations required, one writes for the equation of continuity for the ith component

$$\frac{d}{dx}[n_i(v + V_i)] = K_i \qquad (1.08)$$

where n_i is the concentration of component i, v is the velocity of flow, V_i is the diffusion velocity of the ith component, and K_i is the rate of production by chemical reaction of the ith component.

Let $J_i = n_i(v + V_i)/M$. Then equation 1.08 can be written:

$$M \frac{\mathrm{d}J_i}{\mathrm{d}x} = K_i \qquad \text{where } i = 1, 2, \cdots s \tag{1.09}$$

There are various relations among the K_i. Hence not all the J_i are independent. The number of linearly independent J_i (i.e., the number of equations of continuity required) will be equal to $s - g'$, where g' is the number of independent relations among the K_i. If there are g kinds of atoms present there are g relations of the form

$$\sum_i \nu_{ik} K_i = 0 \qquad \text{where } k = 1, 2, \cdots g \tag{1.10}$$

where ν_{ik} is the number of atoms of the kth kind in a molecule of the ith kind. Equation 1.10 expresses the fact that atoms are conserved in a chemical reaction. Certain groups of atoms may go through the chemical reactions intact and should therefore be treated as single atoms. The number of effective atoms in a system is therefore $r \leq g$. The number of independent equations 1.10, g', is the number of independent components in the sense of the phase rule: $g' = r - s + 2$.

However, if the chemical kinetics of the system involves l chemical reactions and their reverse reactions, it is found that there are at most l linearly independent K_i. This is seen by writing for the chemical reactions

$$\beta_{1j}[1] + \beta_{2j}[2] + \cdots \beta_{sj}[s] \rightleftharpoons \eta_{1j}[1] + \eta_{2j}[2] + \cdots + \eta_{sj}[s] \tag{1.11}$$
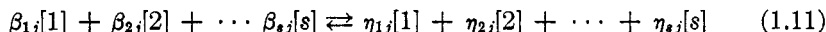
β_{ij} and η_{ij} are constants which are either positive integers or zero. $[i]$ indicates a molecule of i. The subscript j indicates the jth chemical reaction. It can be shown that K_i can be written

$$K_i = \sum_{j=1}^{l} (\eta_{ij} - \beta_{ij}) r_j \tag{1.12}$$

where

$$r_j = f_j(T) y_1^{\beta_{1j}} y_2^{\beta_{2j}} \cdots y_s^{\beta_{sj}}$$

r_j being an expression for the rate of the jth reaction. Thus any K_i is determined by l reactions.

The result of this analysis is that the actual number of linearly independent J_i is either l or $(s - g')$, whichever is smaller.

The third consequence of the changing chemical composition across the flame zone is that since concentration gradients exist across the flame, the effect of diffusion should be included in the equations of continuity and energy. If, as in many theories, all molecules are assumed to have the same size and weight, it is not necessary to include diffusion in the energy equation.

B. *Simplifying assumptions used to effect solutions of the equations for one-dimensional, steady-state, non-viscous flame propagation*

The theories of flame propagation discussed in this paper are concerned with the flow problem as stated in equations 1.01–1.04, but modified according to the generalizations and simplifications (a) to (e) above. However, certain difficulties

are encountered upon attempting to use the equations thus modified, and as a result various further approximations are introduced. The types of assumptions or approximations used distinguish the theories.

The difficulties occur in the problem because the reaction rate is a function of the temperature and of the concentrations of the components taking part in the reaction. The majority of combustion processes consist of a set of reactions proceeding simultaneously, and include not only the molecules of the original components but intermediate particles. It is therefore necessary to have a knowledge of all reactions occurring in the flame and of the dependence of their rates on the temperature and on the concentration of the reacting particles. Studies of chemical kinetics have supplied such complete data in only a few instances. Furthermore, it is not certain that it is valid to use for reaction rates in a flame the rates as measured for the same conditions of temperature and composition in a static system. It may be that in a flame the successive reactions occur so rapidly that the internal degrees of freedom of the intermediate species do not have time to adjust to the local temperature (52, 53).

The expression for dependence of rate on temperature and concentration varies according to the individual reaction. Therefore the differential equations which include the rate expression become dependent on the special form of the equation for the reaction velocity and it is not possible to expect from the solution of the differential equations universal expressions for flame characteristics, since they will vary according to the reaction mechanism.

In general, the rate expression for a single reaction has the form

$$B_1 e^{-E/RT} n_1^{\beta_1} n_2^{\beta_2} \cdots$$

where B_1 is a constant and the β_i represent the number of molecules of species i involved in the reaction. Furthermore, the heat conductivity, the heat capacity, and the diffusion coefficient are functions of temperature and concentration. Consequently the differential equations are non-linear and an exact analytical solution presents great difficulties; hence further simplifying assumptions are required.

Of the further simplifications used, some are of such a nature that one aspect of the mechanism of flame propagation is emphasized to the relative exclusion of another. In fact, current theories can be classed conveniently and more or less sharply according to which of the assumptions listed in the following paragraphs are used.

(f) Generally the limiting case of a constant-pressure flame is assumed. In all theories discussed in this paper it is assumed that u and p_x are small and that the orders of magnitude of u, u^2, $\mu u u_x$, and μu_x with respect to the other terms are such that certain terms may be neglected in equations 1.06–1.07. i is replaced by I to indicate that, since heat is liberated, the enthalpy term must include the heat of formation. Then the momentum and energy equations for a system in which transfer of energy by diffusional processes is not considered are written:

$$p = \text{constant} \qquad \text{(momentum)} \quad (1.13)$$

$$(\rho u I - \lambda T_x)_x = 0 \qquad \text{(energy)} \quad (1.14)$$

Substitution of typical values into equations 1.06 and 1.07 will show that this assumption is not unreasonable (12, 13).

(*g*) A reaction rate law of a relatively simple model, such as the unimolecular or bimolecular rate law, may be used, or a single gross reaction may be substituted for the actual sequence of intermediate reactions.

(*h*) From kinetic theory, the expression $D\rho = \lambda/c_p$, relating thermal conductivity, diffusion coefficient, density, and specific heat, is known to be valid for gas mixtures containing molecules of equal size and weight. This relation, only approximately true when the molecules are not equal, is sometimes employed, with the result that the equations of continuity and energy assume the same form. The mathematical problem is thus reduced to one of solving a single type of differential equation (97, 114, 115, 116).

(*i*) There are two limiting mechanisms for flame propagation (83). *Thermal* theories hold that the process of heat conduction is the most important physical process involved in the transfer of the reaction zone from one layer of gas to the next. Diffusion processes are not considered, and the concentration of a given component at a point is assumed to be governed only by flow and reaction processes.

Very often thermal theories use the concept of *ignition temperature*. It is assumed that heat produced by chemical reaction is conducted to the unburned gas so that the temperature is raised to the ignition temperature, T_i, whereupon the gas begins to react. The zone preceding the point at which the ignition temperature is reached is called the preheating zone, and the zone following the ignition point is called the reaction zone. The early theories (30, 33, 66, 67, 85, 90) regarded the ignition temperature as a characteristic physical constant of the initial gas mixture. It is now known to depend upon the experimental conditions under which the heat is liberated. The reaction rate was assumed to be discontinuous at the ignition point, jumping from zero in the preheating zone to a finite value in the reaction zone. Moreover, the reaction rate was often assumed to maintain a constant value in the reaction zone as the temperature increased from T_i to T_1. In view of the present conception of the dependence of reaction rate on temperature, these ideas are at best approximations to actual conditions. Actually, the rate is not an explicit function of t or x, and its dependence upon these variables cannot be obtained before integrating the equations. Consequently, erroneous or inadequate expressions were introduced for the reaction rate.

The demarcation of the flame zone into two zones is often useful as an approximation for the modern thermal theories (5, 6, 8, 9, 10, 32, 54), as well as for theories which emphasize diffusion processes (42, 43, 97, 115, 116). The combustion process is considered to have an *induction period*, during which the initial mixture must be prepared for ignition, not only by an increase to the required temperature but by the accumulation, through diffusion from burning layers or the establishment of equilibrium with the initial components, of active intermediate particles. During the induction period it is assumed that the chemical decomposition is small, say less than 1 per cent. At the point of ignition the con-

centrations of the active chain carriers and the reaction velocities of the inter-
mediate reactions have become so large that the combustion reaction suddenly
accelerates. At this point the reaction is assumed to begin. The modern concept
does not regard the ignition temperature as a characteristic physical constant
for a mixture. Neither is it expected that the ignition temperatures occurring in
a flame should agree with those obtained for the same initial mixtures by other
methods, such as adiabatic compression of the mixture (61). In those methods
the intermediate products necessary for ignition must be formed solely by thermal
processes. In flames more favorable conditions prevail, since the intermediate
particles are supplied also by diffusion from the reaction zone.

Some modern thermal theories avoid an explicit statement of the expression
for the reaction rate by substituting an experimentally determined value for
the thickness of the reaction zone (32, 42).

(j) The other limiting mechanism holds that the flame velocity is determined
principally by diffusional processes. It is postulated that active atoms and
radicals produced by dissociation in the hot burned gases and by chain branching
diffuse into the fresh gas and cause it to react explosively (4, 9, 42, 43, 104, 105,
106, 107). The diffusional theories generally neglect the energy equation and use
instead an assumed function, frequently an average value, for the temperature.

Diffusional treatments of flame propagation may be classified according to the
treatment of the role of the active particles which participate in the elementary
reactions of the combustion process. The particles are generally chain carriers,
and this fact further complicates the problem, with the result that such simplify-
ing assumptions as the following are made:

(k) If a chain reaction without branching is assumed to occur, two methods
of treatment have been used:

(i) The instantaneous concentration of the active particles is assumed to
be determined everywhere in the flame by the equilibrium of the active
particles with the initial reacting substances (76). The same treatment
may be used when the concentration is determined by the quasi-
stationary methods of Bodenstein, the necessary condition for the
validity of this treatment being the short lifetime of the active particles,
so that the stationary concentrations are established rapidly in com-
parison with the velocity of the reaction (115).

(ii) Equilibrium concentrations of active particles are assumed at only one
point in the flame zone—for instance, at the hot boundary where the
reaction reaches completion—and the particles diffuse from that point
into the colder layers of gas (4, 104, 105, 106, 107). In support of this
viewpoint an estimate by Jost and von Müffling (56, 58) shows that
more than ten times as many particles can reach the colder layers of
the flame zone by diffusion as would be there in equilibrium. Gaydon
and Wolfhard (41) obtained evidence from absorption spectra that in
low-pressure flames the concentration of OH radicals just in front of the
reaction zone is higher than that calculated thermally.

(l) If chain branching is assumed to occur, the velocity of the chain-breaking

reaction is taken to be the limiting factor which determines the flame velocity (108, 109). When there is an accumulation of active particles which are connected with the initial reacting substances not by stoichiometric but by kinetic equations, it is necessary to take account of the recombination of the centers. In order that it may be possible to speak of a chain-branching reaction in which gradual autoacceleration of the reaction occurs, it is necessary that the recombination be small in comparison with the branching when the branching has reached, say, 70 per cent of completion. Otherwise the branching and recombination determine a quasi-stationary concentration of the active centers and one has instead the type described in (k)(i) above (115).

(*m*) The heat capacity, the coefficient of heat conductivity, and the diffusion coefficient are often assigned constant mean values. This is done for reasons of mathematical simplicity, but also because in many instances the exact behavior of the coefficients λ and D for multicomponent gas mixtures is not yet known. Current work on transport properties of multicomponent gas mixtures may provide accurate expressions for λ and D (31, 81, 112).

(*n*) Thermal diffusion, which is caused by the temperature gradient and by which molecules of the heavier gases diffuse in the direction of decreasing temperature and those of the lighter gases in the other direction, is neglected.

(*o*) The gases are assumed to be ideal.

C. Boundary conditions; stability; classification of theories

In order to obtain a particular solution of a set of differential equations it is necessary to specify a single set of boundary conditions. The mathematical problem of determining the values of the dependent variables in a flame is, however, an eigen-value problem, which requires an additional set of boundary conditions. Selection of appropriate boundary conditions, particularly at the cold boundary, is not necessarily simple.

It is generally assumed that the fresh gas moves from $-\infty$ to $+\infty$, with the change from fresh gas to burned gas occurring in a zone contained in this region. Usually pressure is assumed constant and the boundary conditions chosen are the values at the hot and cold boundaries of the variables temperature and concentration and their derivatives with respect to x. The correctness of a theory is often tested by comparing the predicted value of the *flame velocity* with a measured value. The flame velocity or *normal burning velocity*, v_0, is defined as the linear velocity of displacement of the flame front with respect to the fresh gas entering the combustion zone, in a direction normal to the flame front. Detailed discussion of methods of measuring flame velocity may be found in the literature (1, 2, 3, 43, 59, 79, 98).

The inlet or cold-boundary temperature and composition being known, by assuming thermodynamic equilibrium at the hot boundary and either adiabatic combustion or a known heat loss, it is possible to compute the temperature and composition at the hot boundary. Thus the specification of the values of the variables at the two boundaries is relatively simple. Furthermore, it is generally

agreed that temperature and concentration approach asymptotically the equilibrium values at the hot boundary; thus, $dT/dx = 0$ at $x = \infty$.

Specification of the gradients at the cold boundary is more difficult, and a variety of conditions are used. Expressions for chemical reaction rate of the form $B_1\exp(-E/RT)n_1^{\beta_1}n_2^{\beta_2}$ do not vanish at $T = T_0$, so that, mathematically speaking, the gradients are finite, although in actuality no measurable reaction occurs. Some authors nevertheless take the gradients to be zero at $x = -\infty$ and avoid this difficulty by neglecting the contribution to the reaction at the lower temperatures. Others start the solution at a finite point and assign gradients at that point.

It may be that the cold-boundary conditions are related to the stability of the steady state. Frequently a flame travelling down a tube changes from deflagration to detonation, and conceivably this transition is brought about by an instability of the steady state (38, 53). According to Emmons, Harr, and Strong (38), changes in the temperature gradient at the cold boundary can result in a transition to detonation or extinction. Hirschfelder and Curtiss (51, 52, 53) suggest that the presence of a flame holder is necessary to establish a steady state. They define a mathematical flame holder which extracts an amount of heat proportional to the temperature gradient at that point. Lewis and von Elbe (77, 78) have discussed the means by which a two-dimensional flame is stabilized by such a solid object. Their argument is that when the flame is too close to the stabilizing body the flame loses thermal energy and chain carriers to the stabilizer, with the result that the flame velocity is lowered, the gas velocity is everywhere greater than the flame velocity, and the flame is driven back. If the flame is too far from the stabilizer, the flame velocity somewhere exceeds the gas velocity and the flame moves forward. In the equilibrium or stable position, at one point on the flame surface the gas velocity and flame velocity are equal, while everywhere else on the surface the gas velocity exceeds the flame velocity.

No more consideration will be given to the question of stability in this paper, but it should be remembered that the proper choice of boundary conditions may be linked with the question of stability.

The theories of steady-state flame propagation have been divided into three groups according to their major assumptions. Those classed as comprehensive theories have in common the fact that both heat conduction and diffusion processes are considered, with various degrees of rigorousness, and an attempt is made to deduce a priori a complete description of a flame produced by a stated reaction or a stated class of reactions. Ideally, the solution of these equations provides expressions for the temperature, the pressure, the velocity, and the concentration of all components as a function of x.

Thermal and diffusional theories emphasize, respectively, the heat conduction and the diffusion processes of the system. These theories often attempt not the a priori deduction of all properties, but the devising of a general expression for a particular property, usually the flame velocity. Frequently experimentally determined properties such as width of flame zone, induction period, or ignition temperature, or assumed properties such as a temperature, are introduced into the theory.

III. MATHEMATICAL CONSIDERATIONS (25, 40)

e = specific internal energy,

g = energy of formation at absolute zero,

$E = e + g$ = total internal energy,

i = specific enthalpy,

$I = i + g$ = total enthalpy,

S = entropy,

u = velocity of gases in x direction,

U = velocity of reaction front,

ϵ = fraction of burned gas in the mixture,

K = rate of reaction, and

$v = u - U$.

It has long been observed (18, 20, 34, 35, 84, 85) that under ordinary circumstances the flame in a tube filled with combustible gas and ignited at one end propagates at a low velocity of a few meters per second. Under certain circumstances this *normal combustion process* or *deflagration* changes over to a process in which the flame front moves with a very high velocity, 2000 m. or more per second. This high velocity process is called *detonation*. A theoretical explanation based on hydrodynamic processes of these two types of propagation was proposed independently by Chapman (22) and Jouguet (64, 70).

It is not the purpose of this paper to consider the process of detonation in detail, but since the explanations for the phenomena of detonation and deflagration follow from the same mathematical reasoning, detonation will be included in the discussion. A detailed exposition of the mathematical theory of detonation and deflagration waves in gases has been given by Courant and Friedrichs (25, 40), and their treatment will be followed here.

It is assumed initially that the chemical reaction takes place instantaneously, that is, that there is a sharply defined front between fresh and burned gas. This is analogous to the transition of uncompressed to compressed gas across a shock front. The essential difference from a shock transition is that the chemical nature of the gas on one side of the front differs from that on the other; hence (1) the internal energy function $e(\tau, p)$ for the burned gas differs from that of the fresh gas, and (2) the chemical reaction influences the energy balance. After discussing the theory on the basis of this assumption of a sharply defined front, the consequences of assuming that the reaction takes place gradually over a zone will be examined.

The relations describing the transition from state 0 to state 1 correspond to the laws of conservation of mass, momentum, and energy. If the one-dimensional process is observed from a coördinate system moving with the front, the laws of conservation of mass and momentum are identical with those for shock fronts: namely, the jump conditions

$$\rho_0 v_0 = \rho_1 v_1 = M \tag{2.01}$$

where M is the mass flux through the surface, and

$$p_0 + \rho_0 v_0^2 = p_1 + \rho_1 v_1^2 \tag{2.02}$$

The law of conservation of energy for the process is written

$$E^{(0)}(\tau_0, p_0) + p_0\tau_0 + \tfrac{1}{2}v_0^2 = E^{(1)}(\tau_1, p_1) + p_1\tau_1 + \tfrac{1}{2}v_1^2 \qquad (2.03)$$

where the total internal energy is assumed to be a known function $E = E^{(0)}(\tau, p)$ for the fresh gas and $E = E^{(1)}(\tau, p)$ for the burned gas.

From the mechanical conditions (equations 2.01 and 2.01) the relation

$$(p_1 - p_0)/(\tau_1 - \tau_0) = -\rho^2 v^2 = -\rho_0^2 v_0^2 \qquad (2.04)$$

is obtained. Equation 2.04 implies that the pressure and specific volume increase or decrease in opposite directions. From this equation it follows that two different types of processes are compatible with the conservation laws,—those in which both pressure and density increase, called detonations, and those in which both pressure and density decrease, called deflagrations.

Equation 2.02 may be written as

$$(p_1 - p_0)/(u_1 - u_0) = -\rho_0 v_0 = -\rho_1 v_1 \qquad (2.05)$$

which shows that for detonations the velocity of the gas decreases when the reaction front sweeps over it and that for deflagrations the gas is accelerated away from the reaction front.

Certain assumptions concerning the nature of the energy function $E(\tau, p)$ are made: namely, that the partial derivatives of E with respect to p and of I with respect to τ are positive, that is,

$$E_p > 0, \qquad I_\tau > 0 \qquad (2.06)$$

A second assumption is that the relation

$$dE = de = -pd\tau + TdS \qquad (2.07)$$

holds, an assumption which is valid if g is independent of p and τ. Finally, it is required that the process be exothermic, so that for the same pressure and density the total energy and enthalpy for the fresh gas are always greater than for the burned gas.

The velocities may be eliminated from equations 2.01, 2.02, and 2.03 and the so-called Hugoniot relation obtained:

$$E^{(1)}(\tau_1, p_1) - E^{(0)}(\tau_0, p_0) = -\tfrac{1}{2}(\tau_1 - \tau_0)(p_1 + p_0) \qquad (2.08)$$

It is useful to form the Hugoniot function, $H^{(1)}(\tau, p)$, for the burned gas.

$$H^{(1)}(\tau, p) = E^{(1)}(\tau, p) - E^{(1)}(\tau_0, p_0) + \tfrac{1}{2}(\tau - \tau_0)(p + p_0) \qquad (2.09)$$

Employing equation 2.09 in equation 2.08, the latter can be written in the form:

$$H^{(1)}(\tau, p) = E^{(0)}(\tau_0, p_0) - E^{(1)}(\tau_0, p_0) \qquad (2.10)$$

Suppose τ_0 and p_0 are given. Then τ_1 and p_1 will satisfy equation 2.10 in all reaction processes compatible with the conservation laws given in equations 2.01, 2.02, and 2.03. However, not all values of τ and p satisfying equation 2.10

actually correspond to a reaction process compatible with equations 2.01, 2.02, and 2.03, inasmuch as the condition

$$(p_1 - p_0)/(\tau_1 - \tau_0) < 0 \qquad (2.11)$$

derived from equation 2.04, must be satisfied. A plot of points in a (τ,p) plane which satisfy equations 2.10 and 2.11 is called the Hugoniot curve. Such a plot is shown in figure 1.

The significance of the deflagration branch of the Hugoniot curve shown in figure 1 is now examined. Consider a straight line through the point (τ_0,p_0) and its intersection with the Hugoniot curve. If the slope of the ray $(p - p_0)/(\tau - \tau_0)$
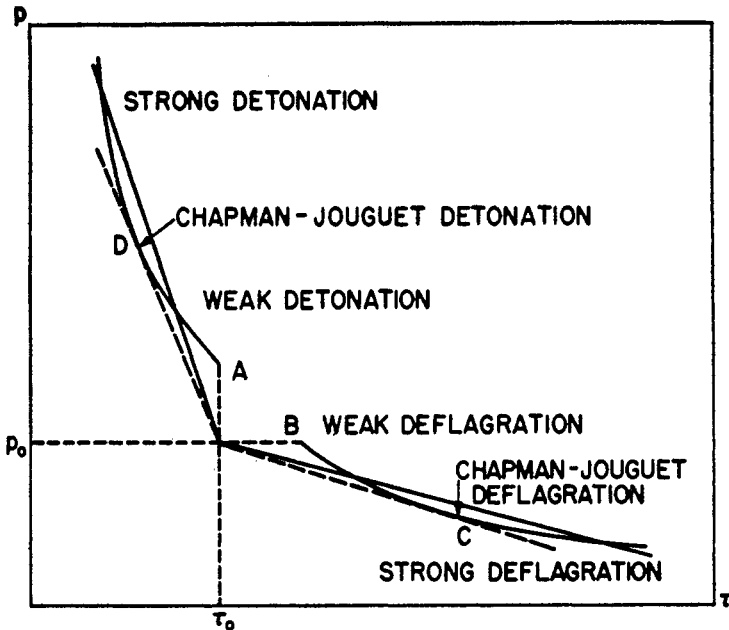
FIG. 1. Hugoniot curve for detonations and deflagrations as given by Courant and Friedrichs (25).

is a small negative number, it will intersect the deflagration branch near the point B, which corresponds to a constant-pressure deflagration. On decreasing the slope a second intersection will occur. It can be shown that not more than two intersections can occur. Deflagrations represented by first intersection points are called weak, and those represented by second intersection points are called strong. Weak and strong deflagrations are separated by the point C, the so-called Chapman–Jouguet deflagration, at which the two points of intersection eventually coalesce if the slope is decreased. Similarly, the point D is the Chapman–Jouguet detonation and separates the regions of strong and weak detonations. It can be shown that in a Chapman–Jouguet process the speed of the burned gas relative to the front is equal to the sound speed of the burned gas. Further-

more, for Chapman–Jouguet deflagrations the reaction front velocity v_0 and the entropy of the burned gas are relative maxima, and for Chapman–Jouguet detonations they are relative minima.

It is seen that reaction processes are not determined by the conservation laws; that is, for a given τ_0 and p_0, a set of deflagrations are mathematically compatible with the laws of conservation across a discontinuity front. To determine a reaction process it is necessary to consider the internal mechanism. By this means it will be shown that strong deflagrations are not possible, and that weak deflagrations are possible only for a well-determined velocity v_0. This velocity is determined by taking into account the transport properties of the gas. Courant and Friedrichs limit the determining property to heat conductivity, but in the general case diffusion must also be considered. Bearing this in mind, the analysis is continued as given by Courant and Friedrichs.

Assume that the change of chemical composition takes place not instantaneously but over a finite zone $x_0 \leq x \leq x_1$. The intermediate compositions are assumed to be mixtures of burned and unburned gas, where ϵ and $(1 - \epsilon)$ represent, respectively, the fraction of burned and unburned gas. Assume that the total energy $E^{(\epsilon)}$ of the mixture is the sum of the total energies for the burned and unburned gases in the mixtures for the same values of τ and p:

$$E^{(\epsilon)}(\tau,p) = (1 - \epsilon)E^{(0)}(\tau,p) + \epsilon E^{(1)}(\tau,p) \qquad (2.12)$$

The equation is valid if the gases are ideal.

The rate of reaction K is assumed to be positive and a function of T, p, and ϵ:

$$d\epsilon/dt = K(T,p,\epsilon) > 0 \qquad (2.13)$$

A steady process has been assumed; hence

$$v \, d\epsilon/dx = K \qquad (2.14)$$

The flow is from left to right, so that $v > 0$. Therefore

$$d\epsilon/dx > 0 \qquad (2.15)$$

It is now argued that the conservation laws (equations 2.01, 2.02, and 2.03) hold throughout the process, the laws being written in the same way, with v_ϵ, p_ϵ, and τ_ϵ replacing v_1, p_1, and τ_1, where the subscript ϵ indicates the value of the quantities at the point x_ϵ where the mixture ratio has the value ϵ.

Relations analogous to equations 2.04 and 2.08 are obtained:

$$(p_\epsilon - p_0)/(\tau_\epsilon - \tau_0) = -M^2 \qquad (2.16)$$

and

$$E^{(\epsilon)}(\tau_\epsilon,p_\epsilon) - E^{(0)}(\tau_0,p_0) = -\tfrac{1}{2}(\tau_\epsilon - \tau_0)(p_\epsilon + p_0) \qquad (2.17)$$

According to equation 2.16 the reaction is represented in the (τ,p) plane by a straight line of slope

$$dp_\epsilon/d\tau_\epsilon = (p_\epsilon - p_0)/(\tau_\epsilon - \tau_0) \qquad (2.18)$$

If we differentiate equation 2.17 and use equations 2.12, 2.18, and 2.07, we obtain:

$$T_\epsilon \cdot \frac{dS_\epsilon}{d\tau_\epsilon} \cdot \frac{d\tau_\epsilon}{dx} = [E^{(0)}(\tau_\epsilon, p_\epsilon) - E^{(1)}(\tau_\epsilon, p_\epsilon)] \frac{d\epsilon}{dx} \tag{2.19}$$

For $\epsilon = 1$, the right-hand side is positive, from equation 2.15 and the assumption that the reaction is exothermic, i.e., that

$$E^{(0)}(\tau_1, p_1) > E^{(1)}(\tau_1, p_1)$$

For a deflagration $d\tau_\epsilon/dx > 0$. Hence equation 2.19 implies

$$dS/d\tau > 0 \text{ for } \epsilon = 1 \tag{2.20}$$

It is now shown that the inequality 2.20 excludes the possibility of strong deflagrations. Consider point C in figure 1, representing the Chapman–Jouguet reaction. For Chapman–Jouguet processes the equation

$$dp/d\tau = (p - p_0)/(\tau - \tau_0) \tag{2.21}$$

holds, in which the differentiation is along the Hugoniot curve. From equations 2.09 and 2.07 one can derive the identity

$$dH^{(1)}(\tau, p) = T dS + \frac{1}{2}[(\tau - \tau_0)dp - (p - p_0)d\tau] \tag{2.22}$$

and using equation 2.21 in equation 2.22 one finds:

$$dS = 0 \quad \text{ at points } C \text{ and } D \tag{2.23}$$

Next differentiate along the Hugoniot curve the relation

$$2T \, dS/d\tau = (p - p_0) - (\tau - \tau_0) \, dp/d\tau \tag{2.24}$$

obtained from equation 2.22. This gives

$$2T \, d^2S/d\tau^2 = -(\tau - \tau_0) \, d^2p/d\tau^2 \quad \text{ at } C \text{ and } D \tag{2.25}$$

since $dS/d\tau = 0$ at points C and D.

Now any ray through (τ_0, p_0) with a slope greater than that of the ray passing through C intersects the Hugoniot curve in two points. Therefore

$$d^2p/d\tau^2 \geq 0 \quad \text{ at } C \text{ and } D \tag{2.26}$$

with the differentiation again being taken along the Hugoniot curve. Since for a deflagration $\tau > \tau_0$ one finds from equation 2.25

$$d^2S/d\tau^2 \leq 0 \text{ at } C, \quad d^2S/d\tau^2 \geq 0 \text{ at } D \tag{2.27}$$

The equality sign of equation 2.27 may now be excluded as follows: The equation of state may be written as a function of τ and S; thus $p = g(\tau, S)$. Differentiating along the Hugoniot curve gives

$$dp/d\tau = g_\tau + g_S S_\tau \tag{2.28}$$

and at C and D, since $S_\tau = 0$,

$$d^2p/d\tau^2 = g_{\tau\tau} + g_S S_{\tau\tau} \quad \text{ at } C \text{ or } D \tag{2.29}$$

Under the assumption that $g_{\tau\tau} > 0$, equation 2.29 shows that $p_{\tau\tau}$ and $S_{\tau\tau}$ cannot vanish simultaneously at C. Equation 2.25 then indicates that they cannot vanish at all. Hence

$$\mathrm{d}^2p/\mathrm{d}\tau^2 > 0 \qquad \text{at } C \text{ or } D \tag{2.30}$$

and

$$\mathrm{d}^2S/\mathrm{d}\tau^2 < 0 \text{ at } C; \qquad \mathrm{d}^2S/\mathrm{d}\tau^2 > 0 \text{ at } D \tag{2.31}$$

From equation 2.31 one sees that equation 2.20 implies that the point (τ_1, p_1) is the first point of intersection of the ray through (τ_0, p_0) with the Hugoniot curve for $\epsilon = 1$. Thus the process is a weak deflagration and strong deflagrations are impossible. Courant and Friedrichs show that the physical meaning of their argument is that a transition from (τ_0, p_0) to the second point of intersection (τ_1, p_1) on the Hugoniot curve for $\epsilon = 1$ is not possible unless the ray passes through a region corresponding to $\epsilon > 1$, and this would be meaningless.

Finally, one wishes to determine if from a set of weak deflagrations one with a particular velocity only is possible. To do this the model of the reaction zone must be refined further. The preceding arguments assumed that no reaction occurs until the point $x = x_0$ is reached and that at that point the reaction rate suddenly assumes a positive value. If one considers the actual process from the point of view of a thermal theory, as the authors do, a picture nearer reality is that the fresh gas is heated by conduction, and only when it has reached a sufficiently high temperature does the reaction rate assume a noticeable value. That weak deflagrations are indeed subjected to one additional condition which depends for a thermal theory essentially on the heat conductivity is illustrated by the following considerations:

The differential equations for the one-dimensional steady-state burning in which there are only two components, reactant and product, and in which heat conductivity and viscosity but not diffusion are considered, may be written

$$\rho v = M \tag{2.32}$$

$$\rho v^2 + p - \mu v_x = P \tag{2.33}$$

$$\rho v(\tfrac{1}{2}v^2 + I^{(\epsilon)}) - \mu v v_x - \lambda T_x = Q \tag{2.34}$$

$$v\epsilon_x = K(T, p, \epsilon) \tag{2.35}$$

where M, P, and Q are constants. Equations 2.32, 2.33, and 2.34 are just the integrated forms of equations 1.05, 1.06, and 1.07, except that the total enthalpy $I^{(\epsilon)}$, which includes the energy of formation and is dependent on ϵ, replaces the enthalpy i of equation 1.07. Equation 2.35 is the same as equation 2.14. The gas is assumed to be ideal; hence $T = p\tau/R'$.

If M, P, and Q are known, equations 2.33, 2.34, and 2.35 are three differential equations of the first order for the variables v, T, and ϵ. All other quantities can be written in terms of these variables. The boundary values $v = v_0$, $\rho = \rho_0$, $p = p_0$, and $\epsilon = 0$ for the fresh gas are prescribed at $x = -\infty$; in the same way

$v = v_1$, $\rho = \rho_1$, $p = p_1$, and $\epsilon = 1$ for the burned gas are prescribed at $x = +\infty$. A solution is sought over the whole range $-\infty < x < +\infty$ which must approach $x = \pm\infty$ in such a way that v_x, T_x, and ϵ_x approach zero. For this to be possible it is required that K vanish for $\epsilon = 1$ and for $\tau = \tau_0$, $p = p_0$, $\epsilon = 0$. Then the constants M, P, and Q can be expressed in terms of the boundary conditions. Since it is required that M, P, and Q have the same values for state 0 and state 1, three conditions are thereby imposed on the boundary conditions.

Now consider a constant-pressure deflagration, so that equations 1.13 and 1.14 replace equations 2.33 and 2.34. Then by introducing ϵ and $T = p\tau/R'$ as independent variables, equations 2.33 and 2.34 become:

$$\lambda T_x - MI^{(\epsilon)} = -MI^{(0)} = -MI^{(1)} = \text{constant} \tag{2.36}$$

$$M\epsilon_x = pK(T,p,\epsilon)/TR' \tag{2.37}$$

Equations 2.36 and 2.37 are combined to give:

$$dT/d\epsilon = M^2(I^{(\epsilon)} - I^{(0)})R'T/\lambda Kp \tag{2.38}$$

The problem is to find a solution of equation 2.38 which satisfies $T = T_0$ for $\epsilon = 0$ and $T = T_1$ for $\epsilon = 1$. The values T_0 and T_1 are restricted by the requirement that the complete enthalpy does not change, i.e., $I^{(0)} = I^{(1)}$. It is now seen that there is only one particular value of M for which the solution just assumes the value $T = T_0$ for $\epsilon = 0$ and $T = T_1$ for $\epsilon = 1$. That is, there is only one point on the deflagration branch of the Hugoniot curve which is possible, and the extra condition to be imposed is that M should have the particular value required for the solution. Thus the flame velocity $v_0 = M/\rho_0$ is completely determined in its dependence on λ, p, T_0, ρ_0, $I^{(\epsilon)}$, and K.

The mathematical problem is thus to find expressions for the dependent variables T, v, ϵ, and ρ which satisfy the differential equations and the two sets of boundary conditions, together with the value of M which makes it possible to satisfy these conditions simultaneously. In other words, it is an eigen-value problem for M.

IV. COMPREHENSIVE THEORIES

A. The theory of Lewis and von Elbe (76)

N_{O_2}, N_O, N_{O_3} = concentration of O_2, O, O_3, respectively,

$E_{O_3}(T)$ = heat of decomposition of 1 mole of ozone,

$E_O(T)$ = heat of recombination of 1 mole of oxygen atoms,

w = rate of formation of oxygen,

K_c, K_p = equilibrium constants in terms of concentrations and partial pressures, respectively,

m = mole ratio (moles O_2/moles O_3) in original mixture,

ϵ = degree of completeness of the reaction, varying from 0 in the unburned gas to 1 in the burned gas,

E = energy of activation, and

Z = number of collisions per unit volume per unit time between O and O_3.

Lewis and von Elbe in this theory were the first (1) to reject the concept of ignition temperature and to introduce explicitly the expression for the reaction velocity as a function of temperature and concentration, (2) to consider the effect of diffusional as well as heat conduction processes and to use the equations of continuity, and (3) to suggest that active atoms and radicals in the flame diffuse into the fresh gas and play an important role in bringing the fresh gas to a reacting state.

The authors consider the simple exothermic ozone-to-oxygen reaction, for which they have measured flame velocities at various pressures and initial temperatures (75). The postulated mechanism is:

(a) $O_3 \rightleftarrows O_2 + O$

(b) $O + O_3 = 2O_2$

The simplifying assumptions are as follows:

Assumption 1: Pressure is assumed constant.

Assumption 2: The heat capacity of the gas mixture is given a constant value equal to the mean heat capacity of O_2 in the temperature range.

Assumption 3: The equilibrium represented by equation (a) is assumed to exist across the whole flame zone. The problem is thus reduced to the case of a single reaction, and the velocity of the flame is determined by the progress of reaction (b). The authors state their intention of developing a theory in which diffusion of atoms or radicals into the unburned gas is decisive in initiating the chemical reaction. However, as Zeldovich, Frank-Kamenetsky, and Semenov (114, 115) point out, because of this assumption of equilibrium (a) it is necessary to consider the diffusion only of the initial reactant (O_3) and the final product (O_2). The single equation of continuity is written:

$$-\frac{d}{dx}(N_{O_2}v) + \frac{d}{dx}\left(D\frac{dN_{O_2}}{dx}\right) + w = 0 \quad \text{(continuity)} \quad (3.1.01)$$

The equilibrium equation is written

$$K_c = N_O N_{O_2}/N_{O_3} \qquad \text{(equilibrium)} \quad (3.1.02)$$

Assumption 4: The diffusion coefficient for the diffusion of oxygen in the gas mixture is taken to be that for its diffusion in a gas consisting entirely of oxygen molecules. It is thus independent of composition, though not of temperature. It is written

$$D = \Omega_{O_2}\lambda_{O_2}/3 \equiv C_1 T^{3/2}/p \qquad (3.1.03)$$

where $\Omega_{O_2}(T)$ is the average velocity of the oxygen molecules at temperature T, λ_{O_2} is the mean free path in a gas consisting of oxygen molecules, and C_1 is a constant numerical factor. This expression is valid for molecules of equal size and weight.

Assumption 5: It is assumed that the total thermal and chemical energy per unit mass is the same at every point in the flame. This assumption, which is expressed in algebraic form, makes it unnecessary to consider the differential equa-

tion of energy, and hence simplifies the mathematical problem. The equation is written as follows:

$$E_{O_3}N_{O_3} + E_O N_O = (N_{O_2} + 1.5N_{O_3} + 0.5N_O)c_p(T_1 - T) \quad \text{(energy)} \quad (3.1.04)$$

This hypothesis is equivalent to the requirement that $D\rho = \lambda/c_p$ (97, 114). Lewis and von Elbe (80) are of the opinion that there is always an excess enthalpy, and that this excess constitutes the energy barrier which prevents ignition of explosive gases by infinitesimal sources. However, the assumption that $D\rho = \lambda/c_p$ is taken as a reasonable approximation.

Assumption 6: If the thermal dissociation of oxygen molecules in the completely burned gas is neglected, the equation of state becomes:

$$N_{O_2} + N_{O_3} + N_O = (N_{O_2})_1 T_1/T \qquad (3.1.05)$$

Equation 3.1.05 is approximated by

$$N_{O_2} = (N_{O_2})_1 T_1/T \qquad \text{(state)} \quad (3.1.06)$$

This approximation is most serious at low temperatures, where the relative concentrations of ozone are high.

Assumption 7: The principle of conservation of mass may be written

$$v/T(1 + 0.5\epsilon + m) = \text{constant} \qquad (3.1.07)$$

where

$$0 \le \epsilon \le 1 \qquad \text{and} \qquad \epsilon = 0 \text{ at } x = x_0$$

$$\epsilon = 1 \text{ at } x = x_1$$

Equation 3.1.07 is approximated by

$$v/T = \text{constant} \quad \text{(conservation of mass)} \quad (3.1.08)$$

Assumption 8: According to the assumption that reaction (b) is the rate-determining reaction, the rate of formation of oxygen by chemical reaction, w, is determined by the frequency of collision between oxygen atoms and ozone molecules and by the probability of reaction occurring upon collision. Every successful collision produces two molecules of oxygen. Therefore the rate is written

$$w = 2Ze^{-E/RT} \qquad (3.1.09)$$

where

$$Z = 2N_O N_{O_3} \sigma^2 \left(2\pi RT \frac{M_O + M_{O_3}}{M_O M_{O_3}}\right)^{1/2} \qquad (3.1.10)$$

σ being the average diameter of the molecules O and O_3, and M_O and M_{O_3} representing the molecular weights of the oxygen atom and the ozone molecule, respectively.

The dependent variables are T, v, N_{O_2}, N_{O_3}, and N_O (or alternatively for N_O, ρ). The set of equations is composed of equations 3.1.01, 3.1.02, 3.1.04, 3.1.06,

and 3.1.08. Equations 3.1.03 and 3.1.09 are substituted into equation 3.1.01. Combining equations 3.1.02, 3.1.04, and 3.1.06 gives

$$N_{O_3} = \frac{(N_{O_2})_1(T_1/T)c_p(T_1 - T)}{K_c E_O/[(N_{O_2})_1(T_1/T)] + E_{O_3}} \tag{3.1.11}$$

and

$$N_O = \frac{K_c c_p(T_1 - T)}{K_c E_O/[(N_{O_2})_1(T_1/T)] + E_{O_3}} \tag{3.1.12}$$

Let $y = (dT/dx)D/T^2$. Then by combining equations 3.1.01, 3.1.06, and 3.1.08 one finds:

$$-y(dy/dT) + Dw/T^2(N_{O_2})_1 T_1 = 0 \tag{3.1.13}$$

Let the cold-boundary condition be $dT/dx = 0$ at $T = T_0$. Then from equation 3.1.13 one finds:

$$y^2 = 2 \int_{T_0}^{T} \frac{D}{T^2} \frac{w}{(N_{O_2})_1 T_1} dT \tag{3.1.14}$$

After introducing equations 3.1.03, 3.1.09, 3.1.10, 3.1.11, and 3.1.12 into equation 3.1.14 and computing the numerical factors, the equation for dT/dx becomes, in degrees per centimeter:

$$\frac{dT}{dx} = 7.17 \times 10^9 \, C_p p^{3/2} \, T^{1/2} \left\{ \int_{T_0}^{T} \frac{[(T_1/T) - 1]^2 \, e^{-15,300/T}}{[1.76 \times 10^{14} \, e^{-12,300/T} + 3.4(10^4)p]^2} \right\}^{1/2} \tag{3.1.15}$$

The curve for T as a function of x is obtained by integrating equation 3.1.15 graphically, plotting dx/dt *versus* T, and again integrating graphically. This procedure implies the introduction of a second boundary condition, two conditions being required for the particular solution of a second-order differential equation. This condition is essentially that $T = T_0$ at $x = -\infty$. Curves for N_{O_3}, N_{O_2}, N_O, and ρ as functions of x are readily obtained.

In order to determine v as a function of x, it is necessary to determine the value of the characteristic constant of equation 3.1.08. This constant, taking into consideration assumption 7, may be considered equivalent to the eigen-value M which, as has been shown previously, should be determined by requiring the solution of the differential equation to fit two sets of boundary conditions. As a result of assumptions 6 and 7 the differential equation 3.1.13 does not contain the variable v or the characteristic constant. Consequently, only one set of conditions, namely $T = T_0$ and $dT/dx = 0$ at $x = -\infty$, was required to obtain a solution of the equation. The physically plausible conditions at the burned end, $T = T_1$ and $dT/dx = 0$ at $x = \infty$, are not imposed. Figure 2 shows T *versus* x as obtained by Lewis and von Elbe (76). It is seen that the curve near the burned side does not behave as it would be expected to from physical considerations.

The flame velocity, v_0, is obtained by considering that the number of ozone

molecules entering the flame front per unit time is equal to the number reacting per unit time. Thus

$$v_0(N_{O_3})_0 = \int_{x_0}^{x_1} \frac{w}{1.5}\, dx = \int_{T_0}^{T_1} \frac{w}{1.5} \frac{dx}{dT}\, dT \qquad (3.1.16)$$

Upon the introduction of expressions for w and dx/dT an expression is obtained for v_0 which can be integrated graphically.
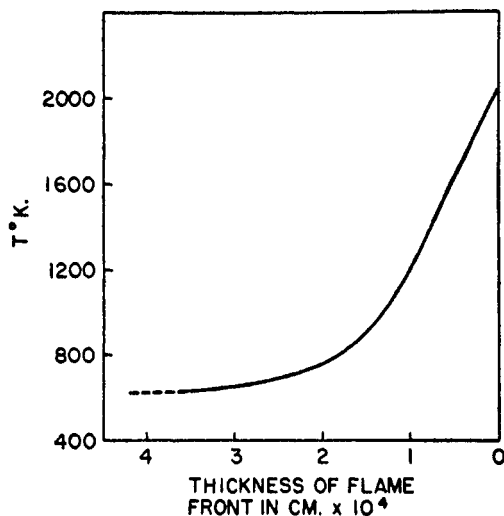

FIG. 2. Dependence of T on x for the ozone flame, as calculated by Lewis and von Elbe (76).

TABLE 1

Comparison of experimental and calculated flame velocities for flames of mixtures of ozone and oxygen according to Lewis and von Elbe (76)

p	T_0	T_1	m	v_0	
				Experimental	Calculated
mm. Hg	°K.	°K.		cm./sec.	cm./sec.
624	300	1239	3.054	55	253
2560	427	1343	3.054	158	451
495	302	1922	1.016	160	333
3760	468	2044	1.016	747	664

Table 1 gives a comparison of observed and calculated flame velocities according to Lewis and von Elbe.

Notwithstanding the fact that the mathematical treatment of the problem is not entirely satisfactory, since the mass flow is not obtained by requiring the solution of the set of equations to fit boundary conditions at both limits of the flame zone, the observed and calculated flame velocities are of the same order

of magnitude. Therefore it would seem that this method of solution gives a first approximation to actual behavior, at least in the lower temperature regions.

B. *The theory of Zeldovich, Frank-Kamenetsky, and Semenov (97, 114, 115, 116)*

L = heat of combustion of 1 g. of initial mixture,
Q' = heat of reaction (calories/molecule of reactant),
h = heat of reaction (calories/gram of reactant),
w = rate of reaction (molecules of reactant/cm.^{3} sec.),
a = molecules of reactant/cm.^{3},
γ = thermal diffusion constant,
S = collision number,
Z = impact coefficient; number of collisions/cm.^{3} sec., and
n_r/n_p = (moles of reactant/moles of product) by the stoichiometric equation.

The theory of flame propagation as developed by Zeldovich and Frank-Kamenetsky (114, 116) has been discussed at length by Semenov (97); the latter's discussion will be followed here for the most part. The theory assumes the reaction model $nA = B + C \cdots$, for which the reaction order may be zero, first, or second with respect to A. Intermediate reactions or particles are not considered.

Assumption 1: Pressure is assumed constant.

Assumption 2: The number of molecules does not vary during the reaction. This restriction is later removed to allow the number to change in the ratio n_r/n_p.

Assumption 3: c_p and λ are constant; hence λ/c_p is constant. This restriction is later partially removed by assuming that λ/c_p has a mean value in region I, defined below, and is equal to the value $\lambda_1/(c_p)_1$ in region II.

Assumption 4: $\lambda/c_p = D\rho$. This assumption has the effect of reducing the number of differential equations from two to one by replacing one of the differential equations with an algebraic equation. Later this restriction is modified to allow

$$(\lambda/c_p)/D\rho = A/B$$

A and B being constants.

Assumption 5: It is assumed that there is a temperature T_i very near to T_1, below which there is practically no reaction. T_i is essentially an ignition temperature which is used not as a physically significant constant but as a mathematical device for approximate computation. T_i does not appear in the final expressions.

The single second-order differential equation is solved by dividing the integrating range into two sub-intervals. In region I, in which the temperature rises from $T = T_0$ to $T = T_i$ and x varies from $-\infty$ to 0, there is no reaction. Region II, in which reaction occurs, extends from $T = T_i$ at $x = 0$ to $T = T_1$ at $x = d$. From $x = d$ to $x = \infty$ the reaction rate is zero, the temperature constant, and the solution obvious.

Assumption 6: It is assumed that in region II for T, near in value to T_1 it is possible to neglect the mass flow term with respect to the reaction and heat conductivity terms.

The equations of continuity, energy, state, and mass are written as follows, after taking into consideration assumptions 3 and 4:

$$D\rho \frac{\mathrm{d}^2 \frac{a}{\rho}}{\mathrm{d}x^2} - M \frac{\mathrm{d} \frac{a}{\rho}}{\mathrm{d}x} - w = 0 \qquad \text{(continuity)} \quad (3.2.01)$$

$$\frac{\lambda}{c_p} \frac{\mathrm{d}^2 T}{\mathrm{d}x^2} - M \frac{\mathrm{d}T}{\mathrm{d}x} + \frac{wQ'}{c_p} = 0 \qquad \text{(energy)} \quad (3.2.02)$$

$$\rho/\rho_0 = T_0/T \qquad \text{(state)} \quad (3.2.03)$$

$$\rho v = M \qquad \text{(conservation of mass)} \quad (3.2.04)$$

By assumption 4 one may obtain an algebraic relation between the temperature and the composition of the mixture in the following way: Define the variables θ and α as follows:

$$\theta = c_p(T - T_0)/Q' \qquad (3.2.05)$$

and

$$\alpha = a_0/\rho_0 - a/\rho \qquad (3.2.06)$$

Substituting equations 3.2.05 and 3.2.06, equations 3.2.01 and 3.2.02 may then be written:

$$D\rho \frac{\mathrm{d}^2 \alpha}{\mathrm{d}x^2} - M \frac{\mathrm{d}\alpha}{\mathrm{d}x} + w = 0 \qquad (3.2.07)$$

and

$$\frac{\lambda}{c_p} \frac{\mathrm{d}^2 \theta}{\mathrm{d}x^2} - M \frac{\mathrm{d}\theta}{\mathrm{d}x} + w = 0 \qquad (3.2.08)$$

The boundary conditions for equations 3.2.07 and 3.2.08 are prescribed as follows:

For $x = -\infty$, $\alpha = 0$, $\theta = 0$

For $x = +\infty$, $\alpha = a_0/\rho_0$, $\theta = c_p(T_1 - T_0)/Q'$

For the condition $D\rho = \lambda/c_p$, equations 3.2.07 and 3.2.08 are identical in form, and if the equations and the boundary conditions for α and θ coincide, i.e., $\alpha = \theta$ over the entire interval, then

$$c_p T + aQ'/\rho = c_p T_0 + a_0 Q'/\rho_0 = c_p T_1 \qquad (3.2.09)$$

The meaning of equation 3.2.09 is that the sum of the thermal and chemical energies per unit mass of the mixture is constant in the combustion zone. That is, the relation between the temperature and the composition of the gas mixture

in the flame is the same as that for adiabatic behavior of the reaction at constant pressure. This is the hypothesis used by Lewis and von Elbe.

One may now replace the differential equation 3.2.01 with the algebraic equation 3.2.09. The problem then reduces to one requiring solution of only one differential equation (equation 3.2.02).

First consider a zero-order reaction, for which it is not necessary to consider the equation of continuity, inasmuch as the rate w is not a function of concentration. Only the energy equation 3.2.02 is necessary. The integrating range is divided into two sub-intervals. In region I, $w = 0$ according to assumption 5 and the energy equation is written

(I) $$\frac{\mathrm{d}^2 T}{\mathrm{d}x^2} - \frac{Mc_p}{\lambda} \frac{\mathrm{d}T}{\mathrm{d}x} = 0 \qquad (3.2.10)$$

where at $x = -\infty$, $T = T_0$, and at $x = 0$, $T = T_i$.

In region II, according to assumption 6, the second term of equation 3.2.02 is neglected and the energy equation is written

(II) $$\frac{\mathrm{d}^2 T}{\mathrm{d}x^2} + \frac{wQ'}{\lambda} = 0 \qquad (3.2.11)$$

where at $x = 0$, $T = T_i$, and at $x = d$, $T = T_1$.

The added condition which determines the eigen-value M is the requirement of continuity of heat flow $q = -\lambda \, \mathrm{d}T/\mathrm{d}x$, where the two regions meet. That is, it is required that

$$(\mathrm{d}T/\mathrm{d}x)_{x=0,\mathrm{I}} = (\mathrm{d}T/\mathrm{d}x)_{x=0,\mathrm{II}} \qquad (3.2.12)$$

Upon solving equations 3.2.10 and 3.2.11 and applying the boundary conditions, one obtains an expression for the flame velocity

$$v_0 = M/\rho_0 = \frac{1}{\rho_0 L} \sqrt{2\lambda Q' \int_{T_i}^{T_1} w \, \mathrm{d}T} = \sqrt{\frac{2\lambda I}{c_p \rho_0 (T_1 - T_0)}} \qquad (3.2.13)$$

where

$$I = \frac{1}{a_0} \int_{T_i}^{T_1} w \, \mathrm{d}T \cong \frac{1}{a_0} \int_{T_0}^{T_1} w \, \mathrm{d}T = \frac{Q'}{\rho_0 L} \int_{T_0}^{T_1} w \, \mathrm{d}T \qquad (3.2.14)$$

Equation 3.2.13 resembles the expressions obtained by the early theories described in Section V,A, if w is set constant over the interval T_i to T_1.

Now let w be a function of T, according to the expression for a zero-order chemical expression

$$w = Se^{-E/RT} \qquad (3.2.15)$$

where S, the collision number, is a constant. It is desired to eliminate T_i from equation 3.2.13, since it has no physical significance.

For sufficiently large energy of activation E, such that $E/RT_1 \gg 1$, the temperature T_i below which the velocity of reaction may be neglected will be near T_1.

Set $\sigma = (T_1 - T)$ and let its values range from $\sigma_1 = (T_1 - T_i)$ to 0. Since $\sigma \ll T_1$,

$$e^{-E/RT} = e^{-E/RT_1} \cdot e^{-E\sigma/RT_1^2} \tag{3.2.16}$$

Then by equations 3.2.15 and 3.2.16 for a zero-order reaction:

$$w = Se^{-E/RT_1} \cdot e^{-E\sigma/RT_1^2} \tag{3.2.17}$$

This expression for w is now introduced into equation 3.2.14 to give

$$I = \frac{Se^{-E/RT_1}}{a_0} \int_{T_i}^{T_1} e^{-E\sigma/RT_1^2} \, dT = -\frac{Se^{-E/RT_1}}{a_0} \int_{\sigma_1}^{0} e^{-E\sigma/RT_1^2} \, d\sigma$$

$$= \frac{Se^{-E/RT_1}}{a_0} \frac{RT_1^2}{E} \int_{0}^{\beta_1} e^{-\beta} \, d\beta = \frac{Se^{-E/RT_1}}{a_0} \frac{RT_1^2}{E} j \tag{3.2.18}$$

where

$$\beta = E\sigma/RT_1^2 \quad \text{and} \quad \beta_1 = E\sigma_1/RT_1^2 \tag{3.2.19}$$

With an accuracy sufficient for the problem, set

$$j = \int_{0}^{\beta_1} e^{-\beta} \, d\beta = 1 - e^{-\beta} \cong 1 \tag{3.2.20}$$

Then the expression for I for a zero-order reaction is written

$$I = (Se^{-E/RT_1}/a_0)/(RT_1^2/E) \tag{3.2.21}$$

whence, according to equation 3.2.13, v_0 for a zero-order reaction is

$$v_0 = \sqrt{\frac{2\lambda}{c_p \rho_0} \frac{Se^{-E/RT_1}}{a_0(T_1 - T_0)} \frac{RT_1^2}{E}} \tag{3.2.22}$$

The order of magnitude of error incurred because of the approximation of equation 3.2.20 may be indicated by the fact that if $\sigma_1 = 2RT_1^2/E$, then $\beta_1 = 2$ and $j = 0.87$, so that there is an error of about 15 per cent in v_0^2.

Reactions in which w is a function of composition as well as of temperature will now be considered. In particular, consider unimolecular reactions for which

$$w = kae^{-E/RT} \tag{3.2.23}$$

and bimolecular reactions for which

$$w = ka^2 e^{-E/RT} \tag{3.2.24}$$

Since a new dependent variable a has been added, one more equation is required. This is equation 3.2.09, which expresses a as a function of T.

By introducing equations 3.2.03, 3.2.09, 3.2.16, and 3.2.23 into equation 3.2.14, an expression for I for a first-order reaction is obtained.

$$I = \int_{T_i}^{T_1} \frac{ka}{a_0} e^{-E/RT} \, dT = ke^{-E/RT_1} \int_{T_i}^{T_1} \frac{T_0}{T} \frac{\sigma}{T_1 - T_0} e^{-E\sigma/RT_1^2} \, dT \tag{3.2.25}$$

T_0/T is taken outside the integral sign and set equal to T_0/T_1, since T_i is near in value to T_1. Set

$$j = \int_0^{\beta_1} e^{-\beta}\beta \, d\beta = 1 - e^{-\beta_1}(\beta_1 + 1) = 1 \qquad (3.2.26)$$

Equations 3.2.19 and 3.2.26 are substituted into equation 3.2.25 and integrated to give an expression for I which, when placed in equation 3.2.13, gives the following expression for v_0 for a first-order reaction:

$$v_0 = \sqrt{\frac{2\lambda k}{\rho_0 c_p}\frac{T_0}{T_1}\frac{e^{-E/RT_1}}{(T_1 - T_0)^2}\left(\frac{RT_1^2}{E}\right)^2} \qquad (3.2.27)$$

For the case of $\beta_1 = 2$, setting j equal to 1 introduces an error of 40 per cent into v_0^2.

Some of the restricting assumptions may now be removed. If one allows the number of molecules to change in the ratio n_r/n_p, assigns λ and c_p the mean values $\bar{\lambda}$ and $\bar{c_p}$ in region I and the value of the burned gases λ_1 and $(c_p)_1$ in region II, and sets $(\lambda/c_p)/D\rho = A/B$, the equation for a unimolecular reaction becomes

$$v_0 = \sqrt{\frac{2\lambda_1(c_p)_1 k}{\rho_0 \bar{c_p}^2}\left(\frac{T_0}{T_1}\right)\left(\frac{n_r}{n_p}\right)\left(\frac{A}{B}\right)\left(\frac{RT_1^2}{E}\right)^2 \frac{e^{-E/RT_1}}{(T_1 - T_0)^2}} \qquad (3.2.28)$$

and for a bimolecular reaction is

$$v_0 = \sqrt{\frac{2\lambda_1(c_p)_1^2 ka_0}{\rho_0 \bar{c_p}^3}\left(\frac{T_0}{T_1}\right)^2\left(\frac{n_r}{n_p}\right)^2\left(\frac{A}{B}\right)^2\left(\frac{RT_1^2}{E}\right)^3 \frac{e^{-E/RT_1}}{(T_1 - T_0)^3}} \qquad (3.2.29)$$

It is desirable to consider the conditions for which this method is valid. Semenov (97) makes an estimate of the range of application to which the solution is limited because of the neglect of the mass flow term in the energy equation 3.2.02 in region II. He concludes that, provided $(T_1 - T_i)/(T_1 - T_0) \leq 0.25$, an error no greater than 8 per cent is incurred in v_0 from this approximation. He next considers the error incurred in neglecting the chemical reaction at temperatures less than $T_i = T_1 - \sigma_1$ while maintaining the condition $\sigma_1 \leq 0.25 \, (T_1 - T_0)$. He concludes that for bimolecular reactions the solution is valid only for $RT_1/E \leq 0.1$. Hence for a bimolecular reaction the application of equation 3.2.29 is restricted to values of E greater than 40 kcal. at $T_1 = 2000°$. For unimolecular reactions the conditions are more favorable.

Belayev (17) applied the theory to the computation of the speed of combustion of the vapor of nitroglycol. The heat of combustion of the vapor phase is conducted to the surface of the explosive and causes the vaporization of the liquid. The mass rate of vaporization is directly measured by the rate of lowering of the meniscus of the liquid, and is assumed equal to the mass rate of combustion of the vapor.

It is assumed that the activated molecule of nitroglycol decomposes by itself and the reaction is possible on impact with any particle. The equation for unimolecular reactions (equation 3.2.28) is used, except that the steric factor k,

instead of being given the first-order value of $\sim 10^{13}$, is replaced by ZN, where N is the number of all molecules in a unit volume. The calculated v_0 agrees well with the measured result, both being about 4×10^{-2} g./sec. cm.^{2}

The theory was also applied to the oxidation of carbon monoxide in the presence of water. The oxidation is assumed to be a chain reaction, the velocity of which very soon attains a stationary value, so that the velocity of the reaction is completely determined by the temperature and concentration at any point in the reaction zone. Zeldovich (97) analyzed the data on the properties of carbon monoxide flames and proposed a mechanism which fits the following kinetic law:

$$\frac{d[CO_2]}{dt} = -2\frac{d[O_2]}{dt} = -\frac{d[CO]}{dt} = Ze^{-25,000/RT}[H_2O][CO] \qquad (3.2.30)$$
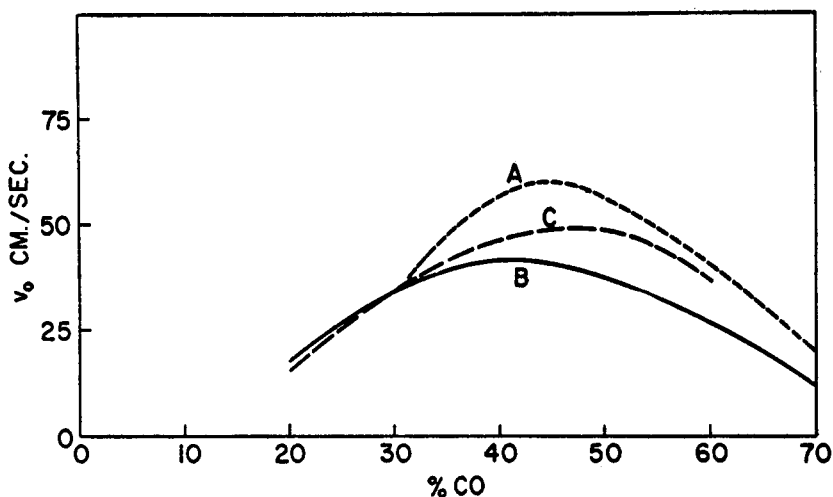

FIG. 3. Experimental and theoretical values of v_0 for carbon monoxide–air mixtures according to Semenov (97). Curve A shows the calculated values; curves B and C give experimental data obtained by Passauer (92) and Jahn (55).

Using this kinetic law the theory accounts satisfactorily for experimental results of measurements of carbon monoxide flames in which carbon monoxide is in excess as well as those in which there is a deficiency of carbon monoxide. According to the expressions obtained for v_0, v_0 should be proportional to $\sqrt{(H_2O)_0}$, where $(H_2O)_0$ is the concentration of water at the original temperature. The results of Fiock and Marvin (39) are replotted in this way and give reasonably good straight lines. The theory also indicates that for constant per cent of moisture content v_0 is independent of pressure, and that for constant water vapor pressure, v_0 varies as $1/\sqrt{p}$. This correlation was observed experimentally. Computed values of v_0 for various ratios of carbon monoxide and air were compared with experimental measurements made by Jahn (55) and Passauer (92). Results are shown in figure 3.

In this treatment of the carbon monoxide flame the diffusion of the active particles H, OH, and O into the fresh gas is neglected. This is in contrast to the treatment of Tanford and Pease, who place the emphasis on the diffusion of active particles, particularly hydrogen atoms, into the fresh gas (104–107).

Dugger (36, 37) measured flame velocity as a function of initial temperature for propane–air and ethylene–air flames, and compared the curves for the experimental data with curves calculated by the Zeldovich–Frank-Kamenetsky
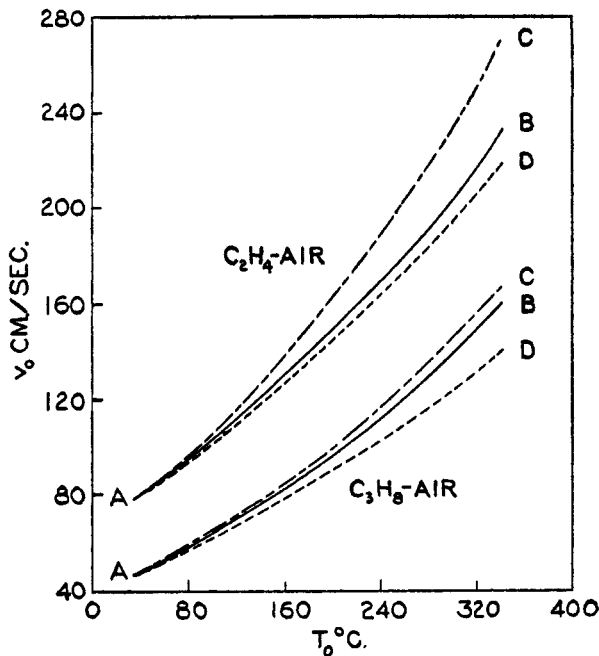

FIG. 4. Dependence of v_0 on T_0 (37). Curves AB show experimental data by Dugger; curves AC are calculated according to the Zeldovich–Frank-Kamenetsky method; curves AD are calculated according to the Tanford–Pease method, using

$$\sum p_i D_{i,r} = 6.5 p_H + p_{OH} + p_O$$

The upper set of curves is for ethylene–air, while the lower set is for propane–air.

theory as well as with curves calculated according to the Tanford–Pease theory. Dugger assumed that the controlling step was a bimolecular reaction. He eliminated from equation 3.2.29 the terms not dependent upon temperature and substituted as approximate relations for the temperature-dependent terms those determined for air. In this way he reduced equation 3.2.29 to the form:

$$v_0 \propto \sqrt{T_0^2 T_1^{4.9} e^{-E/RT_1} / (T_1 - T_0)^3} \tag{3.2.31}$$

Figure 4 shows the curves thus obtained.

C. The theory of Boys and Corner (21, 23)

Q = heat of reaction (calories/gram of product),

E = energy of activation,

ϵ = degree of completeness of the chemical reaction, varying from 0 in the unburned gas to 1 in the burned gas,

$K(\epsilon, T)$ = rate of reaction (gram of product/gram of mixture per second),

W = average molecular weight of reactant,

w = average molecular weight of product, and

$n = W/w = 1$.

Boys and Corner assume a single exothermic chemical reaction. The diffusion of active particles is not considered. In their first paper (21) the diffusion of reactant and product is assumed to be small enough to be neglected; in the second (23) such diffusion is included in the development of the theory. The method being essentially the same in both papers, only the second will be discussed here.

Simplified models allow analytical solutions by a method of successive approximations. Three models are used: a first-order rate from a unimolecular mechanism, a second-order rate from a bimolecular reaction, and the quasi-bimolecular form of a unimolecular reaction at low pressures. The accuracy of the analytical solution is compared with a numerical solution.

Assumption 1: Pressure is constant in the system.

Assumption 2: c_p, λ, and D are assigned constant mean values. Corner points out that D actually varies as T^2 or $T^{7/4}$.

According to the models and the assumptions, the equations of continuity, energy, state, and conservation of mass are written as follows:

$$-D \frac{d}{dx}\left[\frac{M}{v}\frac{d\epsilon}{dx}\right] + M\frac{d\epsilon}{dx} = \frac{MK(\epsilon,T)}{v} \qquad \text{(continuity)} \quad (3.3.01)$$

$$-\lambda \frac{d^2 T}{dx^2} + Mc_p\frac{dT}{dx} = \frac{MQK(\epsilon,T)}{v} \qquad \text{(energy)} \quad (3.3.02)$$

$$pvW/RTM = 1 + n\epsilon \qquad \text{(state)} \quad (3.3.03)$$

$$\rho v = M \qquad \text{(mass)} \quad (3.3.04)$$

The two sets of boundary conditions required to determine the solution of the equations and the characteristic value M are

$$\text{At } x = -\infty, \; T = T_0, \; \epsilon = 0, \; d\epsilon/dx = 0, \; dT/dx = 0$$
$$\text{At } x = \infty, \; T = T_1, \; \epsilon = 1, \; d\epsilon/dx = 0, \; dT/dx = 0$$
$$(3.3.05)$$

Define the variable G as follows:

$$G = \epsilon - (D/v)\, d\epsilon/dx \qquad (3.3.06)$$

so that at $x = \infty$, $G = 1$, and at $x = -\infty$, $G = 0$. By substituting equation 3.3.06 into equations 3.3.01 and 3.3.02 one obtains:

$$dG/dx = K/v \qquad (3.3.07)$$

$$\frac{d}{dx}\left[Mc_p T - \lambda \frac{dT}{dx} - QMG \right] = 0 \qquad (3.3.08)$$

Integration of equation 3.3.08, using the boundary conditions at $x = \infty$, gives:

$$\frac{dT}{dx} = M\{c_p(T - T_1) + Q(1 - G)\}/\lambda \qquad (3.3.09)$$

By combining equations 3.3.03, 3.3.06, and 3.3.09 v and x can be eliminated to obtain an equation for $d\epsilon/dT$ as a function of ϵ, T, and G:

$$\frac{d\epsilon}{dT} = \lambda RT(1 + n\epsilon)(\epsilon - G)/DpW\{c_p(T - T_1) + Q(1 - G)\} \quad (3.3.10)$$

Similarly combine equations 3.3.03, 3.3.07, and 3.3.09, using for $K(\epsilon,T)$ the expression for a first-order reaction

$$K(\epsilon,T) = B_1(1 - \epsilon)e^{-E/RT} \qquad (3.3.11)$$

where B_1 is a constant. This gives an expression for dG/dT in terms of ϵ and T:

$$\frac{dG}{dT} = \frac{\lambda B_1(1 - \epsilon)pWe^{-E/RT}}{\{M^2RT(1 + n\epsilon)[c_p(T - T_1) + Q(1 + G)]\}} \qquad (3.3.12)$$

Equations 3.3.10 and 3.3.12 are exact for the conditions specified.

A first approximation to the solution of equations 3.3.10 and 3.3.12, valid near the burned end of the flame zone, is obtained by retaining in the equations only terms dominant in this region. Thus, near the hot boundary of the flame zone the terms $T - T_1$, $1 - G$, and $1 - \epsilon$ are small, and they determine the behavior of the solution in this region. All other functions of T and ϵ can be given values corresponding to $T = T_1$ and $\epsilon = 1$. The simplified equations have a solution which, where $T - T_1$ and $1 - \epsilon$ are sufficiently small, approaches the solution of equations 3.3.10 and 3.3.12 for the boundary conditions $T = T_1$ where $\epsilon = 1$. This solution is then substituted into exact equation 3.3.12, so that ϵ is eliminated and a separable equation between G and T is obtained which can be integrated. This second approximation to the solution is

$$(1 + n)(G - 1) + \frac{n\theta}{2}(G - 1)^2 = \frac{1 + \beta\theta}{X\beta Q}\int_{T_1}^{T} e^{-E/RT}\frac{dT}{T}$$

$$\cong \frac{1 + \beta\theta}{X\beta Q}\left\{\frac{RT_1}{E}\right\}(e^{-E/RT} - e^{-E/RT_1}) \quad (3.3.13)$$

where

$$X = M^2R/\lambda B_1 pW$$

$$\beta = e^{-E/RT_1}/Xc_pT_1(1 + n)$$

$$\gamma = \lambda RT_1(1 + n)/c_pDpW$$

$$\theta = \frac{\gamma}{2\beta}\left[\left(1 + \frac{4\beta}{\gamma}\right)^{1/2} - 1\right]$$

The solution 3.3.13 satisfies the boundary conditions at the hot boundary, but not necessarily at the cold boundary. The parameter M, for which the solution satisfies conditions at both boundaries, must be determined by requiring the solution 3.3.13 to satisfy the boundary conditions at the beginning of the flame: namely, that $G = 0$ when $T = T_0$. When T is small, near T_0, e^{-E/RT_0} is negligible in comparison with e^{-E/RT_1}. Thus the equation which must be satisfied by M and which determines the properties of the flame is

$$1 + n - \tfrac{1}{2}n\theta = (1 + \beta\theta)(RT_1/E)e^{-E/RT_1}/X\beta Q$$

$$= (1 + \beta\theta)(1 + n)(RT_1/E)c_p T_1/Q \qquad (3.3.14)$$

M is found from X, which can be readily determined by trial. Equation 3.3.14 can be rearranged to give an explicit expression for X, but the expression is cumbersome.

Corner (23) presents calculations which show that for typical values of diffusion rates the flame speed calculated by neglecting diffusion is more than twice the value obtained if diffusion is considered.

A similar solution is given by Corner for a reaction which takes place upon a sufficiently violent collision of a reactant molecule with any molecule of any type, the low-pressure form of a unimolecular decomposition. The rate expression for this type of reaction is

$$K(\epsilon,T) = B_3\rho(1 - \epsilon)(1 + n\epsilon)e^{-E/RT} \qquad (3.3.15)$$

The solution for this reaction type is equation 3.3.14 if, for this case,

$$X = M^2 R^2/\lambda B_3 p^2 W^2$$

and

$$\beta = e^{-E/RT_1}/XT_1^2(1 + n)c_p$$

Also treated is the bimolecular reaction for which

$$K(\epsilon,T) = B_2\rho(1 - \epsilon)^2 e^{-E/RT} \qquad (3.3.16)$$

Its solution involves numerical computation, and Corner gives tables which facilitate the computation.

Comparison between this approximate method of solution and the exact solution obtained by numerical integration, for a first-order reaction with typical values for the parameters, showed that the approximate method gave a flame speed about 5 per cent larger than the numerical method.

Boys and Corner have treated essentially the same models as Zeldovich and Frank-Kamenetsky. This method appears to give a more systematic approximation to the solution. One advantage of the method of the Russian workers is that they consider $D\rho$ to be a constant, an assumption which is more nearly correct than the assumption of Boys and Corner that D is constant.

D. The theory of Hirschfelder and Curtiss (48, 49, 50, 51, 52, 53)

n = number of moles per unit volume,

k = Boltzmann's constant,

$y_i = n_i/n$ = mole fraction of the ith chemical species,

m_i = molecular weight of the ith chemical species,

$\bar{v}$ = mass average velocity at a point (centimeters/second),

$\bar{V}_i$ = diffusion velocity of the ith chemical species,

$G_i = m_i n_i (\bar{v} + \bar{V}_i)/M$ = fraction of the mass rate of flow which is contributed by the ith chemical species.

$w_i = n_i m_i/\rho$ = weight fraction of the ith component,

c_i = specific heat at constant pressure per unit mass of the ith chemical species,

$H_i(T_0)$ = enthalpy per unit mass of the ith chemical species at a reference temperature T_0,

$H_i = H_i(T_0) + \int_{T_0}^{T_1} c_i \, dT$ = enthalpy per unit mass of the ith species,

β_{ij} = number of molecules of the ith species which react stoichiometrically in the jth chemical reaction,

$k_j(T)$ = rate constant for the jth chemical reaction,

$f_j(T) = n^{\Sigma \beta_{ij}} k_j(T)$ = rate constant for the jth chemical reaction modified for use in connection with mole fractions,

$K_i(y_j, T) = \sum_j (\eta_{ij} - \beta_{ij}) f_j(T) y_1^{\beta_{ij}} y_2^{\beta_{ij}}$ = total rate of production of moles of the ith species per unit volume due to chemical reactions,

s = total number of kinds of chemical species,

g = total number of linearly independent G_i, and

E = activation energy.

It is apparent that for chemical process of any complexity, numerical methods of solution of the flame equations are necessary. The laboriousness of the computations has for the most part caused the technique to be neglected. However, recent development of high-speed computing devices offers the opportunity of performing the necessary computations more rapidly. For this purpose Hirschfelder and Curtiss have set up general equations for one-dimensional, steady-state, non-viscous, constant-pressure flames in a form suitable for solution by differential analyzers or high-speed digital computing devices (50, 51, 52, 53).

The equations of these authors differ from those of others in several important respects. First, the equations are completely general with respect to number of components, number of reaction steps, and order of the reactions. Second, the diffusion coefficients are not assigned mean values or set equal to the simple coefficients for binary mixtures. Instead, approximate (50, 51) or exact (52, 53) equations of diffusion in terms of composition gradients are used. Third, the equations are stated in such a way that the chemical kinetics enter only in the continuity equations. Fourth, the authors believe that it is not physically reasonable to separate a stationary flame from the flame holder at which it originates.

They therefore introduce at the cold boundary a mathematical flame holder with specified properties.

Numerical results are given for a unimolecular reaction and a bimolecular reaction for each of which l, the number of chemical reactions with reverse reactions, is equal to 1 (49, 52, 53). The mathematics is much more difficult for flames which are propagated by a sequence of reactions. The authors give a method for developing an asymptotic solution at the hot boundary which in principle could be extended by numerical methods to give a complete solution. For systems with complex chemical kinetics this would involve the simultaneous determination of a number of eigen-values in non-separable equations (52, 53). This is not attempted, but the authors suggest a method for obtaining an approximate solution.

The equations for flame propagation are written, with heat capacity assumed independent of temperature:

$$M \frac{\mathrm{d}G_i}{\mathrm{d}x} = m_i K_i(y_j, T) \qquad \text{(continuity)} \quad (3.4.01)$$

$$\frac{\lambda}{M} \frac{\mathrm{d}T}{\mathrm{d}x} = \sum_i H_i G_i - \left(\sum_i H_i G_i\right)_1 \qquad (3.4.02)$$

or

$$\frac{\mathrm{d}T}{\mathrm{d}x} - (T - T_0) \frac{M}{\lambda} \sum_i c_i G_i = \frac{M}{\lambda} \left[\sum_i H_i(T_0)G_i - \left(\sum_i H_i G_i\right)_1\right]$$

$$\text{(energy)} \quad (3.4.02)$$

$$\frac{\mathrm{d}y_i}{\mathrm{d}x} = \frac{M}{n} \sum_j \frac{1}{D_{ij}} \left(y_i \frac{G_j}{m_j} - y_j \frac{G_i}{m_i}\right) \qquad \text{(diffusion)} \quad (3.4.03)$$

$$n = \sum_i n_i = p/RT \qquad \text{(state)} \quad (3.4.04)$$

The boundary conditions are specified at the hot boundary, $x = \infty$, on the assumption that there is complete thermal and chemical equilibrium. At the cold boundary, $x = 0$, there is inserted the flame holder, which has two properties. It is a semipermeable membrane through which fuel gases flow freely, but through which product molecules cannot pass, so that back-diffusion into the mixing chamber is prevented. Furthermore, it acts as a heat sink, extracting a predetermined amount of heat, $q_0 = -\lambda(\mathrm{d}T/\mathrm{d}x)_0$, from the flame.

The rate of flow of each component, $m_i n_i(\bar{v} + \bar{V}_i)$, is the same on both sides of the membrane, but before the membrane the diffusion velocities are zero since the final composition is constant. Hence the boundary conditions at the cold boundary are:

$$(G_i)_0 = [m_i y_i n/\rho]_{\text{mixing chamber}} \qquad (3.4.05)$$

Note that it is not possible to specify the composition of the gas at the cold boundary (the y_i), because product gases diffuse back to $x = 0$. For this reason it is difficult to integrate the equations from the cold to the hot boundary.

The conditions of equilibrium at the hot boundary are

$$K_i[(y_j)_1, T_1] = 0 \tag{3.4.06}$$

$$\left(\sum_i \frac{n}{\rho} H_i y_i m_i\right)_1 = \left(\sum_i H_i G_i\right)_0 - \frac{1}{M}\left(\lambda \frac{dT}{dx}\right)_0 \tag{3.4.07}$$

$$(G_i)_1 = [m_i y_i n/\rho]_1 \tag{3.4.08}$$

These three equations are equivalent to the following conditions:

$$(dG_i/dx)_1 = 0, \quad (dT/dx)_1 = 0, \quad (dy_i/dx)_1 = 0 \tag{3.4.09}$$

Equations 3.4.06 and 3.4.07 must be solved simultaneously in order to determine T_1, the adiabatic flame temperature, as modified by the heat loss, $(\lambda \, dT/dx)_0$, and the corresponding composition.

The method of solution of the flame equations 3.4.01, 3.4.02, and 3.4.03 is applied to single-stage reactions of the type A → bB, for which the solution is reasonably simple (48, 49, 50, 53). Since only two components are present and $G_a = 1 - G_b$ and $y_a = 1 - y_b$, equations 3.4.01, 3.4.02, and 3.4.03 can be written:

$$M \, dG_b/dx = m_b K_b \qquad \text{(continuity)} \tag{3.4.10}$$

$$\frac{\lambda}{M}\frac{dT}{dx} = (1 - G_b)(H_a - H_b) + H_b - (H_b)_1 \qquad \text{(energy)} \tag{3.4.11}$$

$$G_b = w_b - (\rho D_{ab}/M)(dw_b/dx) \qquad \text{(diffusion)} \tag{3.4.12}$$

If x is treated as a parameter, equations 3.4.10, 3.4.11, and 3.4.12 may be written:

$$dG_b/dT = \lambda m_b K_b/M^2[(1 - G_b)(H_a - H_b) + H_b - (H_b)_1] \tag{3.4.13}$$

$$dw_b/dT = \lambda(w_b - G_b)/\rho D_{ab}[(1 - G_b)(H_a - H_b) + H_b - (H_b)_1] \tag{3.4.14}$$

For a single-stage reaction,

$$K_b = -m_a K_a/m_b \tag{3.4.15}$$

It is convenient to define parameters ϵ and G:

$$\epsilon = [w_b - (w_b)_0]/[1 - (w_b)_0] = 1 - (\rho/n_a)_0(n_a/\rho) \tag{3.4.16}$$

$$G = [G_b - (w_b)_0]/[1 - (w_b)_0] = \epsilon - \rho\frac{D_{ab}}{M}\frac{d\epsilon}{dx} \tag{3.4.17}$$

ϵ represents the degree of completion of the reaction. If the reverse reaction is negligible, both ϵ and G vary from 0 at the cold boundary to 1 at the hot boundary. Finally, define H_{ab} as the heat released per gram of the fuel gas:

$$H_{ab} = m_a(H_a - H_b)(n_a/\rho)_0$$

$$= (H_{ab})_0 + \{m_a(n_a/\rho)_0[(c_p)_a - (c_p)_b]\}\,(T - T_0) \tag{3.4.18}$$

Making use of equations 3.4.15, 3.4.16, 3.4.17, and 3.4.18, equations 3.4.13 and 3.4.14 may be written

$$dG/dT = -\lambda K_a/M^2(n_a/\rho)_0\left[(1-G)H_{ab} - \int_T^{T_1}(c_p)_b\,dT\right] \quad (3.4.19)$$

$$d\epsilon/dT = \lambda(\epsilon - G)/\rho D_{ab}\left[(1-G)H_{ab} - \int_T^{T_1}(c_p)_b\,dT\right] \quad (3.4.20)$$

Equations 3.4.19 and 3.4.20 apply to any form of reaction velocity. Note that they correspond to equations 3.3.10, 3.3.11, and 3.3.12 of Corner, with Corner giving a first-order expression for K_a.

For a unimolecular decomposition the reaction rate is

$$-K_a = Bn_a e^{-E/RT} \quad (3.4.21)$$

Setting the specific heat constant and introducing equation 3.4.21, equations 3.4.19 and 3.4.20 give for a unimolecular reaction

$$d(1-G)/dz = \beta_1(1-\epsilon)/M^2[(1-G)-z] \quad (3.4.22)$$

$$d(1-\epsilon)/dz = \beta_2[(1-G)-(1-\epsilon)]/[(1-G)-Z] \quad (3.4.23)$$

where

$$\beta_1 = B\lambda\rho e^{-E/RT}/(c_p)_b \quad (3.4.24)$$

$$\beta_2 = \lambda/\rho D_{ab}(c_p)_b \quad (3.4.25)$$

$$z = [(c_p)_b/H_{ab}]_1/(T_1 - T) \quad (3.4.26)$$

In carrying out the numerical integration of equations 3.4.22 and 3.4.23 it is helpful to have an approximate value for M. This may be obtained by the Corner method or by a modification of it, or by a method proposed by Adams (48). Furthermore, to perform the integration it is necessary to know the initial derivatives and the solution in the neighborhood of the hot boundary. With this information the equations may be integrated systematically toward the cold boundary. The correct value of M is the one for which the $G-T$ curve approaches $G = 0$ at the cold boundary. This can be determined with any degree of precision by making a sufficient number of trial runs with assumed values for M.

In place of the hot-boundary conditions in which x is the independent variable, it is necessary to state the conditions applicable to equations 3.4.22 and 3.4.23. At the hot boundary $T = T_1$, $\epsilon_1 = G_1 = 1$, and the equations are indeterminate. One must therefore determine

$$\lim_{z\to 0}\left\{\frac{d(1-G)}{dz}\right\} \quad \text{and} \quad \lim_{z\to 0}\left\{\frac{d(1-\epsilon)}{dz}\right\}$$

This is done in the usual way by taking the ratio of the derivative of the numerator to the derivative of the denominator and evaluating at $T = T_1$. The conditions at the hot boundary are found to be

$$[d(1-\epsilon)/d(1-G)]_1 = \theta$$
$$[d(1-G)/dz]_1 = 1 + (\beta_1)_1\theta/M^2 \quad (3.4.27)$$

where

$$\theta = \frac{(\beta_2)_1 M^2}{2(\beta_1)_1} \left[\left(1 + \frac{4(\beta_1)_1}{M^2(\beta_2)_1} \right)^{1/2} - 1 \right] \qquad (3.4.28)$$

Hypothetical flames involving the first-order decomposition of azomethane $(C_2H_6N_2 \rightarrow C_2H_6 + N_2)$ (49) and the bimolecular decomposition of nitric oxide $(2NO \rightleftharpoons N_2 + O_2)$ (49, 53) were studied in detail.

Four cases for the azomethane decomposition were considered: (a) no heat lost to the flame holder, so that $q_0 = 0$; (b) a reasonable amount of heat lost to the flame holder ($q_0 = 10$ cal./cm.^{2} sec.); (c) 50 per cent by volume of inert gases introduced with the fuel; (d) the decomposition assumed to take place by the autocatalytic mechanism $(C_2H_6N_2 + C_2H_6 \rightarrow 2C_2H_6 + N_2)$.

Results indicated that at 1 atm. pressure, for cases (a), (b), and (d), the decomposing azomethane has a large flame velocity and a narrow flame zone. The authors suggest that heat is probably released faster than the flame can dissipate it, with the result that a detonation front is formed. For case (c) the flame velocity was calculated to be 15 cm./sec. and the flame thickness 0.019 cm. Since these are normal values, it is suggested that a stable flame may be possible for a mixture of equal parts of azomethane and nitrogen.

For the decomposition of nitric oxide the equations were modified slightly to take into account the reverse reaction. Since equilibrium is established at the hot boundary the limiting value of ϵ is not unity but is less than 1, the value being determined by the equilibrium constant. For this hypothetical flame it was found necessary to require that the temperature T_0 be $\sim 800°$K. in order to increase the burning rate sufficiently so that even the slow flame speed of 10 cm./sec. be obtained. For $q_0 = 0$, a hot-boundary value $T_1 = 3000°$K. corresponds to an inlet temperature $T_0 = 800°$K.

Figure 5 illustrates the method of determining the eigen-value M. The value of G_{NO} at the cold boundary is 1. At the hot boundary its value is calculated to be 0.0564. If the integration is started from the hot boundary with a value $M = 0.004$, less than the eigen-value, G_{NO} reaches unity at a temperature greater than the inlet temperature. For $M = 0.006$, greater than the eigen-value, the integrated G_{NO} is less than unity at $T_0 = 800°$K. It is found that the eigen-value is $M = 0.0046$. This corresponds to a flame velocity of 10 cm./sec. Curves for ϵ vs. T, ϵ vs. x, and x vs. T are readily calculated. From these curves the width of the flame may be estimated. The flame thickness for the nitric oxide flame was found to be about 0.5 cm.

When the flame is propagated by a sequence or chain of reactions the mathematics is considerably more involved, since there is more than one condition to be satisfied at the cold boundary. It is necessary, as it was for the single-stage problem, to determine the solution in the neighborhood of the hot boundary before numerical integration toward the cold boundary is possible. An asymptotic form of the solution of equations 3.4.01, 3.4.02, and 3.4.03 is developed as follows (52, 53):

In the neighborhood of the hot boundary, equations 3.4.01, 3.4.02, and 3.4.03

may be considered as linear in $(T - T_1)$, $(y_i - (y_i)_1)$, and $(G_i - (G_i)_1)$ if certain requirements of analyticity are fulfilled. Then the functions T, y_i, and G_i may be written:

$$T = T_1 + \sum_k t_k e^{-\alpha_k x} \qquad (3.4.29)$$

$$y_i = (y_i)_1 + \sum_k t_k u_{ik} e^{-\alpha_k x} \qquad (3.4.30)$$

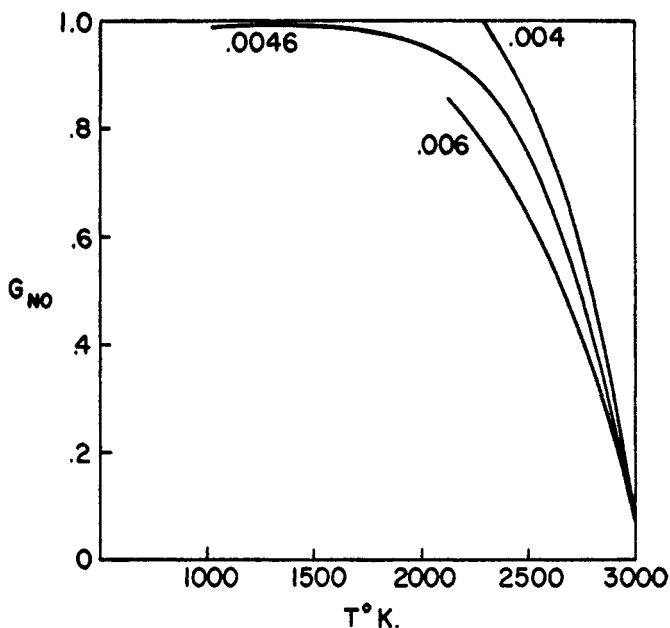$$G_i = (n m_i y_i / \rho)_1 + \sum_k t_k w_{ik} e^{-\alpha_k x} \qquad (3.4.31)$$

Fig. 5. Determination of the eigen-value M for the nitric oxide flame, according to Hirschfelder, Curtiss, Bird, and Spotz (53).

The α_k are roots of the secular equation which will be formed from equations 3.4.33 and 3.4.39, and the u_{ik} and w_{ik} are the constants depending on the kth root.

The t_k are arbitrary constants as far as the hot-boundary conditions are concerned. Therefore, let all $t_k = 0$, except one, and substitute the asymptotic solutions 3.4.29, 3.3.30, and 3.3.31 into equations 3.4.01, 3.4.02, and 3.4.03. The expressions used for the equations of continuity, energy, and diffusion are determined by the substitutions and by considering the limit of the results of these substitutions as $T \to T_1$ (as in equations 3.4.27). This is done since only starting values are desired in the neighborhood of $T = T_1$. The new continuity equation is then combined with the new energy equation and with the new diffusion equation to give an energy equation and a diffusion equation from which the

w_i have been eliminated. Bearing in mind that not all G_i are linearly independent, and that the only linear relation among the u_i is

$$u_s = - \sum_{j=1}^{s-1} u_j \tag{3.4.32}$$

the energy equation becomes

$$\sum_{i=1}^{s-1} L_i u_i = \alpha^2 \lambda^2 + \alpha \lambda MN - Q \tag{3.4.33}$$

where

$$L_i = \sum_{j=1}^{s} H_j (J_{ji} - J_{js}) \tag{3.4.34}$$

$$J_{ik} = \lambda m_i \sum_j (\eta_{ij} - \beta_{ij}) f_j \frac{\beta_{kj}}{y_k} y_1^{\beta_{1i}} y_2^{\beta_{2i}} \cdots \tag{3.4.35}$$

$$Q = \sum_{i=1}^{s} H_i A_i \tag{3.4.36}$$

$$A_i = \lambda m_i \sum_j (\eta_{ij} - \beta_{ij}) \frac{df_j}{dT} y_1^{\beta_{1i}} y_2^{\beta_{2i}} \cdots \tag{3.4.37}$$

$$N = \sum_{i=1}^{s} c_i G_i \tag{3.4.38}$$

Likewise the $s - 1$ diffusion equations become

$$Q_i = \sum_{j=1}^{s-1} (\alpha^2 \lambda n \delta_{ij} + M\alpha\lambda N_{ij} + L_{ij}) u_j \tag{3.4.39}$$

where

$$N_{ij} = \delta_{ij} \sum_{k=1}^{s} \frac{G_k}{m_k D_{ik}} - \frac{G_i}{m_i} \left(\frac{1}{D_{ij}} - \frac{1}{D_{is}} \right) \tag{3.4.40}$$

$$L_{ij} = \frac{J_{ij} - J_{is}}{m_i} \sum_{k=1}^{s} \frac{y_k}{D_{ik}} - y_i \sum_{k=1}^{s} \frac{(J_{kj} - J_{ks})}{m_k} \tag{3.4.41}$$

$$Q_1 = - \frac{A_i}{m_i} \sum_{k=1}^{s} \frac{y_k}{D_{ik}} + y_i \sum_{k=1}^{s} \frac{A_k}{D_{ik} m_k} \tag{3.4.42}$$

There now are s equations 3.4.33 and 3.4.39 and $s - 1$ of the unknowns u_i. For the system to be consistent and a non-trivial solution to exist for these equations, the determinant, $| S_{ij} |$, of the system must equal zero. Since it is assumed that such a solution does exist, the permissible values of α are determined as roots of the secular equation

$$| S_{ij} | = 0 \tag{3.4.43}$$

where the S_{ij} are as follows:

$$S_{ss} = \alpha^2\lambda^2 + \alpha\lambda MN - Q \tag{3.4.44}$$

$$S_{sj} = L_j \qquad j = 1, 2, \cdots, s - 1 \tag{3.4.45}$$

$$S_{is} = Q_i \qquad i = 1, 2, \cdots, s - 1 \tag{3.4.46}$$

$$S_{ij} = \alpha^2\lambda n\delta_{ij} + \alpha MN_{ij} + L_{ij} \qquad \begin{cases} i = 1, 2, \cdots s - 1 \\ j = 1, 2, \cdots s - 1 \end{cases} \tag{3.4.47}$$

Only positive roots, α_k, are significant. The α_k being known, the u_{ik} and therefore the w_{ik} may be determined and an asymptotic solution in the neighborhood of the hot boundary obtained.

In principle this solution can be extended by numerical methods of integrating toward the cold boundary to provide a complete solution. For a flame controlled by complex chemical kinetics this requires finding the value of M such that several cold-boundary conditions are simultaneously satisfied. The amount of computation required, even with the aid of high-speed computing machines, is considerable; hence the authors suggest another method of approximation.

Let the approximate solution be characterized by an approximate mass flow, $M^{(0)}$, and a set of functions $G_i^{(0)}(x)$ which satisfy the known boundary conditions:

$$G_i^{(0)}(0) = (G_i)_0 \tag{3.4.48}$$

and

$$G_i^{(0)}(1) = (G_i)_1 \tag{3.4.49}$$

$M^{(0)}$ may be estimated by the approximate methods previously discussed. By substituting $G_i^{(0)}$ and $M^{(0)}$ into the energy equation 3.4.02 and integrating, approximate $T^{(0)}(x)$ is obtained. Similarly, substitute the $G_i^{(0)}$ and $M^{(0)}$ into the diffusion equation 3.4.03 and integrate to obtain the approximate compositions $y_i^{(0)}(x)$. Each set of approximate solutions thus obtained is in fact an exact solution to a problem for which the chemical kinetics are given by

$$K_i' = \frac{M^{(0)}}{m_i} \frac{\mathrm{d}G_i^{(0)}}{\mathrm{d}x} \tag{3.4.50}$$

The deviation of these K_i' from the K_i obtained by substituting the $T^{(0)}(x)$ and $y_y^{(0)}(x)$ into the actual rate expression, $K = f(y_j, T)$, is a measure of the accuracy of the solution.

V. THERMAL THEORIES

A. The older thermal theories (30, 33, 59, 66, 67, 69, 85, 90); the theory of Damköhler (32, 42)

T_i = ignition temperature,

x_i = point at which ignition occurs,

Q = amount of heat transferred to fresh gas per unit volume per unit time,

δ_r = distance in which the temperature rises from T_i to T_1,

ξ = concentration of products,

w = reaction velocity,

$\bar{w}$ = mean reaction velocity, and

n_r = number of reactant molecules per unit volume.

The earliest expression for flame velocity was derived by Mallard and Le Chatelier (85) and was based on thermal concepts. In addition to the assumptions of constant pressure and of ignition temperature, the following assumptions were made:

Assumption 1: The fresh gas is assumed to have a mean constant heat capacity per unit volume, $c_p\rho$, between T_0 and T_1. The amount of heat which is transferred per unit time by heat conduction is then

$$Q = c_p\rho v_0(T_i = T_0) \qquad (4.1.01)$$

Assumption 2: The temperature gradient at the point x_i is proportional to $(T_1 - T_i)$. Then the heat flow by conduction is

$$Q' = k(T_1 - T_i) \qquad (4.1.02)$$

Here k is a constant which is proportional to the heat conductivity and inversely proportional to the distance, δ_r, in which the temperature rises from T_i to T_1.

Since equations 4.1.01 and 4.1.02 each apply at the ignition point, $Q = Q'$ and

$$v_0 = \frac{k}{c_p\rho}\frac{(T_1 - T_i)}{(T_i - T_0)} = \frac{\lambda}{c_p\rho\delta_r}\frac{(T_1 - T_i)}{(T_i - T_0)} \qquad (4.1.03)$$

Later modifications of this analysis introduce the velocity of the chemical reaction into the energy equation. Following Nusselt (59, 60), let ξ represent the concentration of products, so that the following conditions apply:

$$\text{At } x = x_i,\ T = T_i,\ \xi = 0$$
$$\text{At } x = x_1,\ T = T_1,\ \xi = \xi_1 \qquad (4.1.04)$$

Assumption 3: Nusselt assumes that the degree to which the reaction has proceeded is linear in x. Then

$$d\xi/dx = \xi_1/(x_1 - x_i) = \xi_1/\delta_r \qquad (4.1.05)$$

so that

$$dT/dx = (T_1 - T_i)/\delta_r = [(T_1 - T_i)/\xi_1](d\xi/dx) \qquad (4.1.06)$$

In this way the unknown thickness of the reaction zone, δ_r, is eliminated, but it now becomes necessary to find an expression for the progress of the reaction with respect to x.

Assumption 4: Nusselt assumes that the reaction velocity w is constant; hence also, by assumption 3, the velocity of the gases in the reaction zone, v, is constant, since

$$d\xi/dx = (d\xi/dt)(dt/dx) = w/v \qquad (4.1.07)$$

Assumption 5: For no change in the number of moles, the velocity is expressed as a function of temperature as follows:

$$v = Tv_0/T_0 \qquad (4.1.08)$$

This is inconsistent with assumption 4, which holds v to be constant. Combining equations 4.1.06, 4.1.07, and 4.1.08, Nusselt writes

$$(dT/dx)_{x=x_i} = (T_1 - T_i)wT_0/\xi_1 v_0 T_i \qquad (4.1.09)$$

and since $Q = Q'$, where $Q' = \lambda(dT/dx)_{x=x_i}$, the final equation for flame velocity is written:

$$v_0^2 = \lambda(T_1 - T_i)T_0 w/c_p \rho(T_i - T_0)T_1 \xi_1 \qquad (4.1.10)$$

The theories and expressions of Jouguet and Crussard (66, 67, 69) and of Daniell (33) are essentially the same as those of Nusselt.

Damköhler (32) derives an equation for flame velocity which resembles the equations of Nusselt, Jouguet and Crussard, and Daniell, but modifies the assumptions so that the theory is more realistic. Gaydon and Wolfhard (42) have outlined the following development of the ideas of Damköhler.

Assumption 6: In place of assumption 2 Damköhler makes the approximation that the temperature gradient at the ignition point is related to the average temperature gradient across the reaction zone by a constant F. Then in place of equation 4.1.06, he writes:

$$(dT/dx)_{x=x_i} = (T_1 - T_i)F/\delta_r \qquad (4.1.11)$$

Assumption 7: In place of assumptions 3 and 4 Damköhler defines a mean reaction velocity $\bar{w}$ by the equation

$$n_r v = \int_0^{\delta_r} w \, dx = \bar{w}\delta_r \qquad (4.1.12)$$

where n_r is the number of reactant molecules per unit volume initially present. Note that the contradiction of assumption 5 is avoided.

The final equation is then written in the form

$$\lambda(T_1 - T_i)F/\delta_r = c_p \rho v_0(T_i - T_0) \qquad (4.1.13)$$

or

$$v_0^2 = F\lambda\bar{w}(T_1 - T_i)/c_p \rho n_r(T_i - T_0) \qquad (4.1.14)$$

It is characteristic of these thermal theories that the flame velocity varies as $[\lambda(T_1 - T_i)/c_p\rho(T_i - T_0)]^{1/2}$. A test of the validity of the theory is to compare the flame velocities of two mixtures for which every variable is the same except the heat conductivity. Such experiments were undertaken by Coward and his associates (29). They measured the flame velocities of mixtures of methane and air in which the atmospheric nitrogen was replaced by helium in one case and by argon in the other. The ratio of the flame velocities was found to be $v_0(\text{He})/v_0(\text{A})$

= 1.39. At the time of the experiments the heat conductivities of the mixtures had not been measured. The authors calculated values by the mixing rule from the values for the pure gases at 0°C. The resulting figure for the square root of the ratio of the conductivities was almost twice 1.39, and this was taken as evidence that thermal theories were inadequate for describing observed facts. Jost (62) points out, however, that the method used for calculating the conductivities of the mixtures at the ignition temperatures is not reliable. Bartholomé (6, 8) also stresses the inadequacy of the method of calculation and reports actual measurements. He gives for the square root of the ratio of the heat conductivities the value 1.32, which is very close to the ratio of the flame velocities. Bartholomé therefore concludes that this test of the adequancy of thermal theories holds for the thermal viewpoint rather than against it.

B. The theory of Bartholomé (5, 6, 8, 10, 95)

T_i = ignition temperature,

n_r = number of moles of reactant per unit volume,

$C = c_p \rho R T / p$,

q = heat emitted on reaction of 1 mole of reactant molecules,

m = molecular weight,

$\sum n$ = total number of moles per unit volume at temperature T,

$w = pv/RT$,

u = rate of reaction (moles of reactant per unit volume per unit time), and

E = activation energy.

Bartholomé and Sachsse (5, 6, 95), in order to determine experimentally the variables which have the greatest effect on flame velocity, investigated the combustion of hydrogen, hydrocarbons, alcohols, ethers, nitroparaffins, and alkyl nitrates with air, oxygen, nitrous oxide, and their mixtures. Two observations on the effect of the velocity of the chemical reaction on the flame velocity of fuel–air mixtures (with the fuel–air ratio for the maximum flame velocity) are reported. Gases with large differences in octane number show practically no difference in flame velocity. Addition of knock-promoting and antiknock agents also has little effect. These results indicate a weak functional dependence of flame velocity on reaction velocity. Further, an increase in T_0 by a factor of 5, that is, from 20° to 100°C., produces only a 30 per cent increase in flame velocity. Sachsse (94) showed that for the methane–oxygen flame, preheating to a temperature of 1000°C. caused an increase in flame velocity by only a factor of 3. Since the reaction velocity must somehow increase exponentially with the temperature, the exponential increase must be compensated by a weak functional dependence of the flame velocity on the reaction velocity.

Flame velocities for fuel–air flames were found to have a stronger dependence on T_1. Figure 6 is a plot of v_0 versus T_1 for a number of combustible mixtures. The points arrange themselves on several curves. The flame velocity increases rapidly with temperature, the more rapidly the higher the temperature. It is concluded that for these flames the velocity is essentially determined by the

final temperature. For hotter flames, such as those of hydrocarbons burning with oxygen, in which the end temperature is greater than $\sim 2400°K.$, the flame velocity rises much faster than the final temperature T_1. This is attributed to the fact that dissociation occurs to a perceptible degree at such temperatures and the hydrogen-atom concentration becomes the determining factor. Bartholomé's conception of these hot flames will be summarized in a later section.
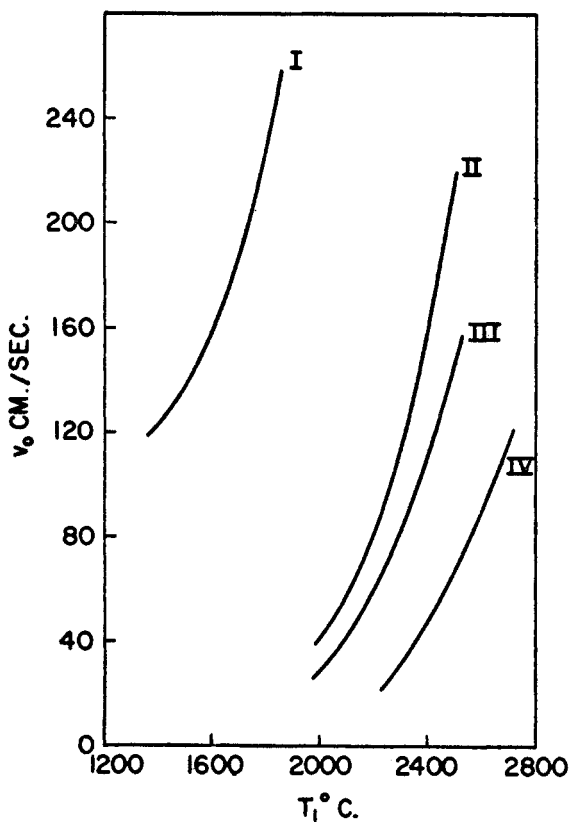

FIG. 6. v_0 *versus* T_1 for flames of various fuels with air, oxygen, nitrous oxide, and their mixtures, as reported by Bartholomé and Sachsse (5, 95). Curve I represents hydrogen flames; curve II represents the flames of gaseous hydrocarbons; curve III includes points for nitrogen compounds and nitrates, alcohol, ether, benzene, carbon disulfide, octane + (oxygen, nitrogen), and others; curve IV includes points for octane + (nitrous oxide, air) and for octane + (nitrous oxide, nitrogen).

On the basis of the foregoing experimental observations Bartholomé proposes a thermal theory of flame velocity (6, 8).

Assumption 1: There is no change in the number of moles during the reaction. The equation of state is written:

$$v = wRT/p \qquad (4.2.01)$$

Then by this assumption w is a constant. w is a version of the parameter M, which appears in other theories.

Assumption 2: Constant pressure is assumed.

Assumption 3: It is assumed that there is no diffusion. Then the equation of continuity is written:

$$(wR/p)[\mathrm{d}(Tn_r)/\mathrm{d}x] + n_r^\alpha \varphi(T) = 0 \qquad (4.2.02)$$

Assumption 4: Constant heat conductivity λ is assumed. Furthermore, the quantity C is assumed to be constant. Then the energy equation is written as:

$$\frac{\lambda}{C}\frac{\mathrm{d}^2 T}{\mathrm{d}x^2} - w\frac{\mathrm{d}T}{\mathrm{d}x} + \frac{Q}{C}n_r^\alpha \varphi(T) = 0 \qquad (4.2.03)$$

Assumption 5: It is assumed that there is an ignition temperature, T_i, which is not less than 90 per cent of the final temperature T_1. Supporting evidence for this assumption is of two kinds. First, neither the octane number of the fuel nor the presence of knock-promoting agents has any appreciable influence on the flame velocity. Since the octane number characterizes the tendency of a fuel–air mixture to explode when heated adiabatically to about 800–900°K., and since a theory of antiknock agents holds that such agents influence the beginning of the explosion in the same temperature region, the evidence suggests that effective reaction does not begin until a temperature at least greater than 900° is attained. Further evidence is based on an extrapolation of induction time measurements of Sachsse (93), which are interpreted to mean that heating of the gas across the flame occurs exclusively by heat conduction until a temperature very near T_1 is reached.

If T_i is very near T_1, the temperature gradient near T_1 is very steep, and the chemical reaction occurs over a very small distance which, if small enough, can be mathematically described as a point. On this assumption Bartholomé holds that it is possible to replace, without great error, the exponential term of the rate expression, $\exp(-E/RT)$, with another function for which the equations are soluble. The form of the function depends upon the order of the reaction and is chosen with a view toward ease of solution of the equations rather than closeness of fit. The expression is written

$$u = n_r^\alpha \varphi(T) = n_r^\alpha \beta T^\alpha \qquad (4.2.04)$$

where $\varphi(T)$, the actual rate expression, contains $\exp(-E/RT)$ and β is a constant prescribed so that the functions fit at one point.

Gaydon and Wolfhard (43) believe, on the basis of experimental data, that the assumption of a very high ignition temperature is not valid. They interpret their measurements of temperature rise for acetylene–air and acetylene–oxygen flames (42) to mean that the reaction commences below 1300°K. and not in the vicinity of 2100°K. Furthermore, they found luminosity due to emission of CC and CH bands beginning at about 1300°K.

For a reaction of second order, $\alpha = 2$ and $\varphi(T)$ becomes βT^2. β is determined so that at $T = 0.95\ T_1$, $\exp(-E/RT) = \beta T^2$. A solution of the differential equations 4.2.03 and 4.2.04 is obtained by dividing the flame zone into two regions.

Region I extends from $x = -\infty$, where $T = T_0$, to $x = 0$, where $T = T_i$. Region II extends from $x = 0$ to $x = \infty$, where $T = T_1$. At $x = \pm\infty$, $dT/dx = 0$. x and dT/dx are continuous at $x = 0$. In region I the reaction velocity is zero and the solution for equations 4.2.03 and 4.2.04 is

(I)
$$Tn_r = T_0 n_{r0} = pn_r/R\Sigma n = \text{constant} \tag{4.2.05}$$

$$T - T_0 = (T_i - T_0)e^{wCx/\lambda} \tag{4.2.06}$$

In region II, setting $u = n_r^2\beta T^2$, equations 4.2.03 and 4.2.04 become, respectively,

$$d(Tn_r)/dx + \beta p(Tn_r)^2/wR = 0 \tag{4.2.07}$$

and

$$d^2T/dx^2 - (wC/\lambda)\,dT/dx + q\beta(Tn_r)^2/\lambda = 0 \tag{4.2.08}$$

Equations 4.2.07 and 4.2.08 are readily integrated for the given boundary conditions to give

(II)
$$(T - T_1) = Ee^{B(x-K)}\epsilon_i[-B(x - K)] \tag{4.2.09}$$

where

$$B = wC/\lambda, \quad E = qw^2R^2/\lambda\beta p^2, \quad K = -wR^2\Sigma n/\beta p^2 n_r,$$

$$\epsilon_i[t] = \int (e^t/t)\,dt \tag{4.2.10}$$

The parameter w is determined by the extra condition that dT/dx be continuous at $x = 0$. Imposing this condition on equations 4.2.06 and 4.2.09, the determining equation is obtained:

$$T_i - T_0 = Ee^{-BK}\epsilon_i[BK] - E/BK \tag{4.2.11}$$

$\epsilon_i[BK]$ is developed into a series which is broken off after the second term and substituted into equation 4.2.11. The resulting equation is solved for v_0^2 to give, for a second-order reaction:

$$v_0^2 = (T_1 - T_0)T_0^2\beta\lambda n_r/(T_i - T_0)C\Sigma n \tag{4.2.12}$$

Similarly an expression for v_0^2 may be found for $\alpha = \frac{3}{2}$, a case which will be illustrated below. The result is

$$v_0^2 = (T_1 - T_0)T_0^2\beta\lambda(R/p)^{1/2}(n_r/\Sigma n)^{1/2}/(T_i - T_0)C \tag{4.2.13}$$

For $\alpha = 1$ the expression is

$$v_0^2 = [(T_1 - T_0)/(T_i - T_0) - 1]T_0^2\beta\lambda R/Cp \tag{4.2.14}$$

Bartholomé calculates the flame velocity for a stoichiometric mixture of methane and air. Following Sachsse (63, 93), it is assumed that the rate is proportional to

the number of collisions between methane molecules and oxygen atoms. Sachsse has given the overall activation energy so that the constant β is determined. In the stoichiometric mixture $[O_2] = 2[CH_4]$, so that $[O]$ is proportional to $\sqrt{2[CH_4]}$. Hence $\alpha = \frac{3}{2}$ and equation 4.2.13 is used for the calculation. Bartholomé reports a calculated value for v_0 of 105 cm./sec. under conditions for which he reports an experimental value of 49 cm./sec.

To test the validity of the assumptions regarding ignition temperature, Bartholomé, Dreyer, and Lesemann (10) solved the differential equations 4.2.02 and 4.2.03 without mathematical simplifications, using a differential analyzer referred to as the "Integrieranlage IPM-Ott" (III). The rate expression $n_r^\alpha \varphi(T)$ was taken from the work of Sachsse (93).

w is obtained as an eigen-value which must be determined by systematic trials. A likely value is assumed and introduced into the equations. The computer is allowed to draw a solution $T(x)$ for that value of w. This will in general not fit the boundary condition that at $T = T_1$, $dT/dx = 0$, but either exceeds the value T_1 or bends off before reaching T_1. For the proper value of w the boundary conditions will be met.

Bartholomé defines ignition temperature in a stationary flame as the point at which the curve $T(x)$ has an inflection. The $T(x)$ curve obtained gives $T_i = 1800°K = {\sim}80$ per cent T_1. This is a lower value than that which has been estimated in the earlier papers (6, 8), but it is the opinion of the authors that it is nevertheless so high that the conclusions drawn from the approximate solution using the high value are valid. The value for the flame velocity as obtained by this computer method is 207 cm./sec., about twice the value of 105 cm./sec. obtained from the approximate analytical solution and about four times the experimental value of 49 cm./sec.

C. The theory of Emmons, Harr, and Strong (38)

ρ_r = density of reacting mixture,
Q = enthalpy change of reaction,
$\alpha = \lambda/c_p\rho$ = thermal diffusivity,
α_r = reaction rate for first-order reaction, and
a_0 = rate constant.

Emmons, Harr, and Strong propose a thermal theory of flame propagation, the equations of which are solved by the use of the Harvard Mark I calculating machine.

Assumption 1: Pressure is assumed constant.

Assumption 2: Heat conductivity, λ, is assumed constant.

Assumption 3: Specific heat, c_p, and hence enthalpy change, Q, are taken to be independent of composition and temperature.

Assumption 4: Density is assumed constant. In view of this assumption the velocity of flow is also constant, and it becomes unnecessary to solve the equations for conservation of mass and of momentum.

Assumption 5: A first-order reaction rate is assumed, for which the reaction rate is given by

$$\alpha_r = \rho_r a_0 e^{-E/RT} \qquad (4.3.01)$$

where ρ_r varies from ρ_{r0} at $x = 0$ to 0 at $x = \infty$.

The sole equation to be solved, the energy equation, is written

$$-\lambda d^2 T/dx^2 + d(\rho v c_p T)/dx + \alpha_r Q = 0 \qquad (4.3.02)$$

The boundary conditions are as follows: at $x = 0$, $T = T_0$, $\rho_r = \rho_{r0}$; at $x = \infty$, $dT/dx = 0$, $\rho_r = 0$.

By setting $\alpha_r = v(d\rho_r/dx)$, substituting into equation 4.3.02, and integrating, using the boundary conditions at infinity, one obtains:

$$-\lambda dT/dx + \rho v c_p T + vQ\rho_r = \rho v c_p T_1 \qquad (4.3.03)$$

At the origin $x = 0$, equation 4.3.03 becomes

$$-\lambda dT/dx \,|^{x=0} + \rho v c_p (T_0 - T_1) + vQ\rho_{r0} = 0 \qquad (4.3.04)$$

which relates the final temperature to the initial temperature and the initial temperature gradient.

Now introduce the variables

$$\eta = (\alpha/v)(dT/dx), \qquad \gamma = a_0\lambda/\rho c_p v^2, \qquad \epsilon = Q\rho_{r0}/c_p\rho \qquad (4.3.05)$$

Then by combining equations 4.3.01, 4.3.02, 4.3.04, and 4.3.05 the following working equation is obtained:

$$d\eta/dT = 1 - \gamma e^{-E/RT}(\eta + T_1 - T)/\eta \qquad (4.3.06)$$

where, according to equation 4.3.04,

$$\eta_0 = \epsilon - (T_1 - T_0) \qquad (4.3.07)$$

For a given η_0 and T_0 there is a unique value of γ which will produce a curve which satisfies the boundary condition at infinity. γ is regarded as specifying the flame speed of the mixture.

γ is found by numerically constructing the solution to equation 4.3.06. Solutions are constructed for chosen values of γ and T_1, that is, the solution curve is produced by numerical integration starting at $T = T_1$. After the integral curves for various γ values have been constructed, T_0 and η_0 may be chosen and the corresponding γ obtained by interpolation. Tables giving ϵ for various values of γ, with $T_1 - T$ as the argument, are presented.

Figure 7 is a plot, for several heating values, ϵ, of flame velocity expressed as $v/(a_0\alpha)^{1/2}$, as a function of temperature gradient expressed as $(\alpha/a_0)^{1/2}(dT/dx)$. For mixtures of high heating value the flame speed is constant over a considerable range of initial temperature gradient, so that for such mixtures there is a most probable flame velocity. For lower heating values, one velocity becomes as probable as another. Emmons suggests that the non-constant flame speed
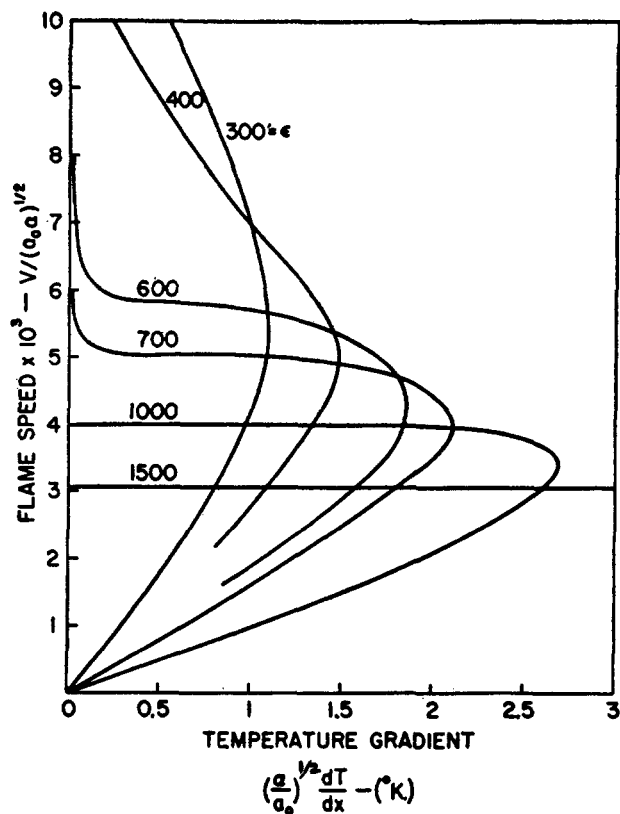
FIG. 7. Flame velocity as a function of temperature gradient for several heating values, as calculated by Emmons, Harr, and Strong (38).

portions of the curve are significant in the explanation of transitions from deflagration to detonation or extinction.

D. The theory of Bechert (11, 12, 13, 14, 15, 16)

n_r, n_p = number of molecules per unit volume of reactant and product, respectively,

M = molecular weight of mixture,

m_r, m_p = mass of molecule of reactant and product, respectively,

a_r = molecular radius of reactant,

E = activation energy,

Z = rate of reaction,

k = Boltzmann's constant, and

q' = heat of gross reaction per molecule of reactant.

The Bechert theory of flame propagation is classed as thermal, since no diffusion terms are included in the continuity and energy equations. Bechert takes diffusion processes into account without introducing terms directly into the

equations by determining E from one measured value of v_0. Detailed accounts of the author's work with respect to reactions between two particles of equal size are given in references 12 and 13. Reference 11 gives a concise review of the most important results. References 14, 15, and 16 discuss the application of the theory to hydrocarbon combustion.

By an approximation method an expression for v_0 in continuous analytical form is obtained as a function of experimental data.

Assumption 1: Pressure is assumed constant.

Assumption 2: Diffusion is neglected, except that it is taken into account in the empirical determination of E from an experimental value of v_0.

Assumption 3: The specific heat at constant pressure is assigned an average constant value $\bar{c}_p$.

Assumption 4: The heat conductivity is assumed to be proportional to the square root of the temperature, so that $\lambda = \lambda_0\sqrt{T}$, where λ_0 is a constant.

Assumption 5: A single overall reaction is assumed.

Assumption 6: A reaction between two similar particles is assumed.

By assumptions 2, 5, and 6 the equation of continuity is written:

$$-\mathrm{d}(n_r v)/\mathrm{d}x = 2Z \tag{4.4.01}$$

By assumption 6 the reaction rate is written:

$$Z = 2(2a_r)^2\, n_r^2 \sqrt{\pi k T/m_r}\; e^{-E/kT} \tag{4.4.02}$$

By assumption 2 and the equation of state, the equation of energy is written

$$\lambda\mathrm{d}T/\mathrm{d}x = \rho_0 v_0 \left[\int_{T_0}^{T} c_v\,\mathrm{d}T + RT/M - RT_0/M_0\right]$$
$$+ q'(n_r v - n_{r0} v_0) + (\lambda\mathrm{d}T/\mathrm{d}x)_0 \tag{4.4.03}$$

Equations 4.4.01, 4.4.02, and 4.4.03 are combined to give

$$-\frac{\mathrm{d}(n_r v)}{\mathrm{d}T} = \frac{4\lambda(2a_r)^2 n_r^2 \sqrt{\dfrac{\pi k T}{m_r}}\; e^{-E/kT}}{\rho_0 v_0\left[\displaystyle\int_{T_0}^{T} c_v\,\mathrm{d}T + \dfrac{RT}{M} - \dfrac{RT_0}{M_0}\right] + q'(n_r v - n_{r0} v_0) + \left(\lambda\dfrac{\mathrm{d}T}{\mathrm{d}x}\right)_0} \tag{4.4.04}$$

The following abbreviations are introduced:

$$\tau = E/kT; \qquad y = \tau - \tau_1; \qquad w = n_r M_0/M D_1; \qquad m^* = n_{p0}/n_{r0}$$

$$\mu = M_1/M_2; \qquad A = 4(2a_r)^2\sqrt{\pi/m_r}\lambda_0 E^2/k^{3/2}q'\tau_0^2$$

$$D_1 = [\rho_0\bar{c}_p E/k\tau_0 + q'n_{r0} - (\lambda\mathrm{d}T/\mathrm{d}x)_0/v_0]/q'\tau_0 \tag{4.4.05}$$

$(\lambda\mathrm{d}T/\mathrm{d}x)_0$ is taken equal to zero. Using this boundary condition, assumptions

1, 3, and 4, and the abbreviations of 4.4.05, the differential equation 4.4.04 is written in final form:

$$\frac{dw}{dy} = \frac{w}{\tau_1 + y} + \frac{A}{v_0^2}\left(\frac{m^* + 1}{m^* + \mu}\right)^2 \cdot e^{-\tau_1}$$

$$\cdot \frac{e^{-y}w^2}{\left[1 - \frac{w(\mu - 1)}{(\tau_1 + y)(m^* + \mu)(1 - \tau_1/\tau_0)}\right]^2 (\tau_1 + y)(w - y)} \quad (4.4.06)$$

The mathematical problem is to determine the value of the parameter v_0 such that two sets of boundary conditions are satisfied: namely, $w = w_0$ for $y = y_0$ and $w = 0$ for $y = 0$.

Bechert plots the direction field of the first-order differential equation 4.4.06 and determines the general properties of the equation. From the direction field is deduced the curve which fits the boundary condition at $w = 0$, $y = 0$ and which, therefore, for the proper value of v_0, also fits the boundary conditions at $w = w_0$, $y = y_0$. Next, as an approximate solution a function is constructed which satisfies the boundary conditions and possesses the properties of the curve sought in good approximation. The substitution of this approximate solution into the differential equation gives an approximate formula for v_0.

Assumption 7: It is assumed that $\tau_0 \gg 1$ and $\tau_0 \gg \tau_1$. (τ_0 is of the order of 30, τ_1 of the order of 5.) The rate of chemical reaction is assumed to be small except near τ_1, i.e., near the hot boundary. Hence the second term at the right of equation 4.4.06 is neglected except at high values of τ.

From a consideration of the plot of the direction field and in view of assumption 7, the following function is chosen as a representation of the desired curve in the w,y plane:

$$w_c = \{y[1 - b(1 + \tau_1)] - b\tau_1\}e^{-y} + b(y + \tau_1) \quad (4.4.07)$$

where $b = 1 - \tau_1/\tau_0$.

The substitution of the approximate solution 4.4.07 into equation 4.4.06 gives a value of the parameter v_0. Different values of v_0 are found, depending upon the choice of the point where the approximate solution is made to satisfy exactly the differential equation. If the approximate solution is a good approximation, the different values will be nearly equal. The following expression for the flame velocity is given:

$$v_0 = \frac{8a_r(\pi/m_r)^{1/4}\sqrt{\lambda_0}\,E}{k^{3/4}\sqrt{q'}} \cdot \frac{m^* + 1}{m^* + \mu} \cdot \frac{e^{-\tau_1/2}}{\tau_0\tau_1\sqrt{1 - \tau_1/\tau_0}} \quad (4.4.08)$$

Equation 4.4.08 is compared with the experimental values for the velocity of the ozone flame as given by Lewis and von Elbe (75). E and a_r are determined from two experimental values of v_0. Table 2 shows selected experimental values for v_0, together with values calculated by Bechert and by Lewis and von Elbe. The values enclosed in parentheses are those used for the calculation of E and a_r.

The theory is applied to the combustion of compounds containing carbon, hydrogen, and oxygen (14, 16). It is assumed that in the region of an excess of air the entire fuel is burned and that in the region of an excess of fuel the entire quantity of oxygen is consumed. Furthermore, it is assumed that reaction occurs upon collision of a fuel molecule and an oxygen molecule. Upon these assumptions an expression for v_0 is obtained by a procedure similar to that leading to equation 4.4.08. The order of magnitude of the flame velocity and its qualitative dependence upon mixture composition are given correctly. No systematic comparison of theoretical and experimental flame velocities is given.

TABLE 2

Comparison of v_0 for ozone–oxygen mixtures measured by Lewis and von Elbe (75) with values calculated by Bechert (11, 12, 13) and by Lewis and von Elbe (76)

m^*	T_0	v_0 (OBSERVED)	v_0		v_0	
			Calculated (Bechert)	Error	Calculated (Lewis and von Elbe)	Error
	°K.	cm./sec.	cm./sec.	per cent	cm./sec.	per cent
3.054	300	55.0	71.7	30	253	360
	361	100.0	108	8		
	427	158	(158)		451	185
1.497	301	141	238	69		
	441	435	467	7		
1.016	302	160	369	130	333	108
	411	615	609	−1		
	468	747	(747)		664	−11.1

VI. DIFFUSION THEORIES

A. *The theory of Tanford and Pease (104, 105, 106, 107)*

n_i = concentration of ith component,

n_r = concentration of combustible,

$A'n_i$ = rate of reaction of ith component,

q_i = mole fraction of ith component,

q_p = mole fraction of potential product,

p_i = equilibrium partial pressure at flame front of ith component,

ϵ = degree of completeness of the chemical reaction, varying from 0 in the unburned gas to 1 in the burned gas,

Q = heat of reaction per gram of unburned gas,

E = energy of activation,

k_i = rate constant appropriate to the ith reaction,

L = molecules per unit volume at 293°K.,

δ = width of flame zone,

N = Avogadro's number, and

θ_m = T_m/T_0.

Tanford and Pease assume that for certain flame reactions the rate of diffusion of active centers into the unburned gas determines the magnitude of the flame velocity. Their work is in three parts. The first part (106) gives calculations of equilibrium atom and free-radical concentrations in moist carbon monoxide flames. The results indicate that the equilibrium concentration of the hydrogen atoms is an important factor in determining the flame velocity. Tanford (104) presents calculations to establish the relative importance of diffusion and heat conduction in creating the hydrogen atoms in the flame zone. The conclusion is that diffusion is the controlling process. The third paper (107) develops an equation for flame velocity based on this conclusion.

Equilibrium concentrations of OH, H, and O at the equilibrium flame temperatures are calculated for moist mixtures of carbon monoxide, oxygen, and nitrogen, and values for flame velocity given by Jahn (55) are plotted against these concentrations. The v_0-[H] plot gives a smooth curve, suggesting that v_0 is a function of hydrogen-atom concentration, while the v_0-[OH] and v_0-[O] plots give scattered points through which no smooth curve can be drawn. It is therefore proposed that burning occurs because free radicals—and in particular for the carbon monoxide reaction, hydrogen atoms—are continuously supplied to the unburned gas.

Two extreme processes are proposed by which radicals appear throughout the flame zone, and an evaluation of the relative importance of the two mechanisms is made (104). The mechanisms are: (1) local production by thermal dissociation, the concentrations being functions of temperature and hence dependent upon the heat conduction process; (2) supply by diffusion from a single point, that at which the reaction has reached equilibrium. Evaluation is made for two mixtures, one consisting of 60 per cent carbon monoxide (containing 1.35 per cent water), 39.4 per cent oxygen, and 0.6 per cent nitrogen, the other consisting of 40 per cent hydrogen, 24 per cent oxygen, and 36 per cent nitrogen.

[H] as a function of x is evaluated for the first mechanism by setting up an energy equation which upon solution gives T as a function of x. From the $T(x)$ curve the maximum possible values of [H] as a function of x are calculated.

Assumption 1: Pressure is constant.

Assumption 2: λ and c_p are constant.

Assumption 3: The chemical reaction term is expressed in terms of $d\epsilon/dx$, with the result that T is the only dependent variable in the equation. Two limiting functions for $d\epsilon/dx$ are used: (a) all heat is released at the flame front, $x = 0$, the flame front being defined as the point where the combustion has reached equilibrium, so that $d\epsilon/dx$ is zero except at $x = 0$; (b) the chemical reaction proceeds evenly across the zone, so that $d\epsilon/dx$ is a constant. The true curve for $T(x)$ is assumed to lie halfway between the solutions obtained for (a) and (b).

Assumption 4: In order to determine the value of $d\epsilon/dx$ under the conditions of assumption 3(b) it is necessary to assume a thickness of the flame zone, δ. Thicknesses of 0.01 cm. for the carbon monoxide flame and of 0.005 cm. for the hydrogen flame are assumed.

Assumption 5: The local equilibrium concentration of hydrogen atoms due to thermal dissociation is calculated by assuming a maximum value for $[H_2]$ at every point. For the moist carbon monoxide flames this concentration is taken to be the equilibrium concentration due to water dissociation at the flame front. For the hydrogen flames it is assumed that the initial $[H_2]$ remains unchanged up to a distance of 0.001 cm. from the flame front.

The energy equation is written:

$$d^2T/dx^2 + (Mc_p/\lambda)(dT/dx) - (MQ/\lambda)(d\epsilon/dx) = 0 \qquad (5.1.01)$$

The gas is here assumed to move toward $x = 0$ from $x = \infty$.

On the basis of assumptions 3, 4, and 5, equation 5.1.01 is solved and $[H]$ is calculated as a function of x. Next a calculation is given of the concentration of hydrogen atoms, as a function of x, due solely to diffusion from the point of completed reaction.

Assumption 6: All of the combustion zone is assumed to be at a constant mean temperature, $T_m = 0.7T_1$. Therefore, since the gases are assumed to be ideal, $\rho = \rho_m$ and $v = v_m = v_0\theta_m$. This assumption has the further consequence that the expression for rate of chemical reaction contains only concentration terms as variables and is not temperature-dependent. The rate of reaction is written as $dn_i/dt = A'n_1$. A' by this assumption is a constant independent of x.

Assumption 7: The diffusion coefficient has a constant value $D_m = D_0\theta_m^2$, where D_0 is the diffusion coefficient for hydrogen atoms into unburned gas at room temperature.

Assumption 8: In reference 104 the chemical reaction term in the continuity equation is written as $A'n_i$, regardless of the order of the processes involved, in order to make the continuity equation linear. For second-order processes, the rates relative to first-order processes are estimated and are taken into account in the first-order term. In reference 105 a numerical solution is made of a non-linear continuity equation containing terms for first-order and second-order reactions. Results are similar to those obtained from the approximated solution, which is the explicit solution of the linear equation.

Assumption 9: It is assumed that for both hydrogen and carbon monoxide combustions, only two reactions are fast enough to have an effect on the hydrogen-atom concentration. They are

(a) $$H + O_2 + M \rightarrow HO_2 + M, \text{ and}$$

(b) $$H + H + M \rightarrow H_2 + M$$
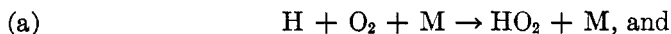
where M represents a third body.

Assumption 10: The mole fraction of oxygen molecules, q_{O_2}, has a constant mean value.

Making use of the appropriate assumptions, the linear continuity equation is written

$$D_m(d^2n_i/dx^2) + v_m(dn_i/dx) + A'n_i = 0 \qquad (5.1.02)$$

Using the boundary conditions $n_i = n_{i1}$ for $x = 0$ and $n_i = 0$ for $x = \infty$, the solution of equation 5.1.02 is

$$n_i = n_{i1} \exp(-B'_i v_m x / D_m) \tag{5.1.03}$$

where

$$B'_i = \tfrac{1}{2}[1 + (1 - 4A'D_m/v_m^2)^{1/2}] \tag{5.1.04}$$

B'_i is evaluated according to the reactions of assumption 9, and the hydrogen-atom concentration as a function of x is computed by means of equation 5.1.03.

This distribution curve is compared with that obtained by assuming the source of hydrogen atoms to be only thermal dissociation. It is found that the partial pressure of hydrogen atoms from thermal dissociation falls to less than 10 per cent of that due to diffusion at a distance of $x \cong 0.004$ cm. and $T \cong 2330°$K. for the carbon monoxide flame, and at $x \cong 0.003$ cm. and $T \cong 1760°$K. for the hydrogen flame. On the basis of these results a theory of flame velocity is developed (107) on the concept that the determining factor is the diffusion of active particles, chiefly hydrogen atoms, from the point at which the combustion has reached equilibrium.

In addition to assumptions 1, 2, 6, 7, and 8, the following assumptions are made for the general theory:

Assumption 11: The rate of formation of the product at any point can be written as a sum of a number of terms, one for each effective radical or atom, each one being of the first order with respect to the radical and to the combustible.

Assumption 12: The only species involved in the process, in addition to the active particles, is the combustible, for which the concentration is represented by n_r. A mean value independent of x is assigned to n_r.

Assumption 13: Chain branching is assumed not to occur.

On the basis of assumptions 11 and 12 the rate of formation of combustion product at any time is written:

$$d(\text{product})/dt = \sum_i k_i n_i n_r \tag{5.1.05}$$

The total rate of formation of product may be computed from the initial composition of the mixture and equated to equation 5.1.05 integrated over the entire range.

$$Lq_p v_0 = \int_0^\infty \sum_i k_i n_i n_r \, dx \tag{5.1.06}$$

Substituting equation 5.1.03 into equation 5.1.06 and integrating gives:

$$Lq_p v_0 = \sum_i k_i n_r n_{i1} D_{mi}/B'_i v_m \tag{5.1.07}$$

Upon replacing n_{i1} with Lp_i/θ_m and making other substitutions called for by assumptions 6 and 7, the expression for v_0 becomes:

$$v_0 = \left(\sum_i k_i n_r p_i D_i/q_p B'_i \right)^{1/2} \tag{5.1.08}$$

Equation 5.1.08 is used to calculate the flame velocities of carbon monoxide mixtures. In accordance with assumption 12, n_r is assigned the mean value $0.7q_{CO}/\theta_m$. q_p is the mole fraction of carbon monoxide or twice the mole fraction of oxygen molecules in the initial mixture, whichever is the smaller. It is assumed that oxygen atoms are not involved in the reaction, so that only hydrogen atoms and OH radicals are considered. Values of the diffusion coefficient are assumed not to vary from mixture to mixture. The flame velocity of carbon monoxide mixtures does not tend to zero with free-radical concentration (106). It is therefore assumed that there is a constant contribution to the flame velocity independent of radical concentration and this constant (17 cm./sec.) is added to equation 5.1.08. Then the form of equation 5.1.08 appropriate for the burning of carbon monoxide is

$$v_0 = 17 + \left\{ \frac{n_r}{q_p} \left(\frac{k_H p_H D_H}{B'_H} + \frac{k_{OH} p_{OH} D_{OH}}{B'_{OH}} \right) \right\}^{1/2} \tag{5.1.09}$$

Flame velocities for the mixtures varied from 25 to 106 cm./sec. The calculated v_0 was never in error by more than 25 per cent and in general the error was much lower.

Equation 5.1.08 was applied to the combustion of hydrogen in a similar way, with results of the same degree of accuracy.

Hoare and Linnett (54) believe that the results of Jahn on the variation in flame velocity with composition of carbon monoxide flames can be accounted for by a thermal theory as adequately as by the theory of diffusion of radicals. They assume that the reaction becomes explosive at an ignition temperature T_i, when the rate of heat release reaches a value H. On the basis of the kinetic results of Hadman, Thompson, and Hinshelwood (47) H is written

$$H = k p_{CO} p_{H_2O} e^{-E/RT_i}/p_{O_2} \tag{5.1.10}$$

The quantity $(T_i - T_0)/(T_1 - T_0)$ is calculated as a function of composition for various values of H/k and E, and the results are plotted against v_0. v_0 increases with $(T_i - T_0)/(T_1 - T_0)$. This correlation is taken as equally good evidence for a thermal theory as is the correlation of v_0 and hydrogen-atom concentration for a diffusion theory.

Dugger (37) compares his experimental curve of flame velocity of propane–air and ethylene–air flames *versus* initial temperature with v_0–T_0 curves calculated from equation 5.1.08. Only p_i, D_i, and L are assumed to be temperature-dependent. Dugger's expression for predicting the relative effect of temperature on flame speed according to the Tanford–Pease theory is

$$v_0 \propto \sqrt{(\Sigma k_i p_i D_{i,r}) T_0^2 T_1^{-1.33}} \tag{5.1.11}$$

where $D_{i,r}$ is the relative diffusion coefficient of the rth radical with respect to other radicals. Figure 4 shows the results for the Tanford–Pease theory as well as for the Zeldovich–Frank-Kamenetsky theory. The effect of initial temperature on the flame velocity appears to be explained equally well by the two theories.

Simon (99) finds the theory to be consistent for thirty-five hydrocarbons the flame velocities of which were reported by Gerstein, Levine, and Wong (44). Equilibrium concentrations of H, O, and OH radicals were calculated at compositions giving maximum flame velocity. The sum of the active particle concentrations each multiplied by the respective relative diffusion coefficient was plotted against v_0, as shown in figure 8. The dotted curve is a similar plot given by Linnett and Hoare (82) for ethylene–oxygen–nitrogen mixtures. Equation 5.1.08 is modified for application to hydrocarbons by including a term r, for the total number of moles of water and carbon dioxide which form per mole of hydro-
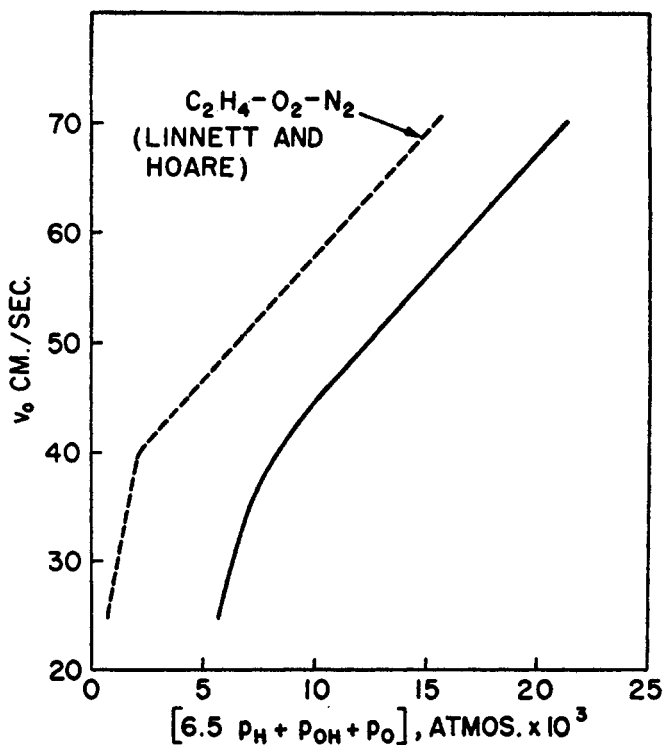

FIG. 8. v_0 versus relative atom and radical concentrations as calculated by Simon (99). The solid line includes points for normal alkanes, branched-chain alkanes, normal alkenes, branched-chain alkenes, alkynes, benzene, and cyclohexane in air.

carbon, and by assuming that H, OH, and O are equally effective as chain carriers. Then equation 5.1.08 becomes:

$$v_0 = \left[\frac{rn_r}{q_p} k \left(\frac{D_H p_H}{B'_H} + \frac{D_O p_O}{B'_O} + \frac{D_{OH} p_{OH}}{B'_{OH}} \right) \right]^{1/2} \tag{5.1.12}$$

From equation 5.1.12 k is found for all hydrocarbons except ethylene to have a value of $1.4 \pm 0.1 \times 10^{11}$ cm.^{3} mole sec. This constancy of k suggests that the rate constants for the oxidation of the hydrocarbons either are the same or are unimportant in the mechanism of flame propagation.

Simon points out that a correlation between flame velocity and flame temperature exists for these hydrocarbons, and that a flame mechanism which depends strongly on flame temperature might give an equally good correlation with flame speed. Therefore a thermal mechanism may not be ruled out.

Badin, Stuart, and Pease (4) calculate ratios for the flame velocities of stoichiometric mixtures of 1,3-butadiene with helium air and with nitrogen air at 1 atm. and 0.5 atm. pressure, assuming that the diffusion of hydrogen atoms is the controlling factor. Table 3 gives the observed and calculated results, as well as results calculated by Manson according to his theory (89).

TABLE 3

Comparison of experimentally determined flame velocity ratios for 1,3-butadiene with nitrogen air and helium air, as measured by Badin, Stuart, and Pease (4), with their calculated ratios and those of Manson (89)

| | RATIO $v_0(He)/v_0(N_2)$ | | | | RATIO $v_0(1 \text{ ATM.})/v_0 (0.5 \text{ ATM.})$ | | |
	Observed	Calculated (Tanford and Pease)	Calculated (Manson)		Observed	Calculated (Tanford and Pease)	Calculated (Manson)
$p = 1$ atm........	3.3	3.2	3.1	Nitrogen air......	0.81	0.88	0.86
$p = 0.5$ atm......	3.4	3.1	3.1	Helium air........	0.80	0.90	0.87

B. The theory of Van Tiggelen (108, 109)

δ = probability of the occurrence of a chain-branching reaction,
β = probability of the occurrence of a chain-breaking reaction,
λ = mean free path,
w = mean velocity of molecules,
d = mean linear displacement of a center,
Z = number of collisions, and
m = molecular weight of active centers.

The theory of flame propagation proposed by Van Tiggelen emphasizes chain branching as the chief reaction mechanism, and an expression for flame velocity is obtained by assuming that the velocity is limited by the rate of chemical reaction rather than by heat conduction.

Assumption 1: For certain slow flames, such as the burning of methane in air, the velocity of the reaction is not great enough to keep up with the heat exchange, so that the rate of reaction determines the flame velocity. Of course, for reactions sufficiently rapid, such as the combustion of hydrogen, heat conductivity may play a preponderant role, since the reaction rate is sufficiently elevated to cause reaction immediately upon attainment, by means of heat conduction, of the necessary reaction temperature.

Assumption 2: The reactions are propagated by chain branching. Van Tiggelen follows Semenov (96) in stating that the active centers which propagate the chains undergo in the course of a molecular collision either (*a*) a branching reaction with probability δ, (*b*) a chain-breaking reaction with probability β, or (*c*) without modification of the total number of active centers, a simple elastic

collision or a reaction of simple propagation of the chain. The condition of burning is established when the probability of branching exceeds that of breaking, i.e., $\delta \geq \beta$. However, that condition, which depends upon the temperature, the concentration of components, and the pressure, is not necessarily sufficient. The condition of burning can be established only if the region is sufficiently extended so that the active centers undergo on the average at least one branching reaction. The region might, for example, be limited by walls on which the centers are destroyed, or by a transition to a cooler region in which the condition $\delta - \beta \geq 0$ does not hold.

Assumption 3: The total pressure and the partial pressures of the reactants are known at the cold boundary and are assumed constant.

Assumption 4: The temperature T_m in the flame zone is assumed constant with a mean value between T_0 and T_1. The complete T–x curve is discontinuous, with a value of T_0 from $x = -\infty$ to $x = 0$ and a discontinuous jump to T_m at $x = 0$. Likewise the velocity v is discontinuous at $x = 0$, jumping from v_0 to v_m, where v_m is the constant mean value at $x > 0$. Assuming ideal gases and no change in the number of molecules upon reaction, the equation of state and the conservation of mass give the following relation:

$$v_0/v_m = \rho_m/\rho_0 = T_0/T_m \qquad (5.2.01)$$

Assumption 5: The molecules are assumed to be equal in size and weight, so that $D = \lambda w/3$.

If λ is the mean free path and d the mean linear displacement which a center can effect in the region where the condition is realized, the number Z of the collisions undergone during the displacement is given by Smoluchowski (100):

$$Z = 3\pi d^2/4\lambda^2 \qquad (5.2.02)$$

In order that maintenance of the critical number of active centers be assured, the following condition, derived from equation 5.2.02 and assumption 2, must be realized:

$$3\pi d^2(\delta - \beta)/4\lambda^2 = 1 \qquad (5.2.03)$$

The displacement d effected by diffusion in a time t is given by the approximate expression:

$$d^2 = 2Dt = 2\lambda wt/3 \qquad (5.2.04)$$

The mean velocity of the molecules, w, is expressed as follows:

$$w = 2\sqrt{2RT_m/\pi m} \qquad (5.2.05)$$

The propagation of the flame is governed by diffusion of the active centers. If the centers have diffused a distance d, the flame shifts a distance fd, essentially equal to the mean value of the projection of d on the perpendicular to the flame front, and the velocity of motion is fd/t. f can be given an approximate value of $2/\pi$.

By combining equations 5.2.03, 5.2.04, and 5.2.05 the velocity of displacement of the flame front in a gas at a temperature T_m becomes

$$v_m = fd/t = 4\sqrt{2RT_m(\delta - \beta)}/\pi\sqrt{3m} \qquad (5.2.06)$$

Since the flame velocity is measured with respect to the fresh gas, combining equations 5.2.01 and 5.2.06 gives the expression for v_0:

$$v_0 = 4T_0\sqrt{2R(\delta - \beta)}/\pi\sqrt{3mT_m} \qquad (5.2.07)$$

For $\delta = \beta$, equation 5.2.07 gives zero for the flame velocity. Thus the expression anticipates the existence of limits of concentration, outside of which the temperature of combustion is not sufficient for the mean temperature T_m to exceed the temperature required for inflammation.

If one neglects β for mixtures the compositions of which are not near the limits, a calculation of v_0 is possible from a knowledge of T_m and δ. The equation is applied in this way to the methane–air flame.

Assumption 6: The branching reaction occurs at the expense of the radical CH_3, and the partner in the branching reaction is O_2. The energy of activation of the reaction is taken to be 40 kcal. The probability δ is written

$$\delta = [O_2] \exp(-40{,}000/RT_m)/p \qquad (5.2.08)$$

so that the expression for flame velocity for this reaction becomes

$$v_0 = 4T_0\sqrt{2R[O_2] \exp(-40{,}000/RT_m)}/\pi\sqrt{3mpT_m} \qquad (5.2.09)$$

From observed values of v_0 for various mixtures of methane and air, the temperature T_m is computed and a curve for T_m *versus* $[O_2]/p$ obtained. The mixtures contained oxygen in excess with respect to methane, and it is assumed that T_m depends uniquely on the percentage of methane and varies linearly with it. This assumption is suggested by the experimental data. Using the temperature–composition curve, flame velocities in mixtures of methane with air having a reduced oxygen content are calculated. The results compare favorably with the experimental values of Coward and Hartwell (28).

C. The theory of Gaydon and Wolfhard (42, 43)

δ_l = thickness of luminous zone between points of maximum rate of change of luminosity,

δ_r = total thickness of luminous region,

d = mean linear displacement of center,

V = diffusion velocity,

n_r = number of reactant molecules per unit volume in the unburned gas,

$\bar{u}$ = mean reaction velocity,

T_i = ignition temperature, and

x_i = point at which ignition occurs.

According to Gaydon and Wolfhard the diffusion of atoms or radicals from the burned gas into the unburned gas is of major importance in the propagation

of hot flames, such as those of hydrocarbons with air or oxygen in mixtures nearly stoichiometric. They point out that heat transfer may also play a role, since the reactions involving atoms or radicals may require an activation energy. Furthermore, while diffusion may be the limiting process in hot premixed flames, other reactions for which heat transfer is important may be rate-determining for other systems.

Assumption 1: The ignition temperature T_i is the point of the beginning of marked exothermic reaction. It is determined by plotting the experimental T–x curve and comparing this curve with the calculated curve for the rise of temperature due solely to heat conduction back from the burned gases. The ignition point x_i is located at the point at which the observed and calculated curves show appreciable divergence. For mixtures of acetylene with air and with oxygen T_i is found to have a value of about 700–800°C.

Assumption 2: The temperature in the flame zone is taken to have a constant average value T_m, equal to $(T_1 + T_i)/2$. There is a discontinuity of $T_m - T_0$ at $x = x_i$.

Assumption 3: The velocity of the gases in the flame zone is taken to have a constant value v_m. There is a discontinuity of $v_m - v_0$ at x_i. Assuming ideal gases and no change in the number of molecules in the course of the reaction, the equations of state and conservation of mass give:

$$v_m = v_0 T_m / T_0 \qquad (5.3.01)$$

Assumption 4: The thickness of the luminous reaction zone δ_l, as measured between points of maximum rate of change of luminosity, is determined for several mixtures. The thickness of the total luminous region, δ_r, is somewhat greater than δ_l, so that $\delta_r \cong \tfrac{3}{2}\delta_l$. δ_r is taken to be the thickness of the reaction zone, as suggested by the measurements described under assumption 1, which show that the beginning of the exothermic reaction corresponds fairly well to the point at which the first impression of light is obtained. The time required for the gases to traverse the zone of thickness δ_r is then $t_r = \delta_r/v_m$. Measurements were made for the mixtures (a) $C_2H_2 + 2.5O_2 + 9.4N_2$, (b) $C_2H_2 + 2.5O_2$, (c) $C_2H_2 + 2.5O_2 + 9.4A$, and (d) $C_4H_{10} + 6.5O_2 + 24.5N_2$.

Assumption 5: The diffusion of hydrogen atoms is assumed to be of major importance. D_0 is the value for the diffusion of hydrogen atoms into a mixture of carbon dioxide and water at standard temperature and pressure and D_m, the constant value of the coefficient in the flame zone, is expressed by $D_0(T_m/T_0)^{3/2}$.

Assumption 6: It is assumed that the ignition point x_i is the limit of diffusion of the hydrogen atoms. An atom starting at the hot boundary x_1 of the reaction zone moves toward x_i by diffusion and is driven back by mass flow. Now if the atom has moved by mass flow and diffusion from x_1 to x_i, a distance δ_r, in a time t_r, and at that time has reached its limit of diffusion so that its diffusion velocity is $V_i = v_m$, the total distance traversed by diffusion is $2\delta_r$. This is seen from the following:

The displacement effected by diffusion is given by the approximate relation

$$d^2 = 2Dt \qquad (5.3.02)$$

Differentiation with respect to t gives the diffusion velocity,

$$V = \sqrt{D/2t} \tag{5.3.03}$$

and at the limit point x_i,

$$V_i = \sqrt{D/2t_r} = v_m = \delta_r/t_r \tag{5.3.04}$$

Then

$$D = 2\delta_r^2/t_r \tag{5.3.05}$$

and

$$d = \sqrt{2Dt_r} = 2\delta_r \tag{5.3.06}$$

This hypothesis is supported by experimental facts. The distance travelled by diffusion in a time t_l for the mixtures listed above is calculated by equation 5.3.02. t_l is the time required for the gases to flow a distance δ_l at a velocity v_m. The ratio d/δ_l was formed for each mixture and was found to be nearly equal to 3 in all cases. Allowing for the fact that $\delta_r > \delta_l$, the results support the hypothesis that $d = 2\delta_r$.

Assumption 7: The expression for reaction velocity is a mean value $\bar{u}$ defined by the equation:

$$n_r v_0 = \int_0^{\delta_r} u \, dx = \bar{u}\delta_r \tag{5.3.07}$$

An expression for flame velocity in terms of the diffusion coefficient may now be derived by combining equations 5.3.01, 5.3.04, 5.3.05, and 5.3.07 to give:

$$v_0^2 = D\bar{u}T_i/2n_rT_m \tag{5.3.08}$$

D. The theory of Bartholomé (6, 9, 95)

As outlined in an earlier section, Bartholomé has given a thermal theory for the flame velocity of fuels burning in air. He found, however, that flame temperature plays a lesser role in determining v_0 for the much hotter flames which are the result of fuels burning in oxygen or oxygen-rich air. For the first group v_0 is 30–70 cm./sec. and T_1 is under 2400°K. For the second group the temperature is not so much greater, 2700°K. and above, but the flame velocities are 400–1200 cm./sec., an order of magnitude faster. The final temperatures for the second group are high enough so that the burned gases are markedly dissociated. If the energy content of the fresh gas is increased, say by increasing the oxygen content of the air, the flame velocity shows a marked increase. The flame temperature rises very little, a large part of the added energy having gone into the dissociation of end products. Thus one can logically seek a dependence of v_0 on the dissociation products.

Bartholomé, like Tanford and Pease, finds a marked correlation of flame velocity with hydrogen-atom concentration and little correlation with concentration of oxygen atoms or hydroxyl radicals. His hypothesis as to the reason for the influence of hydrogen atoms differs from that of Tanford and Pease. Figure

9 is a plot of v_0 versus hydrogen-atom concentration in the burned gases for various fuels. Curve I has points for flames of hydrogen with oxygen, oxygen + nitrogen, and chlorine, as well as the oxyacetylene flame. Curve II represents points for the hydrocarbon–oxygen flames with the exception of the acetylene flame. On the basis of these data the author reaches the following conclusions:

(1) The flame velocity, for this class of flames, is strongly dependent on the hydrogen-atom concentration. The atoms diffuse against the stream into the fresh gas, where they initiate or accelerate the chemical reaction. The influence of the atoms is of another order of magnitude than that of temperature in the
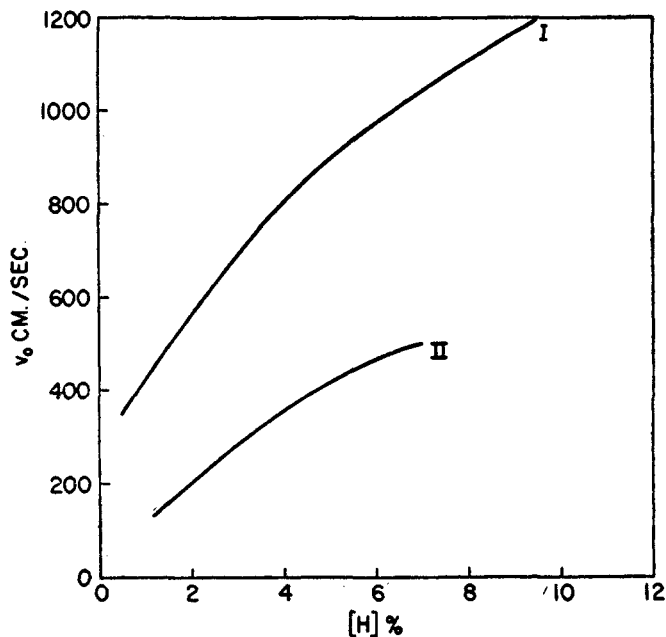

FIG. 9. v_0 versus hydrogen-atom concentration in the burned gases for various combustible mixtures as reported by Bartholomé (9). Curve I includes points for hydrogen–oxygen, acetylene–oxygen, and hydrogen–chlorine mixtures. Curve II includes points for ethene–oxygen, methane–oxygen, and propene–oxygen mixtures.

slower flames. Quantitatively it is found that v_0 is proportional to $[H]^n$, where n is smaller than 1 but larger than the $\frac{1}{2}$ value which Tanford and Pease find in equation 5.1.08.

(2) The influence of the hydrogen atoms is general in nature, similar for all flames and therefore not dependent upon the individual chemical events which may characterize a flame.

(3) The fact that in figure 9 curve II, for the hydrocarbons, lies 50 per cent lower than curve I cannot be understood in terms of the difference of the diffusion coefficient for hydrogen atoms in the different mixtures. This is all the more evident since points for the acetylene flame fall on curve I. The effect is explained

by an assumption of repression of hydrogen atoms in the hydrocarbon flames. Bartholomé suggests that in the hydrocarbon flames reactions of the type $H + CH_4 = H_2 + CH_3$ occur, so that the fast-moving hydrogen atoms are replaced by the more slowly moving alkyl radicals. Since the value for the acetylene flame lies on the curve for the hydrogen flame, it must be assumed either that the radical C—C—H is not formed, or that it decomposes into C_2 and H, so that the concentration of hydrogen atoms is not changed.

Because of the evidence of the general nature of the influence of the hydrogen atoms, Bartholomé suggests that the influence is by virtue of a physical rather than a chemical process. If the atoms recombine after diffusion into the fresh gas, they will have carried over from burned to fresh gas their heat of dissociation. This increase of energy transport may explain the order of magnitude of the difference in flame velocity between thermal and diffusion flames.

The fact that the maximum velocity for flames lies not at stoichiometric quantities of the components, but at fuel excess, is explained by a calculation of hydrogen-atom concentration at various compositions. As the concentration of oxygen decreases, the hydrogen-atom concentration rises with increasing fuel excess. Ultimately the effect of the decreasing temperature, which decreases dissociation, dominates, and [H] again decreases. It is found that at the maximum of the flame velocity, [H] also is at a maximum.

E. The theory of Manson (86, 87, 88, 89)

$\mu = \rho_1/\rho_0$, and

n = number of moles per unit volume.

In contrast to other theories, Manson does not assume that the pressure through the zone is constant. The flame velocity is calculated by obtaining an expression for the pressure and substituting it into the equation

$$v_0 = [\rho_1(p_0 - p_1)/\rho_0(\rho_0 - \rho_1)]^{1/2} \qquad (5.5.01)$$

which is a rearrangement of equation 2.04. The pressure drop is calculated by considering that it arises from the movement of high-energy atoms or radicals, particularly hydrogen atoms, from the reaction zone into the fresh gas.

Assumption 1: Hydrogen atoms are formed in the reaction zone, and they move toward the cold and hot boundaries with a velocity governed by the temperature in the reaction zone.

Assumption 2: The number of atoms crossing per unit area per unit time is the same at the two boundaries, and they move with the same velocity in each direction. Therefore the concentration of the hydrogen atoms is taken to be the same near the hot and the cold boundaries.

Assumption 3: The concentration of hydrogen atoms at the hot boundary is given by the equilibrium partial pressure of the atoms in the burned gases. Then, for ideal gases the partial pressure of the atoms at the cold boundary becomes

$$(p_H)_0 = (p_H)_1 T_0/T_1 \qquad (5.5.02)$$

Assumption 4: The hydrogen atoms in the fresh gas are assumed to undergo recombination according to the equation $2H = H_2 + $ heat. Then the partial pressure in the fresh gas due to the movement of hydrogen atoms from the reaction zone is

$$(p_{H_2})_0 = \tfrac{1}{2}(p_H)_1 T_0/T_1 \tag{5.5.03}$$

Assumption 5: It is assumed that the pressure in region 0 surpasses that in region 1 by the partial pressure of the hydrogen molecules as given by equation 5.5.03, that is,

$$\Delta p = p_0 - p_1 = (p_{H_2})_0 = \tfrac{1}{2}(p_H)_1 T_0/T_1 \tag{5.5.04}$$

TABLE 4

Comparison of experimentally determined flame velocities for various mixtures with the velocities calculated according to the theory of Manson (87, 88)

Mixture................	$H_2 + \tfrac{1}{2}O_2$	$C_2H_2 + O_2$	$C_2H_2 + 5/2\ O_2$	$CH_4 + 2O_2 + 8N_2$
v_0, m./sec. $\begin{cases}$ Calculated...	9.3–9.8	5.8–6.4	3.8–5.7	0.9
 Observed	8.68–10.50	3.5–10	5.75	0.35–0.45

TABLE 5

Comparison of experimentally determined flame velocities for stoichiometric mixtures of 1,3-butadiene with nitrogen air and helium air as observed by Badin, Stuart, and Pease (4) with calculated velocities of Manson (89)

MIXTURE WITH	TOTAL PRESSURE	v_0	
		Calculated	Observed
	atm.	*cm./sec.*	*cm./sec.*
N₂.................................	1	79	43
	0.5	92	53
He.................................	1	246	143
	0.5	282	179

Manson uses equations 5.5.01 and 5.5.04 to calculate flame velocities for a number of gaseous mixtures (87, 88). Some representative results are shown in table 4. When more than one figure for the calculated velocity is given, the values represent calculations with different sets of thermodynamic data. More than one value for the observed velocity indicates that the velocity was measured by more than one observer with different results.

Manson has also calculated v_0, at pressures of 1 and 1.5 atm., for mixtures of 1,3-butadiene with nitrogen air and with helium air (89). Table 3 gives his calculated ratios of flame velocities compared with the calculated and experimental results of Badin, Stuart, and Pease (108). Table 5 shows velocities calculated by Manson compared with experimental results.

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