Flames are gas-phase reactions that can propagate through space and are characterized by strong interactions between convection, molecular transport processes, and chemical reactions. Individual flame processes are well understood and flame theory has been formulated in general, but the study of specific flames is largely experimental. Flame theory provides the model for quantitative interpretation of experimental studies. Structures of several flames have been examined and information derived on the physical processes and chemical kinetics.

FUNDAMENTAL PROCESSES
AND
LAMINAR FLAME STRUCTURE

R. M. Fristrom and A. A. Westenberg

Flames are exothermic gas phase reactions characterized by the ability to propagate through space and obtainable under a wide variety of conditions. Although flames are normally and correctly considered as sources of high temperatures, flame-like reactions occur at temperatures as low as 4°K as, for example, in frozen films of free radicals. Fuel-oxidizer reactions constitute the most common flame systems, but flames can also be obtained from such diverse reactions as those between frozen nitrogen atoms and that of decomposing nitric oxide. Flames have been studied under conditions varying from a thousandth of an atmosphere to several hundred atmospheres. Reaction half-lives can range from from periods of seconds to millimicroseconds.

Flames result from the interaction of the effects of convection, thermal conduction, molecular diffusion, and chemical reaction, proc-esses which are well understood individually. To describe flame systems, therefore, it is possible to write a rigorous set of mathematical relations which are based on the constraints of conservation of energy, matter, and momentum, and incorporate the processes of thermal conductivity, molecular diffusion, and chemical kinetics.

For one-dimensional flames the solution to this set of nonlinear differential equations is related directly to the burning velocity—a parameter used to characterize flames. Figure 1 shows the common method of experimentally determining burning velocities. These equations can be solved in simple cases, but the chemistry is then so unrealistically circumscribed that the results are useful only to the mathematician and physicist. The chemist and chemical engineer must still consider flames from the experimental standpoint even though the flame equations furnish the necessary framework for the quantitative
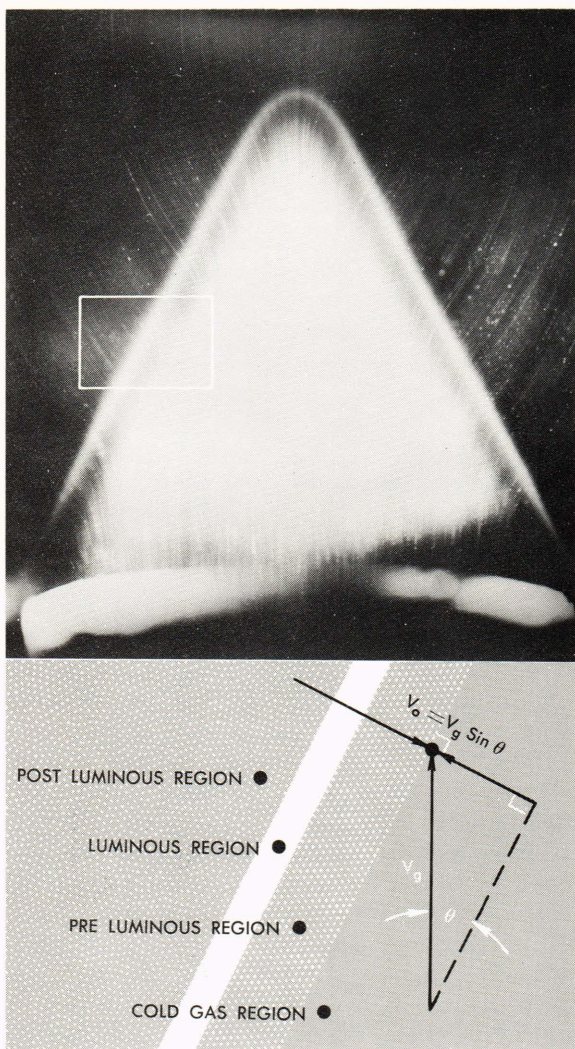
Fig. 1—Burning velocity in a laminar flame. The vector diagram shows the velocity balance used to define burning velocity, with V_o = burning velocity (cm/sec), V_g = approach velocity of the gas in the burner (cm/sec), and θ = angle between the axis and the flame front (half angle of the flame cone.)

flames, the former being a continuum property of the system while the latter is best considered from the molecular standpoint. Flame aerodynamics, considered three-dimensionally, is a complex subject although the principles are straightforward. Flow is governed primarily by considerations of conservation of mass and energy and — for high-velocity flames — of momentum. Flow geometry is usually described in terms of an area parameter, and if this is assumed to be a known variable, the flow is completely specified by the mass continuity equation and a density or temperature profile. Aerodynamics controls gross flame geometry. The flame tends to adjust itself so that there is a balance between the fundamental burning velocity of the system and the component of flow velocity normal to the flame front at any point (Fig. 1). Common flames have velocities which are low compared with the speed of sound and, as a result, the pressure-drops across them are minute, though measurable, and normally neglected. In spite of this, the accelerations of flame gases are large because of the narrowness of the region in which the gas is heated and expanded. In the acetylene torch, for example, the peak gas acceleration exceeds 8000 g.

Table I
TYPICAL FLAME FRONT PARAMETERS

Variable	Functional Dependence	Values		
		Typical	Min.	Max.
Initial temperature	....	300°K	4°K	300°K
Temperature rise	....	1700°K	31°K	4700°K
Final temperature	....	2000°K	35°K	5000°K
Burning velocity	$P^{1/4}$	70 cm/sec	1 cm/sec	10^4 cm/sec
Pressure	....	0.1 atm	10^{-3} atm	10^2 atm
Pressure drop	$P, v_o^{-1/2}$	10^{-5} atm	....	....
Flame thickness	P^{-1}, v_o^{-1}	1 cm	....	....
Duration	P^{-1}, v_o^{-1}	10^{-3} sec	....	....
Maximum logarithmic gradient $1/T \, (dT/dz)$; $1/X \, (dX/dz)$.	P, v_o	70	....	....
Maximum reaction rate	P^2, v_o^2	10^{-2} g-moles/cc/sec	....	....
Maximum heat release rate	P^2, v_o^2	20 cal/cc/sec	....	....

interpretation of combustion systems. Premixed laminar flames are discussed in this paper, but the fundamental processes are the same in all types of flames; thus, in spite of the complications of practical combustion systems, they can usually be related to the simple systems which will be discussed.

Physical Processes

Aerodynamics and transport phenomena are the quantitatively important physical processes in

The other physical processes are considered under the general heading of molecular transport. Of the five known transport processes, only two are important in flames: [1,2] diffusion, which is the transport of matter in a concentration gradient; and thermal conduction, which is the transport of energy in a temperature gradient.

Diffusion has a profound effect upon flame reactions since it provides a mechanism for transporting such reactive species as atoms and free radicals into regions where they are out of equilibrium. The gradients in flame fronts are so steep, as shown in Table I, that a major fraction of the flux is carried by diffusion, as illustrated in Fig. 2.

The effects of diffusion are best visualized by assigning a diffusion velocity to each species in the flame front which is superimposed on the

Fig. 3—Enthalpy fluxes due to thermal conduction and diffusion through the flame zone.

mass average gas velocity. Thus,

$$V_i = (D_i/X_i)\ (dX_i/dz),$$

where V_i is the diffusion velocity (cm/sec), D_i is the diffusion coefficient (cm²/sec), X_i is the concentration (mole fraction), and dX_i/dz is the concentration gradient (mole fraction/cm).

Diffusion coefficients depend on the species involved and upon the temperature. They have been measured for a number of species of interest in flames over a sufficiently wide temperature range to be useful for flame studies.[3] Most of such measurements were made on binary systems, whereas flames generally have many components. However, binary coefficients can be used for many flame analyses because one species is present in excess while the others can be considered as traces in this carrier. In systems where this is not a good approximation, the true multi-component diffusion coefficients can be derived from the binary diffusion coefficients of the system;[1] this, however, is a very laborious computation.

The energy flux due to thermal conduction in flames (as in Fig. 3), is very large, but it is characteristic of such reacting systems that this is almost counterbalanced by the energy flux carried by diffusion. Thermal conductivity is a well-defined parameter at each point in the flame although it has a very complex dependence on composition and temperature. This stems not only from intermolecular forces but also from the contribution of internal molecular energy to heat transfer. These problems are being attacked both theoretically and experimentally at APL.
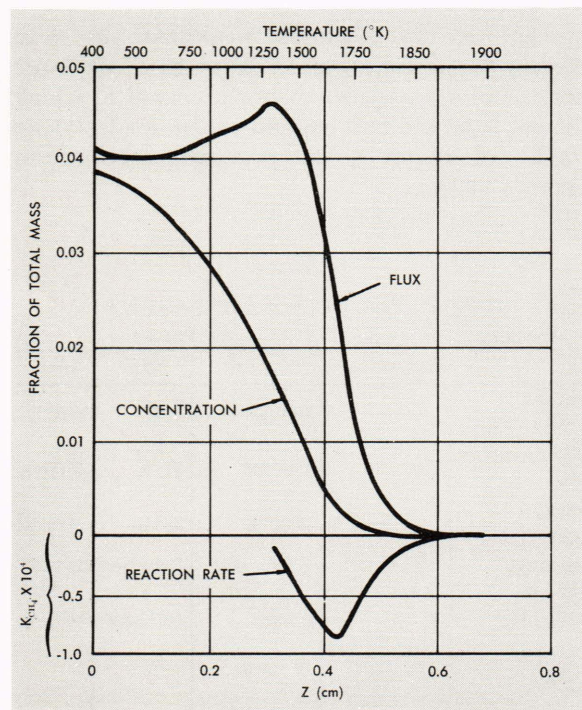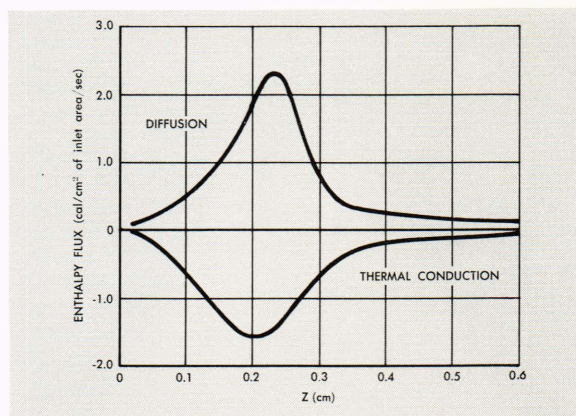

Fig. 2—Profiles of concentration, flux, and rate of reaction for methane in a 0.05-atm 7.8% methane-oxygen flame. The composition variables of concentration and flux are in fractional mass units; rate is in moles/cm²/sec. Concentration is the amount of material per unit volume, and flux is the amount of material passing through a unit area in a unit time.

[1] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, 1954, 756-782.
[2] M. W. Evans, "Current Theoretical Concepts of Steady State Flame Propagation," *Chem. Rev.* 51, 1952, 363-429.
[3] A. A. Westenberg, "Present Status of Information on Transport Properties Applicable to Combustion Research," *Combustion and Flame* 1, 1957, 346-359.

Chemical Processes

The important chemical process in a flame is chemical reaction—the source of energy and the driving force of the system. However, since the equilibrium properties of the burned gases are also often important, mention will first be made of methods for calculating adiabatic flame temperatures, compositions, and heat releases.
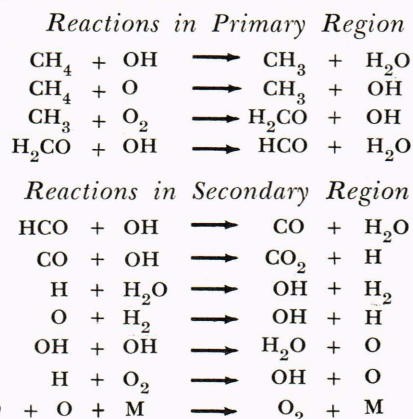
Flames can be considered as adiabatic reactions; so, in principle, it is possible to calculate the final composition and temperatures of fully reacted gases. Such calculations are not meaningful for flame systems which are not adiabatic, which do not go to completion or for which reliable thermodynamic functions are not available. Calculations involving fuel-rich flames and those containing solids are particularly difficult; the information required consists of enthalpies, heat capacities, equilibrium constants, and phase equilibria. There are excellent compilations of thermodynamic functions for most of the species of interest in common flame systems,[4] and these data are among the most precise of physico-chemical information. They are based on equilibrium measurements, calorimetric data, and spectroscopic information.

In the process of chemical reaction the principal differences between flames and homogeneous reaction systems are diffusion effects and the substitution of distance for time as a variable. The diffusion effects are twofold: the concentrations of reactants differ drastically from those of the incoming gas; and reactive species can be transported from later, higher temperature stages of the reaction into the low-temperature initial stages.

Any reaction which liberates heat and has a positive temperature coefficient of reaction rate might, in principle, form a flame system. In practice, however, the rate required to form a reaction zone of convenient laboratory size limits flames to initial reactions of high intrinsic rate. These are primarily bimolecular, usually molecule-radical (or atom) reactions of low-activation energy (Table II). In secondary regions, e.g., see Fig. 4, slower reactions can and do occur, particularly three-body recombination reactions involving radicals.

Because of the extreme rapidity and high temperatures of flame reactions, very little reliable,

[4] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Standards (U.S.) Circ. No. 500, Feb. 1952, 128.

Table II
REACTION KINETIC SCHEME FOR OXYGEN-RICH METHANE-OXYGEN FLAME*

Reactions in Primary Region

$$CH_4 + OH \longrightarrow CH_3 + H_2O$$
$$CH_4 + O \longrightarrow CH_3 + OH$$
$$CH_3 + O_2 \longrightarrow H_2CO + OH$$
$$H_2CO + OH \longrightarrow HCO + H_2O$$

Reactions in Secondary Region

$$HCO + OH \longrightarrow CO + H_2O$$
$$CO + OH \longrightarrow CO_2 + H$$
$$H + H_2O \longrightarrow OH + H_2$$
$$O + H_2 \longrightarrow OH + H$$
$$OH + OH \longrightarrow H_2O + O$$
$$H + O_2 \longrightarrow OH + O$$
$$O + O + M \longrightarrow O_2 + M$$

*As defined from studies shown in Fig. 5.

pertinent, kinetic information is available. Many of the systems of interest have been studied at low temperatures and have shown such low activation energies that their extrapolation to flame temperatures is difficult and often meaningless. In recent years a number of investigators have undertaken the direct study of flame reactions, and much new information is becoming available.

Since even the simplest flames are multicomponent systems involving several reactions, the flame kineticist must immediately face the problem of multiple reactions, both in series and in parallel. Though all conceivable reactions occur to some extent, the problem is to choose the
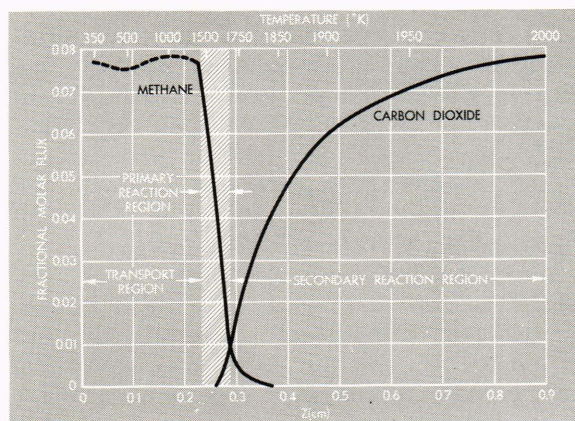

Fig. 4—Profiles of the fluxes of methane and carbon monoxide in the methane flame of Fig. 5, showing the approximate separation of the flame into three regions.

minimum number of reactions which provide a quantitatively satisfactory description of the flame system.

Since the fraction of species disappearing through a particular reaction is proportional to the rate of the reaction, the fastest reaction will dominate. There should be relatively few cases of parallel reactions of comparable importance since this would require that their rates be roughly equal—an unlikely coincidence. Therefore, it can usually be assumed that a flame system can be adequately explained by a simple dominant reaction scheme consisting of a sequence of reactions connecting the initial and final products. Such a scheme for the methane-oxygen flame is illustrated in Fig. 4. In such a sequence, subsequent reactions may be either faster or slower than the previous reaction. If the rate of the following step is rapid compared with the previous reaction, then the intermediate species will be present only as a trace (e.g., formaldehyde in the CH_4 flame) and an adequate representation can be made by considering the over-all reaction, neglecting the fast steps, as is commonly done in reaction kinetics. The second case, that of the subsequent step being slow compared with the initial step, results in a physical separation of the flame into two regions or more. An example of this is the separation of the CO reaction region in the common hydrocarbon flame.

Flame reaction schemes are often considerably simpler than those associated with ignition or cool-flame phenomena and can be used to derive chemical kinetic information.

One-Dimensional Flame Structure

All physically realizable flames are three-dimensional, but it is possible to construct systems in the laboratory which are one-dimensional in the practical sense. This abstraction offers an enormous simplification in the visualization of combustion processes, and such systems have been almost exclusively used for the study of flame structure in the laboratory.

An ideal one-dimensional flame can be considered as a chemical reaction in a flow system. It is completely described by specifying the concentration (in absolute units) of each of the number N of chemical species at every point along the coordinate of propagation z, together with a parameter related to the burning velocity which specifies the mass flow per unit area. In an actual case a profile giving the geometry of the flow pattern is also necessary. This descrip-
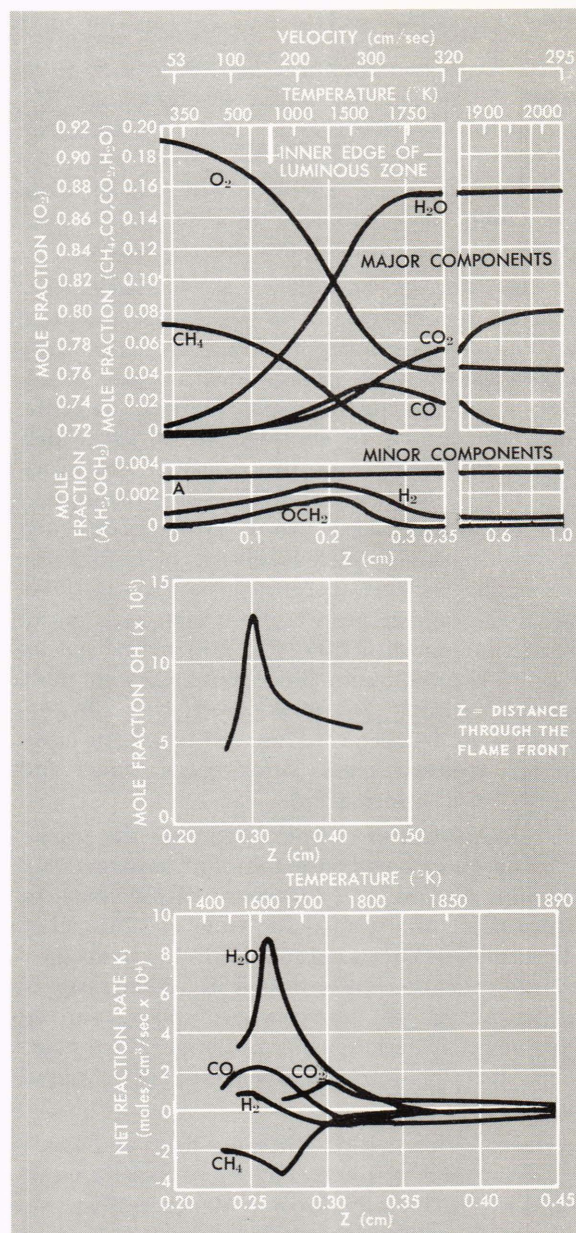

Fig. 5—Characteristic profiles of a premixed flat laminar methane-oxygen flame (7.8% methane; P = 0.1 atm).

tion is best visualized as a family of "profiles," giving the intensive variables as a function of distance through the flame front; this is shown in Fig. 5.

Distance is usually chosen as the independent variable since it is the common experimental one, but it is possible to use any single-valued variable such as time, density, temperature, or one of the compositions. The important point is that a necessary and sufficient set of variables

is given by specifying $N + 1$ of them as functions of a common independent variable. This is analogous to the phase rule used in closed systems. It has been possible to demonstrate that the one-dimensional concept provides a quantitatively adequate model for describing this system.[5]

Several experimental techniques are now available for making flame structure studies, and they have been applied to a number of systems. A typical example is the premixed methane-oxygen flame.[5,6] The characteristic profiles of intensive properties which describe this system are as illustrated. From these experimental data it is possible to derive the fluxes of species and energy and net rates of reactions for the various species.[7]

This flame can be conveniently separated into three spatially distinct regions which are characterized by a few processes, as illustrated in Fig. 4, by considering the reaction path for the oxidation of methane. In the first region no reaction occurs although large temperature and composition changes occur because of diffusion and thermal conduction. In the second region the initial attack of methane occurs (Eq. 1), finally forming carbon monoxide. In the third region this carbon monoxide is oxidized to carbon dioxide (Eq. 2):

$$CO_4 + OH \longrightarrow CH_3 + H_2O \qquad (1)$$
$$CO + OH \longrightarrow CO_2 + H. \qquad (2)$$

This spatial separation is a convenient accident due to the relative rates of the processes involved; however it can be expected to be the normal case. Diffusion tends to mask the effects of reaction, and it is necessary to allow for these effects before even qualitative conclusions can be drawn from flame structure studies.

The energy flux in the flame front is dominated by the transport processes, but the energy flux due to thermal conduction is almost balanced by that due to diffusion. This is a direct result of the dimensionless Lewis number, $\dfrac{\rho C_p D}{\lambda}$, in which ρ is gas density, C_p is heat capacity at constant pressure, D is diffusion coefficient, and λ is thermal conductivity; it is approximately unity for common reacting systems. An interesting consequence of this is that there is a linear relation between temperature rise and "fuel" disappearance. ("Fuel" is defined as a species whose disappearance is directly connected with heat release.)

An important point about the reactions occurring in the methane flame, as shown in Table II, is that they all involve radicals. The initial species, methane and oxygen, do not react with one another except through the agency of these radicals. These reactions are of low-activation energy, with the OH radical being of central importance. In flames, relatively high non-equilibrium radical concentrations exist. For radicals to attain final equilibrium it is necessary to have a three-body recombination reaction which, at normal pressures, is slow compared with bimolecular reactions. These radicals can be transferred, by the agency of diffusion, to low-temperature regions where they are far out of thermal equilibrium. Thus, one might expect that the radical-molecule reaction zone would precede, and be separated from, a radical recombination region.

Many flames can be burned over a wide range of pressures with only a small change in the propagation velocity. This indicates that a flame reaction takes a certain number of collisions to occur, so that if the mean free path is increased, the distance will be scaled to preserve the collision number. For the case of bimolecular reactions, it can be shown that distances in a flame should scale inversely with pressure.[1] Detailed studies have shown that this is a reasonable approximation in some flames.[7,8]

The processes occurring in flame fronts are well understood, and the theory of flames has been formulated in general, although the application to specific flames is primarily an experimental problem since the parameters required are not usually available. However, flame theory provides the model for the quantitative interpretation of experimental flame studies. The structures of several flames have been examined in varying detail, and it appears that the one-dimensional model can quantitatively represent laboratory flames and that reliable information on the physical process and chemical kinetics of flames can be derived. A number of simplifying assumptions used in theoretical flame studies have been verified by such measurements.

[5] R. M. Fristrom, C. Grunfelder, and S. Favin, "Methane-Oxygen Flame Structure I. Characteristic Profiles in a Low Pressure, Laminar, Lean, Premixed Methane-Oxygen Flame," *J. Phys. Chem.* 64, 1960, 1386.

[6] A. A. Westenberg and R. M. Fristrom, "Methane-Oxygen Flame Structure II. Conservation of Matter and Energy in the One-Tenth Atmosphere Flame," *J. Phys. Chem.* 64, 1960, 1393.

[7] A. A. Westenberg and R. M. Fristrom, "Methane-Oxygen Flame Structure IV—Chemical Kinetic Considerations," *J. Phys. Chem.* 65, 1961, 591.

[8] R. M. Fristrom, C. Grunfelder, and S. Favin, "Methane-Oxygen Flame Structure III. Characteristic Profiles and Matter and Energy Conservation in a One-Twentieth Atmosphere Flame," *J. Phys. Chem.* 65, 1961, 587.