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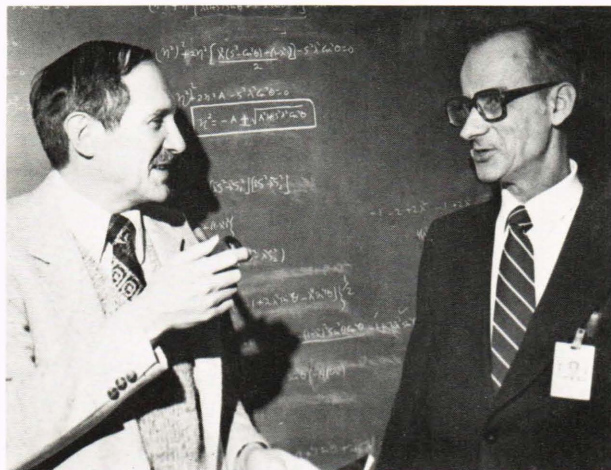
Robert W. Hart (left) and Samuel N. Foner

SAMUEL N. FONER is Vice-Chairman of the Milton S. Eisenhower Research Center and Supervisor of its Electronic Physics Group. Born in New York City (1920), he studied physics and mathematics at what is now the Carnegie-Mellon University, where he received his D.Sc. degree in physics in 1945. He was employed as an instructor in the Physics Department and later as a research associate of the Manhattan Project, working in the laboratory of the Nobelist Otto Stern who instilled in him the use of conceptually simple experiments to answer complex questions.

Dr. Foner joined APL in 1945 and became associated with the Research Center as Supervisor of the Mass Spectrometry Group (1947-52) and the Electronic Physics Group (1953-present). He has made many noteworthy contributions to the mass spectrometry of free radicals and reaction intermediates, to the detection of free radicals stabilized at very low temperatures, and to the ionization of substances by electron impact.

He has served as a member of the NAS/NRC Advisory Committee for the Army Research Office and an Advisor to NATO's Scientific Affairs Division. In 1954, Dr. Foner received the Physical Sciences Award of the Washington Academy of Sciences for work in free radical chemistry and physics. He is a member of the Combustion Institute, the Philosophical Society of Washington, and a Fellow of the AAAS, the American Physical Society, and the Washington Academy of Sciences.

ROBERT W. HART is Chairman of the Milton S. Eisenhower Research Center and Assistant Director of APL for Exploratory Development. Born in Yankton, SD, in 1922, he studied at the University of Iowa and received his Ph.D. degree in physics from the University of Pittsburgh in 1949. After a year of teaching at the Catholic University in Washington, he joined APL in 1950. He has been a member of the Research Center ever since.

During the 1960s, Dr. Hart developed a detailed theory of the complex combustion behavior of solid propellants in rockets in collaboration with the late Frank T. McClure and as member of the Joint Armed Services Committee on Combustion Instability. As Supervisor of the Special Problems Research Group (1954-1975), his interests covered theoretical aspects of wave scattering, the structure of the eye, and other physical and biophysical topics.

Dr. Hart is a member of the American Physical Society and of the Combustion Institute. Outside of professional activities, he is interested in the origin and evolution of civilization and science.

RESEARCH RETROSPECTIVES

THE STRUCTURE OF FLAMES

Flames have been the most important source of heat, light, and power since the earliest days of civilization. At present, the combustion of fuels is, by far, the largest chemical operation under human control. Yet, until quite recently, detailed knowledge of what goes on within a flame did not exist. Although the complexity of combustion is not entirely understood, even today, what was virtually *terra incognita* has been opened up during the past 25 years by the classic studies at APL by Robert M. Fristrom, Arthur A. Westenberg, and their colleagues.

What does one need to know about a flame? Chemists want a detailed accounting of the steps by which fuels (such as oil, natural gas, or coal) and oxidizers (such as air) are converted into products of combustion (water, oxides of carbon, soots, and ash) as well as the intermediate reaction paths that are involved in this transformation. They want to understand why and how inhibitors can extinguish flames or prevent engine "knock" and know how rapidly these transformations can take place. Physicists, on the other hand, are interested in temperature effects, radiation, the flow fields set up by the gases moving into and out of the flames, and countless other physical properties.

What sets flames apart from more conventional chemical transformations is that one is dealing with a very intricate situation in which chemical reactions are closely coupled with the physical flow of substances into and out of a reaction zone, accompanied by a steep rise in temperature, abrupt changes in composition, and numerous optical and electrical phenomena that may be important under specific circumstances. In a distance of less than 1 mm, temperatures can change by thousands of

degrees and gas concentrations can rise or fall abruptly. The thinness of this transformation zone held back experimenters in exploring the detailed structure of flames.

A fundamental advance in understanding the simplest combustion case (where gaseous reactants are mixed prior to combustion and no solid reaction products are formed), came about in the early 1950's. First, a theoretical analysis of flames was made[1] whereby simplified models of combustion processes could be analyzed in detail. This led to suggestions of how one could, in principle, separate the chemical transformations from the simultaneous physical processes (mainly diffusional). Second, it was found that most flames, when stabilized at pressures well below atmospheric, would widen in thickness without altering the sequence of the chemical transformations. This made it possible to introduce sampling probes and thermocouples into the reaction zone and obtain point-by-point samples for subsequent analysis of the concentration of reactants, intermediates, and products as well as temperature profiles.

APL's work pioneered in the development of these experimental tools and their application to the analysis of simple flame systems. Mass spectrometers were found to be useful in identifying the chemical species that survived the sampling process. For highly reactive intermediates such as radicals and atoms, stablizing techniques were developed to preserve them for later analysis. Tiny microprobes and thermocouples were built to obtain spatial resolution in flames whose thickness now extended over several millimeters.[2]

Once the value and workability of these techniques were recognized, they were quickly adopted by others. A vigorous worldwide exploration of many flame systems was started. Much was learned about the intricate interplay by which stable reactants transform into stable products by way of intermediate steps and, in particular, about the crucial role played by free radicals in mediating the rapid transformations.

The picture that has emerged[3] of the structure of, for example, a hydrogen-oxygen flame with excess hydrogen is that initially, as the reactant gases enter the combustion region, they are heated somewhat by conduction as heat flows toward the incoming gases from the hot combustion products. A little later, heat-producing chemical reactions commence. They are initiated by reactive free radicals that diffuse from the hot side of the flame, where they are generated, toward the incoming gases and attack hydrogen molecules, leading to the formation (as well as the disappearance) of the hydroperoxo radical (HO_2) and water. At a still later (and hotter) stage, the relatively slow reaction $O + H_2 \rightarrow OH + H$ becomes important. Because more free radicals are generated than are consumed, this reaction stage is the source of the reactive free radicals that are active earlier in the flame. Finally,

after the main rapid reactions have taken place, a sorting-out zone follows where the free radicals that were formed in excess amounts in the previous stage recombine relatively slowly until the system settles down to an equilibrium state in which reactions respond only to the slow temperature changes brought about by heat losses.

For the "simple" hydrogen-oxygen flame, where most of the possible intermediate steps have now been identified and their reaction rates measured, the overall behavior of the flame can be described by a quite limited number of reaction steps.[4] For hydrocarbon flames, many more chemical interactions are possible because of the presence of carbon in the fuel molecule. An overall description of hydrocarbon flame behavior based on individual steps is now nearly in hand. Here, too, the role of free radicals as crucial mediators (hydroxyl radicals if the flames are deficient in fuel for complete combustion, or hydrogen atoms if there is an excess of fuel) is beyond doubt.

During the combustion of hydrocarbons with excess air, the oxidation of hydrogen and carbon monoxide (which appear as intermediates in the flame) is of particular importance. The hydrogen oxidation furnishes the oxygen and hydrogen atoms and hydroxyl radicals that attack the hydrocarbon molecule to form methyl (CH_3) radicals. The latter subsequently interact with oxygen to form formaldehyde, which reacts in further steps to produce carbon monoxide and, ultimately, carbon dioxide. This sequential formation and disappearance of intermediates (carbon monoxide, hydrogen, formaldehyde, and atoms and radicals) was clearly shown in the experiments of Fristrom and Westenberg[5] and is fully supported by the detailed reaction scheme proposed for hydrocarbon oxidation in flames[6] (Fig. 1).

In fuel-rich flames, many more intermediate steps are possible. Polymerization reactions that lead to the temporary appearance of hydrocarbons that are of higher molecular weight than the initial fuel become important. They give rise, subsequently, to aldehydes and unsaturated hydrocarbons. A complete description of all the individual reaction steps is not yet possible because of the lack of reaction rate data for all of the numerous elementary reactions involved.

One goal of the flame structure work was to obtain quantitative information about individual reaction steps. This turned out to be difficult in practice because so many reactions are proceeding simultaneously even in the simplest flame that it is nearly impossible to single out any one for detailed analysis—with one important exception. In the hot stream of combustion products beyond the active reaction zone, free radicals are still present in measurable amounts. This region can be used as a "hot bath" where the reactions of compounds with free radicals can be studied. It became evident that it was possible to inject traces of well-known flame
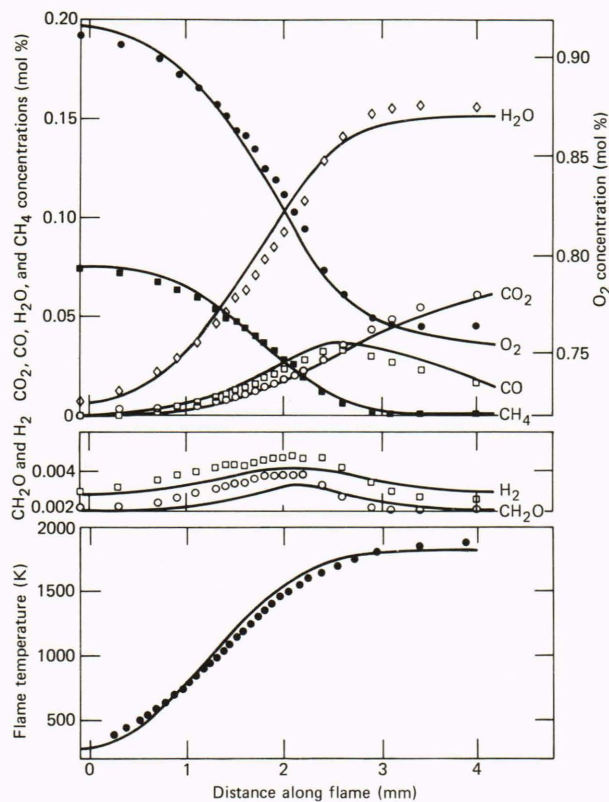
Fig. 1—In 1960, a low pressure fuel-lean flame of methane and air was analyzed by Fristrom et al[5] for the appearance and disappearance of chemical species and for local temperature. The reaction zone was approximately 4 mm thick. Experimental results are shown as individual data points. Recently, J. Warnatz[6] was able to calculate composition and temperature profiles of the same flame from known reaction rates of approximately 80 of the important individual steps that are postulated to occur during the oxidation of methane (solid lines). The agreement between prediction and experiment is excellent.

niques at lower temperature.[7,8] For the first time it was demonstrated that these measurements give concordant results.

Many intriguing and important problems remain, especially in applied areas where fuel/oxidizer mixing limitations, catalytic surface effects, soot formation, and many other subtle interactions may lead to undesirable end effects. However, for the central problem of gas phase combustion, 200 years of flame research have, at long last, brought about a remarkable confluence of theory and experiment. Taking into account the dominant physical processes of diffusion and heat conduction and the numerous interacting chemical reaction steps, the structure of flames can now be viewed in its full intricacy. Complex flame systems can be constructed out of the many individual reactions that proceed within a flame and the overall behavior of such flames can, in principle, be predicted.

WALTER G. BERL

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inhibitors (methyl halides) into this bath, determine their rates of reaction with hydrogen atoms at the high temperature, and compare the results with extrapolations obtained with entirely different techniques at lower temperature.

THE SEARCH FOR HO₂

In more than two hundred years, chemists have isolated and identified about 100 chemical elements and millions of compounds into which these elementary building blocks can be combined. This continuing and unending quest (the number of potential combinations of elements into compounds is virtually limitless) has been accompanied by an intensive effort to learn more about the bonds that hold these building blocks together in recognizable structures and shapes and to discover the rules that determine the rates and the pathways by which one chemical structure changes into another.

Until about 50 years ago, the study of chemistry was based on a belief in stability. To be sure, many levels of stability were identified and techniques were developed to move from one level to another. Some substances were so labile that they would barely survive at room temperature. At high temperatures most compounds would change into a relatively small number of stable products. A few elements like radium and polonium showed signs of instability. But once substances such as hydrogen (H_2) and oxygen (O_2) molecules reacted with each other, they were expected to form only water or, on occasion, hydrogen peroxide (H_2O_2). The details of how such transformations take place were but dimly perceived. It was generally assumed that a direct reaction (commonly written as $2H_2 + O_2 \rightarrow 2H_2O$) occurs that involves no other chemical species.