METHODS OF STUDYING CHEMICAL KINETICS IN FLAMES

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The subject of flames has received considerable attention during the past hundred years, following in the first instance the development of the Bunsen-type premixed stationary flame.[1] Most of the earlier quantitative studies have been concerned with the physical properties of the flame, such as flame temperature, burning velocity, stability, and flammability limits.[2,3] Chemical kinetic studies, on the other hand, have until recently been restricted to qualitative studies of some of the flame chemistry and to quantitative examination of the burnt gas. With the development of better experimental techniques, however, it has recently become possible to examine quantitatively the chemical kinetics in the main reaction zone of the flame, in addition to the burnt-gas properties.

Premixed flames can be classified as stationary or freely propagating flames. In the former the localised reaction zone is fixed in the laboratory system of co-ordinates, and is fed by a flowing stream of fuel plus oxidant mixture. Flame fronts which move with respect to the local co-ordinate system are referred to as freely propagating flames. Flames of both types are thus essentially flowing reaction systems in which the time scale in the usual reaction rate expressions is replaced by a distance scale. Because of the gas velocities in flames which are susceptible to investigation, rapid chemical reactions can be studied. In fact, flames permit the examination of reactions in the range between those studied in the more conventional static systems and those studied by means of flash photolysis or shock tubes. For suitable reactions, flames provide a method of extending investigations towards higher temperature regions where the reaction is too rapid for a simple type of time-resolved study.

In addition to premixed flames, diffusion flames can be obtained in which the fuel and oxidant reach the reaction zone separately, so that mixing and reaction must occur concurrently. A special category of these are the so-called atomic flames in which atoms or free radicals, generated by means of a Wood's tube or an electrodeless discharge, are led into a reaction vessel where they meet the fuel. Studies of this type have yielded much spectroscopic information.[4] However, they are not flames in the true sense since they depend on the external generation of the reactive species. For quantitative studies, diffusion flames present a more complex problem than do premixed flames of suitable geometry, and they will not be considered further in this review.

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[1] Bone and Townend, "Flame and Combustion in Gases," Longmans, London, 1927.

[2] Gaydon and Wolfhard, "Flames," Chapman and Hall, London, 1953.

[3] Lewis and Von Elbe, "Combustion Flames and Explosions," Academic Press, New York, 1961.

[4] Gaydon, "The Spectroscopy of Flames," Chapman and Hall, London, 1957.

1. Relation between measurable flame parameters and reaction kinetics. Conservation equations for one-dimensional premixed flames

A premixed-flame zone can be considered to be a localised reaction zone sandwiched between, on the one side, a cold mixture of fuel and oxidant, and, on the other, a hot equilibrium mixture of burnt gases. If the gas flow through the flame is one-dimensional along, for example, an x axis of co-ordinates, then the flame front will be planar.

The linear burning velocity, S_u, is defined as the normal velocity of approach of the unburnt gas towards the flame front. Alternatively, the mass burning velocity, M, is the mass rate of consumption of gas mixture per unit area of flame surface. By continuity, M is constant throughout the flame and is given by equation (1).

$$M = \rho S = \rho_u S_u = \text{const.} \qquad (1)$$

Here ρ and S are the density and corresponding normal linear flow velocity at any point in the flame, and the subscript u refers to the unburnt gas.

If now the unburnt-gas flow velocity in the x direction is S_u, then the flame front will be in the y,z plane, and the gas properties will depend only on the distance x through the flame. The measured quantities in addition to the burning velocity are the temperature and the weight fractions w_i of each species i in the gas at a number of distances through the flame. The w_i are related with the molar species concentrations n_i by means of equations such as (2), m_i being the molecular weight.

$$[n_i] = \rho w_i / m_i \qquad (2)$$

Reaction rates can be found by the application of the energy and species continuity equations to the measured profiles. These equations have been discussed by Hirschfelder *et al.*,[5] von Kamen and Penner,[6] and others. In the following sections it will be assumed that the pressure remains constant throughout the flame—a valid assumption for all except the fastest flames.

Species Continuity Equations and Diffusion Equations.—Following Hirschfelder *et al.*,[5] we now define the quantity G_i as the weight fraction of species i in the mass rate of flow. The quantity MG_i represents the mass flux of i. Continuity considerations require that the first distance derivative of this mass flux be equal to the chemical rate of formation of the species. The *continuity* equation for the one-dimensional flame is therefore equation (3).

$$M\,\mathrm{d}G_i/\mathrm{d}x = m_i(\partial n_i/\partial t)_{\text{chem}}. \qquad (3)$$

[5] Hirschfelder, Curtiss, and Bird, "Molecular Theory of Gases and Liquids," Wiley, New York, 1954.

[6] Von Kaman and Penner, "Selected Combustion Problems," Butterworths, London, 1954.

Now the total mass flux MG_i is composed of two terms, (i) a convection term (Mw_i) representing the mean mass flow of i, and (ii) a diffusion term ($-\rho D_i \mathrm{d}w_i/dx$).* The G_i terms are therefore expressed in terms of the measured values of w_i by means of the diffusion equations (4). Here D_i is the diffusion coefficient of i in the mixture.

$$MG_i = Mw_i - \rho D_i \mathrm{d}w_i/\mathrm{d}x \qquad . \; . \; . \; . \; . \quad (4)$$

Conservation of Energy.—In this case the appropriate total flux is of the form $M\Sigma G_i H_i - \lambda \mathrm{d}T/\mathrm{d}x$, where H_i is the enthalpy per gram of species i. The chemical rates of production of heat are given by the terms $M\Sigma(\mathrm{d}G_i/\mathrm{d}x)H_i$ in the first distance derivative of this expression, so that for an adiabatic system the conservation of energy is given simply by equation (5) or, on integration, equation (6). The kinetic energy change involved in

$$\mathrm{d}/\mathrm{d}x\{M\Sigma(G_iH_i) - \lambda \mathrm{d}T/\mathrm{d}x\} = 0 \quad . \; . \; . \; . \; . \quad (5)$$

accelerating the gases through the flame front is assumed small enough to be neglected, as also are radiation terms.

$$M\Sigma(G_i\,H_i) - M\Sigma(G_i\,H_i)_u = \lambda \mathrm{d}T/\mathrm{d}x \qquad . \; . \; . \quad (6)$$

Since $H_i = (H_i)_u + \bar{c}_{pi}\,(T - T_u)$, $\bar{c}_{pi}$ being the mean specific heat of i between T_u and T, then equation (6) may in turn be re-arranged to give equation (7).

$$M\Sigma G_i\,\bar{c}_{pi}\,(T - T_u) - \lambda \mathrm{d}T/\mathrm{d}x = M\Sigma\{(G_i)_u - G_i\}\,(H_i)_u \quad . \; . \quad (7)$$

The term on the right-hand side of equation (7) represents the flux of heat liberated by the reaction. This flux is therefore given by the convective thermal energy flux relative to the unburnt gas as standard $[M\Sigma w_i\bar{c}_{pi}(T - T_u)]$ modified to allow for energy transfer by diffusion, which is included in the first term of equation (7), and by thermal conduction.

2. Kinetic Information from Burning Velocity Measurements

It is only within the past ten to fifteen years that attempts have been made accurately to measure temperature and composition profiles in flames. Before this, it was natural that interest should have been focussed on the possibility of obtaining kinetic information from the simpler physical measurements of burning velocity and final flame temperature. The objective of these attempts was to manipulate the flame equations into a form capable of giving an analytical solution relating burning velocity with kinetic parameters such as reaction order, activation energy, and so on. The work of Zeldovich and Frank-Kamenetskii,[7] Zeldovich,[8] and Zeldovich

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* Thermal diffusion and its reciprocal process, the Dufour effect, can be neglected for most ordinary flames, and will not be considered in this review.

[7] Zeldovich and Frank-Kamenetskii, *Compt. rend. Acad. Sci. U.S.S.R.*, 1938, **19**, 693.

[8] Zeldovich, *J. Phys. Chem. U.S.S.R.*, 1948, **22**, 27.

and Semenov,[9] typifies one type of approach. The flame is assumed to be controlled by a single overall reaction obeying the simple Arrhenius rate expression (8) for a reaction of order d.

$$W = A\, n_r{}^d \exp\,(-E/\boldsymbol{R}T) \quad . \; . \; . \; . \; . \; . \; . \quad (8)$$

Here W is the reaction rate and n_r is the reactant concentration. By making a reasonable assumption about the diffusion of reactant, n_r can be expressed as a function of temperature alone, so that diffusion equations are eliminated. For reactions with high activation energy, the reaction is assumed to occur almost exclusively in the immediate neighbourhood of the flame temperature, T_b, and under these conditions, and with a few further small assumptions, the problem can be solved to give an expression of the form of equation (9) for the burning velocity. Here L is the calorific value of the original mixture (cal. g.$^{-1}$), λ^* is the thermal conductivity of

$$S_u{}^2 = \frac{2\,\lambda^*}{\rho_u\, L(n_r)_u} \left\{ \frac{\rho_b (n_r)_u}{\rho_u} \; \frac{(C_p)_b}{L} \; \frac{\boldsymbol{R}T_b{}^2}{E} \right\}^d \frac{\boldsymbol{R}T_b{}^2}{E}\, A \exp\,(-\,E/\boldsymbol{R}T_b) \quad . \quad (9)$$

the equilibrium mixture at the flame temperature, and $(C_p)_b$ is its specific heat. Thus, if the order of the overall controlling reaction is known, then its activation energy can be obtained from the influence of T_b on the burning velocity at constant pressure and fuel concentration. The reaction order can in turn be found from the effect of pressure on the burning velocity under otherwise constant conditions. Equation (9) shows that $S_u \propto p^{(d-2)/2}$

The Zeldovich–Semenov–Frank–Kamenetskii equations have frequently been used for the correlation of burning velocity data and in order to facilitate the postulation of a controlling flame reaction. However, the results need careful interpretation, and the application is of greatest value in the case of simpler flames, such as decomposition flames.

A completely different approach is adopted, for example, by van Tiggelen and Deckers,[10] or by Tanford and Pease.[11] Many flame reactions involve atoms or free radicals, and these approaches consider particularly the diffusion of such centres against the gas flow and into the unburnt gas. In van Tiggelen's approach, chain-branching compensates for radicals lost by terminating reactions or by being swept away with the burnt gas. The burning velocity and reaction-zone thickness must therefore mutually adjust themselves so that each chain centre reproduces itself, on average, once on passing through the flame. The thermal aspects of the flame are not included in the problem except in so far as an average reaction-zone temperature, $T_m = T_u + 0{\cdot}74\,(T_b - T_u)$, is assumed. Equations (10) and (11) result for the burning velocity, S_u, and the reaction-zone thickness,

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[9] Zeldovich and Semenov, *Adv. Phys. Sci. U.S.S.R.*, 1940, **24**, 433.

[10] Van Tiggelen and Deckers, "Sixth Symposium on Combustion," Reinhold, 1956, 61.

[11] Tanford and Pease, *J. Chem. Phys.*, 1947, **15**, 431, 861.

δ, which is again defined in a somewhat arbitrary manner. Here M is the molecular weight of the chain carrier, A and B are partial pressures of fuel and oxidant, respectively, a and b are the partial orders of the reaction,

$$S_u = \frac{4T_u}{\pi}\left[\frac{2R}{3T_mM}\right]^{\frac{1}{2}} \left[\frac{(A)^a\,(B)^b}{P^i} \exp\left(-E/RT_m\right)\right]^{\frac{1}{2}} \quad . \; . \quad (10)$$

$$S_u\delta = \frac{8T_uC\lambda}{3\pi^2T_m} = \frac{8T_u\lambda}{3\pi^2T_m}\sqrt{\frac{8RT_m}{M}} \quad . \; . \; . \; . \; . \; . \quad (11)$$

P is the total pressure, $i = a + b$, and E is an overall activation energy, whilst C and λ are the molecular velocity and mean free path of the chain carrier at T_m. E is regarded primarily as the activation energy of the chain-branching process. Thus, it may be possible to obtain information about the branching process. However, the approach seems to be over-simplified in many respects, and it has not been widely used other than by its originators.

There have been numerous other attempts to formulate expressions relating burning velocity with reaction kinetics, mostly representing advances on the Zeldovich–Semenov–Frank–Kemenetskii approach. However, many of these, like those discussed above, assume only one controlling reaction. For many flames of kinetic interest, this is clearly inadequate. In some cases where the reaction mechanism in the flame is known, radical concentrations have been expressed approximately as functions of temperature by the usual steady-state method of chain-reaction theory, and this has enabled approximate burning velocity expressions to be obtained. Lovachev[12] has used a different type of approximation for the radical concentration, and by making some assumptions about the temperature profile he has obtained explicit equations for some multi-reaction systems; one such equation represents a simplified approach to the hydrogen–oxygen flame system. Approaches of this type are, however, more suitable for experimentally testing the validity of the approximations used than for accurate kinetic studies. For the latter, measurement of the temperature and composition profiles, in addition to the burning velocity, are an essential preliminary.

3. Methods of Supporting the Flames

For kinetic studies, stationary flames supported on burners and fed by a stream of flowing gases are normally used. Early studies were made by using ordinary tubular burners, which produced conical flames, at atmospheric pressure. Spectroscopic studies in emission, by using such burners, showed qualitatively the existence of many free radicals in flames,[4] and it became obvious, by analogy with results from studies of oxidation mechan-

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[12] Lovachev, *Combustion and Flame*, 1960, **4**, 357.

isms in conventional static systems, that the dominant mechanisms in many flames were free-radical processes. However, the flame shape and the gas flows on such burners are not ideally suited to quantitative studies, for which a one-dimensional system would be more convenient. A further difficulty is connected with the thickness of the flame zone. Many flame zones at atmospheric pressure have a total thickness of less than 1 mm., within which the temperature rises by 2000° or more. In order to obtain thicker flames at atmospheric pressure it is necessary to move towards the lowest attainable burning velocities (*e.g.*, 5—10 cm. sec.$^{-1}$) when thicknesses of 4 or 5 mm. may be obtained together with much smaller temperature changes. Fortunately, approximately unidimensional flames satisfying this requirement can be obtained by using one of two different types of flat-flame burner. Both these types of burner were developed some ten to fifteen years ago and the serious quantitative study of chemical kinetics in flame dates from about that time.

In the Egerton–Powling burner[13] very weak or very rich mixtures near the limits of flammability are burnt under approximately adiabatic conditions. The burner is constructed so that the burner port, containing a special matrix, produces a laminar stream of gas and the flame burns as a flat, circular disc in a stationary position a few centimetres above it. The burner is enclosed in a chimney with a perforated plate or gauze which produces aerodynamic stability of the slow-burning flame. More recently a burner has been developed by Botha and Spalding[14] with which it is possible to burn faster flames under non-adiabatic conditions. In this burner the flame sits as a flat, circular disc just downstream of a water-cooled porous sintered-metal plug, which abstracts heat from the flame. By altering the rate of heat abstraction, a given gas composition can be made to produce flames having a range of final gas temperatures—a very useful feature. The rate of heat abstraction must be accurately known if an energy balance is to be made. An advantage of this type of burner is that flames of any required geometry can be obtained, and this has proved useful for the study of spherical flames where the flame is supported by a sintered-metal sphere.[15]

For the study of the reaction zones of faster-burning flames, it is necessary to operate the burners at reduced pressures at which the thickness of the reaction zone increases, the thickness being inversely proportional to a power of the pressure between $\frac{1}{2}$ and 1. The early work on low-pressure flames was carried out by Wolfhard,[16] and burners of this type are described by Gaydon and Wolfhard.[2] Burners of the Powling and Spalding type are also ideally suitable for the study of flames at reduced pressures, and many investigations have been carried out with them.

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[13] Powling, *Fuel*, 1949, **28**, 25; Egerton and Powling, *Proc. Roy. Soc.*, 1948, *A*, **193**, 172.

[14] Botha and Spalding, *Proc. Roy. Soc.*, 1954, *A*, **225**, 71.

[15] Fristrom, *Combustion and Flame*, **1958**; **2**, 103.

[16] Wolfhard, *Z. Phys.*, 1939, **112**, 107.

4. Experimental Determination of the Physical Structure of the Flame

For a complete analysis of the flame it is necessary to know the concentrations through the flame of all the chemical species, both stable molecules and intermediate free radicals and atoms, so that the rates of chemical reaction, given by equation (3), can be derived. In addition, two physical quantities have to be measured. These are (i) the temperature distribution, so that the flame equations can be solved and rates of chemical reactions expressed in the form of the Arrhenius rate equation, and (ii) the burning velocity, which determines the mass rate of consumption of species in the flame and also sets the time scale through the flame.

Temperature Distribution.—A fundamental difficulty now arises because of the extremely rapid reactions in flame zones. As a result, relaxation times may be too long for the distribution of energy amongst the various degrees of freedom of the molecules to follow the equilibrium Maxwell–Boltzmann distribution. In this case, the term "temperature" may have no precise meaning in flames. At present, the only available approach is to assume that an equilibrium energy distribution does exist, and this is usually true for the relatively cooler and slower flames in which chemical kinetics are at present studied. In the absence of full evidence on faster flames, however, it is necessary to bear this in mind. So far, four main methods have been used to determine the temperature distribution in flames.

(*a*) The region of temperature variation is traversed by a thermocouple the dimensions of which are small compared with the flame thickness. Catalytic effects are minimised by coating it with a ceramic material. This method, first used in a flame reaction zone by Klaukens and Wolfhard,[17] has been successfully used in kinetic studies by a number of investigators. A typical temperature profile obtained[18] by this method is shown in Fig. 1. The absence of catalytic effects on the thermocouple is confirmed in this case by independent measurements with a pneumatic probe.

(*b*) The tracks of small, light inert powder particles carried by the flame gases are recorded photographically with stroboscopic light or a high-speed camera. The particles being assumed accurately to follow the gas-flow velocity in magnitude and direction, it is possible from the direction and spacing of the dots to calculate the acceleration of the gases normal to the flame front, and hence their expansion and temperature at various distances through the flame.[19,20] Because of doubts about the assumption this method has not been much used.

(*c*) The refractive index at any distance through a flat flame can be

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[17] Klaukens and Wolfhard, *Proc. Roy. Soc.*, 1948, *A*, **193**, 512.

[18] Fristrom, Grunfelder, and Favin, *J. Phys. Chem.*, 1960, **64**, 1386.

[19] Anderson and Fein, *J. Chem. Phys.*, 1949, **17**, 1268.

[20] Fristrom, Prescott, Neuman, and Avery, "Fourth Symposium on Combustion," Williams and Wilkins, Baltimore, 1953.

determined interferometrically[21] or by measuring the deflexion of a ray of light passing through the flame front in a direction normal to the temperature gradient.[21–23] This method, which can give the complete temperature distribution in one measurement, is limited to slow-burning flames in which composition changes are small.

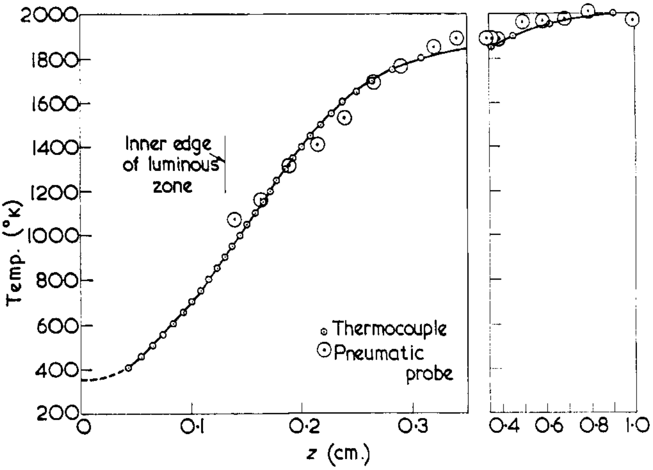

FIG. 1. *Temperature profile of a 7·85% methane–oxygen flame at* 1/10 *atmospheric pressure.*
(Reproduced, with permission, from Fristrom, Grunfelder, and Favin, *J. Phys. Chem.*, 1960, **64**, 1386.)

(*d*) The temperature profile through a flame can be determined by spectroscopic methods.[4] The spectrum of a suitable species, usually a diatomic radical, can be used to determine the vibrational or rotational temperature of that species in the flame. In many cases this temperature corresponds to the flame temperature, but in others excitation is no longer thermal since the radicals may be *formed* in electronically and rotationally activated states. This frequently occurs in low-pressure, high-temperature flames. In lower-temperature flames the absorption spectrum of the rotational structure of the hydroxyl radical has been used to determine the flame temperature.[24,25]

A number of techniques[2] has been developed for determining the temperature of the burnt-gas region of the flame although they are not suitable for studies of the reaction zone. One of the most successful of these is the spectral-line reversal method. On the assumption that the excitation of a chosen spectral line in the flame is purely thermal in origin, the method effectively compares the flame temperature with that of a background

[21] Weinberg, "Optics of Flames," Butterworths, London, 1963.
[22] Dixon-Lewis and Wilson, *Trans. Faraday Soc.*, 1951, **47**, 1106.
[23] Burgoyne and Weinberg, *Proc. Roy. Soc.*, 1954, *A*, **224**, 286.
[24] Kaskan, *Combustion and Flame*, 1958, **2**, 229.
[25] Bonne, Grewer, and Wagner, *Z. phys. Chem. (Frankfurt)*, 1960, **26**, 93.

black-body light source at known temperature. The sodium D lines frequently used for this purpose are produced by adding small amounts of sodium chloride to the flame.

Burning velocities. Numerous studies of burning velocities have been made, but most of the early measurements give differing results depending upon the technique employed. Only in recent years have burning-velocity measurements been made with the accuracy necessary for kinetic studies. The various methods used have been reviewed by Linnett[26] and by Gaydon and Wolfhard;[2] here only those methods relevent to kinetic studies will be discussed.

(*a*) The simplest method of determining the burning velocity is from the volume–area relation, since the laminar burning velocity, S_u, = (volume of gas entering the flame per second)/(area of flame). This method is suitable for flat-flames, flames burning in tubes, and Bunsen-type flames, but in many cases errors can arise because of difficulties in defining the area of the flame, and due to escape of gas around the flame edges.

(*b*) The best technique at present for determining burning velocities is by the flow visualisation technique.[3] In this method, microscopic particles of an inert substance, such as magnesium oxide, are entrained into the gas flow. These are strongly illuminated stroboscopically and photographed by scattered light, producing intermittent tracks on the plate. The velocity of the particles, and hence that of the gas, is determined from the distance between corresponding points on the dotted track and the stroboscopic frequency. Alternatively, the motion of the particles can be followed by means of rotating-drum camera. In either case, corrections must be made for the settling speed of the particles due to the gravitational field.

5. Experimental Determination of Concentration Profiles of Stable Molecules

The bulk of the constituents of a flame are stable molecular reactants and products such as oxygen, methane, hydrogen, oxides of carbon, and water, and an accurate knowledge of their concentration in the various regions of the flame is necessary for kinetic analyses. In simple flames, the composition of the burnt-gas region can be calculated from the known initial gas composition, the reaction stoicheiometry, and equilibrium data. The development of techniques for analysing all regions of the flame including the reaction zone has been a prerequisite of kinetic work.

The most successful technique for examining the chemical structure of a flame has been that of sampling.[27–29] The technique involves removing small samples of the gas from known positions in the flame by inserting a

[26] Linnett, "Fourth Symposium on Combustion," Williams and Wilkins, Baltimore, 1953, p. 20.

[27] Prescott, Hudson, Foner, and Avery, *J. Chem. Phys.*, 1954, **22**, 145.

[28] Friedman and Cyphers, *J. Chem. Phys.*, 1955, **23**, 1875.

[29] Fristrom, Prescott, and Grunfelder, *Combustion and Flame*, 1957, **1**, 102.

small microprobe, usually of quartz. The quartz tube is drawn down to a very fine point with a sampling hole some 10—25μ in diameter. Obviously, unless suitable precautions are taken the probe may affect the composition of the gases studied. Firstly, the choice of quartz minimises catalytic effects, but even then it is never absolutely certain that these are entirely eliminated. Secondly, the velocity through the probe is sonic and the cooling and expansion accompanying the reduction of pressure are sufficient to quench the gases entering the probe. However, in circumstances where radical concentrations are comparatively large, radical recombination or other reactions may affect the apparent concentration of minor constituents. Thirdly, the presence of the probe in the reaction zone may, by slight cooling or aerodynamic effects, cause slight disturbance of the flame position.

A detailed mathematical analysis of this flow perturbation caused by the sampling has shown[30] that with suitable precautions the sample taken by the probe is representative of the true local gas composition. An example of a composition profile obtained[18] by this technique is given in Fig. 2.

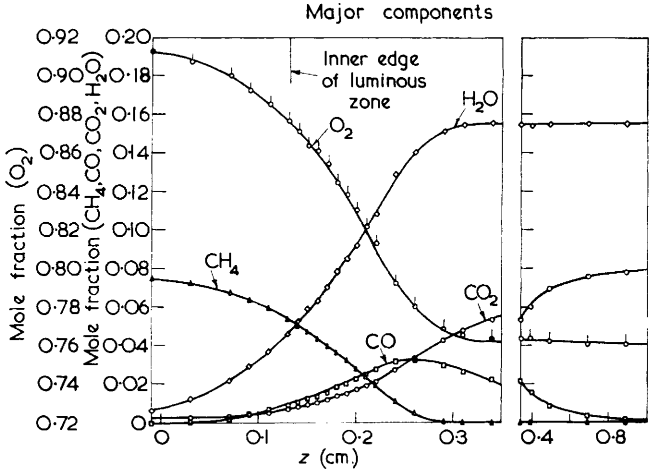

FIG. 2. *Composition profiles of a* 7·85% *methane–oxygen flame at* 1/10 *atmospheric pressure.*
(Reproduced, with permission, from Fristrom, Grunfelder, and Favin, *J. Phys. Chem.*, 1960, **64**, 1386.)

Spectroscopic methods provide an alternative way of determining the composition of the flame gases.[31] They are attractive since they do not involve inserting any foreign body into the flame, and the system is therefore homogeneous. Unfortunately the method suffers from a number of

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[30] Westenberg, Raezer, and Fristrom, *Combustion and Flame*, 1957, **1**, 467.

[31] Minkoff and Tipper, "Chemistry of Combustion Reactions," Butterworths, London, 1962.

experimental difficulties. In order to obtain high spatial resolution light from very small apertures must be used, and this introduces intensity problems. Also, the recorded effect is an integrated effect over whole of the flame and so possible imperfections in the flame shape necessitate shape measurements followed by a complex computational process. The lack of accurate absorption coefficients of the molecules involved at high temperatures also limits the method.

6. Experimental Determination of the Concentrations of Atoms and Free Radicals

Many of the important chemical reactions in flames involve atoms or free radicals and thus accurate methods for their measurement are essential. Four basic techniques are available: mass spectrometry; optical spectroscopy; electron spin resonance; and indicator methods. Of these, optical spectroscopy is potentially the most valuable method since it is very selective, it can give high spatial (and hence time) resolution, and it does not disturb the flame. Because of experimental difficulties, however, its use has been restricted to only a few strongly absorbing radicals, but where spectroscopic methods are used they are usually very successful and reliable. Mass spectrometry is another potentially powerful tool which has had only limited application[31] to flame studies since the pioneer work of Eltenton. Its great advantage is that it can be used to measure quantitatively all species in the flame, including atoms, free radicals, and ions. Its major disadvantage is that sampling is necessary, for this may interfere with the flame and also reactions may occur in the boundary layer surrounding the sampling hole. Electron spin resonance techniques have only recently been applied to flame studies, enabling oxygen atoms[32] and hydrogen atoms[33] to be detected in suitable flames at low pressure. Presumably this method will be restricted to low-pressure flames because only low spatial resolution can be achieved.

The technique which has proved to be of most value so far is based on the addition of a reactive substrate or "indicator" to the flame; this reacts uniquely and at a known rate with one of the radicals or atoms present. The rate of reaction with the indicator is followed spectroscopically or by sampling. In a modification of this method, an indicator which reacts quantitatively with the radical is added immediately the gas is withdrawn into a sampling probe (scavenger method).[34]

Methods of atom and free-radical estimation which have been developed have naturally related to those species which most commonly occur in high concentrations in flames. In particular, the determination of hydrogen and oxygen atoms and hydroxyl radicals has attracted much attention although techniques are at present being developed for other species.

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[32] Azatyan, Akapyan, Nalbandyan, and Ozherel'ev, *Doklady Akad. Nauk, S.S.S.R.*, 1961, **141**, 129.

[33] Azatyan, Panilov, and Nalbandyan, *Kinetika i Kataliz*, 1961, **2**, 295.

[34] Fristrom, "Ninth Symposium on Combustion," Academic Press, New York, 1963.

Hydrogen Atoms.—The determination of the concentration of hydrogen atoms in flames has so far depended upon indirect methods. Optical and direct mass-spectrometric determinations of hydrogen atoms have not yet been successful, but the use of indicators has given excellent results.

Indicator methods. Essentially these involve adding a trace quantity of an indicator which will react with hydrogen atoms at a known rate and whose reaction can be followed. One of the first indicators used in this way was heavy water.[35] Small quantities (0·1—1%) of heavy water are added to the flame; hydrogen atoms present abstract deuterium atoms by the reaction:

$$H + D_2O \rightleftharpoons HD + OD$$

Although additional reactions occur, it can be shown that the hydrogen-atom concentration determines the rate of formation of HD in the flame and hence can be calculated. This method is restricted to rich flames, otherwise the HD would be consumed by excess of oxygen; in lean flames an elegant variation of this method is to add $H_2{}^{18}O$. The initial step is similar:

$$H + H_2{}^{18}O \rightleftharpoons H_2 + O^{18}H$$

and is followed by further exchange reactions leading to the formation of $O^{18}O$. The concentration of hydrogen atoms here is a function of the rate of formation of $O^{18}O$.

Isotope exchanges of this type have also been used in hydrogen flames, a little deuterium being added.[35–37] In the reaction zone, hydrogen atoms abstract deuterium atoms by the processes:

$$H + D_2 \rightleftharpoons HD + D \quad \text{and} \quad D + H_2 \rightleftharpoons HD + H$$

The build up and subsequent decline of HD by oxidation can be followed by sampling; this leads to information on the hydrogen-atom concentration, since the rate constant of the exchange is accurately known.

In suitable flames the reaction of hydrogen atoms with nitrous oxide can be used to determine the concentration of hydrogen atoms:[38]

$$H + N_2O = OH + N_2$$

The rate of decay of nitrous oxide is measured mass spectrometrically and from the known rates of this reaction the concentration of hydrogen atoms can be calculated. The accuracy of the method depends upon the precision of the kinetic data used.

Flame-photometric methods. A number of flame-photometric methods have been developed by Sugden and his co-workers to measure hydrogen

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[35] Fenimore and Jones, *J. Phys. Chem.*, 1958, **62**, 693.

[36] Fenimore and Jones, "Eighth Symposium on Combustion," Williams and Wilkins, Baltimore, 1962.

[37] Fenimore and Jones, *J. Phys. Chem.*, 1959, **63**, 1834.

[38] Fenimore and Jones, *J. Phys. Chem.*, 1959, **63**, 1154.

atoms in the burnt gas from hydrogen–oxygen flames. When small quantities of a sodium (or similiar) salt are added to a flame and if the flame temperature is high enough, sodium D-line emission occurs. At low concentrations this emission is proportional to the concentration of the metal atoms. However, if lithium salts are added to the flame, some hydroxide is formed[39] by the process:

$$Li + H_2O \rightleftharpoons LiOH + H$$

This reaction is sufficiently rapid for the maintenance of equilibrium. Thus the total amount of lithium added to the flame, $[Li]_0$, is equal to $[Li] + [LiOH]$. Now if equal amounts of lithium and sodium salts are added to the same flame then $[Na]_0 = [Li]_0 = [Li] + [LiOH]$, so that if the amount of free sodium $[Na]_0$ and lithium $[Li]$ in the flame are measured spectroscopically the concentration of lithium hydroxide can be deduced. From the known equilibrium constant, it is possible to deduce the concentrations of hydrogen atoms from the equilibrium expression.

A similar technique uses the equilibrium between sodium chloride and hydrogen chloride in the flame.[40] Small quantities of sodium chloride and chloroform are added to the unburnt gases. In the flame, the chloroform is converted into hydrogen chloride and the following equilibria are set up:

$$H + NaCl \rightleftharpoons HCl + Na \quad \text{and} \quad HCl + H \rightleftharpoons H_2 + Cl$$

The free sodium is determined spectroscopically and, from equilibrium data, the concentration of hydrogen atoms is again deduced.

In flames with lower final flame temperatures where the thermal emission of added metal atoms is less, then a chemiluminescence effect[41] may occur. Here, there is a rapid rise of intensity in the reaction zone followed by a steady decay towards the thermal level. This chemiluminescence is due to excitation of the metal (in this case sodium) by the reactions:

$$H + H + Na = H_2 + Na^* \quad \text{and} \quad H + OH + Na = H_2O + Na^*$$

Thus the intensity (I) of the emission is:

$$I = C_1(H)^2 + C_2(H)\,(OH),$$

where C_1 and C_2 are constants involving instrument, quenching, and rate-constant factors. From this intensity the relative concentrations of hydrogen atoms in the burnt gas can be deduced.

Hydroxyl Radicals.—The most successful and accurate method for the determination of the concentration of hydroxyl radicals is direct optical spectroscopy, although a number of indirect flame-photometric techniques, which give relative concentrations, are also available.

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[39] James and Sugden, *Proc. Roy. Soc.*, 1954, *A*, **227**, 312.
[40] Bulewicz, James, and Sugden, *Proc. Roy. Soc.*, 1956, *A*, **235**, 89.
[41] Padley and Sugden, *Proc. Roy. Soc.*, 1958, *A*, **248**, 248.

Absorption spectroscopy. Concentrations of hydroxyl radicals can be determined by measuring their absorption in the ultraviolet $^2\Pi$—$^2\Sigma$ band. The *O,O* band at 3064 Å has been well investigated and is normally used for this purpose.[24,25] Earlier methods[42] used a continuous-background light source with the flame interposed between it and the spectroscope. Because of the very small width of the absorption bands, this necessitated use of a very high resolution monochromator. Often an alternative method requiring only a medium resolution spectrometer is used. In this, the line-absorption method,[43] the background source is a hydroxyl emission spectrum generated by a cooled electrical discharge through water vapour.[24] The line-width in emission in the cooled discharge is small, and these narrow emission lines are partially absorbed by the broader absorption lines of the flame. The absorption coefficient (α) is given by $\ln I/I_0 = -\alpha l$, where I_0 and I are the incident and transmitted energy and l is the path-length through the flame. The concentration of hydroxyl radicals is given by the equation:

$$[\mathrm{OH}] = C_i\, \alpha \exp(E_i/\boldsymbol{R}T),$$

where E_i is the rotational energy of the level i (the chosen line) and C_i is the appropriate constant. The values of both quantities are accurately known so that the concentration of hydroxyl radicals can be calculated.

Photometric indicator methods. These give the relative concentration of hydroxyl radicals in the burnt-gas region from a study of the intensity of the continuous emission from the metal hydroxide formed when sodium or copper salts are added to the flame.[44,45] The following equilibria are set up:

$$\mathrm{Na} + \mathrm{OH} \rightleftharpoons \mathrm{NaOH} \quad \text{and} \quad \mathrm{Cu} + \mathrm{OH} \rightleftharpoons \mathrm{CuOH}.$$

The sodium hydroxide continuum at about 4500 Å and the CuOH continum in the region of 6100 Å have been used[44,45] to follow their concentrations in the flame.

Oxygen Atoms.—The determination of oxygen atoms in flames has not been as successful as that of hydrogen atoms or hydroxyl radicals. The methods used for oxygen in flames all depend upon the use of added indicators.

One of the first methods, described by Gaydon as a qualitative test for oxygen atoms, depends upon the addition of small quantities of nitric oxide to the unburnt gases. If oxygen atoms are present, a whitish yellow-green continuum is emitted due to the overall reaction:

$$\mathrm{NO} + \mathrm{O} = \mathrm{NO_2} + \boldsymbol{h\nu}$$

This radiation can be used as a relative indication of the concentration of

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[42] Oldenberg, *J. Phys. Chem.*, 1937, **41**, 293.
[43] Oldenberg and Rieke, *J. Chem. Phys.*, 1938, **6**, 779.
[44] Bulewicz and Sugden, *Trans. Faraday Soc.*, 1956, **52**, 1475, 1481.
[45] James and Sugden, *Proc. Roy. Soc.*, 1958, *A*, **248**, 238.

oxygen atoms since some success has been obtained[46,47] in making quantitative correlations of the intensity of the emission with the product [NO] [O].

Another photometric method[48] involves the addition of small quantities of iodine to hydrogen flames, the species IO then being formed by the reaction:

$$I + O + M \rightleftharpoons IO + M$$

The IO species is thermally excited, and from the intensity of its emission spectrum it is possible to determine relative concentrations of oxygen atoms in the flame.

In flames containing nitrous oxide, present either as an oxidant or as a trace, it is possible[38,49] to estimate the concentration of oxygen atoms from the rate of the reaction:

$$O + N_2O = 2NO$$

The rate of formation of nitric oxide is followed by sampling and analysis.

Carbon-containing radicals. In addition to the simpler radicals and atoms, the carbon-containing radicals are of great importance to flame chemistry. The emission spectra of flames show the presence of many interesting free radicals, such as CH, C_2, CN, CH_3, C_2H_5, and NH. These emission spectra, however, cannot be used to give an accurate measure of the concentration of these radicals in the flame and absorption spectroscopy must be applied. Although absorption spectra have been obtained for many of these free radicals when they can be generated in high concentrations, as by flash photolysis or high-temperature furnaces, only recently have they been observed in flames. Gaydon[50] *et al.*, have observed, in stationary low-pressure flames, the absorption spectra of C_2, CH, CH_3, and C_2H_5 by means of a multiple reflexion system, and they have obtained an indication of the concentrations.

Although spectroscopic methods are perhaps the best way of determining the concentration of these free radicals in flames, other methods are possible. The concentration of methyl radicals in methane–oxygen flames has been estimated from the rate of dimerisation to ethane and other C_2 hydrocarbons:[51]

$$2CH_3 \rightarrow C_2H_6 \rightarrow \text{other } C_2 \text{ hydrocarbons}$$

and also by the rate of reaction with nitric oxide:

$$CH_3 + NO \rightarrow \tfrac{1}{2}\,(CH_3{\cdot}NO)_2 \rightarrow HCN + \text{other products}$$

The rates of these reactions are followed by sampling and mass spectrometry.

[46] Kaskan, *Combustion and Flame*, 1958, **2**, 286.
[47] Bulewicz and Sugden, *Chem. Soc. Special Publ.*, 1957, No. 9, p. 81.
[48] Phillips and Sugden, *Trans. Faraday Soc.*, 1961, **57**, 914.
[49] Fenimore and Jones, *J. Phys. Chem.*, 1961, **65**, 993.
[50] Gaydon, Spokes, and Van Suchtelen, *Proc. Roy. Soc.*, 1960, *A*, **256**, 323.
[51] Fenimore and Jones, *J. Phys. Chem.*, 1961, **65**, 1532.

7. Application of Flame Studies to Chemical Kinetics

Many investigations have been made of the mechanism of flame propagation, but frequently these have led only to a qualitative outline of the chemical processes involved which had to be generalised in overall rates of reaction for the reaction schemes. More recently, however, the individual reactions have been studied and this has led to considerable information on the rates of the reactions involved. In this section, the results of some of these kinetic investigations are discussed. Also, the chemistry is outlined of some flame systems which have not yet been fully studied kinetically but which are chemically simple and ideal for the purpose.

Self-decomposition Flames.—These are flames in which the decomposition of the fuel maintains a self-supporting flame without additional additive. The initial step is usually the breakdown of the fuel by a unimolecular or pseudo-unimolecular decomposition. Examples of molecules which support self-decomposition flames are hydrazine, some alkyl nitrates and nitrites, ozone, and acetylene.

Studies of the hydrazine self-decomposition have been carried out by a number of investigators, and a detailed kinetic analysis of these results has been made by Gilbert.[52] The mechanism of decomposition changes from first- to second-order kinetics as the pressure is reduced below one atmosphere. This is interpreted by Gilbert[52] in terms of a quasi-unimolecular mechanism in which the initial steps are:

$$N_2H_4 + M = N_2H_4^* + M \quad \text{and} \quad N_2H_4^* = 2NH_2$$

followed by a chain reaction to give the final products, nitrogen, hydrogen, and ammonia. This interpretation is different from that of Szwarc who used the toluene carrier technique to study hydrazine decomposition at low pressures. These results were first interpreted in terms of a simple first-order formation of NH_2, but re-analysis by Gilbert has shown them to be consistent with the mechanism deduced from the flame investigation.

The methyl nitrite self-decomposition flame has been the subject of a number of investigations since its discovery in 1954. This flame is suitable for study at atmospheric pressure since it has a low burning velocity ($3{\cdot}2$ cm. sec.$^{-1}$) and a wide reaction zone. In the isothermal decomposition of methyl nitrite, decomposition is initiated and the overall rate controlled by the endothermic, first-order fission of the oxygen–nitrogen bond:

$$\mathrm{MeONO} \rightarrow \mathrm{MeO} + \mathrm{NO}$$

The activation energy for the isothermal decomposition is $36{\cdot}4$ kcal.mole^{-1} whilst the overall values obtained[53] from burning-velocity studies (Section 2) are $28{\cdot}5$ and 32 kcal.mole^{-1}. A detailed examination of the reaction zone of this flame has been made,[54] but without kinetic analysis.

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[52] Gilbert, *Combustion and Flame*, 1958, **2**, 137, 149.

[53] Gray and Williams, "Eighth Symposium on Combustion," Williams and Wilkins, Baltimore, 1962.

[54] Arden and Powling, *Combustion and Flame*, 1958, **2**, 55.

The self-decomposition flame of ethyl nitrate has been studied in great detail by Hicks.[55] At 3·5 cm. pressure, the burning velocity is 6·5 cm. sec.$^{-1}$ and the reaction-zone thickness is 8 mm. The mechanism, at this pressure, was found to involve a pseudo-unimolecular initial decomposition of ethyl nitrate:

$$EtONO_2 + M \rightarrow EtO + NO_2 + M$$

The rate constant of this step was found[55] to be given by $k = 10^{17 \cdot 7}\exp(-38{,}000/\boldsymbol{R}T)$ l. mole^{-1}sec.$^{-1}$.

Ozone decomposition has been the subject of many theoretical investigations, but little experimental kinetic data have been obtained because of the hazardous nature of the experiments. The mechanism is a relatively simple one, involving only three species:

$$O_3 = O + O_2;\ O + O_3 = 2O_2;\ \text{and } 2O + M = O_2 + M$$

Such a system would be suitable for study by the methods outlined in Sections 4 and 5.

The Hydrogen–Oxygen Flame.—The study of the hydrogen–oxygen reaction has attracted much attention, not only because of its technical importance but because it is the simplest branched-chain reaction. The number of species involved is small—the reactants, hydrogen and oxygen, the product, water, and the intermediates, hydrogen and oxygen atoms and hydroxyl radical. Many studies have been made of the reaction in a closed vessel, and the main steps are understood in detail.[31] However, the mechanism in vessels is greatly complicated by wall reactions, and the absence of these in flames is a great advantage. In the hydrogen–oxygen flame the basic mechanism is:

$$\begin{array}{rl} H + O_2 \rightarrow O + OH & \left.\begin{array}{l}(1)\\(2)\end{array}\right\}\text{branching} \\ O + H_2 \rightarrow OH + H & \\ OH + H_2 \rightarrow H + H_2O & (3)\ \ \text{propagation} \\ H + H + M \rightarrow H_2 + M & \left.\begin{array}{l}(4)\\(5)\end{array}\right\}\text{termination} \\ H + OH + M \rightarrow H_2O + M & \end{array}$$

probably together with reactions forming and destroying HO_2.[56] Studies of the branching reaction (1) have been made in the reaction zone of some hydrogen–oxygen flames by Fenimore and Jones.[38] They obtained a rate constant of $k_1 = 1{\cdot}5 \times 10^8$ l.mole^{-1}sec.$^{-1}$ at 1100°K and, in the range 1100—1500°K deduced a rate expression of $k_1 = 10^{11 \cdot 78}\exp(-18{,}000/\boldsymbol{R}T)$l.mole^{-1} sec.$^{-1}$. These rates agree very well with those obtained at lower temperatures and with the results obtained from shock-tube work; the rate expression representing the results from 300 to 1650°K is $k_1 = 10^{11 \cdot 33}\exp(-16{,}600/\boldsymbol{R}T)$. Lovachev,[12] using his theory of flame propagation in branched systems,

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[55] Hicks, "Eighth Symposium on Combustion," Williams and Wilkins, Baltimore, 1962.

[56] Dixon-Lewis and Williams, *Nature*, 1962, **196**, 1309.

derived a rate expression for this reaction; using burning velocities measured by Jahn, he obtained $k_1 = 1{\cdot}32 \times 10^{11}\exp(-14{,}000/\boldsymbol{R}T)$ whilst results by Bartholome gave $k_1 = 4{\cdot}72 \times 10^{11}\exp(-16{,}300/\boldsymbol{R}T)$ l.mole^{-1} sec.$^{-1}$.

An investigation of the branching reaction (2) has been carried out, also by Fenimore and Jones,[49] in low-pressure flames at 1660° and 1815°K. If the results are combined with other lower-temperature results a rate expression of $k_2 = 2{\cdot}5 \times 10^9 \exp(-7700/\boldsymbol{R}T)$ l.mole^{-1}sec.$^{-1}$ is obtained.

The reaction between hydroxyl and hydrogen [reaction (3)] has received less attention. Fenimore and Jones[35,38] find that the rate expression $k_3 = 2{\cdot}5 \times 10^{11} \exp(-10{,}000/\boldsymbol{R}T)$ l.mole^{-1}sec.$^{-1}$ approximately fits the results they obtained by use of the reverse, isotopic reaction:

$$H + D_2O \rightleftharpoons H_2 + OD \quad . \; . \; . \; . \; . \; . \; . \quad (-3)$$

For this reaction (-3) they deduce $k_{-3} = 10^{12}\exp(-25{,}500/\boldsymbol{R}T)$ l.mole^{-1} sec.$^{-1}$. However, Dixon-Lewis and Williams[57] obtained, from a study of a low-temperature hydrogen–oxygen flame, $k_{-3} \approx 9 \times 10^{11}$ cm.^{3}mole^{-1} sec.$^{-1}$ at 850°K and this agrees with the lower activation energy, $E_3 = 6{\cdot}5$ kcal.mole^{-1}, suggested by studies at room temperatures.

A number of studies[41,58,59] have been made of the chain-terminating combination [reactions (4) and (5)]. The hydrogen atoms and hydroxyl radicals build up to large excesses in the reaction zone and slowly decay to their equilibrium values in the burnt-gas region of the flame; the rate at which they do so depends upon the temperature and the nature of the third bodies available. At 1072°K, the rate constants for the termolecular recombination of hydrogen atoms are of the order[59] of $k_4 = 1 \times 10^{-32}$cm.^{6} mole^{-2}sec.$^{-1}$, whilst the combination of hydrogen atoms and hydroxyl radicals is about twenty-five times faster.

Flames Containing Oxides of Nitrogen.—The flames investigated are usually hydrogen–oxygen flames, to which mixture nitrous or nitric oxide has been added. With nitric oxide, the principal reactions are with oxygen atoms:

$$O + NO = NO_2 + h\nu \quad . \; . \; . \; . \; . \; . \quad (6)$$

$$M + O + NO = NO_2 + M \quad . \; . \; . \; . \; . \; . \quad (7)$$

$$O + NO = O_2 + N \quad . \; . \; . \; . \; . \; . \; . \quad (8)$$

The first of these is the radiative combination responsible for the air afterglow and first used as a test for the presence of oxygen atoms in flames. Broida, Schiff, and Sugden[60] have shown that the mechanism is

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[57] Dixon-Lewis and Williams, Fifth Internat. Symposium on Free Radicals, Uppsala, Sweden, 1961.

[58] Bulewicz and Sugden, *Trans. Faraday Society*, 1958, **54**, 1855.

[59] Dixon-Lewis, Williams, and Sutton, *Discuss. Faraday Society*, 285, **33**, 1962.

[60] Broida, Schiff, and Sugden, *Trans. Faraday Soc.*, 1961, **57**, 259.

more complex than the overall reaction given here. Studies by Kaskan[61] with lean hydrogen flames showed that the emission is proportional to the concentrations of O and NO, with a rate constant of $k_8 = 1{\cdot}2 \times 10^3$ l. mole^{-1}sec.$^{-1}$ at 1290—1840°K. Bulewicz and Sugden[47] worked with rich hydrogen flames up to 2500°K, and their results agree reasonably with those of Kaskan.[61] Studies of the other two reactions have not yet been made in flames.

When nitrous oxide is added to flames it may react with the hydrogen or the oxygen present. Reactions (9) and (10) have been investigated by Fenimore and Jones. Reaction (11) occurs only at very high temperatures and has not yet been investigated. For the reaction with hydrogen atoms Fenimore and Jones[38] obtained $k_9 = 10^{11\cdot6}\exp(-16{,}300/\boldsymbol{R}T)$ l.mole^{-1}sec.$^{-1}$ at 1260—1870°K. For that with oxygen atoms, the rate expression in the range 1400—1900°K is [36] $k_{10} = 10^{11}\exp(-28{,}000/\boldsymbol{R}T)$ l.mole^{-1}sec.$^{-1}$.

$$H + N_2O = OH + N_2 \quad . \; . \; . \; . \; . \; . \; . \quad (9)$$

$$O + N_2O = 2NO \quad . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

$$O + N_2O = N_2 + O_2 \quad . \; . \; . \; . \; . \; . \; . \quad (11)$$

Hydrocarbon and Carbon Monoxide Flames.—The study of hydrocarbon flames has been extensive and the main features of the mechanism have been interpreted. Basically, the hydrocarbon is decomposed by attack by free radicals. In the first stage of the reaction, oxidation to carbon monoxide occurs; in the later stages the carbon monoxide is oxidised to carbon dioxide.

The methane–oxygen flame has been studied in detail and the initia mode of attack has been shown to be reactions (12) and (13):

$$CH_4 + H = CH_3 + H_2 \quad . \; . \; . \; . \; . \; . \; . \quad (12)$$

$$CH_4 + OH = CH_3 + H_2O \quad . \; . \; . \; . \; . \; . \quad (13)$$

reaction (12) predominating in rich flames and reaction (13) in lean flames. For many low-pressure flames, Fenimore and Jones[62] obtained $k_{12} = 2{\cdot}5 \times 10^{11}\exp(-11{,}500/\boldsymbol{R}T)$ and $k_{13} = 3{\cdot}5 \times 10^{11}\exp(-9000/\boldsymbol{R}T)$ l.mole^{-1}sec.$^{-1}$ Values obtained by Westenberg and Fristrom[63] agree with this value for k_{13} at 1750°K. Results have also been obtained[64] for the initial attack of hydroxyl radicals in ethane flames. In ethylene–oxygen flames[64] the initial step is probably addition of an oxygen atom to the double bond:

$$C_2H_4 + O \rightarrow C_2H_4O. \quad . \; . \; . \; . \; . \; . \; . \; . \quad (14)$$

The rate of this reaction has been found[64] to be $10^{10\cdot5}$ l.mole^{-1}sec.$^{-1}$ at 1400—1860°K and does not vary significantly with temperature.

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[61] Kaskan, *Combustion and Flame*, 1958, **2**, 286.

[62] Fenimore and Jones, *J. Phys. Chem.*, 1961, **65**, 2200.

[63] Westenberg and Fristrom, *J. Phys. Chem.*, 1961, **65**, 591.

[64] Fenimore and Jones, "Ninth Symposium on Combustion," Academic Press, New York, 1963.

After the initial stage of hydrocarbon attack, the radical fragment is then oxidised to carbon monoxide by either or both of the paths (15) and (16),

$$R + O_2 \rightarrow RO_2 \rightarrow CO \quad . \; . \; . \; . \; . \; . \; . \; . \quad (15)$$

$$R + O \rightarrow RO \rightarrow CO \quad . \; . \; . \; . \; . \; . \; . \; . \quad (16)$$

then oxidation of carbon monoxide takes place by the reversible reaction (17):

$$CO + OH \rightleftharpoons CO_2 + H \quad . \; . \; . \; . \; . \; . \; . \; . \quad (17)$$

This reaction has been studied both in hydrocarbon oxidation, in carbon monoxide flames, and by means of the reverse reaction wherein carbon dioxide is added to hydrogen flames. Fenimore and Jones[65] obtained $k_{17} = 10^{10\cdot 35}\exp(-10{,}300/\boldsymbol{R}T)$l.mole^{-1}sec.$^{-1}$ at 1200—1350°K. Kaskan[46] has studied the light-producing reaction between carbon monoxide and atomic oxygen in flames; the results could be interpreted by the scheme:

$$CO + O = CO_2 + h\nu$$

$$\text{or } CO + O + M = CO_2{}^* + M \quad \text{and} \quad CO_2{}^* = CO_2 + h\nu$$

The light-emitting reactions have a rate constant of $2{\cdot}7 \times 10^{-19}$cm.^{3} mole^{-1}sec.$^{-1}$

Reactions of Ions and Electrons.—A relatively new aspect of combustion research is that of the reactions of ions and electrons in flames. This has been brought about by the application of mass spectrometry to the analysis of the ions. In hydrogen–oxygen flames very little ionisation takes place, but in hydrocarbon flames there is extensive ionisation, probably by reactions (18) and (19), whilst in the burnt-gas zone the concentrations of ions and electrons fall away because of recombination reactions (such as 20).

$$CH + O \rightarrow CHO^+ + e \quad . \; . \; . \; . \quad (18)$$

$$CHO^+ + H_2O \rightarrow H_3O^+ + CO \quad . \; . \; . \; . \; . \quad (19)$$

$$H_3O^+ + e^- = H_2O + H \quad . \; . \; . \; . \; . \quad (20)$$

Rate constants for these reactions, recently obtained[66] in flame studies, are $k_{18} = 3 \times 10^{-12}$, $k_{19} = 7 \times 10^{-9}$, and $k_{20} = (2{\cdot}2 \pm 1) \times 10^{-7}$cm.^{3}mole^{-1} sec.$^{-1}$.

General Conclusions

The general theory of premixed flames is now well understood and a variety of techniques have been developed to allow study of the structure of suitable flames. However, the experimental methods are more complex

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[65] Fenimore and Jones, *J. Phys., Chem.*, 1958, **62**, 1578.

[66] Green and Sugden, "Ninth Symposium on Combustion," Academic Press, New York, 1963.

than those used for classical closed-vessel studies. One of the limiting factors at present is lack of accurate transport data at high temperatures. On the other hand, flames provide a means of studying chemical reactions at rather high temperatures and velocities and in circumstances where high concentrations of atoms and free radicals can be obtained. Wall-effects are also absent. Thus, it is to be expected that many more chemical reactions will be studied in flames in the near future.