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FLAME INHIBITION RESEARCH

FINAL REPORT

1 NOVEMBER 1960 — 30 JUNE 1965

by

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

FLAME INHIBITION RESEARCH

FINAL REPORT

INTRODUCTION

The Johns Hopkins University Applied Physics Laboratory has had an interest in combustion for many years and has developed a number of techniques for studying flame structure. In November 1960, a program was initiated to apply these techniques to a study of flame inhibition. It was intended to be a small effort parallel to, and drawing on, the more extensive studies of transport coefficients and chemical kinetics supported by the Applied Physics Laboratory and the Advanced Research Projects Agency. The Flame Inhibition Research Program was supported by the U. S. Army Engineering Corps, Fort Belvoir, from 1 November 1960 to 31 October 1963 and from 1 July 1964 to 30 June 1965. Support from the Research Center of the Applied Physics Laboratory allowed the program to be continued between 1 November 1963 and 30 June 1964.

The following section of this report (Background) was adopted from the original program outline and is similar to that found in the quarterly progress reports listed in Ref. 1. It is hoped that this material will aid the unfamiliar reader in following the program without extensive references. The Annual Progress Reports that follow give a historical survey of the accomplishments of the program which are summarized in the Conclusion. For more detailed information on the work done, the reader is referred to the List of Publications which resulted from this program.

BACKGROUND

The goal of these studies was to obtain a better understanding of the mechanism of flame inhibition as a step toward a theory that would permit quantitative predictions.

The research program used flame-structure techniques to determine the detailed microstructure of normal and inhibited flames. These techniques have been discussed in the literature and offer certain advantages for studying chemical reactions: (1) flames offer a steady state for study, (2) there is no wall problem, and (3) there are no mixing problems for studying fast reactions. The disadvantages are: (1) data analysis is complex and (2) high precision is required of the data for obtaining kinetic information. These techniques nevertheless offer an excellent method for studying fast, high-temperature reactions and, in particular, they offer the ideal technique for studying flame inhibition reactions in situ.

To characterize a flame system, it is necessary to specify at least $N + 1$ variables, where N is the number of molecular species. The independent variable usually chosen is distance through the flame front, while the dependent variables are composition, temperature, velocity, or area ratio. Experimentally, it is common to classify the profiles in four categories according to the techniques required to measure them. These are: composition profiles, atom-radical concentration profiles, temperature profiles, and aerodynamic profiles. An example of such a set is given in Fig. 1.

From the chemical standpoint, composition profiles provide the most important information. The most satisfactory technique developed for making the studies that result in this information is microprobe sampling followed by mass spectral

- 2 -
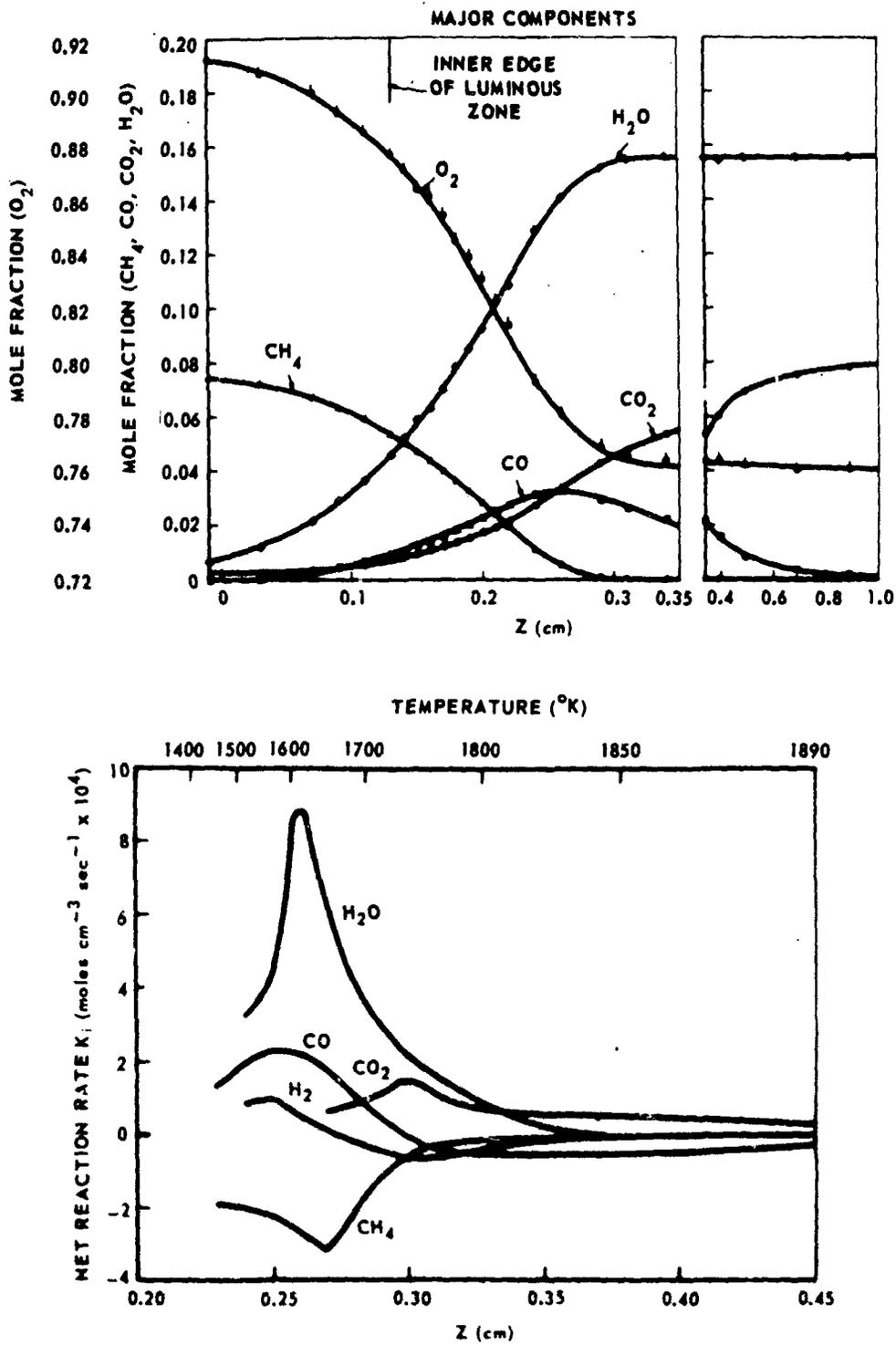
Fig. 1 CHARACTERISTIC PROFILES FOR A METHANE-OXYGEN FLAME.

analysis. The technique consists of withdrawing a sample of gas
from the flame using a small, tapered quartz probe. The probe
can be made small enough so that its effect on the flame is neg-
ligible, and the combination of low pressure as well as rapid
pressure and temperature drop quenches the sample. The gas flows
directly into a mass spectrometer where the composition is deter-
mined.

Logically, atom-radical concentration flame studies
are part of the concentration profile determinations. However,
since their study requires special techniques, they are usually
considered separately.

Temperature profiles are an important parameter for
characterizing flame fronts. Three methods have been used at this
Laboratory: thermocouple traverses, aerodynamic measurements,
and pneumatic probe measurements. Their data are in essential
agreement, although of varying precision.

Flames can be characterized aerodynamically by two
profiles, velocity and area ratio. The area ratio is simply the
geometry of the stream tubes of flow through the flame front.
In the general case it is necessary to make this measurement since
stream-tube expansion through the flame is appreciable. With a
symmetrical geometry such as the spherical flame this measurement
is the geometry of the position determinations. Direct aerody-
namic measurements are made by introducing MgO particles as a
tracer and photographically visualizing their paths through the
flame front, using a Zr flashbulb for the stream-tube measurements
and a pulsed electronic flashlamp for the direct velocity measure-
ments.

Flame systems have relatively complex chemistry, which
makes the identification of the dominant reactions difficult.
For this reason it was desirable to supplement the flame work with

- 4 -

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studies of the individual reactions with simplified chemistry. These could be made at lower temperature, thus permitting more precise estimates of the activation energy.

Prior to interpretation of flame-structure information, it is necessary to calculate the flux profiles and rates of species and heat production profiles by quantitatively accounting for the effects of molecular diffusion and thermal conductivity. The calculation is based on the flame equations that consist of conservation laws and the differential equations of transport and chemical kinetics.

Transport coefficient information is necessary for quantitative interpretation of flame-structure data. The required data are the binary diffusion coefficients for the species being studied and the thermal conductivities of the mixtures. The multi-component diffusion coefficients necessary for the interpretation of such systems are a complex function of all of the binary diffusion coefficients. To avoid this problem it is usual to choose systems in which one species can be considered dominant; in this case the true multicomponent diffusion coefficients can be accurately approximated by a set of binary diffusion coefficients of the individual species with the dominant species. The principal problem is to obtain precise, reliable data at sufficiently high temperatures to be useful in the flame studies. A new technique has been developed at APL, which allows such measurements. Diffusion coefficient data are available for the methane-oxygen system.

Interpretation of the experimental flame structure consists mainly of deriving chemical kinetic data. The analyses also provide data on rates and fluxes of enthalpy and the various molecular species. Such a description is unambiguous and complete, but if the information is to be useful on other systems it is necessary to deduce the detailed reaction scheme and derive the

- 5 -

appropriate kinetic constants, activation energies, and steric factors. This step is largely an art, since in a real system all possible reactions occur to some extent. What is desired is to provide a description of the dominant reactions. For this reason there may be several interpretations with varying levels of sophistication and complexity. For flame inhibition work, what is usually desired is the simplest possible interpretation consistent with a quantitative description.

ANNUAL PROGRESS REPORTS

ACCOMPLISHMENTS FOR THE YEAR 1961

1. The structure of stoichiometric and oxygen-rich methane flames
    was studied with and without traces of a sample inhibitor
    (HBr) (Fig. 2).

2. The data for the stoichiometric (spherical) flame were partial-
    ly analyzed (Fig. 3). Two significant differences - the shift
    of the methane reaction zone to a higher temperature, and a
    reduction in the formaldehyde concentration - were observed.
    However, a significant part of the reaction was occuring on
    the flame holder surface so a complete analysis could not be
    made.

3. A new technique for studying atom-radical concentrations in
    flames was developed. The method combines microprobe sampling
    with chemical scavenging. It was qualitatively successful
    in the study of hydrogen atoms and quantitatively successful
    in the study of oxygen atoms (Fig. 4).

4. The diffusion coefficient of $Ar-H_2$ (trace) was measured between
    $295°K$ and $1079°K$ (Fig. 5).
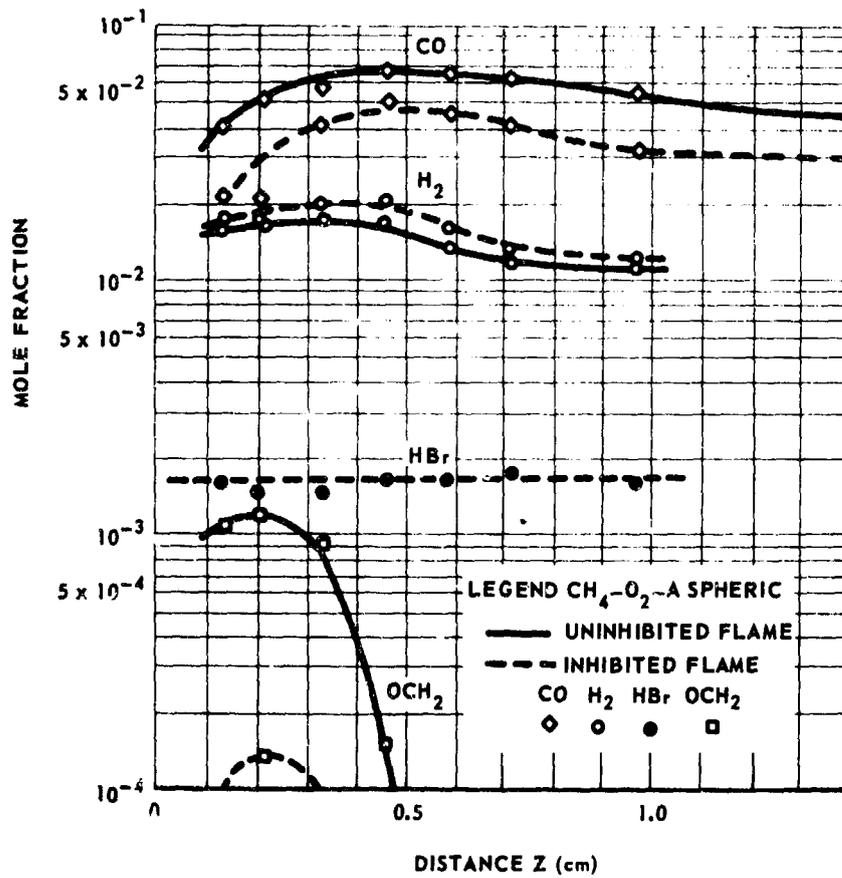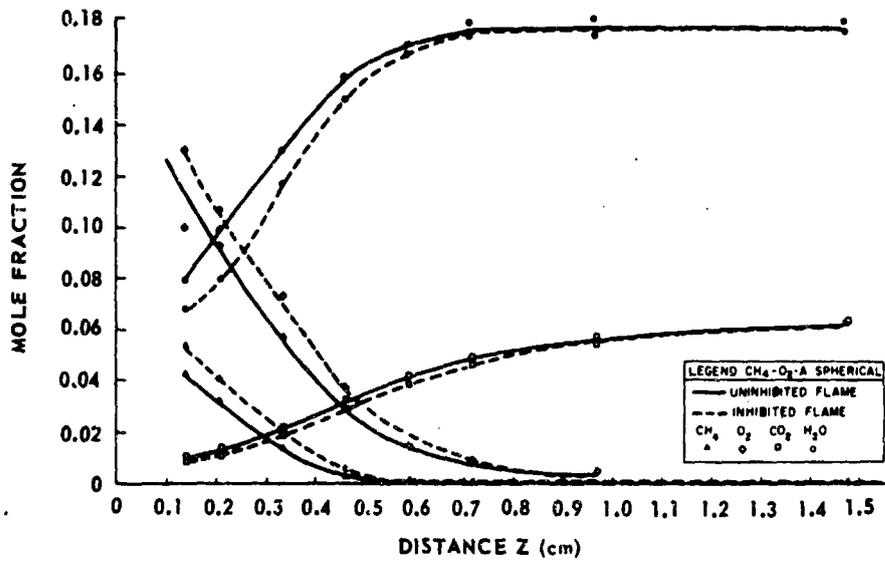
Fig. 2   THE EFFECT OF ADDED HBr ON THE CHARACTERISTIC PROFILES
OF A STOICHIOMETRIC METHANE FLAME.

- 8 -
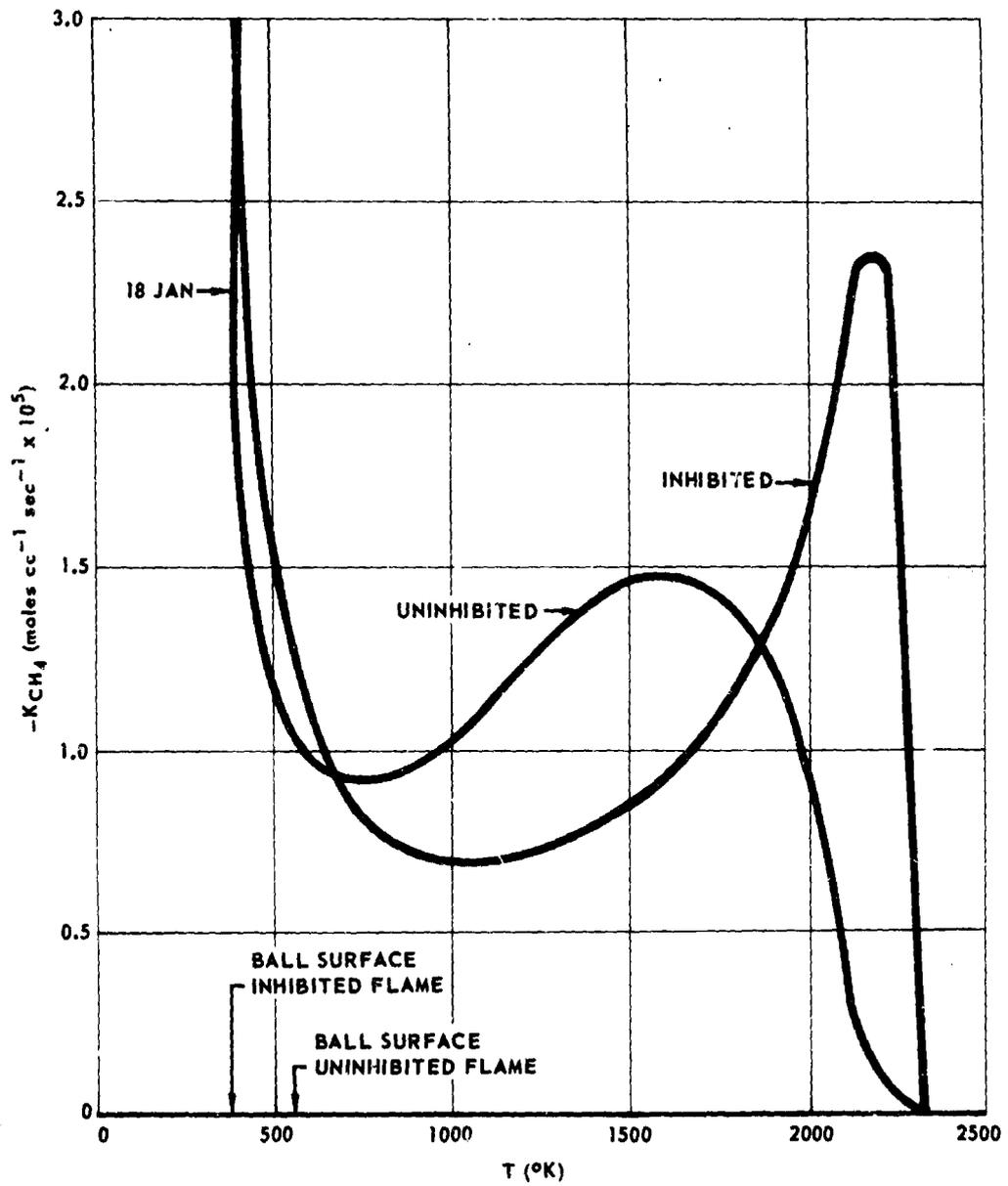
Fig. 3   THE EFFECT OF HBr ON THE RATE OF METHANE DISAPPEARANCE IN A STOICHIOMETRIC FLAME.

- 9 -
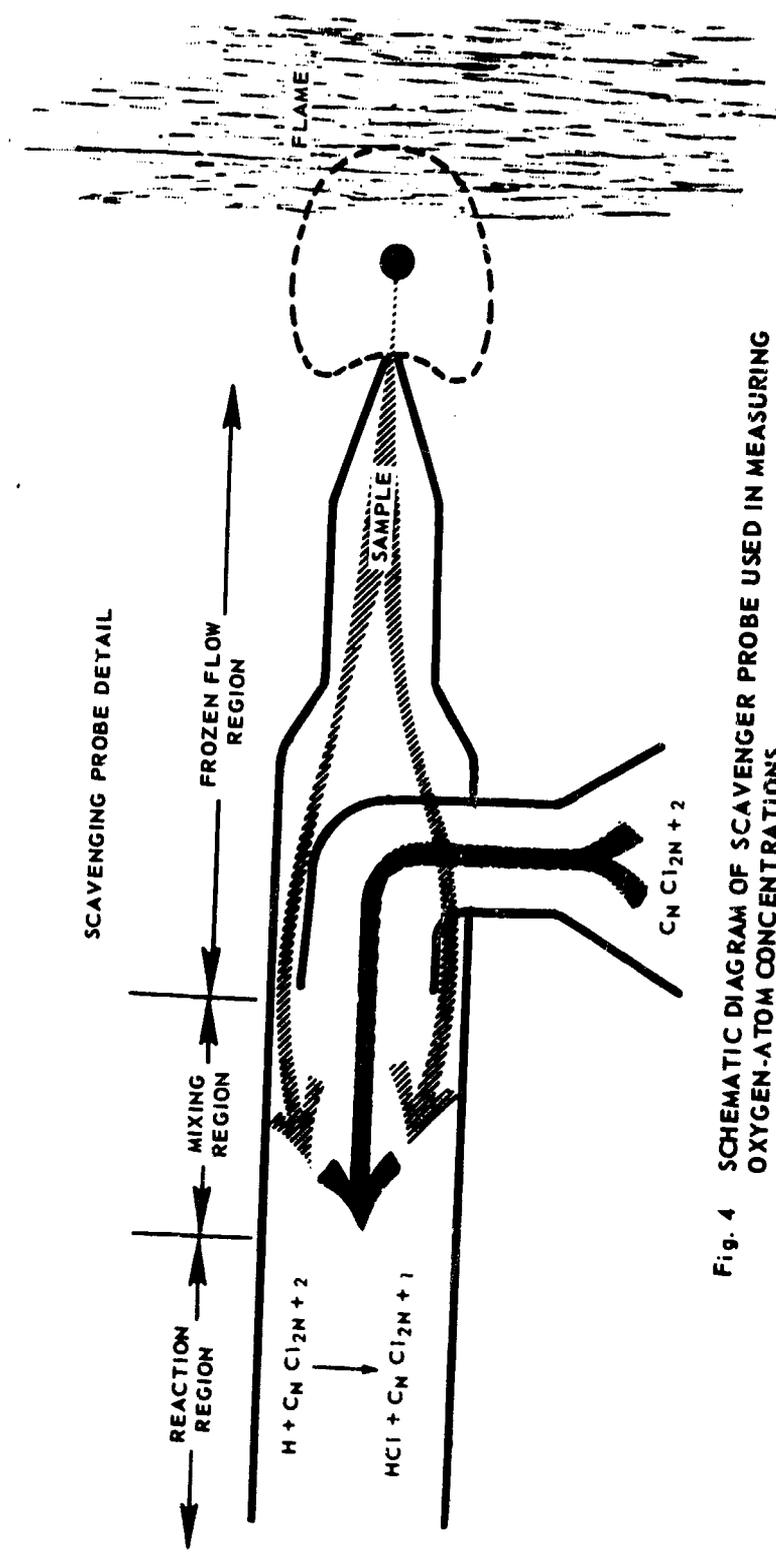
Fig. 4   SCHEMATIC DIAGRAM OF SCAVENGER PROBE USED IN MEASURING OXYGEN-ATOM CONCENTRATIONS.
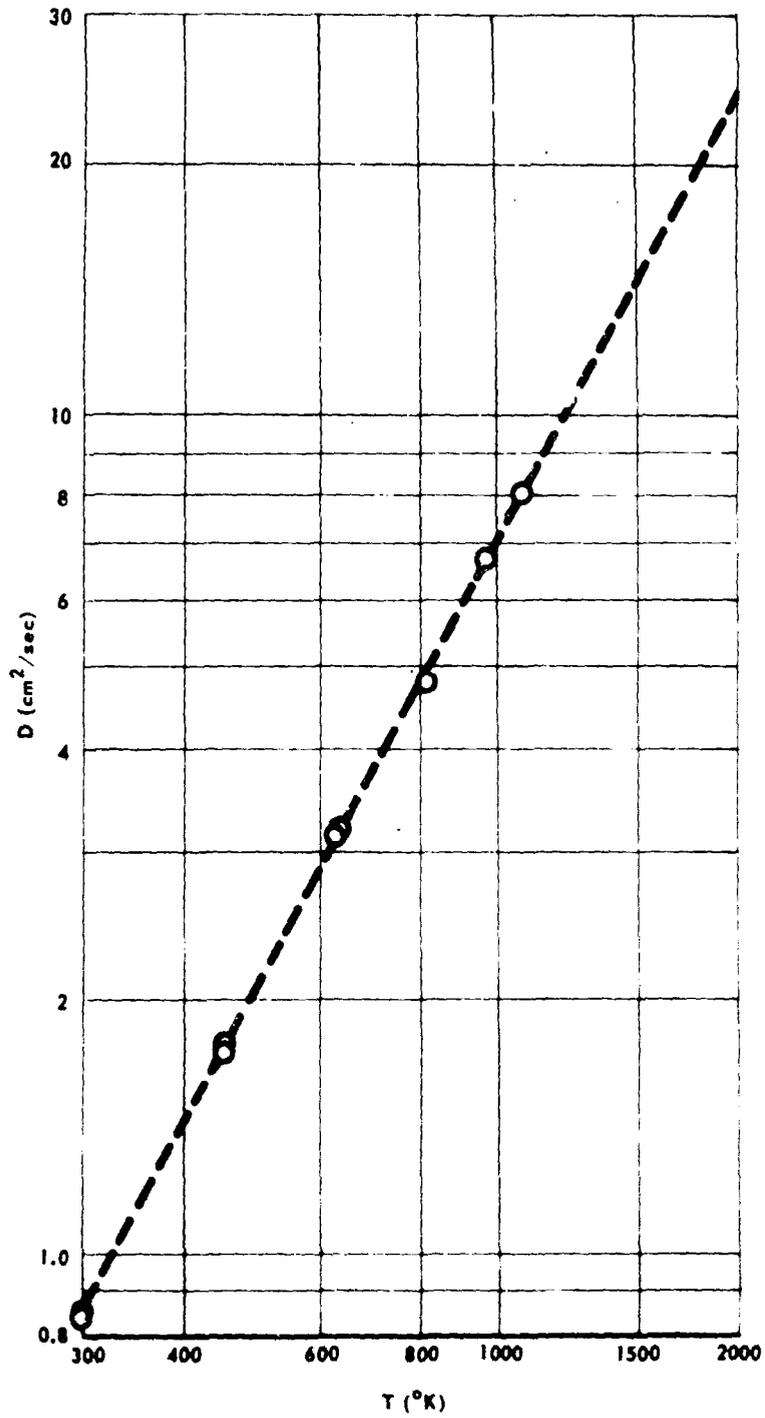
Fig. 5 DIFFUSION COEFFICIENT OF THE SYSTEM H_2 (TRACE)-Ar AS A FUNCTION OF TEMPERATURE.

- 11 -

ACCOMPLISHMENTS FOR THE YEAR 1962

1. A glass-ceramic, flat-flame burner was constructed to over-
    come the problems of corrosion by halogen atoms. Several com-
    position profiles were obtained, showing the effect of hydro-
    gen bromide and methyl bromide on a methane-oxygen flame.
    Qualitative observations were made on the effect of molecular
    iodine on this flame system.

2. A computer program was written for automation of the data
    reduction.

3. The scavenger sampling technique was applied to the study of
    oxygen atoms, hydrogen atoms, and methyl radicals in flames
    (Fig. 6).

4. A machine program for calculating nozzle reactions was modified
    to calculate the effect of inhibition reactions on the chemistry
    of flames. A simple theory has been proposed to connect these
    calculations with conventional flame theory so that prediction
    of the effects of inhibitors on burning velocity can be made.

5. Studies were made of homogenous radical reactions at low tem-
    peratures, using radicals prepared in electric discharges.
    Reactions have been chosen to clarify the chemistry of flames
    and flame inhibition. The reaction of OH with CH_4 has been
    studied, and data have been obtained that should improve the
    determination of activation energy for this reaction (Fig. 7).
    The reactions of D with HBr and the reaction of CH_3I with 0
    atoms were investigated. The chemistry of these reactions
    appears to be too complex for immediate interpretation.

6. HEF Fire Fighting techniques were reviewed and a short survey
    of the field was written.
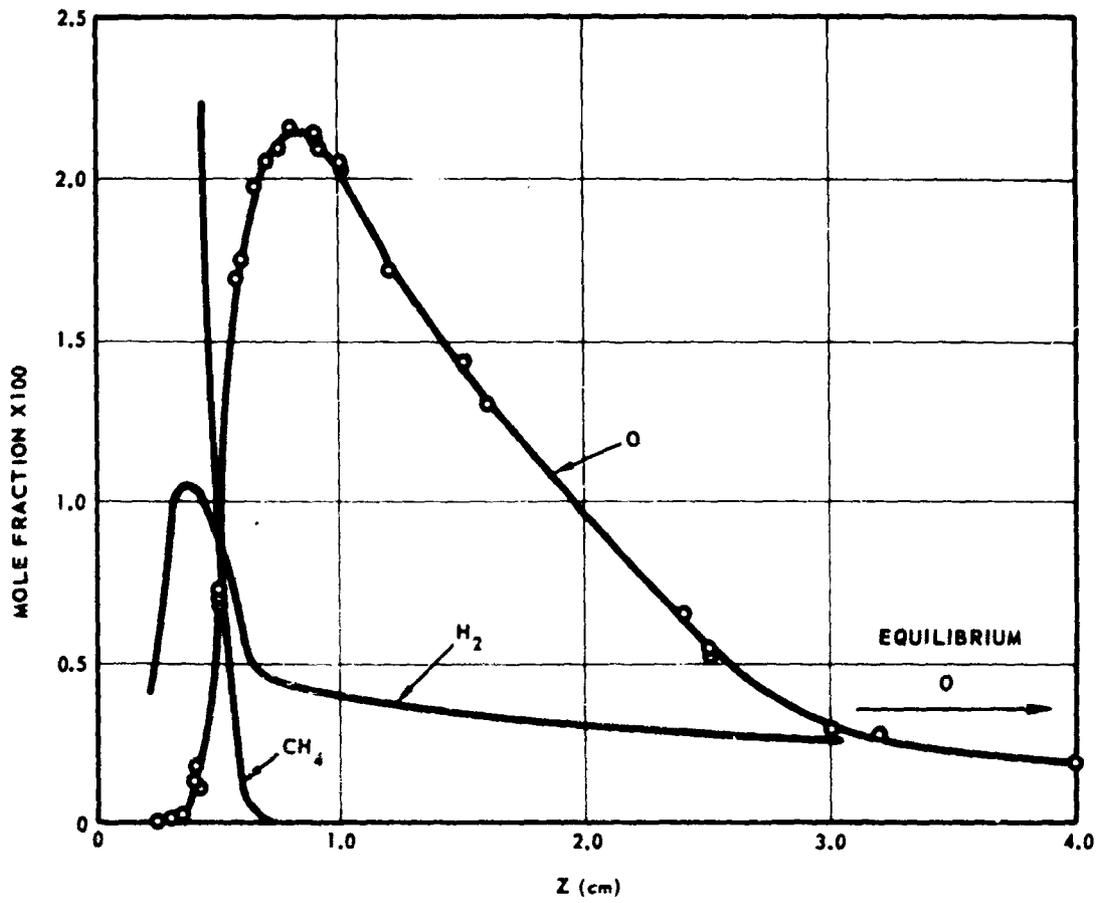
Fig. 6   ATOMIC OXYGEN CONCENTRATION IN METHANE FLAME AS
DETERMINED BY SCAVENGER SAMPLING.

- 13 -
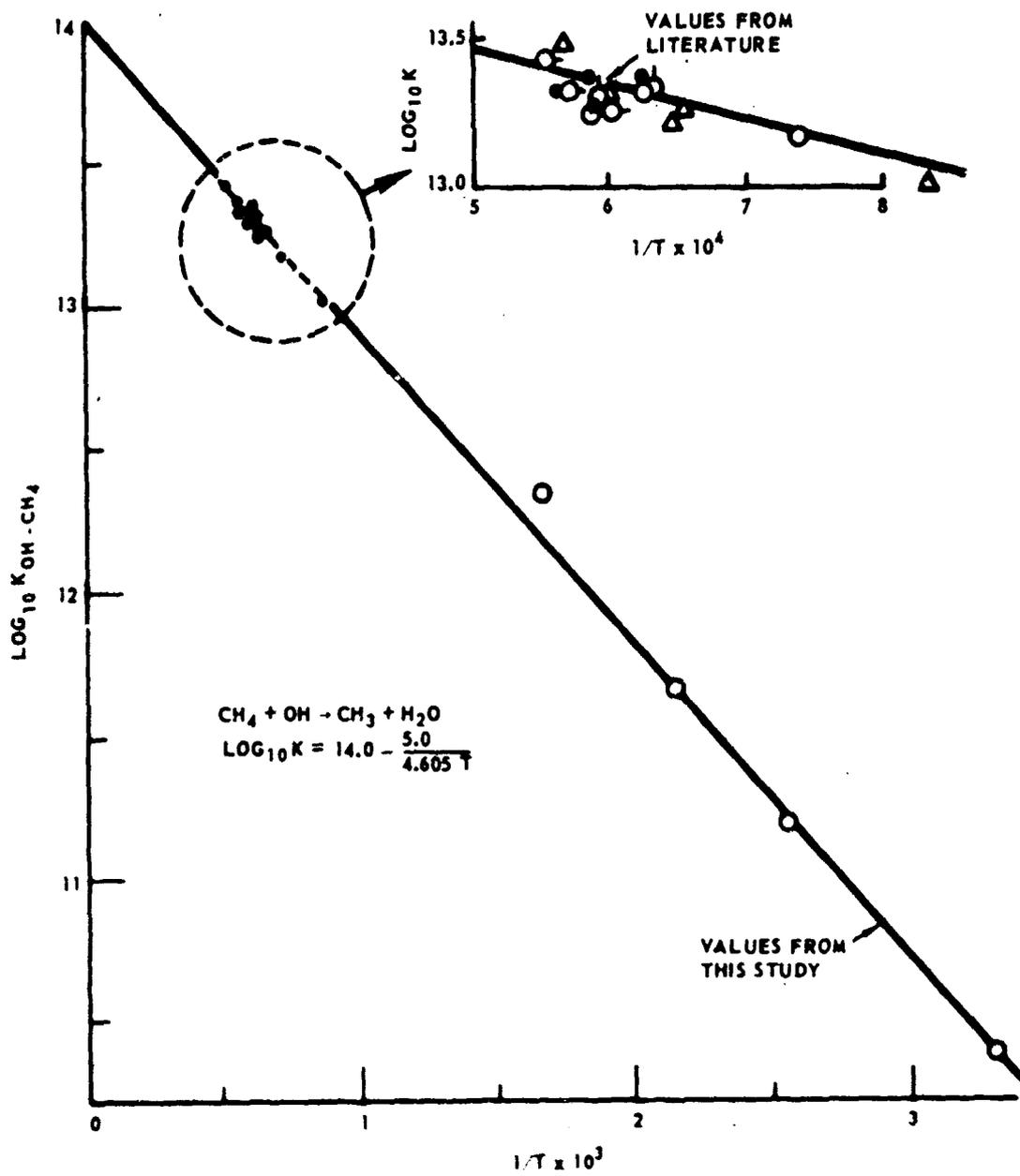
Fig. 7   KINETICS OF THE REACTION $CH_4 + OH \rightarrow CH_3 + H_2O$.

$CH_4 + OH \rightarrow CH_3 + H_2O$

$LOG_{10}K = 14.0 - \dfrac{5.0}{4.605\,T}$

ACCOMPLISHMENTS FOR THE YEAR 1963

1. A flame theory was developed which permits the calculation
    of flame speeds if the diffusivity and elementary reaction
    rates are known. The physical processes of convection, thermal
    conduction, and molecular diffusion are simulated by a simple
    model which assumes that the reaction is confined to a narrow
    region at high temperature and that the Lewis number is unity.
    The chemistry is more rigorously analyzed by use of a computer
    program to make accurate kinetic calculations. The calculated
    velocity of a hydrogen-oxygen flame agreed with the experi-
    mental value. The calculated burning velocity of the hydrogen-
    oxygen flame was independent of the initial radical concentra-
    tion, showing that in an uninhibited flame the composition and
    elementary reactions are the controlling factors, rather than
    the diffusive flux.

    The application of this theory to inhibited flames was
    tested by adding HBr to the H_2-O_2 flame. There was no appre-
    ciable change in the calculated flame velocity, but the igni-
    tion delay increased from 7C μsec (uninhibited) to 770 μsec
    (inhibited). Essentially, the primary flame reactions did not
    begin until after the HBr had been converted to Br, then re-
    action proceeded as if no HBr had been present. This indi-
    cates that the simple model is not applicable to inhibited
    flames (Fig. 8).

2. Experimental profiles of temperature and composition for a
    methane-oxygen flame inhibited with methyl bromide and hydrogen
    bromide were obtained and analyzed in terms of flux and rates
    for each species.

3. Hydrogen atom and hydroxyl radical composition profiles were
    derived for both the HBr and the CH_3Br inhibited flames, using
    known elementary rate expressions and the observed rates and
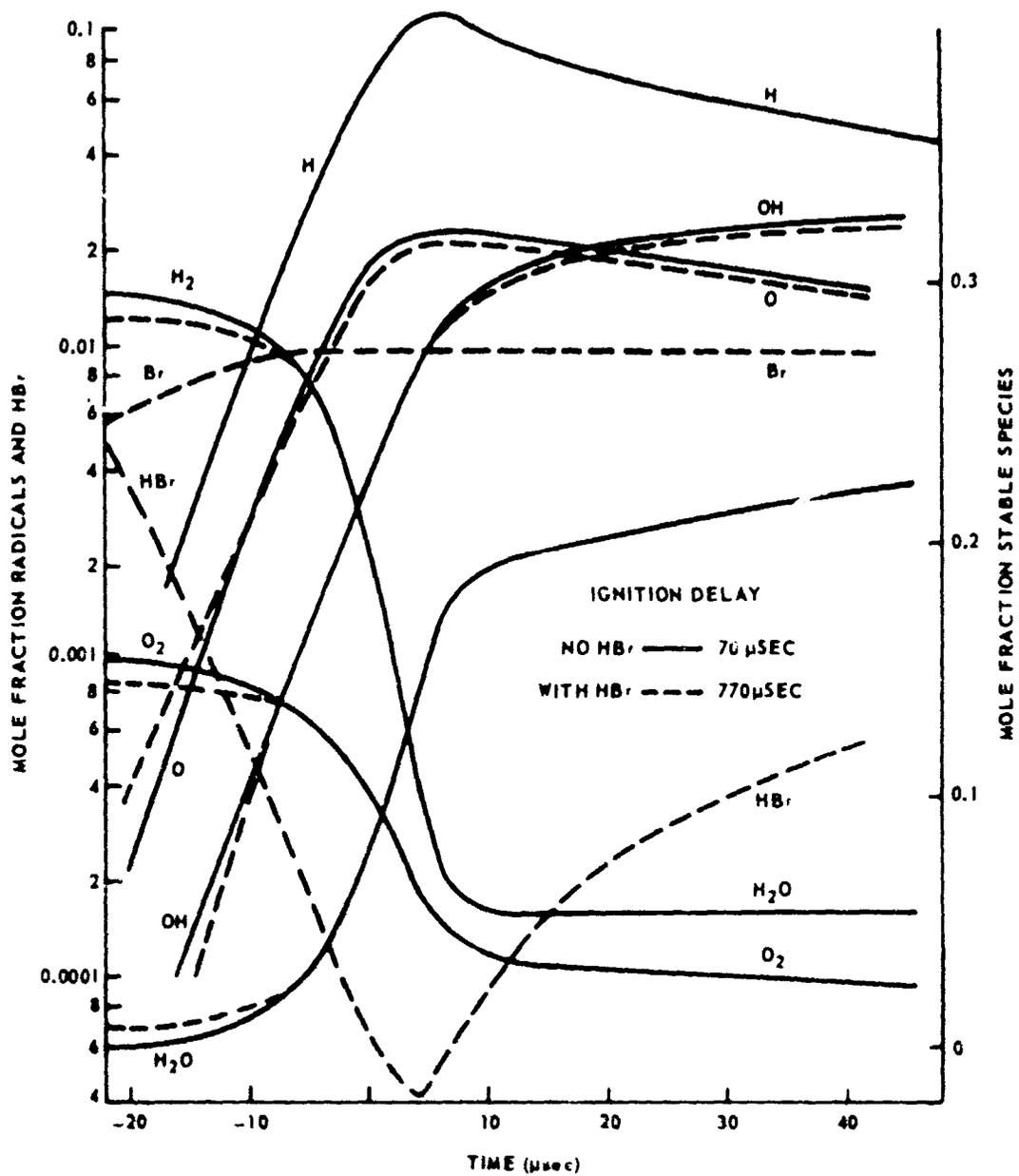
Fig. 8 CALCULATED VALUES OF CONCENTRATION VS TIME FOR IN-
HIBITED AND UNINHIBITED FLAME USING SIMPLIFIED FLAME
THEORY.

compositions.

4. Preliminary kinetic constants were given for the reactions
$HBr + OH \rightarrow H_2O + Br$, and $CH_3Br + OH \rightarrow CH_2Br + H_2O$.
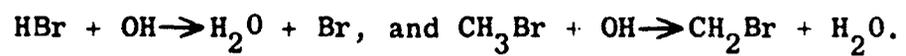
ACCOMPLISHMENTS FOR THE YEAR 1964

1. Analysis of the methane-oxygen flame inhibited with methyl
    bromide was completed. A new theory of flame inhibition of
    halogen compounds was proposed, which emphasizes the pre-igni-
    tion zone and the preferential reaction of radicals with in-
    hibitor which retards chain and chain branching reactions.

    The calculated rates of methane, methyl bromide, and
    hydrogen bromide formed in the early part of the flame show
    that the reaction of methane does not begin until most of the
    hydrogen bromide and part of the methyl bromide have reacted
    (Fig. 9). A comparison of methane rates indicates that the
    primary reaction zone in the inhibited flame is shifted to a
    higher temperature, is narrower, and has a greater absolute value
    than in an uninhibited flame (Fig. 10). These observations
    were used to support a flame-inhibition mechanism in which a
    major effect of the inhibitor is to prolong the pre-ignition
    zone and shift the primary reaction zone to a higher tempera-
    ture. It was suggested that the inhibition reactions have a
    lower activation energy so that radicals which diffuse into the
    pre-ignition zone react preferentially with the inhibitor.
    These reactions do not initiate chains, so the rate of radical
    build-up is decreased and ignition is prolonged until a higher
    temperature is reached. From this mechanism it was predicted
    that a good inhibitor would have a lower activation energy for
    reaction with radicals than either fuel or oxygen, but would
    be sufficiently stable to maintain its existence in the flame
    so that reaction would occur before dissociation.

2. Under the auspices of the Advanced Research Projects Agency,
    a technique was developed for studying the concentrations of
    atoms and free radicals in flames using microprobe sampling

- 18 -
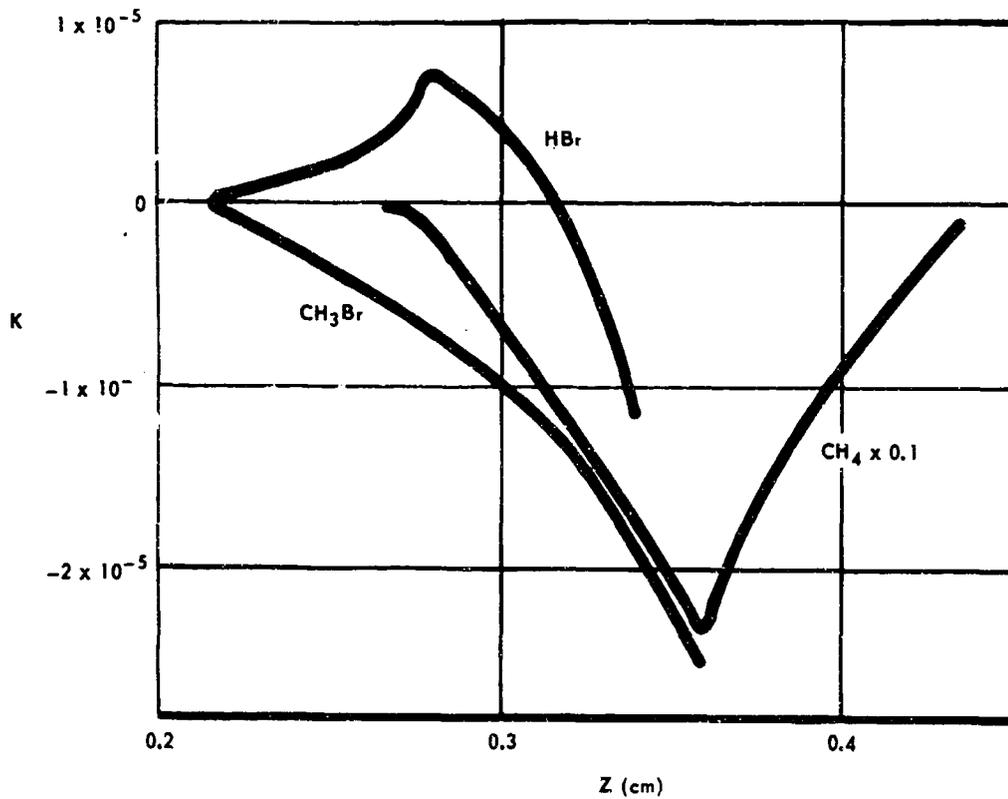
Fig. 9   NET REACTION RATES (K_i, MOLES CC^{-1} SEC^{-1}) FOR HBr, CH_3Br,
AND CH_4. (CH_4 RATES WERE MULTIPLIED BY 0.1 BEFORE
PLOTTING.)
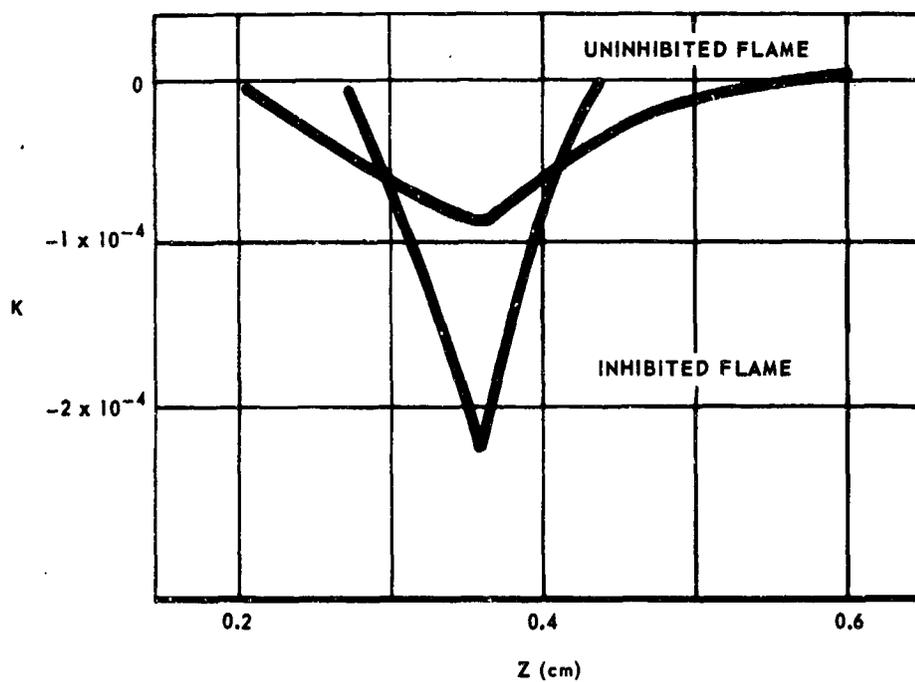
Fig. 10 COMPARISON OF NET REACTION RATE FOR METHANE IN AN INHIBITED AND AN UNINHIBITED FLAME (K_{CH_4}, MOLES CC^{-1} SEC^{-1}).

followed by electron spin resonance (ESR) analysis. The technique used to measure hydrogen and oxygen atom concentrations in an acetylene-oxygen, an ethylene-oxygen, and an ethane-oxygen flame. This technique shows great promise in inhibition studies since it appears clear that the inhibition process is intimately connected with the effects of the inhibitors on radical and atom concentrations in the flame (Figs. 11 and 12).
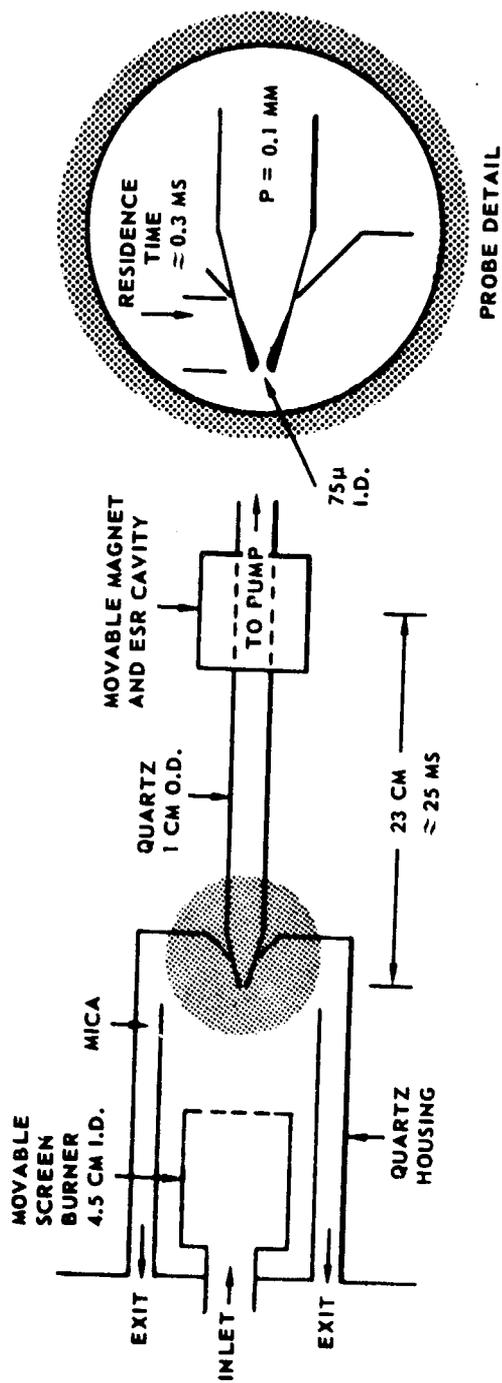
Fig. 11 SCHEMATIC DIAGRAM OF FLAT FLAME AND PROBE FLOW SYSTEM FOR ESR DETERMINATION OF RADICAL CONCENTRATION.

- 22 -
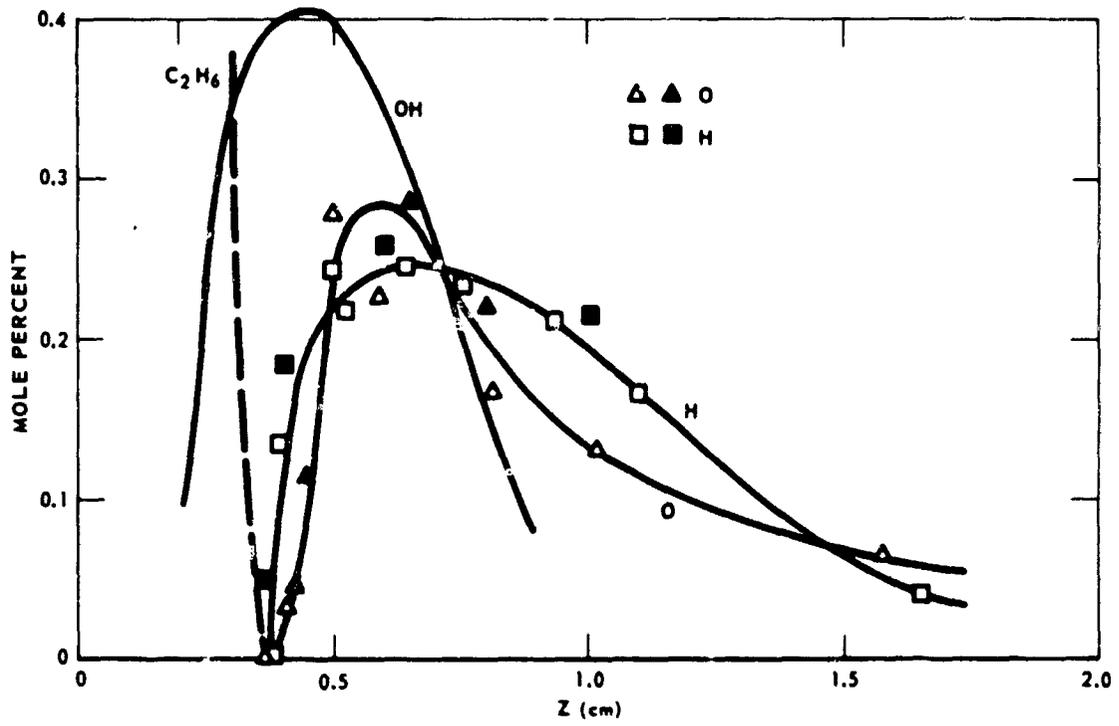
Fig. 12 COMPOSITION PROFILE OF RADICALS IN A $C_2H_6-O_2$ FLAME. O AND
H DETERMINED BY ESR, OH CALCULATED FROM CO_2 APPEARANCE
RATE AND RATE CONSTANT FOR CO + OH $\rightarrow CO_2$ + H. DASHED
LINE SHOWS POSITION OF C_2H_6 PROFILE RELATIVE TO RADICALS.

ACCOMPLISHMENTS FOR THE YEAR 1965

1. <u>Evidence confirming the validity of flame gas sampling for labile atoms/radicals</u>. The prospect the using an ESR spectrometer to make direct measurements of the atom/radical concentrations in a gas sample taken from the reaction zone of a flame with a small quartz probe has provided new possibilities in flame research. However, it was necessary to prove the quantitative validity of the technique. Work on this program was divided into three general phases.

First, an experiment was performed to test the passage of an atom-containing gas through just a small probe tip itself. This was done by sealing a simulated probe with an 0.1-mm-diameter orifice into a simple quartz flow tube, so arranged that the atom concentration could be measured with the ESR spectrometer both upstream and downstream of the orifice (Fig. 13). A stream of oxygen atoms and oxygen molecules from an electric discharge passed over the probe tip. The measured $0/0_2$ concentration ratio was essentially unchanged in changing the ESR cavity from the upstream (1-mm pressure) to the downstream (0.1-mm pressure) position. Since the experiment was done in gas at room-temperature, it proved nothing about the efficiency of such a probe in quenching chemical reactions. The important point, however, is that it showed that labile atoms can be drawn through a tiny orifice <u>without appreciable loss on the walls.</u>

Second, a more stringent test under actual flame conditions was carried out by comparing the sampled atom concentrations against results obtained by an independent technique. Obviously, the most desirable procedure would be to check the sampling result on a system containing a known concentration of atoms. Since this is not possible under flame conditions (except in

- 24 -
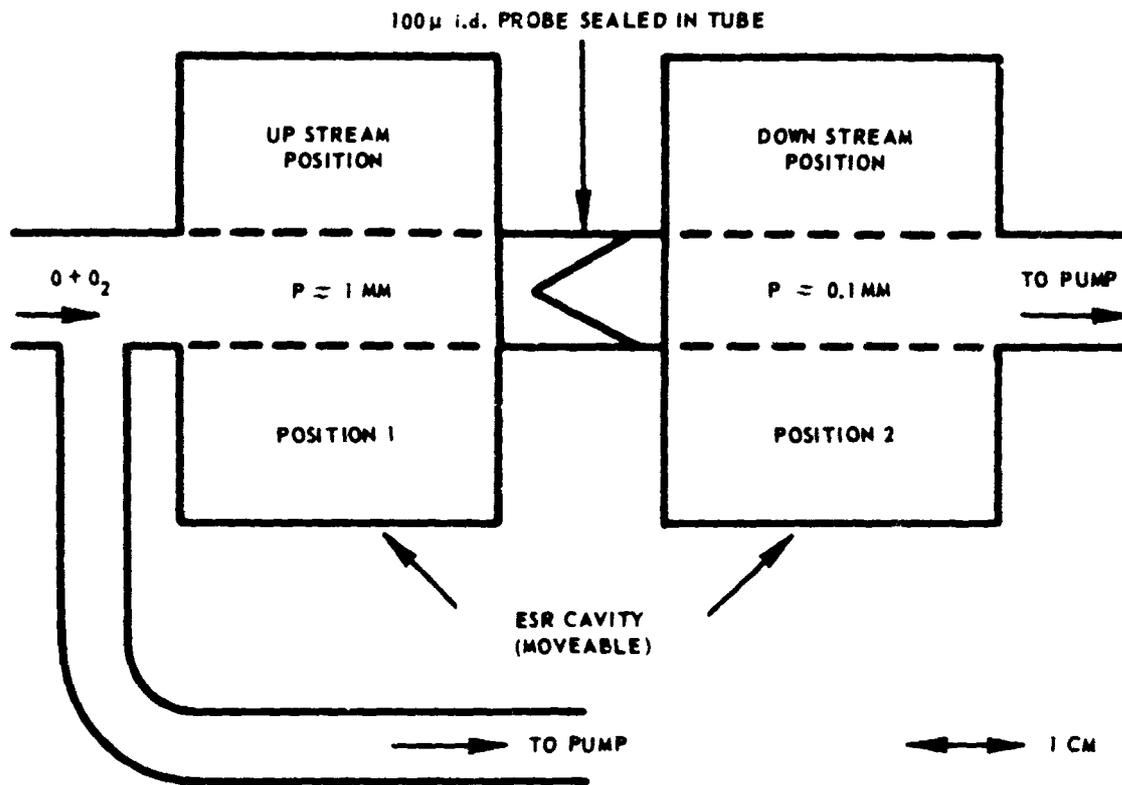
Fig. 13.   SCHEMATIC DIAGRAM OF APPARATUS USED TO SHOW THAT OXYGEN
ATOMS ARE NOT DESTROYED WHEN DRAWN THROUGH A PROBE.

the equilibrium-burned gas where the practically attainable atom concentrations are too low), the next best thing was to use an independent comparison technique. For this the concentration of oxygen atoms in a $C_2H_6-O_2$ flame at 0.1-atm pressure was determined by measuring the rate of formation of nitric oxide by way of the reaction $O + N_2O \rightarrow 2NO$ from an added trace of N_2O and the known rate constant for the reaction. N_2O and NO were determined by mass spectrometry in the sampled gas. The oxygen-atom concentration of about 0.3-0.6 mole-percent measured this way was in good agreement with the value of 0.53 determined by direct ESR in the sampled gas. A similar comparison was made on hydrogen in a rich H_2-O_2 flame, using the tracer reaction $H + D_2 \rightarrow HD + D$. The latter yielded 1-2 mole-percent as compared with 1.2 mole-percent by direct ESR sampling. This is very encouraging agreement.

Third, some numerical calculations (IBM-7094) were carried out to assess the chemical behavior of a non-equilibrium flow through a tiny supersonic nozzle such as a sampling probe. This work indicated the significant point that a non-equilibrium gas very quickly (i.e. a few μsec) freezes at some composition which may or may not be much different from the original inlet composition so far as radicals are concerned. The sampled gas tries to attain a state of "partial" equilibrium where the fast bi-molecular reactions are equilibrated. If the initial gas already has this condition nearly fulfilled (as much of the flame gas does), there will be no significant change in radical concentration in the probe nozzle itself. If the initial gas is not equilibrated, concentration changes should occur, although they may not be drastic.

2. Development of capability for hydroxyl-radical (OH) determination by ESR. This was done in work closely related to this pro-

- 26 -

ject. Since OH gives an ESR spectrum caused by a different type of transition (electric dipole) than the more common atomic spectra (magnetic dipole), it requires a different resonant cavity. A suitable cavity was designed, constructed, and tested on OH radicals generated in a discharge flow system. The theory for calibrating OH radicals against the stable molecule NO was developed, so that our capability of measuring the important radical OH in flame systems how exists.

3. <u>Profiles of H and O atoms in a C_2H_6-O_2 flame</u>. These were determined during this period for comparison with the profiles measured some time ago as a check on long-term reproducibility. The agreement was within a factor of two in absolute magnitude with within 0.5 mm in spatial position in the flame. Presumably the later data are the more reliable because of improvements in the technique.

4. <u>Theoretical ESR intensities for halogen atoms</u>. Preparatory to working with halogenated inhibitors, the necessary intensity relations for ESR measurements of Br, Cl, and I atoms were derived.

5. <u>Analyses of flames inhibited with CH_3Cl, HCl, and Cl_2</u>. These results, compared with those from an uninhibited flame, support the flame-inhibition mechanism suggested by the study of the HBr and CH_3Br inhibited flame. This theory is indicated graphically in Figs. 14 and 15. The activation energy for the reaction of the active flame species H, OH, CH_3, and O with inhibitors is lower than for the chain branching reactions necessary to propagate the flame (the most important being $H + O_2 \longrightarrow O + OH$). Thus, in the early, low-temperature part of the flame, inhibition reactions that result in chain-breaking occur in preference to chain-branching reactions. However, when the temperature becomes high enough for the chain-branching reactions to
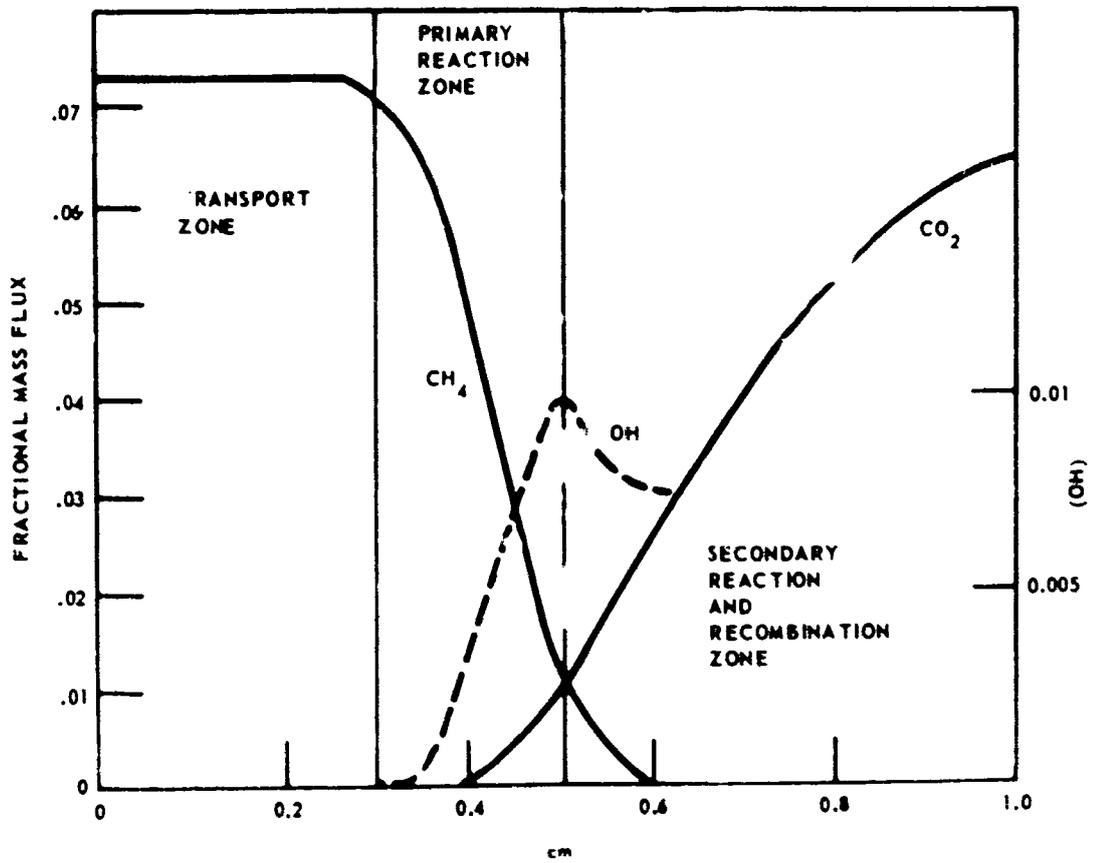
Fig. 14   FLAME ZONES – UNINHIBITED FLAME.
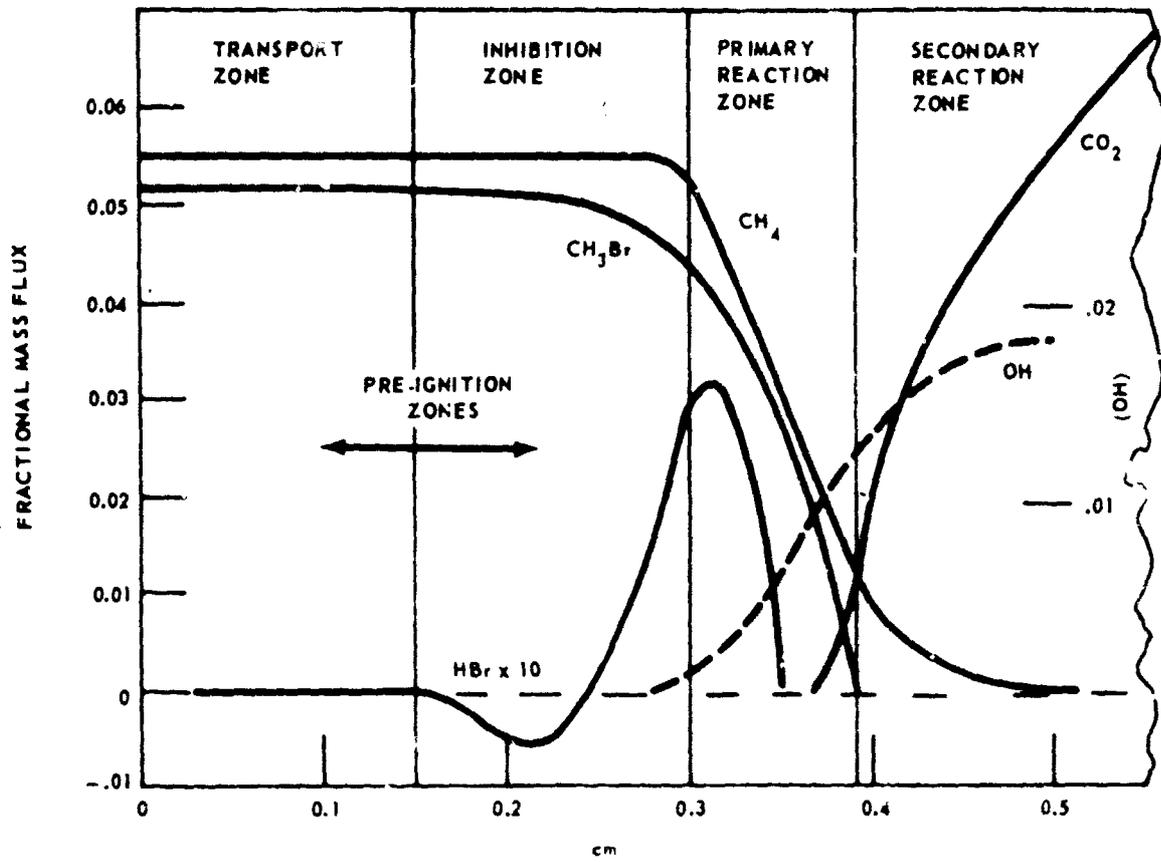
Fig. 15   FLAME ZONES – INHIBITED FLAME.

compete with chain-breaking reactions, the normal flame reac-
tions rapidly become dominant and the fuel reacts at a faster
rate than in a normal flame. Thus, to the normal flame zones
(Fig. 14), i.e., preignition or transport region, primary
reaction zone, and secondary reaction and radical recombina-
tion zone, must be added the inhibition zone in Fig. 15.

6. A summary of rates of inhibition reaction follows:

Reaction	Rate $cm^3 \ mole^{-1} \ sec^{-1}$	Temperature Range
$OH + CH_3Br \rightarrow products$	1.5×10^{13}	1800-2000°K
$OH + CH_3Cl \rightarrow products$	1.3×10^{13}	1800-2100°K
$OH + HBr \rightarrow H_2O + Br$	1.6×10^{13}	1875-2000°K
$OH + HCl \rightarrow H_2O + Cl$	7.7×10^{12}	1925-1950°K

CONCLUSION

Among the accomplishments achieved in the Flame Inhibition Research Program during the past five years, the following are considered of prime importance:

1. Techniques and apparatus for handling and analyzing corrosive additives.

2. Computer techniques for data analysis.

3. Kinetic constants for several inhibition reactions.

4. A new theory to explain the inhibition of flames by halogen compounds.

5. The "scavenger probe" and ESR techniques for direct measurement of free radical concentration.

6. Measurement of the diffusion coefficient of the H_2-Ar system over a wide temperature range.

A number of people at APL have been associated with this project. The project was originally outlined by Drs. W.G. Berl and R.M. Fristrom. During the first years, Dr. Fristrom was the project sponsor. Since 1964, Dr. A.A. Westenberg has been project sponsor. The research was carried out originally by Dr. P. Breisacher and Dr. Fristrom, later by Dr. Wm. E. Wilson, Jr. and Dr. Fristrom, and finally by Dr. Wilson under the direction of Dr. Westenberg. During this time, two associates have contributed to the work. In the initial period the main experimental burden was carried by Mr. C. Grunfelder, but since 1962 Mr. J.T. O'Donovan has been the main experimentalist. The programming and general computations were carried out by Mr. S. Favin.

REPORTS AND PAPERS ON INHIBITION RESEARCH PREPARED AT APL

1. Flame Inhibition Research Quarterly Progress Reports

   (a) 1 Nov 1960 - 31 Jan 1961, TG 376-1, Feb 1961

   (b) 1 Feb 1961 - 30 Apr 1961, TG 376-2, May 1961

   (c) 1 May 1961 - 31 Jul 1961, TG 376-3, Aug 1961

   (d) 1 Aug 1961 - 31 Oct 1961, TG 376-4, Nov 1961
        (Yearly Summary, 1 Nov 1960 - 31 Oct 1961)

   (e) 1 Nov 1961 - 31 Jan 1962, TG 376-5, Jan 1962

   (f) 1 Feb 1962 - 30 Apr 1962, TG 376-6, Apr 1962

   (g) 1 May 1962 - 31 Jul 1962, TG 376-7, Aug 1962

   (h) 1 Aug 1962 - 31 Oct 1962, TG 376-8, Nov 1962
        (Yearly Summary, 1 Nov 1961 - 31 Oct 1962)

   (i) 1 Nov 1962 - 31 Jan 1963, TG 376-9, Feb 1963

   (j) 1 Feb 1963 - 30 Apr 1963, SR 6-1, May 1963

   (k) 1 May 1963 - 31 Jul 1963, SR 6-2, Aug 1963

   (l) 1 Aug 1963 - 31 Oct 1963, SR 6-3, Nov 1963
        (Yearly Summary, 1 Nov 1962 - 31 Oct 1963)

2.* R. M. Fristrom and A. A. Westenberg, "Fundamental Processes and
    Laminar Flame Structure," APL Technical Digest, Vol. 1, (Jan-Feb
    1962), p. 10.

3.* R. M. Fristrom and A. A. Westenberg, Experimental Chemical
    Kinetics from Methane-Oxygen Laminar Flame Structure, Eighth
    Symposium (International) on Combustion, the Williams & Wilkins
    Co., Baltimore, 1962, p. 438.

4.* A. A. Westenberg and G. Frazier, "Molecular Diffusion Studies

in Gases at High Temperature. V. Results for the H_2-Ar System, J. Chem. Phys., Vol 36, 1962, p. 3499.

5.[†] J. T. O'Donovan and R. M. Fristrom, "Research Study on HEF Fire Fighting," APL/JHU CF 3001, Sept 1962.

6.[*] R. M. Fristrom, Radical Concentrations and Reactions in a Methane-Oxygen Flame, Ninth Symposium (International) on Combustion, Academic Press, New York, 1964, p. 560.

7.[‡] G. Frazier, R. M. Fristrom, and J. F. Wehner, "Microstructure of a Hydrogen-Bromine Flame," A.I.Ch.E. Jour., Vol.9, 1963, p 689.

8.[*] R. M. Fristrom, "The Scavenger Probe - A Method for Determining Radical Concentrations in Gaseous Systems," Science, Vol. 140, 1963, p. 297.

9. R. M. Fristrom, "Measurement of Burning Velocity - A Survey," API/JHU TG 481, April 1963.

10. A. A. Westenberg and R. M. Fristrom, H and O Atom Profiles Measured by ESR in C_2 Hydrocarbon-O_2 Flames, Tenth Sympsoium (International) on Combustion, The Combustion Institute, Pittsburgh, 1965, p. 473.

11.[†] W. E. Wilson, Jr., Structure, Kinetics and Mechanism of a Methane-Oxygen Flame Inhibited with Methyl Bromide, Tenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1965, p. 47.

12. R. M. Fristrom, "Definition of Burning Velocity and a Geometric Interpretation of the Effects of Flame Curvature," Phys. Fluids, Vol. 8, 1965, p. 273.

Papers on flames inhibited by HBr, CH_3Cl, HCl, and Cl_2 and on the quantitative validation of the ESR sampling process will be published in the near future.

13. A. A. Westenberg, "Intensity Relationships for Determining Gas-Phase OH, Cl, Br, I, and Free Electron Concentrations by Quantitative ESR," $\underline{J}$. $\underline{Chem}$. $\underline{Phys}$., Vol. 43, 1965, p. 1544.

14. A. A. Westenberg and N. DeHaas, "Quantitative ESR Measurements of Gas-Phase H and OH Concentrations in the $H-NO_2$ Reaction," $\underline{J}$. $\underline{Chem}$. $\underline{Phys}$., Vol. 43, 1965, p. 1550.

- 34 -

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13. ABSTRACT

Flame structure techniques used to determine chemistry kinetics of normal flames were applied to flames inhibited by halogen compounds. A theory was developed to explain this type of inhibition. Free radicals, whose rapid concentration increase through chain and chain branching reactions are responsible for the rapid reaction rates in flames, can react with halogens in chain breaking reactions. As the activation energy for reactions of radicals with halogen compounds is lower than for reaction with fuel or oxidizer, these reactions occur preferentially in the early part of the flame and prevent the rapid increase in free radical concentration. Normal flame propagation cannot begin until all of the halogen inhibitor has been used up through reaction or until the temperature is high enough to make chain branching reactions competitive. Rate constants for a number of reactions or hydroxyl radical with halogen inhibitors were determined. Two new techniques, the scavenger probe and electron spin resonance, were developed which make possible the determination of radical concentrations in flames. Techniques and apparatus for handling and analyzing corrosive additives are described.

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14	KEY WORDS	LINK A		LINK B		LINK C	
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