II. Combustion Research

Fires are a subdivision within the field of combustion. What distinguishes them from the better understood uses of controlled combustion in engines or furnaces are the wide variations in fuel types, fuel arrangements, ignition sources, and gas flow patterns. Insights into the principles of fire ignition, extinction, and propagation permit the setting of design standards that will minimize fire hazards.

Unwanted fires present complex combustion problems whose elements are chemical kinetics, thermodynamics, aerodynamics, and heat and mass transfer. The research problems can be addressed on many levels. On the most abstract level, combustion can be described in terms of molecular processes: collision, radiation, and energy transfer. On the applied level, combustion studies can be as direct as a fire inspector testing the flammability of a building material with his cigar lighter.

Fires can be divided into three phases: ignition, propagation, and extinction. Ignition is the process by which a system passes from a nonburning to a burning state; propagation is the process by which a developed fire consumes the reactants (fuel and air); and extinction is the process in which a developed fire is reduced to the nonburning state.

An understanding of ignition processes would allow better assessment of fire hazard. The understanding of combustion propagation would allow estimates of times available for escape from fires and the response times required for useful fire fighting, and evaluation of the relative safety of areas in a fire and routes through fires. An understanding of extinction would allow estimation of the forces and equipment required and suggest new methods of fire fighting.

Physical and chemical processes are involved in all of these phases. However physical and aerodynamic processes dominate fire propagation, while chemistry dominates ignition and extinction. Since our interests lie in the chemical area, we have emphasized ignition and extinction in our program.

Specific studies have included ignition and extinction of polymer flames using a new method called the "Moving Substrate Technique." Since most domestic fires are ignited or sustained by either natural or synthetic polymer fuels, this represents an important practical problem. A second area has been flame inhibition. Inhibitors are chemicals which reduce the propagation rates of flames and are used in a number of commercial fire extinguishers. The understanding of the chemistry of these processes could provide important clues leading to new extinguishing agents. A third area has been the determination of rates at high temperature of some elementary inhibition reactions. This is useful because fire models use kinetic information which often needs to be extrapolated from low-temperature studies in the absence of high-temperature data. A new technique, the "Point-Source Method," has been developed which allows the study of rates at flame temperatures from which the reliability of extrapolated chemical kinetic information can be assessed. The fourth area involves developing models of simplified flame theories which can be used to predict the chemical effect of inhibitors.

The Moving Substrate Technique—A New Method for Studying Ablation, Ignition, and Extinction of Polymer Flames*

One of the major interests of the fire program has been the understanding of polymer behavior during ignition and extinction. The complexity of solid fuel—gaseous oxidizer systems and the transient nature of ignition and extinction has made quantitative studies difficult heretofore. In the past, systems were commonly studied transiently or critical time-to-ignition parameters were determined, but the short times available for measurements have presented a difficult measurement problem.

A new method called the Moving Substrate Technique (MST) has been developed at APL for studying these transients. The basic concept is to exchange transient time dependence for steady-state position dependence. This is accomplished by moving the material to be ignited relative to a stationary, well-characterized ignition source. The polymer in the form of a wire is drawn through an ignition source such as a flame of known tem-

perature and composition. Positions across the flame in the direction of wire travel correspond to increasing residence times in the ignition medium. Time at a particular point in the flame can be controlled by changing wire velocity. This provides flexible control of ignition and extinction phenomena.

Two classes of behavior are observed: stable and metastable. With stabilized phenomena, there is a one-to-one correspondence between position along the wire coordinate and residence time. Precise measurements are possible because the time available for experiment is primarily limited by convenience. Precision varies with the square root of measuring time. Metastable behavior occurs where a given residence time corresponds to more than one state of the system. This is the result of positive feedback which occurs in many physical systems. In polymer combustion, the feedback results from the coupling between polymer volatilization and the heat released by its combustion. If volatilized polymer enters a suitable oxidizing atmosphere, heat is released. This heat raises the gas temperature, which in turn increases the heat transferred to the polymer surface, resulting in an increased volatilization rate. This process bootstraps itself until a new balance is reached in a stabilized polymer flame. The MST is useful even with such bistable phenomena because it allows definition of the hysteresis loops.

The use of moving systems stabilized in fixed laboratory coordinates to study steady-state combustion is as old as the bunsen burner and the automatically stoked furnace. The concept has also been used in wood cribs, polymers, and fabrics. It appears to be new, however, in the study of ignition and extinction.

Apparatus—Flame-piloted ignition was studied, since flames provide both high temperatures and nonthermal excesses of reactive species such as atoms and radicals. The apparatus can also be adapted to other ignition sources such as hot gas jets, radiant fluxes, or electrical arcs. Polymer ignition requires: (a) volatilization, (b) a second reactant, (c) mixing of volatilized fuel and oxidizer, and (d) high temperature and radical concentrations to initiate combustion. Flames can supply these requirements. Ignition can occur in the wake of a wire if sufficient oxygen is available or at the boundary with an oxidizing atmosphere.
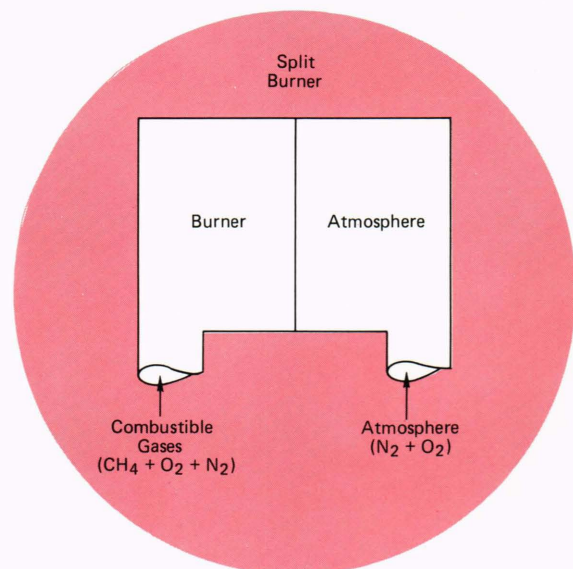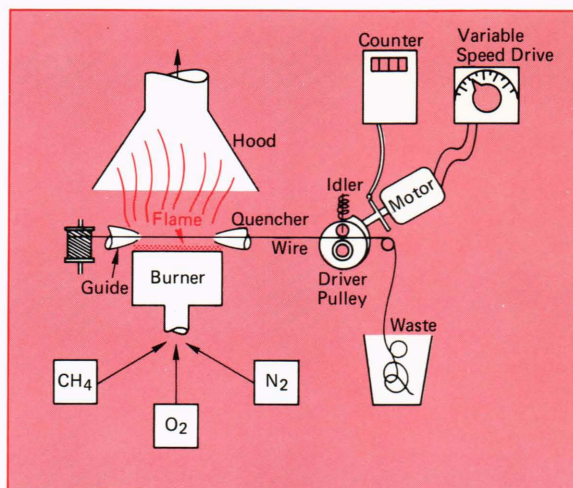
Fig. 14—Schematic diagram of apparatus for the measurement of ignition characteristics of polymer-coated wires.
(A) Premixed flat circular flame as ignition source.
(B) Premixed flat semicircular flame with adjoining atmosphere with adjustable oxygen concentration.

Two versions of our apparatus are used (Fig. 14): an isolated burner (14A) or a burner with an adjacent oxygen-containing atmosphere (14B). The composition and temperature of both the flame and the adjacent atmosphere are controllable and adjustable. The substrate to be ignited is in the form of a polymer-coated wire which is pulled across the flame by a mechanism similar to one used in tape decks. A variable speed motor controls velocity which is measured with an optical counter mounted on the drive shaft. With a precision drive and accurate control of composi-
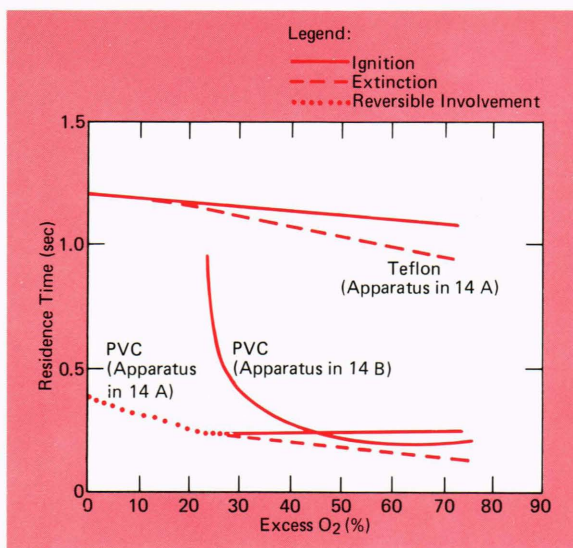
Fig. 15—Ignition and extinction transitions of three commercial polymer-covered wires. Residence time is shown as a function of composition of the ignition gases.

tion of the flame and atmosphere, exposed length of polymer, etc., the transition times are reproducible within a few parts in a thousand.

Data—Characteristic transition times (Fig. 15) determined with the two experimental arrangements are discussed below.

A—Isolated Burner Experiments. Two behaviors are observed: ablation-extinction transitions and ignition-extinction transitions. Ablation-extinction occurs in oxygen-poor flames and is reversible. Here, when the wire speed is decreased, a characteristic velocity is found at which visible attack begins. The involvement length increases with decreasing velocity. Involvement is reversible, and extinction occurs at the same velocity at which ablation began.

Ignition-extinction behavior occurs in oxygen-rich flame atmospheres and shows hysteresis. As the wire velocity is decreased, a sharp involvement point is observed. Movies show that ignition begins at the far edge of the flame and propagates back along the wire. After ignition and at a critical velocity and/or flame size, extinction occurs. The extinguishment velocity is higher than the ignition velocity so that a bistable region exists (Fig. 16). Temperature measurements in the gas phase and on the polymer surface have shown that this hysteresis behavior is reproducible, and that the sharpness and reproducibility increases with oxygen concentration.

B— Flame—Atmosphere Experiments. If a flame is bounded by an atmosphere containing a higher free oxygen concentration, similar behavior is observed. Ignition begins at the flame-atmosphere interface but propagates along the wire into the atmosphere. At a low oxygen concentration, the flame ablatively attacks the wire prior to ignition, and below a minimum oxygen concentration in the atmosphere no ignition is observed. At higher oxygen concentrations, the ablative attack is reduced until, above a certain level, attack is observed prior to ignition in the adjacent atmosphere. If the flame has a higher free-oxygen concentration than the atmosphere, ignition will occur in the flame rather than the atmosphere, and the behavior will be that of the isolated burner.

C—Comparisons Between Experiments. The critical transition times were reproducible and are characteristic of the polymer. The controlling parameter for ablation and ignition is flame contact time rather than wire velocity or flame width. Extinction, in contrast, showed more complex behavior.

In the burner experiments, both flame temperature and the concentration of excess oxygen were important, while in burner-adjacent atmosphere experiments, flame temperature and oxygen concentration of the atmosphere were important variables.

Discussion—The moving substrate apparatus lends itself to many measurements which can be characterized by velocity, temperature, and composition of the ignition source and polymer as a function of position. Such measurments should be interpretable in terms of rates of elementary processes of heat transfer and reaction. This interpretation will require a quantitative model which we are attempting to develop. Preliminary studies suggest that ignition is governed principally by the wire surface temperature.

The correspondence between space and time is not exact in this system. Transport phenomena such as diffusion and thermal conduction behave differently in spatially-varying and time-varying systems. In transient systems, future events do not affect on-going ones. By contrast, in a steady-state moving system, diffusion or conduction can produce a profound effect on spatially earlier parts of the system.

Phenomena which show hysteresis (i.e., bistable systems) can only be held metastably in a moving

system. The MST, however, offers a powerful tool for accurately defining the critical conditions and investigating stability and hysteresis. This technique provides experimental clarification of the physical reasons underlying the asymmetry between ignition and extinction. The behaviors observed seem worthy of comment: (a) ablation which occurs at low oxygen concentration is a reversible attack of the polymer, and (b) ignition-extinction, which occurs at high oxygen concentration, is a bistable phenomenon showing hysteresis (Fig. 16). This clearly shows the contribution of the polymer combustion to produce a bistable
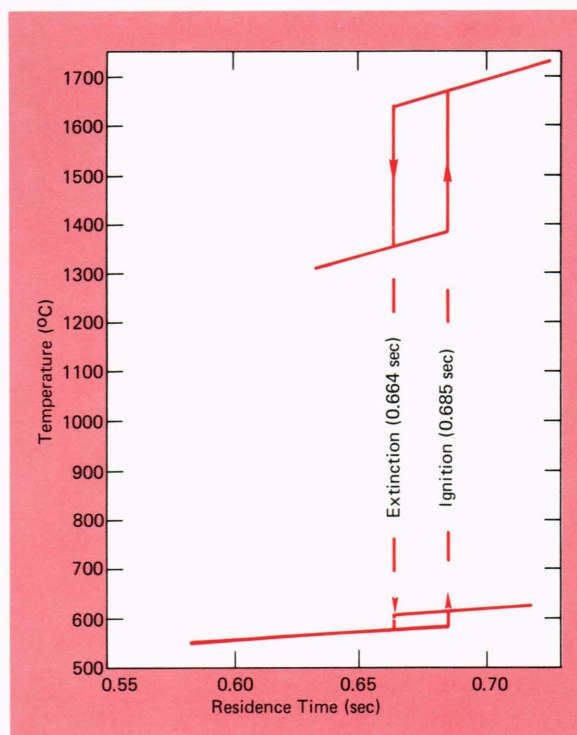

Fig. 16—Temperature hysteresis at ignition and extinction of No. 30 Teflon wire. Arrows indicate irreversible transitions.
Upper curve: gas phase temperature.
Lower curve: wire surface temperature.

situation depending on the presence or absence of the polymer flame. By contrast, in the ablation regime, either the sum of heat required to volatilize the polymer and the heat liberated by its combustion is negative, or the volatilized polymer is swept away from the polymer surface before it has a chance to react. As a result, bootstrapping does not occur, and the behavior is reversible. Most polymers show indications of an ablation regime if sufficiently fuel-rich flames are employed.

The complete interpretation of moving substrate experiments will require extended experimental and theoretical studies. Analysis of the products generated at various positions (or temperatures) in the absence or presence of inhibitors should give information about the function and mode of operation of inhibitors and provide a better, more scientific understanding of flammability tests.

Flame Inhibition Studies*

Fires are commonly extinguished by physical methods. For example, flooding a fire with water cools it below the temperature at which it is self propagating. Water is effective because it has a very high latent heat of vaporization. In addition, it is nontoxic, cheap, and easily available. Extinguishing a fire with carbon dioxide involves another physical process; the flame is blown out or smothered by a blanket of inert gas which separates the fuel from the oxidizing atmosphere. In addition to such physical extinguishants, there are chemical extinguishing agents whose effectiveness is thought to involve interference with some steps in the combustion reactions. The first of these was carbon tetrachloride, used in hand-pumped extinguishers but now ruled out because of its toxic properties. Recently several less toxic chemicals have been substituted (CF_3Br and $C_2F_4Br_2$). These are useful because much less material is required to extinguish a fire than would be the case with CO_2 or water. Such agents are advantageous where weight is important (as in airplanes), where water might cause damage (as in computer installations), and in electrical fires where water could produce hazardous short circuits.

The mechanisms of chemical extinguishment is a subject of some controversy; therefore, we have undertaken studies in chemically simple flames to try to identify the important processes. We chose to study CF_3Br, one of the most widely used chemical extinguishants. In chemical research, flames are studied far short of the extinguishment point, since it is difficult to study flames at the point of extinction. The slowing of flame reactions short of extinction is called inhibition. One common interpretation is that in-

hibitors interfere with radical reactions involving molecular fragments that occur in flames and in other rapidly reacting systems.

Characteristically radicals have an odd number of electrons and show high reactivity. Therefore, molecules which destroy or interfere with the production of radicals might inhibit flame propagation. One common mechanism is called the "scavenger reaction," where the inhibitor reacts with the flame radicals (e.g., H, OH, and O), converting them into unreactive radicals, e.g., Br. An example is the reaction of OH with HBr:

$$OH + HBr \rightarrow H_2O + Br.$$
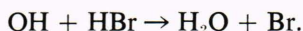
Other radicals, such as H and O, undergo similar reactions with an inhibitor species.

Scavenging reactions neutralize reactive radicals on a one-to-one basis. In another class of reac-
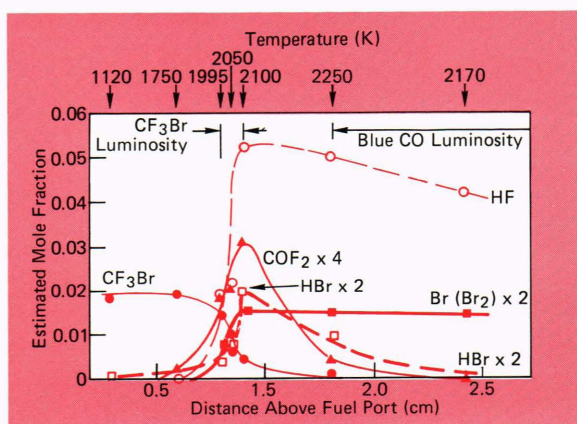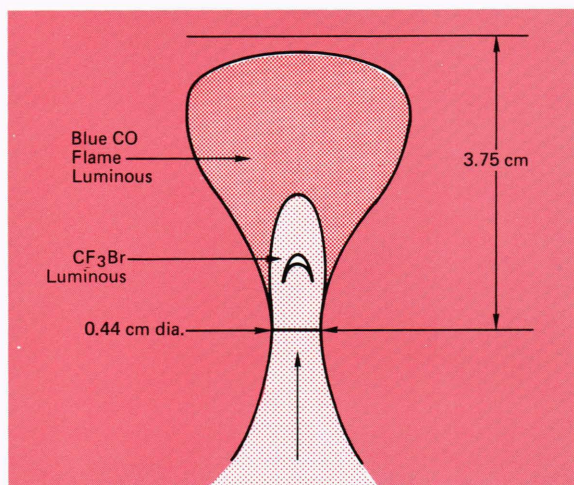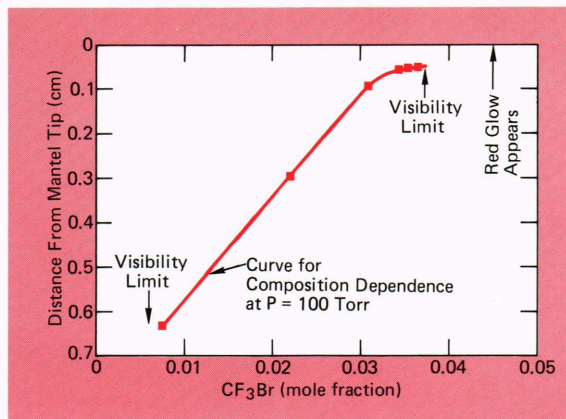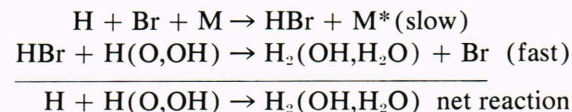

Fig. 18—Variation of position of luminosity as a function of inhibitor concentration.

tions which can destroy radicals by a chain recombination process, one Br atom, for example, can recombine and thus inactivate many radicals. The scheme is as follows:

$$H + Br + M \rightarrow HBr + M^*\,(slow)$$
$$HBr + H(O,OH) \rightarrow H_2(OH,H_2O) + Br\ (fast)$$
$$\overline{H + H(O,OH) \rightarrow H_2(OH,H_2O)\ \ net\ reaction}$$

Note that the net result of the two reactions is the destruction of radicals and that the catalytic agent, Br atoms, is regenerated. The limiting slow step is the three-body recombination.

The APL study has involved a structural measurement of a low pressure CO-H_2 diffusion flame inhibited by CF_3Br (Fig. 17A). At the University of Louvain laNeuve, Belgium, a parallel study of the structure of similar inhibited detonations and premixed flames is underway. Diffusion flames result when fuel and oxidizer are initially separate. The reaction rate is controlled by diffusional mixing. Most industrial flames and fires are of this type. Since fuel and oxidizer are introduced separately, the inhibitor can be added to either the fuel or the oxidizer. Different behaviors are obtained which may have important consequences in fire fighting. The inhibitor was found to be more effective on the fuel side in this system, and studies were concentrated there. Structural studies showed that the inhibitor was destroyed ahead of the main flame reaction zone in a narrow zone associated with a bright azure luminosity (Fig. 17B). The position of this luminosity was a function of the inhibitor concentration but was independent of the pressure (Fig. 18). The attack of CF_3Br was attributed to reaction with H atoms.

Fig. 17—Low pressure carbon monoxide–hydrogen diffusion flame inhibited by CF₃Br.
(A) Flame structure.
(B) Composition and temperature profiles.

A simple theory was developed which explained the observed behavior and allowed an estimate of the level of H atom concentration in the reaction zone. The proposed mechanism for CF_3Br destruction was:

$$H + CF_3Br \rightarrow HBr + CF_3$$
$$H + CF_3 \rightarrow CF_2 + HF$$
$$CF_2 + O_2 \rightarrow COF_2 + O$$
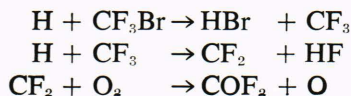
Studies in Elementary Reaction Kinetics*

The driving force in combustion is the energy released from chemical reactions. The information necessary for fire models are the reaction mechanisms and the rates of the elementary steps. In physical chemistry studies, rates usually show an exponential dependence on inverse temperature. This "Arrhenius relation" is commonly used to correlate experimental studies at different temperatures. From the slope of such plots, one derives the activation energy which is related to the energy barrier for the reaction, and from the intercept one obtains the frequency factor which is the rate of reaction given sufficient collisional and internal energy. For many purposes this is a good approximation, but there is some evidence of a breakdown of the relation for reactions that occur at the temperatures found in flames. This is a serious problem in combustion models and fire applications because most high temperature reaction rates are derived by extrapolation from low temperature measurements.

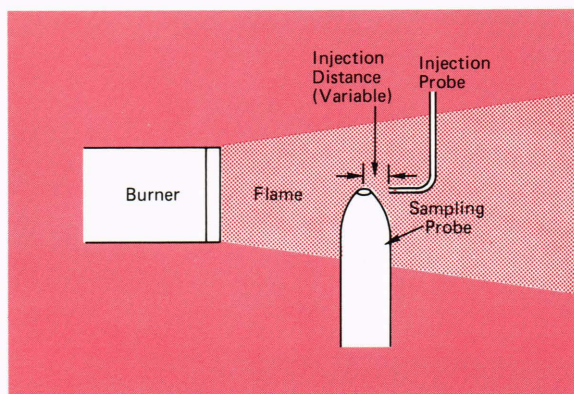To investigate the seriousness of this problem

and add kinetic information of interest in flame inhibition, we developed a new technique called the "Point Source Method." This uses the flame gases as a wall-free high temperature radical source. A small flow of the molecule under study is injected into a flame of suitable and known temperature and radical concentration and the decay of the reactant is measured as a function of distance from the source (Fig. 19). This information can be interpreted in terms of elementary rate constants in a temperature regime (1000 to 2500 K) which is difficult to obtain by other methods. We chose to study the reaction of H atoms with methyl halides.[7]

To further investigate this problem and validate the new technique, a companion study of the same family of reactions was undertaken using the well-established, high-precision Electron Spin Resonance-Flow Reactor Technique.[8] This method consists of a low-pressure flow tube in which reactants are mixed rapidly with a radical in excess, the reactants-radical reaction allowed to proceed, followed by electron spin resonance detection of the unconsumed radical species and mass spectrometric detection of stable species. This technique has generated some of the most precise and
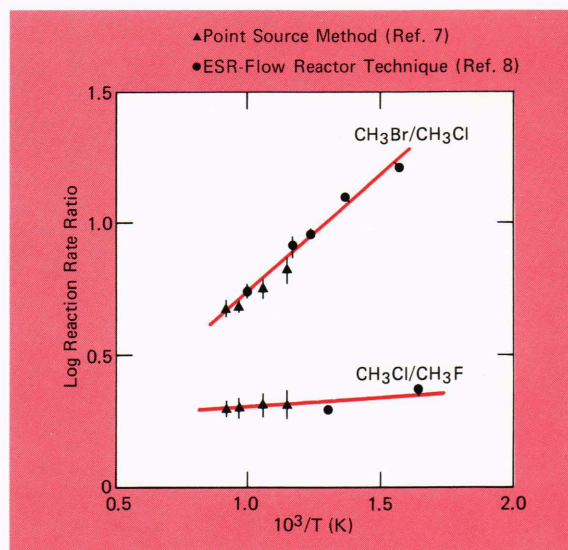

Fig. 19—Schematic diagram of point source injection apparatus for studying radical-molecule reactions in flame environments.

Fig. 20—Rate constant ratios as a function of temperature determined by two independent experimental methods.

reliable elementary kinetic information. The study was aimed at obtaining as wide and as high a temperature range as possible, with measurements extended to 1000 K by heating the flow tube. This allowed an overlap with the point source studies, with gratifying agreement between the two studies (see Fig. 20). In the overlap region, the absolute values agreed within a factor of two and relative rates between species, that did not depend on an absolute measurement of hydrogen atoms, agreed within 30%. This agreement between the two widely differing techniques suggests that the point source method can give precise relative rates, with absolute rates derived with known comparison reactions. It also indicates that the Arrhenius extrapolations of reaction rates to temperatures found in flames are valid.

Flame Theories*

Many fire protection engineering problems require realistic mathematical models of fire situations. The elements of these models are the various basic physical and chemical processes. Fire models can be divided into several interacting parts: flow field, flame reaction region, radiation field, etc. One important component is the flame. Because of the combined complexity of the overall problem and the theory of flames, it is customary to avoid the flame chemistry by treating the flame reactions as a single empirical adjustable parameter. This simplification is desirable because rigorous flame theory, even in a one-dimensional form, is limited to a few chemical steps unless expensive, high-capacity computers are employed.

To improve this situation, we have developed a model for flames which simplifies the physical aspects so that more realistic chemistry can be used.[9] The model assumes that the flame can be approximated as a homogeneous reactor with calculable average properties. The conditions for flame propagation are taken to be those which allow maximum thoughput. In a flame this is equivalent to assuming that the reactions are confined to a narrow homogeneous region, and that the flame propagates at the maximum rate compatible with conservation restrictions. Experimental studies of flame structure support this model, although in some cases more than one reaction zone needs consideration. This reduces the flame problem from the solution of a strongly coupled set of partial differential equations to the solution of a coupled set of algebraic equations. Calculations may be made of the composition, temperature, propagation velocity, and thickness of the primary reaction zone. The computer capacity required for these calculations is reduced by more than an order of magnitude when compared with conventional flame theory calculations.

The model has been applied to hydrogen-air flames where measurements of the burning velocity and hydrogen atom concentration in the reaction zone are available. The agreement between theory and experiment is excellent. By using the second approximation involving coupled reaction zones, it was possible to make the calculation without the use of adjustable parameters. The model has been extended to hydrogen-air flames inhibited with HCl. Again the agreement between predicted and measured changes in burning velocity was good.

Experimental Studies and Survey Papers

Several new experimental techniques have been developed at APL in support of the fire program. They include: (a) a phase-adjustable sampling mass spectrometer for studying the time behavior of repetitive phenomena such as spark ignition;[10] and (b) a large-area, laser-illuminated differential interferometer for investigating flow and density fields around model fires.[11] The extension of this technique to full-scale burns was investigated, and it was concluded that the use of a one-watt continuous-power visible laser would allow study of a field 10 meters by 10 meters. A third technique is a method of sizing particles using interferometric fringes.[12] This could prove a useful tool in soot and smoke studies.

* Dr. Nancy Brown and Professor R. Sawyer (University of California, Berkeley) participated in this study.

[9] N. J. Brown, R. M. Fristrom, and R. F. Sawyer, "A Simple Premixed Flame Model Including Application to H_2 + Air Flames," *Combustion and Flame* **23**, Oct. 1974, 269–275.

[10] R. M. Fristrom, "Flame Sampling for Mass Spectrometry," *Internatl. J. Mass Spectrometry and Ion Phys.* **16**, 1975, 15–32.

[11] J. E. Creeden, R. M. Fristrom, C. Grunfelder, and F. J. Weinberg, "A Large-Area Laser Differential Interferometer for Fire Research," *J. Phys. D: Appl. Phys.* **5**, 1972, 1063–1067.

[12] R. M. Fristrom, A. R. Jones, M. J. R. Schwar, and F. J. Weinberg, "Particle Sizing by Interference Fringes and Signal Coherence in Doppler Velocimetry," *Faraday Symp. Chem. Soc.* **7**, 1973, 183–197.