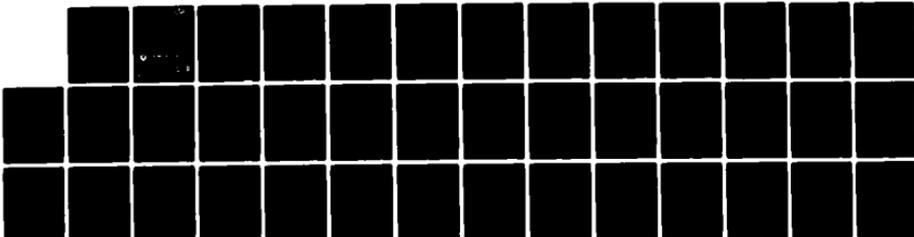


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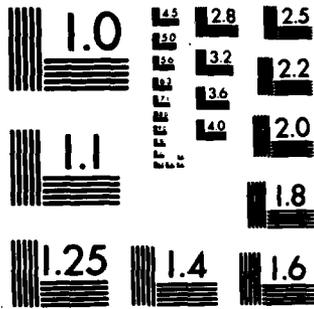
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TECHNICAL REPORT ARBRL-TR-02539

KINETIC MECHANISMS FOR PREMIXED, LAMINAR,
STEADY STATE METHANE/AIR FLAMES

Terence P. Coffee

December 1983



US ARMY ARMAMENT RESEARCH AND DEVELOPMENT CENTER
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) REC 5 A number of kinetic schemes have been used to model premixed, laminar, one-dimensional methane/air flames. Seven such kinetic schemes, including two new models, are compared with one another and with experimental data. The two new models, one with 14 species and one with 20 species, both agree with the experimental data over a range of stoichiometries from lean to rich. (Continued)		

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20. Abstract (Cont'd):

All of the models show good agreement for lean to slightly rich flames. This does not validate any of the models, even for this limited range. Rather, it is shown that the quantities measured are fairly insensitive to much of the mechanism. Therefore, models with incorrect kinetics can agree with the experimental data.

In particular, the contribution of the C_2 species to methane combustion is examined. While these species are important, we conclude that there is insufficient data to determine quantitatively the effects of the C_2 chemistry reactions.

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RESEARCH AND DEVELOPMENT

I. INTRODUCTION

We are interested here in the detailed kinetics governing premixed, laminar, one-dimensional methane/air flames. The earliest such scheme, introduced by Smoot, Hecker and Williams¹ and by Tsatsaronis,² involved 14 species and about 30 reactions. These include the reaction $\text{CH}_2\text{O} + \text{M} \rightarrow \text{CO} + \text{H}_2 + \text{M}$, which is probably not an elementary reaction in atmospheric pressure flames. Warnatz³ introduced a much more complicated scheme involving 23 species and 50 reactions. In particular, he claimed that C_2 species were important for modeling rich or even near stoichiometric flames. Dixon-Lewis⁴ attempted to identify the major reaction channels in large mechanisms such as that of Warnatz. He compares two mechanisms, one with 14 species and one with 18 species (including C_2 chemistry). Both schemes were considered valid for lean or stoichiometric flames. Dixon-Lewis agrees with Warnatz that it is necessary to include C_2 chemistry to adequately model rich flames.

In this paper we introduce two new models. The simpler mechanism (14 species, 39 reactions) does not include C_2 chemistry, but unexpectedly still does a reasonable job of reproducing experimental data for lean and rich flames. The more complicated model (20 species, 63 reactions) is also known to be only an approximation, since a number of species and reactions have been omitted. Nevertheless, it reproduces the experimental data quite well.

Comparisons are made among the seven kinetic models. We conclude that there is insufficient data to validate any particular mechanism at this time.

II. NUMERICAL PROCEDURE

The governing equations for the chemical species and the temperature are given in Reference 5. These equations are integrated in time, using a finite

¹L.D. Smoot, W.C. Hecker, and G.A. Williams, "Prediction of Propagating Methane-Air Flames," *Combustion and Flame*, Vol. 26, pp. 323-342, 1976.

²G. Tsatsaronis, "Prediction of Propagating Laminar Flames in Methane, Oxygen, Nitrogen Mixtures," *Combustion and Flame*, Vol. 33, pp. 217-239, 1978.

³J. Warnatz, "The Structure of Laminar Alkane-, Alkene-, and Acetylene Flames," 18th International Combustion Symposium, The Combustion Institute, Pittsburgh, PA, pp. 369-384, 1981.

⁴G. Dixon-Lewis, "Aspects of the Kinetic Modeling of Methane Oxidation in Flames," 1st Specialists Meeting (International) of the Combustion Institute, France, pp. 284-289.

⁵T.P. Coffee and J.M. Heimerl, "Transport Algorithms for Premixed, Laminar Steady-State Flames," *Combustion and Flame*, Vol. 43, pp. 273-289, 1981.

element method, until the steady-state solution is obtained.^{6,7,8} All calculations have been done on a Cyber 76.

Besides the kinetics information, thermodynamic and transport data are required. For most species, the polynomial fits of Gordon and McBride⁹ are used. For species not included in the above, polynomial fits are made to the data of Benson.¹⁰

The molecular parameters σ , ϵ/k , and μ are from Warnatz.³ The polarizabilities are from Reid and Sherwood.¹¹ These are used to compute the individual species thermal conductivities and the binary diffusion coefficients. A test problem was also computed using the transport parameters of Svehla.¹² The results were virtually identical with the previous calculation using the Warnatz parameters.

The multicomponent mass fluxes ($\rho Y_i V_i$) and heat flux (q) are computed using the methods of Reference 5. All the preliminary work was done using Method V, the simplest procedure. Convergence took from 2 to 12 minutes of computer time, depending on the mechanism and the stoichiometry. In general, very rich or very lean flames (near the extinction point) took longer to converge. Once a particular problem had been solved using one kinetics set, the steady state solution could be used as the start of the time integration for the other kinetics sets. This led to substantial savings.

⁶ T.P. Coffee and J.M. Heimerl, "A Method for Computing the Flame Speed for a Laminar, Premixed, One Dimensional Flame," ARBRL-TR-02212, January 1980 (AD A082803).

⁷ J.M. Heimerl and T.P. Coffee, "The Detailed Modeling of Premixed, Laminar Steady-State Flames. I. Ozone," Combustion and Flame, Vol. 39, pp. 301-315, 1980.

⁸ T.P. Coffee, "A Computer Code for the Solution of the Equations Governing a Laminar, Premixed, One-Dimensional Flame," ARBRL-MR-03165, April 1982.

⁹ S. Gordon and B.J. McBride, "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks and Chapman-Jouguet Detonations," NASA-SP-273, 1971 (1981 program version).

¹⁰ S. Benson, Thermochemical Kinetics, 2nd edition, John Wiley and Sons, NY, 1976.

¹¹ R.C. Reid and J.K. Sherwood, The Properties of Gases and Liquids, 2nd edition, McGraw-Hill, NY, 1966.

¹² R.A. Svehla, "Estimated Viscosities and Thermal Conductivities of Gases at High Temperatures," NASA Technical Report R-132, Lewis Research Center, Cleveland, OH, 1962.

The flame speeds and profiles reported in this paper were computed using transport Method VI. This algorithm is very accurate, but is computationally much more complex. Even using the Method V solutions as starting points, the 14 species model required an additional 30 to 60 minutes of computer time. The 20 species model required an additional 2 to 4 hours.

III. KINETIC SCHEME

The forward reactions used in this paper are listed in Table 1. The rates of the back reactions are computed from the forward rate coefficients and the equilibrium constant for the reaction. Additional species and reactions were considered, but they turned out to have no noticeable effect on the problems considered.

The first 23 reactions are from Dixon-Lewis. These have been checked extensively in earlier studies of $H_2/O_2/N_2$ flames¹³ and $CO/H_2/O_2/N_2$ flames.¹⁴

Reactions 24 through 31 are derived from a series of shock tube experiments by Dean, et al.^{15,16} The formaldehyde reaction rates (28 through 31) are substantially lower than the rates previously used in flame modeling.

The CHO reactions (32 through 35) are not well known. We have more or less arbitrarily chosen the values of Dixon-Lewis.⁴

The next four reactions (36 through 39) are a miscellaneous set from a kinetics data base compiled by Gelinis.¹⁷

These 39 reactions form a 14 species model. Methane is oxidized along the standard pathway $CH_4 \rightarrow CH_3 \rightarrow CH_2O \rightarrow CHO \rightarrow CO \rightarrow CO_2$.

For reaction 40, we begin with the high pressure rate $k = 2.8 \times 10^{14} T^{-0.4}$. This rate is used by both Warnatz³ and Dixon-Lewis.⁴ It must be

¹³G. Dixon-Lewis, "Kinetic Mechanism, Structure, and Properties of Premixed Flames in Hydrogen-Oxygen-Nitrogen Mixtures," Phil. Trans. Roy. Soc. (London), Vol. A292, pp. 45-99, 1979.

¹⁴M.A. Cherian, P. Rhodes, R.J. Simpson, and G. Dixon-Lewis, "Structure, Chemical Mechanism and Properties of Premixed Flames in Mixtures of Carbon Monoxide, Nitrogen, and Oxygen with Hydrogen and Water Vapor," Phil. Trans. Roy. Soc. (London), Vol. A303, pp. 181-212, 1981.

¹⁵A.M. Dean, R.L. Johnson, and D.C. Steiner, "Shock-Tube Studies of Formaldehyde Oxidation," Combustion and Flame, Vol. 37, pp. 41-62, 1980.

¹⁶A.M. Dean and R.L. Johnson, "Shock Tube Studies of the $N_2O/CH_4/CO/Ar$ and $N_2O/C_2H_6/CO/Ar$ Systems," Combustion and Flame, Vol. 37, pp. 109-123, 1980.

¹⁷R.J. Gelinis, "Ignition Kinetics of C1 and C2 Hydrocarbons," Science Applications, Inc., Preprint No. SAI/PL/C279, December 1979.

TABLE 1. REACTIONS IN THE CH₄/AIR SYSTEM

Reaction	A*	B	C	Reference
1. OH + H ₂ → H ₂ O + H	1.17E9**	1.3	1825	4
2. H + O ₂ → OH + O	1.42E14	0.0	8250	4
3. O + H ₂ → OH + H	1.80E10	1.0	4480	4
4. H + O ₂ + M' → HO ₂ + M'	1.03E18	-0.72	0	4
5. H + HO ₂ → OH + OH	1.40E14	0.0	540	4
6. H + HO ₂ → O + H ₂ O	1.00E13	0.0	540	4
7. H + HO ₂ → H ₂ + O ₂	1.25E13	0.0	0	4
8. OH + HO ₂ → H ₂ O + O ₂	7.50E12	0.0	0	4
9. O + HO ₂ → OH + O ₂	1.40E13	0.0	540	4
10. O + HO ₂ → OH + O ₂	1.25E12	0.0	0	4
11. H + H + H ₂ → H ₂ + H ₂	9.20E16	-0.6	0	4
12. H + H + N ₂ → H ₂ + N ₂	1.00E18	-1.0	0	4
13. H + H + O ₂ → H ₂ + N ₂	1.00E18	-1.0	0	4
14. H + H + H ₂ O → H ₂ + O ₂	6.00E19	-1.25	0	4
15. H + H + CO → H ₂ + CO	1.00E18	-1.0	0	4
16. H + H + CO ₂ → H ₂ + CO ₂	5.49E20	-2.0	0	4
17. H + H + CH ₄ → H ₂ + CH ₄	5.49E20	-2.0	0	4
18. H + OH + M'' → H ₂ O + M''	1.60E22	-2.0	0	4
19. H + O + M'' → OH + M''	6.20E16	-0.6	0	4
20. OH + OH → O + H ₂ O	5.75E12	0.0	390	4
21. OH + CO → CO ₂ + H	1.50E7	1.3	-385	4
22. O + CO + M' → CO ₂ + M'	5.40E15	0.0	2300	4

* A is in units of cm³/mole-sec or cm⁶/mole²-sec, k=AT^Bexp (-C/T).

** 1.17E9 = 1.17 x 10⁹.

23.	$\text{H} + \text{CO} + \text{M}' \rightarrow \text{CHO} + \text{M}'$	5.00E14	0.0	755	4
24.	$\text{CH}_4 + \text{O} \rightarrow \text{CH}_3 + \text{OH}$	4.07E14	0.0	7040	15
25.	$\text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2$	7.24E14	0.0	7590	15
26.	$\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	1.55E6	2.13	1230	15
27.	$\text{CH}_4 + \text{M} \rightarrow \text{CH}_3 + \text{H} + \text{M}$	4.68E17	0.0	46910	15
28.	$\text{CH}_3 + \text{O} \rightarrow \text{CH}_2\text{O} + \text{H}$	6.02E13	0.0	0	15
29.	$\text{CH}_2\text{O} + \text{O} \rightarrow \text{CHO} + \text{OH}$	1.82E13	0.0	1550	15
30.	$\text{CH}_2\text{O} + \text{H} \rightarrow \text{CHO} + \text{H}_2$	3.31E14	0.0	5290	15
31.	$\text{CH}_2\text{O} + \text{OH} \rightarrow \text{CHO} + \text{H}_2\text{O}$	7.58E12	0.0	72	15
32.	$\text{CHO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$	3.00E12	0.0	0	4
33.	$\text{CHO} + \text{H} \rightarrow \text{CO} + \text{H}_2$	4.00E13	0.0	0	4
34.	$\text{CHO} + \text{OH} \rightarrow \text{CO} + \text{H}_2\text{O}$	5.00E12	0.0	0	4
35.	$\text{CHO} + \text{O} \rightarrow \text{CO} + \text{OH}$	1.00E13	0.0	0	4
36.	$\text{CH}_2\text{O} + \text{CH}_3 \rightarrow \text{CHO} + \text{CH}_4$	2.23E13	0.0	2590	16
37.	$\text{CH}_3 + \text{OH} \rightarrow \text{CH}_2\text{O} + \text{H}_2$	3.98E12	0.0	0	16
38.	$\text{CH}_3 + \text{HO}_2 \rightarrow \text{CH}_4 + \text{O}_2$	1.02E12	0.0	200	16
39.	$\text{CO} + \text{HO}_2 \rightarrow \text{CO}_2 + \text{OH}$	1.50E14	0.0	11900	16
40.	$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$	4.56E37	-7.65	4250	4,17
41.	$\text{C}_2\text{H}_6 + \text{O} \rightarrow \text{C}_2\text{H}_5 + \text{OH}$	2.51E13	0.0	3200	16
42.	$\text{C}_2\text{H}_6 + \text{H} \rightarrow \text{C}_2\text{H}_5 + \text{H}_2$	5.00E2	3.5	2620	16
43.	$\text{C}_2\text{H}_6 + \text{OH} \rightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O}$	6.63E13	0.0	675	16
44.	$\text{C}_2\text{H}_5 + \text{H} \rightarrow \text{C}_2\text{H}_6$	7.23E13	0.0	0	16
45.	$\text{C}_2\text{H}_5 + \text{H} \rightarrow \text{CH}_3 + \text{CH}_3$	3.73E13	0.0	0	16
46.	$\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H}$	2.29E11	0.0	19120	16
47.	$\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2$	1.53E12	0.0	2446	16
48.	$\text{C}_2\text{H}_4 + \text{O} \rightarrow \text{CH}_2 + \text{CH}_2\text{O}$	2.53E13	0.0	2516	16
49.	$\text{C}_2\text{H}_4 + \text{OH} \rightarrow \text{CH}_2\text{O} + \text{CH}_3$	5.00E13	0.0	3020	16

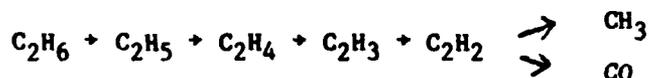
50.	$C_2H_4 + O \rightleftharpoons C_2H_3 + OH$	2.53E13	0.0	2516	16
51.	$C_2H_4 + O_2 \rightleftharpoons C_2H_3 + HO_2$	1.33E15	0.0	27680	16
52.	$C_2H_4 + H \rightleftharpoons C_2H_3 + H_2$	2.00E15	0.0	10000	16
53.	$C_2H_4 + OH \rightleftharpoons C_2H_3 + H_2O$	4.40E14	0.0	3270	16
54.	$C_2H_3 + M \rightleftharpoons C_2H_2 + H + M$	3.01E16	0.0	20380	16
55.	$C_2H_3 + O_2 \rightleftharpoons C_2H_2 + HO_2$	1.57E13	0.0	5030	16
56.	$C_2H_3 + H \rightleftharpoons C_2H_2 + H_2$	7.53E13	0.0	0	16
57.	$C_2H_3 + OH \rightleftharpoons C_2H_2 + H_2O$	1.00E13	0.0	0	16
58.	$C_2H_2 + OH \rightleftharpoons CH_3 + CO$	5.48E13	0.0	6890	16
59.	$CH_3 + H \rightleftharpoons CH_2 + H_2$	2.00E11	0.7	-1500	16
60.	$CH_3 + OH \rightleftharpoons CH_2 + H_2O$	6.00E10	0.7	1010	16
61.	$CH_2 + O_2 \rightleftharpoons CHO + OH$	1.00E14	0.0	1860	16
62.	$CH_2 + O_2 \rightleftharpoons CH_2O + O$	1.00E14	0.0	1860	16
63.	$CH_2 + O_2 \rightleftharpoons CO_2 + H_2$	1.00E14	0.0	1860	16

[M] = total concentration

[M'] = $[H_2] + 0.74 [CO] + 1.47 [CO_2] + 0.35 [O_2] + 6.5 [H_2O] + 0.44 [N_2]$

[M''] = $[H_2] + [CO] + [CO_2] + [O_2] + 5.0 [H_2O] + [N_2]$

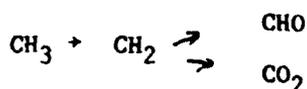
further modified by the fall off method of Luther and Troe.¹⁸ The parameters in Table 1 are a least squares fit of the modified values for a pressure of one atmosphere. This is the primary channel for the formation of C₂ hydrocarbons. The C₂ reactions are 40 through 58.¹⁷ The primary pathway is



There is also a side channel through reactions 48 and 49,



The last five reactions (59 through 63) consist of CH₂ chemistry.¹⁷ The pathway is



This sequence has not been included in previous CH₄/air flame models.

IV. COMPARISON WITH EXPERIMENTAL DATA

Here we compare the seven models discussed above with experimental data. All flames considered in this section are atmospheric pressure, unbounded, methane/air flames with an initial temperature of 298K.

Many measurements have been made on the burning velocity of methane/air flames. Andrews and Bradley¹⁹ have critically reviewed the different experimental techniques. Following their recommendations, we have used the

¹⁸K. Luther and J. Troe, "Weak Collision Effects in Dissociation Reactions at High Temperatures," 17th International Combustion Symposium, The Combustion Institute, Pittsburgh, PA, pp. 535-542, 1979.

¹⁹G.E. Andrews and D. Bradley, "Determination of Burning Velocities: A Critical Review," *Combustion and Flame*, Vol. 18, pp. 133-153, 1972.

results of four experiments.²⁰⁻²³ While there is scatter in the data, the results are generally consistent.

The models of Smoot, Hecker and Williams (SHW14) and Dixon-Lewis (DL14 and DL18) are accurate for lean to slightly rich flames. Tsatsaronis [TS14] modified the model of Smoot, et al, so that it is accurate for rich flames, but the calculated burning velocities are low for stoichiometric to slightly lean flames. The more complicated model of Warnatz (W23) is reasonably accurate over the entire range, although the flame speeds are low for rich flames.

Figure 1 shows the results for the two new models introduced in this paper (CF14 and CF20), the model of Warnatz, and the experimental burning velocities. The results are given in terms of the equivalence ratio $\phi = 2 XCH_4/XO_2$, where X represents the initial mole fraction of the species. All experimental values have been corrected to 298 K. Both new models are accurate over the entire range, although slightly low for very lean or very rich flames. The values calculated here using the Warnatz model (W23) for rich flames are slightly lower than those reported by Warnatz.³ We do not know the reason for the discrepancy.

Laser methods have recently been used to measure species and temperature profiles. Bechtel and Teets²⁴ measured OH profiles using laser-induced fluorescence for $\phi = 0.86, 1.00, \text{ and } 1.25$. In a later paper, Bechtel, et al,²⁵ measured $H_2, CO, CH_4, O_2, CO_2, H_2O,$ and temperature profiles for the same three cases.

These profiles were compared with calculations using the SHW14 model. Agreement was very good except for the H_2 profile. The measured H_2

²⁰G.E. Andrews and D. Bradley, "Determination of Burning Velocity by Double Ignition in a Closed Vessel," Combustion and Flame, Vol. 20, pp. 77-89, 1973.

²¹R. Gunther and G. Janish, "Measurements of Burning Velocity in a Flat Flame Front," Combustion and Flame, Vol. 19, pp. 49-53, 1972.

²²R. Lindow, "Eine verbesserte Brennermethode zur Bestimmung der laminaren Flammgeschwindigkeiten von Brenngas/Luft-Gemischen," Brennstoff Wärme Kraft, Vol. 20, pp. 8-14, 1968.

²³S.B. Reed, J. Mineur, and J.P. McNaughton, "The Effect on the Burning Velocity of Methane of Vitiating of Combustion Air," J. Inst. Fuel, Vol. 44, pp. 149-155, 1971.

²⁴J.H. Bechtel and R.E. Teets, "Hydroxyl and Its Concentration Profile in Methane-Air Flames," Applied Optics, Vol. 18, pp. 4138-4144, 1979.

²⁵J.H. Bechtel, R.J. Blint, C.J. Disch, and D.A. Weinberger, "Atmospheric Pressure Premixed Hydrocarbon-Air Flames: Theory and Experiment," Combustion and Flame, Vol. 42, pp. 197-213, 1981.

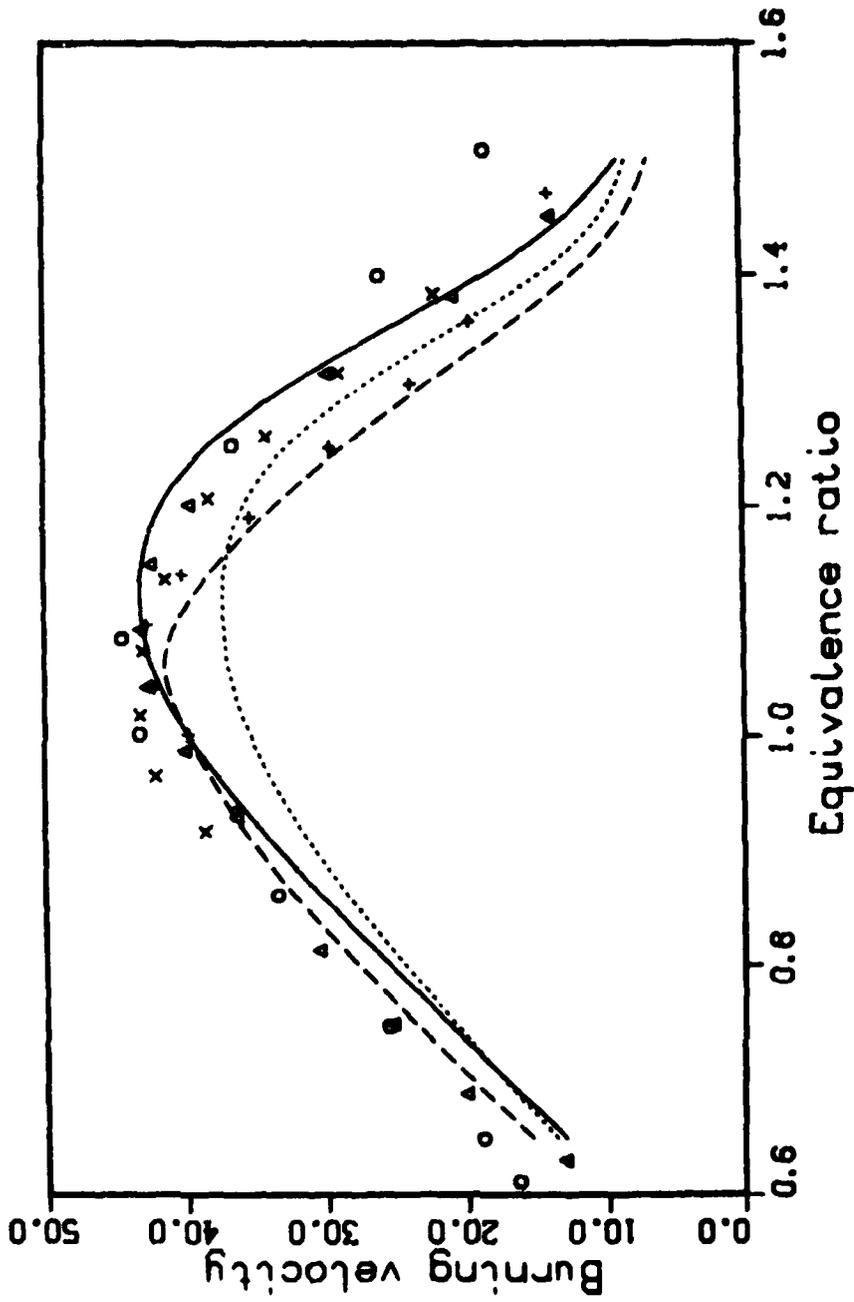


Figure 1. Burning Velocity Versus Equivalence Ratio. Model Values - CF20 (line), CF14 (Dot), and W23 (Dash). Experimental Points - Andrews and Bradley (Circle), Gunther and Janisch (Triangle), Reed (Plus), and Lindow (Times).

concentration was much greater than the calculated H_2 concentration in the leading edge of the flame.

One explanation considered by the authors is an inadequate treatment of the diffusion of H_2 in their model. This appears to be the case. When the SHW14 model was run using our code, agreement for the H_2 profile was very good.

Calculations were made for each of the three cases above for all seven kinetic models. Agreement was excellent for all models for the CO_2 , O_2 , CH_4 , H_2O , and temperature profiles. The primary difference was that the experimental temperature dropped in the post-flame region, while the model temperatures increased. This can be explained by heat lost to the wall.²⁵

Agreement for the H_2 and CO profiles was very good, but with some scatter in the calculated peak heights.

Agreement for the OH profile was good for the lean and stoichiometric cases. For the rich flame, all of the models predicted a higher and earlier peak than that given by the experiment. This suggests either a problem with the experiment or some basic inadequacy in the standard models for rich flames or both.

Figures 2-5 show the experimental profiles for a stoichiometric flame compared to the 3 models including C_2 chemistry. The other models are quite similar.

V. SENSITIVITY ANALYSIS

A sensitivity analysis is useful in trying to understand a complex system like the CH_4 /air kinetics. A procedure for finding sensitivity coefficients for flames was developed in Reference 26.

This analysis was done for a stoichiometric CH_4 /air flame using the CF20 model. The larger logarithmic sensitivity coefficients S_E^i for the flame speed are given in Table 2. These are defined such that if the rate of the reaction is changed by a small factor α , the flame speed will change by α to the S_E^i power, i.e., $v \equiv v_0 \alpha^{S_E^i}$. Analytically, the sum of S_E^i must equal 0.5.²⁶

The flame is most sensitive to the chain branching reaction 2 [$H + O_2 \rightarrow OH + H$]. Radicals must be produced for the flame to propagate, and reaction 2 is the principal bottleneck for reaction production.

The flame is much less sensitive to the corresponding chain branching reaction 3 [$O + H_2 \rightarrow OH + H$]. Since the H_2 concentration is small, this

²⁶T.P. Coffe and J.M. Heimerl, "Sensitivity Analysis for Premixed Laminar, Steady-State Flames," Combustion and Flame, Vol. 50, pp. 323-340, 1983.

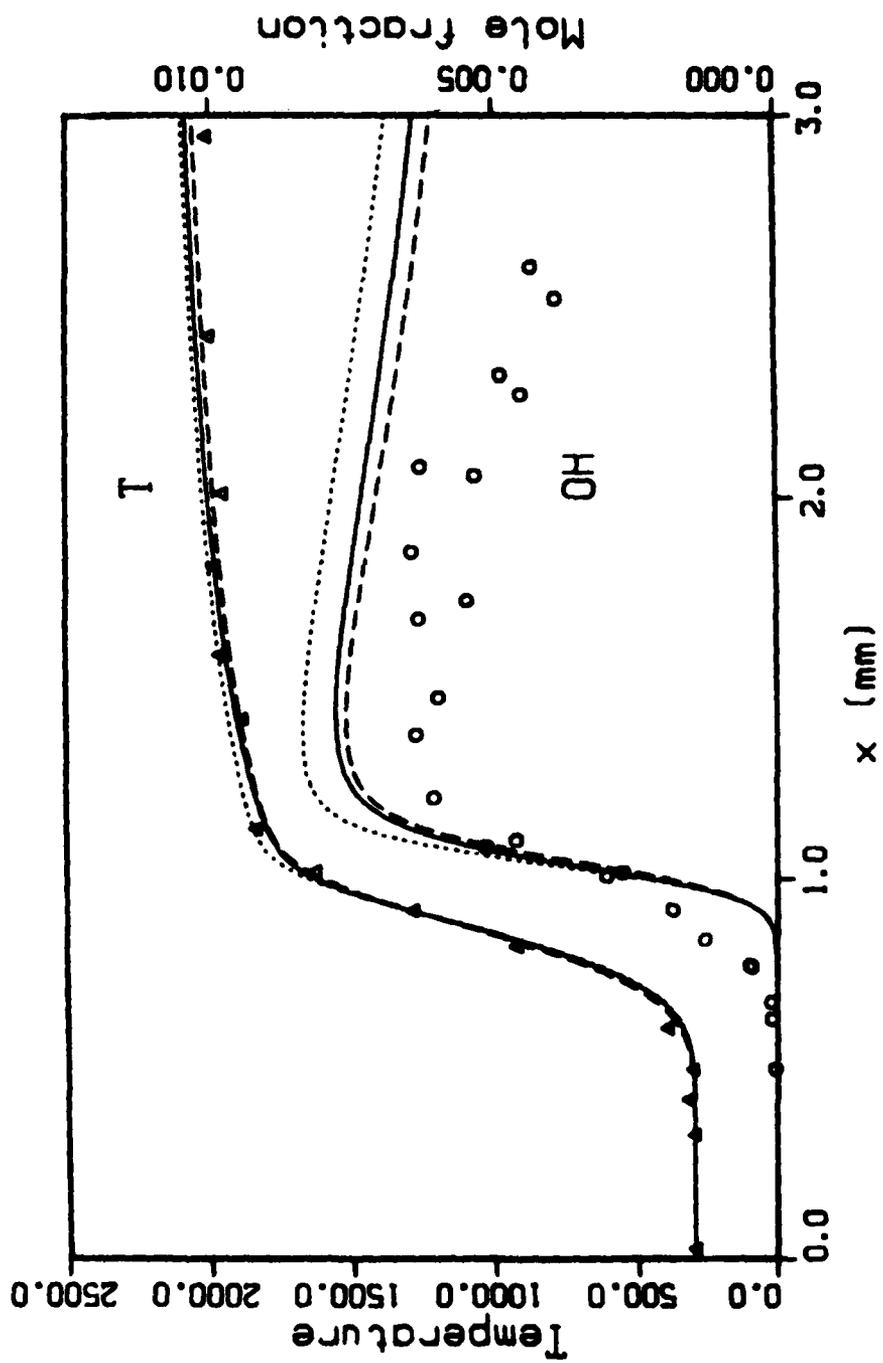


Figure 2. Stoichiometric CH_4/Air Flame. Model Values - CF20 (Line), W23 (Dot), and DL18 (Dash).
Bechtel Experimental Points. T and OH Profiles.

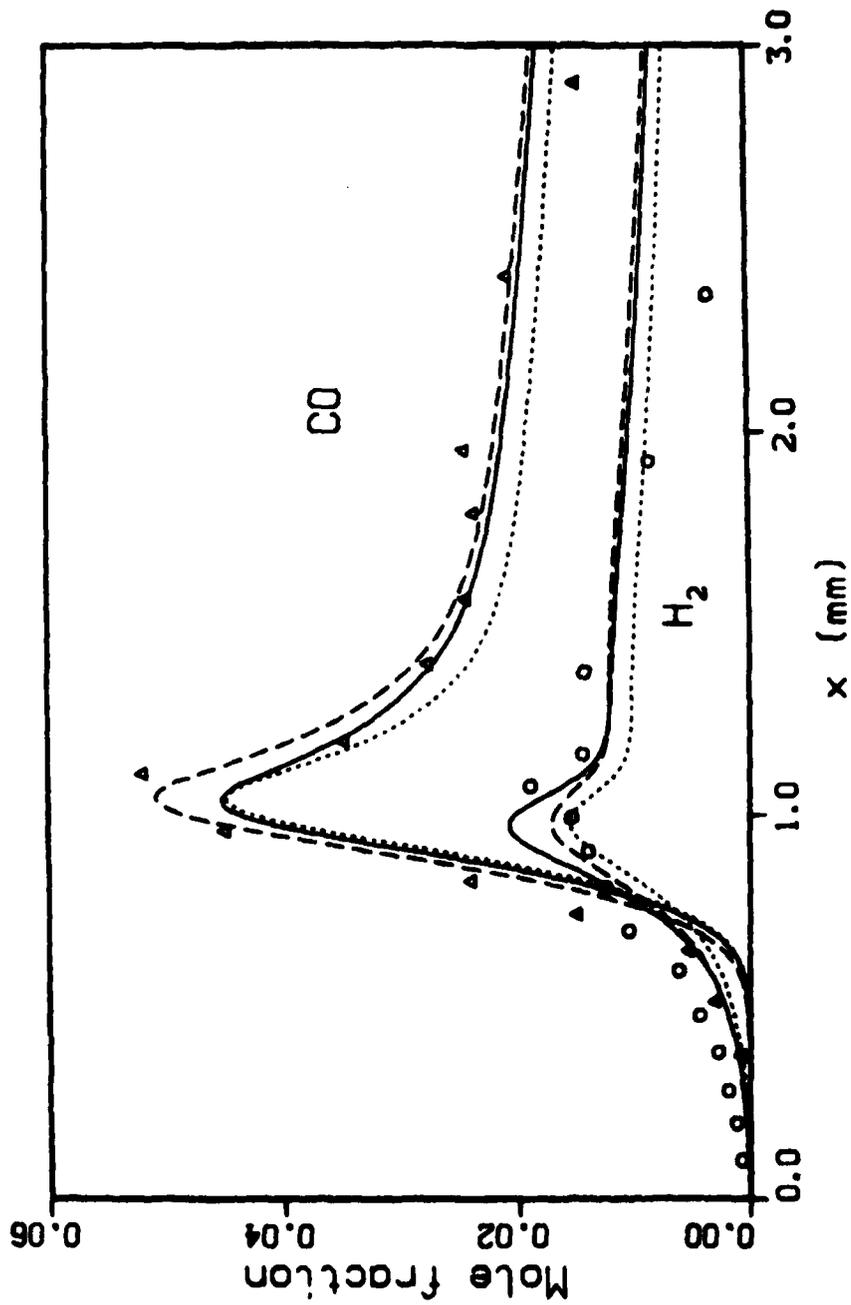


Figure 3. Stoichiometric CH₄/Air Flame. Model Values - CF20 (Line), W23 (Dot), and DL18 (Dash).
Bechtel Experimental Points. H₂ and CO Profiles.

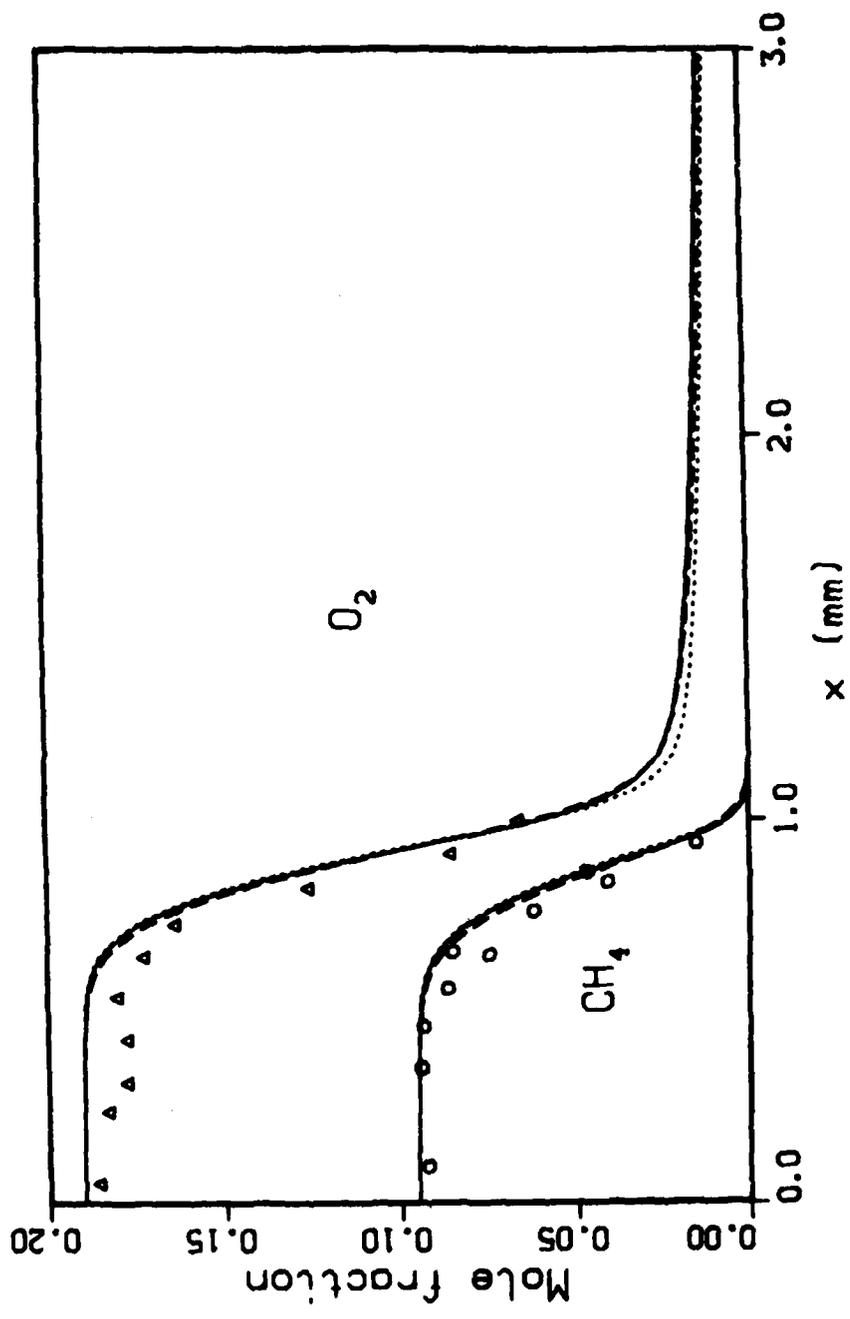


Figure 4. Stoichiometric CH_4/Air Flame. Model Values - CF20 (Line), W23 (Dot), and DL18 (Dash).
Rechtel Experimental Points. O_2 and CH_4 Profiles.

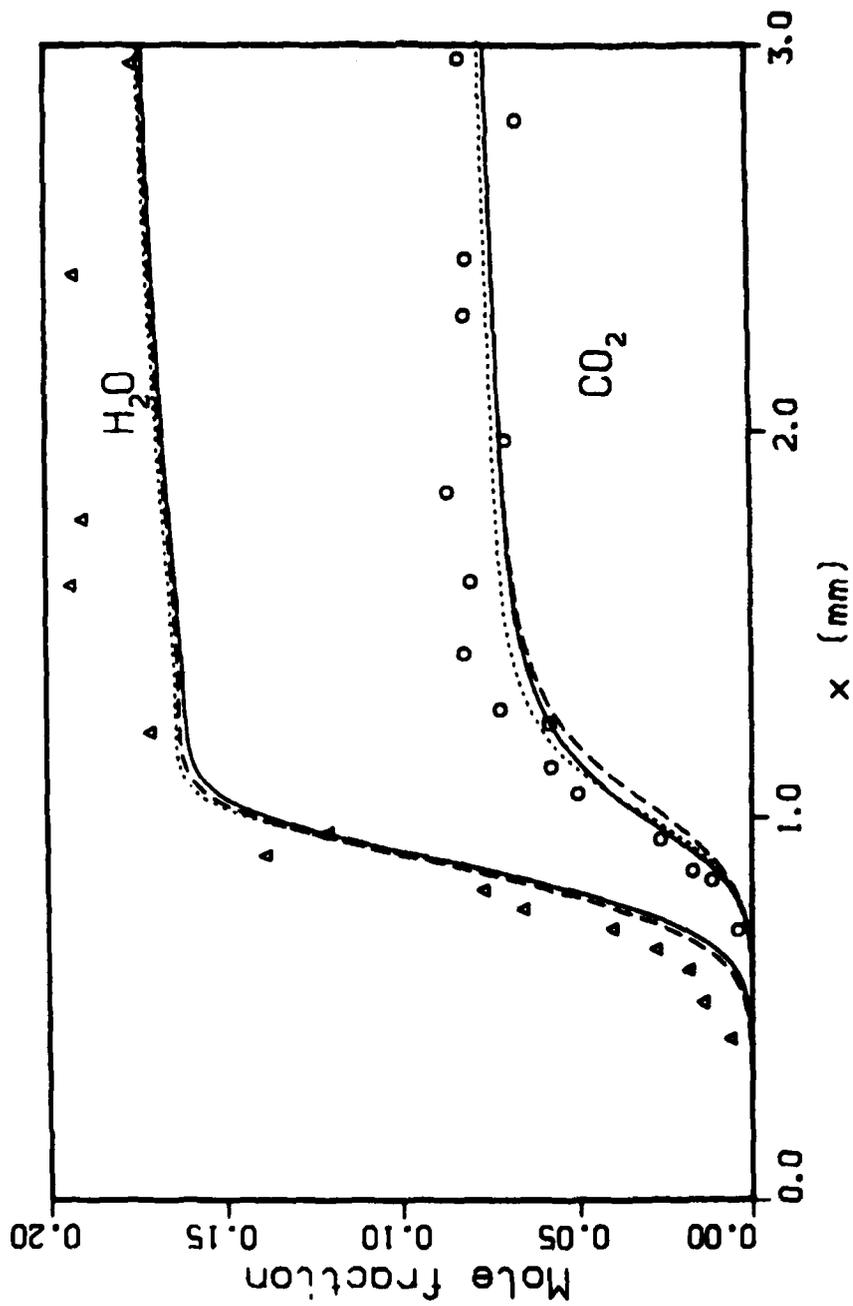


Figure 5. Stoichiometric CH_4/Air Flame. Model Values - CF20 (Line), W23 (Dot), and DL18 (Dash). Bechtel Experimental Points. H_2O and CO_2 Profiles.

TABLE 2. LOGARITHMIC SENSITIVITY COEFFICIENTS FOR A
STOICHIOMETRIC FLAME (CF20 KINETICS SCHEME)

Reaction	S_E^J	Reaction	S_E^J
1	.06	40	-.05
2	.45	59	.09
3	.04	60	.03
4	-.15	61	.03
18	-.05	62	.03
21	.16	63	-.06
23	.07		
25	-.06		
27	-.06		
28	.03		
33	-.04		

reaction is relatively unimportant. Most of the H atoms are generated by other reactions.

Much of the sensitivity analysis can be explained in terms of a shortage of H atoms. Reactions that consume H atoms [4, 18, 25, 27, 33] tend to slow down the flame. Reactions that produce H atoms [1, 3, 21, 23, 28] increase the flame speed. The flame is much more sensitive to the radicals than to the rate at which the intermediates [CH₃, CH₂O, CHO, CO] are formed.

Reaction 40 [CH₃ + CH₃ → C₂H₆] slows down the flame because it leads to the slower C₂ pathway. However, only about 10% of the CH₃ formed goes to C₂H₆. All the other C₂ chemistry rates have very small sensitivity coefficients. For other kinetic schemes, more CH₃ may be converted to C₂H₆, and the C₂ reactions would be more important.

Finally, reactions 59 [CH₃ + H → CH₂ + H₂] and 60 [CH₃ + OH → CH₂ + H₂O] have positive sensitivity coefficients, even though radicals are consumed. This is because CH₂ reacts rapidly with O₂ to produce radicals through reactions 61 and 62. The corresponding reaction 63, which does not produce radicals, has a negative sensitivity coefficient.

In summary, the flame speed is most sensitive to the production of radicals. The $H_2/O_2/N_2$ kinetics is the most important for determining the flame speed. The next most important group is the CO to CO_2 chemistry (reactions 21 and 22). In contrast, the flame is fairly insensitive to the specific hydrocarbon reactions.

The C_2 chemistry (reactions 40 to 58) tends to slow down the flame, while the CH_3 to CH_2 chemistry (reactions 59 to 63) increases the burning velocity. The latter reactions are not standard for CH_4 chemistry models. But if these reactions are omitted, the burning velocity is too low, especially for rich flames. So these reactions are important for the CF20 mechanism. Whether these reactions are actually important in CH_4 combustion is yet to be determined.

Sensitivity coefficients for the species and temperature profiles were also computed (as a function of position). The major species (CH_4 , O_2 , CO_2 , H_2O) were the least sensitive to changes in the rate coefficients. Next comes the intermediate CO and H_2 and the OH radical. The other radicals (H , O, HO_2) were somewhat more sensitive. The intermediates along the main oxidation pathway (CH_3 , CH_2O , CHO) were quite sensitive. The species most affected by rate changes were the C_2 species and CH_2 .

Moreover, the species CH_4 , O_2 , CO_2 , H_2O , CO, H_2 , OH, H, and O are most sensitive to the rate constants 2 and 4. It is the species along the main oxidation pathway (CH_3 , CH_2O , and CHO) that are sensitive to the hydrocarbon reactions.

This explains why all the models are in very good agreement with the profiles measured by Bechtel. The profiles measured are the least sensitive profiles, and in any case, are primarily sensitive to changes in the H_2/O_2 subset. A wide range of hydrocarbon reactions and rates can be assumed, as long as an appropriate pathway exists from CH_4 to CO to CO_2 and the flame speed is reasonable.

VI. DISCUSSION

There is substantial agreement among the models for the profiles measured by Bechtel, et al. It is also useful to see for what profiles the models differ. Experimental measurements of such profiles could help determine which, if any, of the models are correct.

To help analyze the results, a screening analysis is performed.¹⁷ That is, the rate of production and loss for each species as a function of position is partitioned according to the contribution of each reaction. This shows the pathways by which the various species are produced and consumed in the given network. Screening analysis complements a sensitivity analysis, which shows how rate changes can effect the given network.

First, we consider the importance of the C_2 and CH_2 chemistry. Table 3 gives the ratios of the peak mole fractions of the CF20 and CF14 models as a function of stoichiometry, as well as the flame speeds S. The major species

TABLE 3. RATIO OF CF20 PEAK HEIGHTS TO CF14 PEAK HEIGHTS AS A FUNCTION OF EQUIVALENCE RATIO

	<u>0.65</u>	<u>0.86</u>	<u>1.00</u>	<u>1.25</u>	<u>1.40</u>	<u>1.50</u>
H	.86	.94	.95	.91	1.15	1.33
OH	.98	1.00	1.00	.96	1.14	1.06
O	.92	.96	.96	.92	1.86	1.87
HO ₂	1.57	1.41	1.42	1.70	2.20	1.81
CH ₃	.53	.52	.49	.42	.41	.31
CH ₂ O	.89	.99	1.07	1.23	1.51	1.59
CHO	.80	.93	1.00	1.09	1.39	1.09
H ₂	.94	1.02	1.04	1.05	1.02	1.04
CO	.88	.92	.92	.91	.94	1.01
S	.95	1.07	1.12	1.17	1.26	1.07

(CH₄, O₂, CO₂, H₂O) and the temperature are not included as the profiles are virtually identical. The exception is the rich flames ($\phi = 1.40$ or $\phi = 1.50$), where the CO₂ profiles show slight differences.

For lean to slightly rich flames, only the CH₃ and HO₂ profiles show large differences. The CF20 model has less CH₃ since the CH₃ + C₂H₆ and CH₃ + CH₂ reactions deplete this species. The C₂ chemistry then leads to more HO₂ through the reactions 48 [C₂H₅ + O₂ + C₂H₄ + HO₂] and 56 [C₂H₃ + O₂ + C₂H₂ + HO₂].

The similarities between the two models are due to competing effects. The C₂ chemistry tends to slow down the flame. The bulk of the C₂H₆ formed slowly oxidizes to C₂H₂, and then goes to CO through reaction 58 [C₂H₂ + OH + CH₃ + CO]. The concentrations of the radicals and the intermediates CH₂O and CHO are all lowered.

The CH₂ chemistry tends to increase the flame speed. Once the CH₂ forms, it oxidizes fairly rapidly by the reactions 61 [CH₂ + O₂ + CHO + OH], 62 [CH₂ + O₂ + CH₂O + O] and 63 [CH₂ + O₂ + CO₂ + H₂]. The intermediates CH₂O and CHO are increased. The radical concentrations are not greatly affected, although the O atom peak does increase.

For the rich flames, more of the CH₃ goes to C₂H₆ (up to 20%) and also to CH₂ (up to 35%). This leads to slightly higher flame speeds for the CF20 model. The CH₃ peak becomes much smaller. The O and CH₂O concentrations are substantially higher, due to reaction 62 [CH₂ + O₂ + CH₂O + O].

The H_2 profile shows relatively minor differences. For the CF14 model, the H_2 is primarily produced through reactions 25 [$CH_4 + H \rightarrow CH_3 + H_2$] and 30 [$CH_2O + H \rightarrow CHO + H_2$]. For the CF20 model, less H_2 is produced through these reactions, but this is compensated for by reactions 59 [$CH_3 + H \rightarrow CH_2 + H_2$] and 42 [$C_2H_6 + H \rightarrow C_2H_5 + H_2$]. The overall rate of production through the various pathways is about the same. As long as the flame speeds are similar, this will be the case.

Similarly, a decrease in the CO production reaction 23 [$CHO + M' \rightarrow H + CO + M'$] is compensated for by reaction 58 [$C_2H_2 + OH \rightarrow CH_3 + CO$].

Next, we consider comparisons among the three models with C_2 chemistry. To conserve computer time, the solutions are generated using the simplest transport algorithm, Method v.⁵ Tables 4 and 5 show the ratios of the peak mole fractions and flame speeds. Again, the major species and temperature profiles are virtually identical.

The flame speeds generated by the DL18 model agree with those reported by Dixon-Lewis.⁴ The flame speeds generated by the W23 model are lower than those reported by Warnatz (5%-15%).

For the DL18 model, results are not given for $\phi = 1.50$. No steady state solution could be generated, as the computed flame always went out.

For lean to slightly rich flames, all three models agree for the temperature and major species profiles. Lower flame speeds are predicted for $\phi = 1.40$ (DL18 and W23 models) and for $\phi = 1.50$ (W23 model). At these lower speeds, the flame front is spread out and noticeable differences appear in the profiles.

The H, OH, and O profiles are similar for lean to stoichiometric flames. For rich flames, where the models predict lower flame speeds, the radical concentrations tend to be lower (up to a factor of 2). This is reasonable since large amounts of radicals lead to rapid combustion.

There are large differences in the intermediates CH_3 , CH_2O , and CHO . CHO is especially variable because of its low concentration. The C_2 species show relatively low concentrations and large variation. But the H_2 and CO profiles, which have larger concentrations, remain similar throughout.

TABLE 4. RATIO OF DL18 PEAK HEIGHTS TO CF20 PEAK HEIGHTS AS A FUNCTION OF EQUIVALENCE RATIO

	<u>0.65</u>	<u>0.86</u>	<u>1.00</u>	<u>1.25</u>	<u>1.40</u>
H	.93	.98	.99	1.01	38
OH	.98	1.00	1.00	1.01	.50
O	.96	1.00	1.00	.91	.23
HO ₂	.54	.70	.79	.78	.40
C ₂ H ₆	3.35	3.53	3.31	2.26	1.10
C ₂ H ₅	.23	.51	.77	1.08	1.21
C ₂ H ₄	.84	1.71	2.80	3.62	2.30
CH ₃	1.35	1.53	1.62	1.74	1.49
CH ₂ O	.62	.64	.69	.97	1.35
CHO	2.16	2.24	2.11	1.95	.81
H ₂	.79	.82	.83	.87	.88
CO	1.15	1.14	1.12	1.10	.97
S	1.00	1.00	.96	.88	.50

TABLE 5. RATIO OF W23 PEAK HEIGHTS TO CF20 PEAK HEIGHTS AS A FUNCTION OF EQUIVALENCE RATIO

	<u>0.65</u>	<u>0.86</u>	<u>1.00</u>	<u>1.25</u>	<u>1.40</u>	<u>1.50</u>
H	1.12	1.01	.97	.71	.64	1.21
OH	1.10	1.09	1.06	.70	.56	.91
O	1.28	1.20	1.11	.48	.51	.71
HO ₂	.74	.92	1.04	.97	.52	.32
CH ₂	.38	.48	.62	.89	.91	1.45
C ₂ H ₆	2.68	2.07	1.87	1.66	1.66	1.71
C ₂ H ₅	.62	.75	.80	.39	.07	.06
C ₂ H ₄	2.23	2.72	4.08	5.40	3.74	3.00
C ₂ H ₃	2.64	5.44	9.05	10.56	8.59	9.66
C ₂ H ₂	.07	.21	.46	1.20	1.35	1.12
CH ₃	1.42	1.49	1.56	1.40	1.20	1.18
CH ₂ O	.41	.47	.52	.59	.76	.99
CHO	.51	.42	.35	.19	.16	.18
H ₂	.74	.72	.74	.84	.97	.95
CO	1.08	1.00	.97	.96	1.02	1.02
S	1.18	1.05	.96	.73	.69	.72

VII. LOW PRESSURE FLAMES

There have been several experimental studies of low pressure flames using mass spectroscopy. We consider one such experiment due to Fristrom, et al,²⁷ on a 7.85% CH₄/O₂ flame at 0.05 atm pressure. The temperature, CH₄, O₂, H₂, H₂O, H₂, CO, and CH₂O profiles were measured. The flame was stabilized on a circular screen burner. The experimental burning velocity (referenced to 298K, 0.05 atm) was 69 cm/sec.

The flame was modeled as an unbounded flame with the temperature of the unburned mixture as 298K. Computations were made using three kinetics schemes (CF20, W23, and DL18) and the more accurate transport Method VI. Since the flame is very lean, the C₂ chemistry has only minor effects.

The temperature profiles were in very good agreement through the flame front. In the post flame region the experimental temperature measurements were high. For the major species CH₄, O₂, CO₂, and H₂O, all three models were in very good agreement with the experimental results. There were noticeable differences for the other species peak heights and the burning velocities (see Table 6). Dixon-Lewis⁴ tried adjusting the rate constants to match the profiles. He was unable to do so and still match the atmospheric pressure experimental results.

Fristrom, et al, noted that recombination in the sampling probe could distort the trace species. To test this possibility, an ODE code was used. The initial temperature and concentrations were taken as the values at the peak CH₂O concentration, as determined by the CF20 model. A time integration was performed until the CH₂O concentration matched the experimental value, holding the temperature and pressure constant. The results are given in Table 4. The values for H₂ and CO also closely match the experimental values. The major species concentrations also change, but since their concentrations are larger to begin with, this does not affect their agreement with the experimental profiles.

TABLE 6. A COMPARISON OF BURNING VELOCITIES AND PEAK MASS FRACTIONS FOR THE LOW PRESSURE FLAME

	<u>Experiment</u>	<u>CF20</u>	<u>W23</u>	<u>DL18</u>
Burning Velocity	69	55.7	62.1	39.5
CH ₂ O	1.5 E-3	3.1 E-3	1.1 E-3	1.2 E-3
H ₂	2.2 E-4	2.3 E-4	1.3 E-4	9.0 E-5
CO	4.1 E-2	3.4 E-2	3.6 E-2	3.2 E-2

²⁷R.M. Fristrom, C. Granfelder, and S. Favin, "Methane-Oxygen Flame Structure. III. Characteristic Profiles and Matter and Energy Conservation in a One-Twentieth Atmosphere Flame," *J. Phys. Chem.*, Vol. 65, pp. 587-590, 1961.

TABLE 7. RESULTS OF THE TIME INTEGRATION OF THE CF20 MODEL PROFILES.
INITIAL CONDITIONS ARE TAKEN AT THE CH₂O PEAK

	<u>t = 0</u>	<u>t = 3.2 E-4 sec</u>
CH ₂ O	3.1 E-3	1.5 E-3
H ₂	2.3 E-4	2.2 E-4
CO	3.0 E-2	3.8 E-2

So it is possible that the differences between the CF20 model and the experiment are due to recombination within the probe. On the other hand, there is no obvious way recombination could lead to agreement between either the W23 or the DL18 scheme and the experiment. However, reactions on the wall of the probe and the cooling due to the probe have been ignored in this simple model. These assumptions cannot be justified, and the above explanation must be considered tentative.

VIII. CONCLUSIONS

Results for seven kinetic schemes have been compared with a range of data for atmospheric pressure methane/air flames. Three of the models (the two introduced here and the one due to Warnatz) are reasonably accurate over the entire range.

None of the models match the data on low pressure flame obtained by mass spectroscopy. However, if chemistry is assumed to continue for a short time in the probe, the predictions of the two new models are consistent with the experimental data.

None of the models can be considered to be completely validated. In particular, the CF14 models ignores C₂ chemistry, although it is known that C₂ species are formed. However, methane is oxidized in a series of steps. As long as the rate of the overall pathway is accurate, the flame speed, the temperature profiles, and the major species profiles will be accurate. But this does not guarantee that the intermediates CH₃, CH₂O, CHO, CH₂, and the C₂ species will be correct.

A measurement of the CH₃ profile would be especially useful. This would help determine the branching ratio between CH₃ + CH₂O and CH₃ + C₂H₆.

So there are several models that reproduce well the main features of atmospheric flame. Most of the models are accurate for lean to slightly rich flames. But the details of the intermediate reactions in the oxidation of CH₄ are still not well known.

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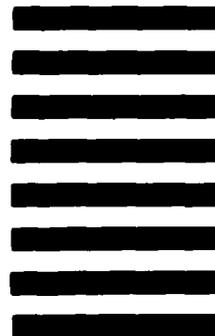
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