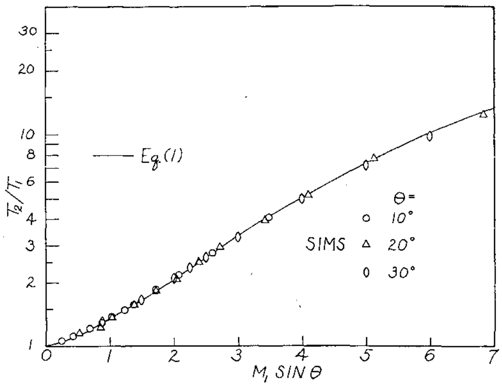

Fig. 1 Cone temperature ratio.

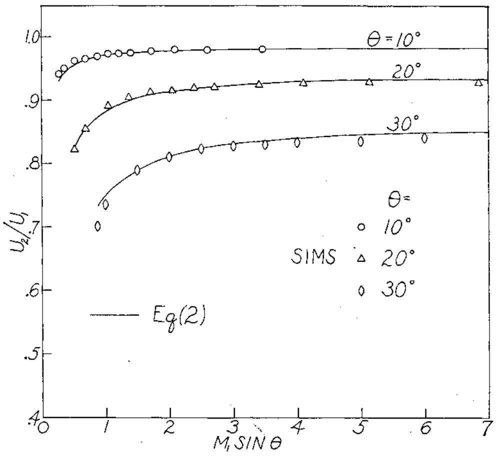

Fig. 2 Cone velocity ratio.

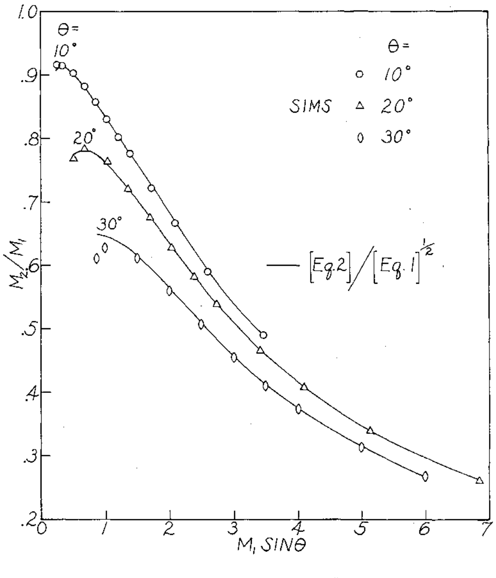

Fig. 3 Cone Mach number ratio.

Previously, Linnell and Bailey,[2] using the similarity concept, obtained the following expression for the pressure coefficient on a cone:

$$C_p = (4 \sin^2\theta)(2.5 + 8\beta \sin\theta)/(1 + 16\beta \sin\theta) \qquad (3)$$

Eq. (3) can be used to obtain the pressure on a cone surface, and this pressure in turn can be used with Eq. (1) and the equation of state to obtain the density on the cone surface.

The accuracy of Eq. (1) and Eq. (2) are questionable above a Mach number of 10, due to the dissociation effects. However, a comparison of Eq. (3) with the results of Romig[3] indicates that Eq. (3) is not affected to any large degree by dissociation.

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Effects of Nitrogen, Excess Hydrogen, and Water Additions on Hydrogen-Air Flames

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Kuehl[1] has measured the effect on the burning velocity of adding nitrogen, excess hydrogen, and steam to a premixed stoichiometric hydrogen–air flame at $\frac{1}{4}$ atm pressure and an initial gas temperature of 800°F (720°K). Whereas addition of nitrogen caused a reduction in burning velocity proportional to the nitrogen added, the addition of excess hydrogen produced increases in the burning velocity. Water caused only about one-third of the reduction produced by an equivalent volume of nitrogen. On replacing the nitrogen in the air by water vapor on a mole-for-mole basis, the burning velocity increased (from around 700 cm-sec^{-1} initially) by about 6 cm-sec^{-1}/mole % water in the over-all mixture.

One approach to the effect of inert additives is to assume that the additive acts as a heat sink, thus reducing the flame temperature, and hence the burning velocity. On this basis alone, it would be expected that all three additives would reduce the burning velocity, whereas heat capacity effects suggest that, mole for mole, water should be more efficient than nitrogen in this way. Assuming the nitrogen to behave in a "normal" fashion, the behavior of both the excess hydrogen and the water vapor is therefore anomalous.

In the case of the *water* additive, Kuehl suggests that the increase in burning velocity when nitrogen is replaced by water may be due to the ability of the unburned gas containing water to absorb radiation from the flame. On the other hand, in a recent note, Levy[2] has drawn attention to a possible chemical kinetic interpretation of the phenomenon. According to this, by analogy with slow reaction studies, the reaction rate in the flame may be increased by such steps as

$$H_2O + HO_2 = OH + H_2O_2 \qquad (1)$$

$$H_2O + H + O_2 = OH + H_2O_2 \qquad (2)$$

Arising from our work on the hydrogen-oxygen flame system, we would like to enlarge on this theme.

First, a slow-burning, hydrogen-rich, hydrogen-oxygen-nitrogen flame at atmospheric pressure has been studied experimentally.[3] The flame temperature was 1072°K and the burning velocity 9.2 cm-sec^{-1}. (Gas flows measured at 18°C and 760 mm.) The initial gas temperature was 336°K. Analysis of the measured temperature profile gave a maximum heat release rate of 20 (±2) cal-cm^{-3}-sec^{-1} at 900°K, whereas the maximum hydrogen atom concentration, measured by studying the rate of the H + D_2 exchange reaction, was about 2.5 × 10^{-8} mole-cm^{-3} at this temperature. Furthermore, at 900°K, $(O_2) \approx 1,1$ $(H_2) \approx 11$, and $(H_2O) \approx 8$ mole %.

Second, the widely accepted basic mechanism used to interpret the explosion limit and slow reaction behavior of

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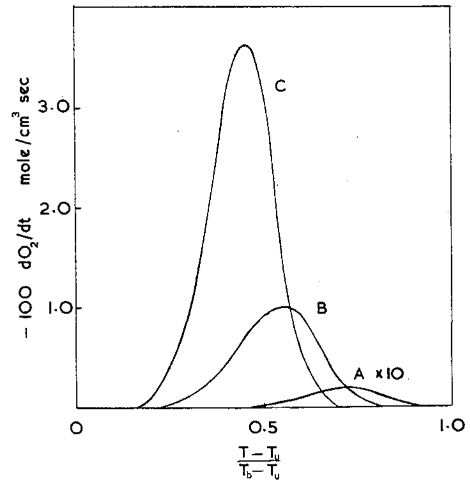

Fig. 1 Rates of oxygen disappearance in three specified flames.

hydrogen-oxygen systems involves the following two oxygen-consuming reactions:

$$H + O_2 = OH + O \tag{3}$$

$$H + O_2 + M = HO_2 + M \tag{4}$$

M in reaction (4) represents any molecule present in the reaction vessel. The second explosion limits in potassium chloride coated vessels at temperatures up to about 850°K are normally assumed to be ultimately controlled by a competition between reactions (3) and (4), so that at the limit the partial pressures of reactants and inert gases obey the relationship $2k_3/k_{4H_2} = (H_2) + k_{O_2}\,(O_2) + k_M\,(M)$. Here $k_M = k_{4M}/k_{4H_2}$. Values of each k_M and of the ratio k_3/k_{4H_2} may be obtained by studying the effect of mixture composition on the second limit. For the molecules relevant to this discussion, it is found[4–6] that $k_{N4_2} = 0.45k_{4H_2}$ and $k_{4H_2O} = 6.5k_{4H_2}$. Reaction (4) with $M = H_2O$ is, therefore, some 14 times as fast as with $M = N_2$; and if reaction (4) contributes appreciably to the flame reaction rate, then an explanation for the observed phenomenon is available. Some possible subsequent reactions of hydroperoxyl in hydrogen–oxygen flames have been discussed by the authors.[7]

To assess the contribution of reaction (4) in flames, it is necessary to consider the ratio k_3/k_{4H_2}. A short extrapolation of the Arrhenius plot for this ratio from second-limit data leads to $k_3/k_{4H_2} = 150$ mm at 900°K. Hence, from the values of k_{N_2} and k_{H_2O} already quoted, it might be expected that, at the position of maximum reaction rate, reaction (4) is some 4 to $4\frac{1}{2}$ times as fast as reaction (3), that is, that reaction (4) is important at least in this particular low-temperature flame. Using a reasonable value for k_3, this conclusion is supported by the results already quoted.

At higher temperatures, the ratio k_3/k_{4H_2} increases at a rate corresponding to an Arrhenius activation energy difference of about 17–20 kcal-mole^{-1}. It is possible, therefore, that reaction (4) and subsequent reactions rapidly become less important in hotter flames, particularly at low pressures. This would be in complete accord with such theories of flame propagation as assume the reaction rate to be a maximum fairly close to the final temperature.

Third, then, some results of numerical solutions of the flame equations for the case of a simplified hydrogen–oxygen reaction mechanism are of interest. The numerical method used has been described by Spalding,[8] Adams and Cook,[9] and others. It consists in integrating the time-dependent heat conduction and diffusion equations controlling the flame by finite difference methods until steady-state composition profiles and propagation velocity are reached. The method takes reasonable account of the diffusion and other properties of the gas mixture. The simplified (but realistic except for HO_2 participation) reaction mechanism employed consisted of the chain branching reactions (5–7) and the radical recombination reaction (8):

$$OH + H_2 = H_2O + H \tag{5}$$

$$H + O_2 = OH + O \tag{6}$$

$$O + H_2 = OH + H \tag{7}$$

$$H + H + M = H_2 + M \tag{8}$$

For oxygen-deficient flames, the controlling reactions are (6) and (8) (see Ref. 3). Using reasonable values for the rate constants of these two reactions, three flames were studied numerically, having the initial compositions and flame temperatures (pressure was atmospheric) shown in Table 1.

Table 1 Parameters of flames studied numerically

	$\%H_2$	$\%O_2$	$\%N_2$	T, °K	T_b, °K
A	18.83	4.60	76.57	336	1072
B	33.33	8.33	58.33	298	1614
C	50.00	10.50	39.50	298	1945

Figure 1 shows the rates of disappearance of oxygen in these flames, plotted as a function of the fractional temperature rise. The maximum rates correspond with temperatures of about 900°, 100°, and 1020°K for flames A, B, and C, respectively. Clearly, the temperature corresponding to this maximum rate does not increase very much in the hotter flames. The "low-temperature" reaction path via H_2O may therefore still retain some importance in the hotter flames, thus making the suggested kinetic effect of water vapor not unreasonable.

The effect of excess *hydrogen* in increasing the burning velocity above that of the stoichiometric mixture is, in our opinion, unlikely to be caused by increased diffusion of H atoms into the unburned gas, as suggested by Kuehl. It has been shown by Giddings and Hirschfelder[10] and by the authors[3] that increasing the diffusion coefficient of H in a specific flame in fact decreases the burning velocity. A more likely explanation of the effect of excess hydrogen may therefore be found in its effect in increasing the thermal conductivity λ of the mixtures, since all theories of flame propagation predict $S\alpha\lambda^{1/2}$.

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