Microstructure of a Low-Pressure Hydrogen-Bromine Flame

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The rate of propagation and the structure of a flame depend on the kinetics of the flame reactions, the interdiffusion of reactants, intermediates, and products, and the thermal conduction of heat from the hot to the cool gases. To determine the relative importance of each of these phenomena experimentally in a particular flame system, one must know the profiles of temperature and of all the independent chemical species throughout the flame front. An analysis of these profiles will permit a determination of the chemical kinetics of all the reacting species in the flame system. A complete study of a flame system in this manner awaits the development of methods for chemical analysis of free radical intermediates. However, a knowledge of the importance of the various processes may be obtained by measuring some of the profiles if sufficient transport coefficient data and some information about the more important chemical reactions are available.

The hydrogen-bromine flame has been studied by several investigators in recent years as an example of a flame whose kinetics are thought to be understood. Anderson and his co-workers measured flame velocities and propagation limits for a variety of compositions by several techniques (*1*). Campbell (*2*) made a theoretical study of the conservation equations specifically governing this flame and showed the numerical difficulties that must be surmounted to analyze this system completely. Gilbert and Altman (*3*) made a theoretical study of the kinetic steady state hypothesis for this flame. Campbell and Fristrom (*4*) summarized the thermodynamic, transport, and chemical kinetic data which apply to this system. Peacock and Weinberg (*5*) described an attempt to study the structure of this flame with optical techniques.

This paper presents the structure of the flame as determined by thermocouple traversing and the chemical analyses performed on the samples withdrawn from the flame zone by fine quartz probes. Some interesting features of this flame and flame theory in general are confirmed experimentally in this work which also demonstrates the feasibility of probing into the hydrogen-bromine system.

EXPERIMENTAL TECHNIQUES

A spherical low-pressure burner with a 1 in. diam. porous ceramic sphere as a flameholder was used successfully to stabilize this flame. The bromine was metered from a reservoir in an isothermal bath regulated to 0.03°C. A heating element immersed in the bromine liquid and powered by a regulated voltage supply furnished the heat of vaporization of the bromine. The hydrogen was metered with a critical orifice. The gases were mixed in a tee and passed through a calming section into the center of the porous sphere. The burned gases (mostly hydrogen bromide) were reacted with ammonia in a baffled tubular reactor and formed ammonium bromide which deposited on the walls of the reactor. The residual gases were passed through several liquid nitrogen traps before being exhausted to a hood by means of a mechanical vacuum pump. This method of chemical pumping allowed the use of a low-capacity mechanical pump where a higher pumping speed was required and eliminated the corrosion problems in an otherwise difficult system. The temperature traverses were made with thermocouples of 0.0005-in. diam. platinum and platinum-10% rhodium wires. They were coated with silica generated from a silicone oil burned in a burner flame (*6*). The chemical analyses were performed with a freeze-out technique in conjunction with light absorption. The samples were obtained with the fine quartz probe described by Fristrom (*7*). The probe had an orifice diameter of 80 μ and was moved through the flame front with a micrometer screw. The bromine partial pressure in the sample was determined in a light-absorption cell by measuring the absorption in a 25-cm. path from a ribbon filament light source with a photocell. This device was calibrated during each run. The hydrogen partial pressure was determined by freezing out bromine and hydrogen bromide from the sample in a bulb with a small cold finger attached and then measuring the residual pressure. Hydrogen bromide was obtained by difference. Sample pressures and hydrogen pressures were measured with a spiral glass manometer used as a null device to prevent the corrosive gases from entering the mercury gauges needed for the particular pressure ranges

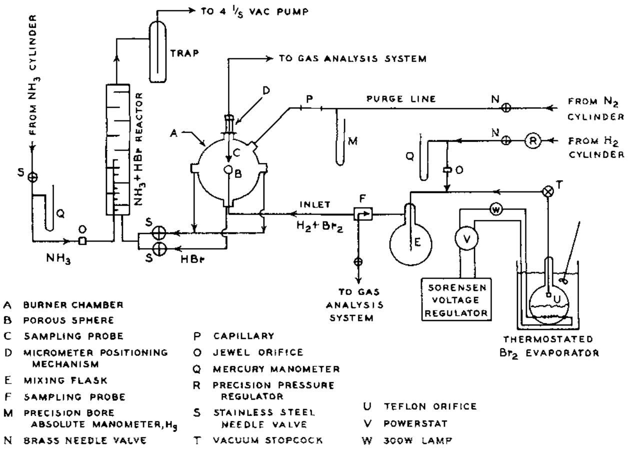

Fig. 1. Burner and flow system.

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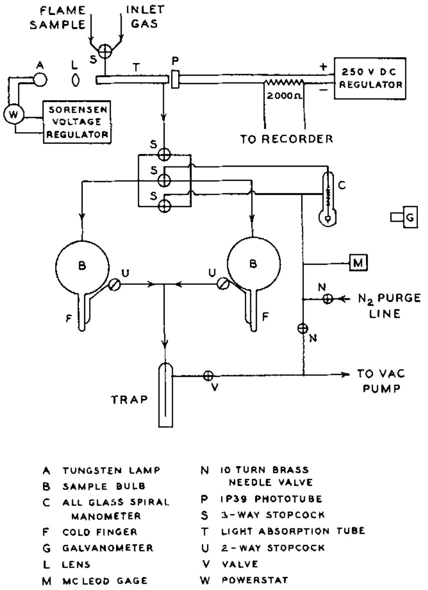

Fig. 2. Gas analysis system.

studied. Other corrosion problems were eliminated by construction of the equipment mostly with glass and nickel; where slow corrosion presented no difficulty, some massive parts were constructed of stainless steel. Schematic diagrams of the flow system and the sampling apparatus are shown in Figures 1 and 2.

RESULTS

The flame studied in this work had an initial composition of 44.2 mole % bromine at 8.87 ± 0.02 cm. mercury total pressure and represents the most stable flame burned by the authors in this pressure region. The concentration of the mixture was controlled to within 0.1%, but the actual concentration was determined only to within 1%. The measured burning velocity of this flame corrected to 25°C. at the actual pressure is 23.4 cm./sec. This flame is nonadiabatic since it loses an appreciable amount of heat by conduction to the porous sphere. The heat is in turn radiated to the surroundings. This heat loss represents about 15% of the heat of reaction. Since the flame temperature is only about 250 deg. below the adiabatic temperature, the characteristics of this flame are similar to those of an adiabatic flame. In Figure 3 temperature profiles uncorrected for thermocouple radiation are presented for several angles around the sphere. At these pressures the resolution of a thermocouple with a bead of 50-μ diam. is sufficient to give a temperature representative of the point at which the thermocouple bead is centered. The disagreement among the profiles at the various positions is attributed to natural convective cooling of the burned gases in the space surrounding the flames. This is inferred from the observation that the surface of the 12-liter glass bulb is hot to the touch at the top of the bulb and cool at the bottom even though the gases are exhausted from the bottom of the vessel. Since the variation in profile is small near the flameholder where the important processes occur, the cap of flame is considered to be a good approximation to a sphere, and all reduction of data was done on profiles measured at the pole of the sphere as they were the best spherical profiles obtainable from this equipment. A spherical burner should be designed to optimize the burned-gas residence time in order to eliminate convection. The performance of the silica coating as a protection against catalytic effects is shown in Figure 4. The difference in final flame temperature is explained by the variation of diameter due to the coating as determined with a microscope. A small amount of catalysis seemingly occurs on the bare thermocouple at the middle of the temperature profile but not on the coated wire.

The resolution of the sampling probes is not as good as that of the thermocouples since the probes are larger. The flame is approximately 50 probe diameters thick; therefore, the position of the composition profile with respect to the temperature profile is uncertain within the resolution of the probes which is unknown but which could be as high as several probe diameters. In this flame, diffusion smooths the composition profiles so that the shape of the curves is measured accurately by the probes. The final results are reasonable enough to suggest that the composition profiles are shifted only slightly. A shift in the profiles will move the maximum of curve A of Figure 5 through a distance equal to the shift, since the rapid rise in heat release before this point is due to the deviation of the temperature profile from that of purely conductive curve. The gradual variations of the composition profiles mask any effect of the shift on other portions of the heat-release curve. The probe diameter was chosen to give a reason-

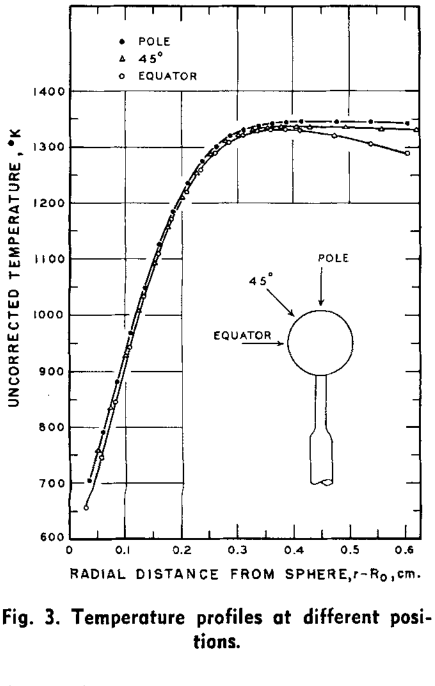

Fig. 3. Temperature profiles at different positions.

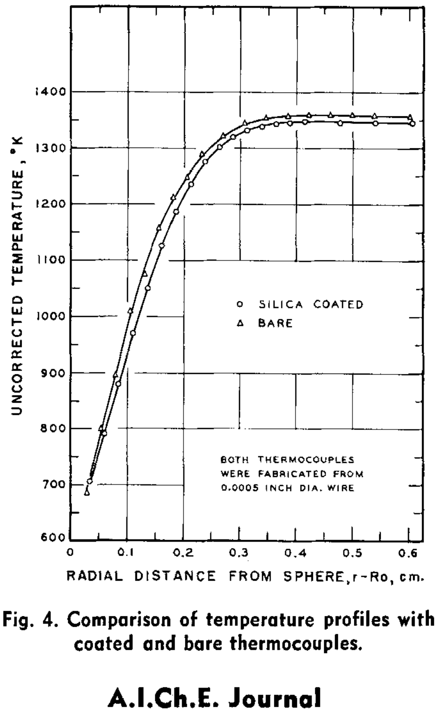

Fig. 4. Comparison of temperature profiles with coated and bare thermocouples.

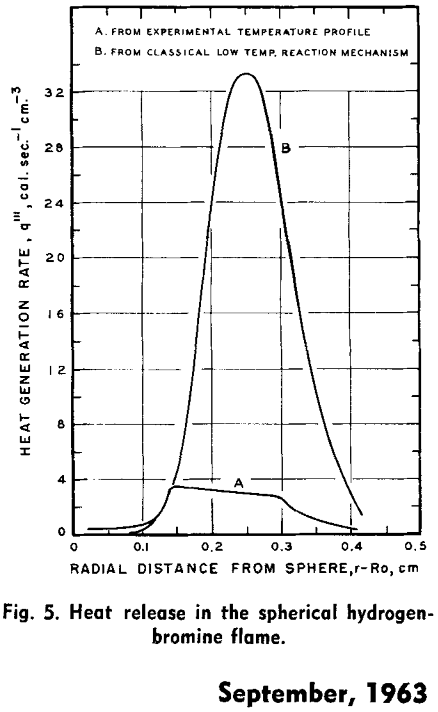

Fig. 5. Heat release in the spherical hydrogen-bromine flame.

able sampling time of 5 min./point which, coupled with chemical analysis time of about 15 min., allowed a reasonable number of points to be obtained in the several hours of running time permitted by the system. Since this diameter was only one order of magnitude greater than the mean free path in the hot gases, the authors were on the borderline of continuum sampling. A set of composition profiles was determined at two positions on the sphere to ascertain the deviation from sphericity. The profiles are shown in Figures 6 and 7. There is a measurable difference in the profiles since the region of unreacted bromine is thicker near the equator. This result was also visibly evident in the color of the bromine in the unburned gases. The profiles are similar enough to permit an analysis to be made with some confidence in the spherical model. Although it seems unlikely, the distortion may be due to flow distribution rather than convection and therefore the mass flow through the region analyzed would be overestimated slightly. This would change the amplitude of all estimated rates proportionally. The importance of diffusion in this flame is shown by the bromine and hydrogen concentrations at the burner surface. The forward diffusion of hydrogen depleted the mixture from an initial hydrogen fraction of 56% down to 28% as shown in the corrected profiles of Figure 8. The back diffusion of hydrogen bromide to the burner surface and the concentration jumps are explained by the velocity change at the surface of the sphere. This effect appears to be an experimental demonstration of a model similar to the mathematical flameholder of Hirschfelder and Curtiss (9) since it is unlikely that the profiles measured near the surface could approach as a limit the premixed mole fractions.

ANALYSIS AND DISCUSSION OF RESULTS

The correction of thermocouple temperatures for radiation losses was made with the correction for losses from a sphere heated by a stream of hot gases in the Reynolds number regime (10^{-1} to 10^{-2}) where the limiting value of the Nusselt number could be used (*8*). An emissivity of 0.9 was assumed for the silica surface which darkened upon exposure to the flame. A particular difficulty which arises in this work is that the thermal conductivity is a strong function of the concentration which is not accurately known since only stable species were measured and since an appreciable amount of the bromine measured is due to bromine atoms in some parts of the flame. The principal effect of the unknown bromine atom concentration is the changing of the mole number and hence of the relative concentration of hydrogen. Therefore the radiation correction could be determined only by an iterative procedure in which the bromine atom concentration is estimated through the equilibrium constant as discusssed later. The thermal conductivity of the mixture was estimated by the method of Mason and Saxena (*10*) with the following relationships:

$$\gamma_{\text{mix}} = \sum_{i=1}^{n} \lambda_i \left[1 + \sum_{\substack{k=1 \\ k=i}}^{n} G_{ik} \frac{X_k}{X_i} \right]^{-1}$$

$$G_{ik} = \frac{1.065}{2\sqrt{2}} \left(1 + \frac{M_i}{M_k} \right)^{-1/2} \left[1 + \frac{\lambda_i^o}{\lambda_k^o} \left(\frac{M_i}{M_k} \right)^{1/4} \right]^{1/2}$$

$$\lambda_i^o = \frac{\lambda_i}{0.115 + 0.354\, C_p/R}$$

All λ_i's were taken from the work of Campbell and Fristrom (*4*) except λ_{Br}, which was replaced by the value of λ_{HBr} as an approximation. The final corrected flame temperature of 1,392°K. and the profile are shown in Figure 8.

The uncorrected composition profiles shown in Figure 6 are based on the compositions of the sample after it is cooled. Since the pressure ratio across the probe is always greater than critical, adiabatic expansion arrests the high-temperature reactions. The mixture entering the probe may contain hydrogen bromide, hydrogen, bromine, hydrogen atoms and bromine atoms. Hydrogen atom concentration is always so low (*2*) that its removal by subsequent reaction with any of the other species does not affect the concentration of that species. Bromine atom concentrations are high; therefore the ultimate fate of the bromine atoms must be considered. The authors assume that they disappear only by recombination since their reactions with each of the stable species are either endothermic or require an activation energy. The apparent mole fraction of bromine (χ'_{Br_2}) in a sample withdrawn from a flame is related to the actual bromine concentration by the relation

$$\chi'_{\text{Br}_2} = \frac{X_{\text{Br}_2} + \frac{1}{2} X_{\text{Br}}}{1 - \frac{1}{2} X_{\text{Br}}}$$

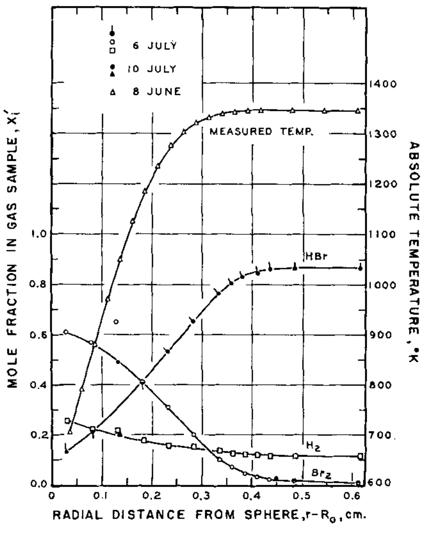

Fig. 6. Hydrogen-bromine flame structure; polar position.

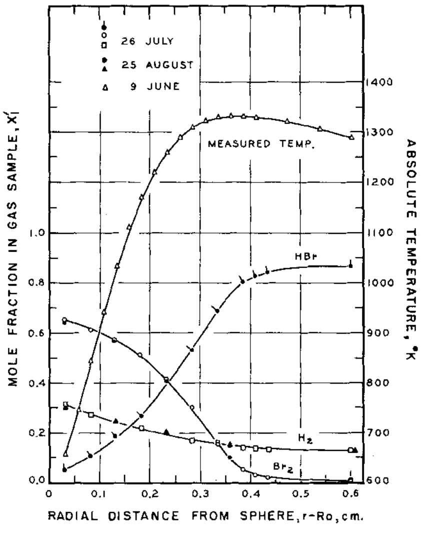

Fig. 7. Hydrogen-bromine flame structure; equator position.

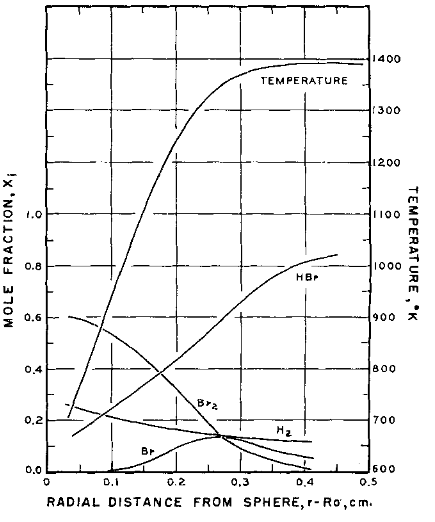

Fig. 8. Corrected profiles based on $\text{Br}_2 = 2\text{Br}$; polar position.

TABLE 1. COMPARISON OF CHEMICAL TIME TO DYNAMICAL TIME

$r\text{-}R_o$ cm.	T °K.	$1/\gamma$ sec.	v cm./sec.	Δr cm.	$1/\gamma/\tau$
0.088	900	0.29	45		
0.130	1,050	0.079	51	0.042	96
0.180	1,200	0.034	59	0.092	22
0.230	1,300	0.025	63	0.142	11

The demoninator also was used to correct the hydrogen bromide and hydrogen profiles. Without additional information concerning bromine atoms, a satisfactory analysis of the data is not possible. Even with measurements of the bromine atom, accurate analysis of the profiles to determine the rate constants requires accurate thermal conductivities and diffusion coefficients, but they are not available. With the known rate constants, it would be possible to derive the transport coefficients from the profiles. At present, one must be satisfied to derive the bromine atom concentration from the profiles with the steady state hypothesis, to compare the heat release determined by thermocouples with that obtained with this profile, and to make some observations with regard to the observed differences.

The hydrogen-bromine flame has received so much attention because only ten plausible chemical reactions (including forward and reverse) may be written among the five possible species:

$$\begin{array}{cl}
Br_2 + M^* \rightleftharpoons 2Br + M & (a) \\
H_2 + M^* \rightleftharpoons 2H + M & (b) \\
Br + H_2 \rightleftharpoons HBr + H & (c) \quad (1) \\
H + Br_2 \rightleftharpoons HBr + Br & (d) \\
H + Br + M \rightleftharpoons HBr + M^* & (e)
\end{array}$$

When the steady state hypothesis for radical concentration is made, a well-known expression for the rate of reaction is obtained (*4*):

$$\frac{d[HBr]}{dt} = \frac{2k_4{}^f\, k_3{}^f \sqrt{K_1}/k_3{}^r\, [H_2][Br_2]^{1/2}}{k_4{}^f/k_3{}^r + [HBr]/[Br_2]} \qquad (2)$$

A consequence of the steady state hypothesis for this system is that the bromine atoms are present in proportion to bromine molecules as related by the equilibrium constant at the particular temperature. With this hypothesis it is possible by an iterative procedure in conjunction with the previously mentioned radiation correction to determine the bromine atom concentration, the corrected temperature, and the corrected bromine concentration with the second iteration. The corrected profiles obtained by this method are shown in Figure 8.

The validity of the steady state hypothesis under flame conditions has been studied by several investigators (*2*, *3*, *9*) and was found not to hold although the magnitude of the deviations is not known quantitatively for this flame. One group of investigators (*3*) think that the deviations are not large.

The volumetric heat release may be calculated from the conservation of energy expressed in spherical coordinates using the temperature profile to obtain the gradient and the concentration profile to obtain the average specific heat of the mixture. The form of the equation is (*11*)

$$r^2\, q'''(r) = \frac{d}{dr}\left[\frac{\dot{m}}{4\pi}\int_{T_o}^{T} C_p\, dT - r^2\, \lambda_{\text{mix}}(T)\, \frac{dT}{dr}\right] \qquad (3)$$

The result of the calculation which involves two differentiations is shown in Figure 5. Also present in this figure is the heat release calculated with the classical reaction rate, Equation (2), and the heat of reaction. The reaction rate constants used in this calculation were taken from those recommended in reference *4*.

The curve *B* may be integrated to give a total heat release several times that given by the heat of reaction. Curve *A*, however, integrates to within about 10% of the theoretical heat release. The difference is due to the use of approximate profiles for composition, and therefore incorrect specific heats, and to the nonadiabatic character of the flame since the heat loss from the surface of the sphere could not be precisely measured.

The excess heat release given by the steady state hypothesis is evidence that this hypothesis is not good for this flame. A comparison of chemical time vs. dynamical time for the dissociation of bromine by a method described by Gilbert and Altman (3) is presented in Table 1. The reciprocal of chemical time γ was estimated from the equation

$$\gamma = [4\rho_m{}^{3/2}]\sqrt{k_1{}^f\, k_1{}^r\, X_{Br2}}$$

The dynamical time τ is given by the relation

$$\tau = \frac{\Delta r}{v}$$

where

$$v = \frac{\dot{m}}{M\rho_m 4\pi r^2}$$

It is evident that sufficient time is not available for the establishment of the steady state in this flame.

TABLE 2. ESTIMATED REACTION RATES

(moles/cc.-sec.)
Endothermic reactions

T, °K.	$\overset{f}{r_1}$	$\overset{f}{r_2}$	$\overset{f}{r_3}$	$\overset{r}{r_4}$	$\overset{r}{r_5}$
1,000	6×10^{-7}	8×10^{-20}	6×10^{-5}	3×10^{-10}	3×10^{-16}
1,075	2×10^{-6}	3×10^{-18}	2×10^{-4}	6×10^{-9}	6×10^{-15}
1,200	1×10^{-5}	2×10^{-16}	7×10^{-4}	6×10^{-8}	3×10^{-13}
1,300	3×10^{-5}	5×10^{-15}	2×10^{-3}	5×10^{-7}	5×10^{-12}

Exothermic reactions

T, °K.	$\overset{r}{r_1}$	$\overset{r}{r_2}$	$\overset{r}{r_3}$	$\overset{f}{r_4}$	$\overset{f}{r_5}$
1,000	6×10^{-7}	3×10^{-15}	3×10^{-6}	6×10^{-5}	1×10^{-10}
1,075	2×10^{-6}	2×10^{-13}	5×10^{-5}	6×10^{-4}	2×10^{-9}
1,200	1×10^{-5}	3×10^{-13}	8×10^{-5}	6×10^{-4}	4×10^{-9}
1,300	3×10^{-5}	3×10^{-12}	3×10^{-4}	1×10^{-3}	2×10^{-8}

TABLE 3. ESTIMATION OF BROMINE ATOM CONCENTRATION

r-R_0(cm.)	T(°K.)	k_3^f	X_{H_2}	$X_{Br}(A)$	$X_{Br}(B)$
0.13	1,050	$10^{10.1}$	0.19	0.018	0.024
0.15	1,105	$10^{10.3}$	0.18	0.024	0.030
0.20	1,240	$10^{10.8}$	0.17	0.010	0.100
0.25	1,325	$10^{11.0}$	0.16	0.007	0.150
0.30	1,365	$10^{11.1}$	0.15	0.006	0.130

A. Calculated from the heat-release curve.

B. Steady state approximation, Figure 8.

An order of magnitude estimation of the rates of the reactions in the reaction zone with the concentrations of Figure 8 and the rate coefficients of reference *4* shows that only reaction (1*a*), (1*c*), and the forward reaction (1*d*) are rapid enough to be important in the region of high heat release. The result of this estimation is shown in Table 2.

If the dissociation of bromine does not follow the steady state, the rates of reaction (1*a*) are not important in the establishment of the bromine atom concentration except in the region of equilibration beyond the heat release. Since only reactions (1*c*) and (1*d*) appear to be important in the region of maximum heat release, the steady state approximation for hydrogen atoms permits the calculation of X_{Br} from the observed heat-release profile in the following manner. Two molecules of hydrogen bromide are formed when a bromine atom reacts in reaction (1*c*) since the steady state requires that each hydrogen atom immediately react with bromine in reaction (1*d*). The observed heat release therefore represents twice the heat of reaction. With the rate constant of reference *4*, the heat of reaction from reference *13*, and X_{H_2} from Figure 8, it is possible to estimate X_{Br} in the reaction zone. The parameters used in this calculation and a comparison with the steady state estimation of X_{Br} are shown in Table 3. This estimation depends only upon the validity of curve *A* of Figure 5 since both the rate constant and X_{H_2} vary slowly through this region of the flame. The magnitude of curve *A* is certainly of the correct order although the shape of the curve is probably not accurate. The magnitude of X_{Br} obtained from the heat-release curve is more reasonable than that estimated from the steady state. The shift of the maximum toward the cold boundary is consistent with a deviation from the steady state and is also in agreement with the calculation of Campbell (*2*). Correction of the profiles by another iterative calculation was not warranted in this type of estimation because of the uncertainties of curve A.

This discussion omits mention of thermal diffusion which is expected to be important whenever ordinary diffusion is important and large temperature gradients occur. An order of magnitude estimate was made of the thermal-diffusion flux at the greatest temperature gradient and was about 30% of the largest ordinary diffusion flux. It should be included in an accurate accounting of transport in a flame of this type. The remarkably small hydrogen gradient appears to be due to thermal diffusion since it adds to the ordinary diffusion in this flame.

The lack of a narrow primary-reaction zone of the type observed in hydrocarbon flames by Fristrom and coworkers (*12*) appears to be a feature which differentiates the two types of flames. It is perhaps due to the low activation energy of the reaction $H + Br_2$ as contrasted to that of $OH + CH_4$; this permits the former reaction to occur in any region into which the hydrogen atom has diffused, and thus the reaction is spread effectively throughout the flame.

Determination of bromine atoms is required to give a complete experimental description of the hydrogen-bromine flame. Precise comparison with theory will be possible when the handling of the transport properties becomes feasible.

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NOTATION

C_p = specific heat at constant pressure, cal./g.-°C.
K_1 = equilibrium constant for bromine dissociation, mole/cc.
k_i^f, k_i^r = rate constants given in reference *4*
M = molecular weight, g./mole
M = any species in mixture
M^* = an energetic species
$\dot{m}$ = mass flow rate, g./sec.
q''' = volumetric heat release rate, cal/cc.-sec.
R = gas constant, cal./g.-°K.
r = radial coordinate measured from center of a sphere, cm.
r_i^f, r_i^r = reaction rates, mole/cc.-sec.
T = absolute temperature, °K.
v = mass average velocity, cm./sec.
X = mole fraction, dimensionless

Greek Letters

γ = reciprocal of chemical time, sec.$^{-1}$
ρ_m = molar density, mole/cc.
τ = dynamical time, sec.
λ_i = thermal conductivity of a component, cal./°C.-cm.

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