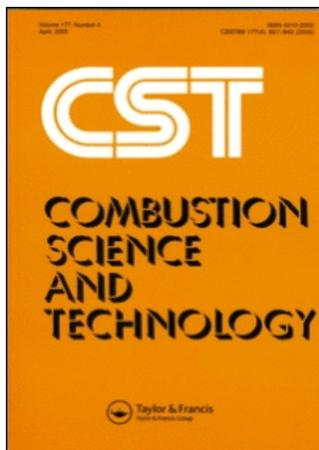


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### Some Studies on Hydrogen - Oxygen Diffusion Flame

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## Some Studies on Hydrogen-Oxygen Diffusion Flame

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**Abstract**—The opposed-jet diffusion flame has been considered with four step reaction kinetics for hydrogen-oxygen system. The studies have revealed that the flame broadening reduces and maximum temperature increases as pressure increases. The relative importance of different reaction steps have been brought out in different regions (unstable, near extinction and equilibrium). The present studies have also led to the deduction of the overall reaction rate constants of an equivalent single step reaction using matching of a certain overall set of parameters for four step reaction scheme and equivalent single step reaction.

### INTRODUCTION

Premixed flames, under certain conditions, are not suitable for the study of combustion kinetics of fuel-oxidant systems, mainly because they have high rates of combustion and small thickness of the flame zone. To overcome the above problems, the fuel and oxidant are burnt in a diffusion flame mode and the flame structure is studied. But in ordinary diffusion flames (e.g. ordinary Bunsen burner with inlet vent closed), the heat and mass transfer rates are usually very low and hence the effect of chemical kinetics is small and cannot be well understood. In such situations strong forced convection is introduced leading to predominant effect of chemical kinetics.

Most of the analytical studies on diffusion flames are restricted to single step reaction. It is often mentioned that the differences in the analytical and experimental results may be due to the fact that realistic kinetic scheme has not been considered. Hence it appears worthwhile to investigate the problem with realistic kinetic scheme. The mechanism of hydrogen-combustion has been studied in great detail and so is considered here.

Da Riva (1966) and Clarke (1968, 1969) have considered hydrogen-oxygen diffusion flames with nine steps and four steps respectively and their results are relevant to near-equilibrium situations. In the practical situations however, the diffusion flames operate with high heat release rates and can be at near-extinction conditions. The analysis by the above authors cannot be extended to near-extinction conditions. Liu and Libby (1970) considered wall-jet diffusion flames with eight step

reaction kinetics. They developed numerical procedure using quasilinearization technique for solution of coupled nonlinear differential equations. Wu and Libby (1972) refined the numerical scheme so that entire range of solution from frozen to equilibrium flow could be obtained.

The work to be presented in this paper is concerned with three aspects described below:

- 1) Results of equilibrium solution and effect of pressure on the equilibrium solution.
- 2) Investigations on the states of different steps—whether they are near equilibrium or not—on different branches—unstable, stable and near extinction.
- 3) Discussion of a methodology for determining the reaction rate constants for equivalent single step reaction and the evaluation of the rate constants for H<sub>2</sub>-air system.

### FORMULATION

#### *The Model and Approximations*

Here we consider the opposed-jet geometry. In the analysis, Fourier's law of heat conduction and Fick's law of diffusion are taken as valid. It has been assumed that: (i) the specific heat at constant pressure is constant, (ii) controlling region of chemical kinetics lies near stagnation point, (iii) jets are of equal diameters and equal velocities, (iv)  $\frac{\mu}{\rho\mu}$  is constant, (v) Lewis number is unity. Marathe (1975) has demonstrated that unity Lewis number assumption is reasonable after examining experimental results by Dixon *et al.* (1973) and Elberius *et al.* (1971) on hydrogen-air flames.

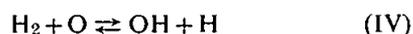
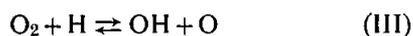
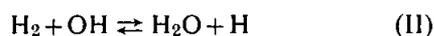
TABLE 1  
Reaction rate constants pertaining to the different steps in the reaction scheme

Reaction	Forward rate constants $k_f^{(1)} = Z_f^{(1)} T^{n_f^{(1)}} \exp(-E_f^{(1)}/T)$			Backward rate constants $k_b^{(1)} = Z_b^{(1)} T^{n_b^{(1)}} \exp(-E_b^{(1)}/T)$		
	$Z_f^{(1)}$	$n_f^{(1)}$	$E_f^{(1)}$	$Z_b^{(1)}$	$n_b^{(1)}$	$E_b^{(1)}$
1. $H_2 + M \rightleftharpoons H + H + M$	$18.5 \times 10^{19}$	-1	54000	$10^{16}$	0	0
2. $H_2 + OH \rightleftharpoons H_2O + H$	$3.0 \times 10^{14}$	0	3200	$1.33 \times 10^{15}$	0	10950
3. $O_2 + H \rightleftharpoons OH + O$	$3.0 \times 10^{14}$	0	8810	$2.48 \times 10^{13}$	0	660
4. $H_2 + O \rightleftharpoons OH + H$	$3.0 \times 10^{14}$	0	4030	$1.30 \times 10^{14}$	0	2490

The units of all the rate constants are  $\text{cm}^3 \text{mol}^{-1} \text{sec}^{-1}$  except for  $k_b^{(1)}$  which is  $\text{cm}^6 \text{mol}^{-2} \text{sec}^{-2}$ ,  $T$  in degrees Kelvin.

#### Reaction Scheme and Data

The following four step reaction mechanism, which is identical to that used by Clarke (1968, 1969), has been considered.



Here  $M$  is any species acting as third body in dissociation-recombination Reaction (I). Reactions (III) and (IV) are bimolecular chain branching having slight endothermicity, while Reaction (II) is the propagating step. The reaction scheme can be considered as moderately realistic since a few third order reactions are not considered.

TABLE 2  
Data for the reaction scheme

Suffix	Species	Molecular weight ( $M_i$ )	$h_i^0$ kcal/gm
1	$H_2$	2	0
2	$O_2$	32	0
3	$H_2O$	18	-3.200
4	H	1	52.100
5	O	16	3.700
6	OH	17	0.590
7	$N_2$	28	0

The reaction rate constants used here are the values given by Ferri *et al.* (1965) and are tabulated in Table 1, Table 2 shows the data pertaining to the reaction scheme.

#### Governing Equations

The governing equations for laminar compressible boundary layer with similarity transformation can be written as (see *e.g.* Lees, 1958; Fay and Riddell, 1958; Jain and Mukunda, 1968)

$$f''' + ff'' + \frac{1}{(k+1)}(1-f'^2) = 0 \quad (1)$$

$$m_i'' + fm_i' = \frac{\dot{w}_i'''}{\rho(k+1)a} \quad (2)$$

$$H'' + fH' = 0 \quad (3)$$

where  $m_i$  = mass concentration of  $i$ th species

$$H = \text{total enthalpy} = c_p T + \sum_{i=1}^6 h_i^0 m_i$$

$c_p$  = specific heat at constant pressure

$T$  = temperature ( $^{\circ}\text{K}$ )

$h_i^0$  = heat of formation of  $i$ th species

$\dot{w}_i'''$  = mass consumption rate of  $i$ th species per unit volume (see Appendix)

## Boundary Conditions

$$\begin{aligned} \eta \rightarrow -\infty, m_1 = 0, m_2 = \beta, \\ m_3 = m_4 = m_5 = m_6 = 0, \\ H = H_{-\infty} = c_p T_{-\infty} + \sum_{i=1}^6 h_i^\circ m_{i-\infty}, \\ f' = 1 \\ \eta = 0, f = 0 \end{aligned} \quad (4)$$

$$\begin{aligned} \eta \rightarrow \infty, m_1 = \gamma, m_2 = m_3 = m_4 = m_5 = \\ m_6 = 0, m_7 = 1 - \gamma, \\ H = H_\infty = c_p T_\infty + \sum_{i=1}^6 h_i^\circ m_{i\infty}, f' = 1 \end{aligned}$$

The set of the governing equations with potential flow approximation ( $f = \eta$ ) and conserved property equations (Spalding, 1962) can be written as (for detail algebra see Marathe, 1975),

$$\begin{aligned} \frac{d^2}{dF^2} \left( \frac{m_1}{M_1} - \frac{m_2}{M_2} + \frac{m_3}{M_3} - \frac{m_5}{M_5} \right) \\ = \frac{D_1}{(F')^2} \left\{ \frac{S_f^{(1)} \rho m_1 \exp(-T_{af}^{(1)}/T_n)}{\rho_\infty M_1 M_\infty T} - \frac{S_b^{(1)} \rho^2 m_4^2}{\rho_\infty M_4^2 M_m} \right\} \end{aligned} \quad (5)$$

$$\begin{aligned} \frac{d^2}{dF^2} \left( \frac{m_3}{M_3} \right) = \frac{D_1}{(F')^2} \left\{ S_f^{(2)} \frac{\rho}{\rho_\infty} \frac{m_1 m_6}{M_1 M_6} \exp(-T_{af}^{(2)}/T_n) \right. \\ \left. - S_b^{(2)} \frac{\rho}{\rho_\infty} \frac{m_3 m_4}{M_3 M_4} \exp(-T_{ab}^{(2)}/T_n) \right\} \end{aligned} \quad (6)$$

$$\begin{aligned} \frac{d^2}{dF^2} \left( \frac{m_2}{M_2} \right) = \frac{D_1}{(F')^2} \left\{ S_f^{(3)} \frac{\rho}{\rho_\infty} \frac{m_2 m_4}{M_2 M_4} \exp(-T_{af}^{(3)}/T_n) \right. \\ \left. - S_b^{(3)} \frac{\rho}{\rho_\infty} \frac{m_5 m_6}{M_5 M_6} \exp(-T_{ab}^{(3)}/T_n) \right\} \end{aligned} \quad (7)$$

$$\begin{aligned} \frac{d^2}{dF^2} \left( \frac{m_2}{M_2} + \frac{m_5}{M_5} \right) \\ = \frac{D_1}{(F')^2} \left\{ S_f^{(4)} \frac{\rho}{\rho_\infty} \frac{m_1 m_5}{M_1 M_5} \exp(-T_{af}^{(4)}/T_n) \right. \\ \left. - S_b^{(4)} \frac{\rho}{\rho_\infty} \frac{m_4 m_6}{M_4 M_6} \exp(-T_{ab}^{(4)}/T_n) \right\} \end{aligned} \quad (8)$$

$$2m_1 \frac{M_1}{M_4} + 2m_3 \frac{M_3}{M_4} + m_6 \frac{M_6}{M_4} + m_4 = 2\gamma \frac{M_1}{M_4} F \quad (9)$$

$$2m_2 \frac{M_2}{M_5} + m_3 \frac{M_3}{M_5} + m_5 + m_6 \frac{M_6}{M_5} = 2\beta \frac{M_2}{M_5} (1 - F) \quad (10)$$

$$\begin{aligned} T_n = (1 - T_{n-\infty})F + T_{n-\infty} \\ + B_3 m_3 + B_4 m_4 + B_5 m_5 + B_6 m_6 \end{aligned} \quad (11)$$

where the following nondimensional transformations have been used.

$$\begin{aligned} T_n = T/T_\infty, \quad B_i = h_i^\circ / c_p T_\infty \\ T_{af}^{(i)} = E_f^{(i)} / T_\infty, \quad T_{ab}^{(i)} = E_b^{(i)} / T_\infty \end{aligned}$$

$$D_1 = \text{Damköhler Number} = \frac{\sum_{i=1}^4 [Z_f^{(i)} + Z_b^{(i)}] \rho_\infty}{8(k+1)a}$$

$$S_f^{(i)} = \frac{8Z_f^{(i)}}{\sum_{i=1}^4 (Z_f^{(i)} + Z_b^{(i)})} \quad S_b^{(i)} = \frac{8Z_b^{(i)}}{\sum_{i=1}^4 (Z_f^{(i)} + Z_b^{(i)})}$$

Here  $F = 1/2[1 + \text{erf}(\eta/\sqrt{2})]$  transformation is used to change the independent variable ( $\eta$ ) range from  $(-\infty$  to  $\infty)$  to independent variable ( $F$ ) range (0 to 1).

## Boundary Conditions

$$\begin{aligned} F = 0, m_1 = 0, m_2 = \beta, \\ m_3 = m_4 = m_5 = m_6 = 0, \\ m_7 = 1 - \beta, T_n = T_{n-\infty} \\ F = 1, m_1 = \gamma, m_2 = m_3 = m_4 = m_5 = m_6 = 0, \\ m_7 = 1 - \gamma, T_n = 1.0 \end{aligned} \quad (12)$$

## Solution

1) *Equilibrium Solution* Equilibrium model is represented by  $D_1 \rightarrow \infty$ , leading to the result that forward and backward reaction rates are equal. This solution does not show any discontinuity of

concentration and temperature gradients. This model shows the broadening of the flame, which is called "equilibrium broadening". The flame width can be represented by the region where the temperature profile shows significant curvature. To get the equilibrium solution bracketed terms in Eqs. (5) to (8) are set to be equal to zero. Along with these four conditions, Eqs. (9) to (11) are solved for various values of  $F$ . To solve these seven transcendental equations for seven unknowns, Newton's method for multivariables has been used. The iterations are continued till the accuracy of 0.01 per cent is obtained in all the seven variables.

2) *Finite Kinetics*. All the possible nonequilibrium solutions must lie between the frozen solution ( $D_1 \rightarrow 0$ ) and equilibrium solution ( $D_1 \rightarrow \infty$ ). It may be noticed that Wu and Libby (1972) solved the problem of wall jet-diffusion flame with a rather general kinetic scheme. In their example, however, the injection rate was rather small ( $-f_w \sim 0.0932$ ). The present problem is in a sense an extreme limit of wall jet diffusion flame with the nondimensional injection parameter ( $-f_w/f''(0)$ ) tending to infinity. In the present problem wherein a four step reaction scheme has been adopted, several numerical techniques of solutions were tried, (e.g. trial and error method, quasilinearization—cubic spline technique) but not with much success.

Approximate technique such as Modified Flame Surface Theory (e.g., see Peskin and Wise, 1966; Mukunda, 1968) was utilized to obtain solutions which could be used for interpretation of the various chemical kinetic effects. It is believed that these solutions form a fairly accurate representation of the actual behaviour, certainly qualitatively, presumably even quantitatively. The extinction-ignition phenomena which is due to finite  $D_1$  can be studied with this approximate analytical method.

In single step, irreversible reaction kinetics, the flame position is governed by the condition of stoichiometric ratio of fuel and oxidant mass fluxes. But in the present analysis four reversible step mechanism is considered for which straight application of above condition is not possible as we cannot precisely differentiate the fuel, oxidant and product species. So it is assumed here that the flame position is governed by the overall irreversible reaction, namely  $\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$ . The justification for this assumption comes from the result of Clarke (1968) that in the asymptotic limit of  $D_1 \rightarrow \infty$ , the overall reaction is essentially  $\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$ .

The solution of differential equation gives:

$$\frac{m_1^* - \gamma F^*}{M_1} + \frac{m_3^*}{M_3} + \frac{\beta(1 - F^*) - m_2^*}{M_2} - \frac{m_5^*}{M_5} = -F^*(1 - F^*)L_1^* \quad (13)$$

$$\frac{m_3^*}{M_3} = F^*(1 - F^*)L_2^* \quad (14)$$

$$\frac{m_2^* - \beta(1 - F^*)}{M_2} = -F^*(1 - F^*)L_3^* \quad (15)$$

$$\frac{m_2^* - \beta(1 - F^*)}{M_2} + \frac{m_5^*}{M_5} = -F^*(1 - F^*)L_4^* \quad (16)$$

where  $F^*$  = flame position

$$= \frac{\beta}{\beta + \gamma(M_2/2M_1)} \quad (17)$$

$L_j^*$  ( $j = 1$  to 4) are right hand sides of Eqs. (5) to (8) calculated at flame position, for example

$$L_1^* = \frac{D_1}{(F^*)^2} \times \left\{ \frac{S_f^{(1)} \rho^* m_1^* \exp(-T_{af}^{(1)}/T_n^*)}{\rho \infty T^* M_1 M_m^*} - S_b^{(1)} \frac{\rho^{*2} m_4^{*2}}{M_4^2 M_m^*} \right\}$$

and so on.

Thus the final set of equations to be solved is given by Eqs. (13) to (16) and (9) to (11) which are seven in number with eight unknowns i.e.,  $m_i^*$  ( $i = 1$  to 6),  $T_n^*$  and  $D_1$ .

Thus, if we assume the value of one of the unknowns at flame position ( $F^*$ ), the values of the other unknowns can be determined by solving seven (linear and nonlinear transcendental) equations. For ease of computation, the value of  $T_n^*$  has been assumed to be between the frozen and equilibrium values in steps and the values of the other unknowns are subsequently determined. Here again Newton's method has been used for the solutions of nonlinear equations with multivariables.

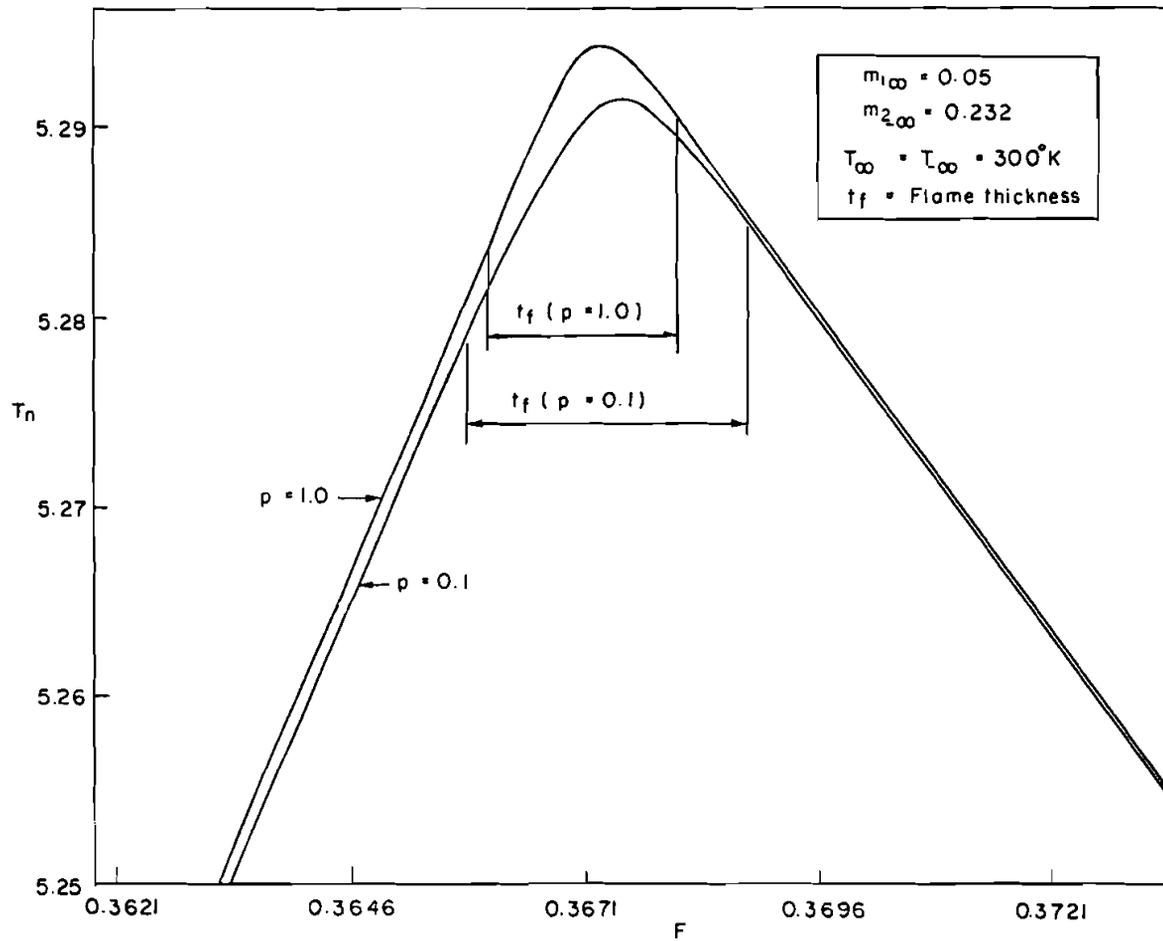


FIGURE 1 Profiles of temperature with  $F$  showing the effect of pressure in equilibrium kinetics.

## RESULTS AND DISCUSSION

### *Equilibrium Model*

Figure 1 contains the variation of temperature ( $T_n$ ) with  $F$  for two values of pressures near the flame position because it is here that there is a departure from a straight line profile. Flame broadening reduces as pressure increases (flame width is defined for the present purpose as the width over which temperature profile shows significant curvature). Hence, as the pressure increases, the equilibrium solution will approach the flame sheet solution. This can be ascribed to the suppression of dissociation of H atoms at high pressures. The equilibrium constant of the first reaction decreases as pressure increases due to increase of density.

This reduces the equilibrium model to that of flame sheet.

Variations of concentrations of species are plotted in Figures (2) and (3) for two different pressures. The results show that the concentrations of intermediate species (H, O, OH) decrease as pressure increases. In the limit of pressure tending to infinity we can expect that these concentrations will tend to zero and equilibrium solution will be identical to the flame sheet solution. Hence, the four step reaction scheme will tend to single irreversible reaction with  $\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$  in the limit as pressure becomes large. This limit is true in the assumed reaction scheme only. In actuality other three body collisions can be expected to be dominant and the resulting limit may be different.

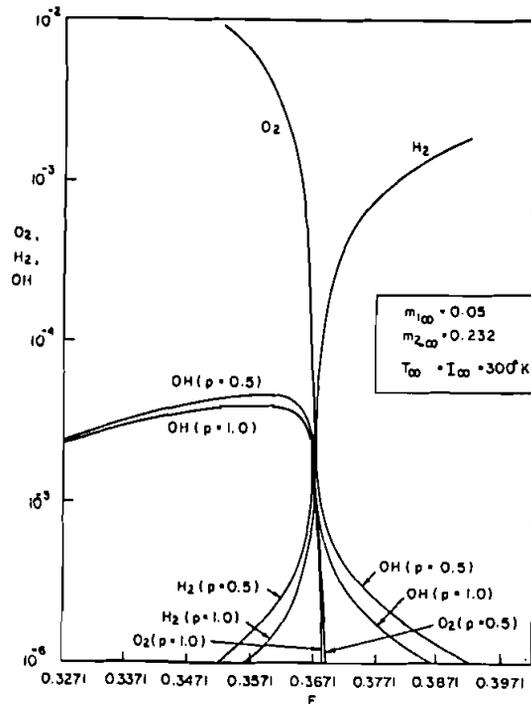


FIGURE 2 Profiles of concentrations of  $O_2$ ,  $H_2$  and  $OH$  with  $F$  showing the effect of pressure in equilibrium kinetics.

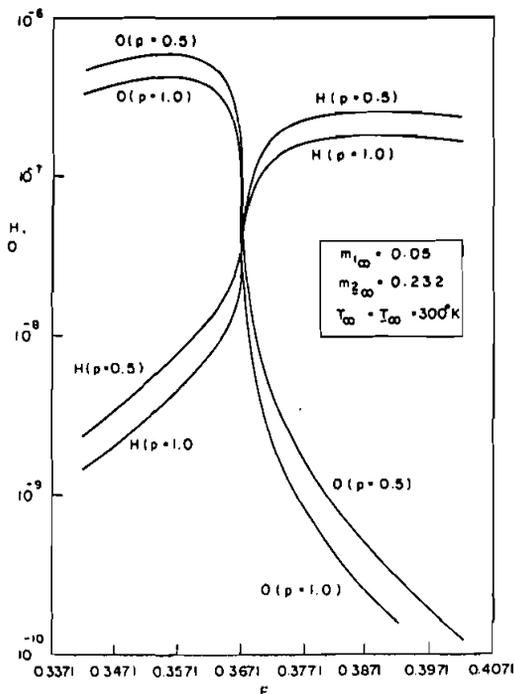


FIGURE 3 Profiles of concentrations of  $O$  and  $H$  with  $F$  showing the effect of pressure in equilibrium kinetics.

#### Importance of Different Steps in Mechanism

In the four step mechanism considered here, different reactions will have different states of non-equilibrium—some nearer to equilibrium than others. Bulewicz and Sudgen (1958) showed that the second reaction  $H_2 + OH \rightleftharpoons H_2O + H$  is in equilibrium in premixed one-dimensional hydrogen flames. Fowler (1962) has suggested that all bimolecular processes are in equilibrium because the forward and backward rates are very large and very nearly equal to each other. Kaskan (1958) suggested that bimolecular reactions reach a state of equilibrium very quickly beyond the luminous zone. Clarke (1969) studied a similar reaction scheme analytically to obtain the reaction broadening (for the case of large  $D_1$ ). Using the perturbation technique he found that all bimolecular reactions (Reactions II, III and IV) are in equilibrium on the oxidant side while Reactions II and IV are in equilibrium on the hydrogen side of flame. All these results show that the recombination process is rate determining step in the overall kinetics.

The above comments of different authors refer to situations arising out of their investigations when a stable flame is present in the system. No study seems to have been made at near extinction conditions. Clarke (1969), for instance, cannot make any comments on near-extinction conditions since the asymptotic analysis which he has used is invalid in this region.

In the present paper, in order to study the problem analytically and in the complete range (unstable and stable branches) MFST has been used. The solutions obtained by this technique are plotted as  $D_1$  versus  $T_n^*$ . Now in order to study the role of each reaction step, each reaction step is individually assumed to be in equilibrium and MFST solutions are obtained. Variations of  $D_1$  versus  $T_n^*$  are plotted in Figure 4 (see Table 3). If it is necessary to obtain the solution, say with second reaction only, in equilibrium (Case RE2), the equations to be solved simultaneously are (9), (10), (11) and (13), (15), (16) along with  $L_2^* = 0$ . Table 3 shows the values of  $D_{1,ext}$  and  $T_{n^*,ext}$  for different reactions in equilibrium.

From Figure 4, it is evident that the second and fourth reaction steps are in equilibrium as there is deviation of less than 10 percent as far as  $D_{1,ext}$  is concerned between the Cases REN, RE2, RE4 and RE24. The third reaction which governs the consumption rate of  $O_2$ , will be in equilibrium in high temperature region only, while in the low temper-

TABLE 3  
Effect of different steps in equilibrium on  $D_{1,ext}$  and  $T_n^*,_{ext}$

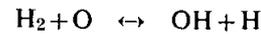
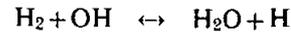
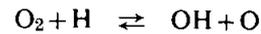
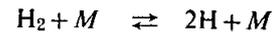
MFST solution for	$p = 1 \text{ atm}$ $T_\infty = T_{-\infty} = 300^\circ\text{K}$ $m_{1\infty} = 0.1$ $m_{2-\infty} = 0.232$		$p = 1 \text{ atm}$ $T_\infty = T_{-\infty} = 300^\circ\text{K}$ $m_{1\infty} = 0.05$ $m_{2-\infty} = 0.232$		$p = 0.5 \text{ atm}$ $T_\infty = T_{-\infty} = 300^\circ\text{K}$ $m_{1\infty} = 0.05$ $m_{2-\infty} = 0.232$		$p = 1 \text{ atm}$ $T_\infty = T_{-\infty} = 400^\circ\text{K}$ $m_{1\infty} = 0.1$ $m_{2-\infty} = 0.232$	
	$D_{1,ext}$	$T_n^*,_{ext}$	$D_{1,ext}$	$T_n^*,_{ext}$	$D_{1,ext}$	$T_n^*,_{ext}$	$D_{1,ext}$	$T_n^*,_{ext}$
REN: NO Reaction in equilibrium	0.753 E12	3.925	0.254 E13	3.775	0.267 E13	3.600	0.396 E12	2.975
RE1: 1st Reaction in equilibrium $\text{H}_2 + M \leftrightarrow \text{H} + \text{H} + M$	0.436 E15	5.800	0.209 E17	4.950	0.216 E17	4.780	0.112 E15	4.550
RE2: 2nd Reaction in equilibrium $\text{H}_2 + \text{OH} \leftrightarrow \text{H}_2\text{O} + \text{H}$	0.702 E12	3.925	0.240 E13	3.800	0.250 E13	3.625	0.367 E12	3.000
RE3: 3rd Reaction in equilibrium $\text{O}_2 + \text{H} \leftrightarrow \text{OH} + \text{O}$	0.208 E12	3.050	0.504 E12	2.950	0.669 E12	2.850	0.102 E12	2.120
RE4: 4th Reaction in equilibrium $\text{H}_2 + \text{O} \leftrightarrow \text{OH} + \text{H}$	0.726 E12	3.925	0.246 E13	3.775	0.259 E13	3.600	0.381 E12	2.975
RE24: 2nd and 4th Reactions in equilibrium $\text{H}_2 + \text{OH} \leftrightarrow \text{H}_2\text{O} + \text{H}$ $\text{H}_2 + \text{O} \leftrightarrow \text{OH} + \text{H}$	0.694 E12	3.925	0.233 E13	3.800	0.243 E13	3.625	0.353 E12	3.000

ature region this does not seem to be in equilibrium as differences in the results between RE3 and REN are large. Setting the third reaction in equilibrium (Case RE3) will not lead to reasonable prediction of the extinction characteristics. As far as the recombination reaction is concerned it is found that this is not in equilibrium even at high temperatures. These results agree well with the results of other workers described earlier.

Similarly, if we plot the variations of concentrations of major species ( $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ) at the flame position against  $D_1$  (Figure 5), it is observed that the conclusions which are drawn earlier are valid *i.e.*, (i) second and fourth reactions are in equilibrium on stable as well as unstable branch, (ii) the third reaction is not in equilibrium near extinction but on stable branch, it can be assumed to be in equilibrium, (iii) the recombination of H atom reaction is not in equilibrium even on stable branch.

The above studies imply that the four step reaction mechanism can be simplified to one with two

kinetic steps and the other two in equilibrium as below:



The above simplification is a reasonably good approximation for most applications where detailed kinetics has to be considered.

#### Overall Reaction Constants

The simplification of the mechanism as above is still quite involved for many applications. Most engineering analysis of combustion problems assume a single step reaction or equivalent single step reac-

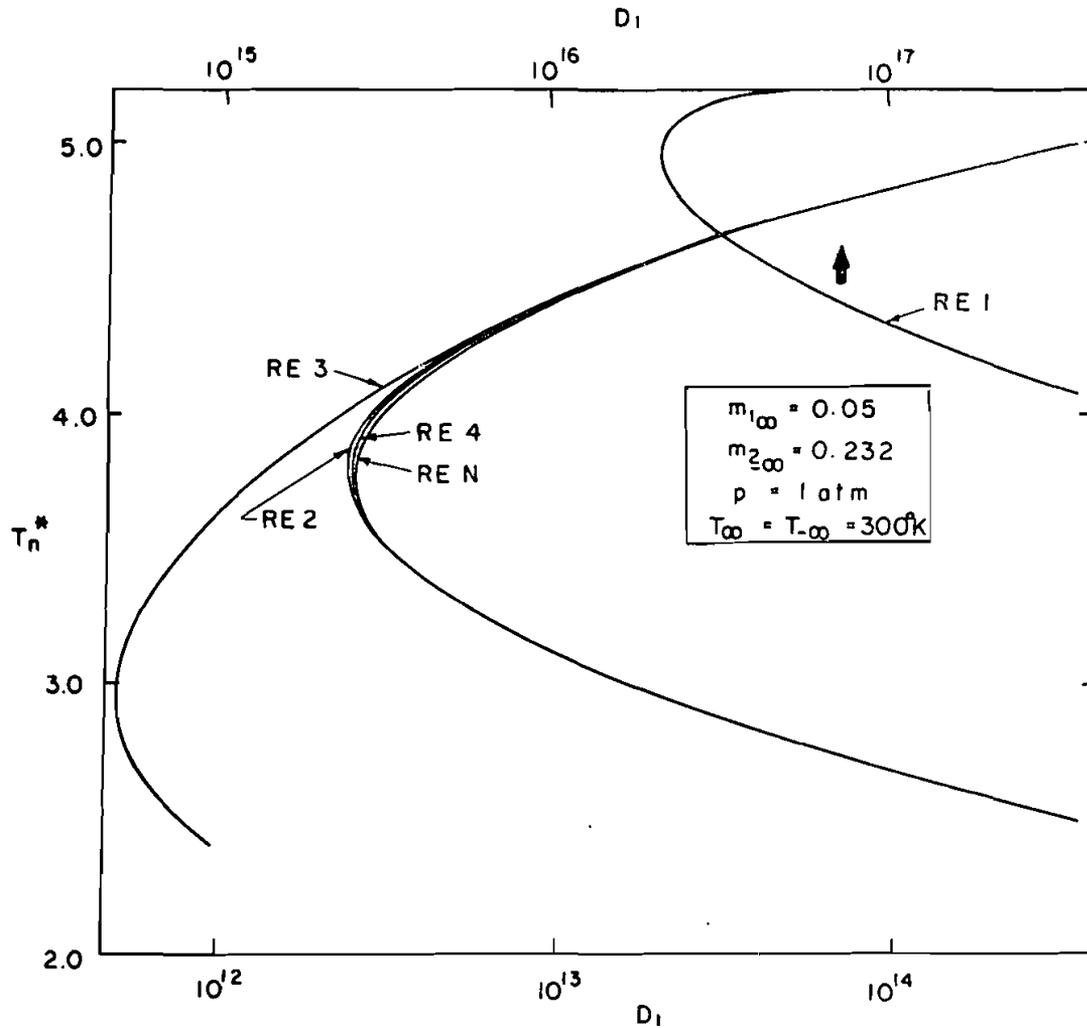
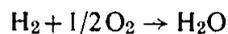


FIGURE 4 Importance of different reaction steps ( $T_n^*$  versus  $D_1$ ).

tion (ESSR). For instance, studies on (i) maximum heat release rates in premixed reactions and (ii) combustion of rocket propellants use this approximation. Further, the detailed kinetic steps and their rates have been a subject of many discussions and controversy even today. Under these circumstances it will be useful to examine if an ESSR which will constitute a good approximation to the original mechanism can be obtained. The reference quantities for comparison are certain overall measurable parameters like extinction conditions, maximum flame temperature etc.

The overall reaction in the present case is



The reaction rate of  $\text{H}_2$  is given by

$$\dot{w}(\text{H}_2) = M(\text{H}_2) Z_0 \rho^{\alpha+\beta} \frac{m(\text{H}_2)^\alpha m(\text{O}_2)^\beta}{M(\text{H}_2)^\alpha M(\text{O}_2)^\beta} \exp(-E_0/RT)$$

where  $Z_0$  = frequency factor

$E_0$  = activation energy

$\alpha$  and  $\beta$  = orders of reaction with respect to species  $\text{H}_2$  and  $\text{O}_2$ .

The problem is now one of estimating  $Z_0$ ,  $\alpha$ ,  $\beta$  and  $E_0$ , such that predictions of overall performance parameter like maximum temperature,  $D_{1,\text{ext}}$  for single step reaction model are in reasonable agree-

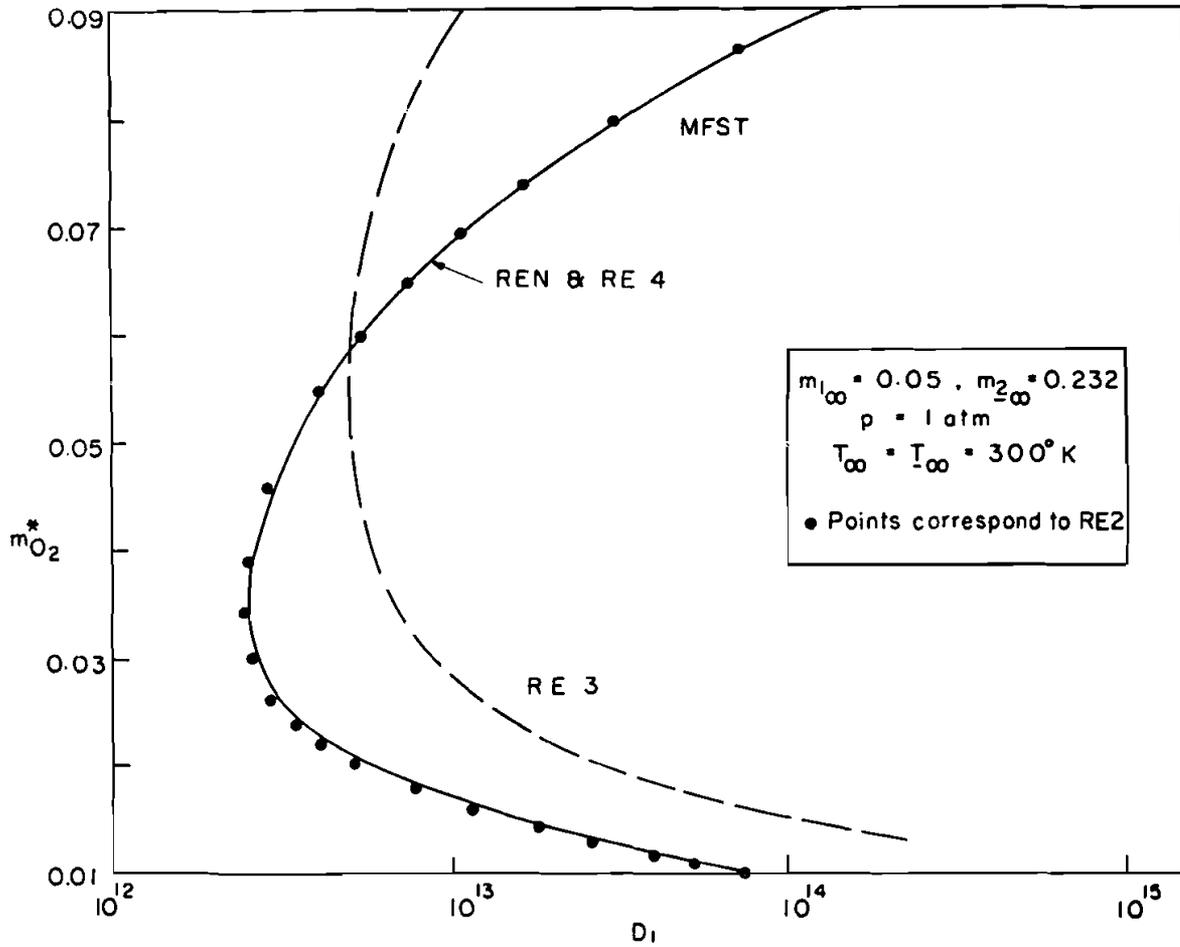
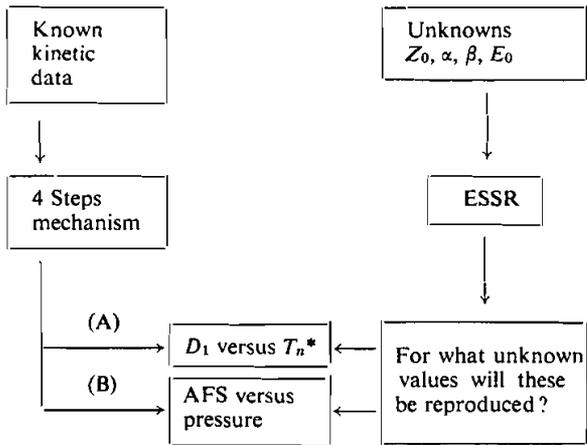


FIGURE 5 Importance of different reaction steps ( $m(O_2)^*$  versus  $D_1$ ).

ment with those for four step mechanism as is represented below:



The prediction of parameters of ESSR will therefore depend on the criterion chosen for comparison. The problem can be viewed as a form of "generalized curve fitting" to estimate unknown quantities. It is desirable if all the principal concentration profiles, temperature profiles for all  $D_1$  are reproduced. This, however, is too much to ask for, since number of unknowns is finite (4), but the number of criteria to be satisfied is multiply infinite. Hence, it is imperative that the number of points of comparisons be reduced. The two criteria which have been used are (A) the reproduction of  $D_1$  versus  $T_n^*$  profile or (B) AFS versus pressure.

*D1 versus Tn\* profiles* The actual  $D_1$  versus  $T_n^*$  profile to be reproduced is seen in Figure 4. The

data on single step reaction are

$$r = \text{stoichiometric ratio} = 8$$

$$H = \text{heat of combustion} = 28800 \text{ cal/gm of } O_2$$

$$c_p = \text{specific heat at constant pressure} = 0.41 \text{ cal/gm } ^\circ\text{K.}$$

The MFST solution for single step reaction (for general Lewis number) is given by (Marathe and Jain, 1972)

$$\frac{D_1}{C_1} = \exp\left(\frac{E_0}{RT_n^*}\right) \quad (18)$$

where

$$C_1 = m(O_2)_{-\infty} \sqrt{(2Sc)} \left\{ [1 - \text{erf}(\eta^* \sqrt{(Sc/2)})] - \frac{2m(O_2)^*}{m(O_2)_{-\infty}} \right\} \\ \times T_n^* \exp(-\eta^{*2} Sc/2) / \\ \sqrt{\pi m(H_2)^{\alpha} m(O_2)^{\beta} [1 - \text{erf}^2(\eta^* \sqrt{(Sc/2)})]} \quad (19)$$

$$T_n^* = 1/2 \left\{ (1 + T_{n-\infty}) + (1 - T_{n-\infty}) \right. \\ \times \text{erf}(\eta^* \sqrt{(Sc/2)}) \sqrt{Le} \\ \left. + B \sqrt{Le} \exp[\eta^{*2} Sc(Le-1)/2] \right. \\ \times \frac{[1 - \text{erf}^2(\eta^* \sqrt{(Sc/2)}) \sqrt{Le}]}{[1 - \text{erf}^2(\eta^* \sqrt{(Sc/2)})]} \\ \left. [1 - \text{erf}(\eta^* \sqrt{(Sc/2)}) - m(O_2)^*/m(O_2)_{-\infty}] \right\} \quad (20)$$

$$m(H_2)^* = m(O_2)^*/r \quad (21)$$

$$B = Hm(O_2)_{-\infty}/rc_p T_\infty \quad (22)$$

$$\text{erf}(\eta^* \sqrt{(Sc/2)}) = \frac{m(O_2)_{-\infty} - r m(H_2)_\infty}{m(O_2)_{-\infty} + r m(H_2)_\infty} \quad (23)$$

A value of  $m^*(O_2)$  is assumed and Eqs. (19) and (20) are used to obtain  $T_n^*$  and  $C_1$  respectively.  $D_1$  can be obtained for any given  $T_n^*$  from Figure 4, i.e. the value given by four step reaction mechanism. Thus,  $D_1/C_1$  is obtained against  $T_n^*$ . The slope of the curve  $[\ln(D_1/C_1)$  versus  $1/T_n^*]$  will give  $E_0/R T_\infty$  (Figure 6), the frequency factor can be obtained

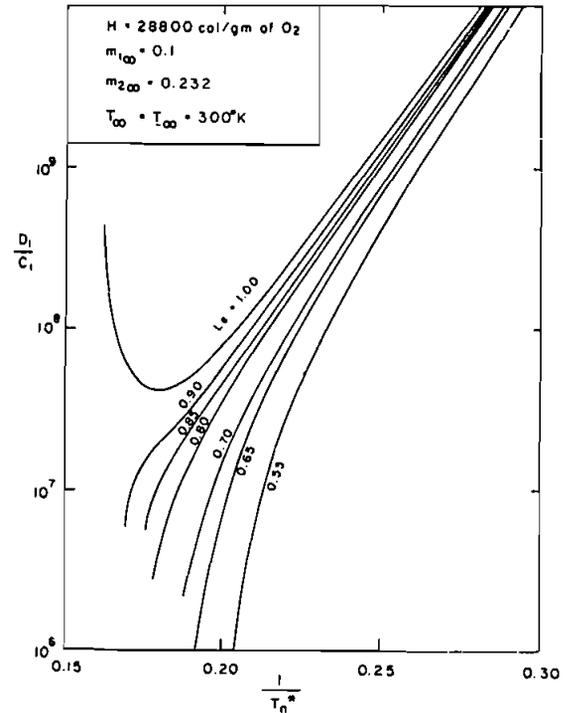
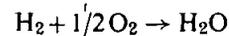


FIGURE 6 Plots of  $(D_1/C_1)$  versus  $(1/T_n^*)$  for various values of Lewis numbers.

later. It is to be pointed out that the value of Lewis number is as yet kept variable and will be chosen for the profile which gives straight line on  $\ln(D_1/C_1)$  versus  $1/T_n^*$  plot. This implies that the equivalent transformation into a single step reaction, if it occurs at all, could occur in one with  $Le$  other than unity. From Figure 6 it is clear that  $Le$  is less than unity. The plot shows that in no case is it a straight line over the entire range of  $T_n^*$  and  $D_1$ , though over most of the range it is straight. Further, values of  $T_n^*, \max$  which actually occur in four reaction scheme are unapproachable in ESSR since  $Le$  is less than unity.

This implies that this approach of obtaining ESSR is ruled out, because the data used for reproduction are overspecified.

*Apparent flame strength (AFS) versus pressure (p)*  
For the equivalent single step reaction (ESSR)



with orders of reaction  $\alpha$  and  $\beta$  with respect to  $H_2$  and  $O_2$  respectively, the reaction rate term in the

governing equation will be

$$\frac{R^\circ}{\rho(k+1)a} = \frac{Z_0 \rho^n m(\text{H}_2)^\alpha m(\text{O}_2)^\beta \exp(-E_0/RT)}{\rho(k+1)a M(\text{H}_2)^\alpha M(\text{O}_2)^\beta} \quad (24)$$

where  $E_0$  and  $Z_0$  are activation energy and frequency factor respectively for ESSR,  $n$  is the overall order of reaction =  $\alpha + \beta$ .

First Damköhler numbers of ESSR is defined as

$$D_1^\circ = \frac{Z_0 \rho_\infty^{n-1}}{(k+1)a} \quad (25)$$

The reaction rate will be

$$\begin{aligned} \frac{R^\circ}{\rho(k+1)a} &= D_1^\circ \frac{m(\text{H}_2)^\alpha m(\text{O}_2)^\beta}{M(\text{H}_2)^\alpha M(\text{O}_2)^\beta} \exp(-E_0/RT) \\ &\times \left(\frac{\rho}{\rho_\infty}\right)^{n-1} \end{aligned} \quad (26)$$

For axisymmetric jet with diameter 'd', the value of  $a$ , the stagnation velocity gradient (for potential distribution) is given by

$$a = U_{-\infty}/d = U_\infty/d \quad (27)$$

Thus

$$D_1^\circ = \frac{Z_0 \rho_\infty^{n-1} d}{(k+1)U_\infty} = \frac{Z_0 \rho_\infty^n d}{(k+1)\rho_\infty U_\infty} \quad (28)$$

At extinction with  $D_1^\circ = D_{1^\circ, \text{ext}}$  and  $(\rho_\infty, U_\infty)_{\text{ext}} = \text{AFS}$

$$D_{1^\circ, \text{ext}} = \frac{Z_0 \rho_\infty^n d}{(k+1) \text{AFS}}$$

Thus

$$\text{AFS} = \frac{Z_0 d \rho_\infty^n}{(k+1) D_{1^\circ, \text{ext}}} \quad (29)$$

For a given set of data  $(m(\text{H}_2)_\infty, T_\infty, m(\text{O}_2)_{-\infty}, \rho_\infty, p)$ , hence:

$$\text{AFS} \sim p^n \quad (30)$$

Thus, the slope of  $\ln(\text{AFS})$  versus  $\ln(p)$  will give us the order of reaction ( $n$ ). It should be noted, however, that the individual orders of reactions with respect to fuel and oxidant are not obtainable as the corresponding reaction of equivalent single step is obtained by invoking MFST (the condition of stoichiometric flux rates of fuel and oxidant at flame position leads to  $m(\text{H}_2)^* = m(\text{O}_2)^*/r$  and

thus only overall order appears in the rate expression). The procedure for obtaining  $n$  is now described below.

The AFS can be expressed in terms of known variables as

$$\text{AFS} = \rho_\infty U_{\infty, \text{ext}} = \frac{Z \rho_\infty^2 d}{(k+1) D_{1, \text{ext}}}$$

For axisymmetric stagnation point geometry  $k = 1$

$$\text{AFS} = \frac{Z M_\infty^2 d}{(RT_\infty)^2} \frac{1}{2} \frac{p^2}{D_{1, \text{ext}}} \quad (31)$$

here,

$Z$  = averaged frequency factor for 4-step reaction scheme defined by

$$\frac{\sum_{i=1}^4 (Z_f^{(i)} + Z_b^{(i)})}{8}$$

Thus

$$\text{AFS} = \frac{p^2 L}{D_{1, \text{ext}}} \quad (32)$$

where

$$L = \frac{Z M_\infty^2 d}{2(RT_\infty)^2} = \text{constant.}$$

Hence for a given set of data  $(m(\text{H}_2)_\infty, m(\text{O}_2)_{-\infty}, T_\infty, T_{-\infty}, D_{1, \text{ext}})$  is evaluated from four step reaction scheme and AFS is deduced from expression (31).  $p$  is then varied and corresponding values for AFS are obtained. It is worth noting that significant variations of AFS as a function of pressure occur through the dissociation reaction  $\text{H}_2 + M \rightleftharpoons 2\text{H} + M$ . Figure (7) shows the plot of  $\ln(\text{AFS}/L)$  versus  $\ln(p)$ . The slope of the curve varies with pressure.

At a pressure of one atmosphere the value of order of reaction so obtained is 1.92. This value compares well with a figure of 1.9 quoted by Lewis and von Elbe (1961). Further, Sawyer and Glassmann (1969) have performed experiments on determining the order of reaction with respect to fuel ( $\text{H}_2$ ) by using mixtures with large excess oxidant ( $\text{O}_2$ ). They showed that an order with respect to  $\text{H}_2$  is unity. A combination of these results leads us to conclude that the order with respect to  $\text{O}_2$  is 0.92.

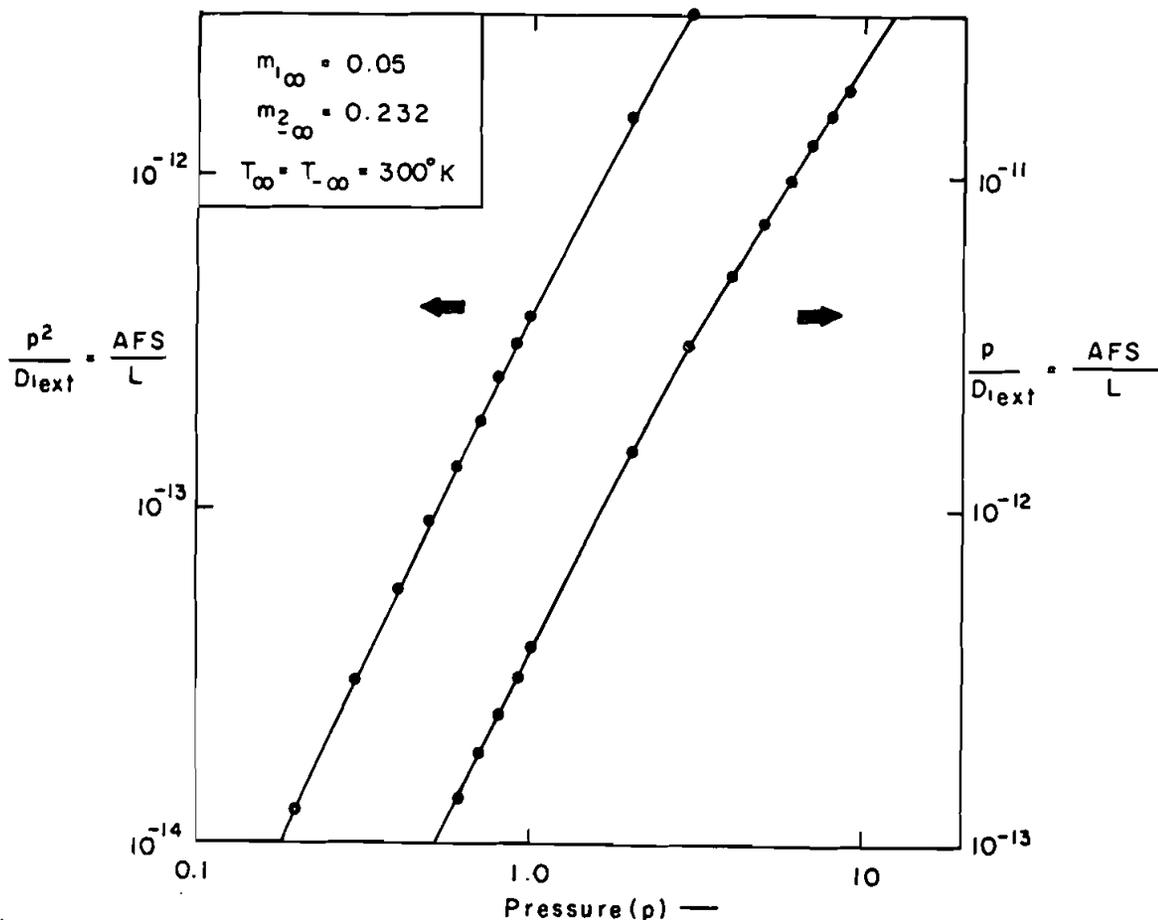


FIGURE 7 The variation of AFS with pressure.

Thus, we obtain that  $\alpha = 1.0$  and  $\beta = 0.92$  (at normal pressures).

The overall order of reaction becomes much larger, of the order of 2.5 at low pressures ( $\sim 0.001$  to  $0.1$  atm. range) and much smaller of the order of 1.0 or so, at pressures of the order of 100 atm. Potter and Berlad (1956), using burning velocity and quenching distance criterion to evaluate the value of overall order of reaction, found that at pressures less than one atm., the order of global reaction ( $H_2 + \text{air}$ ) is around 2.17. This agrees well with the values obtained by analytical solutions in this study. The above selected mechanism is not expected to be valid at pressures much larger than 60–70 atm., since three body collisions become important and most of such reactions have been excluded in the mechanism considered. Table 4 shows the values of order of reaction at different pressures.

TABLE 4

Values of order of ESSR at different pressures

Pressure ( $p$ )	Order of ESSR ( $n$ )
0.01	2.50
0.10	2.38
1.00	1.92
10.00	1.43
100.00	1.00

*Activation energy ( $E_0$ )* Instead of tracing the full curve of  $\ln(D_1/C_1)$  versus  $1/T_n^*$  for activation energy as mentioned earlier, the values of  $D_1$  for different values of hydrogen concentration in free stream ( $m_{1\infty}$ ) at extinction are matched with single step reaction.  $m_{1\infty}$  is varied between 0.05 to 0.25 in steps of 0.05. MFST solution with four step mech-

TABLE 5

Comparison of ( $D_{1,ext}/D_{1,ext,0.05}$ ) versus  $m_{1\infty}$  obtained by four reaction mechanism and ESSR

$m_{1\infty}$	$D_{1,ext}/D_{1,ext,0.05}$ Four reaction mechanism	$D_{1,ext}/D_{1,ext,0.05}$ for ESSR				
		Order 1.92			Order 2.0	Order 1.8
		$E_0 = 13200$	$E_0 = 13800$	$E_0 = 14000$	$E_0 = 13800$	$E_0 = 13800$
0.05	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.10	0.2966	0.3102	0.3070	0.2920	0.2980	0.3060
0.15	0.1790	0.1834	0.1770	0.1690	0.1735	0.1800
0.20	0.1314	0.1325	0.1275	0.1205	0.1242	0.1300
0.25	0.1065	0.1042	0.1000	0.0945	0.1000	0.1020

The unit of  $E_0$  is cal/mole

anism is used to find  $D_{1,ext}$ . Using different values of activation energy ( $E_0$ ),  $D_{1,ext}$  is calculated for single step reaction with unity Lewis number (the assumption is also used for four step mechanism) for different  $m_{1\infty}$  values. The results are obtained at a pressure of one atm., and overall order of reaction as 1.92.  $D_{1,ext}/D_{1,ext}(m_{1\infty} = 0.05)$  versus  $m_{1\infty}$  is tabulated (Table 5). This table shows that activation energy lies between 13.2 kcal/mole and 14.4 kcal/mole which agrees with the value 16 kcal/mole given by Fenn and Calcote (1953). Recently similar procedure has been used by Ablow and Wise (1974) to determine activation energy.

Further, one would like to know how the prediction of activation energy will be affected by a change of the overall order of reaction. It can be seen (Table 5) that even with the order of reaction taken as 1.8 or 2.0 the prediction of the activation energy is more or less the same as that corresponding to an order 1.92. Thus, even if the overall order of reaction is not predicted precisely,  $E_0$  (activation energy) appears to be predicted reasonably accurately.

**Frequency factor ( $Z_0$ )** Once the activation energy and order of reaction are determined, the values of  $D_{1,ext}$  given by four step mechanism and single step reaction are matched. The ratio of  $D_{1,ext}$  with these two schemes (four reaction scheme and ESSR) will give the ratio of frequency factor as:

$$Z_0 = \frac{\sum_{i=1}^4 (Z_f^{(i)} + Z_b^{(i)}) D_{1,ext}(\text{single step})}{8 D_{1,ext}(\text{four steps})}$$

In the calculations we have selected the different values of  $m_{1\infty}$  for determining frequency factors. The values are calculated with  $E_0 = 13.80$  kcal/mole,  $\alpha = 1$  and  $\beta = 0.92$ . Table 6 shows values of  $Z_0$  for different values of  $m_{1\infty}$ . The average value  $2.96 \times 10^{11}$  shows a maximum departure of 5 per cent.

TABLE 6

Values of frequency factor of ESSR for different  $m_{1\infty}$

$m_{1\infty}$	Frequency factor $Z_0$
0.05	3.02 E11
0.10	3.08 E11
0.15	2.96 E11
0.20	2.93 E11
0.25	2.84 E11
Average	2.96 E11

Finally we can write the expression for volumetric consumption rate of species in ESSR ( $H_2 + 1/2 O_2 \rightarrow H_2O$ ) at pressure of one atm., as

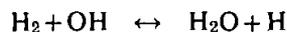
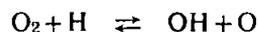
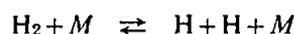
$$\frac{2.96 \times 10^{11} \rho^{1.92} m(H_2) m(O_2)^{0.92}}{M(H_2) (M(O_2))^{0.92}} \exp \left[ -\frac{13800 \pm 600}{RT} \right]$$

## CONCLUSIONS

Based on the work reported here, the following conclusions can be drawn.

1) The equilibrium broadening increases with a decrease in pressure.

2a) The four four step mechanism is equivalent to following simplified mechanism:



2b) On the stable branch  $\text{O}_2 + \text{H} \rightleftharpoons \text{OH} + \text{O}$  is also in equilibrium.

2c) At all points on  $D_1$  versus  $T_n^*$  curve, reaction involving recombination of H atoms is in non-equilibrium and is the rate determining step.

3) For equivalent single step reaction (ESSR)  $\text{H}_2 + 1/2 \text{O}_2 \rightarrow \text{H}_2\text{O}$  the kinetic constants are

Order with respect to  $\text{H}_2(\alpha) = 1.0$

Order with respect to  $\text{O}_2(\beta) = 0.92$

Overall order ( $n$ ) = 1.92

Activation energy ( $E_0$ ) =  $13.8 \pm 0.6$  kcal/mole

Frequency factory ( $Z_0$ ) =  $2.96 \times 10^{11}$  (cm<sup>3</sup>/mole sec)<sup>0.92</sup>

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## Appendix

The explicit expressions for consumption terms associated with the considered model of hydrogen-air system are

$$\dot{w}_1'' = M_1(R_1 + R_2 + R_4)$$

$$\dot{w}_2'' = M_2(R_3)$$

$$\dot{w}_3'' = M_3(-R_2)$$

$$\dot{w}_4'' = M_4(-2R_1 - R_2 + R_3 - R_4)$$

$$\dot{w}_5'' = M_5(-R_3 + R_4)$$

$$\dot{w}_6'' = M_6(R_2 - R_3 - R_4)$$

Here  $R_j$  is rate of progress of  $j$ th reaction. Using the law of mass action, we can write down  $R_j$  for all the

reversible steps as follows

$$R_1 = k_f^{(1)} \frac{\rho^2 m_1}{M_1 M_m} - k_b^{(1)} \frac{\rho^3 m_4^2}{M_4^2 M_m}$$

$$R_2 = k_f^{(2)} \frac{\rho^2 m_1 m_6}{M_1 M_6} - k_b^{(2)} \frac{\rho^2 m_3 m_4}{M_3 M_4}$$

$$R_3 = k_f^{(3)} \frac{\rho^2 m_2 m_4}{M_2 M_4} - k_b^{(3)} \frac{\rho^2 m_5 m_6}{M_5 M_6}$$

$$R_4 = k_f^{(4)} \frac{\rho^2 m_1 m_5}{M_1 M_5} - k_b^{(4)} \frac{\rho^2 m_4 m_6}{M_4 M_6}$$