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FLAME INHIBITION RESEARCH

QUARTERLY PROGRESS REPORT

1 May 1962 - 31 July 1962

LIST OF INVESTIGATORS

Project Coordinator:	R. M. FRISTROM
Project Advisor:	W. G. BERL
Flame Structure Studies:	W. E. WILSON J. T. O'DONOVAN R. M. FRISTROM S. FAVIN
Atoms and Radicals in Flames:	R. M. FRISTROM C. GRUNFELDER
Isotope Preparation:	J. WAGNER W. E. WILSON

THE JOHNS HOPKINS UNIVERSITY
APPLIED PHYSICS LABORATORY
8621 GEORGIA AVENUE   SILVER SPRING, MARYLAND

SUMMARY OF PROGRESS 1 May 1962 - 31 July 1962

(1) The flat flame burner system is in operation. Two runs have been been made on the lean uninhibited methane-oxygen flame to study the concentration of methyl radical. Methyl radicals were detected using iodine in the scavenger sampling probe, and a preliminary composition profile is presented. A traverse was made of this flame inhibited by elementary iodine. Among the interesting products found were methyl iodide (CH_3I) and iodic acid (HIO_3).

(2) The low pressure flow reactor has been modified for the study of radical reactions in the range 300-600°K. An investigation was made of methods for preparing "pure" H, OH, O and CH_3 in known concentrations using electric discharges and chemical reactions as sources. "Pure" indicates freedom from complicating radical impurities.

A study of the products of reaction of HBr with the effluent from a heavy water discharge (D, OD, and O) suggests that the reactions of O and/or OD may be more complex than the usually assumed: $OD + HBr \rightarrow HDO + Br$ and $O + HBr \rightarrow OH + Br$. Detailed runs using pure O and OH with DBr are planned.

It was found that O atoms react with methyl iodide to give a bright yellow "atomic" flame. Formaldehyde is a major product.

The reaction of methane with OH radicals has been studied from 300°K - 600°K. A tentative activation energy of 4.5 ± 1.5 kcal/mole was derived from the temperature dependence of the methane disappearance and formaldehyde formation. This is in agreement with the value 6.5 kcal/mole derived from flame structure studies.

(3) Methods have been investigated for the preparation of DBr for isotopic tracer studies in flames. Several tests have been made of the

reaction $3H_2O + PBr_3 \rightarrow HBr + H_3PO_3$. The apparatus is being set up for the final preparation using heavy water.

(4) Arrangements have been made for the testing of some new inhibitors and fire fighting techniques in connection with the destruction of certain surplus supplies of boron containing fuels.

(5) During the past quarter a paper previously reported in (TG376-6) was published.

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FLAME INHIBITION RESEARCH

I. BACKGROUND MATERIAL

REPORT ORGANIZATION

This report is divided into four sections: I. Background Material, II. Program Outline, III. Summary of the program to the beginning of the reported quarter, and IV. Quarterly Progress. Only the fourth section contains new material (although Section III is updated quarterly). It is hoped that the background material will aid the unfamiliar reader in following the program without extensive references. Those who are familiar with the work may find it profitable to turn directly to the fourth section (Page 11).

PROGRAM OBJECTIVE

The objective of this program is to obtain a scientific understanding of the mechanism of chemical inhibition of flames. Although this research is primarily restricted to the fundamental aspects of the problem, there are several potentially practical by-products. A quantitative understanding of flame inhibition should allow the prediction of the relative effectiveness of inhibitors on a flame system from their known chemical kinetics. Thus, a rational initial choice of inhibitor should be possible without extensive empirical studies. (This factor may become of increasing importance as "exotic" fuels become common.) It would also seem possible to set an absolute upper limit for the effect of an inhibitor, so that their efficiencies can be evaluated.

HISTORICAL SUMMARY

Over the past two decades, a number of studies have been made on flame inhibition of hydrocarbon-oxygen flames by halogen-containing compounds (Refs. 1 and 2). The experimental evidence suggests that the effectiveness of these materials is due to an effect on the chemical reactions in such flames. It has been established that the inhibition is a function of the concentration of the halogen, and that the order of effectiveness of the halogens is inverse to the reactivity of the free atoms, i.e., $F < Cl < Br < I$. Most practical extinguishers contain bromine compounds. Iodine compounds are usually unstable and expensive.

It is generally accepted that the mechanism for such flame inhibition is the exchange reactions between the inhibitor and the free radicals that are responsible for the primary propagation reactions in flames. Such reactions lead to the formation of stable molecules and free halogen atoms, which are much less reactive than the flame radicals. In hydrocarbon-oxygen flames the important radicals are hydrogen atoms, oxygen atoms, hydroxyl radicals, and possibly methyl radicals. Other radicals exist in flames, but these are probably less important to the flame propagation. On this hypothesis one would expect that the following reactions would be important in flame inhibition:

1) $RX + H\cdot \rightarrow HR + X\cdot$

2) $RX + OH\cdot \rightarrow ROH + X\cdot$

3) $RX + O\cdot\cdot \rightarrow RO\cdot + X\cdot$

Here, R represents a hydrogen or hydrocarbon radical, and X represents a halogen. Dots indicate unpaired electrons. Reactions of this type are well known (Ref. 3), but much of the available data is too fragmentary to allow extrapolation of the kinetic information from the low-temperature regime of most laboratory studies to radical reactions at the high temperatures encountered in flames.

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1. R. Friedman and J. R. Levy, "Survey of Fundamental Knowledge of Mechanisms by Action of Flame Extinguishing Agents, "WADC Tech. Report 56-568, Jan. 1957, Supplement I, Sept. 1958, Supplement II, April 1959.

2. W. A. Rosser, H. Wise, and J. Miller, "Mechanism of Combustion Inhibition by Compounds Containing Halogen", Seventh Symposium (International) on Combustion, pp. 175-82, Butterworths Scientific Publications, London (1959).

3. E. W. R. Steacie, Atomic and Free Radical Reactions, Reinhold Publ. Co., New York (1954) (2 volumes).

II. PROGRAM OUTLINE

The research program will utilize studies of the detailed microstructure of flames (Ref. 4) with and without added inhibitor, together with such other chemical and physical studies as seem necessary to elucidate the detailed mechanisms of chemical inhibition of flames. The relation between these studies can be visualized in Fig. II-1. Following this figure the report will be divided into five major sections (flame structure studies, simple reaction studies, analysis, interpretation, and recommendations of flame inhibition), and eight minor sections (temperature profiles, composition profiles, aerodynamic profiles, and atomic and free-radical composition profiles). This is a long-range program of modest scale whose completion is expected to take from three to five years. Therefore, although work is planned in all of these categories, current work will usually occupy only a few of these sections.

The number of possible inhibitors and the number of possible flame systems are both large, and the number of flame-inhibitor systems which may be of interest is even larger since it is the product of these two numbers. The situation can be represented by a very large "matrix" in which one index of the terms represents the flame system and the other represents the inhibitor system. (See Fig. II-2). Since it is impractical to study such a large number of systems, two possible approaches suggest themselves: The synthetic method, in which one would study the chemistry of inhibitors with radicals, and a separate study of the uninhibited flame systems. This is equivalent to studying the initial row and initial column in the "matrix". A satisfactory theory would allow the prediction of the effect of any inhibitor on any flame from this information. The other approach is the statistical technique, which is often used in agriculture. Studies would be made of a randomized set of these systems using one of the patterns of experiment design, such as the Latin square. By studying this fraction of the systems, a satisfactory theory should allow the derivation of information sufficient to predict the effect of any specific inhibitor on any specific flame system.

Both approaches assume that an adequate theory is developed. Therefore, a judicious combination of these two approaches seems in order. Early studies should be aimed at developing a theory, subsequent studies should be aimed at making a randomized statistical test of the efficacy of the theory, and final studies should be aimed at the accumulation of data. On this basis we propose to make a very detailed study

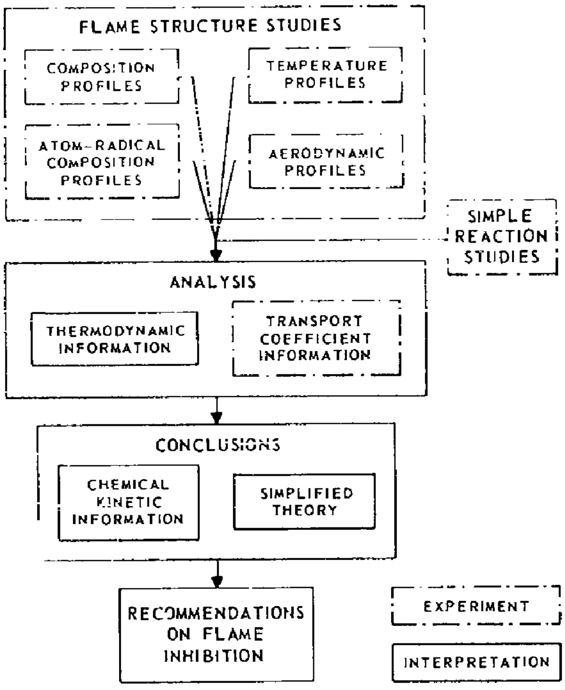
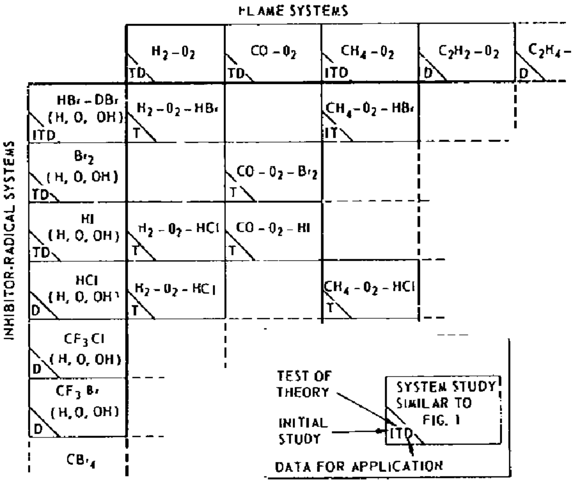


Figure II-1 FLOW OF INFORMATION IN THE PROGRAM TO STUDY FLAME INHIBITION



Initial Study, I – An intensive study of one inhibitor-flame system is directed toward the goal of a simplified theory of flame inhibition. The chosen system is methane-oxygen with HBr (and or DBr) as an inhibitor.

Test of Theory, T – The theory from the initial study should then be tested on representative inhibitor-fl[illegible]systems to confirm its generality.

Data for Application, D – If the theory seems satisfactory, then a store of data should be developed to permit its broad application. Such data is most readily obtained from simple systems–the flame systems alone and inhibitor-radical reaction systems. The required data include those of chemical kinetics, transport coefficients, and thermodynamic properties.

Figure II-2 OVER-ALL PROGRAM TO STUDY FLAME INHIBITION

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4. R. M. Fristrom, and W. G. Berl. "Proposal for the Study of Flame Inhibition", proposal submitted by the Johns Hopkins University Applied Physics Laboratory, in response to WADC Request [illegible]

of the methane-oxygen flame with a simple inhibitor (probably HBr) to develop the theory. This will be followed by a randomized test on a restricted number of systems, and finally by a systematic study of parameters. The program is illustrated by Fig.II-2. It is discussed in more detail in Ref. 4.

FLAME STRUCTURE EXPERIMENTAL STUDIES

It is planned to use flame structure techniques in this research, on flames both with and without inhibitors. These techniques have been discussed in the literature (Refs. 5 and 6) and offer certain advantages for studying chemical reactions: 1) flames offer a steady-state for study, 2) there is no wall problem, 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, 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 (Ref. 5). 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, atomic and free-radical composition profiles, temperature profiles, and aerodynamic profiles. An example of such a set is given in Fig. II-3.

Composition Profiles

From the chemical standpoint, the most important information is the concentration profiles. The most satisfactory technique developed for making such studies is the microprobe sampling technique, which is followed by mass spectral 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 negligible, and the low pressure and rapid pressure drop in such a tapered probe quenches the sample so that reproducible meaningful samples can be obtained. Radical concentrations are not obtained by these techniques and are discussed in the next section. This technique is discussed in detail in the literature (Ref. 7).

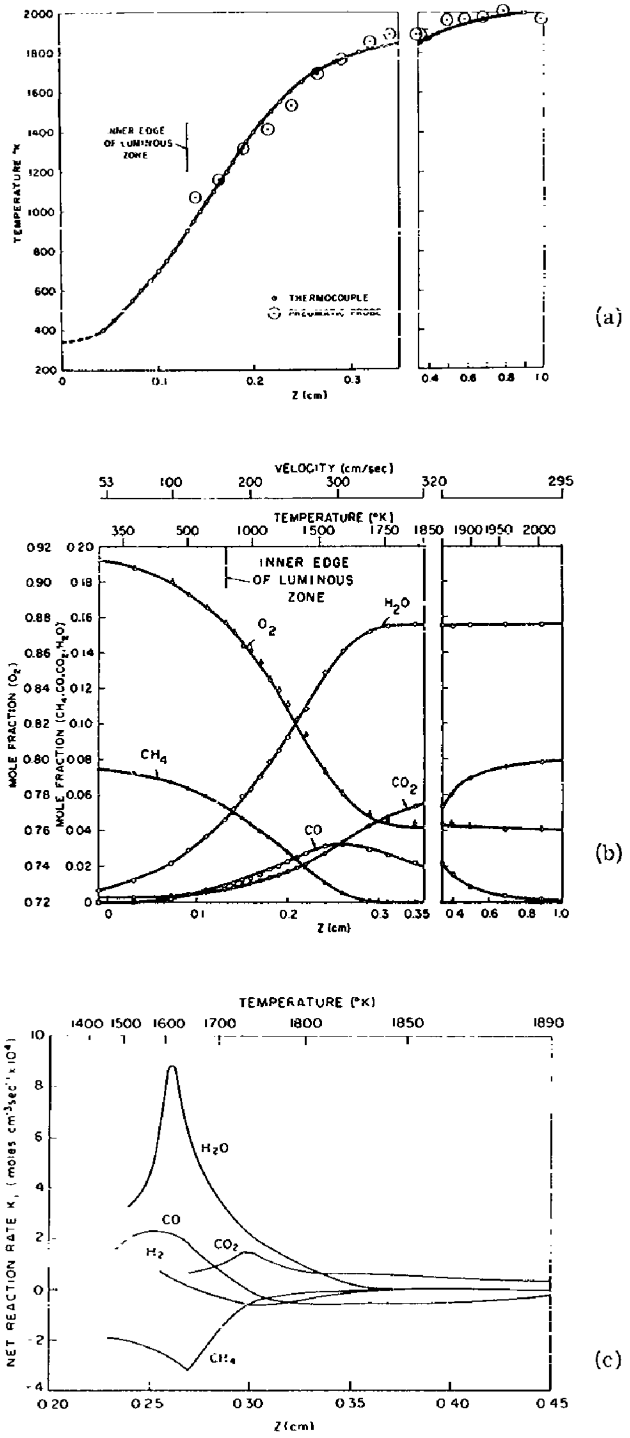

Figure II-3 CHARACTERISTIC PROFILES FOR A METHANE-OXYGEN FLAME

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5. R. M. Fristrom, "Structure of Laminar Flames", Sixth Symposium (International on Combustion), pp. 96-110, Reinhold Publ. Co., New York (1957).

6. R. M. Fristrom, C. Grunfelder, and S. Favin, "Methane-Oxygen Flame Structure I - Characteristic Profiles in a Low-Pressure, Laminar, Lean, Premixed Methane-Oxygen Flame", J. Phys. Chem. 64, 1386-92 (1960).

Radical-Atom Concentration Profiles

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

Radicals and atoms are not susceptible to conventional sampling techniques because of their extreme reactivity which transforms them into stable species before analysis is possible. In most flame structure studies (Refs. 5 and 7) these concentrations are considered (usually correctly) to be negligible compared with the concentrations of the stable species, and are therefore neglected in the analysis. This reasonable approximation is, of course, only a stopgap measure to obtain information while satisfactory methods are developed for determining atom and radical concentrations. None of the techniques thus far developed (Refs. 8 through 10) possess the generality and spatial resolution necessary for the quantitative interpretation which we wish to make. Therefore, we are developing a new technique for studying radical concentration profiles under a companion flame structure study supported by ARPA (Task R). This is the scavenger probe method, which combines the techniques of probe sampling with those of chemical scavenging. A sample is taken through a probe, and the radical-containing gases are mixed rapidly with a large excess of a suitable "scavenger" gas which reacts with the radical to produce a characteristic product. Scavenger studies are well known in radiochemistry and photochemistry (Ref. 11), and mass spectrometer studies (Ref. 12) have indicated that radicals can be sampled successfully through orifices.

An absolute measurement of concentration can be made if 1) there is a one-to-one correspondence between the reaction product and the precursor radical and, 2) the analytical system (mass spectrometer) can be calibrated for the stable reaction product. This is a significant advantage since it is notoriously difficult to obtain absolute radical concentrations. Spatial resolution will be limited by the probe diameter, and sensitivity should be as high as the analytical system allows for stable species. As this technique is developed it will be used in these studies.

Temperature Profiles

Temperature profiles offer an important technique 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 (Ref. 6), although of varying precision.

The most precise method is that with thermocouple traverses in which temperatures are measured with fine (0.0005") Pt-Pt 10% Rh thermocouples coated with silica. Profiles with a precision of 10°K and excellent spatial reproducibility are obtained.

Temperature can be determined by using aerodynamic measurements of velocity and area ratio, deriving the point-by-point density through the continuity relations, and then applying the perfect gas law. The results are not of high precision (2-4%), but within their limits, they provide a reliable measure of the translational temperature of the gas.

Temperatures can also be measured with a pneumatic probe (Ref. 13). This device is a quartz probe similar to those used in the composition studies. If gas flows under choking conditions through two orifices in series, and the temperature is known at the second orifice, temperature at the inlet orifice of such a probe can be derived from the relation between ambient pressure and the pressure between the two orifices. This technique provides a moderately precise (1-2%) and reliable method for determining temperature and has the added advantage that it can be directly associated with a composition, since it can also be used for composition sampling.

Aerodynamic Profiles

Flames can be characterized aerodynamically by two profiles - velocity and area ratio. As mentioned under temperature measurements, these can be combined to derive a density profile. 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

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7. R. M. Fristrom, "Experimental Determination of Local Concentrations in Flames", APL JHU CM-978.

8. C. G. James and T. M. Sugden, "Photometric Investigations of Alkali Metals in Hydrogen Flame Gases I - A General Survey of the Use of Resonance Radiation in the Measurement of Atomic Concentration", Proc. Roy. Soc. A-227, p. 312 (1955).

9. W. E. Kaskan, "Hydroxyl Concentrations in Rich Hydrogen-Air Flames Held on Porous Burners", Comb. and Flame 2, 229-43 (1958).

10. T. Grewer and H. G. Wagner, "Die Reaktionszone von Flammen", Zeit. fur Phys. Chem. (Neue Folge) 20, 371-74 (1959).

11. R. H. Schuler, "Scavenger Methods for Free Radical Detection in Hydrocarbon Radiolysis", J. Chem. Phys. 62, 37-41 (1958).

12. S. Foner and R. Hudson, "The Detection of Atoms and Free Radicals in Flames by Mass Spectrometric Techniques", J. Chem. Phys. 21, 1374-82 (1953).

the flame is appreciable. With a symmetrical flame, such as the spherical flame, it is unnecessary to make this measurement, since it can be obtained directly from the geometry of the position determinations. Direct aerodynamic 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 measurements (Ref. 14).

SIMPLE REACTION STUDIES

Flame systems have relatively complex chemistry (see Table I) which makes the identification of the dominant reactions difficult. For this reason it is desirable to supplement the flame studies with studies of the individual reactions with simplified chemistry. A second reason for doing so is that these studies will be made at lower temperature, thus enabling more precise estimates to be made of the activation energy.

The activation energy of most flame reactions lies below 10 kilocalories per mole, so that at flame temperatures the rate is a very insensitive function of the activation energy. On the other hand for this very reason, flame studies allow an accurate determination of the steric factor and may ultimately allow a determination of its temperature dependence - a problem which has plagued chemical kineticists for many years.

The techniques we propose to use are the conventional discharge tube-mixing techniques, with the addition of direct measurement of radical concentrations using the scavenger probe technique being developed. This work has been summarized by Steacie (Ref. 3) to 1954. More recent work has been carried out by a number of authors (Ref. 15).

DATA ANALYSIS

To make quantitative interpretation of flame structure information it is necessary to analyze the data. An analysis consists of calculating the actual flux profiles and rate of species and heat production profiles by quantitatively accounting for the effects of molecular diffusion and thermal conductivity. This step is necessary to avoid false impressions of the rate processes involved (Fig.II-3), since in many flames the effects of diffusion and thermal conduction are large.

Table I

Methane-Oxygen Flame Reaction Kinetic Constants

Reaction	Activation Energy, E (kcal mole^{-1})	Frequency Factor, A (10^{14}cm^3 mole^{-1} sec^{-1})
$CH_4 + OH \rightarrow CH_3 + H_2O$	8.5	2
$CH_4 + O \rightarrow CH_3 + OH$	8	2*
$CH_3 + O_2 \rightarrow OH + H_2CO$	0	1
$H_2CO + OH \rightarrow HCO + H_2O$	0	2
$HCO + OH \rightarrow CO + H_2O$	0	2
$CO + OH \rightarrow CO_2 + H$	7	0.3
$H + H_2O \rightarrow OH + H_2$	25	1
$OH + H_2 \rightarrow H_2O + H$	18	5
$O + H_2 \rightarrow OH + H$	10	1
$OH + OH \rightarrow H_2O + O$	10	1
$O + O + M \rightarrow O_2 + M$	0	-
$H + O_2 \rightarrow OH + O$	18	5

* The value given is an estimate, normal for this type of reaction.

This analysis is based on the flame equations consisting of conservation laws and the differential equations of transport and chemical kinetics. They have been formulated in generality by Hirschfelder (Ref. 16) and adapted for flame structure analysis by Westenberg (Refs. 17 and 18).

Thermodynamic Information

The thermodynamic functions of interest are enthalpies, and heat capacities. This information is generally available for almost all of the species

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13. C. Gunfelder, Jr., "Instruments for the Measurement of Local Flame Temperatures in High-Velocity Streams", APL JHU CM-768 (1953).

14. R. M. Fristrom, W. H. Avery, R. Prescott, and A. Mattuck, "Flame Zone Studies by the Particle-Track Technique I - Apparatus and Technique", J. Chem. Phys. 22 106-9 (1954).

15. Symposium on Some Fundamental Aspects of Atomic Reactions, Can. J. of Chem., Vol. 38, October (1960), pp. 1643-2032.

16. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, John Wiley and Sons, New York, pp. 756-83, (1954).

17. R. M. Fristrom and A. A. Westenberg, "Flame Zone Studies IV - Microstructure and Material Transport in a Laminar Propane-Air Flame Front", Comb. and Flame 1, 217-8 (1957).

found in flame inhibition studies over the temperature range of interest. Several standard reference sources are available (such as Ref. 18) which provide data of sufficient accuracy for our purposes.

Transport Coefficient Studies

Transport coefficient information is necessary for the 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 multicomponent diffusion coefficients necessary for the interpretation of such systems are a complex function of all of the binary diffusion coefficients (Ref. 19). 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 coefficient of the individual species with the dominant species. The general case, with no single dominant species, could also be handled, but only at the expense of an order of magnitude increase in the necessary diffusion coefficient information (in the general multicomponent case, it is necessary to know the diffusion coefficients of all of the possible pairs of species) (Ref. 20).

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 (Ref. 21). Diffusion coefficient data are available for the methane-oxygen system (Ref. 22).

The problem of thermal conductivities of mixtures is in a less satisfactory state, but fortunately this information is unnecessary for kinetic studies. An analogous "point source" technique is being developed at APL under Task R for making such measurements (Ref. 23).

INTERPRETATION

The interpretation of this information on flame structure consists of deriving chemical kinetic information and information on flame processes (Refs. 24 through 26). The analysis provides 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 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.

Chemical Kinetic Information

Once a mechanism is assigned, the derivation of chemical kinetic data from flame structure and simple reaction rate information is straightforward. The choice of mechanism is largely a subjective process. We will not discuss the process other than to point out that a useful beginning is often a systematic collection of the possible reactions. The data which we have available from flame structure and simple reaction studies are: temperature, concentrations, and rates. The constants which are of interest are: the activation energy E, the steric factor P, and the temperature dependence of the steric factor n. In most kinetic studies, and probably in our initial work, the precision is not sufficient to allow separation of the temperature dependence factor from the exponential dependence of the activation energy. Flame studies, however, do offer information in a temperature regime which may ultimately allow such a separation to be made. If this is possible, it will represent an important addition to kinetic information. The relation of the exponential and power dependence of the reaction rate on temperature is best visualized by expanding the Arrhenius exponential factor as a series:

$$R_i = R_j = X_i\,X_j\,Z\,P\,T^n\,e^{-E/RT}$$

$$= X_i\,X_j\,\frac{Z_o}{T_o^{1/2}}\,P\left\{T^{n-1/2} - E/R\,T^{n-3/2} + \frac{E^2}{2!\;R^2}\,T^{n-5/2} + ------\right\}$$

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18. A. A. Westenberg and R. M. Fristrom, "Methane-Oxygen Flame Structure II - Conservation of Matter and Energy in the One-Tenth Atmosphere Flame", J. Phys. Chem. 64 1393-8 (1960)

19. F. D. Rossini, et. al, Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, Carnegie Press, Pittsburgh, Pa. (1953).

20. R. E. Walker, N. deHaas, and A. A. Westenberg, "Measurements of Multicomponent Diffusion Coefficients for the CO_2-He-N_2 System Using the Point-Source Technique", J. Chem. Phys. 32, 1314-16 (1960).

21. R. E. Walker and A. A. Westenberg, "Molecular Diffusion Studies in Gases at High Temperature I - The 'Point Source' Technique", J. Chem. Phys. 29, 1139-46 (1958)

22. R. E. Walker and A. A. Westenberg, "Molecular Diffusion Studies in Gases at High Temperature IV - Results and Interpretation of the CO_2-O_2, CH_4-O_2, and H_2O-O_2 Systems", J. Chem. Phys. 32, 436-42 (1960).

Since the species are interrelated, a number of cross checks should be possible on the derived kinetic constants, so that there will be a reasonable assurance of the essential correctness of the derived mechanism.

Simplified Theory

The goal of these studies is to provide a description of flame inhibition which is relatively simple and yet still will yield quantitative predictions. This may not always be possible, but it appears that in the case of the methane-oxygen flame a start can be made. The goal of such a simplified theory would be to enable quantitative predictions to be made of the effect of inhibitor on flame reactions (and hence burning velocity) with a precision of 20 per cent. In a sense this simply represents the limit of interpretations, since all mechanisms represent abstractions of the true system.

RECOMMENDATIONS OF FLAME INHIBITION

As a result of this work it is hoped that it will be possible to make some practical recommendations on flame inhibition. It is hardly possible to predict in advance what such recommendations will be, but it seems reasonable to expect that they will include recommendations of specific inhibitors for specific flame systems.

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23. R. E. Walker, N. deHaas, and A. A. Westenberg, "New Method of Measuring Gas Thermal Conductivity", Phys. of Fluids 3, 482 (1960).

24. R. M. Fristrom, A. A. Westenberg, and W. H. Avery, "Etude du Mechanisme de la Reaction Propane-Air par l' Analyse de Profils de Fronts de Flamme", de l' Institut Francais du Petrole et Annales de Combustibles Liquids, Vol. XIII, No. 4, pp. 544-53 (1958)

25. A. A. Westenberg and R. M. Fristrom, "Methane-Oxygen Flame Structure IV - Chemical Kinetic Considerations", J. Phys. Chem. to be published Feb. 1961.

26. R. M. Fristrom and A. A. Westenberg, "Experimental Chemical Kinetics from Methane-Oxygen Laminar Flame Structure", Presented at the Eighth Symposium (International) on Combustion, Sept. 1960.

III. SUMMARY OF PREVIOUS WORK

SUMMARY OF WORK PRIOR TO 1 NOV. 1960

The work prior to the initiation of this contract (on 1 November 1960) consisted of a survey of the possibilities of applying flame structure data to flame inhibition studies, and a suggested program for such studies. This work was summarized in a proposal submitted to the U. S. Army Engineering Research and Development Laboratory in October 1960 (Ref. 4, on page 2).

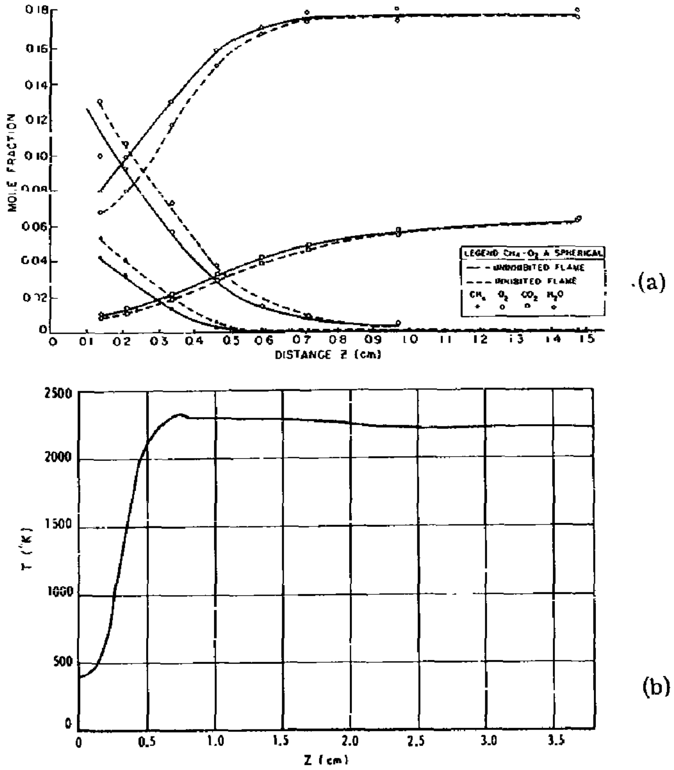


Figure III-1 THE EFFECT OF ADDED HBr ON THE CHARACTERISTIC PROFILES OF A STOICHIOMETRIC METHANE FLAME. COMPOSITION OF THE MAJOR SPECIES (mole fractions) AND TEMPERATURE IS PLOTTED AGAINST DISTANCE, Z (cm.).

SUMMARY OF PROGRESS, 1 NOV. 1960 - 31 JAN. 1961

(1) A flat flame burner was set up for flame inhibition studies. The previously studied methane flame (CH_4 - 0.078, O_2 - 0.92; pressure 0.05 atm) was successfully stabilized with added inhibitor (HBr) up to concentrations of 0.0035 mole fraction.

(2) Using the uninhibited flame, two flame composition profiles were run on the new time-of-flight mass spectrometer. A third run was made on an inhibited flame to test the sensitivity of the instrument for HBr. From these test runs it was concluded that the instrument requires the addition of a trap current regulator to allow quantitative work and a forepump trap to shorten the HBr pump-out time. These items have been ordered, and the inhibitor studies have been temporarily transferred to the CEC magnetic-deflection spectrometer.

(3) A computing machine routine for the automatic reduction of flame structure data has been developed.

(4) A report on the flame inhibition program was presented 15 November 1960 at the meeting on "Inhibition of Ignition and Flames with Chemicals." This meeting was sponsored by the Committee on Fire Research of the National Academy of Sciences, National Research Council.

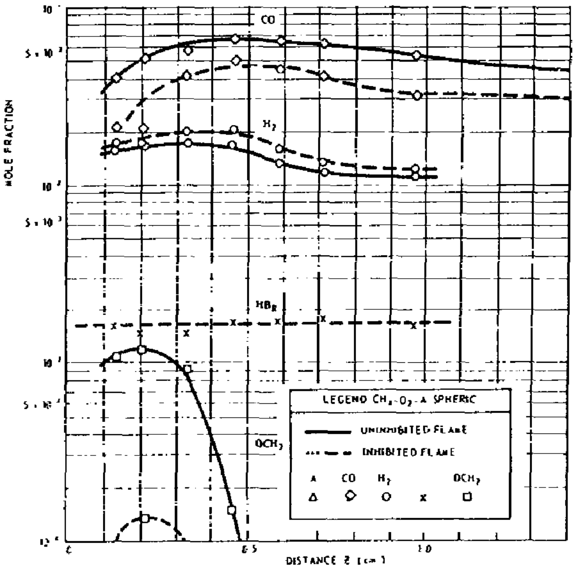


Figure III-2 THE EFFECT OF ADDED HBr ON THE CONCENTRATIONS OF INTERMEDIATE SPECIES IN A STOICHIOMETRIC METHANE FLAME.

SUMMARY OF PROGRESS, 1 FEB. - 30 APR. 1961

(1) A spherical flame apparatus was set up for inhibition studies on the system (CH_4 - 0.09, O_2 - 0.179, Ar - 0.727, pressure 0.05 atm). Composition profiles were measured for both the inhibited and uninhibited flames with the same total mass flow. In addition to measuring the concentrations of the species which were stable to sampling, an attempt was made to measure hydrogen-atom concentration profiles using a new device, "the scavenger sampling probe." Qual-

itative consideration of these results yields the following information:

(a) The addition of this amount of inhibitor ($X(HBr) = 0.0015$) appreciably lowers the rate of reaction of the major species (CH_4, O_2, and CO).

(b) Peak concentrations of the intermediate species (OCH_2, CO, and H_2) are changed and shifted relative to the major species. When data on diffusion and temperature become available, a quantitative interpretation may yield H, OH, and CH_3 radical concentration data.

(c) The apparent concentration of H atoms was depressed almost five-fold by the addition of HBr even in the equilibrium region.

(d) HBr was the only bromine-containing compound detected ($X(Br_2) < 10^{-4}$).

These latter two results are probably artifacts of the techniques. They may, however, yield useful information and provide a guide for subsequent work.

(2) A series of computer calculations were made of the adiabatic temperatures and compositions of the equilibrium burned gases of some CH_4 - O_2 - Ar mixtures and of the effect of adding small amounts of HBr. A routine developed by the U. S. Naval Ordnance Test Station was used on the APL computer to determine these flame properties. One of the most interesting points developed was that the HBr is almost completely dissociated and that bromine atoms are the commonest inhibitor species in the burned gases.

SUMMARY OF PROGRESS, 1 MAY - 31 JULY 1961

(1) A set of composition and temperature profiles was determined for a flat methane-oxygen flame (CH_4 - 0.078, O_2 - 0.92, P = 0.05 atm) with and without added HBr. Corrosion was so severe that the burner assembly became unusable. A new teflon-glass-ceramic system including traps to protect the pumps has been designed and is being fabricated.

(2) A program to measure the high-temperature diffusion coefficients for the analysis of the inhibited flames has been started. The apparatus has been activated and tested at 300°K and 500°K on the well-known $He-N_2$ system. Measurements have been started on the $Ar-H_2$ system.

(3) Scavenger probe studies of radical concentrations in flames have been continued. The use of chlorinated hydrocarbons as scavenger for H atoms has been shown to be proportional to H, but the scavenging efficiency was found to be only 10%. Studies of oxygen-atom concentration using NO_2 as a scavenger have been made.

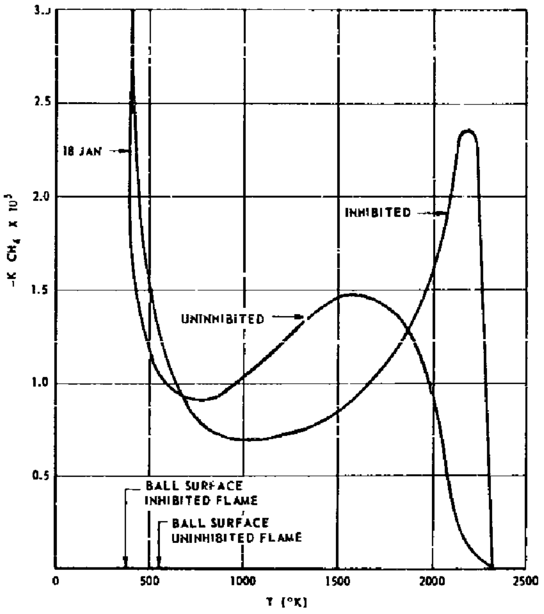


Figure III-3 THE EFFECT OF HBr ON THE RATE OF METHANE DISAPPEARENCE IN A STOICHIOMETRIC FLAME (CH_4 - 0.09 O_2-0.179 A-0.727; P = 0.05 Atm.). K_{CH_4} (MOLES PER CUBIC CM. PER SEC x 10^5) VERSUS TEMPERATURE (°K)

NOTE THAT AN APRECIABLE PART OF THE REACTION APPEARS TO BE OCCURING AT OR NEAR THE SURFACE OF THE BALL. THE PRINCIPLE EFFECT OF THE ADDED HBr APPEARS TO BE A SHIFT OF THE REACTION TO THE HIGH TEMPERATURE REGION.

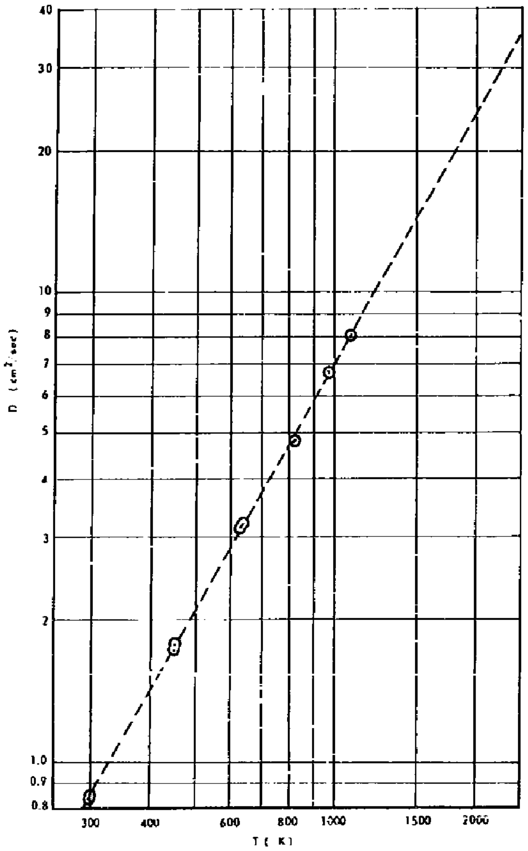


Figure III-4 DIFFUSION COEFFICIENT OF THE SYSTEM H_2 (trace) -Ar AS A FUNCTION OF TEMPERATURE

The efficienty of scavenging appears to be high and may approach 100%.

SUMMARY OF PROGRESS 1 AUG. - 31 OCT. 1961

(1) A temperature profile was measured on the spherical stoichiometric methane-oxygen-argon flame system whose composition structure was reported in TG 331-2. (See pp 9)

(2) The diffusion coefficient of the system A-H_2 (tract) was measured at atmospheric pressure over the range 300 - 1070°K. (See pp 12)

(3) An analysis was made of the effect of added HBr on the fluxes and rates on the stoichiometric methane flame. (See pp 14). This indicated that a significant fraction of the reaction occurred on the surface of the ball.

Table III-I

Test of Oxygen-Atom Scavenger Probe*

System						
CH_4	O_2	Ar	T_o (°K)	P (atm)	Expt'l.	Calculated**
0.078	0.92	0.002	313	4.1	0.0019	0.0020
0.10	0.18	0.72	313	3.8	0.0030	0.00325

* Using the reaction $O + NO_2 \cdot NO - O_2$ for scavenging in flame microprobe-sampling studies (see Figure III-5a below), the O-atom concentrations were found in the equilibrium burned gas region.

** Values interpolated from calculation made using T_o = 400°K.

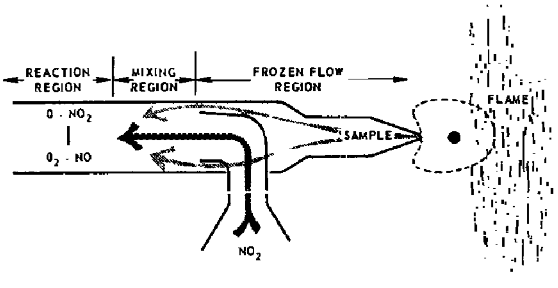


Figure III-5a SCHEMATIC DIAGRAM OF SCAVENGER PROBE USED IN MEASURING OXYGEN ATOM CONCENTRATIONS

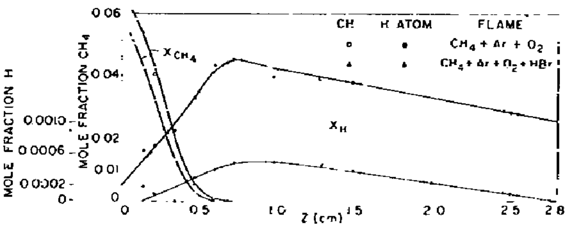


Figure III-5b EFFECT OF ADDED HBr ON COMPOSITION PROFILES OF METHANE AND HYDROGEN ATOMS IN A METHANE FLAME

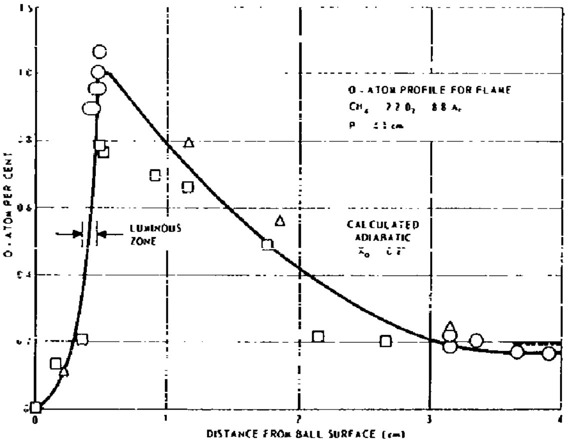


Figure III-5c TEST OF OXYGEN-ATOM SCAVENGER PROBE

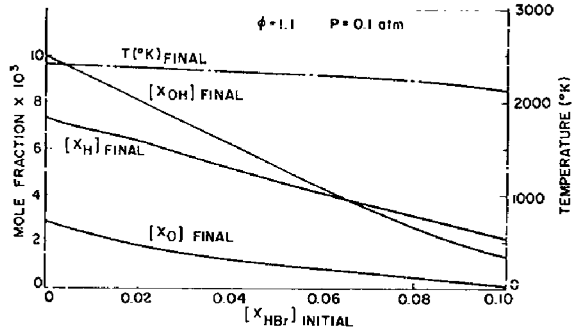


Figure III-6a EFFECT OF ADDED HBr ON FLAME RADICAL CONCENTRATIONS (H, O, OH)

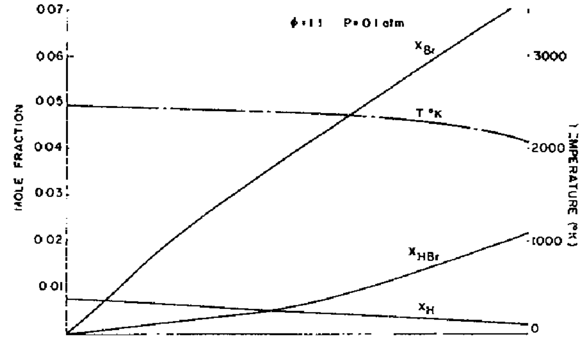


Figure III-6b EFFECT OF HBr CONCENTRATION ON INHIBITOR SPECIES CONCENTRATIONS (HBr, Br, Br_2)

SUMMARY OF PROGRESS 1 November 1961 - 31 January 1962

(1) To circumvent the corrosion problems encountered in previous metal burner systems a new spherical flame apparatus has been designed and constructed using exclusively glass, Teflon, and ceramic materials. The sampling probe has been modified to allow temperature measurements to be made by the pneumatic probe method, thus allowing the direct association of temperature and composition measurements.

(2) The problem of handling and precisely measuring small amounts of corrosive materials has been solved by the construction of a new type of pressure transducer whose critical parts are constructed of Teflon and glass.

(3) The scavenger probe studies of atom concentrations have continued. A newly designed apparatus has been constructed and tested in studies of oxygen atom concentration in a spherical methane flame. The results were satisfactory in reproducibility. Quantitative comparison of these results with equilibrium calculations were frustrated by serious enthalpy losses through conduction of the flask walls.

SUMMARY OF PROGRESS 1 February - 30 April 1962

(1) The spherical flame was operated under maximum pressure and flow conditions in an effort to circumvent the wall cooling problems previously reported. Studies of this flame indicated that the adiabatic temperature maximum was attained but that oxygen atom concentration remained out of equilibrium. It was concluded that the solution to the problem was either an increase in flask size or the use of a flat flame; therefore, an all glass, ceramic, and Teflon burner has been constructed and tested. The system employs a flat flame burner and the sampling system has been designed so that temperatures can be measured using the pneumatic probe technique; and provision has been made to determine radical concentrations using the scavenger sampling probe technique.

(2) The scavenger sampling probe technique for oxygen atoms has been compared with gas phase titration in an electric discharge. The two techniques agreed very well, provided certain precautions are taken. Some limitations of the gas phase titration technique are discussed.

FLAME INHIBITION RESEARCH

IV. Report of Progress
1 May - 31 July 1962

FLAME STRUCTURE STUDIES

W. E. Wilson, J. T. O'Donovan and R. M. Fristrom

Some difficulty has been encountered in developing a corrosion resistant burner that is sufficiently rugged to hold together for the duration of a complete run. The first burner used glass mesh screens fastened with Sauerisen cement. This was satisfactory for runs of a few minutes but with prolonged use the increase in burner temperature caused the screen and cement to crack.

Next a ceramic plate, Alundum RA98, was tried. First is was cemented to a glass tube with Sauerisen. The pressure drop across the Alundum plate was fairly large and the cement was too porous to make a satisfactory seal. Next a Teflon fitting was machined to hold the Alundum plate on the glass tube. This worked fine at first but the Teflon lost its dimensional stability when it got hot and began to leak around the edges. A new glass-ceramic burner is being fabricated which will use a glass plate and a Viton "O" ring or gasket seal. In addition a burner will be constructed from a porous porcelain plate sealed in a porcelain funnel.

While efforts continue to develop a corrosion resistant burner, some studies are being made on a glass burner with a nickel mesh screen. Three runs have been made with a CH_4-O_2 flame, two using I_2 as a scavenger and one with I_2 added to the fuel-air mixture prior to burning. The major purpose was to see if it is possible to determine the H atom and CH_3 free radical concentration by the reactions:

$$I_2 + H^{\cdot} \rightarrow HI + I^{\cdot} \text{ and } I_2 + CH_3^{\cdot} \rightarrow CH_3I + I^{\cdot}.$$

In the first run I_2 was added through the scavenger probe. The mass spectrometer was run at maximum pressure for the most efficient detection of trace species. No HI was detected. A small amount of CH_3I was observed, 5 units when O_2 was 30,000 units. Although this is too small a peak to be reliable it did appear to be present and show a profile through the flame.

In the second run I_2 was added to the fuel-air mixture in the hope of seeing a larger quantity of HI and CH_3I. The CH_3I was about the same and there was no HI. An unexpected observation was that the I_2 formed solid HIO_3 which deposited on the outside of the probe.

For the third run the following technique was tried. I_2 was added in the scavenger probe and was frozen out in a dry ice trap before reaching the mass spectrometer. After being analyzed the gas stream was pumped through a trap cooled with liquid nitrogen so that all species except O_2, H_2 and CO were frozen out. After a sufficiently large sample was collected, the spectrometer was closed, the trap allowed to warm up, and the batch sample analyzed. This technique gives a 10 fold magnification of the frozen out species and thus makes it possible to obtain a more accurate analysis of the minor components.

For this run the CH_3I and OCH_2 peaks give a very nice profile. (Fig. IV-1). Although the technique needs more testing it appears to be a useful analytical tool.

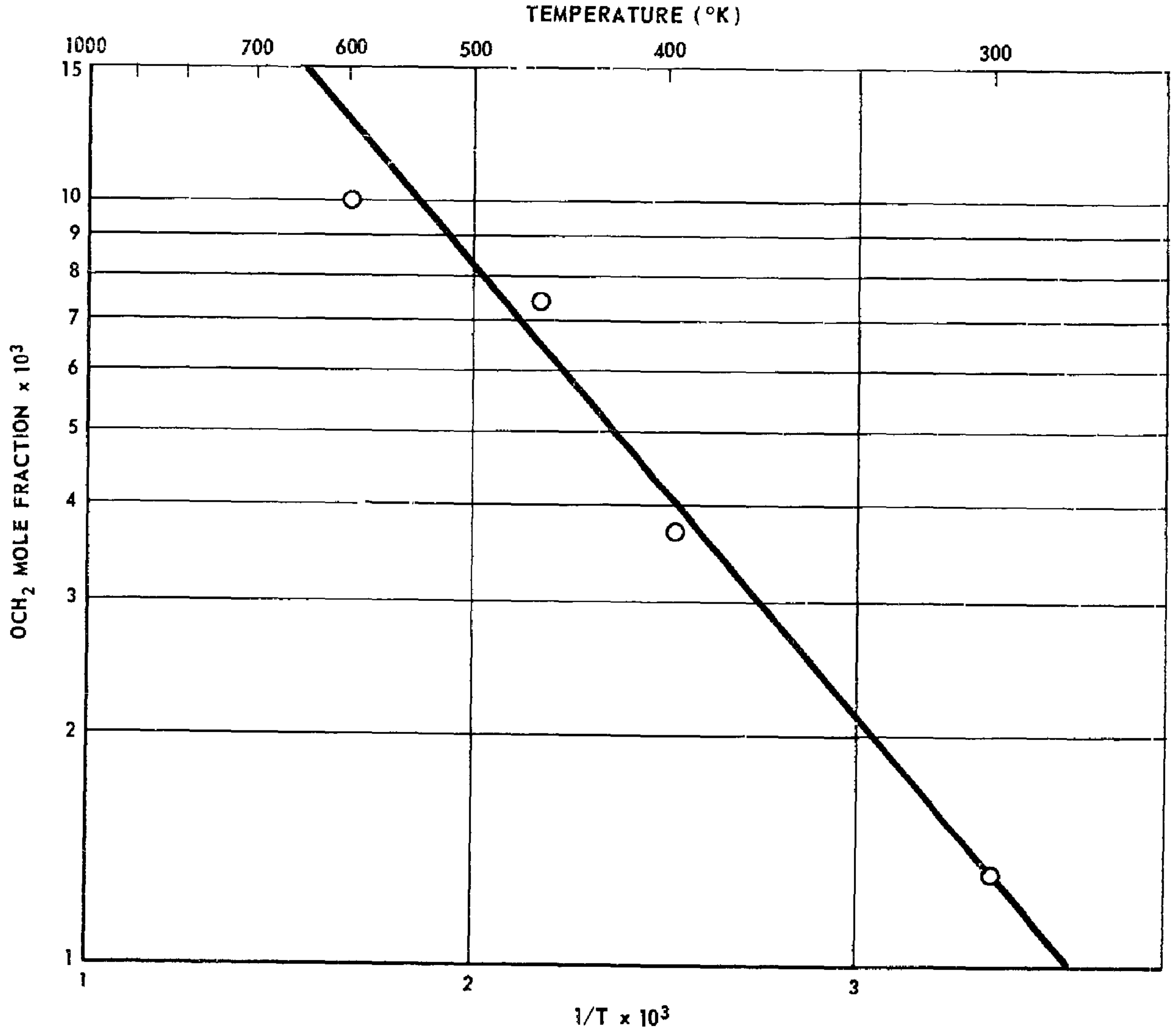


Fig. IV-1 METHYL IODIDE, FORMALDEHYDE, METHANE, AND TEMPERATURE PROFILES THROUGH A TWENTIETH ATMOSPHERE METHANE-OXYGEN FLAME

ELEMENTARY REACTION STUDIES

R. M. Fristrom and C. Grunfelder

Flame reactions and inhibition reactions are closely coupled and it is difficult to unambiguously identify and study the reaction path. The HBr inhibited methane flame is such a case. The main outline of the reactions seems established, but several ambiguities remain and some of the reactions appear to have such low activation energies that it is difficult to derive accurate values from high temperature studies.

A number of these problems could be solved by companion studies of the radical reactions at lower temperatures in simpler systems. This can be accomplished by preparing radicals in electric discharges (or by chemical means) and mixing them with reactants in a low pressure reaction tube.

An apparatus of this type was constructed to test the scavenger probe (Ref. 1). It has been modified to allow operation in the range between 300 and 600°K. Provision has been made for varying the residence time with constant mass flow and pressure, for doing gas phase titration and for scavenger sampling.

With this set up we plan to obtain information on: (1) Kinetics of the inhibition reactions of HBr and Br_2; (2) try to establish the activation energy of the reaction $CH_4 + OH \rightarrow H_2O + CH_3$; (3) determine the relative importance of oxygen atoms and molecules in reactions with methyl radicals; (4) clarify the reactions of formaldehyde in the methane flame.

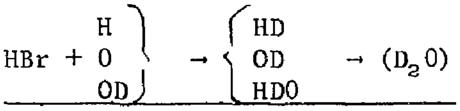
Initial trials with the apparatus were aimed at testing methods for preparing known concentrations of "pure" radicals. "Pure" meaning free from other radicals. The radicals of interest in the methane flame are H, O, OH, and CH_3. A number of techniques have been evaluated.

TABLE 1

REACTIONS FOR PRODUCING "PURE" RADICALS

RADICAL	REACTION	REMARKS
H	$K + HBr \rightarrow KBr + H$	Difficult to keep system free of K and KBr.
0	$N + NO \rightarrow N_2 + 0$	Requires high energy discharge to form N from N_2.
OH	$H + NO_2 \rightarrow OH + NO$	Half life of OH very short.
CH_3	$H + CH_3I \rightarrow HI + CH_3$	Half life of CH_3 very short.
CH_3	$K + CH_3I \rightarrow KI + CH_3$	Half life of CH_3 very short.

A study of the reactions of flame radicals with inhibitors has been initiated. Two runs have been made: the reactions of HBr with the products of a D_2O discharge and oxygen atoms with methyl iodide.



$$HBr + \left.\begin{matrix} H \\ 0 \\ OD \end{matrix}\right\} \rightarrow \left\{\begin{matrix} HD \\ OD \\ HDO \end{matrix}\right. \rightarrow (D_2O)$$

The study of HBr reactions with the products of a heavy water discharge was initiated with the hope that the relative importance of the reactions of HBr with these three radicals could be determined from the concentrations of HD, H_2O, HDO, and D_2O. Kinetic constants for the reactions with 0 and OH could be deduced by comparison with the known kinetics of the D-HBr reactions, (Ref. 2). The interpretation of the data was made difficult by wall exchange in the sampling system which disturbed the various water concentrations. The initial data is shown in Table 2.

TABLE 2

PEAK HEIGHTS FOR D_2O DISCHARGE PRODUCTS

Product	HD	D_2	HDO	O_2
Without HBr	37	2600	470	4100
With HBr	314	2700	345	5100

These results are puzzling and indicate that the reaction of HBr with the radicals D, OH and O may be more complex than we have presumed above. In particular, the addition of HBr to the discharge effluent actually decreased the formation of HDO (some HDO is formed in the pure D_2O discharge because of liberation of H_2O from the walls due to the action of the discharge). This could not be due to HBr entering the discharge region because the discharge was isolated by a choking orifice. The other peculiarity is that the production of molecular oxygen went up sharply. This is an unexpected result and presumably due to some unknown reaction:

$$HBr + \left\{\begin{array}{l} H \\ O \\ OH \\ ? \end{array}\right. \rightarrow O_2 + ?$$

To surmount the exchange problem a teflon lined sampling system and spectrometer inlet is being constructed. The rate of formation of HD in our system confirmed previous studies of the $D + HBr \rightarrow HD + Br$ reaction. The reaction is rapid at room temperature and must have a low activation energy. The usually accepted value is 1.1 k cal/mole, (Ref. 3).

$O + CH_3I \rightarrow OCH_2$ + other products.

The reaction of oxygen atoms with methyl iodide has been surveyed. Appreciable reaction occurs with the emission of yellow light. The system is complicated, yielding formaldehyde, traces of ethane (c.a. 5 percent of the reaction product) and golden colored solid. This solid is similar in appearance to that which accumulates in the reaction between hydrogen atoms and carbon tetrachloride. It is a by-product of the same importance as the ethane. Possible it is a polymer of the teflon, polyethylene family with a CHI unit. This system appears to be too complex for immediate study.

A study is being made of the reaction of OH with methane. This is the principle reaction of methane in lean flames; it has been studied at this laboratory (Ref. 4) and others (Refs. 5 and 6). There is excellent agreement in the absolute rates measured in the various flames, but there is considerable disagreement as to the choice of activation energy, (Ref. 4), Fig. 1. The reason is the high temperature range in which the studies were made. The addition of low and moderate temperature studies should allow clarification of this point and improve the precision of the kinetic constants.

The OH radicals were prepared by the reaction of NO_2 with hydrogen atoms (formed in a microwave discharge). By measuring the amount of NO formed the initial OH flux could be determined. Methane was of research grade containing a few tenths of a percent of ethane as an impurity. The products of reaction were primarily methyl alchol and formaldehyde rather than ethane (from methyl radical recombination) or HCN from the reaction $CH_3 + NO \rightarrow H_2O + HCN$.

Because of the rapidity of the recombination of OH it was not feasible to make direct measurements of rate by varying the residence time. Therefore, the reaction was followed by allowing it to go to completion in competition with $OH + OH \rightarrow H_2O + O$; $O + OH \rightarrow H_2O + H$ and $2H \rightarrow H_2$. Kinetic constants have recently become available for these reactions.

To derive a preliminary activation energy it was assumed that the fraction of OH reacting with methane is proportional to the mole fraction of formaldehyde produced (within the limits of error this checks with the methane disappearance). This amount is small compared with the OH disappearing by recombination; therefore, the logrithmic slope of the fraction converted as a function of temperature should be related to the difference in activation energy, (see Fig. IV-2), between the two processes. This slope corresponds to a difference of 3 k cal/mole which corresponds to 4.5 k cal/mole for the OH + CH_4 reaction (Ref. 6).

References

1) Flame Inhibition Research Quarterly Progress Report No. 6, The Johns Hopkins Applied Physics Laboratory, TG-376-6, pp 14-20, May 1963.

2) E. S. Campbell and R. M. Fristrom, "Reaction Kinetics, Thermodynamics and Transport in the Hydrogen-Bromide System", A Survey of Properties for Flame Studies", Chem. Rev. 58, 206, (1958).

3) F. Kaufmann and F. P. Del Greco, "Fast Reactions of OH Radicals", Preprint No. 12 Discussion Fundamental Flame Processes" IXth International Symposium on Combustion (Cornell), Chairman, W. H. Avery, The Applied Physics Laboratory, Silver Spring, Md., (June 1962).

4) R. M. Fristrom, "Radical Concentrations and Reactions in a Methane-Oxygen Flame", Preprint No. 2, "Discussion on Fundamental Flame Processes", IXth International Symposium on Combustion (Cornell), Chairman, W. H. Avery, The Applied Physics Laboratory, Silver Spring, Md., (June 1962).

5) C. P. Fennimore and G. W. Jones, "The Rate of Reaction of Methane with H atoms and OH radicals", J. Phys. Chem. 65, 591 (1961).

6) E. W. R. Steacie, Atomic and Free Radical Reactions (vol. 2) p 605, 2nd ed., Reinhold Pub. Co., New York, (1954).

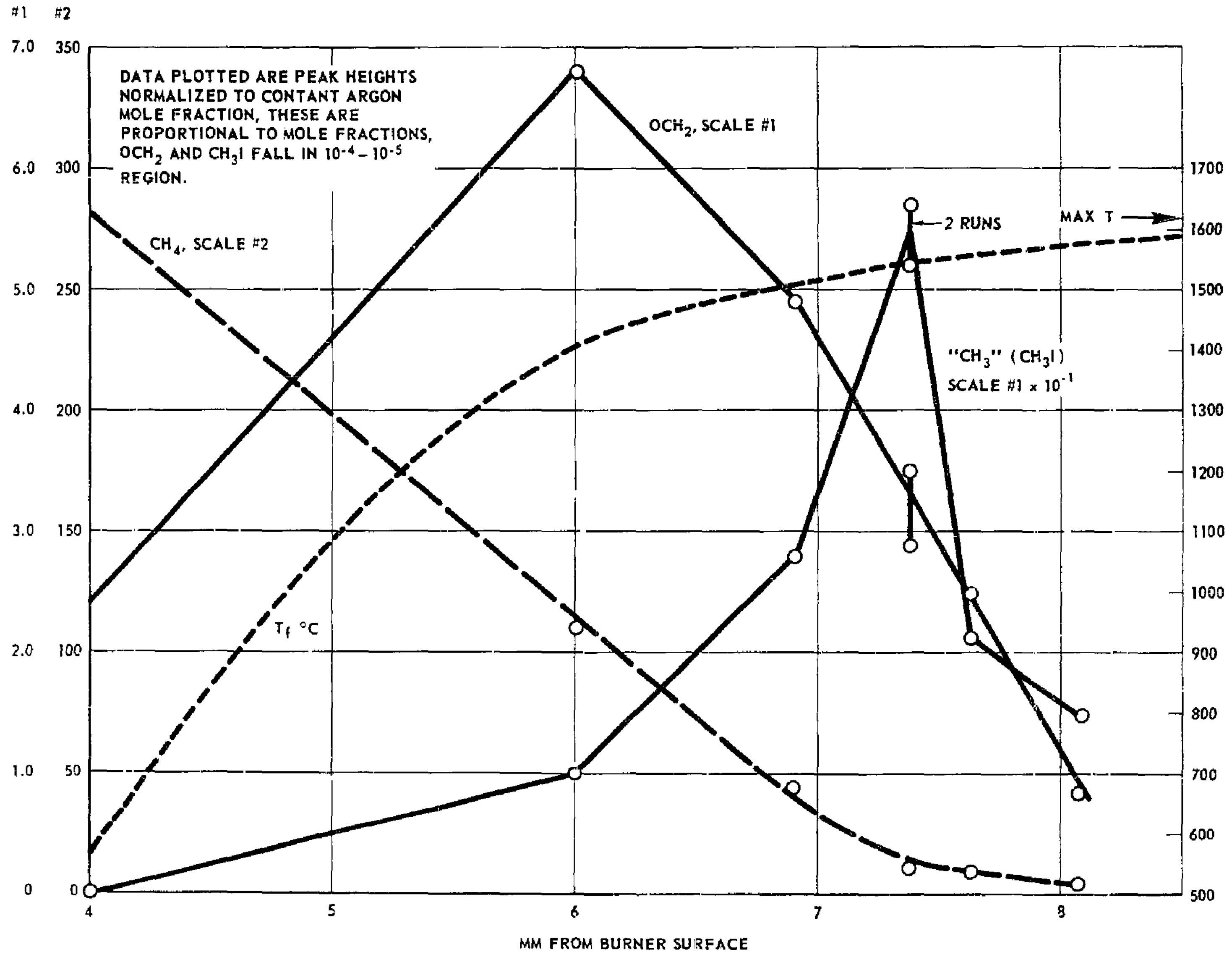


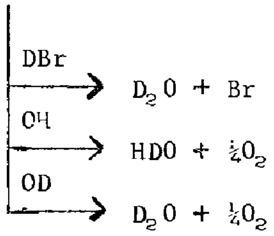
Fig. IV-2 MOLE FRACTION OF FORMALDEHYDE FORMED BY REACTION OF METHANE WITH OH AS A FUNCTION OF TEMPERATURE

PREPARATION OF DBr

W. E. Wilson and John Wagner

Work is progressing in the preparation of DBr for use in flame inhibition studies. As shown in the following equations isotopic labeling may be used to clarify the reactions of radicals with halogen compounds and to determine the rates of these reactions:

$$DBr + CH_3^{\cdot} \rightarrow CH_3D + Br^{\cdot}$$
$$DBr + H^{\cdot} \rightarrow HD + Br^{\cdot}$$
$$DBr + OH^{\cdot} \rightarrow HDO + Br^{\cdot}$$
$$DBr + O^{\cdot\cdot} \rightarrow OD^{\cdot} + Br^{\cdot}$$



It is planned to study these reactions in flame systems and simple radical flow reaction systems.

DBr will be prepared by the reaction:

$$D_2O + PBr_3 \rightarrow H_3PO_3 + DBr$$

The apparatus is shown in Fig. IV-3.

The reaction has been tested with H_2O and goes smoothly. Preliminary mass spectrometric analyses showed that PBr_3 and H_2O impurities were less than a few percent if present at all. A more exhaustive analysis for purity will be made. To prevent the formation of HBr by wall exchange the DBr will be prepared in a glass system in which most of the hydrogen in hydrogen containing species adsorbed on the wall will have been replaced with deuterium. It will then be transferred to a stainless steel pressure vessel for storage.

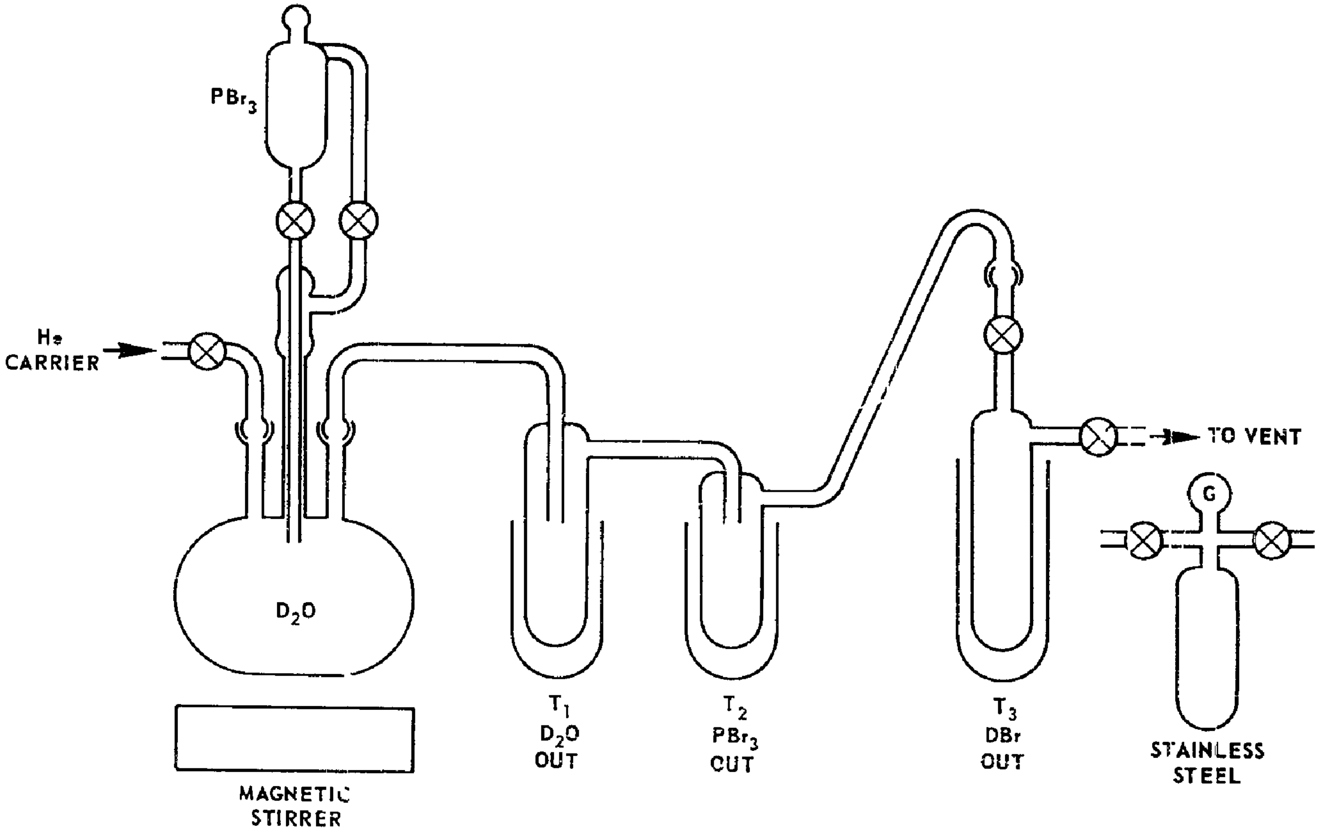


Fig. IV-3 APPARATUS FOR PREPARATION OF DBr

HIGH ENERGY FUEL FIRE FIGHTING STUDY

J. T. O'Donovan, R. M. Fristrom, and W. E. Wilson

The Laboratory has declared certain quantities of high energy fuel surplus. From this stock fifty pounds of HEF-2 and/or pentaborane have been set aside for fire fighting tests. Preliminary arrangements have been made with the technical disposal center at Indian Head, Maryland, for assistance in this project. The purpose is to study the effects of various inhibitors on high energy fuel fires.

A set-up is planned for small scale fires in the one to two pound range. The apparatus will consist of a stainless steel pan to confine the fire. Separate metering systems will be used for the fuel and the inhibitors. The instrumentation will consist primarily of photographic coverage. Figure IV-4 is a preliminary sketch of the apparatus.

Some of the materials now under consideration are exploded mica which would absorb the fuel; ammonium bicarbonate, liquid ammonia, and ammonium hydroxide froth.

Mr. Neil Sateer of Liquid Propellant Information Agency has written to various authorities in the field of fire fighting to obtain additional information concerning new techniques and/or inhibitors. All contributions will be reviewed and those ideas considered most promising and feasible will be tested.

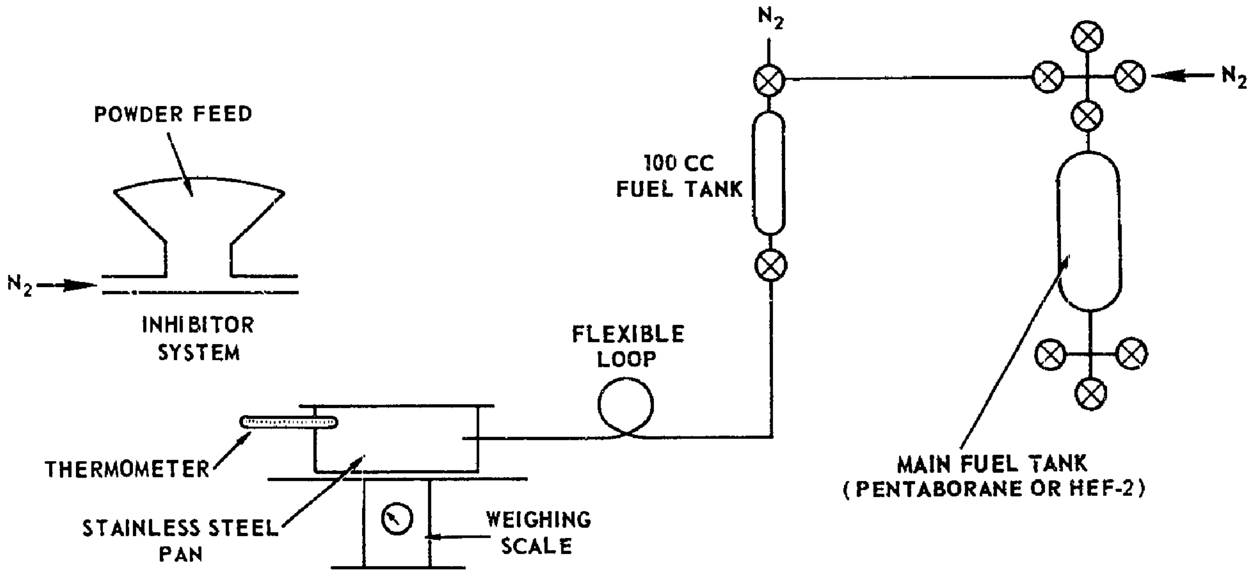


Fig. IV-4 APPARATUS FOR FIRE FIGHTING STUDIES

PAPERS FOR EXTERNAL PUBLICATION

During the past quarter a paper previously reported in (TG376-6) was published.

A. A. Westenberg and G. Frazier "Molecular Diffusion Studies in Gases at High Temperatures. V. Results for the H_2-A System." J. Chem. Phys. 36 p. 3499 (1962).