

Lecture 6

Asymptotic Structure for Four-Step Premixed Stoichiometric Methane Flames

Previous lecture:

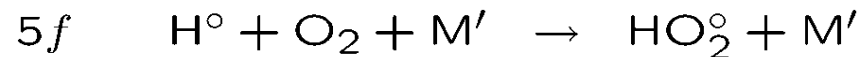
- Asymptotic description of premixed flames based on an assumed one-step reaction
 - Basic understanding of the flame structure when a large sensitivity to temperature was built into the model
- There is no chemical basis for the one-step assumption
 - Results must be regarded with caution when conclusions are drawn about the dependence of the burning velocity on pressure and reactant concentrations, as well as flammability and extinction limits
- While numerical calculations based on full and reduced mechanisms are able to predict these properties, they contribute little to the understanding of the fundamental parameters that influence flame behavior

- Therefore there is a need to **fill the gap** between the numerical calculations based on mechanisms with elementary kinetics and asymptotic analysis based on assumed chemistry models
- The asymptotic description of stoichiometric methane-air flames based on a **four step reduced mechanism** will be presented in this lecture
- Since the basic chemical parameters were retained, this mechanism has been quite successful in describing the dependence of the burning velocity on pressure and pre-heat temperature

- A similar asymptotic analysis was also carried out for lean methane flames (Seshadri 1991)
- This description may, with some modifications, also serve as a model for other hydrocarbon flames
- This will be shown by using analytical approximation formulas (Göttgens 1992) that are based on the asymptotic description of methane flames for flames of C_2H_6 , C_2H_4 , C_2H_2 and C_3H_8 in air

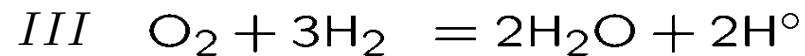
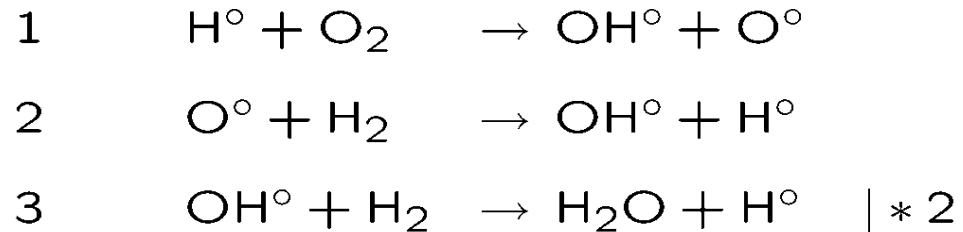
The Four-Step Model for Methane-Air Flames

- Systematically reduced mechanism using quasi steady state approximations
- Non steady state components:
 - Stable components CH_4 , O_2 , H_2O , CO_2 , H_2 , CO
 - H° -radical
 - Representing effect of radicals on flame structure
 - Competition between chain branching and chain breaking
 - Typically H-radical because of its importance in main radical reactions

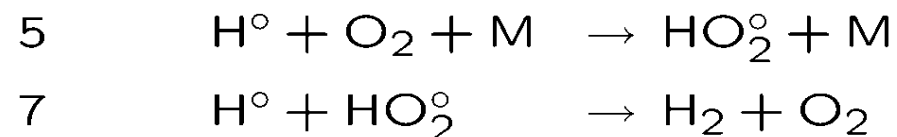


- These reactions lead with steady state assumptions for OH and O lead to global reactions III and IV

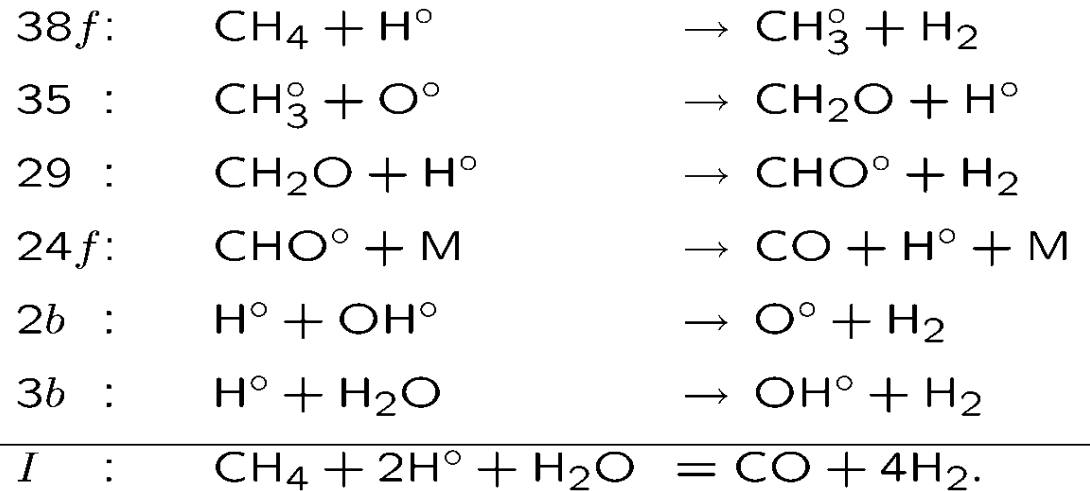
- Global **reaction III** with the rate of reaction 1f describes **chain branching**



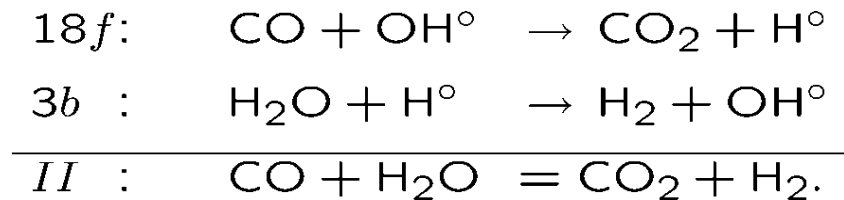
- Global **reaction IV** with the rate of reaction 5f describes **chain breaking**



- Global **reaction I** with the rate of reaction 38f describes **fuel consumption**

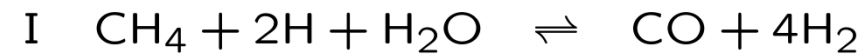


- Radical consuming because of CH3 consumption reaction
- Global **reaction II** with the rate of reaction 18f describes **CO oxidation (water gas shift reaction)**



The Four-Step Model for Methane-Air Flames

- The four-step model for methane flames is in summary

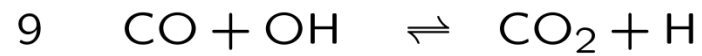


- The principal rates governing these global reactions are

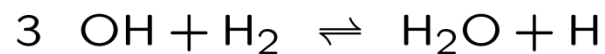
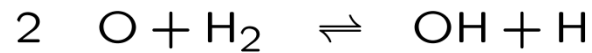
$$\omega_{\text{I}} = \omega_{11}, \quad \omega_{\text{II}} = \omega_9$$

$$\omega_{\text{III}} = \omega_5, \quad \omega_{\text{IV}} = \omega_1$$

- They correspond to the elementary reactions



- We neglect the influence of the other reactions here in order to make the algebraic description more tractable
- Since OH and O appear in this formulation as reactants we need to express them in terms of the species in the four-step mechanism by using the **partial equilibrium assumption** for the reaction such that



$$[\text{O}] = \frac{[\text{H}][\text{OH}]}{K_2[\text{H}_2]}$$

$$[\text{OH}] = \frac{[\text{H}_2\text{O}][\text{H}]}{K_3[\text{H}_2]}$$

where K_2 and K_3 are the equilibrium constants of reactions 2 and 3, respectively

- This leads to the following reaction rates of the global steps I-IV:

$$\omega_{\text{I}} = k_{11}[\text{CH}_4][\text{H}]$$

$$\omega_{\text{II}} = \frac{k_{9f} [\text{H}]}{K_3 [\text{H}_2]} \left([\text{CO}][\text{H}_2\text{O}] - \frac{1}{K_{\text{II}}} [\text{CO}_2][\text{H}_2] \right)$$

$$\omega_{\text{III}} = k_5[\text{H}][\text{O}_2][\text{M}]$$

$$\omega_{\text{IV}} = k_1 \frac{[\text{H}]}{[\text{H}_2]^3} \left([\text{O}_2][\text{H}_2]^3 - \frac{1}{K_{\text{IV}}} [\text{H}]^2[\text{H}_2\text{O}]^2 \right)$$

which is explicit in terms of the concentrations of species appearing in the four-step mechanism

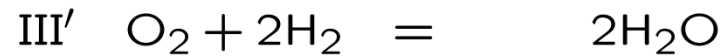
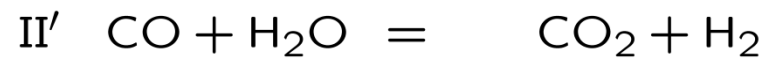
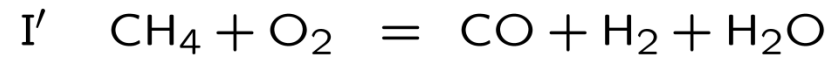
- The equilibrium constants in these rates are given by

$$K_3 = 0.216 \exp(7658/T)$$

$$K_{\text{II}} = 0.035 \exp(3652/T)$$

$$K_{\text{IV}} = 1.48 \exp(6133/T).$$

- We now want to go one step further and assume steady state of the radical H
- Adding reaction IV to I and III leads to the three steps



with the first three rates given at the previous slide

- [H] must now be determined from the [steady state equation](#) for H
- Taking the H balance in the four-step mechanism and setting H steady state leads to

$$L(H) = -w_I - w_{II} + w_{IV} = 0$$

and

$$\omega_I + \omega_{III} = \omega_{IV}$$

- This may be written as

$$[H] = [H_{eq}] \left(1 - \frac{k_5[M]}{k_1} - \frac{k_{11}[CH_4]}{k_1[O_2]} \right)^{1/2}$$

where $[H_{eq}]$ based on partial equilibrium of reaction IV

$$[H_{eq}] = K_{IV}^{1/2} \frac{[O_2]^{1/2} [H_2]^{3/2}}{H_2O}$$

- The equation

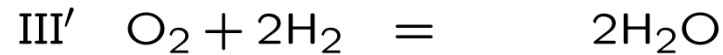
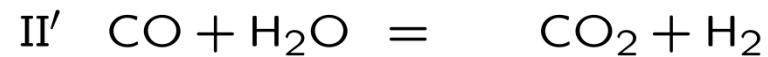
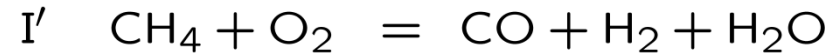
$$[H] = [H_{eq}] \left(1 - \frac{k_5[M]}{k_1} - \frac{k_{11}[CH_4]}{k_1[O_2]} \right)^{1/2}$$

shows an interesting structure

- At temperatures of 1400 K and above, the second term in the brackets is small while the ratio k_{11} / k_1 is much larger than unity
- It follows that $[CH_4]/[O_2]$ must be much smaller than unity, if $[H]$ is to remain real
- This will be used to develop an asymptotic description of the inner layer below, but also shows that the equation cannot be valid in the preheat zone upstream of the inner layer where CH_4 is entirely consumed
- It also follows that $[H]$ vanishes in the preheat zone which is therefore chemically inert

Two-Step Mechanism

- A further approximation that will reduce the three step mechanism



effectively to a two-step mechanism is the assumption of **partial equilibrium of II**

- Assuming $[\text{H}_2\text{O}]$ and $[\text{CO}_2]$ to be known this leads to a coupling between $[\text{CO}]$ and $[\text{H}_2]$ of the form

$$[\text{CO}] = \alpha' [\text{H}_2], \quad \alpha' = \frac{[\text{CO}_2]}{[\text{H}_2\text{O}]} K_{\text{II}}(T).$$

- By introducing partial equilibrium of reaction II one assumes that the effective rate coefficient k_{gf}/K_3 in

$$\omega_{II} = \frac{k_{gf}}{K_3} \frac{[H]}{[H_2]} \left([CO][H_2O] - \frac{1}{K_{II}} [CO_2][H_2] \right)$$

tends to infinity while the term in parenthesis tends to zero and ω_{II} remains finite

- Since ω_{II} is undefined, the rate ω_{II} must be eliminated from the balance equations

- In order to show this the balance equations for the three-step mechanism are written in operator form

$$\text{Species} \quad L_i(Y_i) \equiv \rho u s L \frac{dY_i}{dx} - \frac{1}{Le_i} \frac{d}{dx} \left(\frac{\lambda}{c_p} \frac{dY_i}{dx} \right) = W_i \sum_{l=I'}^{III'} \nu_{il} \omega_l$$

$$\text{Temperature} \quad L_T(T) \equiv \rho u s L \frac{dT}{dx} - \frac{d}{dx} \left(\frac{\lambda}{c_p} \frac{dT}{dx} \right) = \frac{1}{c_p} \sum_{l=I'}^{III'} Q_l \omega_l$$

- In terms of the variable $G_i = Y_i/W_i$ the balance equations for the concentrations are written

$$L_{CH_4}(\Gamma_{CH_4}) = -\omega_I$$

$$L_{CO}(\Gamma_{CO}) = \omega_I - \omega_{II}$$

$$L_{O_2}(\Gamma_{O_2}) = \omega_I + \omega_{III}$$

$$L_{H_2O}(\Gamma_{H_2O}) = \omega_I - \omega_{II} + 2\omega_{III}$$

$$L_{H_2}(\Gamma_{H_2}) = \omega_I + \omega_{II} - 2\omega_{III}$$

$$L_{CO_2}(\Gamma_{CO_2}) = \omega_{II}$$

- The rate ω_{II} may be eliminated from

$$\begin{array}{ll}
 L_{\text{CH}_4}(\Gamma_{\text{CH}_4}) = -\omega_{\text{I}} & L_{\text{CO}}(\Gamma_{\text{CO}}) = \omega_{\text{I}} - \omega_{\text{II}} \\
 L_{\text{O}_2}(\Gamma_{\text{O}_2}) = \omega_{\text{I}} + \omega_{\text{III}} & L_{\text{H}_2\text{O}}(\Gamma_{\text{H}_2\text{O}}) = \omega_{\text{I}} - \omega_{\text{II}} + 2\omega_{\text{III}} \\
 L_{\text{H}_2}(\Gamma_{\text{H}_2}) = \omega_{\text{I}} + \omega_{\text{II}} - 2\omega_{\text{III}} & L_{\text{CO}_2}(\Gamma_{\text{CO}_2}) = \omega_{\text{II}}
 \end{array}$$

by combining the balance equations of H_2 , H_2O , and CO_2 with that of CO

$$\begin{array}{l}
 L_{\text{H}_2}(\Gamma_{\text{H}_2}) + L_{\text{CO}}(\Gamma_{\text{CO}}) = 2\omega_{\text{I}} - 2\omega_{\text{III}} \\
 L_{\text{H}_2\text{O}}(\Gamma_{\text{H}_2\text{O}}) - L_{\text{CO}}(\Gamma_{\text{CO}}) = 2\omega_{\text{III}} \\
 L_{\text{CO}_2}(\Gamma_{\text{CO}_2}) + L_{\text{CO}}(\Gamma_{\text{CO}}) = \omega_{\text{I}}
 \end{array}$$

- We will anticipate that in the thin reaction layers to be considered below, the diffusive terms dominate for the same reason as in the thin reaction zone for the one-step model
- Therefore we will neglect the convective terms in

$$\text{Species} \quad L_i(Y_i) \equiv \rho_u s_L \frac{dY_i}{dx} - \frac{1}{Le_i} \frac{d}{dx} \left(\frac{\lambda}{c_p} \frac{dY_i}{dx} \right) = W_i \sum_{l=I'}^{III'} \nu_{il} \omega_l$$

$$\text{Temperature} \quad L_T(T) \equiv \rho_u s_L \frac{dT}{dx} - \frac{d}{dx} \left(\frac{\lambda}{c_p} \frac{dT}{dx} \right) = \frac{1}{c_p} \sum_{l=I'}^{III'} Q_l \omega_l$$

for the thin reaction zones and consider only the diffusive terms

- This suggests that the concentrations should be scaled with the Lewis numbers

- We introduce the non-dimensional variables

$$X_i = \frac{Y_i W_{\text{CH}_4}}{Y_{\text{CH}_4 u} W_i} , \quad x_i = \frac{X_i}{\text{Le}_i}$$

$$T^* = \frac{T - T_u}{T_b - T_u} , \quad x^* = \rho_u s_L \int_0^x \frac{c_p}{\lambda} dx$$

$$\omega_l^* = \frac{\lambda W_{\text{CH}_4} \omega_l}{c_p Y_{\text{CH}_4 u} (\rho v)_u^2} , \quad Q_l^* = \frac{Q_l Y_{\text{CH}_4 u}}{c_p (T_b - T_u) W_{\text{CH}_4}}$$

and redefine the parameter α'

$$\alpha = \alpha' \frac{\text{Le}_{\text{H}_2}}{\text{Le}_{\text{CO}}}$$

- With $x_{\text{CO}} = \alpha x_{\text{H}_2}$ one obtains the following balance equations of the two-step mechanism (the asterisks will be removed from here on)

$$-\frac{d^2 x_{\text{CH}_4}}{dx^2} = -\omega_{\text{I}}$$

$$-\frac{d^2 x_{\text{O}_2}}{dx^2} = -\omega_{\text{I}} - \omega_{\text{III}}$$

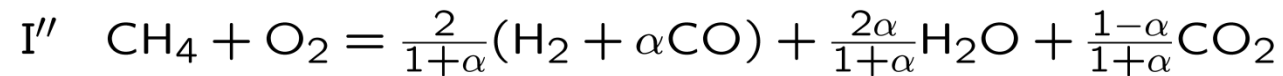
$$-\frac{d^2 x_{\text{H}_2}}{dx^2} = \frac{2}{1+\alpha}(\omega_{\text{I}} - \omega_{\text{III}})$$

$$-\frac{d^2 x_{\text{CO}}}{dx^2} = \frac{2\alpha}{1+\alpha}(\omega_{\text{I}} - \omega_{\text{III}})$$

$$-\frac{d^2 x_{\text{H}_2\text{O}}}{dx^2} = \frac{2\alpha}{1+\alpha}\omega_{\text{I}} + \frac{2}{1+\alpha}\omega_{\text{III}}$$

$$-\frac{d^2 x_{\text{CO}_2}}{dx^2} = \frac{1-\alpha}{1+\alpha}\omega_{\text{I}} + \frac{2\alpha}{1+\alpha}\omega_{\text{III}}$$

- The stoichiometric coefficients are those of the two global reactions



- Here the combination $\text{H}_2 + \alpha \text{CO}$ appears as an intermediate which is formed in I'' and consumed in III''
- The rates of these reactions are still the same as of I and III in the four-step mechanism

- If the balance equations

$$\text{I}'' \quad \text{CH}_4 + \text{O}_2 = \frac{2}{1+\alpha}(\text{H}_2 + \alpha\text{CO}) + \frac{2\alpha}{1+\alpha}\text{H}_2\text{O} + \frac{1-\alpha}{1+\alpha}\text{CO}_2$$

$$\text{III}' \quad \text{O}_2 + \frac{2}{1+\alpha}(\text{H}_2 + \alpha\text{CO}) = \frac{2}{1+\alpha}\text{H}_2\text{O} + \frac{2\alpha}{1+\alpha}\text{CO}_2$$

are used to determine x_{CH_4} and x_{H_2} , all other concentrations and the temperature can be determined deriving the following coupling equations in addition using the corresponding temperature equation

$$\frac{d^2}{dx^2}[(1 + \alpha)x_{\text{H}_2} + 4x_{\text{CH}_4} - 2x_{\text{O}_2}] = 0$$

$$\frac{d^2}{dx^2}[x_{\text{H}_2} + 2x_{\text{CH}_4} + x_{\text{H}_2\text{O}}] = 0$$

$$\frac{d^2}{dx^2}[x_{\text{H}_2} + x_{\text{CH}_4} + x_{\text{CO}_2}] = 0$$

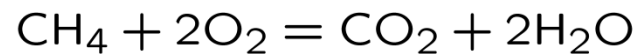
$$\frac{d^2}{dx^2}[(q_{\text{H}_2} + \alpha q_{\text{CO}})x_{\text{H}_2} + x_{\text{CH}_4} + T] = 0$$

- Here the reduced heats of reaction are

$$q_{\text{H}_2} = \frac{1}{2} \frac{Q_{\text{III}}}{Q} = 0.3116$$

$$q_{\text{CO}} = \frac{(\frac{1}{2}Q_{\text{III}} + Q_{\text{II}})}{Q} = 0.3479$$

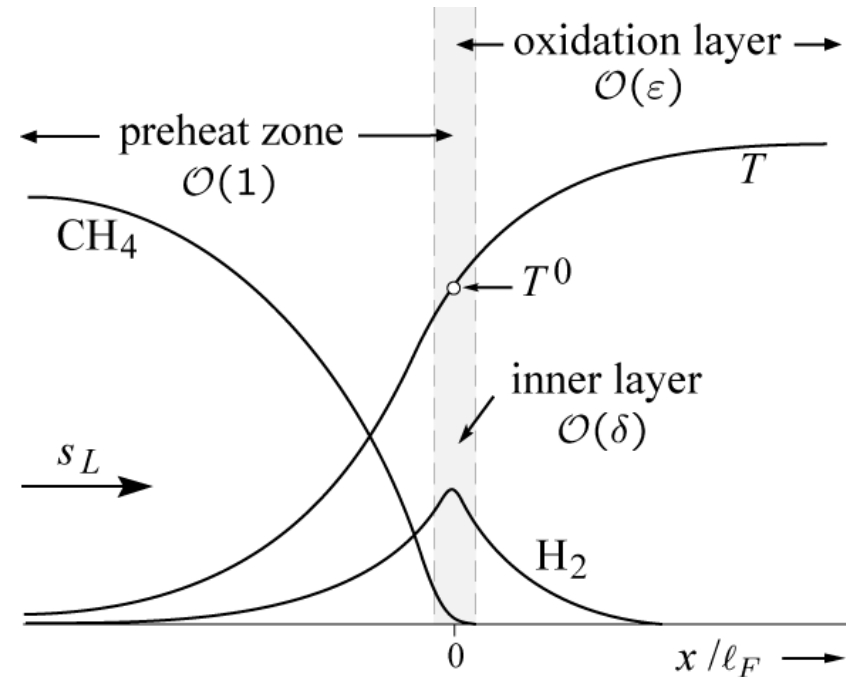
where Q is the heat of reaction of the global step



- In the following we approximate both q_{H_2} and q_{CO} by $q = 0.33$ for simplicity

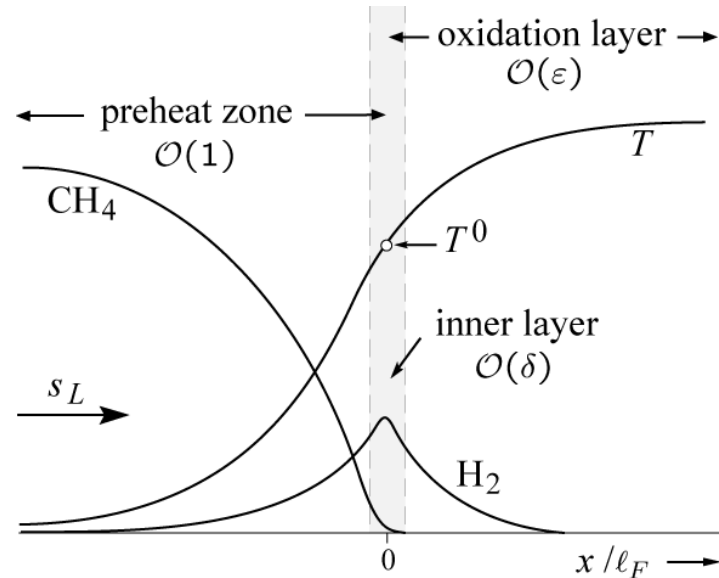
The Asymptotic Structure of Stoichiometric Methane-Air Flames

- Flame structure of the two-step mechanism
- It contains three layers
 1. A chemically inert preheat zone of order 1 upstream
 2. A thin inner layer of order δ in which the fuel is consumed and the intermediates H_2 and CO are formed according to the global step I''
 3. A thin oxidation layer of order ε downstream where H_2 and CO are oxidized according to global step III''



Details of the Asymptotic Analysis

- At first the inner layer shall be analyzed



- We will denote quantities at the inner layer with a subscript 0 but the inner layer temperature as T^0
- In this layer all concentrations except that of the fuel, which is depleted, may be assumed constant to leading order

- Introducing

$$[H] = [H_{eq}]$$

into

$$\omega_I = k_{11}[\text{CH}_4][H]$$

leads to

$$\omega_I = \text{Da}_I x_{\text{CH}_4} \left(1 - \frac{x_{\text{CH}_4}}{\delta}\right)^{1/2}$$

where the Damköhler number is

$$\text{Da}_I = \frac{\rho_0^2 Y_{\text{CH}_4} u \lambda_0 (K_{IV} X_{\text{O}_2} X_{\text{H}_2}^3)_0^{1/2}}{\rho_u^2 s_L^2 W_{\text{CH}_4} c_{p0} X_{\text{H}_2\text{O}}} \text{Le}_{\text{CH}_4} k_{11}(T^0)$$

- The small parameter δ was defined as

$$\delta = \frac{k_1(T^0)X_{O_2,0}}{k_{11}(T^0)L_{eCH_4}}$$

- It denotes the ratio of the rate coefficients of reaction I and II
- Thereby it describes the competition of these two reactions in producing and consuming H-radicals according to the global steps IV and I
- Since it happens that the reaction rate k_1 is typically smaller than k_{11} , and since also X_{O_2} in the inner layer $X_{O_2} < 1$, $\delta \approx 0.1$ and sufficiently small for an asymptotic expansion.

- If δ is small, since ω_1 must be real it follows from

$$\delta = \frac{k_1(T^0)X_{O_2,0}}{k_{11}(T^0)Le_{CH_4}}$$

$$\omega_I = Da_I x_{CH_4} \left(1 - \frac{x_{CH_4}}{\delta}\right)^{1/2}$$

the term in paranthesis that x_{CH_4} must not exceed the value of δ

- The flame structure shows that the fuel is of order 1 in the preheat zone but decreases rapidly towards the inner layer

- In the inner x_{CH_4} is then of order δ and one may introduce the scaling

$$y = \frac{x_{\text{CH}_4}}{\delta}$$

and the stretched variable

$$\zeta = \frac{x}{\delta}$$

- Introducing these into $-\frac{d^2 x_{\text{CH}_4}}{dx^2} = -\omega_{\text{I}}$

it leads to the differential equation that governs the structure of the inner layer

$$\frac{d^2 y}{d\zeta^2} = (\delta^2 \text{Da}_{\text{I}}) y (1 - y)^{1/2}$$

- The downstream boundary condition of this equation is

$$y = 0 \quad \text{as} \quad \zeta \rightarrow +\infty$$

since reaction I is irreversible

- The matching with the preheat zone should, as for the one-step asymptotic problem, provide the second boundary condition
- The solution for the fuel concentration in the preheat zone is

$$x_{\text{CH}_4} = 1 - \exp(\text{Le}_{\text{CH}_4} x)$$

which leads to the expansion $x_{\text{CH}_4} = -x$ around $x = 0$

- It is shown in (Peters 1987), however, that the inner layer and the preheat zone are separated by an additional thin layer, the **radical consumption layer**

$$y = 0 \quad \text{as} \quad \zeta \rightarrow +\infty$$

- In this layer the steady state approximation for the H-radical breaks down
- This layer occurs at $y = 1, \zeta = -1$ in terms of the inner layer variables
- Since the fuel is not consumed in this radical layer the slope of the fuel concentration is continuous and matching across this layer leads to

$$y = 1, \quad \frac{dy}{d\zeta} = -1 \quad \text{at} \quad \zeta = -1$$

- With the boundary conditions

$$y = 0 \quad \text{as} \quad \zeta \rightarrow +\infty$$

and

$$y = 1, \quad \frac{dy}{d\zeta} = -1 \quad \text{at} \quad \zeta = -1$$

the equation

$$\frac{d^2y}{d\zeta^2} = (\delta^2 \text{Da}_I) y(1 - y)^{1/2}$$

can be integrated once to obtain the eigenvalue

$$\delta^2 \text{Da}_I = \frac{15}{8}$$

- With

$$\delta^2 \text{Da}_I = \frac{15}{8}$$

one could now determine the burning velocity s_L if the temperature T^0 and all other properties at the inner layer were known

- In order to determine these, the structure of the oxidation layer also must be resolved
- In the oxidation layer $x_{\text{CH}_4} = 0$ and therefore $\omega_1 = 0$
- The temperature varies only slowly in this layer and since the activation energy of k_5 is small, temperature variations may be neglected

- Since most of the chemical activity takes place in the vicinity of the inner layer, all properties shall be evaluated at $x = 0$
- Choosing x_{H_2} as the dependent variable in the oxidation layer and scaling it in terms of a new variable z as

$$x_{\text{H}_2} = \frac{\varepsilon z}{(1 + \alpha)q}$$

- One may use the coupling relations

$$\frac{d^2}{dx^2}[(1 + \alpha)x_{\text{H}_2} + 4x_{\text{CH}_4} - 2x_{\text{O}_2}] = 0,$$

$$\frac{d^2}{dx^2}[x_{\text{H}_2} + 2x_{\text{CH}_4} + x_{\text{H}_2\text{O}}] = 0,$$

$$\frac{d^2}{dx^2}[x_{\text{H}_2} + x_{\text{CH}_4} + x_{\text{CO}_2}] = 0,$$

$$\frac{d^2}{dx^2}[(q_{\text{H}_2} + \alpha q_{\text{CO}})x_{\text{H}_2} + x_{\text{CH}_4} + T] = 0$$

to show that the downstream boundary conditions are satisfied by

$$x_{\text{O}_2} = \varepsilon z / 2q, \quad T = 1 - \varepsilon z$$

- In these expansions ε is the small parameter related to the thickness of the oxidation layer.

- Introducing $x_{\text{H}_2} = \frac{\varepsilon z}{(1 + \alpha)q}$ and $\omega_{\text{III}} = 2q\text{Da}_{\text{III}}\varepsilon^3 z^3$

into

$$\omega_{\text{III}} = k_5[\text{H}][\text{O}_2][\text{M}]$$

leads to

$$\omega_{\text{III}} = 2q\text{Da}_{\text{III}}\varepsilon^3 z^3$$

where the Damköhler number of reaction III is defined as

$$\text{Da}_{\text{III}} = \frac{\rho_0^2 Y_{\text{CH}_4 u} \lambda_0}{\rho_u^2 s_L^2 W_{\text{CH}_4} c_{p0}} \left(\frac{K_{\text{IV}} \text{Le}_{\text{O}_2}^3 \text{Le}_{\text{H}_2}^3}{2^5 (1 + \alpha)^3} \right)^{1/2} \frac{k_5[\text{M}]}{q^4 X_{\text{H}_2\text{O}}}$$

- The concentration of the third body in reaction 5 may be determined approximately by using the third body efficiencies evaluated at the burnt gas conditions
- This leads to

$$[M] = \frac{1.6p}{\mathcal{R}T}$$

which introduces a pressure dependence of Da_{III} and will finally determine the pressure dependence of the burning velocity.

- Introduction of a stretched coordinate

then leads with $\omega_I = 0$ from $\eta = \frac{2qx}{\varepsilon}$

$$-\frac{d^2 x_{H_2}}{dx^2} = \frac{2}{1+\alpha}(\omega_I - \omega_{III})$$

to the governing equation of the oxidation layer

$$\frac{d^2 z}{d\eta^2} = (\varepsilon^4 Da_{III}) z^3$$

- This suggests the definition

$$\varepsilon = Da_{III}^{-1/4}$$

- It turns out that for $p \geq 1$ atm ε is smaller than unity but typically larger than δ

- Even though δ is not very small, we will consider it as small enough to justify an asymptotic description of the oxidation layer

$$\eta = \frac{2qx}{\varepsilon}$$

- The downstream boundary condition of equation $\frac{d^2z}{d\eta^2} = (\varepsilon^4 \text{Da}_{\text{III}})z^3$

is $z = 0$ for $\eta \rightarrow \infty$

since reaction III is irreversible

- The upstream boundary condition must be determined from jump conditions across the inner layer

- Since the fuel is depleted and H₂ is formed in the inner layer following reaction I'', the stoichiometry of this reaction also determines the change of slopes of the H₂ in comparison of those of the fuel
- This is written as

$$\frac{dx_{\text{CH}_4}}{dx} \Big|_{0-} - \frac{dx_{\text{CH}_4}}{dx} \Big|_{0+} = \frac{1 + \alpha}{2} \left(\frac{dx_{\text{H}_2}}{dx} \Big|_{0-} - \frac{dx_{\text{H}_2}}{dx} \Big|_{0+} \right)$$

- Since the thickness of the preheat zone is of order 1 and that of the oxidation layer of order ε the upstream slope of the H₂ concentration can be neglected compared to the downstream slope

$$\frac{dx_{\text{H}_2}}{dx} \Big|_{0+} \ll \frac{dx_{\text{H}_2}}{dx} \Big|_{0-}$$

- It then follows with $x_{H_2} = \frac{\varepsilon z}{(1 + \alpha)q}$ and $\eta = \frac{2qx}{\varepsilon}$

that the upstream boundary condition of $\frac{d^2 z}{d\eta^2} = (\varepsilon^4 Da_{III})z^3$ reads

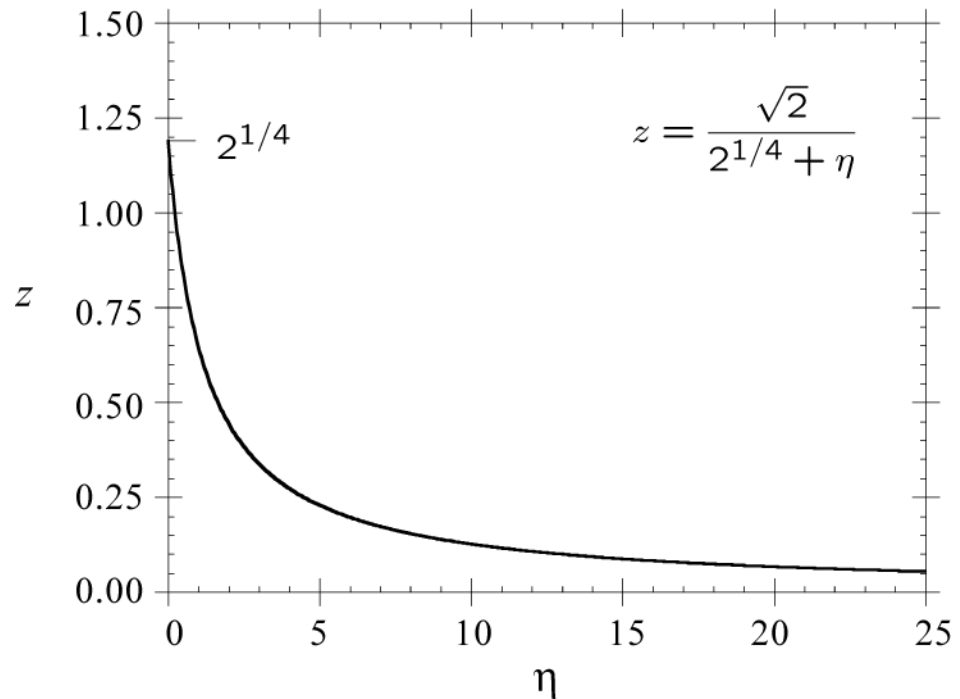
$$\frac{dz}{d\eta} = -1 \quad \text{at} \quad \eta = 0$$

Then the solution is

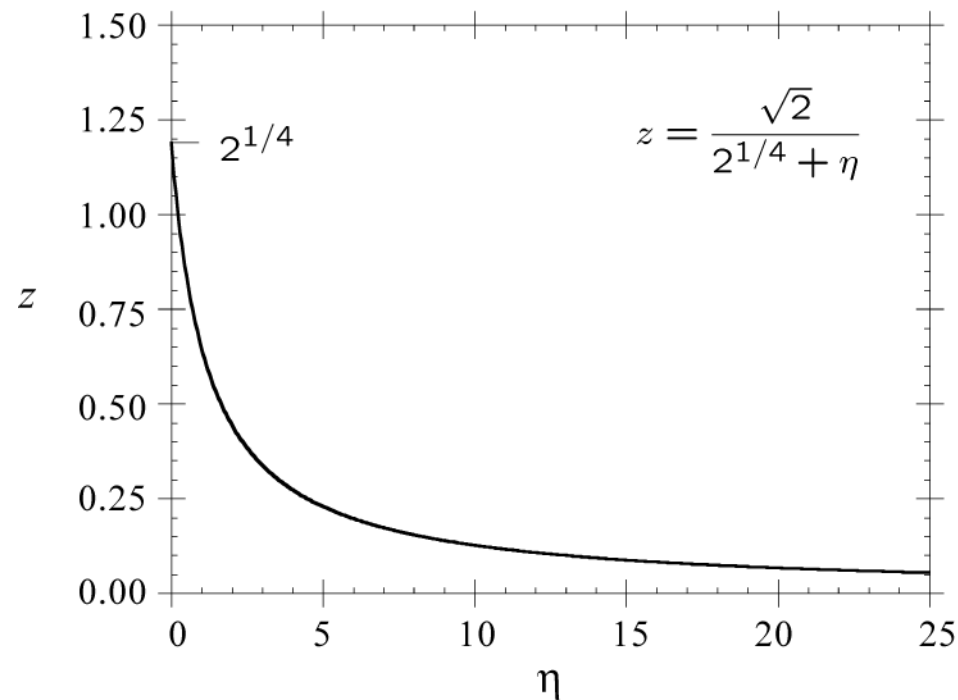
$$z = \frac{2^{1/2}}{2^{1/4} + \eta}$$

with

$$z_0 = 2^{1/4} \quad \text{at} \quad \eta = 0$$



- The profile shows a very slow decrease of z towards $\eta \rightarrow \infty$



- This may explain why in numerically and experimentally obtained concentration and temperature profiles the downstream conditions are approached only very far behind the flame

An Analytic Expression for the Burning Velocity

- The result $z_0 = 2^{1/4}$ at $\eta = 0$

may now be used in $x_{\text{H}_2} = \frac{\varepsilon z}{(1 + \alpha)q}$

and $\omega_{\text{III}} = 2q\text{Da}_{\text{III}}\varepsilon^3 z^3$

to determine the quantities required in

$$\text{Da}_I = \frac{\rho_0^2 Y_{\text{CH}_4} u \lambda_0 (K_{\text{IV}} X_{\text{O}_2} X_{\text{H}_2}^3)_0^{1/2}}{\rho_u^2 s_L^2 W_{\text{CH}_4} c_{p0} X_{\text{H}_2\text{O}}} \text{Le}_{\text{CH}_4} k_{11}(T^0).$$

and thereby the burning velocity s_L

- By dividing

$$\text{Da}_I = \frac{\rho_0^2}{\rho_u^2 s_L^2} \frac{Y_{\text{CH}_4 u} \lambda_0 (K_{IV} X_{\text{O}_2} X_{\text{H}_2}^3)_0^{1/2}}{W_{\text{CH}_4} c_{p0} X_{\text{H}_2\text{O}}} \text{Le}_{\text{CH}_4} k_{11}(T^0)$$

by

$$\eta = \frac{2qx}{\varepsilon}$$

one can eliminate s_L and obtain a relation of the form

$$\frac{k_1^2(T^0)}{k_{11}(T^0)k_5(T^0)/(\mathcal{R}/T^0)} = 1.5p \frac{\text{Le}_{\text{CH}_4}}{\text{Le}_{\text{O}_2}}$$

- Here the universal gas constant must be used as $\mathcal{R} = 82.05 \text{ atm cm}^3/\text{mol/K}$ in order to be consistent with the units of the reaction rates and the pressure

- The equation

$$\frac{k_1^2(T^0)}{k_{11}(T^0)k_5(T^0)/(\mathcal{R}/T^0)} = 1.5p \frac{Le_{\text{CH}_4}}{Le_{\text{O}_2}}$$

shows that with the rate coefficients fixed, the inner layer temperature is function of the pressure only

- It does not depend on the preheat temperature, the dilution of the fuel concentration in the unburnt mixture and thereby the adiabatic flame temperature

- After some algebraic manipulations the expression for the burning velocity reads

$$s_L^2 = \frac{8 k_1^2}{15 k_{11} q^4} \frac{1}{X_{H_2O}} \frac{Y_{CH_4,u}}{W_{CH_4}} \frac{\lambda_0}{c_{p0}} \left(\frac{Le_{O_2}^5 Le_{H_2}^3 K_{IV}(T^0)}{Le_{CH_4} 2^5 (1 + \alpha_0)^3} \right)^{1/2} \frac{T_u^2 (T_b - T^0)^4}{T_0^2 (T_b - T_u)^4}$$

where $z_0 = 2^{1/4}$ at $\eta = 0$ and $\omega_{III} = 2q Da_{III} \varepsilon^3 z^3$

were used to relate ε to the difference between T_b and T^0

$$\varepsilon z_0 = \frac{T_b - T^0}{T_b - T_u}$$

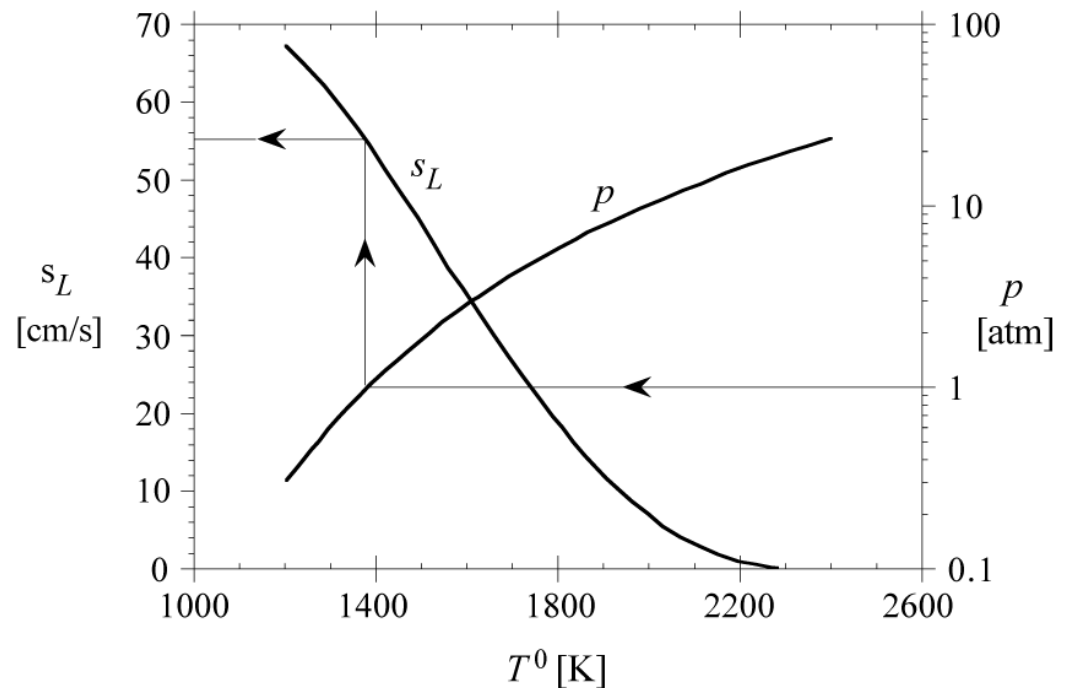
Results of the Asymptotic Analysis

Asymptotic Analysis leads to analytic expression for laminar burning velocity

$$s_L^2 = \frac{8 k_1^2}{15 k_{11} q^4 X_{H_2O}} \frac{1}{W_{CH_4}} \frac{\lambda_0}{c_{p0}} \left(\frac{Le_{O_2}^5 Le_{H_2}^3 K_{IV}(T^0)}{Le_{CH_4} 2^5 (1 + \alpha_0)^3} \right)^{1/2} \frac{T_u^2 (T_b - T^0)^4}{T_0^2 (T_b - T_u)^4}$$

- Pressure obtained from $\frac{k_1^2(T^0)}{k_{11}(T^0)k_5(T^0)/(\mathcal{R}/T^0)} = 1.5p \frac{Le_{CH_4}}{Le_{O_2}}$,

- For an undiluted flame with $T_u = 300$ K and $p = 1$ atm, determining T^0 , one obtains a laminar burning velocity of 54 cm/s for stoichiometric methane flames



- This value is satisfactory in view of the many approximations that were made and the few kinetic rates that were retained
- In fact, it is seen from

$$\frac{k_1^2(T^0)}{k_{11}(T^0)k_5(T^0)/(\mathcal{R}/T^0)} = 1.5p \frac{Le_{CH_4}}{Le_{O_2}}$$

and

$$s_L^2 = \frac{8}{15} \frac{k_1^2}{k_{11} q^4} \frac{1}{X_{H_2O}} \frac{Y_{CH_4,u}}{W_{CH_4}} \frac{\lambda_0}{c_{p0}} \left(\frac{Le_{O_2}^5 Le_{H_2}^3 K_{IV}(T^0)}{Le_{CH_4} 2^5 (1 + \alpha_0)^3} \right)^{1/2} \frac{T_u^2 (T_b - T^0)^4}{T_0^2 (T_b - T_u)^4}$$

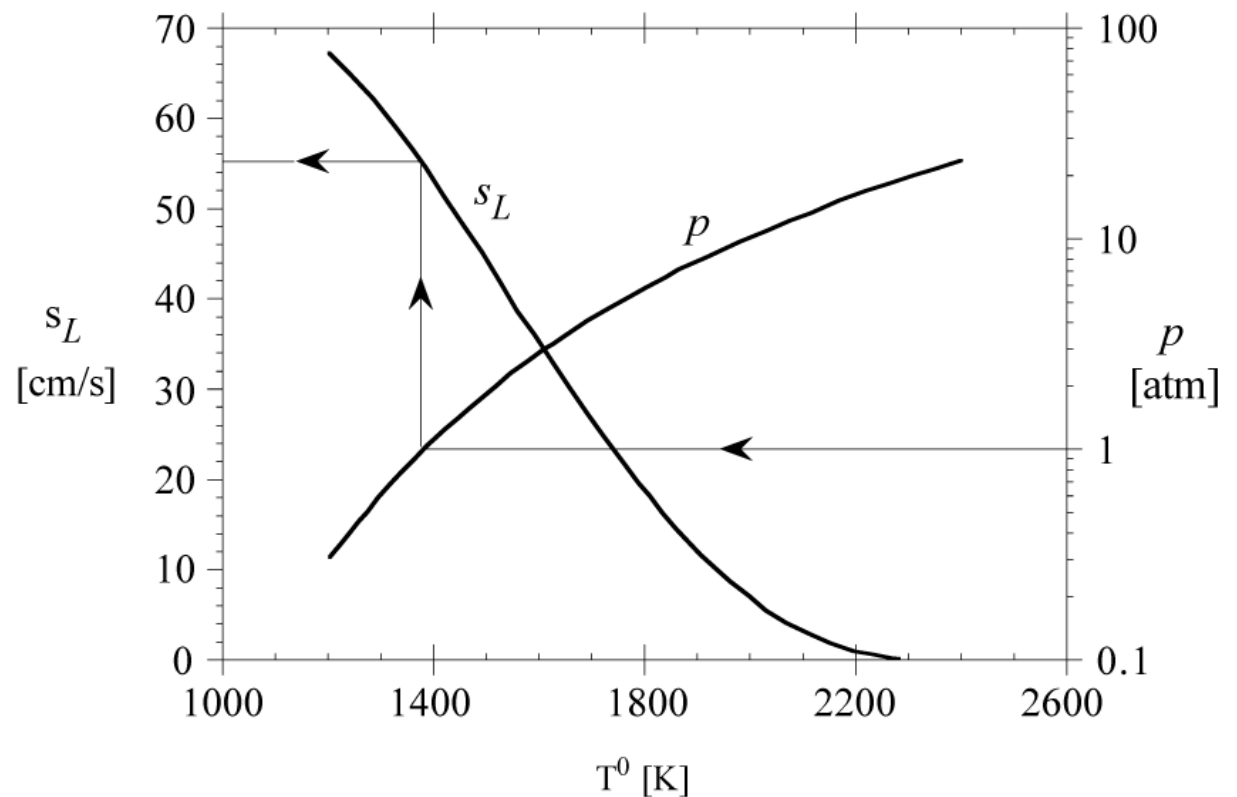
that only the rates of reactions 1, 5, and 11 influence the burning velocity in this approximation

- A further consequence of equation

$$s_L^2 = \frac{8 k_1^2}{15 k_{11} q^4 X_{H_2O}} \frac{1}{W_{CH_4}} \frac{Y_{CH_4,u} \lambda_0}{c_{p0}} \left(\frac{Le_{O_2}^5 Le_{H_2}^3 K_{IV}(T^0)}{Le_{CH_4} 2^5 (1 + \alpha_0)^3} \right)^{1/2} \frac{T_u^2 (T_b - T^0)^4}{T_0^2 (T_b - T_u)^4}$$

is that the **burning velocity vanishes as T^0 reaches T_b**

- With $T_b = 2320$ K, T^0 reaches T_b when the pressure is larger than approximately 20 atm



- Different values of T_b would have been obtained for a diluted or preheated flame
 - The fact that at a fixed pressure T^0 is fixed by the rate of rate coefficients points towards the possibility to explain flammability limits at least in terms of dilution for stoichiometric flames
- ➔ If the amount of fuel is so low that in the unburnt mixture the corresponding adiabatic flame temperature is lower than T_0 , a premixed flame cannot be established

Relation to the Activation Energy of the One-step Model

- Using the burning velocity expression from the preceding lecture

$$\rho_u s_L = \sqrt{2 \frac{B \rho_b^2 \lambda_b \mathcal{R}^2 T_b^4}{c_p (T_b - T_u)^2 E^2} \exp\left(-\frac{E}{\mathcal{R} T_b}\right) S}$$
$$S = \frac{\nu'_{\text{CH}_4} Y_{\text{O}_2,b}}{M_{\text{O}_2}} + \frac{\nu'_{\text{O}_2} Y_{\text{CH}_4,b}}{M_{\text{CH}_4}} + \frac{2 \nu'_{\text{O}_2} \nu'_{\text{CH}_4} c_p \mathcal{R} T_b^2}{(-\Delta H) E},$$

one may plot the burning velocity in an Arrhenius diagram over $1/T_b$

- Then in the limit of a large activation energy, the slope in this diagram is given by

$$\frac{d \ln s_L^2}{d(1/T_b)} = -\frac{E}{\mathcal{R}} \quad \text{or} \quad \frac{d \ln s_L^2}{d \ln T_b} = \frac{E}{\mathcal{R}T_b}$$

- Applying this form to

$$s_L^2 = \frac{8 k_1^2}{15 k_{11} q^4 X_{\text{H}_2\text{O}}} \frac{1}{W_{\text{CH}_4}} \frac{Y_{\text{CH}_4,u} \lambda_0}{c_{p0}} \left(\frac{\text{Le}_{\text{O}_2}^5 \text{Le}_{\text{H}_2}^3 K_{\text{IV}}(T^0)}{\text{Le}_{\text{CH}_4} 2^5 (1 + \alpha_0)^3} \right)^{1/2} \frac{T_u^2 (T_b - T^0)^4}{T_0^2 (T_b - T_u)^4}$$

with T^0 fixed leads to

$$\frac{d \ln s_L^2}{d \ln T_b} = \frac{4T_b}{T_b - T^0} - \frac{4T_b}{T_b - T_u}$$

- Since the second of the terms is much smaller than the first,

with $\varepsilon z_0 = \frac{T_b - T^0}{T_b - T_u}$, where z_0 is the scaled hydrogen mass fraction in the inner layer,

and when T^0 approaches T_b and ε is small, one obtains

$$\frac{E}{RT_b} = \frac{4T_b}{T_b - T_u} \frac{1}{\varepsilon z_0}$$

- Therefore the Zeldovich number $Ze = \frac{E(T_b - T_u)}{\mathcal{R}T_b^2}$

introduced in the previous lecture may be expressed as

$$Ze = \frac{E(T_b - T_u)}{\mathcal{R}T_b^2} = \frac{4}{\varepsilon z_0}$$

- In the one-step model the thickness of the reaction zone was of the order of the inverse of the Zeldovich number
- This corresponds for the two-step model for methane flames to the thickness of the oxidation layer
- Therefore the oxidation layer seems to play a similar role in hydrocarbon flames as the reaction zone in one-step asymptotics

Analytic Approximations of Burning Velocities for Lean CH₄, C₂H₆, C₂H₄, C₂H₂, and C₃H₈ Flames

- The burning velocity expression

$$s_L^2 = \frac{8 k_1^2}{15 k_{11} q^4 X_{H_2O}} \frac{1}{W_{CH_4}} \frac{Y_{CH_4,u} \lambda_0}{c_{p0}} \left(\frac{Le_{O_2}^5 Le_{H_2}^3 K_{IV}(T^0)}{Le_{CH_4} 2^5 (1 + \alpha_0)^3} \right)^{1/2} \frac{T_u^2 (T_b - T^0)^4}{T_0^2 (T_b - T_u)^4}$$

$$\frac{k_1^2(T^0)}{k_{11}(T^0) k_5(T^0) / (\mathcal{R}/T^0)} = 1.5p \frac{Le_{CH_4}}{Le_{O_2}}$$

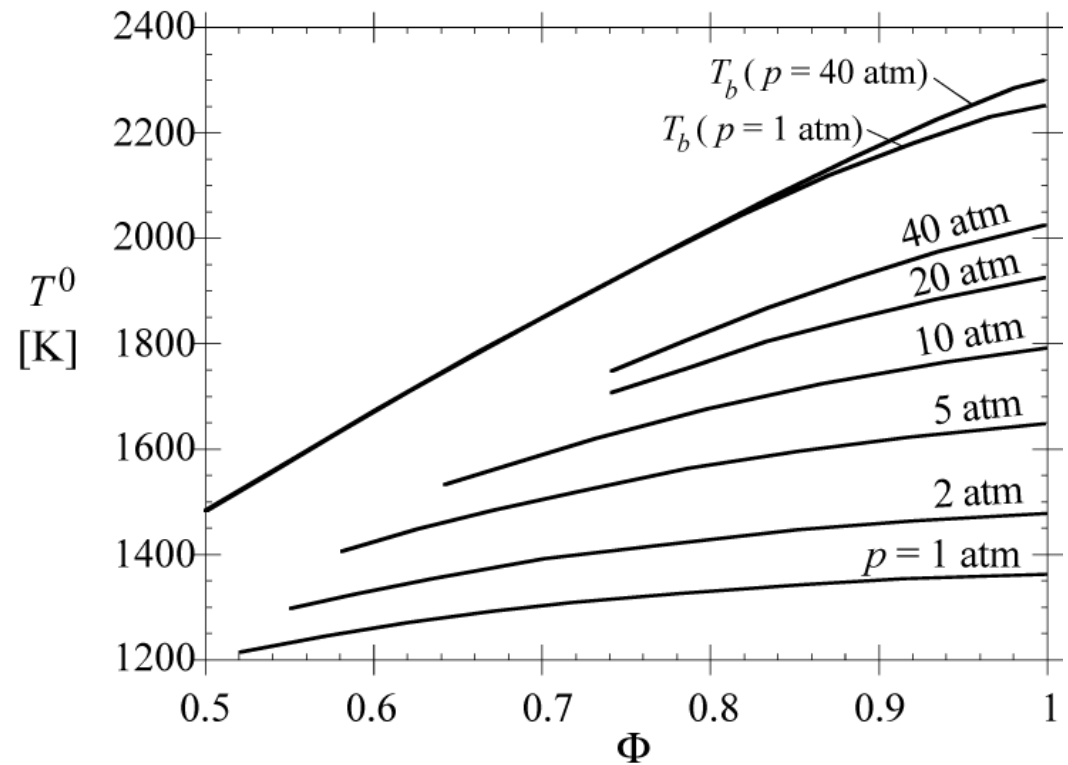
presented may be generalized by writing an approximation formula for burning velocities as

$$s_L = Y_{F,u}^m A(T^0) \frac{T_u}{T^0} \left(\frac{T_b - T^0}{T_b - T_u} \right)^n \quad \text{and} \quad p = P(T^0)$$

where the functions $A(T^0)$ and $P(T^0)$ are determined by fitting numerical or experimental data and the values $m = 1/2$ and $n = 2$ would correspond to the previous expressions for premixed methane flames

- $p = P(T^0)$ assumes that the inner layer temperature is a function of pressure only, and it does not depend, for instance, on the equivalence ratio

- This is a fairly crude approximation as may be seen when inner layer temperatures obtained from asymptotic analysis (Seshadri 1991) are plotted together with the adiabatic temperatures as a function of the equivalence ratio



- If the structure of any other hydrocarbon fuel is similar to that of methane, these exponents should not differ very much from these numbers
- Since $A(T^0)$ and $B(T^0)$ contain essentially the temperature dependence due to rate coefficients, we express them in Arrhenius form

$$A(T^0) = F \exp(-G/T^0) \quad P(T^0) = B \exp(-E/T^0)$$

- This concept was tested by Göttgens 1992
- The basis of the approximation was a data set of 197, 223, 252, 248, and 215 premixed flames for CH_4 , C_2H_6 , C_2H_4 , C_2H_2 and C_3H_8 , in the range between $p = 1$ atm and 40 atm, T_u between 298 K and 800 K, and the fuel-air equivalence ratio between $\phi = 0.4$ and 1.0.

- A nonlinear approximation procedure was employed, yielding the following values for the coefficients:

fuel	B [bar]	E [K]	F [cm/s]	G [K]	m	n
CH ₄	3.1557e8	23873.0	22.176	-6444.27	0.565175	2.5158
C ₂ H ₂	56834.0	11344.4	37746.6	1032.36	0.907619	2.5874
C ₂ H ₄	3.7036e5	14368.7	9978.9	263.23	0.771333	2.3998
C ₂ H ₆	4.3203e6	18859.0	1900.41	-506.973	0.431345	2.1804
C ₃ H ₈	2.2502e6	17223.5	1274.89	-1324.78	0.582214	2.3970

- The approximation was surprisingly the best for C₂H₂, yielding a standard deviation for s_L of 2.3%, followed by C₂H₄ with 3.2%, C₂H₆ and C₃H₈ with 6.2%, and CH₄ with 7.4%

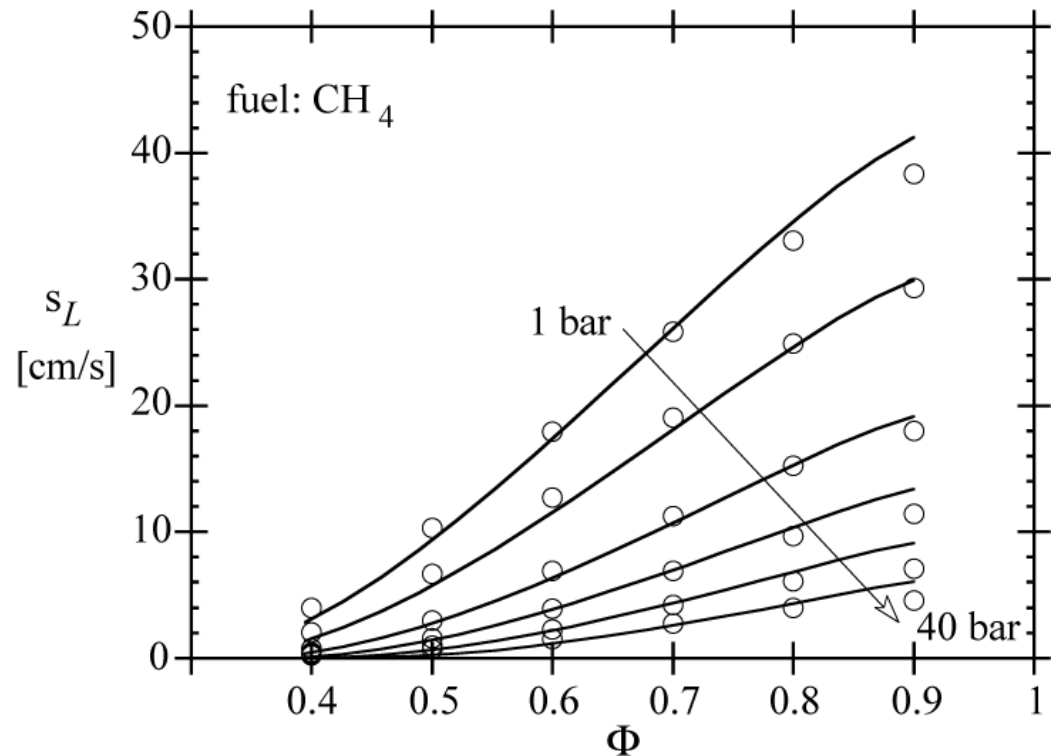
- These deviations may be considered extremely small in view of the fact that such a large range of equivalence ratios, pressures and preheat temperatures has been covered with an approximation formula containing only six coefficients
- A closer look at the exponents m and n shows that m is close to $1/2$ for CH_4 and C_3H_8 , but close to unity for C_2H_2 and C_2H_4
- This suggests that the asymptotic model for these flames should differ from the one for CH_4 in some important details
- The exponent m lies around 2.5 and thereby sufficiently close to 2 for all fuels

- Burning velocities for methane calculated from

$$s_L = Y_{Fu}^m A(T^0) \frac{T_u}{T^0} \left(\frac{T_b - T^0}{T_b - T_u} \right)^n \quad \text{and} \quad p = P(T^0)$$

are plotted as a function of equivalence ratio for different pressures at $T_u = 298$ K and compared with the values obtained from the numerical computations.

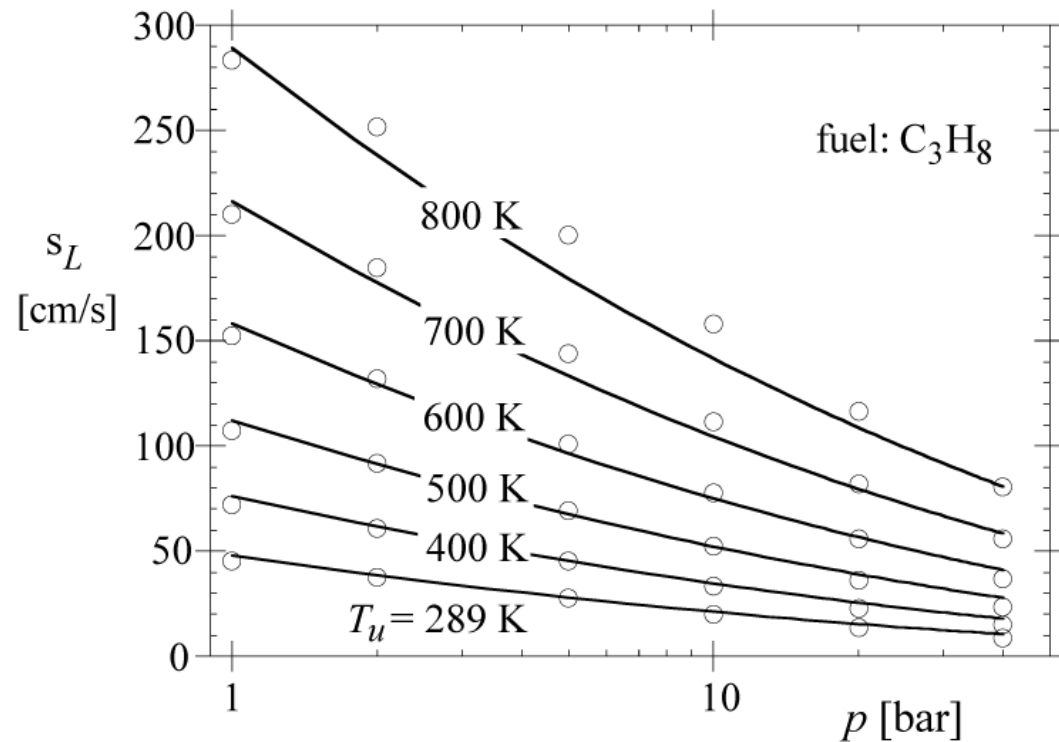
- Generally the largest deviations from the numerical computations occur around $\phi = 1$



- Burning velocities for methane calculated from

$$s_L = Y_{F_u}^m A(T^0) \frac{T_u}{T^0} \left(\frac{T_b - T^0}{T_b - T_u} \right)^n \quad \text{and} \quad p = P(T^0)$$

- The pressure and unburnt temperature variation of s_L at stoichiometric mixture are plotted for propane



Example

- From the approximation $s_L = Y_{F,u}^m A(T^0) \frac{T_u}{T^0} \left(\frac{T_b - T^0}{T_b - T_u} \right)^n$

calculate in comparison with

$$\rho_u s_L = \sqrt{2 \frac{B \rho_b^2 \lambda_b \mathcal{R}^2 T_b^4}{c_p (T_b - T_u)^2 E^2} \exp\left(-\frac{E}{\mathcal{R} T_b}\right) S}$$
$$S = \frac{\nu'_F Y_{O_2,b}}{M_{O_2}} + \frac{\nu'_{O_2} Y_{F,b}}{M_F} + \frac{2 \nu'_{O_2} \nu'_F c_p \mathcal{R} T_b^2}{(-\Delta H) E}$$

those activation energy, which describes the change of the reaction rate as function of the change in T_b

- Thereby T_u and T^0 should be considered constant

Solution

- If one writes
$$\rho_u s_L = \sqrt{2 \frac{B \rho_b^2 \lambda_b \mathcal{R}^2 T_b^4}{c_p (T_b - T_u)^2 E^2} \exp\left(-\frac{E}{\mathcal{R} T_b}\right) S}$$
$$S = \frac{\nu'_F Y_{O_2,b}}{M_{O_2}} + \frac{\nu'_{O_2} Y_{F,b}}{M_F} + \frac{2 \nu'_{O_2} \nu'_F c_p \mathcal{R} T_b^2}{(-\Delta H) E}.$$

approximately as $(\rho_u s_L)^2 = \text{const} \exp(-E/\mathcal{R} T_b)$

and logarithmizes this expression:

$$2 \ln(\rho_u s_L) = \ln(\text{const}) - \frac{E}{\mathcal{R} T_b},$$

one can determine the activation energy by differentiation with respect to $1/T_b$

- This leads to

$$\frac{E}{\mathcal{R}} = -2 \frac{d \ln(\rho_u s_L)}{d(1/T_b)} = 2T_b^2 \frac{d}{dT_b} (\ln(\rho_u s_L))$$

- Using this in

$$s_L = Y_{F,u}^m A(T^0) \frac{T_u}{T^0} \left(\frac{T_b - T^0}{T_b - T_u} \right)^n$$

for $\rho_u = \text{const}$, it follows

$$2T_b^2 \frac{d}{dT_b} (\ln(\rho_u s_L)) = \frac{2nT_b}{T_b - T^0} - \frac{2nT_b}{T_b - T_u}$$

- Therefore one obtains for the Zeldovich number Ze

$$Ze = n \left(\frac{T_b - T_u}{T_b - T^0} - 1 \right)$$

- Here, following

$$p = P(T^0)$$

T^0 is only dependent on pressure, while T_b follows

$$T_b(Z) = T_u(Z) + \frac{Q_{\text{ref}} Y_{F,1}}{c_p \nu'_F W_F} Z, \quad Z \leq Z_{st},$$

$$T_b(Z) = T_u(Z) + \frac{Q_{\text{ref}} Y_{O_2,2}}{c_p \nu'_{O_2} W_{O_2}} (1 - Z) \quad Z \geq Z_{st}$$

depends both on T_u and on the fuel-air ratio $\phi = 1/\lambda$

- If the difference $T_b - T_0$ is small compared with $T_b - T_u$, the second term in the parenthesis can be neglected