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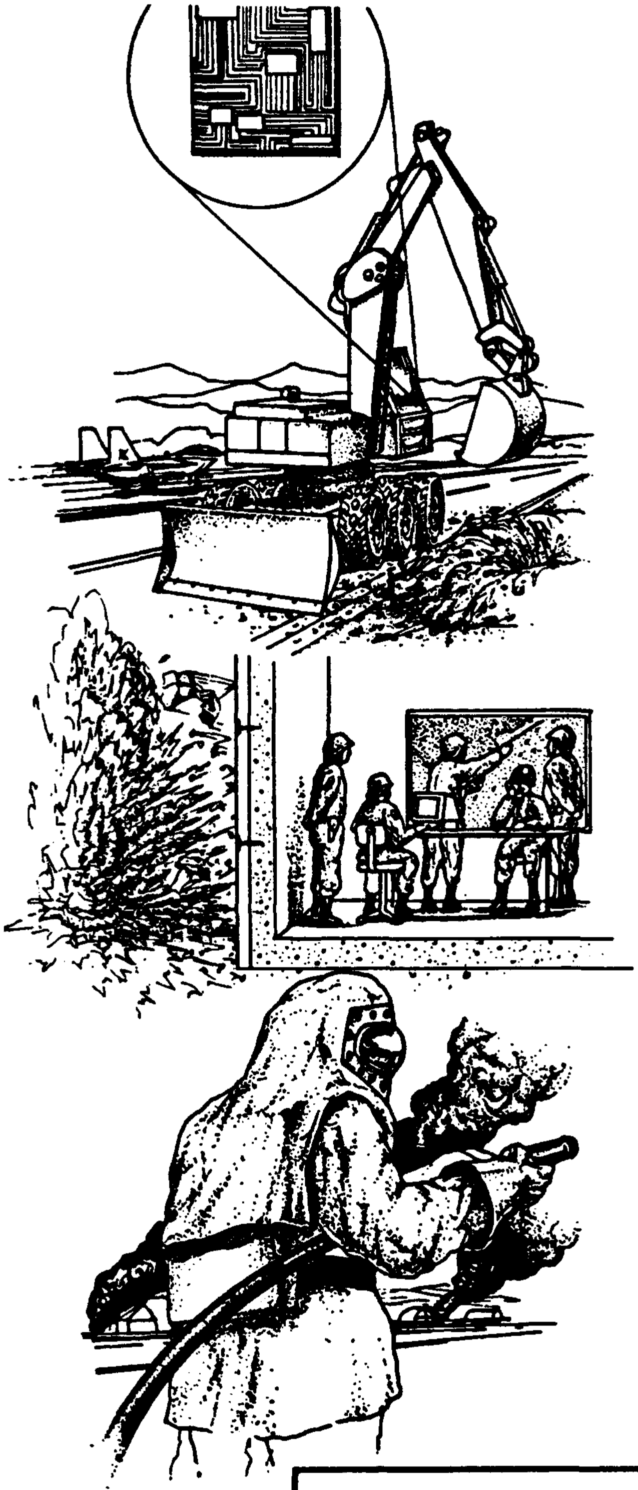

INITIAL FIRE SUPPRESSION REACTIONS OF HALONS PHASE I-DEVELOPMENT OF EXPERIMENTAL APPROACH

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13. ABSTRACT (Maximum 200 words)

The objective of this effort was to develop an experimental approach for identification and characterization of the first reactions occurring when halon fire extinguishing agents enter flames. This report reviews technologies available for measurement of flame temperatures and concentrations of chemical species in flames. Methods reviewed for measurement of flame temperatures include use of thermocouples, laser Raman and coherent Anti-Stokes Raman (CARS) spectroscopy, and silicon carbide filaments with optical monitoring. Methods assessed for applicability to measurement of concentrations of chemical species in flames include laser Raman spectroscopy, isolation of fragments and products on a frozen argon matrix followed by analysis by Fourier-transform infrared spectroscopy, and photoionization followed by mass spectrometry. An experimental approach for studying reactions of halons in flames is developed. This approach consists of four elements: (1) construction of an information database, (2) an investigation of the relative importance of physical and chemical processes in halon fire extinguishment, (3) development of flame extinguishment diagnostics and characterization, and (4) time-dependent studies of free-radical reactions.

14. SUBJECT TERMS
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EXECUTIVE SUMMARY

A. OBJECTIVE

The objective of the overall effort is to identify and characterize the first reactions occurring when halon fire extinguishing agents enter flames. The objective of this Phase I effort is to develop the experimental approach.

B. BACKGROUND

Halon firefighting agents have been used for many years because they are effective, clean, and relatively nontoxic and inexpensive. However, they have been implicated in the depletion of stratospheric ozone, and the United States Air Force is now investigating alternatives to replace halons. Knowledge of the initial reactions occurring when halons enter flames is needed both to advance the development of halon alternatives and to aid in the development of techniques and hardware to reduce the quantities of halons used.

C. SCOPE

The scope of the project is to develop an experimental approach (Phase I), evaluate the experimental methodology (Phase II), and apply the experimentation to the determination of initial reactions of flames with halons (Phase III). This Phase I effort develops the approach, prepares the experimental plan, and sets up the instrumentation and facilities necessary to initiate Phase II of the project.

D. METHODOLOGY

A comprehensive technology search was conducted to collect and analyze approaches to flame characterization and flame reaction determinations.

Spectroscopic approaches were emphasized. This information was used to develop an experimental approach to determine the initial fragmentation and abstraction reactions occurring in flame/halon interactions. A plan was prepared for experimentation to identify and characterize the initial chemical reactions occurring when halons enter flames. The plan included laser Raman spectroscopic studies, isolation of fragments and products on a frozen argon matrix with identification of products by FTIR, and photoionization with analysis by mass spectrometry.

E. TEST DESCRIPTION

This report contains the results of the technology search, the proposed experimental procedures, the rationale for the approach selected, and a description of facilities. The laboratory facilities, equipment, and supplies needed to initiate Phase II of the project were obtained, set up, and reconfigured as needed.

F. RESULTS

Techniques for temperature measurement in flames were reviewed, including use of thermocouples and nonintrusive laser Raman spectroscopy. Techniques for characterizing flame species were assessed, including use of microprobes with gas chromatography, molecular beam mass spectrometry, laser-induced fluorescence, and laser Raman spectroscopy.

G. CONCLUSIONS

From the technology review three experimental approaches appear promising for measurement of concentrations of chemical species in flames: laser Raman spectroscopy, isolation of fragments and products on a solid argon matrix followed by analysis by Fourier-transform infrared spectroscopy, and photoionization followed by mass spectrometry. Raman techniques lack high sensitivity and therefore can only be used to measure concentrations of major flame species. Possible techniques for measurement of flame temperatures include use of thermocouples, laser Raman and coherent Anti-Stokes Raman (CARS), or a silicon carbide filament with optical monitoring.

H. RECOMMENDATIONS

A recommended program is described that will provide a fundamental understanding of extinguishment mechanisms by halons, verify the applicability of experimental techniques, and develop concepts for alternative firefighting agents. This program consists of four elements: (1) construction of an information database, (2) an investigation of the relative importance of physical and chemical processes in halon extinguishment, (3) flame extinguishment diagnostics and characterization, and (4) time-dependent studies of free-radical reactions. It is recommended that three techniques be tested to compare their usefulness for determining the concentrations of chemical species in flames: laser Raman spectroscopy, matrix isolation with Fourier-transform infrared spectroscopy, and photoionization with mass spectrometry.

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PREFACE

This report was prepared by the New Mexico Engineering Research Institute (NMERI), University of New Mexico, Albuquerque, New Mexico 87131, under contract F29601-84-C-0080, for the Engineering and Services Laboratory, Air Force Engineering and Services Center, Tyndall Air Force Base, Florida 32403.

This report summarized work done between March and June 1988. The HQ AFESC/RDCF Project Officers were Capt E. Thomas Morehouse, Jr. and Capt John R. Floden.

Professors Edward A. Walters, Donald R. McLaughlin, Thomas M. Niemczyk, and Fritz S. Allen, of the University of New Mexico Department of Chemistry, provided valuable criticism, comments, and suggestions. John May, Marcus S. Butler, Rosa E. Rivera, Monica L. Rodriguez, and Joanne P. Moore were the project technicians.

This report has been reviewed by the Public Affairs Officer (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

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SECTION I
INTRODUCTION

A. OBJECTIVE

The objective of this project is to identify and characterize the first reactions occurring when halon fire extinguishing agents enter flames. The objective of the Phase I effort is to develop the experimental approach.

B. BACKGROUND

Halon firefighting agents have been used for many years. The United States Air Force uses two primary halon agents: Halon 1301, bromotrifluoromethane (CF_3Br), which is used as an indoor agent in total and partial flood applications, and Halon 1211, bromochlorodifluoromethane (CF_2BrCl), which is used in both indoor and outdoor streaming applications. Because halons are effective, clean, safe, and relatively inexpensive, little incentive for development of new chemical agents has existed. Recently, however, halons, along with fully halogenated chlorofluorocarbons (CFCs), have been implicated in the depletion of stratospheric ozone. The United States Air Force is now investigating alternative agents to replace halons (Reference 1). Knowledge of the initial reactions occurring when halons extinguish flames is needed to advance this halon replacement work. Moreover, knowledge of the initial reactions will aid in the development of techniques and hardware to reduce the amount of halon needed.

Halon fire suppression agents extinguish fires chemically by terminating free-radical chain reactions and physically by absorbing heat. Though the final chemical reactions are relatively well understood, the initial reactions occurring when halons enter flame fronts are unclear. It is these initial reactions, however, that determine differences in halon performance, the effect of physical state on suppression, and the effect of fire parameters on agent activity. Investigations are needed to characterize the initial reactions leading to flame suppression by halons.

C. SCOPE

The scope of the project is to develop an experimental approach (Phase I), evaluate the experimental methodology (Phase II), and apply the experimentation to the determination of initial reactions of flames with halons (Phase III). The Phase I work develops the approach, prepares the experimental plan, and sets up the instrumentation and facilities necessary to initiate Phase II of the project.

D. TECHNICAL APPROACH

A comprehensive technology search was conducted to collect and analyze approaches to flame characterization and flame reaction determinations. Emphasis was placed on spectroscopic approaches. This information was used to develop an experimental approach to determine the initial fragmentation and abstraction reactions occurring in flame/halon interactions.

A plan was prepared for experimentation to identify and characterize the initial chemical reactions occurring upon impingement of halons with flames. The plan includes laser Raman spectroscopy studies. The plan also includes selected photoionization and matrix isolation FTIR studies. The laboratory facilities, equipment, and supplies needed to initiate Phase II of the project were obtained, set up, and reconfigured as needed.

The following report contains the results of the technology search, the experimental procedure proposed, the rationale for the approach selected, the plan of experimentation, and a description of facilities.

SECTION II

TECHNOLOGY REVIEW

A. PRIMARY PROCESSES IN FLAMES

Since flames have been described in careful detail by several workers (Reference 2), only the most important flame processes are discussed here. These processes are illustrated schematically in Figure 1.

1. Chain Branching

The chemistry of flames is dominated by free-radical reactions. Since free radicals are lost by a variety of mechanisms (including diffusion out of the flame and recombination in the flame), free radicals must be generated continually if the flame is to be sustained. In a stable flame, the rate of loss of free radicals is balanced by the rate of generation. The principal path generating free radicals is the chain branching reaction, in which a single free radical reacts with a molecular species to yield two free radicals. The following reactions (one unique to CH_4 combustion) are some of the most important chain branching reactions. The reaction enthalpies, ΔH, given in kilojoules, kJ, are taken from the JANAF tables (Reference 3). The temperature used for most enthalpies presented in this report is 298 K. The temperature is always specified.

$$H + O_2 \rightarrow OH + O, \ \Delta H(298\ K) = 70\ kJ \qquad [1]$$

$$O + H_2 \rightarrow OH + H, \ \Delta H(298\ K) = 8\ kJ \qquad [2]$$

$$O + CH_4 \rightarrow OH + CH_3, \ \Delta H(298\ K) = 10\ kJ \qquad [3]$$

The net, very large, heat release by the recombination reactions (vide infra) provides the energy required to sustain these endothermic chain branching reactions.

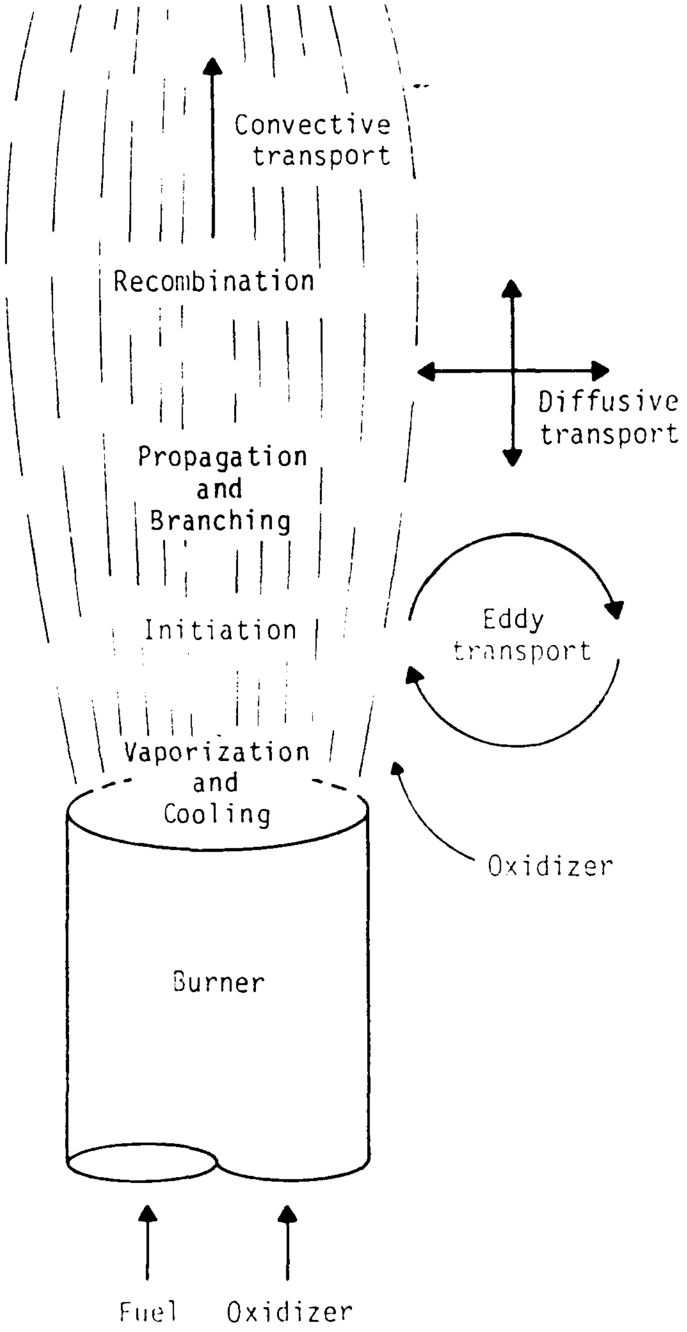

Figure 1. Processes in Flames.

2. Radical Initiation

Radical initiation reactions, such as the pyrolysis of hydrocarbons, also serve as sources of free radicals. For example, pyrolysis of methane gives hydrogen and methyl free radicals.

$$CH_4 \rightarrow CH_3 + H,\ \Delta H(298\ K) = 439\ kJ \qquad [4]$$

Again, the source of the energy needed to drive this reaction is the heat released by the flame. Since the reaction enthalpies of these pyrolysis reactions are much larger than those for typical chain branching reactions, the latter are the dominant reactions by which radicals are generated in a flame.

3. Propagation

Many reactions serve to propagate free-radical chains without changing the total number of radicals in the flame. The following reactions are typical.

$$CH_4 + H \rightarrow CH_3 + H_2,\ \Delta H(298\ K) = 3\ kJ \qquad [5]$$

$$OH + H_2 \rightarrow H_2O + H,\ \Delta H(298\ K) = -63\ kJ \qquad [6]$$

These propagation reactions are usually bimolecular and may be either endothermic or exothermic.

4. Recombination

Recombination reactions differ in two important respects from the reactions described above. They are highly exothermic and they require a third body (M) to carry off part of the energy (consider the following).

$$H + H + M \rightarrow H_2 + M,\ \Delta H(298\ K) = -436\ kJ \qquad [7]$$

$$H + OH + M \rightarrow H_2O + M,\ \Delta H(298\ K) = -499\ kJ \qquad [8]$$

As suggested earlier, these reactions are the primary sources of energy to sustain the endothermic chain branching reactions. Moreover, since these reactions are termolecular and the probability of a three-body collision is much smaller than the probability of a bimolecular collision, recombination reactions are much slower than other flame reactions. Radicals are, therefore, relatively long-lived in a flame and may diffuse significant distances before they undergo reactive encounters.

5. Convective Transport

Although it seems trivial to note that flames rise, the consequences are profound. Convective transport is a principal loss mechanism both for radicals (which might otherwise become engaged in chain branching reactions) and for thermal energy (which is required to sustain the chain branching reactions).

6. Eddy Transport (Entrainment)

As the hot gases rise, they accelerate with respect to the surrounding gases and generate small eddies that may evolve into large-scale turbules. The eddies not only result in a counterflow movement of flame species, they also entrain gases (oxidizers, diluents, suppressants) into the flame. Entrainment can increase burning rates by facilitating the mixing of fuel and oxidizer and by assisting chain branching reactions (by mixing free radicals present in the combustion products with the fuel and oxidizer mixture). However, high turbulence can also decrease burning rates by causing separation of pockets of burning gas, which are only slowly consumed. Eddy transport provides an important but little studied mechanism for entrainment of extinguishing agents in fires. Once the initial momentum of a discharged fire suppressant has been lost, further penetration into the flame depends almost entirely on entrainment. Studies in two areas are needed: (1) mathematical modeling of the coupled physical/chemical processes in combustion and extinguishment and (2) experimental characterization of the role of turbulence in fire extinguishment.

7. Diffusive Transport

Along with entrainment, diffusive transport accounts for the fact that a flame propagates upstream from the zone of high free-radical concentration. As expected, atomic and small molecular species (especially hydrogen atoms) diffuse at the highest rates. Convincing evidence of the importance of diffusive transport of radicals into the preheat zone of a premixed C_2H_4/air flame has been presented by Weinberg and Wilson (Reference 4). These workers compared the heat released in the preheat zone of an ignited C_2H_4/air mixture with that released by an unignited mixture of the same two gases, which had been heated to the same temperature. At 700 $^{\circ}C$, the heat released by the ignited mixture was about 12 times that released by the unignited mixture. This work presents clear evidence for the importance of exothermic reactions involving radicals that diffuse upstream from the reaction zone.

8. Radiation

Although radiation (including radiation at IR and UV wavelengths) clearly results in energy loss, measurements indicate that radiation is not a primary mechanism for flame propagation. This conclusion is based on the extensive work by Gaydon and others (Reference 2). Two factors seem to be important. First, the energy required to break a bond in a typical fuel or oxidizer molecule is of the order of 400 kJ/mole and requires photons in the ultraviolet ($k < 300$ nanometers). At wavelengths shorter than 200 nanometers, diatomic oxygen and nitrogen absorb strongly. Thus only a narrow band of wavelengths, which have enough energy to contribute to bond breaking, can be transmitted. Second, flames are not very dense from an optical standpoint. Thus, even those photons generated with appropriate energies are unlikely to be absorbed by a reactive molecule. With luminous flames, on the other hand, radiation plays an important role in heat loss. Moreover, in large fires and in fires having high particulate concentrations, radiation plays a primary role in fuel vaporization.

9. Heat Loss to the Burner and to the Fuel Pool

Burners and pools of liquid fuels represent heat sinks. For flames supported on surfaces (e.g., burners) or on pools of fuel, the temperature and, therefore, the flame speed in the vicinity of the heat sink must be lower than that in the hottest part of the flame. As a result, it is necessary to describe the dynamics of a flame in terms of the relative velocities of the flame and of the fuel/oxidizer/diluent stream. Since the adiabatic flame velocity is typically larger than the linear stream velocity, the flame will tend to propagate upstream toward the burner or fuel pool. However, the heat loss to these heat sinks will reduce the flame speed until it equals the stream velocity. At this point equilibrium is established. This equilibrium accounts for the fact that a flame can take up a stable position a short distance above the burner or fuel pool, and that a change in stream velocity or in diluent ratio can have a significant influence on the location and/or stability of the flame.

Heat losses to burner heads and fuel surfaces can greatly influence the behavior of flames and fires; this must be taken into account in designing, conducting, and interpreting combustion and extinguishment experiments. The laboratory experiment is an idealized situation; the laboratory burner is often water-cooled. By contrast, a real fire is sustained on a pool of fuel, the temperature of which may approach the boiling point. A Class A fire is an extreme case in that the smoldering fuel provides a hot "flame holder" very different from a laboratory cup burner. Moreover, the interface between a cold fuel and a flame represents a fragile equilibrium, which can be easily disturbed by introduction of even small amounts of extinguishing agent. By contrast, the latter stages of a flame are more robust. For this reason, it may be important to study the introduction of a fire suppressant as a function of distance from the burner surface.

B. TYPICAL LABORATORY FLAMES

Over the past four decades, numerous tests have been performed in an effort to characterize the relative effectiveness of candidate fire suppressants. While many of these tests have been conducted on a large scale with attempts to simulate realistic fire environments, others have been conducted at small scale in laboratories in attempts to bring some of the experimental variables under control. It should be noted that, to the degree that experimental parameters are brought under control, the laboratory experiments depart from the real world. As a consequence, one is required to extrapolate from laboratory experiments to real-world expectations. Nevertheless, carefully controlled laboratory experiments are essential if one is to characterize reliably the important processes and to determine the point at which intervention is most effective.

Several flame types will be discussed in the following paragraphs. While it is tempting to identify one type of flame as "best" for experimentation, such an assessment cannot be made. Each flame type is suited for a different objective. Thus, for example, a premixed flame allows one to monitor the concentrations of important species as functions of flame location, but does not permit an examination of the chemistry in either side of the interface between a fuel stream and and oxidizer stream.

A technique for grouping the various laboratory experiments is presented in Figure 2, in which two of the principal variables -- the stoichiometry of the fuel stream and the velocity of the environmental stream -- are selected as axes. The circled numbers on this diagram represent important sets of experimental parameters; each is discussed separately below.

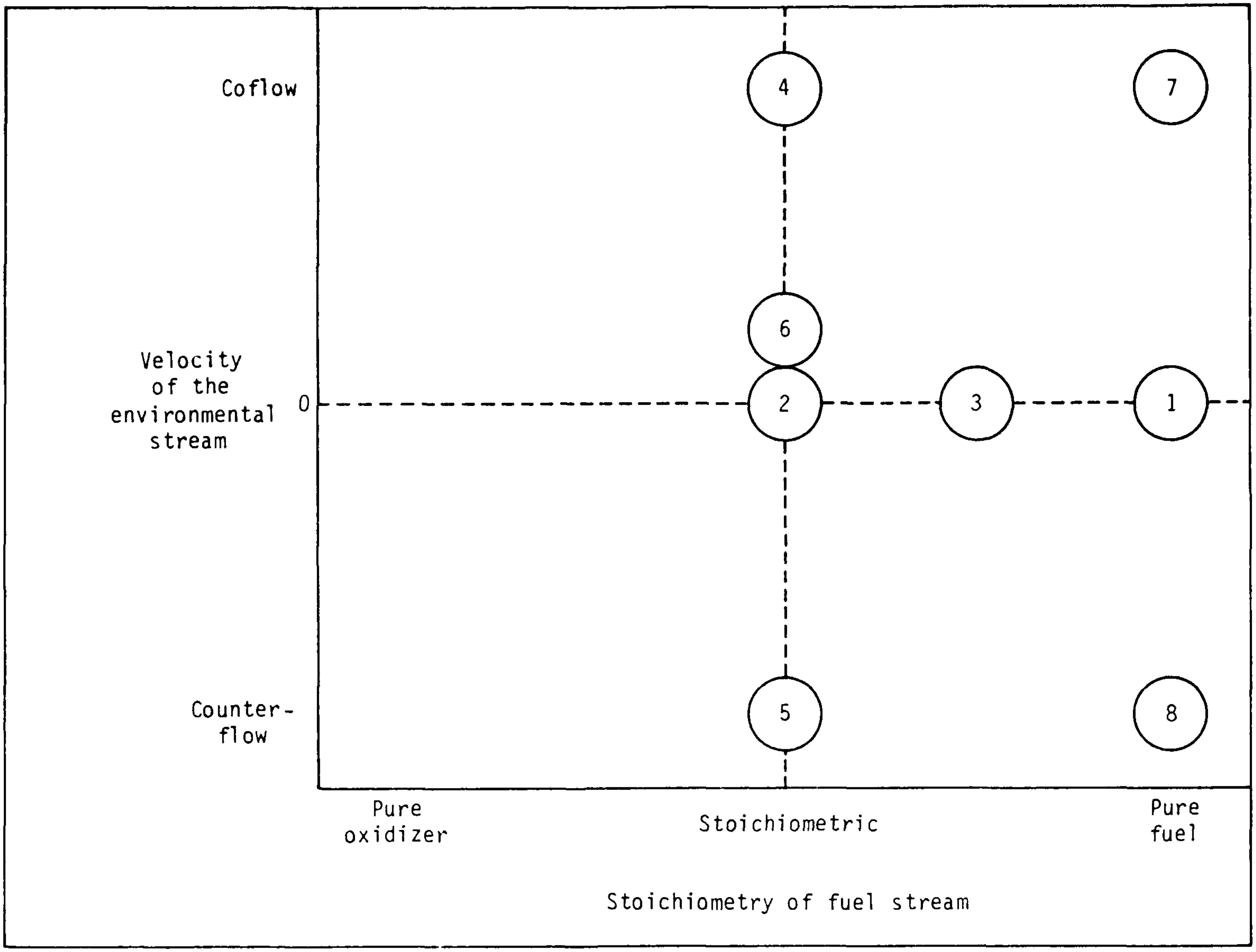

Figure 2. Typical Laboratory Flames

1. Point 1: Natural Flames

Point 1 represents a pan fire burning in a quiescent atmosphere and, as such, approaches a real fire. In this configuration, the chemical (nonlinear) processes are tightly coupled with the mass and energy transport processes (largely, linear). Since neither the chemical processes nor the transport processes dominate, this flame is the most difficult to analyze and characterize. It is difficult to uncouple chemical and physical processes; however, the remaining points in the diagram represent efforts in this direction. Permitting one process to dominate simplifies the study and understanding of combustion and extinguishment.

2. Point 2: Premixed Flames

Premixed flames, among the most thoroughly studied, typically use a porous plug or similar configuration in the burner to prevent the flame from flashing back into the mixing zone (Figure 3). The advantage of premixing the fuel and oxidizer is immediately apparent. Since the fuel and oxidizer are intimately mixed, reaction distances (i.e., the distances species must move before encountering reactive events) are very short, and the overall rate of combustion will be dominated by the rates of the individual chemical processes and not by the rates of transport of the reactive species. Moreover, since the fuel/oxidizer mixture is introduced at the bottom of the combustion zone and the combustion products exit at the top, the important chemical processes are spatially separated and can be studied separately. Thus, one can identify a preheat zone in which the temperature of the reaction mixture rises but the reactions are relatively slow, a reaction zone that is dominated by bimolecular chain branching and chain propagation reactions, and a recombination zone in which heat continues to be released (largely through termolecular reactions) and where the final composition of the exhaust gases is determined.

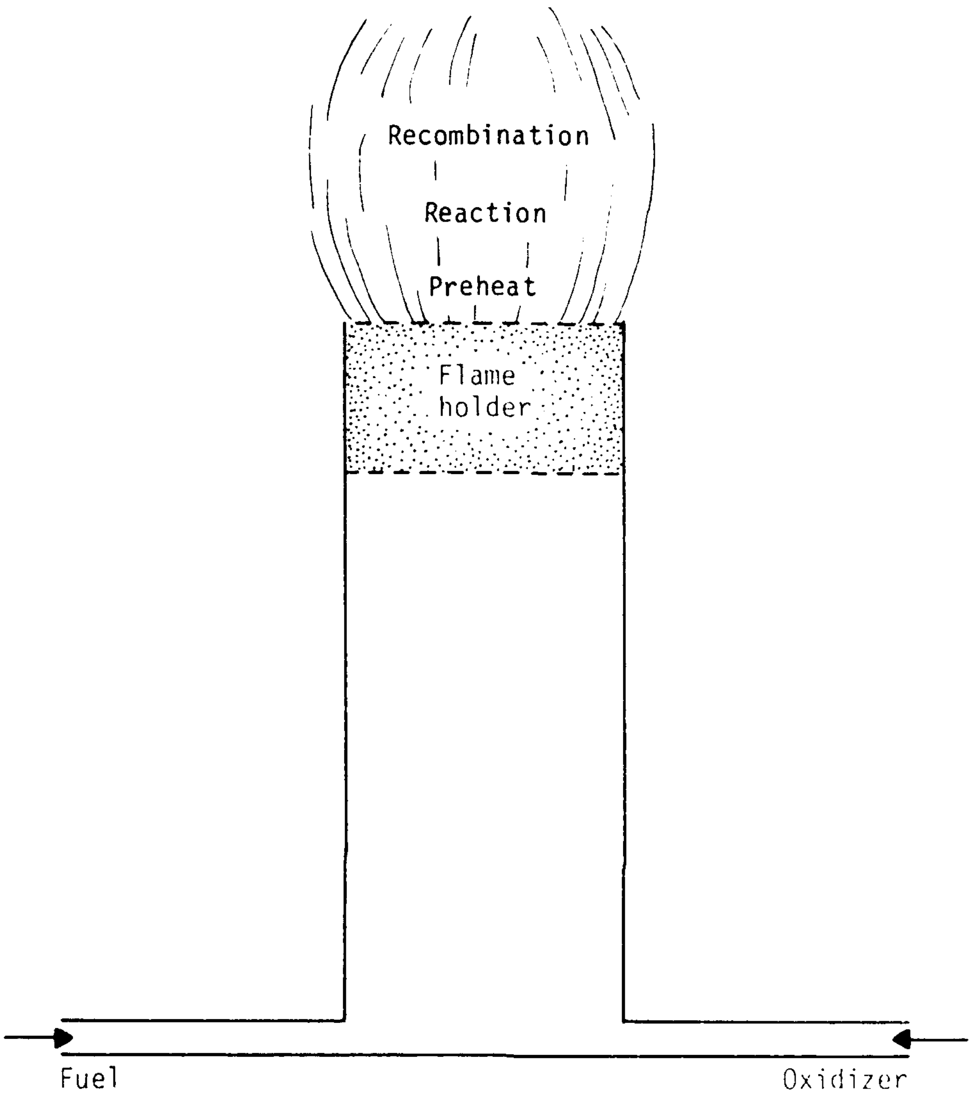

Figure 3. Premixed Burner.

Though premixed flames allow partial separation of physical and chemical processes, they may not relate well to real-world fires, which are nearly always diffusive and turbulent. Nevertheless, premixed flames are ideal for characterizing the basic chemistry of combustion and extinguishment. The two sets of interrelated processes that characterize a real flame are chemical processes and transport processes. Premixed flames allow one to explore the chemical processes, freed to a large extent from the complications of those transport processes that involve the mixing of fuel and oxidizer. Once the basics are understood, the information can be refined in studies involving other types of flames.

3. Point 3: Bunsen Flames

The classic premixed flame is the Bunsen flame, located at Point 3 on Figure 2. Note that it lies in the fuel-rich region as shown on this figure. As a consequence, introduction of secondary oxidant (largely, by eddy transport in the outer sheath of the flame) is needed for completion of combustion. This type of flame, therefore, provides an opportunity for introduction of oxygen mass transport into flame characterization.

4. Point 4: Premixed, Coflow Flames

Points 2 and 3, described in the previous paragraphs, represent the introduction of a flame into a stagnant environment and are characterized by a velocity differential between the flame and the environment. The velocity differential results in eddy transport of environmental gas into the flame, which complicates characterization. This complication can be ameliorated by providing an environmental sheath that flows in the same direction and at the same rate as the flame. Since the flame accelerates as it rises from the burner, velocity matching is only approximate, and eddy transport typically becomes important as the distance from the burner increases.

For low stream velocities, the flame will appear to be attached to the burner. For larger stream velocities, on the other hand, a dark space separates the flame from the burner. This latter situation represents a tenuous dynamic equilibrium and is, therefore, difficult to reproduce. Such separated flames are rarely studied; however, lift-off is sometimes used as an indicator of extinguishment.

5. Point 5: Premixed, Counterflow Flames

As suggested earlier, the presence of a burner (or pool of liquid fuel) will have a significant effect on the observed characteristics of a flame. A novel technique for avoiding this effect is to inject a high velocity stream of premixed fuel and oxidizer into a counterflowing stream. The fuel-oxidizer stream velocity is large enough to prevent the flame from attaching to the burner; however, the presence of a counterflowing environmental gas stream creates a stable stagnation zone, where the flame chemistry can be observed. In this configuration, the effect of the cold burner is largely removed. Figure 4 illustrates a variant in which the environmental stream is injected into the rapidly flowing premixed combustion gases.

6. Point 6: Well-Mixed Reactor

In many respects, a "well-mixed reactor" is a premixed flame (Point 2); however, the experimental configuration, illustrated by Figure 5, is sufficiently different to warrant a separate discussion. In this configuration, the jet of premixed fuel and oxidizer is introduced into a stagnant reaction mixture at such a high rate that nearly instantaneous mixing occurs throughout the entire reactor volume. This configuration is very different from that at Point 2. At Point 2, the various zones of the flame are separated spatially; at Point 6, the flame is nearly homogeneous. Thus, fuel and oxidizer molecules are exposed directly to the combustion products (especially to the species normally found in the recombination zone), and one expects to observe different chemistries.

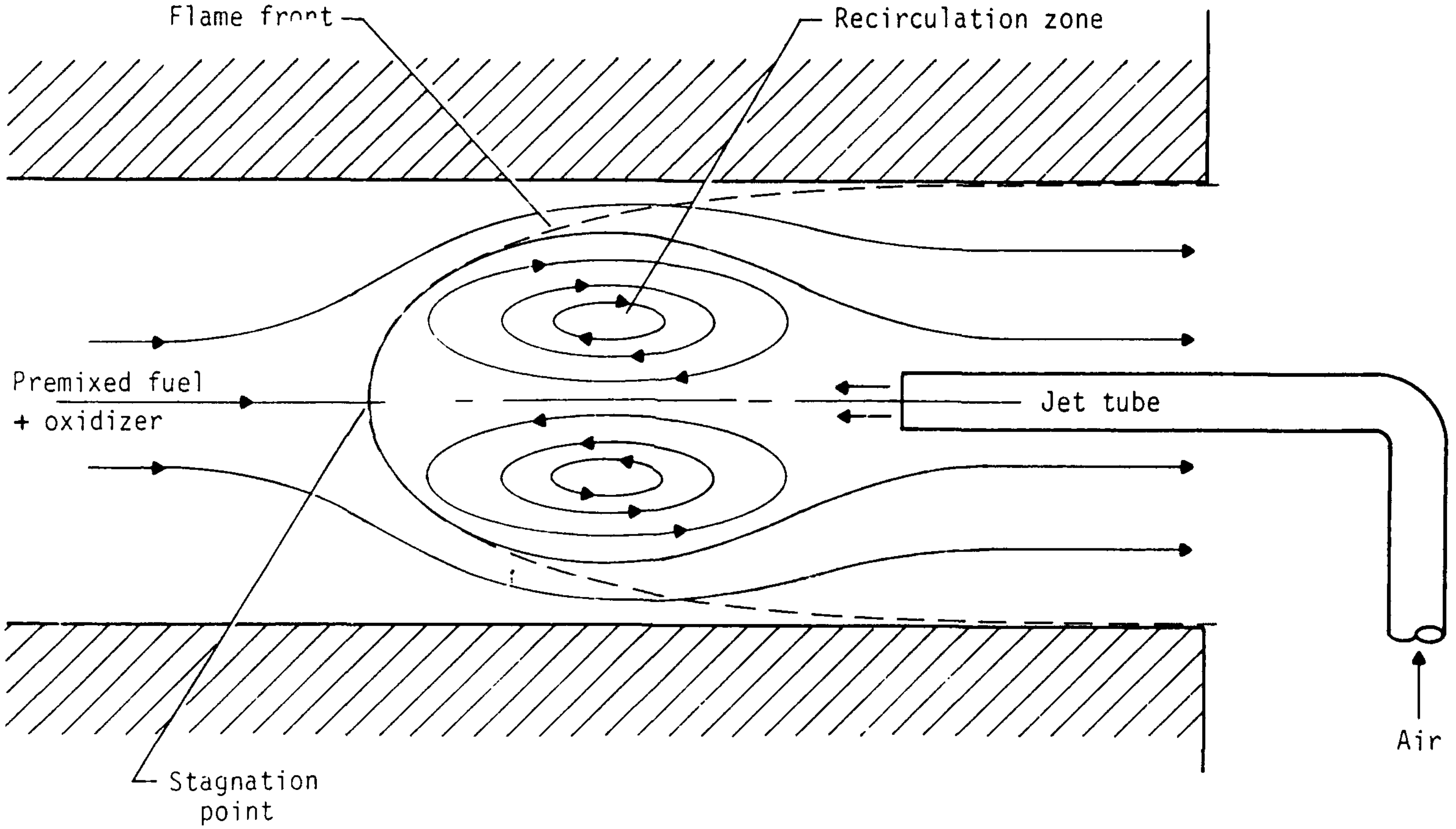

Figure 4. Counterflow Flame Experiment (redrawn from Reference 5).

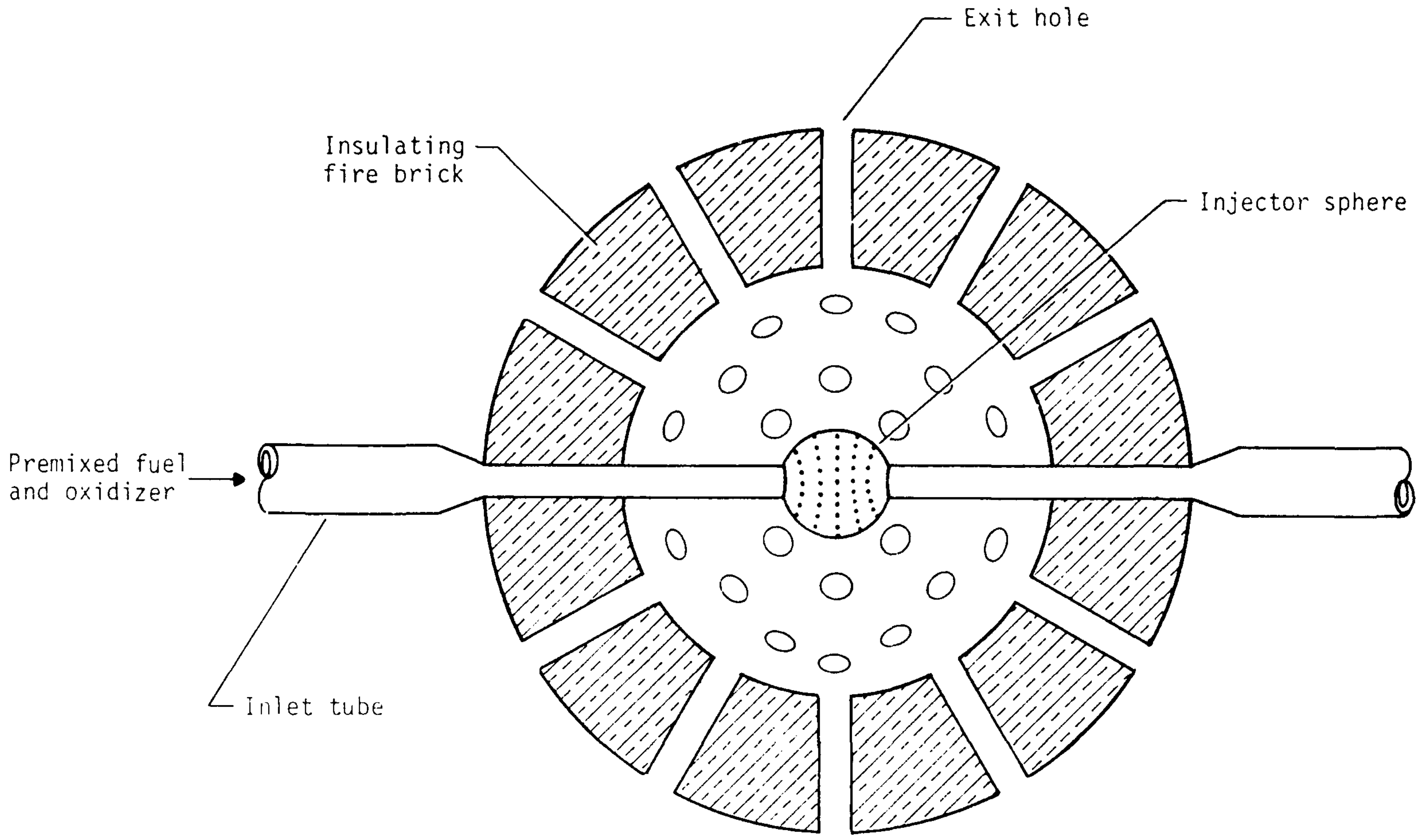

Figure 5. Well-Mixed Reactor (redrawn from Reference 6).

7. Point 7: Diffusion Flames

In a "natural flame," Point 1, mixing is the result of a combination of molecular and eddy transport processes. To a first approximation, one can eliminate the complication of the eddy transport processes by matching the velocities of the fuel and oxidizer streams. This process is found at Point 7 on the diagram. In an ideal experiment, a fuel stream flows out of a burner while a sheath of oxidizer flows at the same velocity along the side of the fuel stream. As the result of molecular diffusion, the two streams slowly mix and react. A typical experimental configuration is illustrated in Figure 6. This configuration permits one to investigate the diffusion processes, which are characteristically slow with respect to the chemical processes. In addition, this configuration provides the opportunity to examine the important species on either side of the stoichiometric reaction zone. The situation is complicated by the fact that, since the flame is hotter than either the fuel stream or the oxidizer stream, the flame accelerates with respect to the two individual streams. Thus, the flame may not be free of eddy transport processes for its entire length.

The following comment on diffusion flames is instructive. One cannot say that either "the chemistry drives the mixing" or "the mixing drives the chemistry." Both statements are true. The chemistry can only occur when the reactants diffuse together, but diffusion is possible only owing to the presence of concentration gradients established by reaction. Once again, chemical and physical processes are coupled. In this case, however, the characteristic times are such that separate study is possible.

8. Point 8: Counterflow Mixing Flames

One may view a premixed flame as a configuration in which the mixing speed of the fuel and oxidizer is infinitely fast. Nearly the same result can be achieved if the mixing zone is so turbulent that the rates of the chemical processes are slow by comparison with the rate of mixing. This

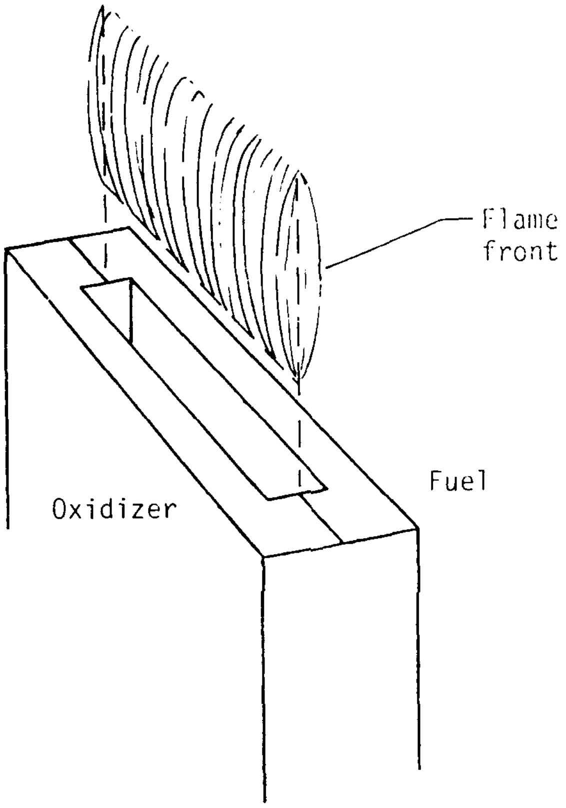

Figure 6. Diffusion Flame Burner.

situation is represented by Point 8. As at Point 5, the introduction of a counterflowing gas stream creates a stagnation zone in which the combustion can be studied. A typical experimental configuration is shown in Figure 7. In this arrangement, the combustion actually proceeds from the center of the combustion disc to the periphery, and the combustion products escape radially.

C. OTHER EXPERIMENTAL CONFIGURATIONS

Figure 2 is a two-dimensional slice in which only two of the many possible variables are treated. To treat other variables, one can imagine a three-dimensional (or n-dimensional) arrangement in which the change in another variable places one in a parallel two-dimensional plane. Here are some of the other variables.

1. Pressure

Although atmospheric pressure flames have been implied by the previous paragraphs, many of the experiments were actually performed at reduced pressures. For these experiments, the partial pressures (and densities) of the various species are reduced. Two principal results can be expected. First, since the chemical rate equations are written in terms of the partial pressures of the reacting species, one expects the rates of the chemical reactions to be slowed. This is accompanied by a concomitant reduction in flame velocity and flame temperature, which could result in the reordering of the importance of the various chemical reactions. In particular, termolecular reactions are expected to be much slower. Bimolecular reactions would show smaller velocity decreases. Second, because of the lowered density, the times between reactive collisions are longer, and diffusion processes become more important as rate limiting steps.

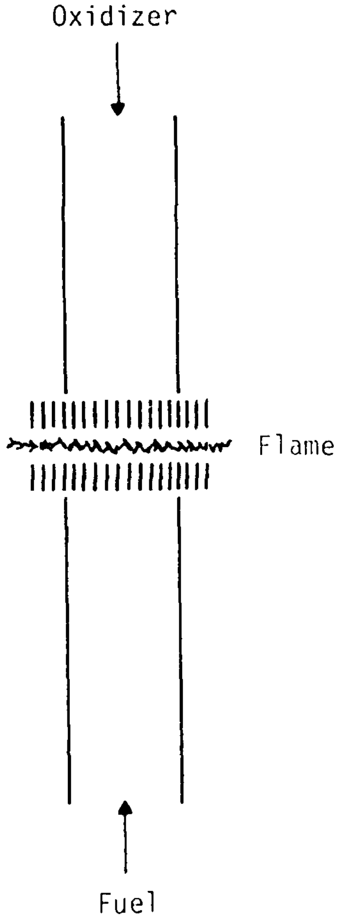

Figure 7. Counterflow Mixing Flame Experiment.

From a practical point of view, low-pressure flames are much easier to study than atmospheric flames. This results, in part, from the fact that low-pressure flames are stretched out in space. Thus, a reaction zone which is 1 or 2 millimeters thick in an atmospheric flame may be as long as a centimeter in a reduced-pressure flame. It is easier to characterize the sequence of important reactions in a flame in which the reaction zone is elongated. Much of the success of the splendid work by Biordi and coworkers can be attributed to the fact that they worked at approximately 0.04 atmosphere (Reference 7).

The extrapclation from low-pressure flames to real-world, atmospheric-pressure flames must be done with care. Since chemical processes are not linear functions of pressure, they are not easily extrapolated. However, the nonlinear dependence can be handled with relative ease by available computer algorithms. This fact alone is one of the most compelling arguments for complementing laboratory experiments with computer simulations.

2. Reynolds Number

The Reynolds number is a measure of the degree of turbulence of a flow. To a degree, turbulence (or lack of it) has already been taken into account by Figure 2. For example, one usually strives for laminar flow conditions in coflow flame experiments and for turbulence in counterflow experiments. Nevertheless, the degree of turbulence clearly can be an important parameter. In particular, as suggested earlier, the penetration of extinguishing agent into the body of a flame and the mixing of an agent with flame gases are strong functions of turbulence.

3. Reversed Flames

Curiously, although many experiments have been done with lean flames (i.e., slightly to the left of the stoichiometric mixture in Figure 2), the authors are not aware of any experiments corresponding to the far left of Figure 2. In such experiments, the oxidizer would be contained in the "burner" and would be injected into the fuel-rich environmental stream. It may be that no new understanding would be gained by exploring this region; however, the range of possibilities is intriguing. In this regard, it should be noted that real-world flames are fuel-rich except around the edges (where there is sufficient oxidizer to balance the fuel present). This accounts for the highly luminescent, sooty character of real-world flames. Since these characteristics make the fuel-rich portions of flames difficult to study with conventional techniques, they may account for the fact that few studies have systematically explored fuel-rich behavior. However, from the point of view of extinguishment, the fuel-rich zone may be the most important to study.

D. OVERVIEW OF LABORATORY STUDIES OF FLAME SUPPRESSION

Each flame type represented in Figure 2 has been used to study the effectiveness of halogenated fire suppressants. In premixed flames, the suppressant is usually introduced into the premixed fuel-oxidizer stream. However, no a priori reason exists to show why the suppressant cannot be mixed with the environmental stream. In diffusion flames, the suppressant can be mixed with either the fuel stream or the oxidizer stream (or both). The results of all experiments are surprisingly consistent; the amount of suppressant required to extinguish a flame is nearly independent of the stream into which the suppressant is introduced.

In many studies, the objective is limited to a determination of the amount (typically, mass fraction or mole fraction) of suppressant required to extinguish a flame. Usually, the extinguishment is observed visually. One exception is the H_2/O_2 flame. Because this flame is nearly invisible, some workers have used infrared detectors to sense extinguishment (Reference 8). A second exception is encountered in certain experimental setups in which the flame lifts off from the burner and takes up an equilibrium position some distance above the burner. Lift-off is often taken as the point of extinguishment (Reference 9).

In many other studies, the flame is not actually extinguished; rather, some characteristic of the flame (e.g., temperature, velocity, species concentration) is examined as a function of the amount of suppressant added, and inferences are drawn regarding the mechanism of suppression. The three most commonly used techniques for profiling the concentrations of important species in the flame are gas chromatography, mass spectrometry, and optical spectroscopy. The first of these is limited to the measurement of stable compounds, while both mass spectrometry and optical spectroscopy can detect both radicals and stable molecules.

E. MECHANISMS OF EXTINGUISHANT ACTION

Since the key reactive species in the principal chain branching reactions are the hydrogen and oxygen atoms, and since these reactions are endothermic, the flame may be extinguished by any process which either reduces the concentrations of these atoms or reduces the temperature of the flame (and thus reduces the energy available to drive the endothermic reactions). Table 1 lists mechanisms for fire extinguishing agents. Clearly, each interferes with the chemistry of the flame; nevertheless, it is convenient to consider the first four mechanisms as "physical" and the last as "chemical."

TABLE 1. EXTINGUISHANT MECHANISMS

Mechanism	Effect
Dilution	Reduces concentrations of reactive species
Vaporization	Absorbs energy from flame; reduces temperature
Heat Transfer	Absorbs energy from flame; reduces temperature
Translation	
Rotation	
Vibration	
Electronic Excitation	
Dissociation	Absorbs energy from flame; reduces temperature
Reaction	Removes reactive species from flame

By way of illustration, consider the chain branching reaction shown in Reaction [1]. Its rate equation is

$$\text{rate} = k[H][O_2] \tag{1}$$

where the square brackets, [ ], represent the concentration (e.g., moles/liter, molecules/cm^3, etc.) of the species in the brackets. Since the rate is proportional to the concentration of each of the reactants, any agent that dilutes the reaction mixture necessarily reduces the concentrations of the reactive species and, thus, reduces the rate of the reaction. At some point, the rate becomes so slow that the rate of generation of radicals falls below the rate of loss and the flame goes out.

An extinguishant not only dilutes the reactants in the flame, but also absorbs energy from the flame. In this process, energy is removed from the reactant species and the fraction of reactant molecules (and atoms) having enough energy to surmount the activation energy barriers is reduced. Once again, the consequence is a reduction in the rate of generation of radicals. The degree to which a particular molecule may act as a heat sink for thermal energy in the flame depends on the molecular properties of the heat-sink molecule. Vaporization is unique to liquid phase extinguishants. Once the extinguishant is in the gas phase, the energy from the flame may be transferred to translational, rotational, vibrational, and/or electronic degrees of freedom in the extinguishant molecule. The amount of energy that may be transferred to each molecule depends on its number of degrees of freedom and on the separation between the energy levels in each degree of freedom. By way of illustration, consider the molecules in Table 2.

Atomic species, such as He, have no rotational or vibrational degrees of freedom and have electronic energy levels so high in energy that they are virtually inaccessible in normal flames. Thus the atoms may absorb energy in translation but in no other degrees of freedom. Exceptions include the alkali metals, which have low-lying electronic energy levels and are, in fact, appreciably ionized in normal flames.

TABLE 2. MOLAR HEAT CAPACITIES OF REPRESENTATIVE GASEOUS EXTINGUISHANTS.[a]

Extinguishant	Heat Capacity at 298 K, J/K-mole	Heat Capacity at 1900 K, J/K-mole
He	20.79	20.79
N_2	29.12	35.80
H_2O	33.59	50.50
CO_2	37.13	60.05
CF_4	61.05	105.28
CF_3Br	69.33	105.94
CCl_4	83.40	107.14

[a] Reference 3.

The average translational energy of an atom or molecule depends only on its temperature. Thus, if both hydrogen atoms and CF_3Br molecules are in thermal equilibrium in a flame, both will have the same kinetic energy. With respect to translational energy alone, both H atoms and CF_3Br molecules are equally good thermal sinks; however, hydrogen atoms will have much higher velocities and can, therefore, transport energy much more rapidly than can CF_3Br molecules. On the other hand, CF_3Br molecules have degrees of freedom which hydrogen atoms do not have.

Linear molecules, such as N_2 and CO_2, have two rotational degrees of freedom, while the remaining molecules in Table 2 are nonlinear and have three rotational degrees of freedom. As expected, the molar heat capacities of these species are significantly greater than those of helium.

The number of vibrational degrees of freedom may be calculated by the formulas 3N-5 for linear molecules and 3N-6 for nonlinear molecules, where N is the number of atoms in the molecule. However, it is not sufficient to simply know the number of vibrational degrees of freedom; one must also know the energy of each vibrational energy level. With this information, one can estimate the ratio of molecules in an excited vibrational energy level to those in the ground state by the Boltzmann distribution formula $e^{-\Delta E/0.695T}$, where ΔE is the energy of the vibrational energy level expressed in wavenumbers, cm^{-1}, and T is the absolute temperature expressed in degrees Kelvin. As a rule of thumb, if ΔE (in wavenumbers) is one half T (in Kelvin units), the ratio of molecules in the excited state to those in the ground state is approximately one half (48.7 percent). Moreover, since the vibrational frequency of a particular mode is inversely related to the square root of the reduced mass, it follows that molecules with heavy atoms will have a larger number of low-energy vibrational modes and thus have a larger molar heat capacity than lighter molecules with the same number of atoms. In this light, one can understand why CF_3Br has a larger molar heat capacity than, for example, CF_4.

The dissociation of a molecule typically requires a substantial input of energy. For this reason, dissociation rarely serves as a significant heat sink.

By contrast with the four physical extinguishment mechanisms described in the preceding paragraphs, the chemical mechanism actually removes key free radicals from the flame. Perhaps the most thoroughly studied of the chemical fire suppressants is Halon 1301, CF_3Br. Despite considerable debate on the detailed extinguishment mechanism, it is generally agreed that the first step is the abstraction of the bromine atom by a hydrogen atom.

$$CF_3Br + H \rightarrow CF_3 + HBr, \Delta H(298\ K) = -76\ kJ \qquad [9]$$

This reaction is then followed by a set of reactions such as the following.

$$H + HBr \rightarrow H_2 + Br, \Delta H(298\ K) = -70\ kJ \qquad [10]$$

$$Br + HR \rightarrow HBr + R, \Delta H(est, 298\ K) = 46\ kJ \qquad [11]$$

In Reaction [11], HR represents a fuel molecule from which the bromine atom abstracts a proton. The net result is the catalyzed recombination of H atoms to form H_2 gas (Reaction [12]).

$$H + H \rightarrow H_2,\ \Delta H(298\ K) = -436\ kJ \qquad [12]$$

Reactions [9] through [11] thus interfere with the key chain branching reactions in which hydrogen atoms react with oxygen molecules (Reaction 1). The authors do not have information at hand which indicates the relative importance of the direct removal of H atoms (Reaction [9]) and the catalytic recombinations (Reactions [10] and [11]); however, computer modeling would provide a good indication of their relative importance.

The bromine atoms from the halon catalyze the hydrogen atom recombination. Each bromine atom is used over and over owing to recycling reactions such as those shown in Reactions [13] and [14]. The exceptional effectiveness of halons is attributable to this catalytic process.

$$Br + Br + M \rightarrow Br_2 + M,\ \Delta H(298\ K) = -224\ kJ \qquad [13]$$
$$H + Br_2 \rightarrow HBr + Br,\ \Delta H(298\ K) = -143\ kJ \qquad [14]$$

Being very exothermic, Reaction [14] accounts for the fact that, while Br_2 is an end product of the extinguishment process, the concentration of molecular bromine is very small in flames.

Of course, the extinguishment mechanism is more complex than suggested by the above equations. Other reactions, such as the following, certainly contribute as well.

$$R + Br_2 \rightarrow RBr + Br,\ \Delta H(298\ K) = -69\ kJ \qquad [15]$$
$$CF_3Br + Br \rightarrow CF_3 + Br_2,\ \Delta H(298\ K) = 67\ kJ \qquad [16]$$

The importance of the CF_3 radical in the extinguishment of flames is less clear. Among the several plausible reactions are the following, which have been deduced from products found in typical flames.

$$H + CF_3 + M \rightarrow HCF_3 + M, \Delta H(298\ K) = -445\ kJ \qquad [17]$$
$$OH + CF_3 \rightarrow OCF_2 + HF, \Delta H(est,\ 298\ K) = -339\ kJ \qquad [18]$$

In addition, CF_3Br may react directly with other important radicals in the flame.

$$O + CF_3Br \rightarrow CF_3 + OBr, \Delta H(est,\ 298\ K) = +56\ kJ \qquad [19]$$
$$OH + CF_3Br \rightarrow CF_3 + HOBr, \Delta H(est,\ 298\ K) = +60\ kJ \qquad [20]$$

The effectiveness of halogenated fire suppressants increases as the atomic weight and number of halogen atoms increase. Effectiveness increases in the following order: F < Cl < Br < I. Furthermore, a molecule containing two atoms of a given halogen is usually more effective than a molecule containing only one (Reference 10).

The relative importance of the physical and chemical mechanisms has been strongly debated. Perhaps because much of the work has been done by chemists, the majority of the published works have emphasized the chemical mechanism. However, advocates of the physical mechanisms periodically point out that most of the available fire suppression data can be correlated without the need to invoke chemical processes (References 11, 12). It should be noted in this regard that the ability to correlate fire suppression effectiveness with the physical attributes (notably, the molar heat capacity) of a fire suppression agent does not necessarily abrogate the need to invoke a chemical mechanism. The molecules that have the highest molar heat capacities are precisely those that contain the heavy atoms (Br and/or I), which are important in the chemical mechanism.

F. OPTICAL TECHNIQUES

Of the many techniques available for exploring the chemistry of extinguishants in flames, optical techniques, being nonintrusive, are particularly attractive. Table 3 lists the four principal techniques along with their characteristics.

In addition to being nonintrusive, the techniques listed in Table 3 share other characteristics. Spatial resolution of optical techniques is typically of the order of 1 millimeter or better. In addition, by using pulsed lasers (or other gating techniques), time-resolved results can be obtained. The techniques also share the ability to determine the temperature of the flame, often simultaneously determining the concentration of one or more species. An excellent review of laser techniques is contained in a paper by Penner and coworkers (Reference 13).

TABLE 3. PRINCIPAL OPTICAL TECHNIQUES

LASER ABSORPTION SPECTROSCOPY	Measures concentrations directly
LASER INDUCED FLUORESCENCE (LIF)	Suitable for minor constituents (≈ 10^{11}/cc) Quantitative work requires treatment of collisional quenching
SPONTANEOUS LASER RAMAN SPECTROSCOPY	Signal is linear with number density Signal is not perturbed by collisional quenching Not suitable for sooting flames
COHERENT ANTISTOKES RAMAN SCATTERING (CARS)	Suitable for major constituents (≈ 0.5%) Can be used in sooting flames

1. Laser Absorption

This is conceptually the simplest of the techniques. Each photon in a laser cavity passes through the gain medium several times. The principal problems with this technique stem from the fact that, to measure small concentrations of a species, it is necessary to compare two large signals. One technique for improving the sensitivity of laser absorption experiments is to include the flame in the cavity, thus using the absorption of the species of interest to spoil the gain at the absorption wavelength. This method is explained as follows. As a photon passes through the gain medium, it stimulates the emission of one or more additional photons (thus the name, "light amplification by stimulated emission of radiation, laser"). If one places a gas, such as a flame, which absorbs photons at the laser wavelength, between the laser mirrors, the gas will absorb photons that would otherwise stimulate emission of additional photons at the same wavelength. The net result is termed "spoiling the gain" of the laser, and it results in a much larger decrease in the size of the observed signal than would be the case if the output of the laser were simply passed through an absorbing flame.

2. Laser-Induced Fluorescence

LIF is intrinsically the most sensitive of the techniques. Since collisional quenching competes with radiative decay of the excited state, it has been necessary to develop complex experimental and/or data reduction techniques in order to permit quantitative estimates of the concentrations. One technique uses laser power sufficient to saturate the absorption. This is relatively easy for atomic species, much more difficult for diatomic molecules, and essentially impossible for polyatomics. Among the species that have been measured by LIF are OH, CH, CO, C_2, NH_2, and CN.

3. Raman Spectroscopy

Raman techniques (spontaneous Raman and coherent Anti-Stokes Raman spectroscopy) are potentially more versatile than either laser absorption or laser-induced fluorescence spectroscopy since virtually all molecules and many atoms have accessible Raman transitions. The principal drawback of the Raman techniques is their lack of sensitivity. These techniques are, therefore, used almost exclusively for principal species such as N_2, O_2, H_2, fuels, and extinguishants.

4. Other Optical Techniques

Because no single technique mentioned above is ideally suited for characterization of flames, intense activity over the past decade to develop additional optical techniques has resulted.

A case in point is the optogalvanic technique for detection of atomic oxygen and hydrogen (References 14, 15). In this technique, the atom is ionized by multiphoton absorption and detected by a biased microprobe in or near the flame. Concentrations as low as a few parts per million can be detected. Thus, this technique appears to have substantially greater sensitivity than Raman or LIF techniques for these atoms.

G. OTHER EXPERIMENTAL TECHNIQUES

1. Other Diagnostic Techniques

Much of the early work on characterizations of flames used spectroscopic techniques to identify the important species and their flame distributions. Then, with the advent of gas chromatography, this technique was used to good advantage to make quantitative estimates of the fixed gases (O_2. N_2, CO, CO_2, light hydrocarbons, etc.) in the flame. At about the same time, mass spectrometry was introduced as a diagnostic technique, and it dominated the area throughout the 1970s. As described in detail below, mass spectrometry is an intensive method, but it has the advantage of being able to detect both transient species (ions and free radicals) and stable species. Finally, it should be noted that somewhat more esoteric techniques, such as electron paramagnetic resonance (EPR), are useful in instances in which specific physical properties, such as densities of unpaired spins, are of interest.

2. Alternatives to Flames

Because of the inherent complexities of flames it is often useful to abandon flames altogether and adopt techniques in which variables of interest can be carefully controlled. Of particular note are experiments conducted with flow tubes, shock tubes, and molecular beams. These experiments are especially well suited for measurement of the rates of individual flame reactions.

The value of flow tube experiment stems from the ability to prepare a reactant of interest (often a radical) upstream of the reaction zone. In the reaction zone, a second reactant is introduced. The course of the reaction is then followed as the reaction mixture continues to flow down the tube, and the rate of the reaction is inferred from the rate of decay of one of the reactants or from the rate of appearance of a product. A variety of diagnostic techniques can be used to measure the concentrations of the species of interest.

Molecular beam experiments share many of the characteristics of flow tube experiments except that they are performed at much lower densities and are not perturbed by wall effects. In an especially difficult experiment, one molecular beam may be crossed with another molecular beam. Alternatively, a molecular beam may be injected into a reaction zone containing a stagnant reactant gas (at low pressure, of course). Because of the low densities characteristic of molecular beam experiments, very sensitive diagnostic techniques, such as mass spectrometry and laser-induced fluorescence, must be employed.

Shock tube experiments, like molecular beam experiments, require highly specialized equipment. Since temperatures equal to those observed in flames are easily achieved in shock tubes, shock tube experiments are especially well suited for measuring the temperature coefficients of reactions in temperature ranges of importance in flame chemistry. By using fast optical techniques, the experimentalist can measure concentrations of important species even though the duration of a typical experiment is very short.

3. Characterization of Flame Flow Fields

The characterization of small-scale and large-scale turbulence in flames has a rich history and has been of extraordinary importance in improving combustion efficiency. Modern techniques use lasers to illuminate small particles in the flames. Provided the particles are small enough, they follow the flow of the gases in the flame. Particularly noteworthy are the experiments in which $TiCl_4$ is premixed either with the fuel or with the oxidant. The water naturally present in the flame reacts with the $TiCl_4$ to form small TiO_2 particles which, in turn, scatter the laser light, which enables one to observe the formation and evolution of turbulent structures in the flame.

SECTION III

CONCLUSIONS AND APPROACH

A. SCOPE OF THE PERTINENT LITERATURE

Because of the significant level of experimental activity over the past four decades, the literature contains several hundred papers pertaining directly to the extinguishment of flames by halogenated agents. When one adds the papers that treat general combustion and flame characterization and diagnostic techniques, the total number of papers is immense. For this reason, it is important that new research efforts be thoroughly examined before initiation and that experimental details be assessed by a comprehensive technology review.

B. TEMPERATURE MEASUREMENT

Although time and spatially resolved measurement of the temperature in a flame is not a trivial task, several techniques have been well worked out. The earliest methods used thermocouples, which can be made quite small and can be coated to prevent catalytic and/or reactive effects. The results can be corrected for radiation losses. Laser-optical techniques, especially laser Raman and Coherent Anti-Stokes Raman (CARS), are nonintrusive. These technologies take advantage of the fact that for a molecule in equilibrium in the flame, the relative populations of the various energy levels are directly related to the temperature. A recent technique combines physical (intrusive) sensing with optical monitoring. In this technique, a very thin silicon carbide filament is placed in the flame, and optical pyrometric methods are used to determine the radiant emission temperature at each location along the filament.

C. TECHNIQUES FOR CHARACTERIZING FLAME SPECIES

Although one thinks in terms of the use of nonintrusive techniques to replace the older intrusive ones, nonintrusive optical techniques actually predate intrusive methods for characterizing flames. Thus, flame emission spectroscopy is a traditional method for characterizing species present in various flame zones. Early on, this method was complemented with optical absorption experiments. A summary of much of this early work is contained in a book by Gaydon and Wolfhard (Reference 2).

Relatively recently probes have been inserted into flames to remove species from selected flame locations. Two quite different types of probes have been used. Microprobes, which are very thin and long, are well suited for removing stable molecules but not for sampling radicals or ions (since these react on the walls of the probe before reaching the analytical instrument). Large probes, with diameters of up to 1 centimeter, can be used to sample both stable species and radicals. In these latter probes, the flame species are drawn through a small orifice into the evacuated interior of the probe, thus forming a molecular beam that does not impinge on the walls of the probe and within which the various species do not collide.

The diagnostic instrument of choice for the microprobe experiments is the gas chromatrograph since it is well suited for separating and detecting small, stable molecules. The mass spectrometer is the instrument of choice for the molecular beam probe experiments. This instrument couples very high sensitivity, needed to detect species in the relatively low density molecular beam, with the ability to register both stable molecules and transient species such as radicals.

The application of molecular beam mass spectrometry to the characterization of flames peaked in the 1970s, and excellent work using this technique continues to the present. In recent years, attention has turned to laser-spectroscopic techniques because of their nonintrusive nature and their potential for high spatial and temporal resolution. Caution is warranted, however. These techniques, powerful as they are, have not proven to be suitable for all tasks. It should be noted, for example, that spectroscopic monitoring of oxygen and hydrogen atom concentrations is difficult at best. Since the atoms absorb in the vacuum ultraviolet region of the spectrum, atmospheric gases must be rigorously excluded from the optical path. Even with this precaution, it may not be possible to monitor these atoms because of the strong absorption of normal flame components (O_2, N_2, etc.) in the vacuum ultraviolet region of the spectrum. Clear exceptions are shock tube and some reduced pressure experiments in which the flame gases are controlled to assure optical transparency at the wavelengths where hydrogen and oxygen atoms absorb.

Of all the optical techniques, laser-induced fluorescence (LIF) is the most sensitive. This technique is well suited for atoms and such small molecules as OH. The prerequisite for any fluorescence experiment is the existence of a suitable absorption band, one which permits excitation of the fluorescing state in the molecule (or atom) of interest. To excite the two most important flame species, hydrogen and oxygen atoms, one must use either multiphoton excitation or traditional vacuum ultraviolet atomic resonance fluorescence techniques. The latter technique is particularly applicable to shock tube studies, where it is easy to rigorously exclude air from the optical path.

While fluorescence techniques are well suited to some atoms and small molecules, laser Raman techniques have been applied to a large number of molecules and even to some atoms. The general applicability of Raman techniques stems from the fact that the species of interest is excited to a virtual state; the existence of a real state to which the species can be excited by the available laser wavelength is not required. This fact also accounts for the most severe limitation of laser Raman techniques: They are not very sensitive. Of the two most common Raman techniques, CARS differs from the simpler Spontaneous Raman spectroscopy in that the CARS signal is coherent and emitted in a single direction. This gives CARS the potential for greater sensitivity. In addition, CARS can be applied to sooting flames, where other techniques are severely degraded. The applicability of CARS to sooting flames is especially significant since the addition of a halon generally increases the visible luminescence and soot generating characteristics of a flame.

Since Raman techniques are significantly less sensitive than fluorescence techniques, the former are best for examination of major flame species, but are not well suited for trace species. Consequently, much of the important chemistry can only be inferred from Raman experiments, while fluorescence techniques, at least in principle, permit direct observation of all species involved in the most important elementary reactions.

D. NUMERICAL MODELING

The inherent limitations of the available observational tools are of less importance today than they were in the past because of the substantial advances in numerical modeling of flames. Present models can include not only all of the elementary chemical reactions known to be important, but also the molecular and thermal transport processes for the flame species. As a result, it is possible to draw inferences from available experimental data with increasing confidence. Indeed, while one still would like to measure all of the species involved in elementary reactions, it now may be possible to gain sufficient insight from the measurement of a subset. In particular, one may ask whether it is adequate to couple a Raman technique (for the measurement of fuel, oxidizer, and extinguishant) with LIF (for the measurement of OH) and computer modeling (to fill in the missing information about hydrogen atom and oxygen atom concentrations, mechanisms, etc.).

E. MECHANISMS OF EXTINGUISHMENT

Both physical and chemical mechanisms are believed to contribute to the extinguishment of flames by halons; however, the relative importance of each mechanism is debatable. Moreover, even though it is possible to draw a correlation between extinguishment efficiency and such physical properties as heat capacity, the importance of a chemical mechanism (which also correlates with physical properties) cannot be discounted. An obvious experiment, one which would shed light on the relative importance of the two mechanisms, would compare the extinguishment efficiency of a preheated halon sample with that of a room temperature sample.

Substantial evidence supports the conclusion that the principal role of CF_3Br is to provide bromine atoms which, in turn, catalyze the recombination of hydrogen atoms. It has also been suggested that, under some conditions, CF_3Br reacts with the OH radical (Reference 9) as shown in Reaction [19], although the evidence is much less conclusive. Further exploration of the importance of this reaction should be pursued using flow tube, bulb, or beam experiments. Frozen argon matrix isolation experiments might be considered as well. For these experiments, one may consider the thoroughly explored reaction of hydrogen atoms with NO_2 as a source of OH radicals (Reference 16).

$$H + NO_2 \rightarrow OH + NO \qquad [21]$$

One could monitor the disappearance of OH in a bulb or flow-tube experiment or search for reaction products by matrix isolation.

Though hydrogen bromide is a principal product of this experimental system, hydrogen fluoride is only a minor product. This observation suggests that Reactions [20] and [21] are but a part of a much more complex dynamic process. Important reactions leading to the production of HBr probably include the bromine abstraction reactions [9] and [13], although the direct involvement of the H_2 molecule cannot be entirely discounted.

A summary of the present understanding of chemical extinguishment mechanisms follows: A principal mechanism is the catalytic recombination of hydrogen atoms by bromine atoms; however, this reaction may not be dominant at all stoichiometries. An alternate mechanism could be important in the less studied fuel-lean region (Figure 2), which characterizes the boundary g50ween a "natural" fire and the environment. In this context, it is likely that a search for alternative mechanisms may prove of great value.

F. TIME-RESOLVED EXPERIMENTS

Flame experiments conducted to date have been steady-state, where the effect of introducing the extinguishing agent has been studied as a function of the amount of extinguishant added. Many of these experiments have been done very well, and it would be of little value to repeat them. On the other hand, in order to understand fully the role the extinguishant plays, it is essential to resolve the elementary reactions physically and to learn their reaction rates and temperature dependence. By doing so, intelligent alternatives to the simple halons might be identified. Such experiments are not straightforward; nevertheless, worthwhile approaches may involve the use of molecular beams or flow systems. Both of these techniques are powerful but instrumentation and manpower intensive. In addition, both require considerable preparatory work before appropriate combinations of reagents and conditions can be established. This preparatory work could consist of a set of bulb experiments in which early reaction products of reactive free radicals, such as H, OH, Br, Cl, and I, are allowed to combine with halons. These radicals may be prepared by discharge methods or by laser multiphoton dissociation of precursors. Analysis of the products by infrared (IR) spectroscopy, mass spectrometry (MS), or gas chromatography (GC) will allow identification. Another technique particularly suited to free-radical studies is electron paramagnetic resonance (EPR). Coupled with a flow system, EPR can give quantitative estimates of radical concentrations.

G. ALTERNATE EXTINGUISHMENT MECHANISMS

To this point, the emphasis has been placed primarily on experiments that focus on the extinguishment mechanism in which the concentration of hydrogen atoms is sharply reduced. However, it would be wise to complement these experiments with a set of experiments that focuses on the reduction of hydroxyl free radicals. Two factors commend this approach. First, it is known that the O/H/OH system is essentially in equilibrium in the flame. Thus, any agent that reduces hydroxyl concentration (or oxygen atom concentration) will also reduce the hydrogen atom concentration and thus extinguish the flame. Second, the primary mechanism for destruction of potential depleters of stratospheric ozone during their passage through the troposphere is reaction with hyroxyl radicals. (Photolysis by wavelengths longer than 300 mm also plays an important role.) Thus, any agent that reacts with the hydroxyl radical not only should be an effective fire suppressant but also should be prevented from reaching the stratosphere by reactions with hydroxyl radicals in the troposphere. Indeed, it is conceivable that an agent that reacts with hydroxyl radicals as its primary extinguishment mechanism may not be a threat to the ozone layer. While such a research program is admittedly of higher risk than programs that focus on modification of conventional halon suppressants, such a program could provide the "ultimate" solution to the current ozone depletion problem.

SECTION IV
EXPERIMENTAL PLAN

A. RECOMMENDED PROGRAM

The objective of this program is to provide a fundamental understanding of the microscopic processes that result in flame extinguishment by halons, and to verify experimentally the applicability of these microscopic processes to candidate next-generation fire suppression agents. The program consists of four elements: (1) construction of an information data base, (2) an investigation of the relative importance of physical and chemical processes in halon extinguishment, (3) flame extinguishment diagnostics and characterization, and (4) time-dependent studies of free-radical reactions.

1. Information Base

The first element of the program is to codify the flame extinguishment information base that has already been created and to develop a methodology for continual information base expansion during this project. Because of the large volume of literature, simple paper collection is insufficient to ensure access to needed extinguishment information. The proposed Information Base will be generated using an existing data base management system (Software "REF-11" by DG Systems is proposed) and will provide the user with ready access to the literature. In the Information Base, the papers will be indexed as follows:

Type of investigation (experimental, computational, ...)
Extinguishant (CF_3Br, CF_2BrCl, ...)
Experimental technique (Mass spec., Raman, LIF, ...)
Species monitored (O_2, N_2, H, O, OH, CF_3, ...)
Microscopic process (cooling, H-atom recombination, ...)

The Information Base will be prepared for PC desk-top computer use and will be available to users on 5 1/4 inch floppy disks.

2. Physical Versus Chemical Mechanisms

The second element of the program will investigate the relative importance of the physical and chemical extinguishment mechanisms. The experimental study will take advantage of the fact that the amount of heat that can be removed from a flame by an extinguishant is inversely related to the initial temperature of the extinguishant. Extinguishants at various initial temperatures will be injected into the flame, and the relative extinguishment efficiencies will be compared. An early decision in this element of the program will be whether to use a premixed or diffusion flame for these studies. At the time of this writing, it appears that a diffusion flame may be more suitable.

The vital importance of this element of the program stems, at least in part, from the fact that very little is known about the relative importance of physical versus chemical extinguishment mechanisms. If on the one hand, the chemical mechanism is dominant, then the thrust of future research must place strong emphasis on understanding chemical mechanisms and searching for alternate chemical mechanisms. If, on the other hand, the physical mechanism is dominant, it may be relatively easy to abandon those molecules that contain those atoms (bromine and chlorine) most deleterious to the ozone layer. Thus the course of future research will be strongly dependent on the findings of this element of the program.

3. Flame Extinguishment Characterization and Diagnostics

The third element of the program will provide the ability to make partially resolved measurements of the temperature and principal species in flames. Laser Raman spectroscopy will be used to obtain temperature and major species concentrations, and laser-induced fluorescence (LIF) will be used to monitor the OH radical concentration. CF_3Br (Halon 1301) will be the primary agent studied. Study of other agents appears to be important in view of recent electric discharge supported flame studies in which it has been found that Halon 1211 is much more readily fragmented than Halon 1301.

4. Free-Radical Reactions

The investigation of free-radical reactions can be conveniently divided into three parts.

a. Investigation of Hydrogen Atom Depletion Mechanisms

In this part, the current understanding of presently proposed mechanisms will be extended. Attention will be given not only to the primary species (chlorine and bromine atoms), which are important in fire extinguishment, but also to secondary species such as the CF_3 radical, which appear to be important. Evidence for catalytic cycles will be sought and the number of cycles per catalytic molecule will be determined.

b. Investigation of Molecules Susceptible to Hydroxyl Scavenging

In this part, chlorine- and bromine-containing molecules that have been modified to be susceptible to hydroxyl radical attack (in the troposphere) will be studied. Of particular importance is the relative effectiveness of these molecules as compared with conventional extinguishants (Halon 1301 and 1211).

c. Search for Molecules that Scavenge Hydroxyl Radicals

This is the long-range part of the study and involves the front end of a search for agents that use an entirely different mechanism to extinguish flames. Since many molecules are known to extinguish flames, but the mechanisms are known for only a few, it may be that this work will elucidate the mechanisms for molecules already known to be effective and thus shed light on the process of selecting new molecules for study as possible "ultimate" replacements for current agents.

Identification and characterization of the initial reactions between halons and flame reactive intermediates, most notably H and OH, will add to and elucidate the existing knowledge of the primary extinguishment events. It is proposed that this portion of the study consist of two stages. The first of these is a set of static gas experiments in which H or OH free radicals are generated from appropriate precursors by multiphoton dissociation with a laser. Halons will be introduced into the chamber at various pressures so that early reaction products can be identified. For instance, it will be particularly significant to identify HBr at low halon pressures and, if possible, products of CF_3, such as C_2F_4. The results of these experiments will provide guidance for the more complex, but more informative, Phase III studies. These will consist of molecular beam or flow experiments using oriented clusters of reagents. Such experiments will allow free-radical reactions to be conducted under very controlled conditions. In the molecular beam case, clusters will be prepared and characterized in a supersonic nozzle, pulsed, and analyzed with time-of-flight mass spectrometry or laser-induced fluorescence. Various combinations of halons with fuel or oxidizer with pulsed radical generation will permit elucidation of the detailed role that halons play in extinguishment.

In this element of the program, we will also develop diagnostic matrix isolation tools for studying such transient species as the CF_3 and CF_2 radicals. A series of experiments designed to shed some light on the importance of CF_3 is planned using matrix isolation Fourier Transform Infrared (FTIR) spectroscopy. In these experiments, the CF_3 radical is generated in a molecular beam by an electric discharge through an argon/CF_3Br mixture. The CF_3 (and other products) are trapped in frozen argon and examined in the infrared. By adding varying amounts of H_2 to the discharge, it is expected that information about fluorine abstraction reactions, such as those shown below, will be obtained.

$$CF_3 + H \rightarrow CF_2 + HF \qquad [22]$$

$$CF_2 + H \rightarrow CF + HF \qquad [23]$$

B. FACILITIES

1. Information Base Construction and Modeling Support

Zenith Model 150 desk-top PC computers are available for creation, storage, and manipulation of information files. The computers are tied into the University of New Mexico Chemistry computer system consisting of two MicroVAX II computers. One computer has an ULTREX 1.2 operating system and the other has a VMS version 5.0 operating system. The Chemistry Department system is part of a local ether net, which is, in turn, tied into the University of New Mexico Broad-Band LAN system. The local desk-tops have access to the the Department of Defense TECNET system and, through the University system, New Mexico Rio Grande Corridor Tecnet, BITNET, and Internet. The local system also has access to online Chemical Abstract Services and to the University of New Mexico computerized library catalog.

2. Physical Versus Chemical Mechanism Studies

A fire laboratory is available on the University of New Mexico main campus. This laboratory contains a cup burner apparatus, which will be used for diffusion flame, liquid fuel experiments involving preheated agents.

3. Flame Studies

A laser Raman spectrometer with a burner attachment has been set up. The apparatus also performs well for collection of emission data from hot flames and fluorescence spectra. The apparatus, consists of a laser light source, a monochromator, a detector, and data acquisition and storage electronics. A sample cell, laser optics, and sample-to-monochromator coupling optics are also present. A high power argon ion laser has been chosen as the light source, a triple monochromator with high stray light rejection is used, and an Optical Multichannel Analyzer (OMA) is employed as the detector.

The Coherent, I-52-4 wavelength-selectable, Argon Ion laser can produce a nominal 4 watts of continuous lasing in the multiline mode, and approximately 1.8 watts in the single-line modes at 488 nanometers and 514.5 nanometers. A Spex model 1877 spectrometer provides light dispersion. Triple monochromators, such as this one, are ideal for Raman spectroscopy and for multichannel detectors since they provide high stray light rejection for Raman experiments and a flat, undistorted focal plane for the detectors.

The coupling of the Raman signal generated by the laser beam to the monochromator slit requires two high reflectivity, first-surface mirrors, a 7.5-centimeter quartz lens, and a 350-nanometer band pass filter. The two mirrors are used to move the horizontal path of the laser beam as it passes through the flame to the vertical direction of the monochromator slit. This configuration allows for maximum filling of the slit.

A filter is placed in the optical path to block the OH emission spectrum in the 600 to 700-nanometer spectral range. The shift in the OH spectrum from its normal 300- to 600-nanometer spectral range to these higher wavelengths can be attributed to the passage of the second-order spectrum of the gratings. Since the gratings in this monochromator are designed to be used in first order, the higher-order spectra can normally be ignored unless the intensity of the spectral species is very high.

4. Free-Radical Reaction Investigations

The free-radical investigations will employ a photoionization mass spectrometer using an excimer pumped dye laser for performing multiphoton dissociation and GC or GC/MS for sample analysis. A completely equipped laboratory is available; however, for some specific experiments, reconfiguration may be needed. Construction of a pulsed nozzle and completion of a time-of-flight mass spectrometer are planned.

A matrix isolation apparatus using FTIR as a probe is available for work involving matrix isolation of free radicals and their products.

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