

Flame Theory and Combustion Technology

FRANK E. MARBLE*

California Institute of Technology

SUMMARY

The study of combustion processes is in a sufficiently early stage so that there is no strong connection between combustion theory and the technology of combustion chamber development. To clarify such a connection is the principal task of workers engaged in establishing combustion as an engineering science.

The equations of aerothermochemistry are reviewed for the case in which temperature and composition gradients are small. Solutions have been obtained in very few cases and under very restrictive circumstances; most detailed considerations are restricted to the plane laminar flame front. The current situation in the theory of plane laminar flames is discussed. The few extensions that have been made to two-dimensional problems are then described. Several directions of work which would assist in establishing theoretical results approaching technological requirements appear possible.

INTRODUCTION

BEFORE THE STUDY of combustion processes can assume its position as a branch of engineering science, it is necessary to clarify the relationships between the aerothermodynamic and chemical-kinetic fundamentals underlying combustion and the complex processes that take place in combustion chambers. According to the spirit of engineering science, it need not be expected that the performance of combustors shall be predicted from fundamentals but, rather, that the thread connecting fundamental processes on the one hand with combustion technology on the other shall be thoroughly sound. Only then may valid approximations be made, appropriate experimental results introduced, and proper similarity criteria developed.

At the moment, this ideal seems to be a long way from realization. The instances where a realistic combustion process may be deduced from first principles are singular indeed. Furthermore, the fundamental information is not always available. Chemical kinetics is still unable to cope with many complex reactions of technological interest; fluid dynamics does not yet present a picture of the turbulence mechanism adequate enough to infer its influence on combustion processes; and basic experimental difficulties have rendered progress slow in obtaining reliable detailed information on combustion systems. On the one hand, there exists considerable information concerning the performance of combustion chambers for jet propulsion units; on the other hand, there has been considerable scientific study into the description of combustion details, particularly that of the laminar flame in combustible gaseous mixtures through application of chemical and thermodynamic fundamentals. But at this time there exists no clear

connection between the two. This state is one through which most fields of engineering science have passed at one time or another during their development. Consequently, the present circumstances should not cast shadows on future possibilities. Aeronautical engineers are still aware of the period when the theory of ideal fluid motion appeared as a monstrosity having little bearing on the observed phenomena.

Under these circumstances, it is to be expected that Dr. von Kármán would, during recent years, devote a portion of his time to the clarification of this field of engineering. His interest is a natural outgrowth of his early and extensive work in the jet propulsion sciences. The impact of Dr. von Kármán's efforts in this field has been twofold. First, he has contributed his own deep insight and clear thought to formulation of key problems in the bridge between fundamentals and practice. Second, he has attracted the enthusiastic participation of workers disciplined in aerothermodynamics to problems formerly of interest principally to physical chemists. In assuring this cooperation between practitioners of the individual sciences and instructing them by example of the directions in which to work, it seems probable that Dr. von Kármán is at present accomplishing the essential step in developing aerothermochemistry into a mature engineering science.

The following paper describes briefly some of the contributions made by Dr. von Kármán and his collaborators and attempts to show how they fit into the present state of combustion theory. The author is indebted to his colleague, Prof. S. S. Penner, for advice concerning the contents of this review. In particular, the author acknowledges his deep gratitude to Dr. Hsue-shen Tsien from whose conversations many ideas have been drawn. Without the benefit of this material, the author's interpretation of Dr. von Kármán's current efforts would be far more faulty than it is.

AEROTHERMODYNAMIC AND CHEMICAL FUNDAMENTALS

Combustion processes are described by the motion of nonuniform gaseous mixtures in which chemical reaction produces concentration gradients and, consequently, diffusion of chemical species. Following the methods of Chapman and Cowling¹ or of Hirschfelder, Bird, and Curtiss,² appropriate mean values for the velocity, density, temperature, etc., of the gas mixture may be defined so that a gross continuity equation for the gas mixture may be written in the usual fashion

$$(\partial p / \partial t) + \operatorname{div}(\rho V) = 0 \quad (1)$$

Likewise, in the absence of external forces, the Navier-

* Associate Professor of Jet Propulsion and Mechanical Engineering, Daniel and Florence Guggenheim Jet Propulsion Center.

Stokes equations of motion assume their familiar form

$$\rho(\partial V/\partial t) + (\rho V \cdot \nabla) V = -\text{grad } p + \text{div } \tau \quad (2)$$

With the exception that τ is here the stress tensor for the nonuniform gas mixture; hence it includes contributions which arise from the fact that velocities of individual gaseous components differ from the mean velocity because of differential diffusion rates.

In dealing with the principle of energy conservation, it is convenient to introduce the concept of the total gas enthalpy, defined as the sum of the usual thermodynamic enthalpy $\int_{T_0}^T C_p dT$ and the enthalpy $h^{(0)}$ required to form the chemical species from its constituents at a fixed temperature T_0 . Then, for a given chemical species, the total enthalpy h_i may be written

$$h_i = \int_{T_0}^T c_{p,i} dT + h_i^{(0)} \quad (3)$$

while the enthalpy for a gas mixture having a fraction Y_i of its weight contributed by the i th chemical species is

$$h = \sum Y_i h_i = \sum Y_i \left\{ \int_{T_0}^T C_{p,i} dT + h_i^{(0)} \right\} \quad (4)$$

the sum being taken over all chemical species. Now in a process involving an exothermic chemical reaction, the heat evolved arises from molecular binding energy released during the chemical rearrangement, and, clearly, this appears as a change in energy of formation between initial and final chemical species. Consequently, the heat associated with an exothermic reaction is explicit in this definition of the enthalpy. The energy conservation relation appears then as

$$\rho \frac{\partial}{\partial t} \left(h + \frac{|V|^2}{2} \right) + (\rho V \cdot \nabla) \left(h + \frac{|V|^2}{2} \right) + \nabla \cdot \sum \rho Y_i h_i V_{a,i} - \frac{\partial p}{\partial t} = \text{div } (\lambda \text{ grad } T) + \Phi \quad (5)$$

Aside from the definition of the enthalpy h , the only unusual term appearing is the divergence of $\sum (\rho Y_i V_{a,i}) h_i$. The mass transport of the i th species due to its diffusion velocity $V_{a,i}$ is just $\rho Y_i V_{a,i}$ and, consequently, the enthalpy transport is $(\rho Y_i V_{a,i}) h_i$ and, consequently, the enthalpy transport is $(\rho Y_i V_{a,i}) h_i$. The total enthalpy transport due to diffusion is then simply the sum of the individual transports $\sum (\rho Y_i V_{a,i}) h_i$. The quantity Φ is the viscous dissipation given in terms of velocity gradients and viscosity coefficients. Actually, this energy equation is correct for only terms linear in the diffusion velocities, and this restriction has been considered by von Kármán³ whose results are quoted by Penner.⁴ It appears that these higher order terms have not been deduced directly from the Boltzmann equation.

The gross continuity equation is not adequate to describe the conservation of each chemical species. For individual species, the motion differs from the mean motion by the local diffusion velocity $V_{a,i}$, and the spe-

cies is manufactured locally at the rate w_i . Then clearly

$$(\partial/\partial t)(\rho Y_i) + \text{div}[\rho Y_i(V + V_{a,i})] = w_i \quad (6)$$

and in virtue of the gross continuity relation of Eq. (1)

$$\rho \left(\frac{\partial Y_i}{\partial t} + V \cdot \text{grad } Y_i \right) + \text{div}(\rho Y_i V_{a,i}) = w_i \quad (7)$$

The diffusion velocity V_i arises from gradients in concentration, pressure, and temperature. In most combustion problems, the variations in pressure are sufficiently small so that this effect may be neglected. The diffusion caused by temperature gradients or thermal diffusion depends upon the existence of large temperature gradients and large differences of molecular weight between the interdiffusing species. A very interesting physical description of thermal diffusion is given by Jost.⁵ Usually, but not invariably, this effect may be neglected in combustion problems and will be discounted in the following considerations. Then it is not difficult to show that, to the first-order perturbation of the Boltzmann distribution, the diffusion velocities of the i th and j th species are related as

$$\sum_j \frac{Y_i Y_j}{M_i M_j} \left(\frac{V_{a,j} - V_{a,i}}{D_{ij}} + \frac{1}{Y_i} \text{grad } Y_i - \frac{1}{Y_j} \text{grad } Y_j \right) = 0 \quad (8)$$

where D_{ij} is the binary diffusion coefficient between the i th and j th species, and M_i, M_j are their corresponding molecular weights. In addition, it is clear that the momenta associated with the diffusion velocities must sum to zero, and hence

$$\sum Y_i V_{a,i} = 0 \quad (9)$$

The rates of production w_i of the various chemical species are governed by the laws of chemical kinetics. The gross chemical reaction is described by the numbers ν_i of initial atoms or molecules that react to produce ν_i' of the product molecules. If a chemical species is denoted by the symbol C_i , and all species entering into either the reactants or products are ordered $C_1 \dots C_i \dots C_N$, then the mass balance of atoms is written

$$\sum \nu_i C_i \rightarrow \sum \nu_i' C_i \quad (10)$$

This is known as the stoichiometric relation; ν_i and ν_i' are the stoichiometric coefficients. Relations of this sort are usually inadequate to describe the detailed course of a reaction because the atoms or molecules of the left-hand side do not produce the final products through elementary collisions. Rather, they produce intermediate products which, in turn, react in a complex manner to produce the final products. Since the rates of reaction are related to the probability of "successful" molecular collisions, the entire set of elementary reactions must be known as

$$\sum \nu_i^{(k)} C_i \rightarrow \sum \nu_i^{(k)'} C_i \quad (11)$$

The overall result of Eq. (11) is the gross stoichiometric relation given by Eq. (10).

Associated with each elementary step is a rate at which it is carried out. For a given system, the probability of a successful collision depends upon (a) the fraction of molecules having sufficient energy—i.e., temperature—to engage in a successful process, and (b) the concentration of reacting species. The rate of a simple reaction may be expressed according to the law of mass action which states that the rate is proportional to the concentrations of reacting species. Thus, if the stoichiometric balance contains a species C_i, ν_i times, the reaction rate contains the concentration $[C_i]$ as $[C_i] \cdot [C_i] \cdot [C_i] \dots \equiv [C_i]^{\nu_i}$. Consequently, the reaction rate may be written for the k th equation of type (11)

$$r^{(k)} \prod_i [C_i]^{\nu_i^{(k)}} \quad (12)$$

where $r^{(k)}$ is the specific reaction rate constant giving the probability for success of a given molecular encounter. Early in the study of chemical reaction rates, Svante Arrhenius⁶ indicated that the specific reaction rate could be written

$$r = BT^\alpha e^{-E/RT} \quad (13)$$

where the activation energy E , the exponent α , and the frequency factor B depend upon the details of the particular reaction.

These basic processes, recently reviewed and clarified by von Kármán,⁷ describe the details of ordinary aerothermochemical processes. The relations hold under the general assumptions that the Maxwell-Boltzmann distribution is not severely disturbed by the processes and that the changes of state encountered are sufficiently slow that equipartition of energy among all internal degrees of freedom of the molecule is satisfied at all times.

THE LAMINAR FLAME

One of the simplest problems arising from the complex aerothermochemical system described in the previous section is the plane flame front in a uniform parallel flow of a laminar gas stream. Consider the gas flowing in the direction of positive x axis; it is desired to calculate the gas speed required to produce a stationary reaction zone normal to the direction of flow and to determine some details of the reaction zone. This problem has been considered a classical one since the pioneering investigations of Mallard and Le Chatelier,⁸ an excellent survey of the early theoretical attack on the problem has been given by Evans.⁹ For this one-dimensional steady process, the gross continuity condition, Eq. (1), reduces simply to $\rho u = m = \text{constant}$. The momentum equations reduce to a single one that relates the pressure gradient in the direction of flow to the stream velocity and velocity gradient. It may be shown, a posteriori, that the normal velocities of flames in laminar gas mixtures are so low that the resulting pressure variations are negligible. Hence, the momentum equation need not enter in the analysis.

The fact that the flame propagation velocity is low also introduces simplifications into the energy conserva-

tion relation. In the first place, the work done against the infinitesimal pressure gradients may be neglected; in the second place, the dissipation, equal to $(4/3)\mu \times (\partial u/\partial x)^2$, may be dismissed as unimportant in comparison with heat transferred by conduction. Then it is clear, from this simplified energy relation, continuity equations for individual species, and knowledge of the chemical-kinetic processes, that the details of the reaction zone may be expressed as distributions of temperature and chemical species. Boundary conditions are easily established on the problem since initial temperature and composition is given, and final temperature and composition may be determined from chemical equilibrium calculations. Furthermore, no heat or chemical species may be conducted or diffused from the field at points far upstream and downstream of the flame zone. Consequently, it is required that

$$\left. \begin{aligned} T &= T_0; & (dT/dx) &= 0 \\ Y_i &= Y_{i,0}; & (dY_i/dx) &= 0 \end{aligned} \right\} \quad \text{at } x = -\infty$$

$$\left. \begin{aligned} T &= T_f; & (dT/dx) &= 0 \\ Y_i &= Y_{i,f}; & (dY_i/dx) &= 0 \end{aligned} \right\} \quad \text{at } x = \infty$$

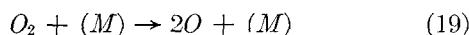
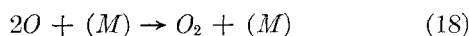
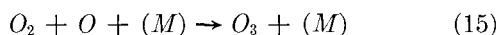
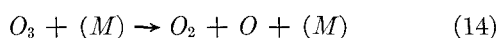
A certain difficulty is immediately apparent. If the initial reactable mixture exists at a temperature T_0 , then, according to the specific reaction rate of Arrhenius [Eq. (13)] the mixture will be reacting at a finite rate. Unless the initial gas temperature has the unlikely value of absolute zero, the spatial variations of composition and the consequent heat release make it impossible to satisfy the conditions $(dT/dx) = (dY_i/dx) = 0$ far upstream of the flame zone. This essential incompatibility of boundary conditions and chemical-kinetic principles is known as the problem of the "cold boundary." The mathematical implications of this were discussed by Emmons¹⁰ and by Adamson;¹¹ they investigated what must necessarily be prescribed far ahead of the flame to make the problem soluble and indicated that the flame itself was not too sensitive to conditions far upstream. In an effort to reconcile physical reality with mathematical accuracy, Hirschfelder and his collaborators¹² introduced an artificial "flame holder" endowed with the properties of absorbing heat and certain chemical species so that the flame could exist and still not alter the prescribed conditions far ahead of the reaction zone.

Later, von Kármán and Millan¹³ discussed the cold boundary difficulty in detail for a reaction zone without diffusion. They first showed that the existence of a fixed flame speed in the mixture was equivalent to assuming an ignition temperature T_i —that is, a temperature below which no chemical reaction takes place. Thus, the most involved devices introduced to force a solution to the cold boundary problem were finally no more penetrating than the ignition temperature concept employed by the pioneers in the field. Of more importance to the solutions of combustion problems was their demonstration that the calculated flame speed was quite insensitive to the value assumed for the ignition temperature over a surprisingly wide range that depends upon the chemical details of the reaction. This confirmed the assumption made by Boys and Corner¹⁴ that a good esti-

mate of the flame speed could be made by an approximation accurate near the hot boundary of the flame and relatively inaccurate at the cold boundary.

The technique for approximate integration of the aerothermochemical relations starting from the hot flame boundary was extensively developed by von Kármán and Millan¹³ for a system described by a single global reaction without diffusion. The extension to more complex systems of chemical kinetics and to flames with diffusion of chemical species has been undertaken by von Kármán and Penner^{15, 16} for two examples where reasonable knowledge of the kinetic details is known. Clearly, as the number of important elementary steps [Eq. (11)] increases, the problem becomes less tractable analytically. For complex systems, the only possibility for reasonable solution lies in simplifications that may arise because some of the elementary reactions are very fast while others are relatively slow.

To illustrate the simplifications that may be made in this way, consider the kinetics of ozone decomposition which were used by von Kármán and Penner¹⁶ in their most detailed example. The decomposition of O_3 proceeds according to the elementary steps



where (M) indicates any massive body that does not take part in the reaction. In Eq. (14), the decomposition of ozone proceeds at a rate $10.56 \times 10^{12} (p/RT) \times \sqrt{T} X_3 \exp(-24140/RT)$, while the reverse reaction, Eq. (15), goes with a rate $0.23 \times 10^{12} (p/RT)^2 \sqrt{T} X_1 X_2$. The chain-breaking reaction given by Eq. (16) proceeds at a rate $7.15 \times 10^{12} (p/RT) \sqrt{T} X_1 X_3 \exp(-6000/RT)$, while its reverse, Eq. (17), has a rate $2.93 \times 10^{12} \times (p/RT) \sqrt{T} X_2^2 \exp(-99210/RT)$. Finally, the association of oxygen atoms, Eq. (18), has a rate $0.482 \times 10^{12} (p/RT)^2 \sqrt{T} X_1^2$, while the dissociation of oxygen molecules follows the law $8.92 \times 10^{12} (p/RT) \sqrt{T} X_2 \times \exp(-117350/RT)$. Here the mole fractions of O , O_2 , and O_3 have been denoted X_1 , X_2 and X_3 , respectively. No effective global reaction is obvious largely because of the significant role played by oxygen atoms, the chain carrier.

After its manufacture, during the decomposition of ozone—according to Eq. (14)—the oxygen atoms enter again into reaction with ozone—according to Eq. (16)—to produce additional molecular oxygen. Through a little analysis, an effective global reaction may be found. For, when the mole fraction X_1 of atomic oxygen is small while the mole fractions X_2 and X_3 of molecular oxygen and ozone, respectively, are not small, the decomposition of ozone—according to Eq. (14)—strongly dominates its inverse given by Eq. (15). Similarly, due

to the low activation energy for reaction of ozone with atomic oxygen—according to Eq. (16)—this reaction predominates over its inverse, Eq. (17), provided only that $X_1 \gg 10^{-19}$. Between the dominant reactions given by Eqs. (14) and (16), atomic oxygen is manufactured and consumed at about the same rates; for, if O accumulated, it would retard the first reaction and accelerate the second until equilibrium was restored. Conversely, the second reaction would be retarded if the supply of atomic oxygen became depleted. Since these two reactions take place much faster than the dissociation of oxygen, Eqs. (18) and (19), at flame temperatures, it is clear that the rates of manufacture and utilization of atomic oxygen are nearly equal over that portion of the flame where X_2 and X_3 are of order unity while $10^{-3} > X_1 \gg 10^{-19}$. Therefore, with good approximation, the two rates are equal.

$$10.56 \times 10^{12} \sqrt{T} X_3 \exp(-24140/RT) \approx 7.15 \times 10^{12} \sqrt{T} X_1 X_2 \exp(-6000/RT)$$

which determines the concentration of oxygen atoms as

$$X_1 \approx (10.56/7.15) \exp(-18140/RT) \quad (20)$$

For temperatures of interest in flame studies, this value of X_1 satisfies the restrictions $10^{-3} > X_1 \gg 10^{-19}$, and, consequently, the approximate balance above is justified. This result means that for every O_3 molecule that decomposes—according to Eq. (14)—an oxygen atom is produced which destroys another O_3 molecule—according to Eq. (16). Hence, the rate of disappearance of ozone is just twice the rate of the reaction given by Eq. (14), and, since this rate involves only the concentration of O_3 , it will suffice as the global reaction treated by von Kármán and Millan.

This analysis, given here in a rather intuitive form, is carried out in detail by von Kármán and Penner.¹⁶ They observe, furthermore, that this condition constitutes simply an example of the so-called steady-state hypotheses—introduced by Bodenstein,¹⁷ and now familiar to all chemists—that the rates of change of some intermediate products may be neglected in comparison with rates of change of primary constituents. The success of its application to the ozone flame has encouraged von Kármán and his collaborators, as well as other investigators,* to explore how far this principle may be used to simplify further examples in the theory of laminar flames.

Toward the hot boundary of the flame, however, the ozone concentrations become so small that the decomposition of ozone—according to Eq. (14)—comes nearly to a balance with its inverse. Then the decomposition of ozone proceeds according to Eq. (16), consuming the available supply of atomic oxygen until both O_3 and O approach their equilibrium concentrations at the adiabatic flame temperature. Thus, the last small portion of the reaction proceeds at roughly half

* Recently M. Gilbert and D. Altman of the Jet Propulsion Laboratory at California Institute of Technology have been investigating its application to the Hydrogen-Bromine flame.

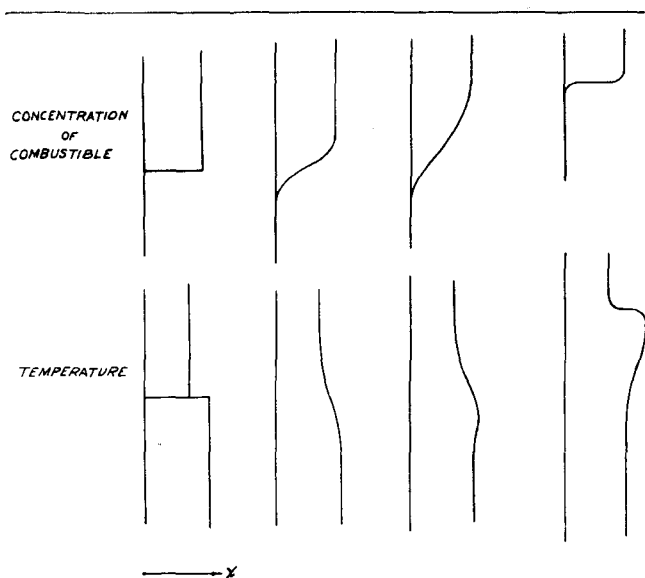


FIG. 1. Development of temperature and concentration profiles during ignition in a laminar mixing zone.

the rate of the larger part. It is not difficult to show that this final portion accounts for less than 1 per cent of the temperature rise and, consequently, is not influential in determining the flame speed. The more important consequence of this change in the kinetic process toward the end of the flame zone is that the reactions taking place at the hot boundary are not representative of those in the bulk of the flame zone. Therefore, an approximation beginning at the hot boundary with the conditions there would be grossly in error for the principal flame zone. Accurate application of the approximate integration techniques of Boys and Corner or of von Kármán and Millan require recognition of the differences between this thin, hot boundary zone and main flame region.

LAMINAR COMBUSTION AND THE BOUNDARY LAYER

Combustion processes of a two- or three-dimensional character may be constructed when the combustion zone is replaced by a discontinuity imparting a fixed temperature rise to the gas and moving into the unburned gas with a fixed normal velocity. Such flow fields have been constructed by Tsien,¹⁸ by Barrere and Mestre,¹⁹ and by Gross and Esche.²⁰ This approximation provides an adequate description when the flame radii of curvature are large in comparison with the flame thickness and when no strong temperature gradients, composition gradients, or other conditions are imposed which upset seriously the local structure of the flame zone. When the combustion front is not uniform over its length, the problem becomes very difficult since the one-dimensional analysis described previously cannot be applied locally. However, with the knowledge gained through analytic solution of the plane flame front and the use of approximation techniques introduced by von Kármán, some progress may be made in discussing some particular cases of the true two-dimensional combustion zone.

Investigation of these problems is facilitated by introduction of the boundary-layer approximation. As a matter of fact, the preponderant number of technically important two-dimensional combustion zones originates in regions where the gradients of important quantities normal to the direction of flow are much larger than those in the direction of flow. Examples of this circumstance occur in the quenching of flames near cold surfaces, the erosive burning of solid propellants, the ignition of a combustible stream or jet by laminar mixing with an adjacent stream of hot gas moving at a different velocity, etc. Employing the boundary-layer approximation and certain of the techniques used by von Kármán, the ignition and combustion in the laminar mixing zone between two streams was investigated by Adamson and the present author.²¹ Let one stream be of combustible mixture at temperature T_1 flowing with velocity U_1 , the other of reaction products at temperature T_2 , $T_1 < T_2 < T_f$, moving with a velocity U_2 . From the start of mixing at $x = 0$, the streams develop velocity, temperature and composition profiles due to simple shear, heat conduction and diffusion—Fig. 1. Farther downstream, sufficient combustible material has been heated so that the chemical reaction produces its own peculiar changes in the temperature and concentration profiles. At first the combustion zone is quite diffuse, but gradually it contracts into a zone resembling the laminar flame. Since the mixing zone grows roughly as \sqrt{x} , the reaction zone will eventually move out of the laminar mixing region and develop into a true plane flame front. If the velocities of the two gas streams are such that the laminar flame makes a very small angle with respect to the x axis, the boundary-layer approximation is applicable throughout the region of flame development.

Under the boundary-layer approximation, only dynamic equilibrium in the direction of flow need be considered, and, because of the low value of laminar combustion velocity, the pressure variations over the field are negligible. Therefore

$$\rho u(\partial u/\partial x) + \rho v(\partial u/\partial y) = (\partial/\partial y)[\mu(\partial u/\partial y)] \quad (21)$$

and the gross continuity equation is

$$[\partial(\rho u)/\partial x] + [\partial(\rho v)/\partial y] = 0 \quad (22)$$

The temperature field is described by the energy equation. If the enthalpy is separated into its thermodynamic and chemical portions, the energy equation may be written

$$\rho u(\partial/\partial x)(C_p T) + \rho v(\partial/\partial y)(C_p T) = (\partial/\partial y)[\lambda(\partial T/\partial y)] - qw \quad (23)$$

where q is heat released through consumption of a unit mass of combustible gas. Assuming a simple global reaction involving only the mass fraction of combustible mixture Y , the "rate of appearance" of combustible matter is

$$w = -(\rho Y/\tau) \exp(-E/RT) \quad (24)$$

where τ , the characteristic time of the reaction, is re-

lated to the frequency factor. By virtue of the gross continuity condition, Eq. (22), only the conservation of combustible species need be considered. If D is the diffusion coefficient of combustible gas into the combustion products, the continuity of the reactable species is given by

$$\rho u(\partial Y/\partial x) + \rho v(\partial Y/\partial y) = (\partial/\partial y)[\rho D(\partial Y/\partial y)] + w \quad (25)$$

The set of relations given by Eqs. (21) through (25), together with limiting conditions of velocity, temperature, and concentration in the two streams, describe completely the process of ignition in the laminar mixing zone between two parallel streams.

The initial development of the combustion process is calculated most easily by expansion in powers of x , the so-called Blasius series. The fact that this approximation breaks down in excess of a certain distance downstream from the start of mixing implies that a characteristic time or distance must be implicit in the problem. Certainly this is related to the characteristic time τ of the reaction; a detailed calculation of time required in this problem before a significant rate of heat release is achieved gives the characteristic time as

$$t = \tau(E/RT)[1 - (T_1/T_2)] \exp(E/RT_2) \quad (26)$$

so that it depends not only upon the time constant τ but very strongly upon the activation energy. The power series breaks down when $(x/u_1 t)$ becomes of the order unity. The solution is extended beyond this region through application of the integral technique introduced by von Kármán into the calculation of boundary-layer flows.

Another problem of great technical significance, flame-quenching near a cool surface, may be investigated with the aid of boundary-layer approximations. Although this problem is of historic interest in combustion theory and experiment, the first effort at its analysis from first principles was undertaken by von Kármán and Millan.²² In addition to Eqs. (21) through (25), there are the boundary conditions: (a) no gas velocity normal to or parallel to the wall at the wall surface, (b) the temperature at the wall surface is constant and equal to T_w , and (c) no net diffusion of species into or away from the wall. This latter condition is equivalent to the assumption that the process is entirely one of thermal quenching—that is, the wall removes heat from the combustion process at a rate depending upon the local temperature gradient, but individual chemical species are reflected from the wall unmodified by the collision; no surface reaction takes place. This restriction on the formulation of this problem should be removed when chemical kineticists provide conclusive information on the processes taking place at the surface.

Von Kármán and Millan consider a normal combustion front moving into a stationary gas bounded by a constant temperature wall; the process is made stationary by allowing the wall to move at the speed of normal flame propagation. The fluid dynamic aspects are

approximated by assuming the velocity normal to the wall to vanish uniformly over the field. They obtained the position of the flame front through an approximate calculation of the temperature field and assumed the flame to lie along the isotherm corresponding to the "ignition temperature" in the sense of their laminar flame calculation. Their results are shown in Fig. 2; the lengths are given in terms of the heat conduction length $(\lambda/\rho_0 u_0 C_p)$ so that the horizontal coordinate is $\xi = (\rho_0 u_0 x C_p/\lambda)$, while the vertical coordinate is $\eta = (\rho_0 u_0 y C_p/\lambda)$, and the temperature field as a ratio of local temperature to the flame temperature is $\vartheta = (T/T_f)$. The vertical isotherm at $\xi = 0$ corresponds to the normal flame in the free stream. The temperature field for $\xi > 1.5$ is adequately approximated by that which would exist if the normal flame extended to the wall.

The geometry of the isotherms joining these two limiting states was approximated by the integral techniques that von Kármán introduced into boundary-layer problems and which was applied successfully in the problem of ignition in a laminar mixing region. It is clear that a certain difficulty occurs in describing this portion of the field. For the normal flame, the gradients are predominantly in the direction of flow; for the region far downstream, the gradients are predominantly normal to the flow direction since this portion of the field is established by heat conduction to the wall. The transition region between the two limiting states does not satisfy the criteria for employing the boundary-layer approximation. Thus, Eq. (23) does not necessarily hold in the transition region. Von Kármán consequently included the thermal conduction $\lambda(\partial T/\partial x)$ in the direction of flow which is omitted in classical boundary-layer considerations. Aeronautical engineers will recognize here a situation reminiscent of that arising in the problem of shock wave-boundary layer interaction. The isotherm $\vartheta = 0.7$, corresponding to the ignition

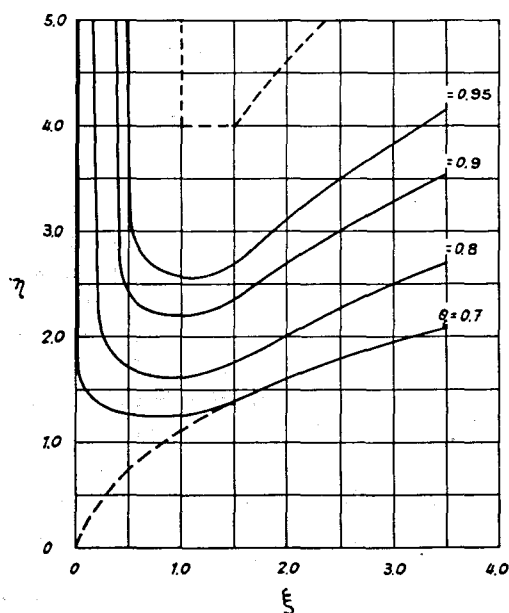


FIG. 2. Isotherms near a laminar flame front quenched by a cool wall.

temperature and hence the approximate position of the flame front, passes much closer to the wall than the usually accepted quenching distance. Numerical conclusions, however, can hardly be drawn since the chemistry employed was arbitrary and somewhat oversimplified, and the measurements cannot be considered precise.

CONCLUSION

Although these investigations that have been described fall far short of the needs of combustion technological practice, they do treat some of the key questions that arise in a wide variety of problems. Only through complete answers to some of these elementary questions will sufficient information be obtained to permit really sound similarity considerations. In a field so involved as combustion, it is likely that similarity rules will always constitute the most widely used results.

REFERENCES

- ¹ Chapman, S., and Cowling, T. G., *The Mathematical Theory of Non-Uniform Gases*, 2nd Ed., Cambridge Univ. Press, 1952.
- ² Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B., *Molecular Theory of Gases and Liquids*; John Wiley, New York, 1954.
- ³ von Kármán, Theodore, Sorbonne Lectures, 1951–52, Sorbonne, Paris.
- ⁴ Penner, S. S., *Chemical Reactions in Flow Systems*, Advisory Group for Aero. R&D, Butterworths Sci. Pub., London, 1955.
- ⁵ Jost, W., *Diffusion in Solids, Liquids, Gases*; Academic Press, New York, 1952.
- ⁶ Arrhenius, Svante, *Über die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Säuren*, Zeitschrift für Physikalische Chemie, Vol. 4, pp. 226–248, 1889.
- ⁷ von Kármán, Theodore, *Fundamental Equations in Aero-thermochemistry*, Proc. of Second AGARD Combustion Colloquium, Liege, Belgium, December, 1955.
- ⁸ Mallard, E., and Le Chatelier, H., *Recherche Experimentelles et Théoriques sur la Combustion des Melanges Gaseuses Explosifs*, Ann. Min., Paris, Series 4, Vol. 8, p. 274, 1883.
- ⁹ Evans, M. W., *Current Theoretical Concepts of Steady-State Flame Propagation*, Chem. Rev., Vol. 51, pp. 363–429, 1952.
- ¹⁰ Emmons, H. W., *Thermal Flame Propagation*, Computation Lab. of Harvard Univ., Contract No. AT(30-1)-497, December, 1949.
- ¹¹ Adamson, Thomas C., Jr., *On the Theory of One-Dimensional Flame Propagation*, J. Am. Rocket Soc., Vol. 22, No. 1, pp. 38–39, January–February, 1952.
- ¹² Hirschfelder, J. O., Curtiss, C. F., and Campbell, D. E., *The Theory of Flame Propagation, IV.*, University of Wisconsin, Rept. No. CM-756, November, 1952.
- ¹³ von Kármán, Theodore, and Millan, Gregorio, *The Thermal Theory of Constant Pressure Deflagration*, Biezeno Anniversary Volume, Delft, 1953.
- ¹⁴ Boys, S. F., and Corner, J., *The Structure of the Reaction Zone in a Flame*, Proc. Roy. Soc. A, Vol. 197, p. 90, 1949.
- ¹⁵ von Kármán, Theodore, and Penner, S. S., *The Thermal Theory of Constant Pressure Deflagration for First-order Global Reactions*, Max Born Commemorative Volume, Univ. of Edinburgh Press, 1953.
- ¹⁶ von Kármán, Theodore, and Penner, S. S., *Fundamental Approach to Laminar Flame Propagation*, Selected Combustion Problems, AGARD, Butterworths Sci. Publ., London, 1954.
- ¹⁷ Bodenstein, Max, *Eine Theorie der Photochemischen Reaktionsgeschwindigkeiten*, Zeitschrift für Physikalische Chemie, Vol. 85, pp. 329–397, 1913.
- ¹⁸ Tsien, H. S., *Influence of Flame Front on the Flow Field*, J. Appl. Mech., ASME, vol. 18, pp. 188–194, 1951.
- ¹⁹ Barrere, M., and Mestre, A., *Stabilisation des Flammes par des Obstacles*, Selected Combustion Problems, AGARD, Butterworth Sci. Pub., London, 1954.
- ²⁰ Gross, Robert A., and Esche, Robin, *Low Speed Combustion Aerodynamics*, J. Am. Rocket Soc., Vol. 24, No. 2, March–April, 1954.
- ²¹ Marble, Frank E., and Adamson, Thomas C., Jr., *Ignition and Combustion in a Laminar Mixing Zone*, Selected Combustion Problems, AGARD, Butterworths Sci. Pub., London, 1954.
- ²² von Kármán, Theodore, and Millan, Gregorio, *Thermal Theory of a Laminar Flame Front near a Cold Wall*, Proc. of the Fourth Symposium (International) on Combustion, pp. 173–177; William and Wilkens Co., 1953.