

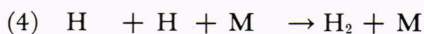
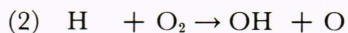
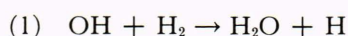
RADICALS

in

W. E. Wilson, Jr. and R. M. Fristrom

Radicals are an essential chemical species in flames. Although present in low concentrations, they are responsible for ignition and for the rapid reaction rates observed in flames. A radical is an atom or group of atoms, which, in chemical terms, has a free valency and may react to form a more stable molecule. Except for unusual cases or extreme environments, radicals may be considered as highly reactive, transient chemical species. Some of the important radicals in hydrogen and hydrocarbon flames are hydrogen atoms (H), hydroxyl radicals (OH), oxygen atoms (O), and methyl radicals (CH₃).

An illustration of how radicals enhance the rate of a reacting system may be had by examining the hydrogen-oxygen flame. An undisturbed mixture of H₂ and O₂ is quite stable at room temperature. However, if a few H or OH radicals are introduced, the following reactions take place with sufficient rapidity to maintain a flame:



These illustrate several peculiarities of radical reactions. In (1), we see that a radical-molecule reaction may generate a new radical, which in turn may react with another molecule, regenerating the original radical. This is called a chain reaction. Reactions (2) and (3) are examples of chain branching where one radical may generate two more. Trimolecular chain-breaking reactions, such as reaction (4), are much slower than the bimolecular reactions. This mechanism, whereby one active species gives rise to many more, is responsible for the rapid rate of reactions involving radicals. While chain-branching reactions are essential to ignition,

in a steady-state flame it is only necessary that chain branching balance chain breaking.

These species are so reactive that their lifetimes are very short. It is necessary, therefore, to utilize unusual techniques to study them. Cochran, Adrian, and Bowers, in a recent article, discussed the use of liquid helium to stabilize at low temperature radicals formed by ultraviolet photolysis.¹ The present paper will discuss the study of radicals in the high-temperature environment of flames. Since the general problem of studying flames has been discussed previously by Fristrom and Westenberg,² only the determination of radicals in flames and the application of these results to the study of chemical kinetics will be considered here.

Determining Radical Concentrations in Flames

Determination of the concentrations of atoms and radicals has been a major problem in chemical kinetic studies for a number of years, and has usually been avoided by application of the "steady-state approximation." This assumes that radicals

TABLE I
ATTAINMENT OF STEADY STATE IN A
HYDROGEN-BROMINE FLAME

Temperature (°K)	Required Time Available (%)
1050	1
1200	5
1300	10

¹ E. L. Cochran, F. J. Adrian, and V. A. Bowers, "Trapped Free Radicals," *APL Technical Digest*, **2**, Jan.-Feb. 1963, 2-9.

² R. M. Fristrom and A. A. Westenberg, "Fundamental Processes and Laminar Flame Structure," *APL Technical Digest*, **1**, Jan.-Feb. 1962, 10-15.

FLAMES

Radicals in flames may be studied by: direct, molecular-beam, mass spectrometry; optical spectroscopy; scavenger probe techniques; or by derivation from kinetic constants. It has been shown that radical concentrations greatly exceed equilibrium values and that active species diffuse from the reaction zone back into cool gases. Profiles of hydrogen, oxygen, hydroxyl, and methyl radicals in a methane-oxygen flame are given as examples. The chemical kinetic constants of elementary reactions are the most important information to be derived.

react at the same rate at which they are formed and that their concentration may be determined from equilibrium considerations. The validity of this assumption in rapidly reacting systems is highly questionable. An illustration of this point is given in Table I, in which the reaction time required to reach the steady state is compared to the actual time available in a hydrogen-bromine flame.³ Clearly, in this flame there is not sufficient time available for operation of the steady-state approximation. The determination of radicals in flames becomes, therefore, an experimental problem.

Free radicals have been investigated in several ways: microwave absorption, paramagnetic resonance, mass spectrometry, gas-phase titration, optical spectroscopy, and recently, a new technique developed at APL called "scavenger sampling."

For two important reasons, only a few of the experimental techniques mentioned above are suitable for quantitative flame studies. The experimental problems are complicated by the high temperatures in flames; and for quantitative work,

local concentrations must be determined with considerable precision point by point through the flame front. The latter requirement is quite stringent since flame fronts are normally only a few millimeters thick.³ Because a number of separate determinations of local concentration are necessary, the primary requirement is spatial resolution well below a fraction of a millimeter.

Although none of the present methods is completely satisfactory, they have enabled investigators to make much progress on a problem once thought to be completely impossible. We will discuss briefly the methods that have been used, with emphasis on the techniques we have used and with which we are most familiar.

RADICAL CONCENTRATIONS DETERMINED BY DIRECT MASS SPECTROMETRY—One of the most reliable methods for determining radical concentrations in flames is direct mass spectrometry. The radicals must enter the spectrometer ion chamber with only a few, or preferably no, collisions after sampling. This is best accomplished by using a molecular beam-sampling mass spectrometer of the type developed by S. N. Foner and R. L. Hudson at APL (Fig. 1).⁴ This system has been used primarily for studying radical reactions induced by electric discharge, but it has also been successfully applied to the study of radicals in diffusion flames and to the study of stable species in flames.⁵ Through use of the apparatus, it was established that HO₂ was not present in detectable amounts in diffusion flames of hydrogen and oxygen, but could be produced in substantial quantities in discharge-tube systems.

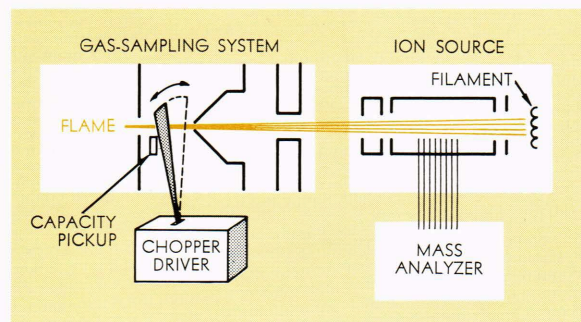


Fig. 1.—The determination of atoms and radicals by direct mass spectrometry.

³ G. C. Frazier, Jr., R. M. Fristrom, and J. F. Wehner, "Microstructure of a Low Pressure Hydrogen-Bromine Flame," *A.I.Ch.E. Journal* (accepted for publication, 1963).

⁴ S. N. Foner and R. L. Hudson, "The Detection of Atoms and Free Radicals in Flames by Mass Spectrometric Techniques," *J. Chem. Phys.*, **21**, Aug. 1953, 1374-1382.

⁵ R. Prescott, R. L. Hudson, S. N. Foner, and W. H. Avery, "Composition Profiles in Pre-Mixed Laminar Flames," *J. Chem. Phys.*, **22**, Jan. 1954, 145-146.

The instrument was intended for identification of radicals and is not suitable in its present form for quantitative studies of flame structure. The inlet disturbs the flame and gives poor distance resolution. While it should be possible to design a molecular-beam probe that would circumvent many of the problems of determining radicals, molecular-beam mass spectrometers are expensive and difficult to build, requiring, in particular, powerful vacuum pumps to maintain high pumping speeds at low pressures.

RADICAL CONCENTRATIONS DERIVED FROM SPECTROSCOPIC STUDIES—Radical concentrations have been determined spectroscopically in flames, using both absorption and emission, a technique that has the virtue of not disturbing the flame. Its major disadvantages are the difficulties in finding suitable absorption lines, interpreting the emission spectra, and obtaining sufficient spatial resolution. It has been limited in practice to the study of hydroxyl radicals (absorption) (Fig. 2)⁶ and hydrogen atoms (emission). Absorption spectroscopy is quite straightforward in principle, although the experimental problems are moderately complex. The absorption of light is directly related to the concentration, i.e. partial pressure, of the absorbing molecule. The interpretation of emission data is more complex, the most successful studies having been made by an ingenious technique that involves introducing a trace ($\approx 10^{-5}$ mole fraction) of a pair of the alkali metals, one of which forms a stable hydride, the other, not. The concentration of hydrogen atoms can be derived from measurements of the relative intensity of the resonance lines of the two alkali metals and the known equilibrium constant of the reaction. This latter technique has been used to study the radical recombination region in hydrogen-air flames.⁷

RADICAL CONCENTRATIONS BY THE SCAVENGER PROBE TECHNIQUE—A method recently developed at APL for the study of radical concentrations in flames, the "scavenger sampling probe technique" (Fig. 3A), combines the techniques of microprobe sampling and chemical scavenging.⁸ The quartz microprobe used for studying stable species in flames consists of a small, uncooled, quartz tube with a tapered tip ending in a small sampling orifice

10 to 50 microns in diameter. A large pressure drop is maintained across the probe by pumping on it, with the result that the system acts as a miniature supersonic nozzle. The sample being withdrawn experiences a rapid adiabatic decompression, and within a few microseconds the temperature and pressure are so low that reaction rates in the gas phase become negligible. This is the well-known frozen flow that occurs in rocket nozzles. Even reactive radical species survive a number of centimeters down the probe before they recombine on the probe walls (gas-phase recombination is negligible under these conditions).

In some cases it is possible to inject into the sampled gas stream a stable substance that reacts quantitatively and specifically with the radical species under study to give a stable product that can be analyzed by mass spectrometry; the injected reactant is called a "scavenger." Thus, the radical concentration can be deduced from its one-to-one correspondence with the product species. This technique has been used successfully to study hydrogen atoms by reaction with chlorinated hydrocarbon, methyl radicals by scavenging with iodine, and oxygen atoms by scavenging with nitrogen dioxide. Its extension to the study of other radicals depends on finding suitable scavenger reactions.

DERIVATIONS FROM KINETIC CONSTANTS—It is possible to deduce radical concentration in flames from the measured concentration of stable species

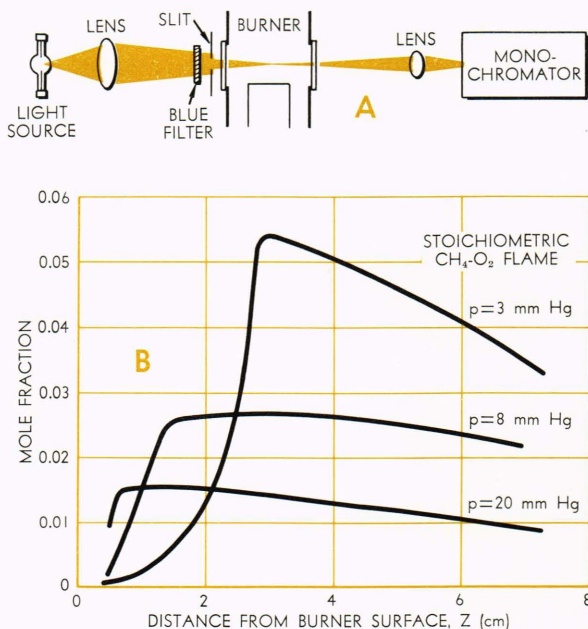


Fig. 2.—The determination of hydroxyl radical concentrations in low-pressure flames. (A) Schematic of the apparatus; and (B) OH profiles for several stoichiometric methane-oxygen flames.

⁶ U. Bonne, T. Grever, and H. Gg. Wagner, "Messungen in der Reaktionszone von Wasserstoff—Sauerstoff—und Methan—Sauerstoff-Flammen," *Zeitschrift für Physikalische Chemie*, Frankfurt, **26**, 1960, 93-110.

⁷ C. G. James and T. M. Sugden, "Photometric Investigation of Alkali Metals in Hydrogen Flame Gases. I—A General Survey of the Use of Resonance Radiation in the Measurement of Atomic Concentrations," *Proc. Roy. Soc.*, **227**, 1955, 312-329.

⁸ R. M. Fristrom, "Scavenger Probe Sampling: A Method for Studying Gaseous Free Radicals," *Science*, **140**, Apr. 19, 1963, 297.

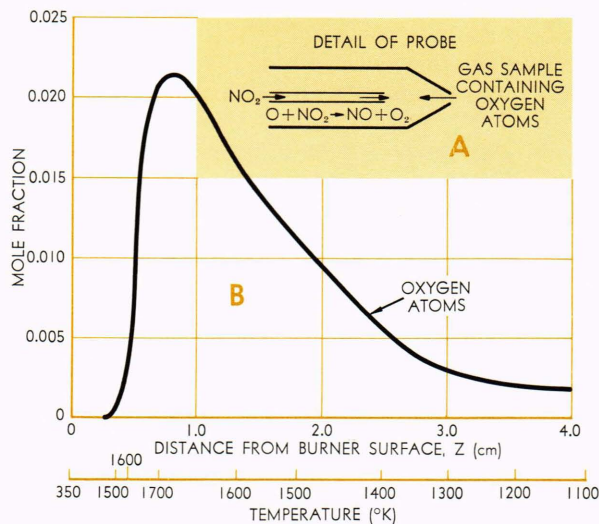


Fig. 3.—Scavenger probe technique for determining radical concentrations in flames. (A) Schematic of the apparatus for studying oxygen-atom concentrations; and (B) an oxygen-atom concentration profile in a methane-oxygen flame.

if the kinetic constants of the species that react with the radical are known. This procedure is valuable since it allows estimates, not otherwise available, to be made of radical concentrations.

For example, consider the reaction given by the chemical equation



For this reaction it is possible to write a mathematical equation,

$$R = K_f[\text{CO}][\text{OH}] - K_r[\text{CO}_2][\text{H}], \quad (2)$$

where R is the rate of formation of CO_2 , K_f is the rate constant in a forward direction, K_r is the rate constant in a reverse direction (where K is a function of temperature), and the terms in brackets indicate the concentration of the mixture components.

Measurements of R , $[\text{CO}]$, and $[\text{CO}_2]$ can be made. If K_f is known, and $K_r[\text{CO}_2][\text{H}]$ is small compared with the forward rate, it is possible to calculate $[\text{OH}]$ from the equation

$$[\text{OH}] = \frac{R}{K_f[\text{CO}]} \quad (3)$$

This approximation is to be distinguished from the steady-state method that assumes that the radical concentration can be expressed in terms of the stable species and equilibrium constants. The assumption that the reverse reaction can be neglected is usually better in the early stages of a flame.

Results of Radical Concentration Studies in Flames

One of the first results of quantitative studies was the discovery that the radical concentration in flames was much higher than that predicted by thermal equilibrium. This led to the realization that the rapid bimolecular reactions involving free radicals do not reduce the overall radical concentration but merely change one radical into another, and that the radicals must be removed by slower trimolecular reactions. Consider the reactions of the H_2 — O_2 flame mentioned earlier. In the later stages of the flame, the reverse reactions must be considered also. However, reactions such as (1), (2), and (3) do not reduce the number of radicals; they maintain a quasi-equilibrium among the bimolecular steps so that the ratio of H , OH , and O is the same as in thermal equilibrium, hence calculable from thermodynamics, while the total radical concentration may be far out of equilibrium.⁷

When two small radicals combine, as in reaction (4), they release more energy than can be absorbed internally so that the molecule would be dissociated unless there were a third body available to carry away the excess energy. Such trimolecular reactions are slower because of the lower probability of three molecules colliding simultaneously than of two molecules doing so. At atmospheric pressure the number of three-body collisions is only one for every thousand bimolecular collisions; this ratio is proportional to pressure. Below a tenth of an atmosphere, the recombination is so slow that the flame gases may reach the walls of the apparatus before recombination can occur. In many such systems, the heat losses to the wall cool the flame gases so rapidly that the radical concentration may be frozen far out of thermal equilibrium.

Another aspect of radicals in flames is that because of diffusion effects they can often react in a region of a flame upstream of, and hence earlier in the reaction path than, the point at which they are formed. This peculiarity is responsible for the rapidity of the reactions and for the elimination of many of the slow, complex steps found in lower-temperature oxidations. In order to give a mathematical description of this effect, it is necessary to introduce a new variable, flux, which is the amount of a species passing through a unit area in a unit time, as opposed to concentration, which is the amount of species per unit volume at a point. The two variables are related by the equations

$$G_i = f_i(v + V_i)/v \quad (4)$$

and

$$V_i = -(D_i/f_i) (df_i/dz), \quad (5)$$

where G is fractional mass flux, D is the diffusion coefficient, f is mass fraction, v is mass average velocity, V is diffusion velocity, z is distance, and subscript i refers to species i . In flames in which the concentration gradients are very steep and the effects of diffusion are appreciable, V_i can become greater than v . This means that for this species the diffusional flow due to concentration gradients is larger than the overall species mass flow; overall mass flow remains unchanged, of course. An example of this behavior is given by the oxygen atoms in a methane-oxygen flame. Oxygen atoms are formed in the main flame reaction zone but diffuse back into the unburned gases to initiate reactions (Fig. 4). In the ordinary flow system, where df_i/dz is very small, the two variables are identical when expressed in dimensionless units (such as mass fraction and fractional mass flux).

The Spherical Premixed Methane-Oxygen Flame

The most complete information on radical concentrations has been obtained from a spherical, low - pressure, methane - oxygen flame⁹ having spherical symmetry and supported on a spherical ball in a large flask. At low pressure the radical recombination is so slow that radical equilibrium is not attained until the walls of the flask are reached. The flame is not adiabatic because of heat

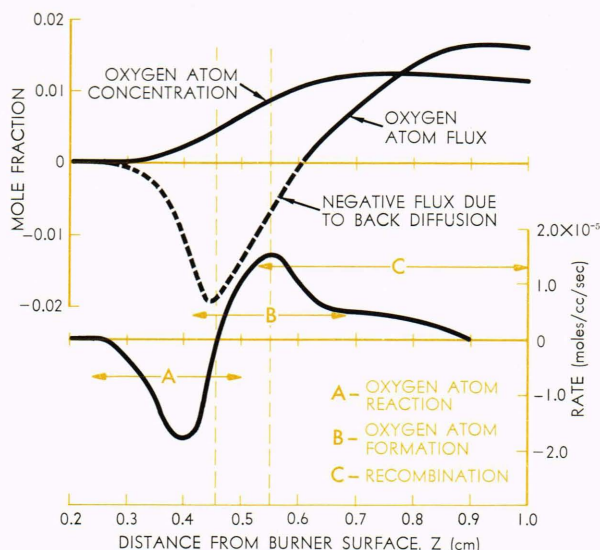


Fig. 4.—Reaction of oxygen atoms in a methane-oxygen flame, showing (top) concentration and flux fraction and (bottom) reaction rates.

⁹ R. M. Fristrom, Sec. 2.1 of *Experimental Methods in Combustion Research*, J. Surugue, ed., Pergamon Press, New York, 1961.

transfer to the walls, resulting in partially “frozen radical concentrations;” characteristic profiles for this system are shown in Fig. 5. Temperature profiles were measured with small, silica-coated, Pt, Pt-10% Rh thermocouples. Composition profiles of the stable species were determined by micro-

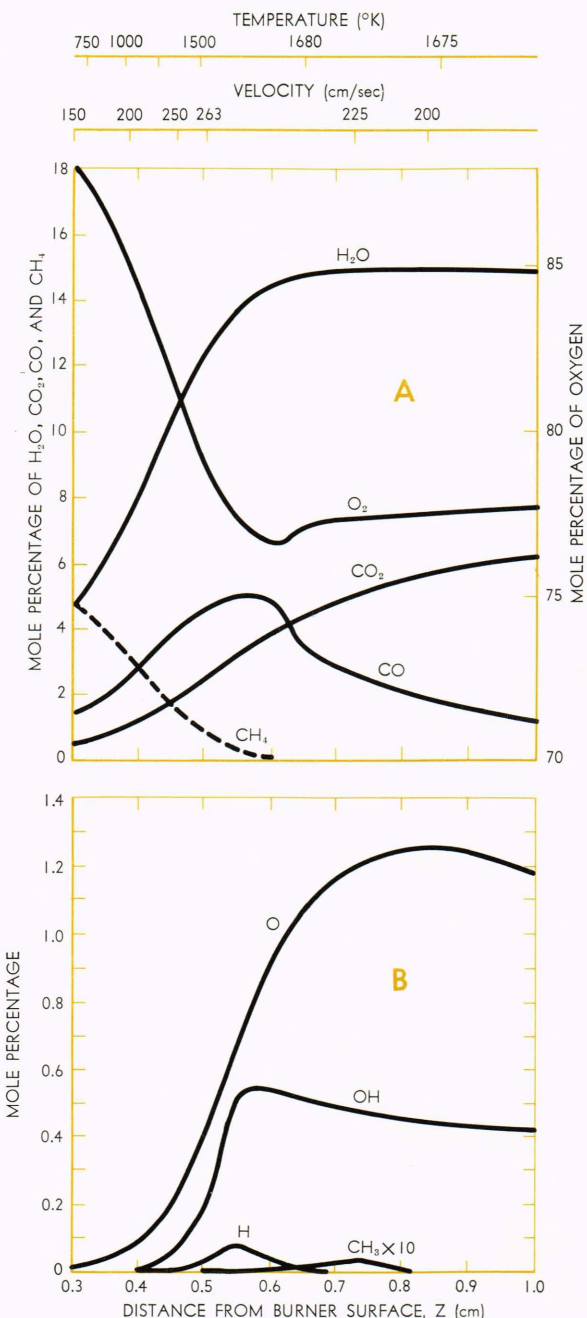


Fig. 5.—Characteristic profiles of a premixed, spherical, methane-oxygen flame (CH₄—7.8% O₂—92%; P = 0.05 atm); (A) stable species, and (B) radical species.

probe sampling and mass spectral analysis,¹⁰ velocity was calculated from the density and area.

The radical concentrations for the methane-oxygen flame were derived by several techniques. Hydrogen atoms were estimated from the disappearance rate of oxygen, assuming known kinetic constants and that the reaction $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ is responsible for oxygen disappearance. The order of magnitude of the results was confirmed by scavenger probe studies on a similar flat flame. Oxygen atom concentrations were measured using scavenger probe sampling based on the scavenger reaction $\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$. The OH concentration was derived from the rate of appearance of CO_2 , assuming that the rate is due to the reaction $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$. The validity of the assumption was confirmed by comparison with a spectroscopically measured profile of a flat flame with the same composition and final temperature. The methyl-radical concentration was determined by scavenger sampling on a similar flat flame using the scavenger reaction $\text{CH}_3 + \text{I}_2 \rightarrow \text{CH}_3\text{I} + \text{I}$.

Applications

The most important information to be derived from radical concentration studies are the chemical kinetic constants of the elementary reactions. If it is possible to obtain a profile of the radical concentration as well as the stable species and rate profiles, then it is possible to compute K (see Eq. 3). An example of this procedure is given by the reaction of the hydroxyl radical in methane-oxygen flames. Here it has been established that both carbon monoxide and methane react primarily with the hydroxyl radical. Since the kinetic constants for carbon monoxide are reasonably well known, the hydroxyl concentration may be calculated. This in turn may be used to determine the kinetic constants of the methane-hydroxyl radical reaction. By combining high-temperature data from flame-structure studies with low-temperature data from the reaction of methane in a discharge tube, it has been possible to derive kinetic constants of good precision (Fig. 6). The excellent agreement between these two temperature extremes demonstrates that the identification of these reactions is essentially correct and that simple collision models of chemical reactions are adequate for describing such systems in the extremes of temperature found in flames.

It has been possible to identify and obtain kinetic constants for a number of elementary reactions in flames, and to write reaction schemes for some of

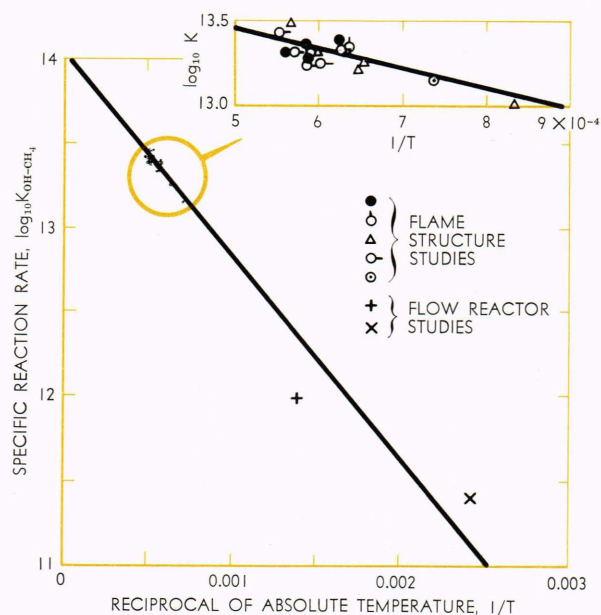


Fig. 6.—Rate constants for the reaction $\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ as a function of $1/T$.

the simpler flame systems that can account quantitatively for the observed behavior. One of the interesting points is that in all of the reaction schemes proposed, radicals play a dominant role.

Since radicals are so important in the propagation of flames, yet are present in small amounts, we may properly wonder if flames cannot be influenced by manipulation of radical concentrations. It is possible, for example, to double the flame speed of the carbon-monoxide-oxygen flame by changing the water concentration from 0.1% to 0.2%. The water provides a source of OH and H radicals. This allows CO to be oxidized by the reaction $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$, which is much faster than any set of reactions utilizing $\text{CO} + \text{O}_2$ or $\text{CO} + \text{O}$. The OH is regenerated by the reaction $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ to permit a rapid chain reaction.

In the opposite direction, a small research effort at APL is devoted to the study of slowing down flames by removing radicals or substituting unreactive radicals for the chain carriers. The method of operation of such chemical fire extinguishers as carbon tetrachloride and bromotrifluoromethane (CF_3Br), now used in many fire extinguishers on aircraft, is the substitution of the less reactive chlorine or bromine atom radical for the oxygen, hydroxyl, or hydrogen radical. Since chlorine and bromine atoms are relatively stable and unreactive, they do not propagate the chain reactions. Similarly, the lead tetraethyl added to gasoline is a free radical scavenger that controls the free radical distribution and concentration in the internal combustion engine, preventing too early ignition.

¹⁰ A. A. Westenberg and R. M. Fristrom, "Methane-Oxygen Flame Structure. IV. Chemical Kinetic Considerations," *J. Chem. Phys.*, **65**, Apr. 1961, 591-601.