The Chemistry of Flames

Research in the field of combustion chemistry focuses mainly on the intermediate substances created as hydrocarbon fuels burn to produce carbon dioxide, water and trace pollutants

by William C. Gardiner, Jr.

The key discovery in the scientific effort to understand fire was made in 1774, when Antoine Laurent Lavoisier recognized that the apparent disappearance of matter in flames is an illusion. Instead, Lavoisier showed, an invisible component of the air (which he later named oxygen) reacts chemically with matter at high temperature, yielding heat and a variety of combustion products. Today this concept defines a fuel: a substance that can participate in an exothermic (heat-releasing) chemical reaction with oxygen.

Combustion science has taken on added significance in recent years, owing to increased public awareness of the finite supply of comparatively inexpensive fossil fuels and of the injurious effects of some combustion products on the environment and human health. With the aid of modern laboratory techniques it is possible to detect not only the end products of combustion processes but also many substances that appear transiently in the course of burning. As a result fire has come to be understood chemically as an intricate network of molecular events. The practical objective of this work remains what it was for prehistoric man: to learn how to burn the cheapest available fuels as efficiently, intensely and cleanly as possible.

Some fuels, such as wood or camel dung, are too complex to deal with in detail at the molecular level. Others, such as aluminum and ammonia, require more energy to produce than they liberate when they burn, and so they are normally considered impractical as fuels. Combustion scientists are primarily concerned with the fuels most often burned as energy sources: coal, petroleum products and natural gas. Such fuels are not pure chemical substances. Coal, which is mainly composed of elemental carbon, also has a variety of other components, both combustible and noncombustible. Petroleum fuels and natural gas are mixtures of hydrocarbons (compounds consisting of hydrogen and carbon in a roughly two-to-one ratio) with traces of other substances. In addition to these common fuels combustion chemists study special-purpose fuels such as acetylene for welding torches, powdered metals for fireworks and hydrogen for rocket engines.

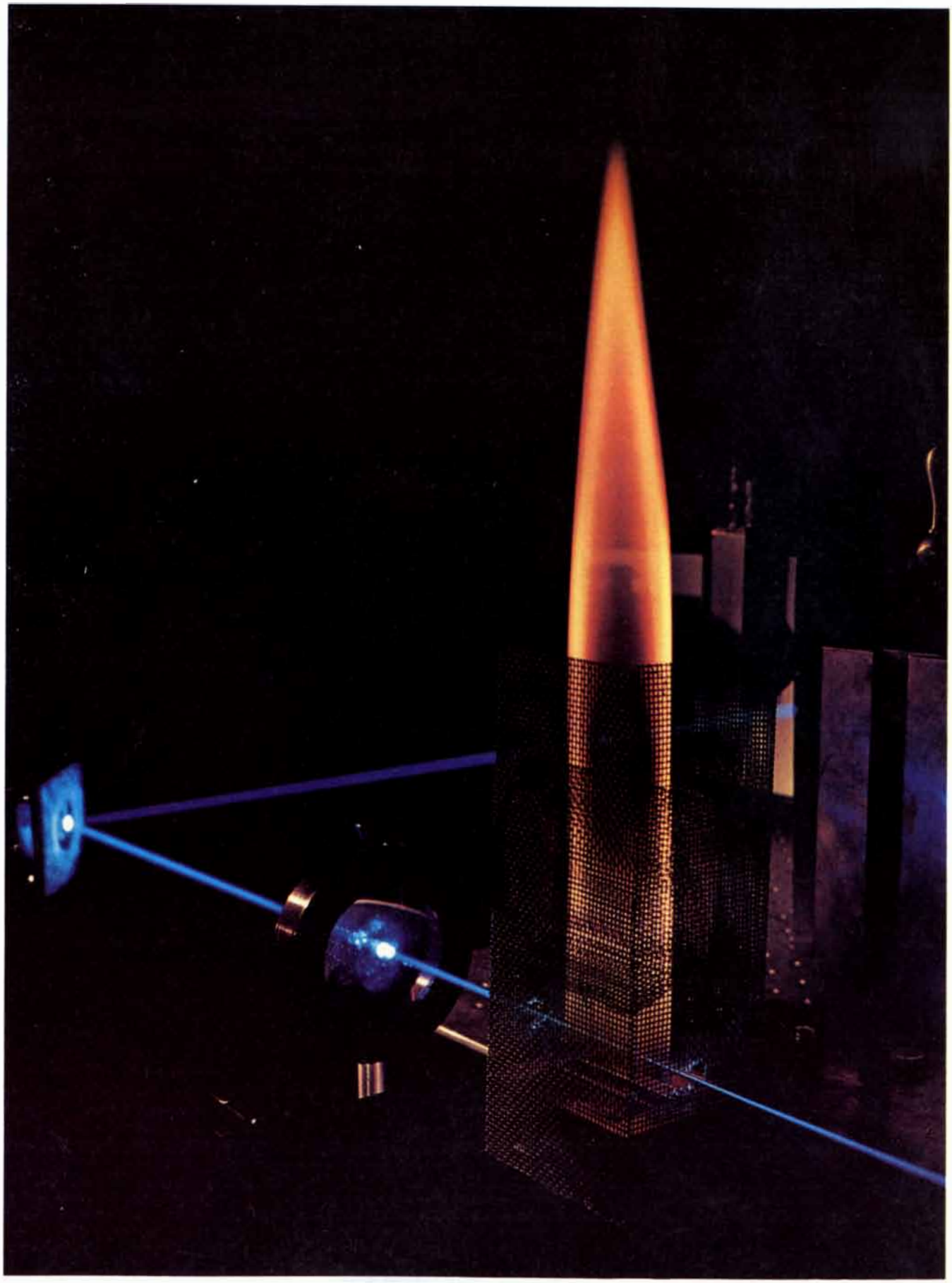
Although fuels have the ability to burn, they rarely do so spontaneously. A mixture of acetylene and oxygen, for example, could be stored for hundreds of years with no perceptible reaction. If the mixture were to be exposed to a flame or a spark, however, it would detonate in a microsecond. The layman's explanation is simple: A fire has to be lighted first, and it will then sustain itself until either the fuel or the oxygen runs out or until it is extinguished. The task of combustion science is to put the basic notions of ignition, propagation and extinction into precise chemical and physical terms. Doing so requires more details than are provided by merely identifying the overall chemical reaction involved in a fire.

The first combustion chemists believed temperature change alone would explain the phenomena of ignition and propagation. They reasoned that the chemical reactions involved in combustion are simply too slow to be perceived at normal temperatures; if the ignition temperature is reached in one place, however, the rate at which the ensuing chemical reaction releases heat becomes high enough to raise the temperature in the adjacent region to the ignition temperature too. This interpretation, which lumps all the chemistry into a single heat-releasing process whose rate depends on temperature, begs the question of why such a temperature dependence exists. Nevertheless, when the question is framed in quantitative terms, it does provide models that agree with experiments and are useful to engineers for designing combustion devices. Such models explain how burning rates depend on temperature, but not why. That is because they do not deal with the molecular events underlying the combustion process.

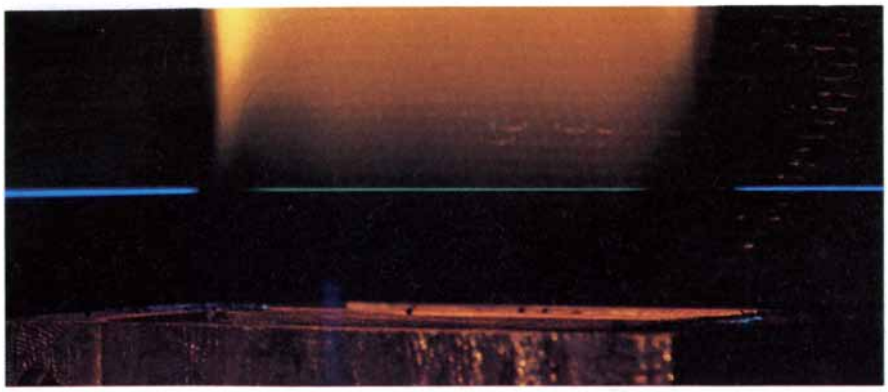
Before proceeding further some definitions are needed. In combustion science the term fire is generally applied to any accidental or deliberate combustion event in the "real" world (that is, the world outside the laboratory). In such an event, say a forest fire or a furnace fire, air is supplied and combustion products and heat are removed by means of large-scale, unsteady flows. Flames are the subunits of fire. They in turn can be broken down into two classes: premixed flames, in which the fuel is mixed with oxygen prior to combustion, and diffusion flames, in which the fuel and the oxygen meet in the combustion zone.

Gasoline and air (which is about 20 percent oxygen) mix in the carburetor of a conventional internal-combustion engine and burn later (after compression and spark ignition in the cylinder) as a premixed flame. Vaporized wax and air meet above a candlewick to burn as a diffusion flame. Premixed flames and diffusion flames can be either turbulent or laminar, depending on the flow rates of the substances involved. Turbulent flow increases the burning rate and so is advantageous when fast combustion is desired. Laminar, or smooth, flow is easier to describe mathematically and is usually better suited for laboratory experiments. In all the flames mentioned so far the fuel is in the form of a vapor before combustion begins. If it is not, then one is dealing with a more complicated physical situation: either heterogeneous combustion, such as takes place at the surface of a burning piece of coal, or a combined vaporization-combustion process, such as takes place in a diesel engine or a jet-aircraft engine.

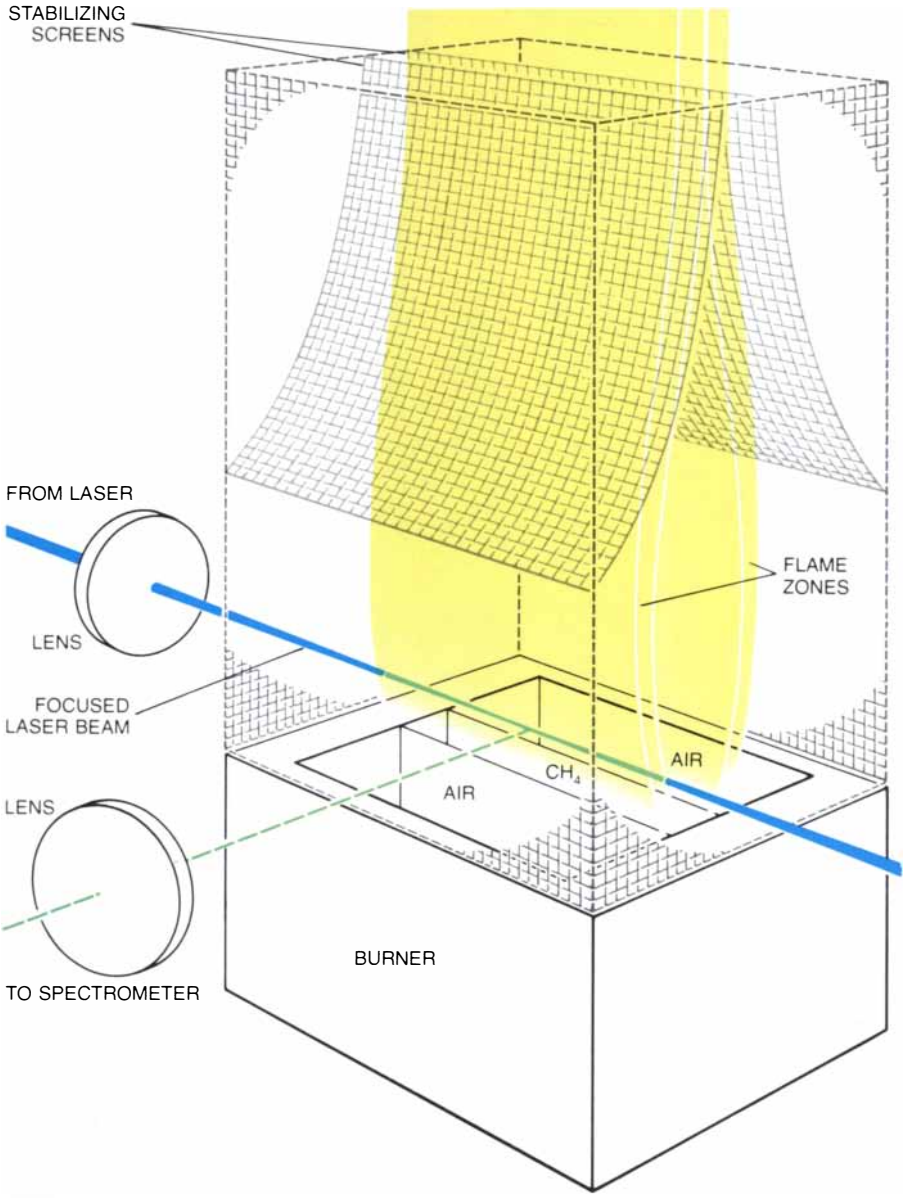
Of all these types of flames only the laminar premixed flame offers the possibility of conducting a quantitative study of chemical processes in spite of concurrent physical processes, in particular the diffusive movement of heat and matter. Even the comparatively simple reaction zone of a Bunsen-burner flame is not optimal for studying combustion chemistry, however; the flow pattern around such a flame is two-dimensional, which is one dimension more than can be dealt with in simple flow equations. Moreover, the reaction zone is very thin, so



LAMINAR DIFFUSION FLAME is stabilized with the aid of screens in this demonstration of the laser-probe technique, photographed by Fritz Goro at the Fire Research Center of the National Bureau of Standards. In a flame of this type the fuel and the oxidizer meet in the combustion zone; here the fuel is methane and the oxidizer is air. A closeup view of the flame, showing the green fluorescence excited by the blue laser beam from large organic molecules that may be soot precursors, is shown at the top of the next page.



THIN GREEN LINE of fluorescing gas molecules excited by the passage of a blue laser beam through the reaction zone of a methane-air diffusion flame was captured by Goro in this close-up photograph of the flame. The front stabilizing screen has been removed; the rear one is dimly visible through the flame. The brass flame holder is approximately four centimeters long.



FLUORESCENCE FROM FLAME can be analyzed by means of a spectrometer, as is shown in this schematic diagram of the experimental setup seen in the photograph on the preceding page. The methane fuel flows out of a slot in the middle of the burner; the fuel outlet is flanked by two laminar sheets of air flowing from channels along the sides of the burner. Combustion takes place in the two reaction zones at the interface of the fuel and the air. The laser beam is focused on the fuel side of reaction zone on near side of burner. The experiments on soot formation at the Fire Research Center are being done by W. Gary Mallard and Kermit C. Smyth.

that it is difficult to do chemical analyses within the flame. For laboratory studies of the structure of flames a one-dimensional flow pattern can be generated by replacing the tube of a Bunsen burner with a large, flat flame holder fitted with a porous plug. The reaction zone can then be stretched by reducing the pressure of the fuel-oxidizer mixture to less than atmospheric pressure.

In low-pressure premixed flames the course of the chemical reactions can be followed with suitable probes of the composition and the temperature of the gas in the combustion zone. Intrusive probes, such as quartz gas-sampling tubes and thermocouples, provide spatially resolved information about composition and temperature at the cost of disturbing the flow, often significantly and in a way that is difficult to describe mathematically. Optical probes, such as laser beams, have the advantage that the flame itself is undisturbed and the disadvantage that the path of the light beam is bent by density gradients in the flame. A variety of flames have been probed by a variety of methods since the late 1950's, when the technology of generating stable, low-pressure flames was developed. These continuing studies have provided a chemical description of the changes that take place in flames.

The variation in concentration of the molecular components in a flame as a function of distance from the burner can be represented by a set of graphs known as flame profiles. The mathematical analysis of such profiles, pioneered by Joseph O. Hirschfelder and Charles F. Curtiss of the University of Wisconsin at Madison in the 1950's, enables one to separate changes in molecular concentrations into two classes: changes resulting from diffusion and changes resulting from chemical reactions. One can then derive net chemical-reaction rates for each substance found in the flame; the resulting set of reaction-rate profiles serves as the basic chemical description of the flame. Even before combustion chemists developed the techniques for getting reaction profiles reliably, however, they knew that no set of flame profiles, however complete, would suffice to identify the molecular events responsible for the profiles. They knew already that the diversity of molecular events was far greater than the number of flame profiles they could ever hope to compile.

The molecules of most fuels have far too many atoms for combustion to proceed as a concerted event. Imagine the tangle that would arise if the eight carbon atoms and the 18 hydrogen atoms of an octane molecule (C_8H_{18}) were to disengage from one another and combine all at once with the surrounding molecules of diatomic oxygen (O_2), forming the new chemical bonds of car-

FLAME	CHEMICAL REACTION	TEMPERATURE (DEGREES KELVIN)	ENERGY RELEASE (JOULES PER GRAM)
HYDROGEN-OXYGEN	$2\,H_2 + O_2 \rightarrow 2\,H_2O$	3,100	24,000
METHANE-OXYGEN	$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$	3,000	10,000
METHANE-AIR	$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$	2,200	2,700
OCTANE-OXYGEN	$2\,C_8H_{18} + 25\,O_2 \rightarrow 16\,CO_2 + 18\,H_2O$	3,100	9,900
ACETYLENE-OXYGEN	$2\,C_2H_2 + 5\,O_2 \rightarrow 4\,CO_2 + 2\,H_2O$	3,300	11,800
CYANOGEN-OXYGEN	$C_2N_2 + O_2 \rightarrow 2\,CO + N_2$	4,800	6,300
PRODUCER GAS–AIR	$2\,CO + 4\,H_2 + 3\,O_2 \rightarrow 2\,CO_2 + 4\,H_2O$	2,400	4,100
METHYLHYDRAZINE – NITROGEN TETROXIDE	$CH_4N_2 + N_2O_4 \rightarrow 2\,H_2O + CO_2 + 2\,N_2$	3,000	7,500

FLAME CONDITIONS depend on both the fuel and the oxidizer. The temperatures listed for the chemical reactions in this table refer to flames burning at atmospheric pressure. At higher pressures the dissociation of the combustion products would be suppressed, leading to higher flame temperatures. The value given for the energy released by each reaction refers to the amount of energy liberated per gram of fuel and oxidizer together (including the inert components in the case of air) after the product gases have cooled back to ambient temperature. Hydrogen and cyanogen flames are important in the laboratory for high-temperature spectroscopic studies. Producer gas is a comparatively cheap fuel mixture prepared from coal and water. Methylhydrazine is burned with nitrogen tetroxide as the oxidizer in the attitude-control engines of the space shuttle; unlike most fuel-oxidizer combinations, these two substances ignite instantly on contact.

bon dioxide (CO_2) and water (H_2O). No fuel burns that way. Instead the breakdown of fuel molecules and the formation of combustion products proceed in long sequences of steps; each step involves only a small rearrangement of chemical bonds.

A step of this type is termed an elementary reaction; the various molecules created along the way are called reactive intermediates, and the set of all elementary reactions that together account for the net chemical transformation is the reaction mechanism. The equation describing the overall chemical reaction that takes place in a flame gives no hint of what the individual molecular changes are; the equations describing elementary reactions, however, do represent real chemical events at the molecular level. Only when all the important elementary reactions are known can the path from fuel to combustion products be accurately described in terms of the rearrangements of atoms in molecules.

Discovering the elementary reactions is the key to understanding how combustion proceeds. In order to get this key, however, it is not enough to identify particular elementary reactions as possible chemical events. One must also know what the probability is that the molecules concerned will indeed react when their paths cross, since most of their encounters do not lead to a chemical reaction. That probability turns out to depend on the relative speed with which the molecules collide. Usually the more violent the collision, the more likely it is to lead to a chemical reaction. Since both the frequency and the speed of molecular encounters depend on the temperature of the gas, the reaction probability increases, often quite sharply, with increasing temperature.

The study of reaction probabilities and their dependence on temperature falls into the area of chemical kinetics, a field in which it is the custom to express such probabilities in terms of the temperature-dependent proportionality constants called rate coefficients. The reaction rate is the rate coefficient multiplied by the concentration of each of the reactant molecules. Since the temperature-dependent values of the rate coefficients of most flame reactions have not been measured for the temperature range of flames, extrapolations are usually required. Fortunately the theory of rate coefficients has been thoroughly tested and is (with minor reservations) reliable enough for accurate extrapolations to be made.

The goals of combustion chemistry are therefore to identify the elementary reactions of a flame, to determine the rate coefficient of each reaction as a function of temperature and to assemble this information into flame models that provide testable predictions. To arrive at such predictions one employs computer programs in which the equations describing the diffusive and reactive rates of change in concentration of all the molecules in the flame are combined with the equations describing the flow of the reacting gases.

In searching for the elementary reactions of flames combustion chemists knew in advance the kinds of reaction they would have to identify. Early in this century it was recognized that the intermediate substances participating in most chemical reactions are present in extremely small amounts that are usually undetectable. This is particularly true when the intermediates are highly reactive compared with the other molecules present and when they enter readily into elementary reactions that produce other reactive intermediates. An example that proves to be very important in flame chemistry is the elementary reaction that converts carbon monoxide into carbon dioxide: $CO + OH \rightarrow CO_2 + H$. The reactive intermediate entering into the elementary reaction, the hydroxyl radical (OH), yields another reactive intermediate, atomic hydrogen (H), with the result that there is no change in the number of intermediates. (The term radical is used by chemists to denote reactive fragments of molecules.)

The hydrogen atom subsequently participates in other elementary reactions, some of which may in turn yield a hydroxyl radical, making it possible for the reaction with carbon monoxide to recur. Because of the repetition of the same molecular events this kind of reaction mechanism is called a chain reaction; the elementary reactions are called chain-propagating steps, and the atoms and radicals that participate in the propagation of the chain are called chain centers. A very small number of chain centers can lead to a large amount of chemical reaction.

Chain-propagating steps alone are insufficient to account for flames. It was recognized in the 1930's that chain-initiating, chain-terminating and chain-branching steps are also necessary. The 1956 Nobel prize in chemistry was awarded jointly to Cyril N. Hinshelwood of the University of Oxford and Nikolai N. Semenov of the Institute of Chemical Physics in Moscow for their leading roles in showing how the main features of oxidation reactions could be explained in terms of branched-chain reaction mechanisms. (At the time of their research chemists had only provisional ideas about what the actual elementary reactions might be and almost no information at all about the values of the rate coefficients.)

A chain-initiating step is an elementary reaction in which one or two normally stable molecules react to form one or two chain centers. An example is the reaction $C_3H_8 \rightarrow C_2H_5 + CH_3$, in which the stable molecule propane (C_3H_8) decomposes spontaneously, when it is

raised to a high energy by collisions with other molecules in a hot gas, to form the two radicals C_2H_5 and CH_3, each of which can in turn serve as a chain center.

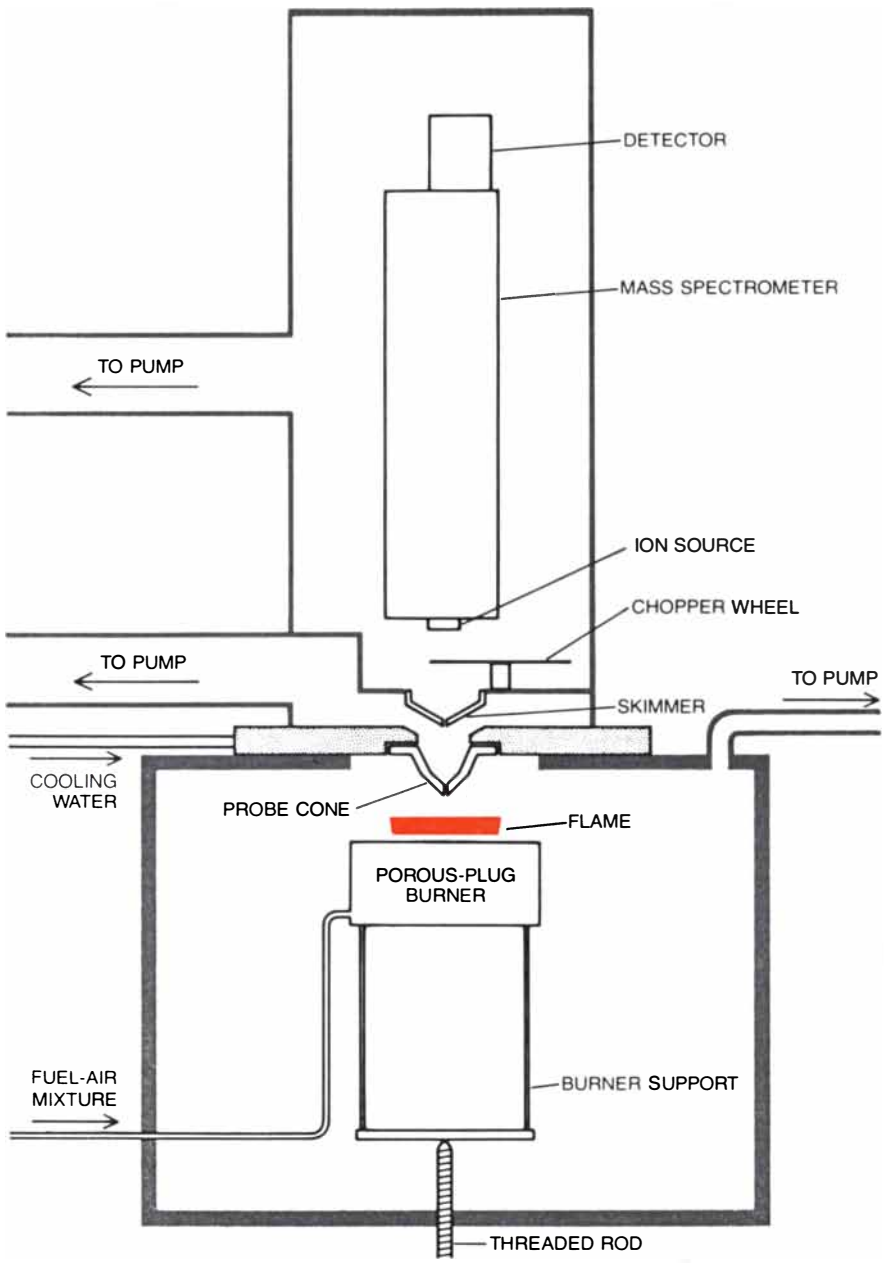
A chain-terminating step is an elementary reaction that has the opposite effect. For example, in the reaction $H + OH + N_2 \rightarrow H_2O + N_2$ two chain centers, a hydrogen atom and a hydroxyl radical, simultaneously encounter the chemically stable molecule nitrogen (N_2) to form another chemically stable molecule: water. Here the nitrogen molecule acts as a kind of chaperon, absorbing some of the energy that is liberated when the new chemical bond of the water molecule is formed.

The distinctive chemical feature of flames, however, is the participation of chain-branching steps: elementary reactions in which the number of chain centers increases from one to two or perhaps even three. The most important chain-branching reaction is $H + O_2 \rightarrow O + OH$, in which atomic hydrogen reacts with molecular oxygen to yield atomic oxygen and a hydroxyl radical.

This much basic theory has been known for half a century. To develop it into a detailed description of flame chemistry, however, two more factors were needed. The first was a set of practical mathematical procedures to find the combined effects of all the elementary reactions on observable chemical and physical properties. Expressing the physical processes of diffusion, heat conduction, chemical reaction and flow in mathematical form was only the start; the resulting simultaneous differential equations present two difficulties, one obvious and the other subtle.

The obvious difficulty is that an exact description of diffusion and heat conduction requires that one provide the values for certain parameters (called multicomponent transport coefficients) that cannot be measured in the laboratory. Approximate descriptions of them can be made only by relying on assumptions of questionable accuracy. Fortunately recent computer-modeling research has shown that approximations made in describing diffusion and heat conduction have only minor effects on the results.

The subtle difficulty is that the differential equations have a property called stiffness, which means that some of the concentration variables are held to nearly constant values by very rapid reactions, while others change. The effect of this factor is to require intolerably long computer time if the set of simultaneous differential equations is to be solved numerically on a digital computer by standard methods. Special computer techniques for dealing with stiff differential equations were developed in the 1970's, most of them based on pioneering research by Charles W. Gear of the University of Illinois at Urbana. The advent of stiffly stable numerical techniques made it feasible to model one-dimensional flames, taking detailed account of the flame chemistry, on large digital computers.



SAMPLING PROBE is used to follow the progress of combustion reactions in flames burning at low pressure. The rapid expansion of the gas entering the cone-shaped probe has a cooling effect that "freezes" the flame reactions. Accordingly the gas sample taken through the probe can be analyzed outside the reaction zone by conventional analytic methods, such as the mass spectrometer employed in this apparatus, devised by Joan C. Biordi, Charles P. Lazzara and John Papp at the U.S. Bureau of Mines Research Center in Pittsburgh. For obtaining flame profiles of substances too reactive to survive such a probing process, optical methods are required.

A computer simulation is only as good as its input data, in this case the rate coefficients for all the elementary reactions. Since flames themselves are too complex to define these coefficients, one must find them in less complex environments. Hence the second requirement was to measure the rate coefficients of the elementary reactions experimentally. How?

In spite of the world's reliance on gas-phase combustion for energy, scientists studying gas reactions (gas kineticists) epitomize "small science": small groups (sometimes as small as one person working alone) with small laboratories and small budgets, scattered over the globe, meeting one another personally mostly at the fringes of scientific gatherings whose main purpose requires some input of basic gas kinetics. When the theory of flame reactions was first being developed, gas kineticists studied oxidation reactions in glass bulbs, where the reactions could be made to proceed slowly by maintaining lower tempera-

SCIENCE/SCOPE

The first carbon-dioxide laser rangefinder developed in the U.S. for tactical military use offers several advantages over existing solid-state lasers to improve the first-round accuracy of tank gunners. The new laser, being developed at Hughes for the Army's M1 main battle tank, will penetrate battlefield smoke and dust much better. Because the laser is harmless to the human eye and requires minimal safety restrictions to be operated, gunners will have more training time than they do with the solid-state unit and will become more proficient. The Army is evaluating an advanced development model.

A new adaptive radar, using technology that could be applied in the future to many different weapon control systems, has completed feasibility tests. The radar, called FLEXAR (Flexible Adaptive Radar), uses a multimode transmitter and a programmable signal processor that are now in production, plus a new lightweight, low-cost electronically-scanned antenna. The antenna rotates once each second while the beam electronically scans up and down and back and forth. Waveforms are selected automatically to match the environment. Such flexibility enables the radar to adapt its waveform beamwidth and scan rate as needed to acquire and track targets. Hughes developed FLEXAR for the U.S. Navy.

Besides taking pictures of clouds every 30 minutes, a new satellite provides meteorologists with other important information. The GOES-5 spacecraft relays data from more than 1,500 stations that monitor sea ice conditions and water and snow distribution in remote areas, providing flood warning, among other services. It also measures solar winds and detects solar flares and fluctuations in the earth's magnetic field. This data, besides being useful in weather predictions, is used in communications and electrical power distribution. GOES-5 is the second of three Geostationary Operational Environmental Satellites built by Hughes for the National Oceanic and Atmospheric Administration.

Hughes Industrial Electronics Group offers the advantages and opportunities of a small company backed by the resources of a $2-billion company. Our facilities are in the Southern California communities of Carlsbad, Irvine, Newport Beach, Torrance, and Sylmar. Our programs incorporate 34 different technologies. They include silicon and GaAs semiconductor technologies, fiber optics, microwave and millimeter-wave communications, microprocessors, lasers, and solar cells. Send resume to B.E. Price, Hughes Industrial Electronics Group, Professional Employment, Dept. SSA, P.O. Box 2999, Torrance, CA 90509. Equal opportunity employer.

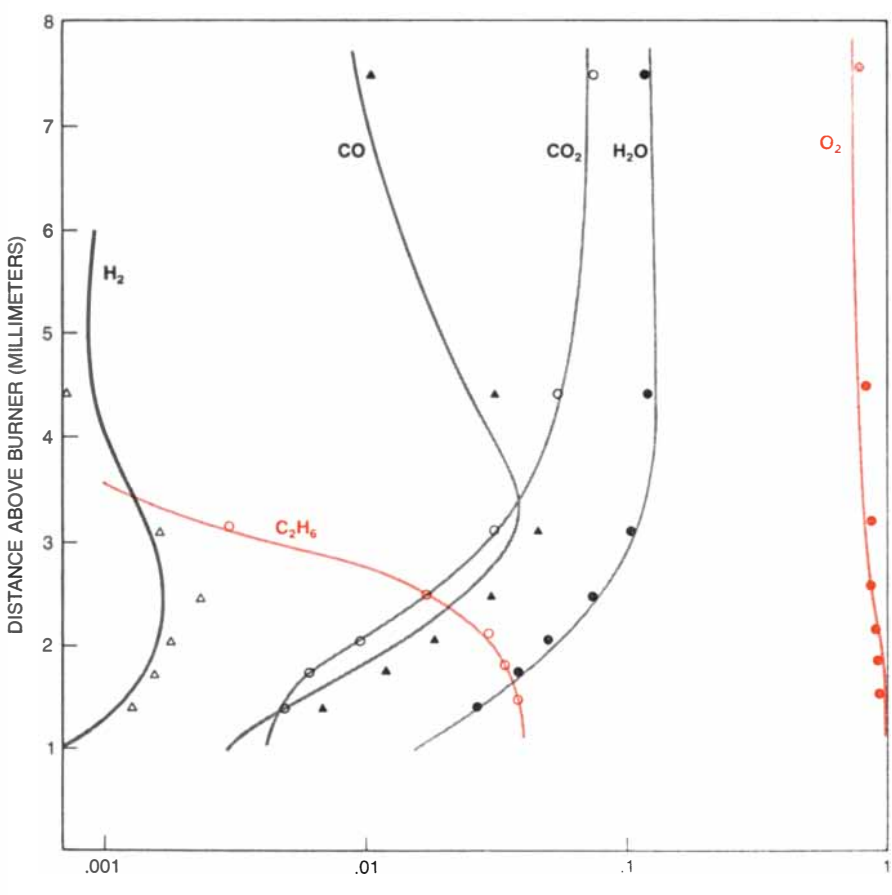
Better and timelier weather forecasts will be possible when a microwave sensor is launched aboard a military satellite in the mid-1980s. The instrument will tell how hard rain is falling in a specific area rather than simply how much has fallen over a wide area within 24 hours. It also will determine wind speed, atmospheric water content, soil moisture, and sea ice conditions. Because the satellite will follow a low polar orbit, the sensor will gather important data on the little-studied polar regions and oceans. Hughes will soon deliver the prototype Special Sensor Microwave/Imager to the U.S. Air Force.

tures and pressures than normally prevail in flames. As the result of long years of painstaking work it became possible to identify a large number of elementary reactions in this way and to deduce rate coefficients for them. Virtually all this effort, however, bypassed the central chain reactions, because they are too fast to be studied by such methods.

The development of sophisticated laboratory techniques has made it possible to study even the fastest elementary reactions. No single experimental technique and no single laboratory has dominated the field; the new knowledge of elementary combustion reactions was generated by many investigators, working with various techniques. To give the flavor of this research I shall describe three experiments based on three techniques that have been responsible for major contributions. The set of three elementary reactions studied in these experiments constitutes the main chain reaction of the hydrogen-oxygen flame.

A shock wave traversing a gas heats it rapidly. The temperature can jump thousands of degrees Kelvin in a billionth of a second. In a shock tube, a laboratory device in which shock waves of controlled strength are passed through a test gas, chemical reactions resulting from shock heating can be monitored by fast analytical methods. In 1966 David Gutman and Garry L. Schott of the Los Alamos Scientific Laboratory used a shock tube to generate shock-heated mixtures of hydrogen and oxygen that were highly diluted with the chemically inert gas argon in order to maintain a constant temperature during the reaction. The growth of the chain centers could be followed by fluorescence spectroscopy on a time scale of microseconds.

Gutman and Schott provided an analytical probe by adding to the test gas some carbon monoxide, which emits a blue luminescence with an intensity proportional to the concentration of oxygen atoms present. The rate at which the intensity of the luminescence increased was extrapolated to an O_2-to-H_2 ratio of zero, where the rate of chain branching would be governed exclusively by the rate of the reaction $H + O_2 \rightarrow OH + O$. The result was a determination over the temperature range from 1,100 to 1,700



COMPUTED FLAME PROFILES (*curves*) **can be compared with laboratory measurements** (*data points*) **for low-pressure laminar flames. The profiles shown here were computed by Jürgen Warnatz of the Technical University in Darmstadt for a reaction mechanism with 58 elementary reactions, taking into account the diffusion of all 20 substances involved in the overall reaction. The experimental data, for an ethane-oxygen flame burning at one-tenth atmospheric pressure, were obtained by Robert M. Fristrom, William H. Avery and C. Grunfelder of Johns Hopkins University. Laser analyses of similar flames by James H. Bechtel and his co-workers at the General Motors Research Laboratory have confirmed the mass-spectrometer profiles.**

degrees K. of the rate coefficient of the elementary reaction responsible for chain branching in hydrogen-oxygen flames.

Reactive atoms can be made at low temperatures by decomposing molecules in electric discharges. Fast reactions of atoms produced in this way can be studied by mixing them with other gases and flowing the mixture rapidly past an observation station downstream. In 1968 Arthur A. Westenberg and Newman deHaas of the Johns Hopkins University Applied Physics Laboratory made a small amount of atomic oxygen in a microwave discharge of molecular oxygen diluted with the inert gas helium. The mixture of atomic oxygen and helium was added to a stream of hydrogen flowing down a tube maintained at a desired reaction temperature. Downstream from the mixing point the loss of oxygen atoms due to reaction with hydrogen molecules was measured with an electron-spin-resonance spectrometer. The result was a determination over the temperature range from 500 to 900 degrees K. of the rate coefficient of the second elementary reaction of hydrogen-oxygen flames, namely $O + H_2 \rightarrow OH + H$.

Another way to decompose stable molecules is with ultraviolet radiation. In 1980 Frank P. Tully and Akkihebbal R. Ravishankara of the Georgia Institute of Technology developed an apparatus in which a small amount of water vapor in hydrogen at a desired reaction temperature could be irradiated with an intense flash of ultraviolet radiation. The hydroxyl radicals created by the flash could then react with the hydrogen molecules in the third elementary reaction of the hydrogen-oxygen flame, namely $OH + H_2 \rightarrow H_2O + H$. The decay in the concentration of OH was followed by ultraviolet analytical spectroscopy. The result was a determination of the rate coefficient of this reaction over the temperature range from 500 to 1,000 degrees K.

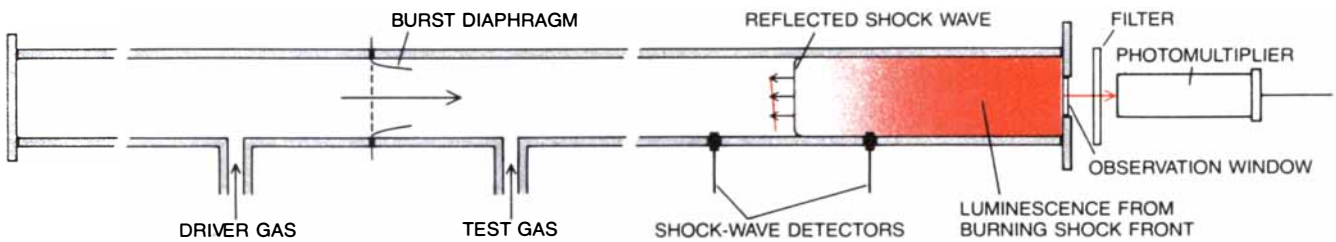
Dozens of experiments such as these have collectively provided chemists with a set of rate coefficients for the elementary reactions of the hydrogen-oxygen flame, thereby making it possible to model these flames accurately on a computer. In addition to the three elementary reactions discussed above some 20 more, mostly concerned with the roles of the secondary intermediates hydrogen peroxide (H_2O_2), the hydroperoxyl radical (HO_2) and ozone (O_3), can be included to construct models that describe even the minor details of the hydrogen-oxygen reaction.

Hydrogen-oxygen flames are scientifically interesting as prototype combustion processes, but their only application outside the laboratory is in rocket engines. Practical flames burn hydrocarbons. What is known about them?

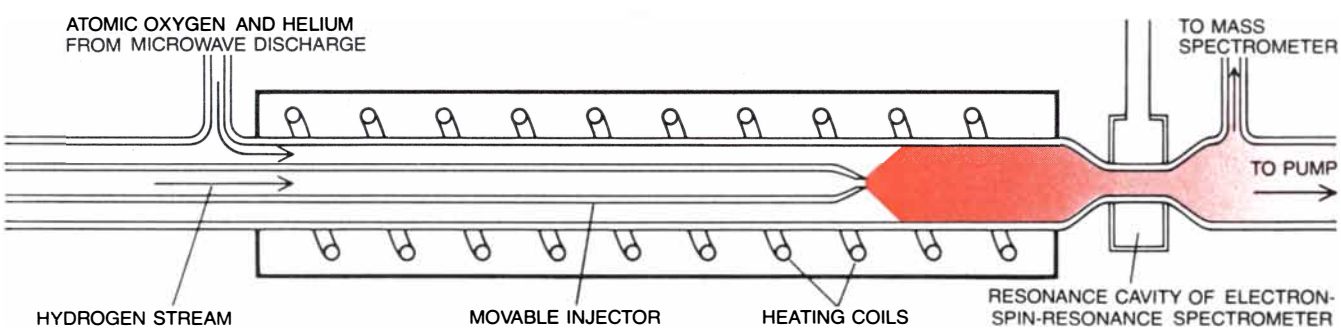
A current chemical description of a hydrocarbon flame would resemble a book with an almost complete introduction (the reactions of the fuel molecules themselves) a complete last chapter (the oxidation of H_2 and CO) and only fragments of everything in between. The number of chapters in the book would increase with the number of carbon atoms in the fuel molecules, except that the simplest fuels, those with one or two carbon atoms, share common reaction pathways and therefore have the same combustion mechanism. Chapter headings could be taken from the fuels and the known intermediates: CH_4, CH_3, CH_2, CH, C_2H_6, C_2H_5, C_2H_4, C_2H_3, C_2H_2, C_2H, CH_3O, CH_2O, CHO, C_2H_4O, C_2H_3O, C_2H_2O....

Trial models of hydrocarbon flames are made by combining the elementary reactions an investigator feels are important, employing both measured and estimated rate coefficients. They are then tested against a variety of experimental facts: flame-propagation speeds, shock-tube ignition measurements, flow-reactor molecular-concentration profiles and so on. Even for the smallest hydrocarbons, however, the list of elementary reactions considered important for one reason or another soon has more than 100 entries, and the only way to keep track of the process is with the aid of flow diagrams.

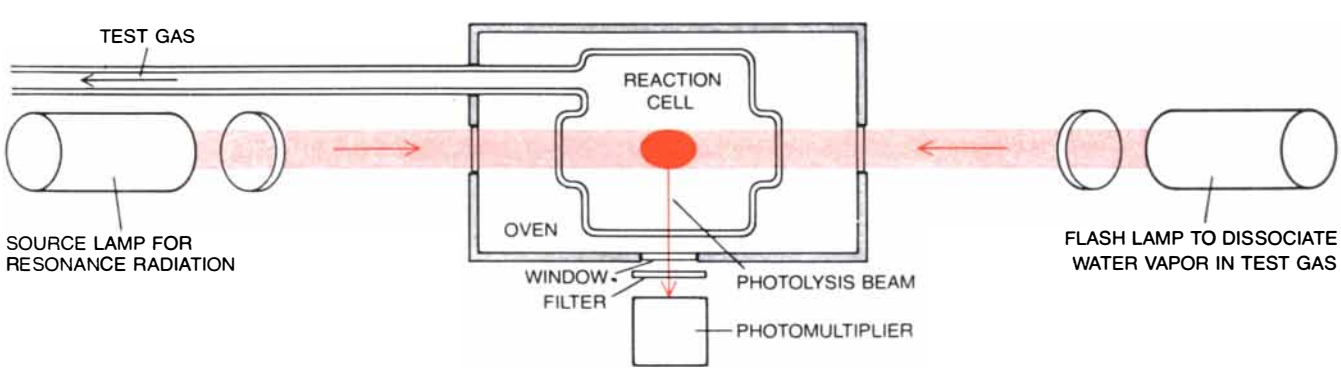
The details of hydrocarbon-flame models are still in dispute, but many general features are clear. First, most of the elementary reactions are types



SHOCK-TUBE EXPERIMENTS are carried out by heating a test gas with a shock wave passing down a long tube and then observing the ensuing reaction in the hot test gas. The apparatus shown was used by David Gutman and Garry L. Schott of the Los Alamos Scientific Laboratory in 1966 to determine the rate coefficient of the reaction $H + O_2 \rightarrow OH + O$. The test gas was a mixture of diatomic molecules—hydrogen (H_2), oxygen (O_2) and carbon monoxide (CO)—highly diluted in the inert gas argon. The shock wave was generated by bursting the thin metal diaphragm separating the high-pressure driver gas (in this case H_2) from the low-pressure test gas. The chemical reaction began when the shock wave was reflected from the end wall of the tube, heating the test gas in a billionth of a second to the reaction temperature. The intensity of the luminescence from the $CO + O$ reaction, which is proportional to the concentration of oxygen atoms in the test gas, was recorded by a photomultiplier tube through a window in the end wall of the shock tube. The rate of the chemical reaction, measured on a scale of microseconds, was deduced from the rate of increase in the intensity of the luminescence.



DISCHARGE-FLOW EXPERIMENTS make it possible to study fast reactions by streaming the reacting gas at high speed past a fixed observation point. In this experiment, done in 1968 by Arthur A. Westenberg and Newman deHaas of Johns Hopkins, atomic oxygen was generated in a microwave discharge and was mixed with molecular hydrogen flowing through a heated tube. The rate coefficient of the reaction $O + H_2 \rightarrow OH + H$ was determined by measuring the concentrations of the reactants and the products with the aid of an electron-spin-resonance spectrometer situated downstream from the mixing point. Measurements were also made by mass spectrometry.



FLASH-PHOTOLYSIS EXPERIMENTS are done by initiating the reaction with an intense flash of ultraviolet radiation. The apparatus depicted here was used by Frank P. Tully and Akkihebbal R. Ravishankara of the Georgia Institute of Technology in a 1980 study of the reaction $OH + H_2 \rightarrow H_2O + H$. Hydroxyl radicals (OH) were obtained by the photodissociation of a trace of water vapor inside the heated reaction cell by means of a secondary flash lamp (*right*). The reaction rate was determined by monitoring the intensity of the fluorescence from a small fraction of the hydroxyl radicals that had been excited to a radiating energy state by the primary flash lamp (*left*).

GIANT GOURMET MUSHROOMS LIKE THESE INDOORS YEAR 'ROUND'

the majestic Shiitake mushroom - revered by gourmets for its flavor, revered in the Orient as the Elixir-of-Life

by Hal Taub (At Lovin' Spoonful, I'm Chief Cook & Bottle Washer)

Like most Americans, I love mushrooms. Mushrooms on steak...in an omelet...stuffed mushrooms...as part of my salad...mushroom gravy—you name it, I eat 'em up.

When I can afford it!

With the price of mushrooms *mushrooming* to over $2 a pound for the small button type—when you can find them—and the fancy dried imported kind going for $20-$40 a pound and more, I think twice before indulging myself. Is it any wonder that I've even tried growing them myself? What I got for my labors was a handful of tiny buttons, along with some nasty comments and dirty looks from my neighbors. (Our American or "button" mushrooms require large amounts of manure to grow.)

A TASTE EXPERIENCE

Do I love my food? Let's just say that I very seldom miss a meal. Recently, on a business trip to California, I was treated to a business lunch at an absolutely delightful restaurant in Beverly Hills. Of course I ordered a mushroom salad. It was incredible! I had never tasted anything like it before. Not even the imported mushrooms came close. I can only describe the flavor as being somewhere between filet mignon and lobster! I not only ate my salad, I ordered two more to boot. In fact I almost OD'd on mushroom salad!

THEY ARE CALLED SHIITAKE'S

That was my introduction to the Shiitake Mushroom. Let me tell you, I did not leave that restaurant without learning their source. I discovered they were being raised in very limited supply by a Chinese American botanist, Dr. Henry Mee. I called Dr. Mee thinking I could tote a few pounds home with me. He most graciously invited me out to his facilities. I went to buy mushrooms, but instead, received an education.

ELIXIR OF LIFE

The first Shiitake spawned during the misty era of a hundred million years ago. Early Chinese sages attributed great powers to the Shiitake and it was often called the Emperor's Food. In ancient China and Japan, it was eaten by royalty to fend off old age, revered as an aphrodisiac and fought over by Japanese warriors who fiercely guarded the growing sites.

In their natural habitat, it takes two years to bring a Shiitake crop to harvest. They grow on oak logs in the remote mountain forests of Japan. After 25 years of study and labor Dr. Mee has developed a method that cuts the time down to 45 days. He now produces some 100 pounds daily, of which the entire crop is taken by a relatively small handful of gourmet restaurants and shops.

MORE THAN I BARGAINED FOR

Rather than sell me a few pounds of mushrooms, Dr. Mee suggested I grow my own. He had perfected his process to the point where he claimed anyone who could water a house plant could enjoy fresh, luscious "Shiitake" mushrooms. Simply stated, he simulates their natural habitat by producing a "log" fabricated of 100% sterilized organic plant material, with nothing artificial, and no chemicals added. The log is then innoculated with pure culture of the "Shiitake" mushroom spore...and then cured or "aged" to hasten fruition under home environment with the addition of nothing but water. When Dr. Mee said I would not require any manure or fertilizer of any kind, I decided to give it a try.

SIMPLE AS A.B.C.

The instructions were simple. Start by soaking the log in water for 24 hours. Then simply place the tree in its own wooden planter-stand and set on a foam rubber pad, which is supplied with each log and acts as a moisture "reservoir". After that just mist it once a day. And, unlike buttons, Shiitakes thrive in daylight.

INCREDIBLE RESULTS

In only 5 days I actually saw mushrooms start budding, 10 days later I picked my first giant Shiitake. One month later I had enough for not only myself but my friends as well. What's more, Dr. Mee has informed me that I can expect the log to keep producing for the next 10 to 12 months. If you're growing more mushrooms than you can use, simply store the tree in the frig (or outdoors if the weather is cool) and it will stop growing. When you want more mushrooms, just place it at room temperature and it will start producing.

NUTRITION

With a virtually unlimited supply of my favorite food I've become something of an expert. Mushrooms are nature's unique low cal fat-free food. One pound contains fewer calories than a single apple! Shiitake mushrooms have more than twice as much protein and fiber as common button mushrooms, almost 3 times the minerals. Calcium, Phosphorous and Iron are present in large quantities, as are high levels of B Vitamins and Vitamin D2.

A FEAST

All of this nutrition stuff is great. But the eating is even better! One ounce of Shiitake will equal the flavor of an entire pound of buttons. They are super meaty, super mushroomy in taste, succulent, heady and 100% edible from cap to stem.

One of two slices turn an ordinary pot roast into a gourmet delicacy...an ordinary salad into an extraordinary taste sensation...a gravy into a nectar for the gods. And spaghetti; let me tell you about my spaghetti. I serve it with a mushroom meat sauce that is truly memorable!

My guests insist that Julia Child had come in to cook for me!

AM I SELFISH?

My friends (and my wife) have accused me of being selfish. I admit to being somewhat of a miser when it came to sharing my mushroom crop. It seems every time I gave my friends a super-size Shiitake, they would come back and pester me for more. I finally had to ask Dr. Mee for additional mushroom logs to save my sanity and several valued friendships.

Dr. Mee is now producing a limited number of Shiitake Mushroom Log kits. We at the Lovin' Spoonful are fortunate in being chosen to introduce it to the general public. As a measure of our enthusiasm and our confidence we offer it to you at our risk. If the Shiitake is not every bit as delicious as we claim, or for any reason, you are not satisfied with the production of the log, return it for a full refund of purchase price. The cost is only $19.95, complete with everything you need to grow a bumper crop. We also include a selection of fabulous mushroom recipes. I guarantee it will be the most delicious investment you will have ever made.

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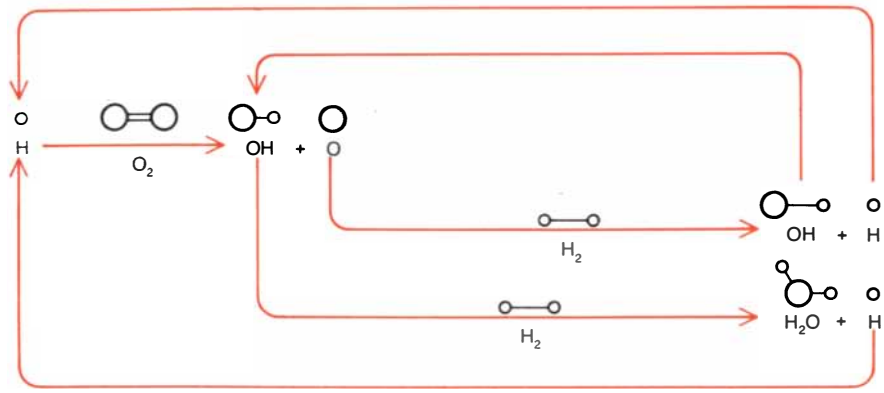
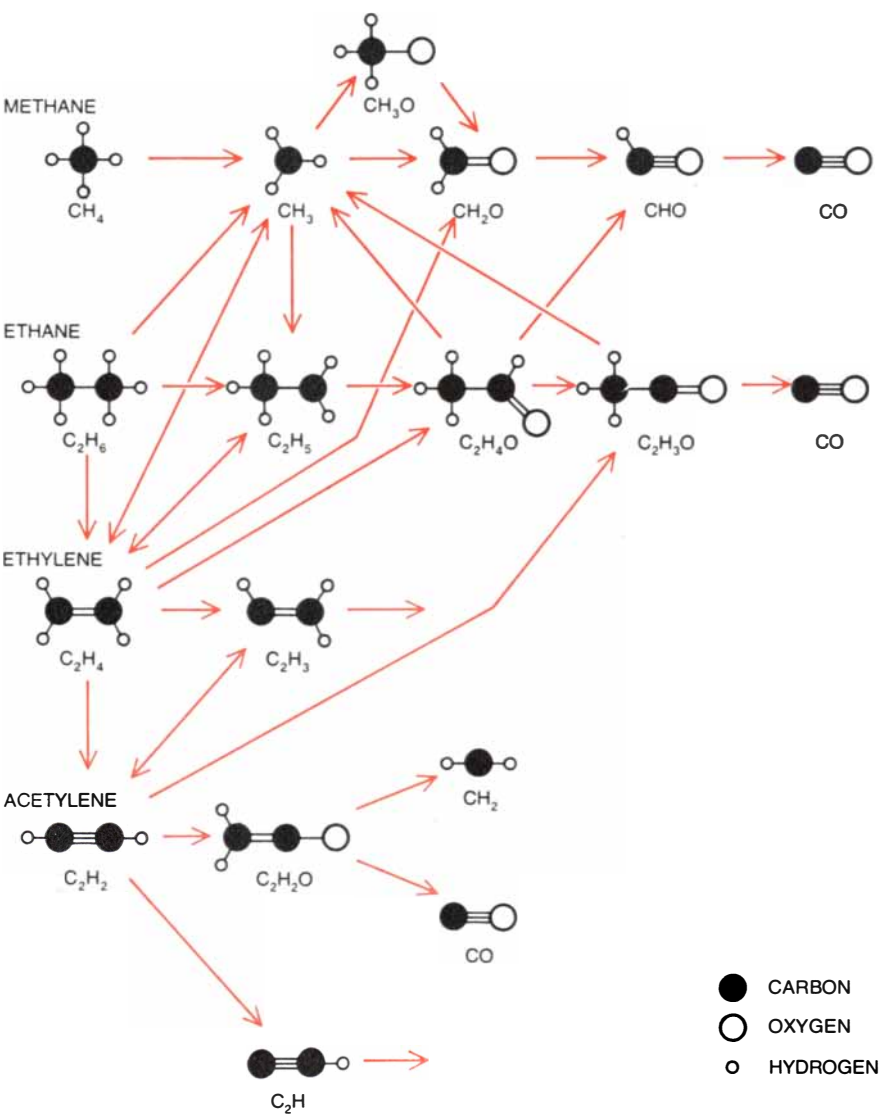


ELEMENTARY REACTIONS of a hydrogen flame involve the intermediate substances H, O and OH. This set of reactions exhibits a typical "chain branching" effect: for each hydrogen atom entering the sequence three hydrogen atoms are generated. This phenomenon is what gives combustion reactions their explosive speed. The rate coefficients of all these reactions have been measured. At low temperatures and high pressures there are other reactions that produce and consume hydrogen peroxide (H_2O_2), the hydroperoxyl radical (HO_2) and ozone (O_3).



HYDROCARBONS BURN by a complex network of combustion routes involving so many elementary reactions that a flow diagram is needed to keep track of the overall course of the reaction mechanism. This comparatively simple flow diagram shows the major transformations that take place in the combustion of the small hydrocarbons methane (CH_4), ethane (C_2H_6) and ethylene (C_2H_4). The intermediates O, H, H_2 and OH and the combustion products CO_2 and H_2O are omitted from the diagram for the sake of clarity. Also not shown are the further reactions of acetylene (C_2H_2) and the reactions of the intermediate hydrocarbons C_2H, C_2H_3 and CH_2, some of which lead to the formation of larger hydrocarbons and soot.

long known in chemical kinetics. Atom-transfer reactions such as $OH + C_2H_6 \rightarrow H_2O + C_2H_5$ constitute the main attack on hydrocarbon fuels. Larger fuel molecules, however, usually do not reach the reaction zone intact, because they are decomposed by heat faster than they diffuse. The commonest type of decomposition involves the loss of two carbon atoms at a time, as in the decomposition of octane by the reaction $C_8H_{18} \rightarrow C_2H_5 + C_6H_{13}$. Most intermediates with an odd number of hydrogen atoms, such as the C_2H_5 radical, quickly lose one of them to form intermediates in the class of hydrocarbons called olefins, in this case ethylene (C_2H_4). Others may lose hydrogen atoms to form intermediates in the class called ethynes; a typical product of this kind is acetylene (C_2H_2).

Olefins and ethynes have been found to undergo some kinds of elementary reactions in flames that are not known in traditional chemical kinetics. For example, Jürgen Warnatz of the Technical University in Darmstadt has recently concluded from modeling the speed of acetylene flames that CH_2 radicals that are formed when oxygen atoms react with acetylene by the reaction $O + C_2H_2 \rightarrow CH_2 + CO$ can fly to pieces in reacting with molecular oxygen by the reaction $CH_2 + O_2 \rightarrow CO_2 + H + H$. Such complex transformations of chemical bonds in single elementary reactions rarely occur except in flames.

Computer models for the combustion of methane (CH_4) already include more than 100 elementary reactions. Is there any hope, then, of constructing one for octane (C_8H_{18}), even assuming the availability of vast computer power? The answer is that there is no hope at all if the model is to take explicit account of all the intermediates: the number of elementary reactions required increases geometrically with the size of the fuel molecule and becomes excessive long before one reaches octane. If the octane-combustion model is only intended to account quantitatively for the central chemical events at the molecular level, however, present-day computers could handle the job by grouping the intermediates by their structure and the reactions by their type. Whether the rate coefficients for such a model can be established in the laboratory remains for the next generation of combustion chemists to discover.

Combustion adds pollutants to the atmosphere: oxides of nitrogen and sulfur, incompletely burned hydrocarbons and particulates such as soot. On a more or less pragmatic engineering basis the suppression of pollutant emissions can be achieved by adjusting the conditions of combustion, by selecting low-nitrogen and low-sulfur fuels, by pretreating fuels or by posttreating combustion gases. Scientifically the goal is

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to discover what elementary reactions create or remove pollutants.

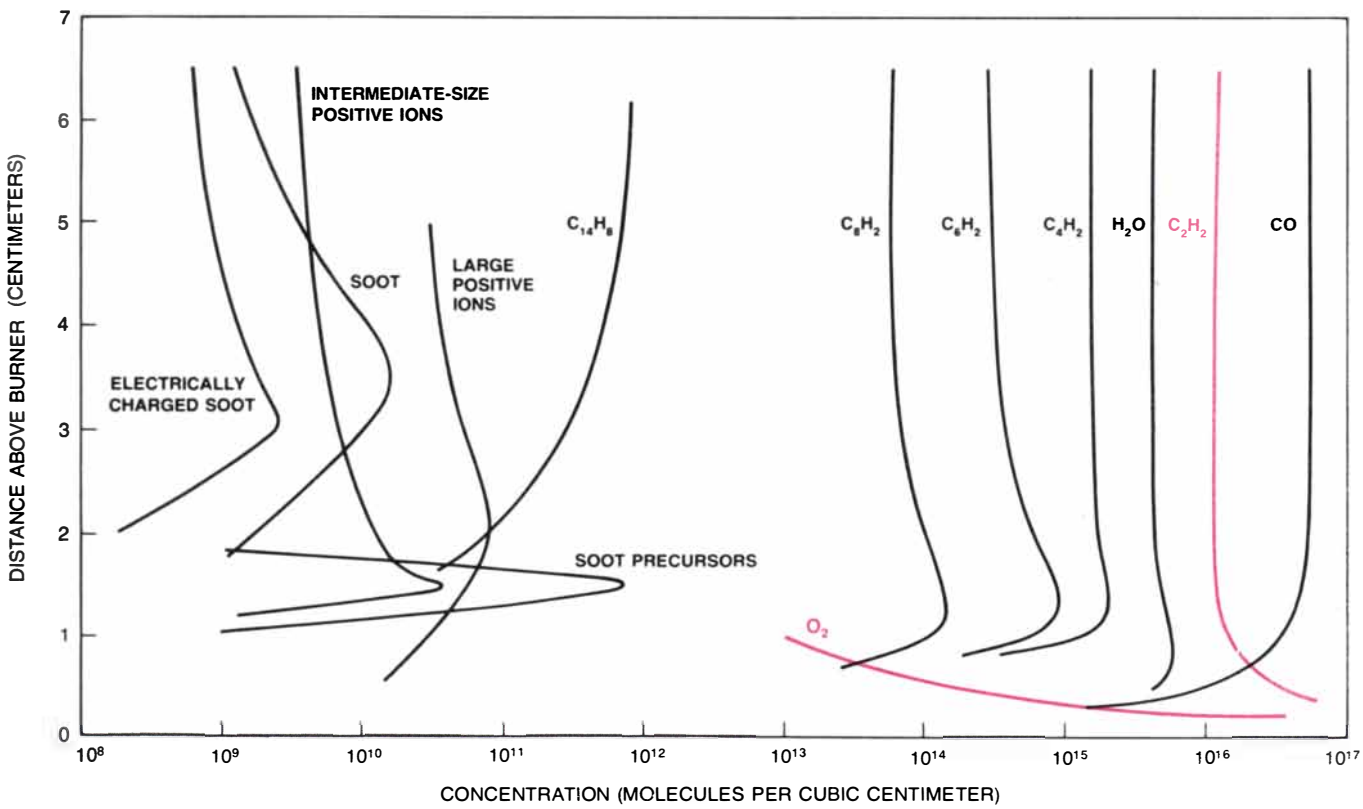
The best-understood aspect of combustion-generated pollution is the formation of oxides of nitrogen with the generic formula NO_x in very hot flames (at temperatures above 2,000 degrees K.). Nitric oxide (NO) is apparently the only oxide of nitrogen formed directly in flames; nitrogen dioxide (NO_2) arises later through slower reactions with atmospheric oxygen, which take place even at room temperature. In very hot flames molecular nitrogen from the air loses its inert character and is split by oxygen atoms in the reaction $O + N_2 \rightarrow NO + N$. Nitrogen atoms rapidly attack molecular oxygen to form nitric oxide and atomic oxygen in the reaction $N + O_2 \rightarrow NO + O$, thereby completing a two-reaction chain known as the Zeldovich mechanism (after Yakov B. Zeldovich of the Institute of Chemical Physics in Moscow, who first proposed it in 1947). Direct shock-tube measurements of the rate coefficient for the $O + N_2 \rightarrow NO + N$ reaction, reported by Jamie Monat, Ronald K. Hanson and Charles H. Kruger, Jr., of Stanford University in 1980, make it possible to model the production of nitric oxide accurately by this route.

At temperatures low enough to suppress the Zeldovich reactions other reactions still generate nitric oxide. Traces of it were shown by Charles Fenimore of the General Electric Research Laboratory to appear very early in flames, leading him to coin the term "prompt NO." What intermediate is energetic enough and plentiful enough then to attack N_2 is unclear. One suggestion is that it is the CH radical, perhaps by the reaction sequence: $O + C_2H_2 \rightarrow CH + CHO$, followed by $CH + N_2 \rightarrow HCN + N$, followed by $N + O_2 \rightarrow NO + O$. Hydrogen cyanide (HCN) is also thought to be an important intermediate when nitric oxide is formed from fuel nitrogen (the generic term for a variety of nitrogen-containing compounds found in small concentrations in petroleum). The reactions leading from hydrogen cyanide to nitric oxide are not yet known. Most of the nitric oxide generated early in flames never escapes into the atmosphere, however, but is converted into molecular nitrogen. How? No one knows. There is obviously ample room for further research on the formation and removal of NO_x compounds in flames.

Basic understanding of reactions involving nitric oxide has led to an ingenious method for removing nitric oxide from postcombustion gas. The method, which has been developed into a commercial process by Richard K. Lyon of the Exxon Research and Engineering Corporation, calls for the injection of ammonia (NH_3) into the postflame gas at a particular point in the cooling process. This leads quickly to the formation of NH_2 radicals, mainly by the reaction $NH_3 + OH \rightarrow H_2O + NH_2$. One of the elementary reactions of NH_2, characterized in 1972 by Manfred Gehring, Karlheinz Hoyermann, Helmut Schacke and Jürgen Wolfrum of the University of Göttingen, is $NH_2 + NO \rightarrow N_2 + H_2O$. In this subsequent step both of the nitrogen atoms in the reactant molecules end up in molecular nitrogen, effectively eliminating the nitric oxide.

A sulfur compound entering a flame quickly forms the stable sulfur dioxide molecule (SO_2), since SO, the sulfur analogue of NO, reacts directly with oxygen by the reaction $SO + O_2 \rightarrow SO_2 + O$, even at room temperature. Chemists studying sulfur reactions that form SO and SO_2 have the problem that sulfur in the gas phase generates a bewildering array of reactive and stable compounds, all of them acidic and all of them unpleasant additions to the atmosphere. There is thus little practical incentive to pursue the identification of specific elementary reactions of sulfur in flames. Pollution control for sulfur means removing all forms of the element prior to combustion or removing all the acidic oxides of sulfur later.

Finally there is soot, the formation and oxidation of which are currently the



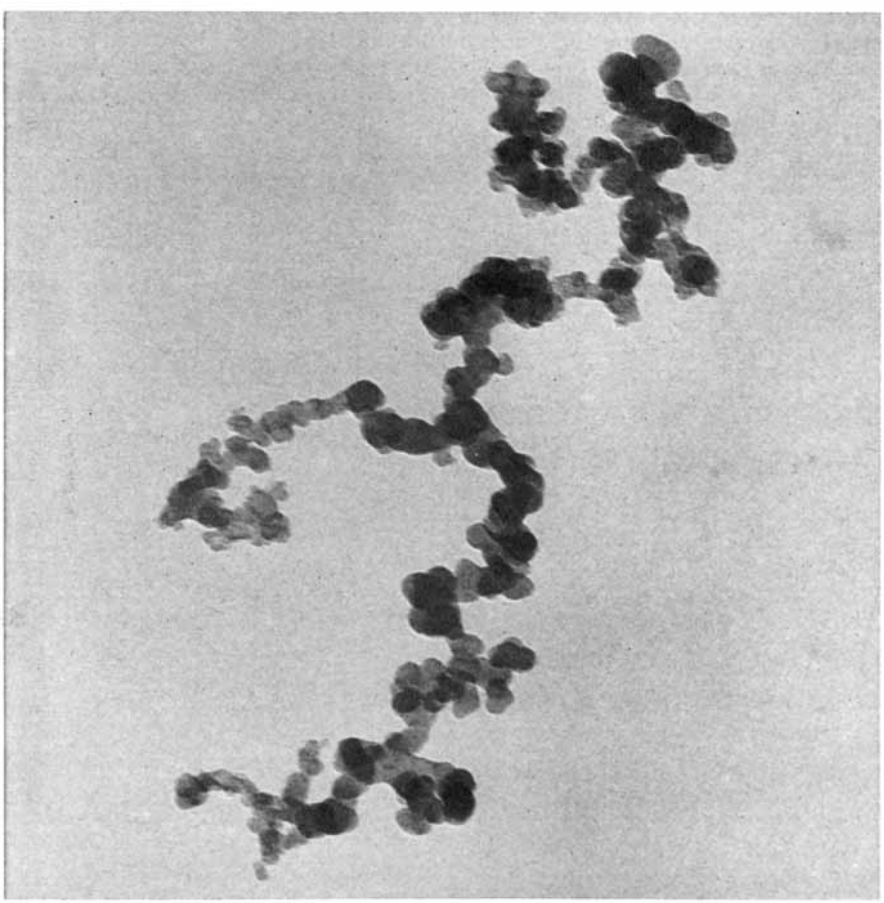
MOLECULAR COMPOSITION of a typical soot-producing laboratory flame varies as a function of distance above the burner. This set of logarithmic concentration profiles, for an acetylene-oxygen flame, combines the results of measurements made by Ulrich Bonne, Klaus H. Homann and Heinz-Georg Wagner of the University of Göttingen, Douglas B. Olson and Hartwell F. Calcote of the Aerochem Research Laboratories and Jack B. Howard and his co-workers at the Massachusetts Institute of Technology. The group of intermediates labeled "soot precursors" consists of a variety of hydrocarbons with between 20 and 50 carbon atoms. Unlike polyaromatic, or multiple-ring, hydrocarbon molecules (such as $C_{14}H_8$), whose flame profiles continue to rise, the soot precursors vanish when soot appears.

two most actively studied processes in combustion chemistry. At one time the main use of petroleum was for kerosene lamps, which require the intermediate formation of soot to provide luminescence and the subsequent oxidation of soot to avoid the blackening of the lamp chimney. Nowadays light can be produced more conveniently by electricity, so that the soot in most flames is just a nuisance. The factors that enhance the production of soot are well known: high fuel-to-air ratios, fuel containing compounds with low hydrogen-to-carbon ratios, erratic ignition and poor mixing of fuel and air. It appears that much of the future supply of liquid fuels will come from oil shale and liquefied coal, which are intrinsically low-hydrogen fuels. Can they be burned on a large scale without burying us all in soot?

Soot is formed in three stages. In all hydrocarbon flames there is a decrease in the hydrogen-to-carbon ratio of the hydrocarbon molecules and radicals as they are successively decomposed by heat and chemical attack. The last of them are typically molecules such as acetylene (C_2H_2) and fragments such as the ethynyl radical (C_2H). In a soot-producing flame such molecules and radicals are not oxidized; in the first stage of soot formation they mostly polymerize to form polyacetylenes and their radicals by reactions such as $C_2H + C_2H_2 \rightarrow C_4H_2 + H$, followed by $C_2H + C_4H_2 \rightarrow C_6H_2 + H$. Other large molecules characteristic of a soot-producing flame are a variety of polyaromatic compounds (in which the carbon atoms are arranged in multiple rings) and positive hydrocarbon ions.

After a characteristic delay time some of these molecules vanish and in the second stage a soot aerosol appears: spherical particles of carbon containing varying amounts of hydrogen and trapped hydrocarbons, depending on the flame. The aerosol particles give sooty flames their opacity and are therefore responsible for their yellow glow. The spheres cannot grow beyond about a tenth of a micron in diameter, because of the depletion of carbon in the flame gas, and so the larger particles that constitute black smoke form in the third stage by the agglomeration of the aerosol particles. Both the particles and their agglomerates anneal as long as they are hot, losing hydrogen and organic material and forming increasingly rigid structures that in some flames begin to resemble the layered structure of graphite. They can also oxidize readily, and in many flames, such as those of candles or well-run industrial furnaces, they vanish completely.

The evidence supporting this picture comes from two sources: analyses of the molecular and ionic composition of flame gases and related soot-forming systems prior to the appearance of a soot aerosol, and microscopic and chemical studies of soot particles recovered from the later stages of the process. The investigator of soot is therefore isolated from two key aspects of the flame: the steps by which hydrocarbon molecules, radicals and ions first nucleate to form an aerosol, and the competition among the annealing, agglomeration and oxidation of aerosol particles later in the flame. The largest molecules that can be detected in flames have some two or three dozen carbon atoms; the smallest particles able to exist as aerosols have perhaps a million. Agreement on a coherent picture of how the molecules become soot particles has not yet been reached. The aerosol particles must be a beehive of chemical activity, the chemical characterization of which may never be achieved.



EXTENDED STRUCTURE OF SOOT is evident in a transmission electron micrograph made by Robin Stevenson of the General Motors Research Laboratories. Soot particles of this type are formed in a fuel-rich hydrocarbon flame by the agglomeration of an aerosol of minute carbon spheres containing varying amounts of hydrogen and trapped hydrocarbons. In flames producing a yellow glow but no black smoke the soot aerosol is oxidized by the flame gases faster than it agglomerates. This particular particle was collected on an amorphous carbon substrate from the exhaust of a diesel engine. The image was deliberately underfocused to enhance the contrast. The magnification of the micrograph is some 110,000 diameters.

Petroleum and natural gas will not continue to dominate the energy scene for many more years; alcohol is already in use as a fuel, and other "synfuels" made from coal, biomass, shale, tar sands and garbage may soon be common. Will they be so expensive that they become luxuries, or will noncombustible energy reservoirs such as batteries or fuel cells replace them?

There is good reason to think that liquid fuels will continue to be hydrocarbons and that they will continue to be burned much as they are now at least for mobile energy sources, even if they have to be synthesized. The reason is that no one has discovered any promising substitute for their unique combination of convenience and high energy density. Coal, charcoal and uranium are suitable for burning in stationary power plants, and substitutes for natural gas in space heating may become economical, but liquid hydrocarbons are likely to remain the optimal form of energy storage for powering automobiles and airplanes. The main difference between the petroleum liquids we burn and the synfuels our descendants will burn will probably be that the synfuels will have less hydrogen and hence a greater tendency to produce soot. What to do about that problem is going to be the next challenge of combustion engineers, and how to understand it will be the next challenge of combustion chemists.

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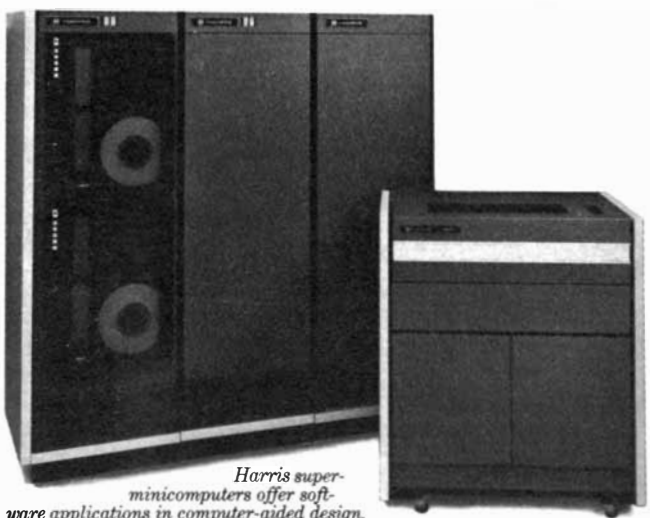

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