

Laminar Premixed Flames: Flame Structure

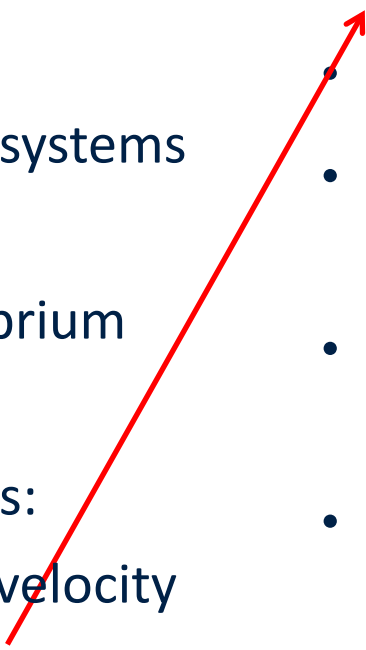
Combustion Summer School
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Course Overview

Part I: Fundamentals and Laminar Flames

- Introduction
 - Fundamentals and mass balances of combustion systems
 - Thermodynamics, flame temperature, and equilibrium
 - Governing equations
 - Laminar premixed flames: Kinematics and burning velocity
 - **Laminar premixed flames:**
Flame structure
 - Laminar diffusion flames
 - FlameMaster flame calculator
 - **Thermal flame theory**
 - Flame thickness and flame time
 - Four-step model for methane-air flames
 - Three-step model for methane-air flames
 - Asymptotic structure of stoichiometric methane-air flames
 - Analytic expression for the burning velocity of methane and other hydrocarbon flames
 - Flammability limits
- 

Thermal Flame Theory

The first theoretical treatment of stationary one dimensional flames:

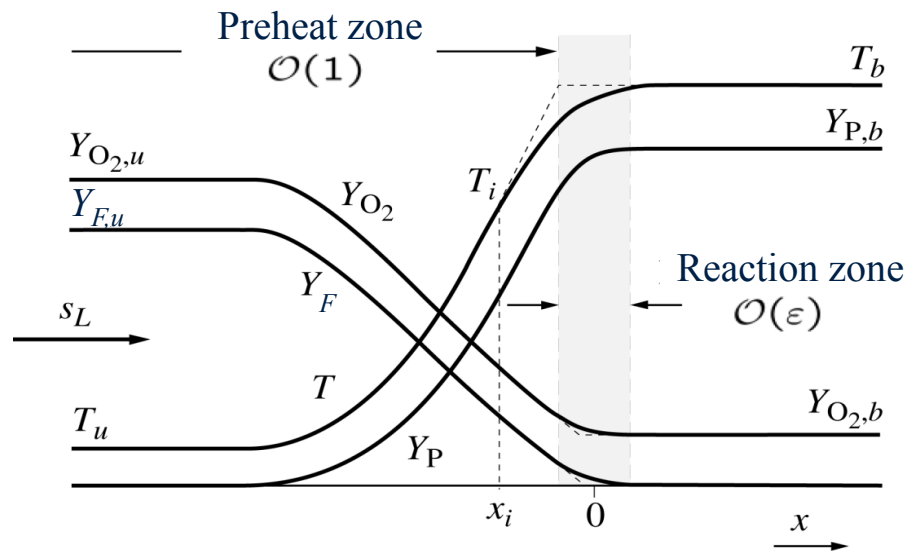
Thermal Flame Theory of Zeldovich and Frank-Kamenetzki (1938)

- A classical example of a mathematical description of the combustion of premixed gases
- Assumption of a one step global reaction with high activation energy
→ Mathematically solveable form of the governing equations
- This theory is the origin of a development, which placed combustion science on a mathematical basis

Thermal Flame Theory

- Starting point:
 - Stationary and flat flame front
 - Absolute values of the flow velocity and the burning velocity are identical, and in opposite direction

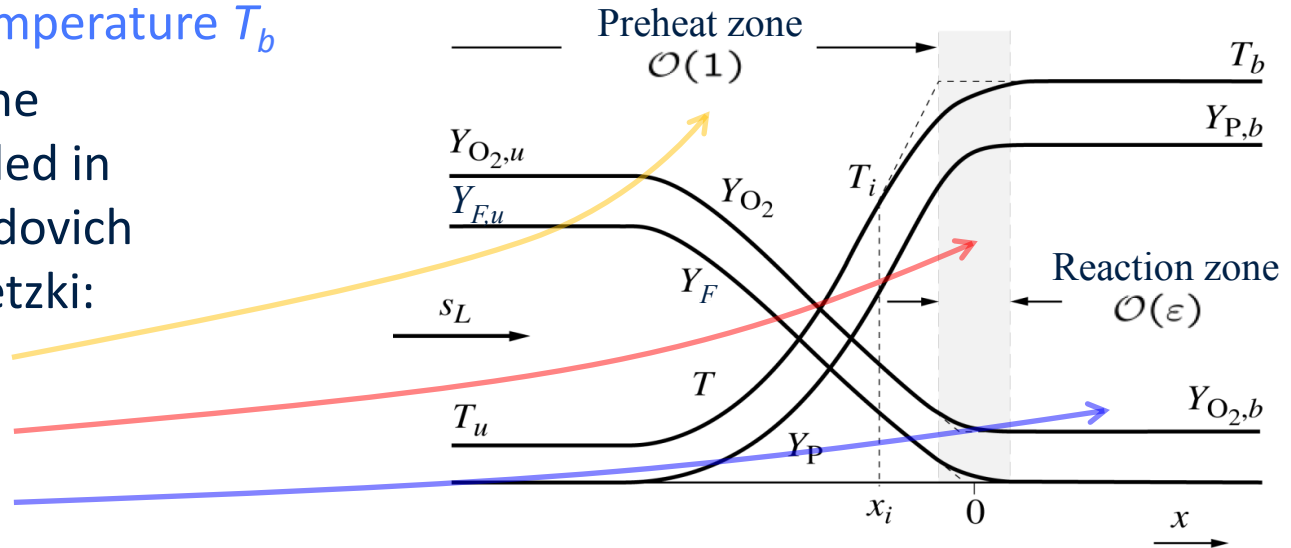
Temperature and concentration profiles, schematically for a lean mixture



Thermal Flame Theory

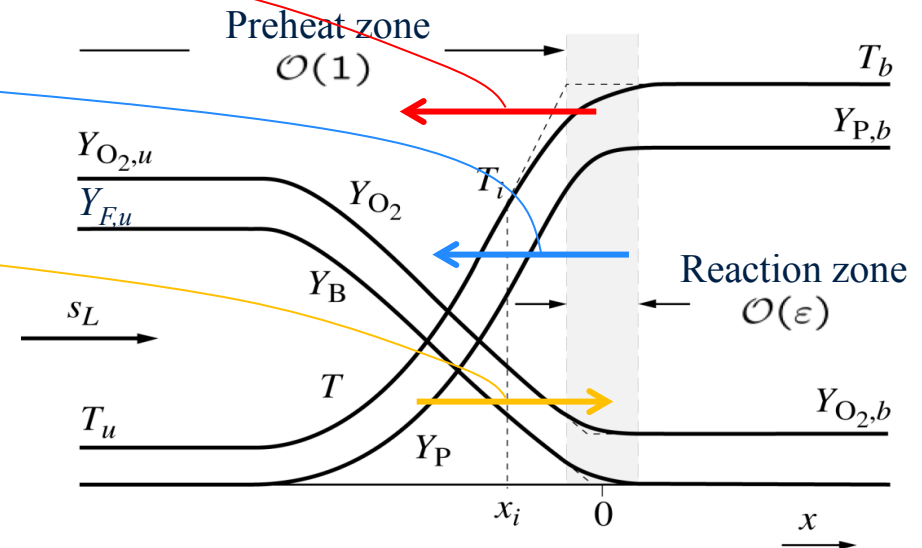
Flame front (lean mixture):

- Complete fuel conversion
- Excess oxygen remains
- Temperature rises from the initial value T_u to the **adiabatic flame temperature T_b**
- The area around the flame front is divided in **three zones** by Zeldovich and Frank-Kamenetzki:
 - **Preheat zone**
 - **Reaction zone**
 - **Equilibrium zone**



Thermal Flame Theory

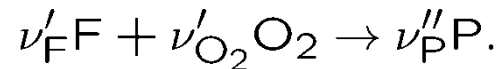
- Heat conduction out of reaction zone
→ Mixture in the preheat zone is continuously heated
- Diffusion of combustion products back into the unburnt mixture
- Diffusion of reactants (fuel and oxygen), into the reaction zone
- Transition
 - Position x_i
 - Temperature T_i
- Reaction zone: chemical reactions



Thermal Flame Theory

- Simplification:

- Global reaction equation



- Reaction rate

$$\omega = B \frac{\rho Y_F}{W_F} \frac{\rho Y_{O_2}}{W_{O_2}} \exp\left(\frac{-E}{\mathcal{R}T}\right)$$

- Behind the flame front:

- No chemical conversion → Reaction rate = 0

- Complete consumption of:

- Fuel (for lean mixtures)
- Oxygen (for rich mixtures)
- Both reactants (for stoichiometric mixtures)

- In the equilibrium zone:

$$Y_{F,b} \cdot Y_{O_2,b} = 0.$$

Thermal Flame Theory

- Further simplifications:
 - Specific heat is constant and identical for all components
 - Constant enthalpy of reaction
 - Lewis-Number $Le = 1$
 - Enthalpy is constant
- Coupling functions between the concentrations and the temperatures:

$$Y_F = -\frac{\nu'_F W_F c_p}{Q} (T - T_b) + Y_{F,b}$$

$$Y_{O_2} = -\frac{\nu'_{O_2} W_{O_2} c_p}{Q} (T - T_b) + Y_{O_2,b}$$

Thermal Flame Theory

- Momentum equation, limit of small Mach-Numbers → constant pressure

$$p = \text{const}$$

- With the ideal gas law and the coupling functions:

- Density
- Thermal conductivity
- Reaction rate

as function of temperature

- Solution of the continuity equation for one dimensional flows:

$$\rho v = \rho_u v_u = \rho_u s_L$$

Thermal Flame Theory

- Only one differential equation: Temperature equation in x-direction

$$\rho_u s_L \frac{dT}{dx} = \frac{d}{dx} \left(\frac{\lambda}{c_p} \frac{dT}{dx} \right) - \frac{Q}{c_p} \omega$$

- Solution of this equation with the following **assumptions** suggested by Zeldovich and Frank-Kamenetzki:
 1. Preheat zone, $T < T_i$: no reactions: $\omega = 0$
 2. Reaction zone, $T > T_i$: Convective term on the left hand side is negligible compared to the diffusive term and the reaction term
- Validity of the second assumption:
 - Asymptotic theory
 - Nature of the reaction zone: very thin boundary layer
 - Mathematical justification by singular asymptotic expansion

Thermal Flame Theory

- First assumption yields

$$\rho_u s_L \frac{dT}{dx} = \frac{d}{dx} \left(\frac{\lambda}{c_p} \frac{dT}{dx} \right) - \frac{Q}{c_p} \omega \quad \rightarrow \quad \rho_u s_L \frac{dT}{dx} \approx \frac{d}{dx} \left(\frac{\lambda}{c_p} \frac{dT}{dx} \right)$$

- Integration of the simplified differential equation in the preheat zone
- For the first derivative, with boundary conditions at $x = -\infty$

$$\frac{dT}{dx} = \frac{c_p \rho_u s_L}{\lambda} (T - T_u)$$

$$\text{At } x = x_i : \quad \left. \frac{dT}{dx} \right|_{x_i}^V = \frac{c_p \rho_u s_L}{\lambda_i} (T_i - T_u)$$

Thermal Flame Theory

- Second assumption yields

$$\rho_u s_L \frac{dT}{dx} = \frac{d}{dx} \left(\frac{\lambda}{c_p} \frac{dT}{dx} \right) - \frac{Q}{c_p} \omega \quad \rightarrow \quad 0 \approx \frac{d}{dx} \left(\frac{\lambda}{c_p} \frac{dT}{dx} \right) + \frac{(-\Delta H)}{c_p} w(T)$$

- Heat conduction term can be substituted by

$$\frac{d}{dx} \left(\frac{\lambda}{c_p} \frac{dT}{dx} \right) = \frac{dT}{dx} \frac{d}{dT} \left(\frac{\lambda}{c_p} \frac{dT}{dx} \right) = \frac{c_p}{\lambda} \frac{1}{2} \frac{d}{dT} \left(\frac{\lambda}{c_p} \frac{dT}{dx} \right)^2$$

- The differential equation then becomes

$$\frac{1}{2} \frac{d}{dT} \left(\frac{\lambda}{c_p} \frac{dT}{dx} \right)^2 = - \frac{(-\Delta H) \lambda}{c_p^2} w(T)$$

Thermal Flame Theory

- Integration of the differential equation with BC: $x = +\infty, T = T_b$

$$\frac{dT}{dx} = \sqrt{2 \frac{(-\Delta H)}{\lambda^2} \int_T^{T_b} \lambda w(T) dT}.$$

$$\text{At } x = x_i : \quad \left. \frac{dT}{dx} \right|_{x_i}^R = \sqrt{2 \frac{(-\Delta H)}{\lambda^2} \int_{T_i}^{T_b} \lambda w(T) dT}$$

- Zeldovich und Frank-Kamenetzki: derivatives of the temperature in the preheat zone and reaction zone at position x_i are equal:

$$\left. \frac{dT}{dx} \right|_{x_i}^V = \left. \frac{dT}{dx} \right|_{x_i}^R$$

- Relations for preheat and reaction zone have boundary conditions at infinity and need to be equal → Eigenvalue → Burning velocity

Thermal Flame Theory

- Evaluation of the integral in complete form is possible, only if further simplifications are introduced
- Series expansion of the exponential term in

$$\omega = B \frac{\rho Y_F}{W_F} \frac{\rho Y_{O_2}}{W_{O_2}} \exp\left(\frac{-E}{\mathcal{R}T}\right)$$

centered at T_b and neglecting terms of higher order leads to:

$$-\frac{E}{\mathcal{R}T} = -\frac{E}{\mathcal{R}T_b} + \frac{E(T - T_b)}{\mathcal{R}T_b^2}$$

Thermal Flame Theory

- Reaction zone: T differs only slightly from T_b
- Introduce **dimensionless temperature**

$$\Theta = \frac{E(T - T_b)}{\mathcal{R}T_b^2}$$

□ Even for high $E/(\mathcal{R}T_b^2)$, order of magnitude is one

- In the reaction zone: **material properties** assumed **constant**
- **Reaction becomes**

$$\omega = B\rho_b^2 \frac{c_p \mathcal{R}T_b^2}{(-\Delta H)E} \exp\left(-\frac{E}{\mathcal{R}T_b}\right) \left[-\left(\frac{\nu'_F Y_{O_2,b}}{M_{O_2}} + \frac{\nu'_{O_2} Y_{F,b}}{M_F}\right) \Theta + \frac{\nu'_{O_2} \nu'_F c_p \mathcal{R}T_b^2}{(-\Delta H)E} \Theta^2 \right] \exp \Theta$$

Thermal Flame Theory

- Integration yields:

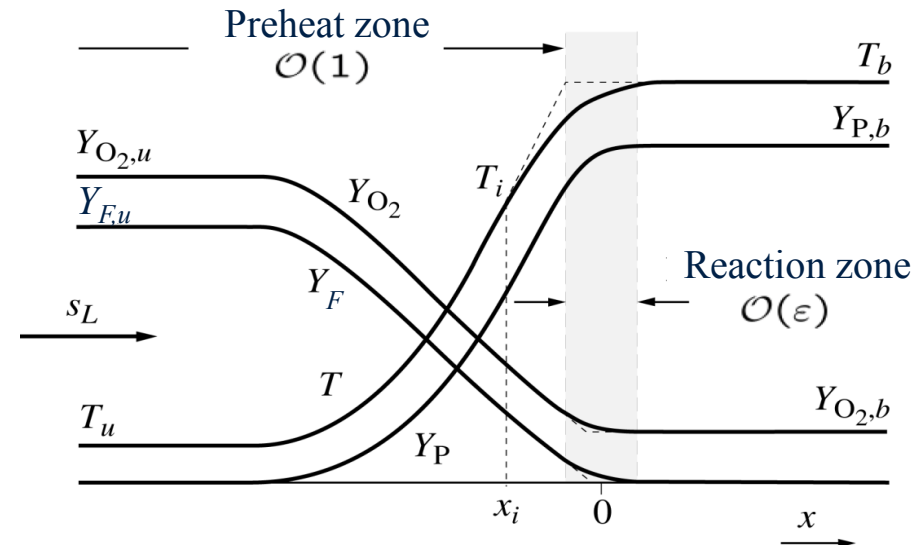
$$\begin{aligned}
 \int_{T_i}^{T_b} \lambda \omega dT &= \lambda_b \frac{\mathcal{R} T_b^2}{E} \int_{\Theta_i}^0 w(\Theta) d\Theta \\
 &= \frac{\lambda_b B \rho_b^2 c_p \mathcal{R}^2 T_b^4}{(-\Delta H) E} \exp\left(-\frac{E}{\mathcal{R} T_b}\right) \left[\left(\frac{\nu'_{\text{F}} Y_{\text{O}_2, b}}{M_{\text{O}_2}} + \frac{\nu'_{\text{O}_2} Y_{\text{F}, b}}{M_{\text{F}}} \right) (1 + (\Theta_i - 1) \exp \Theta_i) \right. \\
 &\quad \left. + 2 \frac{\nu'_{\text{O}_2} \nu'_{\text{F}} c_p \mathcal{R} T_b^2}{(-\Delta H) E} \left(1 - \left(1 - \Theta_i + \frac{\Theta_i^2}{2} \right) \exp \Theta_i \right) \right]
 \end{aligned}$$

Thermal Flame Theory

- Integral:
$$\int_{T_i}^{T_b} \lambda \omega dT = \lambda_b \frac{\mathcal{R} T_b^2}{E} \int_{\Theta_i}^0 w(\Theta) d\Theta$$
$$= \frac{\lambda_b B \rho_b^2 c_p \mathcal{R}^2 T_b^4}{(-\Delta H) E} \exp\left(-\frac{E}{\mathcal{R} T_b}\right) \left[\left(\frac{\nu'_F Y_{O_2,b}}{M_{O_2}} + \frac{\nu'_{O_2} Y_{F,b}}{M_F} \right) (1 + (\Theta_i - 1) \exp \Theta_i) \right. \\ \left. + 2 \frac{\nu'_{O_2} \nu'_F c_p \mathcal{R} T_b^2}{(-\Delta H) E} \left(1 - \left(1 - \Theta_i + \frac{\Theta_i^2}{2} \right) \exp \Theta_i \right) \right]$$

- With:
 - Asymptotic limit of high activation energies
 - Overlapping process of the solution from preheat and reaction zones

- Substitution of θ_i by θ_u
 → Assumption: Reaction zone also valid in the preheat zone



Thermal Flame Theory

- Physical explanation: Below T_i , the integral of the reaction rate is negligible because of the high temperature dependence
→ No difference between integration from T_i to T_b or from T_u to T_b
- θ_u has a high negative values for high activation energies
- In terms, which include $\exp(\theta_u)$, θ_u can be replaced by $-\infty$
→ Terms disappear

$$\begin{aligned}
 \int_{T_i}^{T_b} \lambda w dT &= \lambda_b \frac{\mathcal{R} T_b^2}{E} \int_{\Theta_i}^0 w(\Theta) d\Theta \\
 &= \frac{\lambda_b B \rho_b^2 c_p \mathcal{R}^2 T_b^4}{(-\Delta H) E} \exp\left(-\frac{E}{\mathcal{R} T_b}\right) \left[\left(\frac{\nu'_B Y_{O_2,b}}{M_{O_2}} + \frac{\nu'_{O_2} Y_{B,b}}{M_B} \right) (1 + (\Theta_i - 1) \exp \Theta_i) \right. \\
 &\quad \left. + 2 \frac{\nu'_{O_2} \nu'_B c_p \mathcal{R} T_b^2}{(-\Delta H) E} \left(1 - \left(1 - \Theta_i + \frac{\Theta_i^2}{2} \right) \exp \Theta_i \right) \right].
 \end{aligned}$$

$$\text{At } x = x_i : \quad \left. \frac{dT}{dx} \right|_{x_i}^R = \sqrt{2 \frac{(-\Delta H)}{\lambda^2} \int_{T_i}^{T_b} \lambda w(T) dT}$$

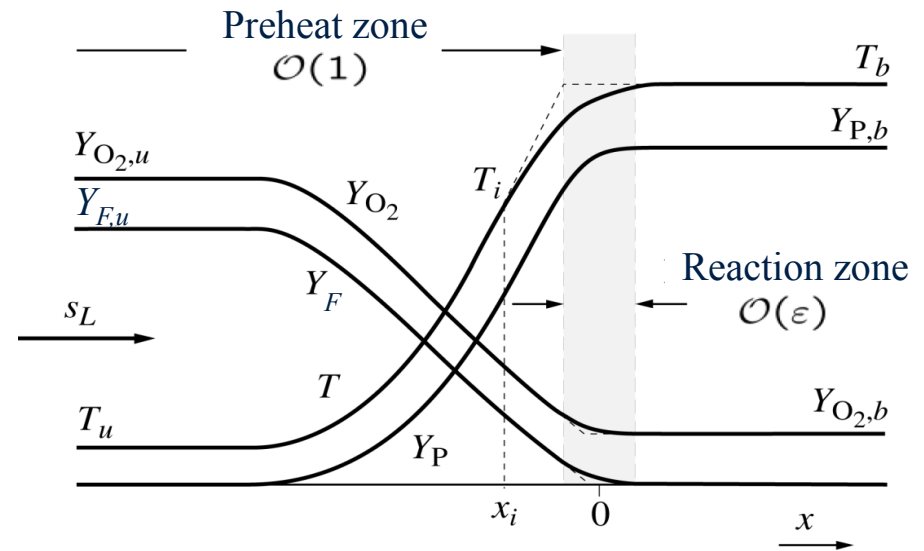
Thermal Flame Theory

Preheat zone:

- Replacing T_i by T_b and λ_i by λ_b

$$\rightarrow \left. \frac{dT}{dx} \right|_{x_i}^P = \frac{c_p \rho_u s_L}{\lambda_b} (T_b - T_u)$$

- Assumptions:
 - Reaction zone is so thin that the preheat zone reaches till T_b
 - T_i differs only minimally from T_b



Thermal Flame Theory

- Equating the following expressions

$$\left. \frac{dT}{dx} \right|_{x_i}^V = \frac{c_p \rho_u s_L}{\lambda_b} (T_b - T_u) \quad \left. \frac{dT}{dx} \right|_{x_i}^R = \sqrt{2 \frac{(-\Delta H)}{\lambda^2} \int_{T_i}^{T_b} \lambda w(T) dT}$$

leads to:

$$\rho_u s_L = \sqrt{2 \frac{B \rho_b^2 \lambda_b \mathcal{R}^2 T_b^4}{c_p (T_b - T_u)^2 E^2} \exp\left(-\frac{E}{\mathcal{R} T_b}\right) S}$$

with

$$S = \frac{\nu'_F Y_{O_2,b}}{M_{O_2}} + \frac{\nu'_{O_2} Y_{F,b}}{M_F} + \frac{2 \nu'_{O_2} \nu'_F c_p \mathcal{R} T_b^2}{(-\Delta H) E}.$$

- Terms in S depend on **equivalence ratio ϕ** :
 - Lean mixture \rightarrow Oxygen mass fraction high, $Y_{B,b} \approx 0$
 - Rich mixture \rightarrow Fuel mass fraction high, $Y_{O_2,b} \approx 0$
 - Stoichiometric mixture $\rightarrow Y_{O_2,b} \approx Y_{B,b} \approx 0$

Thermal Flame Theory

$$\rho_u s_L = \sqrt{2 \frac{B \rho_b^2 \lambda_b \mathcal{R}^2 T_b^4}{c_p (T_b - T_u)^2 E^2} \exp\left(-\frac{E}{\mathcal{R} T_b}\right) S}$$

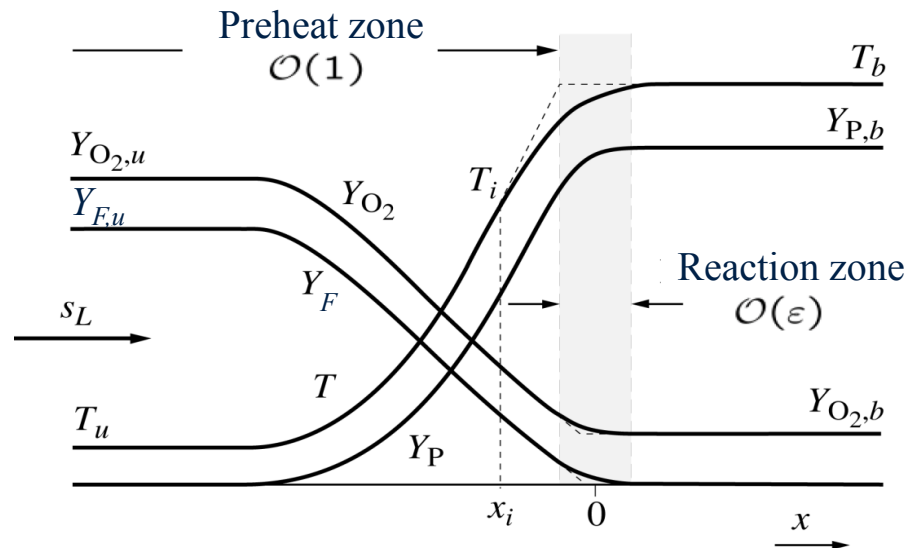
$$S = \frac{\nu'_F Y_{O_2,b}}{M_{O_2}} + \frac{\nu'_{O_2} Y_{F,b}}{M_F} + \frac{2 \nu'_{O_2} \nu'_F c_p \mathcal{R} T_b^2}{(-\Delta H) E}.$$

- In a stoichiometric mixture, the last term is dominant
→ Approximation:

$$S = \begin{cases} \frac{\nu'_F Y_{O_2,b}}{M_{O_2}} & \text{für } \phi \ll 1, \\ \frac{2 \nu'_{O_2} \nu'_F c_p \mathcal{R} T_b^2}{(-\Delta H) E} & \text{für } \phi = 1, \\ \frac{\nu'_{O_2} Y_{F,b}}{M_F} & \text{für } \phi \gg 1. \end{cases}$$

Thermal Flame Theory (Summary)

- Preheat zone: reaction rate is neglected
- Reaction zone: convection term is neglected
- Approximation of the reaction rate by a series expansion centered at T_b , only the exponential term is expanded
- Material properties are set to their values at T_b
- Integration over the reaction zone \rightarrow Integral between $T = -\infty$ und $T = T_b$
- When using the solution from the preheat zone, T_i is set equal to T_b .



Thermal Flame Theory (Summary)

- Original derivation of the thermal flame theory of Zeldovich and Frank-Kamenetzki not for **reaction rate** in the form of

$$\omega = B \frac{\rho Y_F}{W_F} \frac{\rho Y_{O_2}}{W_{O_2}} \exp\left(\frac{-E}{\mathcal{R}T}\right)$$

which is **of first order** with respect to both **fuel** and **oxygen**

- Rather, different results for reaction rate of **zeroth, first, and second order** were derived



Comparison with present result shows that first order valid for either very lean or very rich

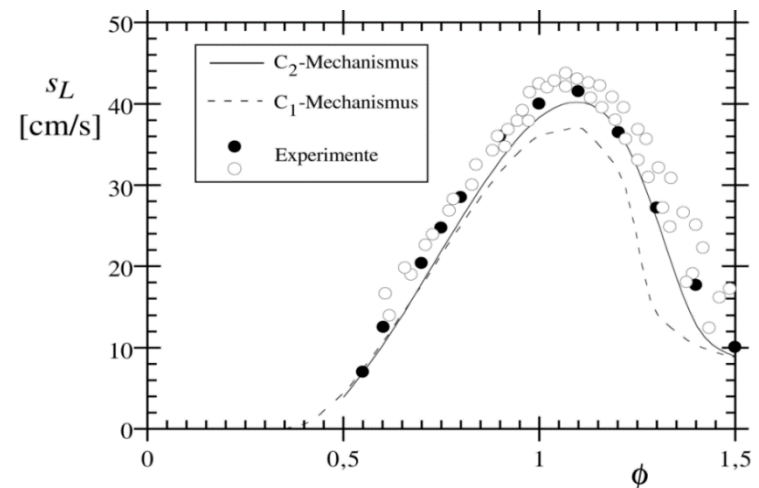
Thermal Flame Theory (Summary)

- Comparison with the following result:

$$\rho_u s_L = \sqrt{2 \frac{B \rho_b^2 \lambda_b \mathcal{R}^2 T_b^4}{c_p (T_b - T_u)^2 E^2} \exp\left(-\frac{E}{\mathcal{R} T_b}\right) S},$$


- Very rich/very lean mixture: reaction of first order
 - The component in shortage determines the conversion
- Stoichiometric mixture: Reaction of second order
 - Both components are reaction rate-determining

$$S = \begin{cases} \frac{\nu'_F Y_{O_2,b}}{M_{O_2}} & \text{für } \phi \ll 1, \\ \frac{2 \nu'_{O_2} \nu'_F c_p \mathcal{R} T_b^2}{(-\Delta H) E} & \text{für } \phi = 1, \\ \frac{\nu'_{O_2} Y_{F,b}}{M_F} & \text{für } \phi \gg 1. \end{cases}$$



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Flame Thickness and Flame Time

- Thermal flame theory:

$$\rho_u s_L = \sqrt{2 \frac{B \rho_b^2 \lambda_b \mathcal{R}^2 T_b^4}{c_p (T_b - T_u)^2 E^2} \exp\left(-\frac{E}{\mathcal{R} T_b}\right) S}$$

$$S = \frac{\nu'_F Y_{O_2,b}}{M_{O_2}} + \frac{\nu'_{O_2} Y_{F,b}}{M_F} + \frac{2 \nu'_{O_2} \nu'_F c_p \mathcal{R} T_b^2}{(-\Delta H) E}.$$

- Burning velocity s_L : Eigenvalue, results from the solution of the one-dimensional balance equation
- Assumptions:
 - One step reaction → Only one chemical time scale
 - $Le = 1$, thermal diffusivity $\alpha = \lambda/(\rho c_p)$ equal to the mass diffusivity D
- Solution for the burning velocity s_L :

$$s_L = \sqrt{D/t_c}$$

links the parameters diffusivity and chemical time scale

Diffusivity and Chemical Time Scale

- D: thermal diffusivity $D = \frac{\lambda_b}{\rho_u c_p}$,
- Dimensional analysis

$$s_L = \sqrt{D/t_C} \quad \longrightarrow \quad t_F = l_F/s_L = t_C$$

$$l_F = \sqrt{D \cdot t_C}$$

- Chemical time scale:

$$t_c = \frac{\rho_u E^2 (T_b - T_u)^2}{2B \rho_b^2 (\mathcal{R} T_b^2)^2 S} \exp\left(\frac{E}{\mathcal{R} T_b}\right)$$

$$= \frac{1}{2} \cdot \frac{\rho_u}{\rho_b} \cdot \text{Ze}^2 \cdot \underbrace{\left[\nu'_B B \left(\frac{\rho_b Y_{O_2,b}}{M_{O_2}} \right) \exp\left(-\frac{E}{\mathcal{R} T_b}\right) \right]^{-1}}_{\text{For lean mixtures}}$$

Time scale of global reaction: $\nu'_B \text{B} + \nu'_{O_2} \text{O}_2 \rightarrow \text{Produkte}$

- Square of Zeldovich-Number appears

$$\text{Ze} = \frac{E(T_b - T_u)}{\mathcal{R} T_b^2} \quad \longleftarrow \quad \text{Ze is order 10}$$

\longrightarrow t_c determined not only by chemistry, but also by flame structure

Flame Time t_F

$$t_F = \frac{l_F}{s_L}$$

- Time, during which the flame front moves by one flame thickness

- Comparison:

$$s_L = \sqrt{D/t_c}$$

$$l_F = \frac{D}{s_L} = \frac{\lambda_b}{c_p \rho_u s_L}$$

$$t_F = \frac{l_F}{s_L}$$

- t_c is the flame time:

$$t_c = \frac{D}{s_L^2} = \frac{l_F}{s_L} = t_F$$

Flame Thickness

- Definition of **flame thickness**:

$$l_F = \frac{D}{s_L} = \frac{\lambda_b}{c_p \rho_u s_L}$$

- Graphical determination of the flame thickness from the temperature profile:
 - Place **tangent in the turning point** of the profile
 - Intersections** of the tangent with the horizontal lines at T_u and T_b
 - Length l_F at the abscissa

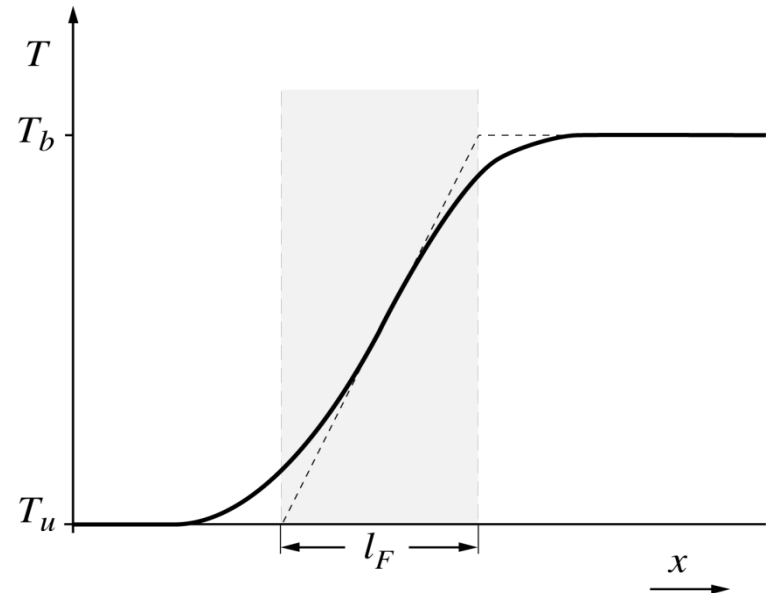
- From analysis
 - Replace LHS of

$$\frac{dT}{dx} = \frac{c_p \rho_u s_L}{\lambda} (T - T_u)$$

by $(T_b - T_u) / l_F$


and evaluate RHS at $T = T_b$ yields

$$l_F = \frac{\lambda_b}{c_p \rho_u s_L}$$



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- 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, especially
 - Dependence of the **burning velocity** on pressure and composition
 - **Flammability and extinction limits**
- **In contrast to simple analysis**
 - Numerical calculations based on **full and reduced mechanisms** are able to predict these properties, **but they contribute little** to the understanding of the fundamental parameters that influence flame behavior

Understanding Combustion Chemistry

- Initiation reaction (**Production of chain carriers** from stable components)



- Chain propagation reaction (**No change in number of radicals**)



- Chain branching reaction (**Increase in number of radicals**)



- Chain breaking reaction (**Decrease in number of radicals**)



Understanding Combustion Chemistry

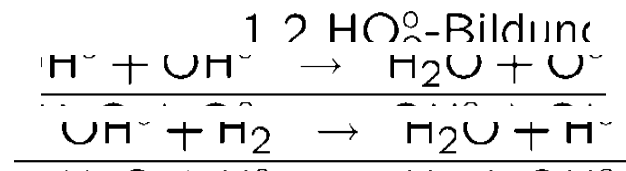
Five Rules for understanding combustion chemistry of hydrocarbon fuels

1. **Reaction progress** mostly determined by radicals
2. **Radical balance** most important aspect
3. Most reactions are **chain propagating**
4. Chain branching and chain breaking reactions are most important
5. The most important radicals are H^\bullet , OH^\bullet , O^\bullet , and for radical-poor situations also HO_2^\bullet

One more rule:

6. **O-radical counts twice!**

Reason: Fast Shuffle Reactions



Nr.	Reaktion	B	n	E
		in mol, cm ³ , s		kJ/mol
1.1 H ₂ /O ₂ -Kettenreaktionen				
1f	H° + O ₂ → OH° + O°	2,000E+14	0,00	70,30
1b	OH° + O° → O ₂ + H°	1,568E+13	0,00	3,52
2f	O° + H ₂ → OH° + H°	5,060E+04	2,67	26,30
2b	OH° + H° → H ₂ + O°	2,222E+04	2,67	18,29
3f	OH° + H ₂ → H ₂ O + H°	1,000E+08	1,60	13,80
3b	H ₂ O + H° → H ₂ + OH°	4,312E+08	1,60	76,46
4f	OH° + OH° → H ₂ O + O°	1,500E+09	1,14	0,42
4b	H ₂ O + O° → OH° + OH°	1,473E+10	1,14	71,09
1.2 HO ₂ °-Bildung und -Verbrauch				
5f	H° + O ₂ + M' → HO ₂ ° + M'	2,300E+18	-0,80	0,00
5b	HO ₂ ° + M' → H° + O ₂ + M'	3,190E+18	-0,80	195,39
6	H° + HO ₂ ° → OH° + OH°	1,500E+14	0,00	4,20
7	HO ₂ ° + H° → H ₂ + O ₂	2,500E+13	0,00	2,90
8	OH° + HO ₂ ° → H ₂ O + O ₂	6,000E+13	0,00	0,00
9	HO ₂ ° + H° → H ₂ O + O°	3,000E+13	0,00	7,20
10	HO ₂ ° + O° → OH° + O ₂	1,800E+13	0,00	-1,70

Nr.	Reaktion	B	n	E
		in mol, cm ³ , s		kJ/mol
1.3 H ₂ O ₂ -Bildung und -Verbrauch				
11	$\text{HO}_2^\circ + \text{HO}_2^\circ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	2,500E+11	0,00	-5,20
12 ^f	$\text{OH}^\circ + \text{OH}^\circ + \text{M}' \rightarrow \text{H}_2\text{O}_2 + \text{M}'$	3,250E+22	-2,00	0,00
12 ^b	$\text{H}_2\text{O}_2 + \text{M}' \rightarrow \text{OH}^\circ + \text{OH}^\circ + \text{M}'$	1,692E+24	-2,00	202,29
13	$\text{H}_2\text{O}_2 + \text{H}^\circ \rightarrow \text{H}_2\text{O} + \text{OH}^\circ$	1,000E+13	0,00	15,00
14 ^f	$\text{H}_2\text{O}_2 + \text{H}^\circ \rightarrow \text{H}_2 + \text{HO}_2^\circ$	1,700E+12	0,00	15,70
14 ^b	$\text{H}_2 + \text{HO}_2^\circ \rightarrow \text{H}_2\text{O}_2 + \text{H}^\circ$	1,150E+12	0,00	80,88
1.4 Rekombinationsreaktionen				
15	$\text{H}^\circ + \text{H}^\circ + \text{M}' \rightarrow \text{H}_2 + \text{M}'$	1,800E+18	-1,00	0,00
16	$\text{OH}^\circ + \text{H}^\circ + \text{M}' \rightarrow \text{H}_2\text{O} + \text{M}'$	2,200E+22	-2,00	0,00
17	$\text{O}^\circ + \text{O}^\circ + \text{M}' \rightarrow \text{O}_2 + \text{M}'$	2,900E+17	-1,00	0,00

Nr.	Reaktion	B	n	E
		in mol, cm ³ , s		kJ/mol
2. CO/CO ₂ -Mechanismus				
18f	CO + OH° → CO ₂ + H°	4,400E+06	1,50	-3,10
18b	CO ₂ + H° → CO + OH°	4,956E+08	1,50	89,76
3.1 CH°-Verbrauch				
19	CH° + O ₂ → CHO° + O°	3,000E+13	0,00	0,00
20	CO ₂ + CH° → CHO° + CO	3,400E+12	0,00	2,90
3.2 CHO°-Verbrauch				
21	CHO° + H° → CO + H ₂	2,000E+14	0,00	0,00
22	CHO° + OH° → CO + H ₂ O	1,000E+14	0,00	0,00
23	CHO° + O ₂ → CO + HO ₂ °	3,000E+12	0,00	0,00
24f	CHO° + M' → CO + H° + M'	7,100E+14	0,00	70,30
24b	CO + H° + M' → CHO° + M'	1,136E+15	0,00	9,97

Nr.	Reaktion	B	n	E
		in mol, cm ³ , s		kJ/mol
3.3 CH ₂ ^o -Verbrauch				
25f	CH ₂ ^o + H ^o → CH ^o + H ₂	8,400E+09	1,50	1,40
25b	CH ^o + H ₂ → CH ₂ ^o + H ^o	5,830E+09	1,50	13,08
26	CH ₂ ^o + O ^o → CO + H ^o + H ^o	8,000E+13	0,00	0,00
27	CH ₂ ^o + O ₂ → CO + OH ^o + H ^o	6,500E+12	0,00	6,30
28	CH ₂ ^o + O ₂ → CO ₂ + H ^o + H ^o	6,500E+12	0,00	6,30
3.4 CH ₂ O-Verbrauch				
29	CH ₂ O + H ^o → CHO ^o + H ₂	2,500E+13	0,00	16,70
30	CH ₂ O + O ^o → CHO ^o + OH ^o	3,500E+13	0,00	14,60
31	CH ₂ O + OH ^o → CHO ^o + H ₂ O	3,000E+13	0,00	5,00
32	CH ₂ O + M' → CHO ^o + H ^o + M'	1,400E+17	0,00	320,00

Chemical mechanism for methane oxidation

Nr.	Reaktion	B	n	E
		in mol, cm ³ , s		kJ/mol
3.5 CH ₃ ^o -Verbrauch				
33f	CH ₃ ^o + H ^o → CH ₂ ^o + H ₂	1,800E+14	0,00	63,00
33b	CH ₂ ^o + H ₂ → CH ₃ ^o + H ^o	3,680E+13	0,00	44,30
34	CH ₃ ^o + H ^o + (M) → CH ₄ + (M) k_{∞} k_0	2,108E+14	0,00	0,00
		6,257E+23	-1,80	0,00
35	CH ₃ ^o + O ^o → CH ₂ O + H ^o	7,000E+13	0,00	0,00
36	CH ₃ ^o + CH ₃ ^o + (M) → C ₂ H ₆ + (M) k_{∞} k_0	3,613E+13	0,00	0,00
		1,270E+41	-7,00	11,56
37	CH ₃ ^o + O ₂ → CH ₂ O + OH ^o	3,400E+11	0,00	37,40
38f	CH ₄ + H ^o → CH ₃ ^o + H ₂	2,200E+04	3,00	36,60
38b	CH ₃ ^o + H ₂ → CH ₄ + H ^o	8,391E+02	3,00	34,56
39	CH ₄ + O ^o → CH ₃ ^o + OH ^o	1,200E+07	2,10	31,90
40f	CH ₄ + OH ^o → CH ₃ ^o + H ₂ O	1,600E+06	2,10	10,30
40b	CH ₃ ^o + H ₂ O → CH ₄ + OH ^o	2,631E+05	2,10	70,92
4.1 C ₂ H-Verbrauch				
41f	C ₂ H + H ₂ → C ₂ H ₂ + H ^o	1,100E+13	0,00	12,00
41b	C ₂ H ₂ + H ^o → C ₂ H + H ₂	5,270E+13	0,00	119,95
42	C ₂ H + O ₂ → CHCO ^o + O ^o	5,000E+13	0,00	6,30

Nr.	Reaktion	B	n	E
		in mol, cm ³ , s		kJ/mol
4.2 CHCO°-Verbrauch				
43f	CHCO° + H° → CH ₂ ° + CO	3,000E+13	0,00	0,00
43b	CH ₂ ° + CO → CHCO° + H°	2,361E+12	0,00	-29,39
44	CHCO° + O° → CO + CO + H°	1,000E+14	0,00	0,00
4.3 C ₂ H ₂ -Verbrauch				
45	C ₂ H ₂ + O° → CH ₂ ° + CO	4,100E+08	1,50	7,10
46	C ₂ H ₂ + O° → CHCO° + H°	4,300E+14	0,00	50,70
47f	C ₂ H ₂ + OH° → C ₂ H + H ₂ O	1,000E+13	0,00	29,30
47b	C ₂ H + H ₂ O → C ₂ H ₂ + OH°	9,000E+12	0,00	-15,98
48	C ₂ H ₂ + CH° → C ₃ H ₃ °	2,100E+14	0,00	-0,50
4.4 C ₂ H ₃ °-Verbrauch				
49	C ₂ H ₃ ° + H° → C ₂ H ₂ + H ₂	3,000E+13	0,00	0,00
50	C ₂ H ₃ ° + O ₂ → C ₂ H ₂ + HO ₂ °	5,400E+11	0,00	0,00
51f	C ₂ H ₃ ° + (M) → C ₂ H ₂ + H° + (M)	k_∞	0,00	166,29
		k_0	-7,50	190,40
51b	C ₂ H ₂ + H° → C ₂ H ₃ °	k_∞	0,00	3,39

Nr.	Reaktion	B	n	E
		in mol, cm ³ , s		kJ/mol
4.5 C ₂ H ₄ -Verbrauch				
52 <i>f</i>	C ₂ H ₄ + H° → C ₂ H ₃ ° + H ₂	1,500E+14	0,00	42,70
52 <i>b</i>	C ₂ H ₃ ° + H ₂ → C ₂ H ₄ + H°	9,605E+12	0,00	32,64
53	C ₂ H ₄ + O° → CH ₃ ° + CO + H°	1,600E+09	1,20	3,10
54 <i>f</i>	C ₂ H ₄ + OH° → C ₂ H ₃ ° + H ₂ O	3,000E+13	0,00	12,60
54 <i>b</i>	C ₂ H ₃ ° + H ₂ O → C ₂ H ₄ + OH°	8,283E+12	0,00	65,20
55	C ₂ H ₄ + M' → C ₂ H ₂ + H ₂ + M'	2,500E+17	0,00	319,80
4.6 C ₂ H ₅ °-Verbrauch				
56 <i>f</i>	C ₂ H ₅ ° + H° → CH ₃ ° + CH ₃ °	3,000E+13	0,00	0,00
56 <i>b</i>	CH ₃ ° + CH ₃ ° → C ₂ H ₅ ° + H°	3,547E+12	0,00	49,68
57	C ₂ H ₅ ° + O ₂ → C ₂ H ₄ + HO ₂ °	2,000E+12	0,00	20,90
58 <i>f</i>	C ₂ H ₅ ° + (M) → C ₂ H ₄ + H° + (M)	k_∞	0,00	166,00
		k_0	0,00	130,00
58 <i>b</i>	C ₂ H ₄ + H° → C ₂ H ₅ °	k_∞	0,00	12,61

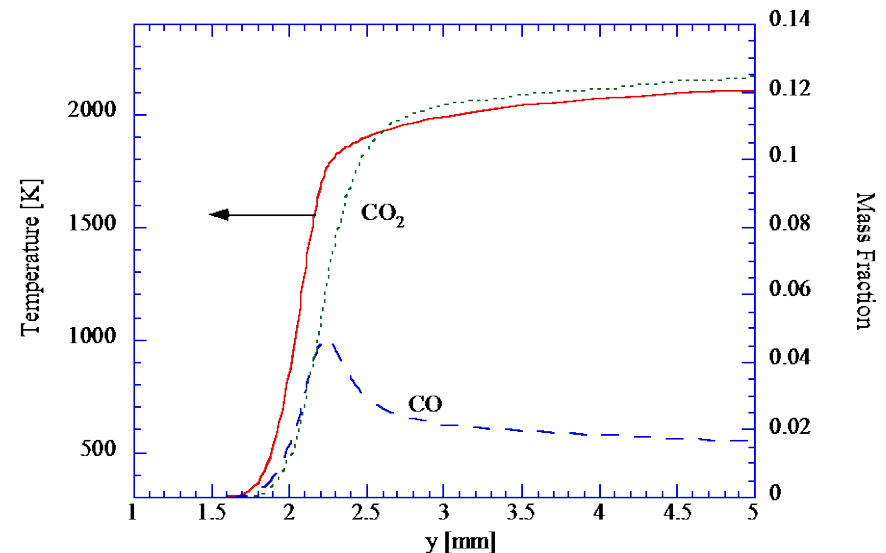
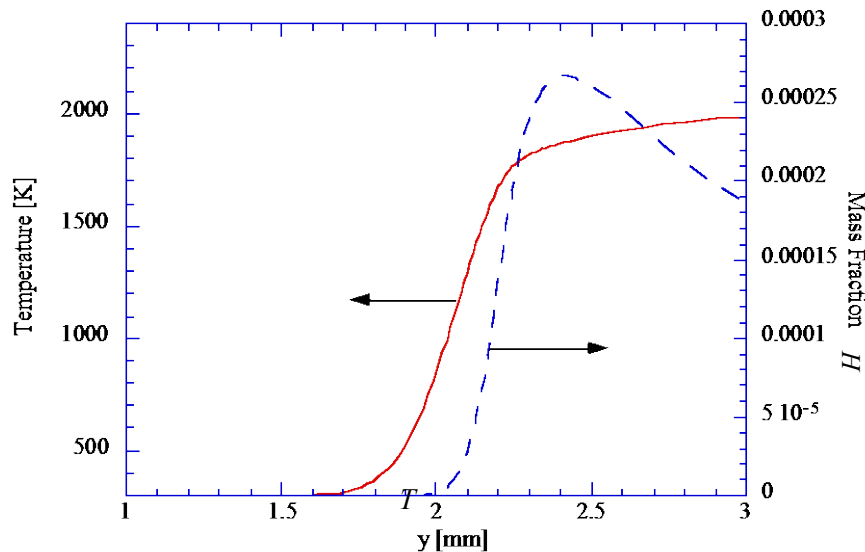
Nr.	Reaktion	B	n	E
		in mol, cm ³ , s		kJ/mol
4.7 C ₂ H ₆ -Verbrauch				
59	C ₂ H ₆ + H° → C ₂ H ₅ ° + H ₂	5,400E+02	3,50	21,80
60	C ₂ H ₆ + O° → C ₂ H ₅ ° + OH°	3,000E+07	2,00	21,40
61	C ₂ H ₆ + OH° → C ₂ H ₅ ° + H ₂ O	6,300E+06	2,00	2,70
5.1 C ₃ H ₃ °-Verbrauch				
62	C ₃ H ₃ ° + O ₂ → CHCO° + CH ₂ O	6,000E+12	0,00	0,00
63	C ₃ H ₃ ° + O° → C ₂ H ₃ ° + CO	3,800E+13	0,00	0,00
64f	C ₃ H ₄ → C ₃ H ₃ ° + H°	5,000E+14	0,00	370,00
64b	C ₃ H ₃ ° + H° → C ₃ H ₄	1,700E+13	0,00	19,88
5.2 C ₃ H ₄ -Verbrauch				
65	C ₃ H ₄ + O° → C ₂ H ₂ + CH ₂ O	1,000E+12	0,00	0,00
66	C ₃ H ₄ + O° → C ₂ H ₃ ° + CHO°	1,000E+12	0,00	0,00
67	C ₃ H ₄ + OH° → C ₂ H ₃ ° + CH ₂ O	1,000E+12	0,00	0,00
68	C ₃ H ₄ + OH° → C ₂ H ₄ + CHO°	1,000E+12	0,00	0,00

Nr.	Reaktion	B	n	E
		in mol, cm ³ , s		kJ/mol
5.3 C ₃ H ₅ ^o -Verbrauch				
69f	C ₃ H ₅ ^o → C ₃ H ₄ + H ^o	3,980E+13	0,00	293,10
69b	C ₃ H ₄ + H ^o → C ₃ H ₅ ^o	1,267E+13	0,00	32,48
70	C ₃ H ₅ ^o + H ^o → C ₃ H ₄ + H ₂	1,000E+13	0,00	0,00
5.4 C ₃ H ₆ -Verbrauch				
71f	C ₃ H ₆ → C ₂ H ₃ ^o + CH ₃ ^o	3,150E+15	0,00	359,30
71b	C ₂ H ₃ ^o + CH ₃ ^o → C ₃ H ₆	2,511E+12	0,00	-34,69
72	C ₃ H ₆ + H ^o → C ₃ H ₅ ^o + H ₂	5,000E+12	0,00	6,30
5.5 C ₃ H ₇ ^o -Verbrauch				
73	$n - \text{C}_3\text{H}_7^{\text{o}}$ → C ₂ H ₄ + CH ₃ ^o	9,600E+13	0,00	129,80
74f	$n - \text{C}_3\text{H}_7^{\text{o}}$ → C ₃ H ₆ + H ^o	1,250E+14	0,00	154,90
74b	C ₃ H ₆ + H ^o → $n - \text{C}_3\text{H}_7^{\text{o}}$	4,609E+14	0,00	21,49
75	$i - \text{C}_3\text{H}_7^{\text{o}}$ → C ₂ H ₄ + CH ₃ ^o	6,300E+13	0,00	154,50
76	$i - \text{C}_3\text{H}_7^{\text{o}} + \text{O}_2$ → C ₃ H ₆ + HO ₂ ^o	1,000E+12	0,00	20,90

Nr.	Reaktion	B	n	E
		in mol, cm ³ , s		kJ/mol
5.6 C ₃ H ₈ -Verbrauch				
77	$C_3H_8 + H^\circ \rightarrow n - C_3H_7^\circ + H_2$	1,300E+14	0,00	40,60
78	$C_3H_8 + H^\circ \rightarrow i - C_3H_7^\circ + H_2$	1,000E+14	0,00	34,90
79	$C_3H_8 + O^\circ \rightarrow n - C_3H_7^\circ + OH^\circ$	3,000E+13	0,00	24,10
80	$C_3H_8 + O^\circ \rightarrow i - C_3H_7^\circ + OH^\circ$	2,600E+13	0,00	18,70
81	$C_3H_8 + OH^\circ \rightarrow n - C_3H_7^\circ + H_2O$	3,700E+12	0,00	6,90
82	$C_3H_8 + OH^\circ \rightarrow i - C_3H_7^\circ + H_2O$	2,800E+12	0,00	3,60

$$C_{M'} = 6,5 C_{CH_4} + 6,5 C_{H_2O} + 1,5 C_{CO_2} + 0,75 C_{CO} + 0,4 C_{O_2} + 0,4 C_{N_2} + 1,0 C_{sonstige}$$

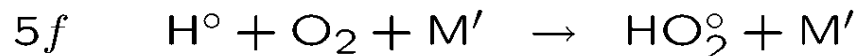
- Structure of an unstretched premixed methane/air flame at standard conditions from numerical simulations



- Asymptotic description of stoichiometric methane-air flames based on **four step reduced mechanism** will be presented in this lecture
- Similar asymptotic analysis was also carried out for lean, moderately rich, and rich methane flames (e.g. Seshadri 1991)
- 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



The cross-over (inner layer) temperature

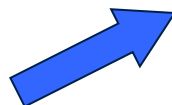
- Most important chain branching and chain breaking reactions hydrogen and hydrocarbon combustion



- Competition of 1f and 5f leads to

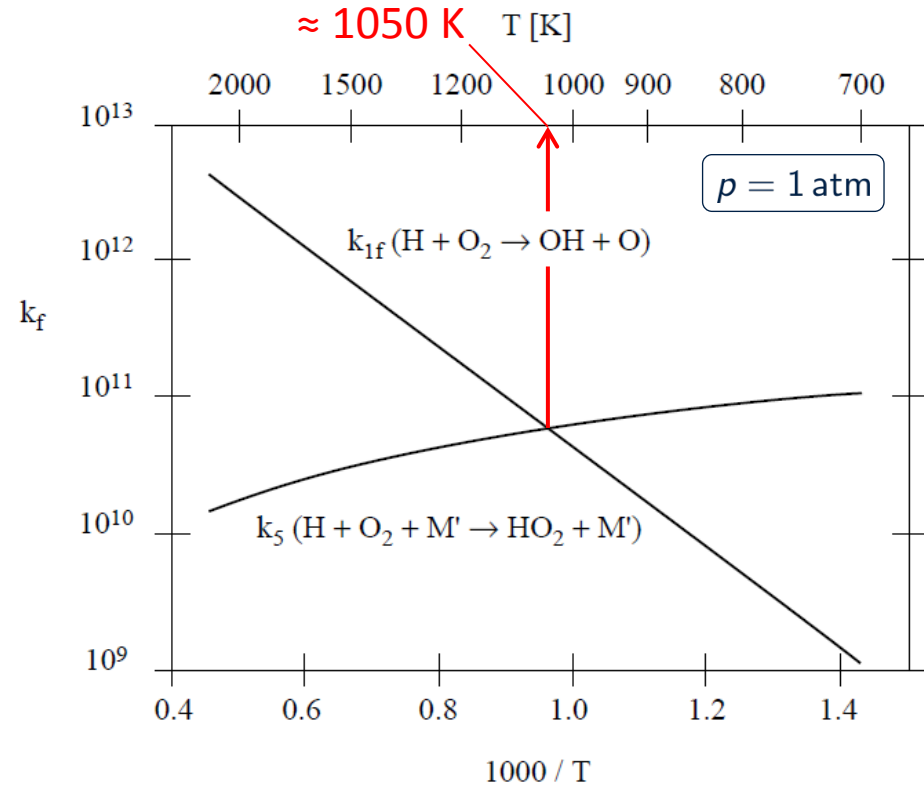
$$\frac{\omega_1}{\omega_5} = \frac{k_1 C_{\text{O}_2} C_{\text{H}}}{k_5 C_{\text{O}_2} C_{\text{H}} C_{\text{M}}} = \frac{k_1}{k_5 C_{\text{M}}}$$

$$\left. \frac{\omega_1}{\omega_5} \right|_0 = \frac{k_1(T^0) \mathcal{R} T^0}{k_5(T^0) p} \equiv 1$$



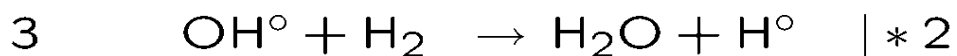
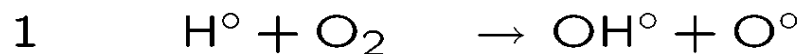
Cross-over temperature T^0
(aka: Inner layer temperature)

- $T < T^0$: Chain termination, **extinction**
- $T > T^0$: Chain branching, e.g. **explosion**



The Four-Step Model for Methane-Air Flames

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

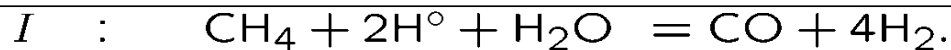
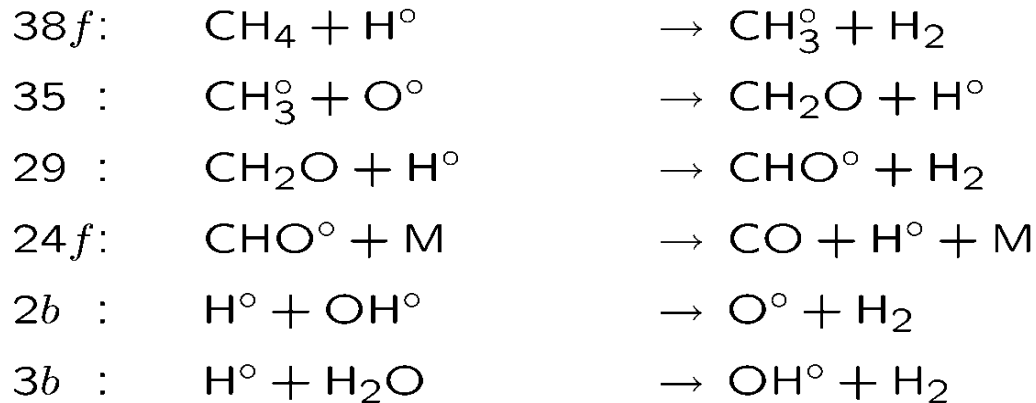


- Global **reaction IV** with the rate of reaction 5f describes **chain breaking**



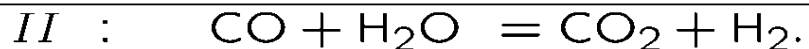
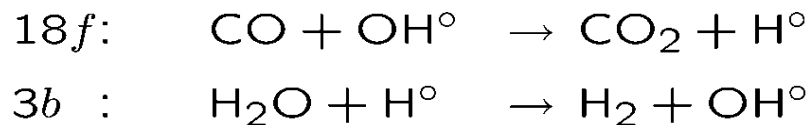
The Four-Step Model for Methane-Air Flames

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



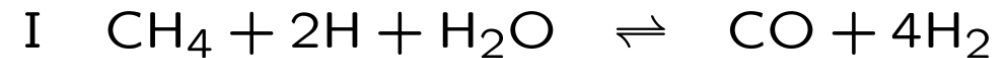
Radical consuming because of CH_3 consumption reaction

- Global **reaction //** 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



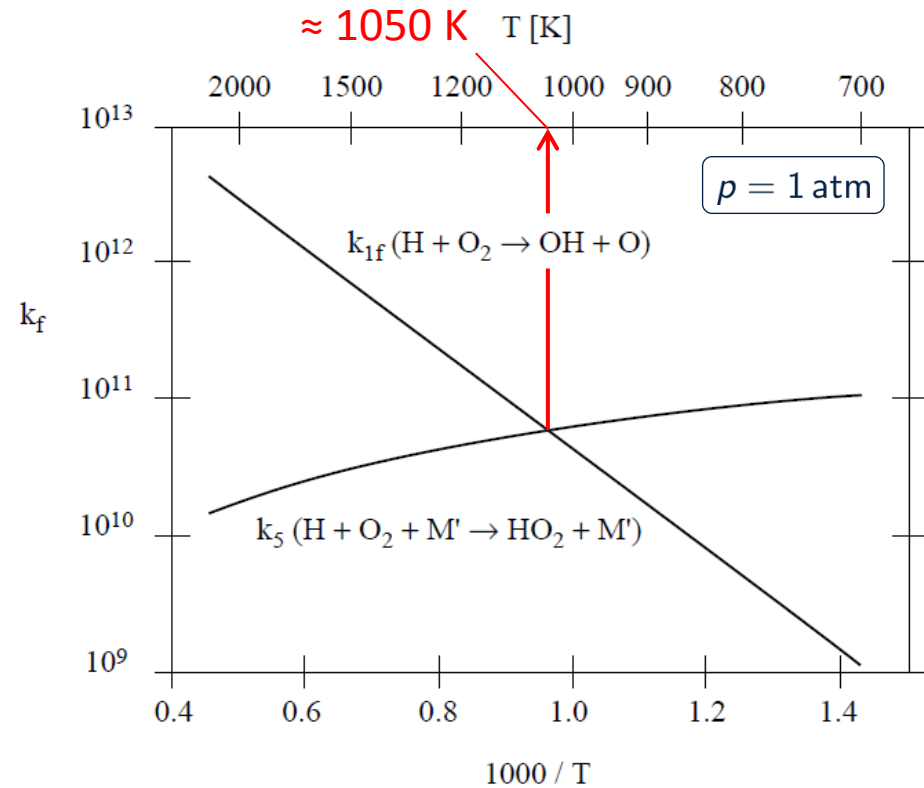
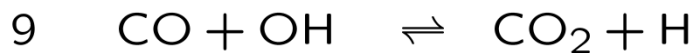
The Four-Step Model for Methane-Air Flames

- 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



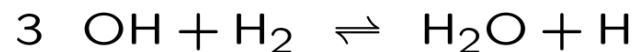
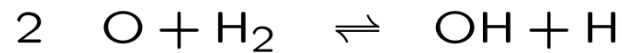
Inner layer Temperature T^0

$$\frac{\omega_1}{\omega_5} = \frac{k_1 C_{\text{O}_2} C_{\text{H}}}{k_5 C_{\text{O}_2} C_{\text{H}} C_{\text{M}}} = \frac{k_1}{k_5 C_{\text{M}}}$$

$$\left. \frac{\omega_1}{\omega_5} \right|_0 = \frac{k_1(T^0) \mathcal{R} T^0}{k_5(T^0) p} \equiv 1$$

The Four-Step Model for Methane-Air Flames

- 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

The Four-Step Model for Methane-Air Flames

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

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

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

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

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

which only depends on concentrations of species appearing in the four-step mechanism

- Equilibrium constants are given as:

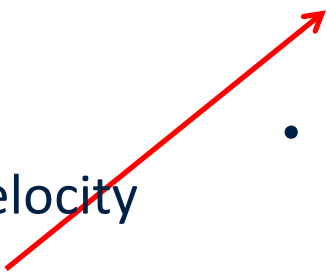
$$K_3 = 0.216 \exp(7658/T)$$

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

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

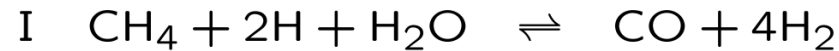
Course Overview

Part I: Fundamentals and Laminar Flames

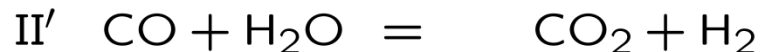
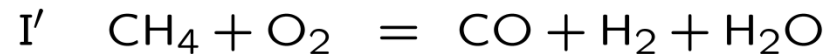
- Introduction
 - Fundamentals and mass balances of combustion systems
 - Thermodynamics, flame temperature, and equilibrium
 - Governing equations
 - Laminar premixed flames: Kinematics and burning velocity
 - **Laminar premixed flames: Flame structure**
 - Laminar diffusion flames
 - FlameMaster flame calculator
 - Thermal flame theory
 - Flame thickness and flame time
 - Four-step model for methane-air flames
 - **Three-step model for methane-air flames**
 - Asymptotic structure of stoichiometric methane-air flames
 - Analytic expression for the burning velocity of methane and other hydrocarbon flames
 - Flammability limits
- 

The Three-Step Model for Methane-Air Flames

- Start from four-step mechanism and assume steady state of the radical H



- Adding reaction IV to I and III leads to the three steps



The Three-Step Model for Methane-Air Flames

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

$$L(H) = -\omega_I - \omega_{III} + \omega_{IV} = 0$$

and

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

$$\begin{aligned}\omega_I &= k_{11}[\text{CH}_4][\text{H}] \\ \omega_{II} &= \frac{k_{9f}[\text{H}]}{K_3[\text{H}_2]} \left([\text{CO}][\text{H}_2\text{O}] - \frac{1}{K_{II}}[\text{CO}_2][\text{H}_2] \right) \\ \omega_{III} &= k_5[\text{H}][\text{O}_2][\text{M}] \\ \omega_{IV} &= k_1 \frac{[\text{H}]}{[\text{H}_2]^3} \left([\text{O}_2][\text{H}_2]^3 - \frac{1}{K_{IV}}[\text{H}]^2[\text{H}_2\text{O}]^2 \right)\end{aligned}$$

- This leads to

$$[\text{H}] = [\text{H}_{eq}] \left(1 - \frac{k_5[\text{M}]}{k_1} - \frac{k_{11}[\text{CH}_4]}{k_1[\text{O}_2]} \right)^{1/2}$$

where $[\text{H}_{eq}]$ based on partial equilibrium of reaction IV

$$[\text{H}_{eq}] = K_{IV}^{1/2} \frac{[\text{O}_2]^{1/2}[\text{H}_2]^{3/2}}{\text{H}_2\text{O}}.$$

The Three-Step Model for Methane-Air Flames

- The equation

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

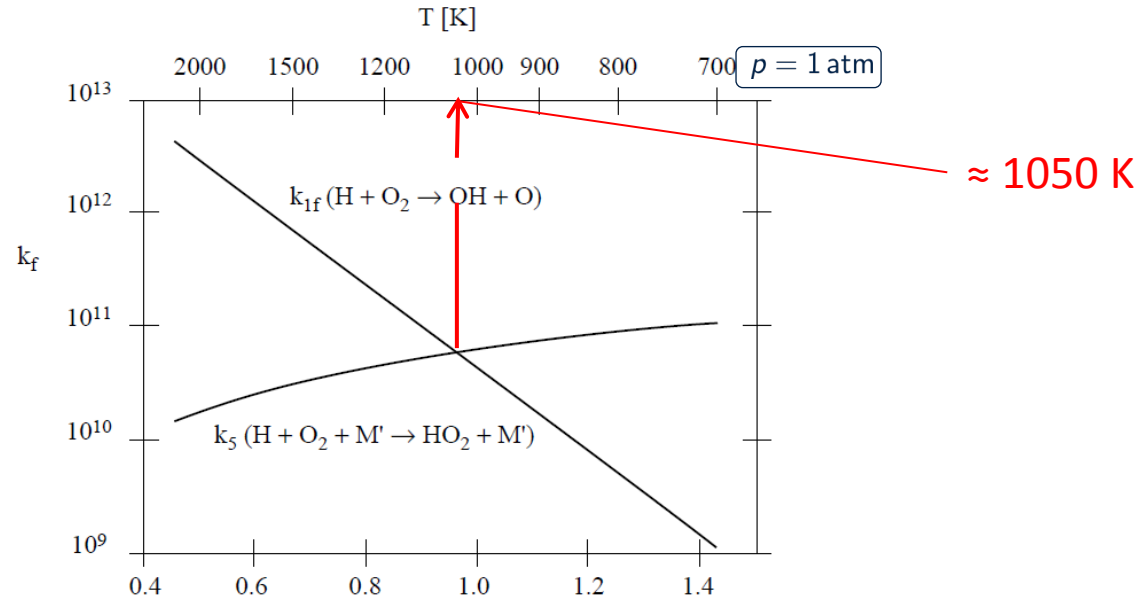
shows an interesting structure

- 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

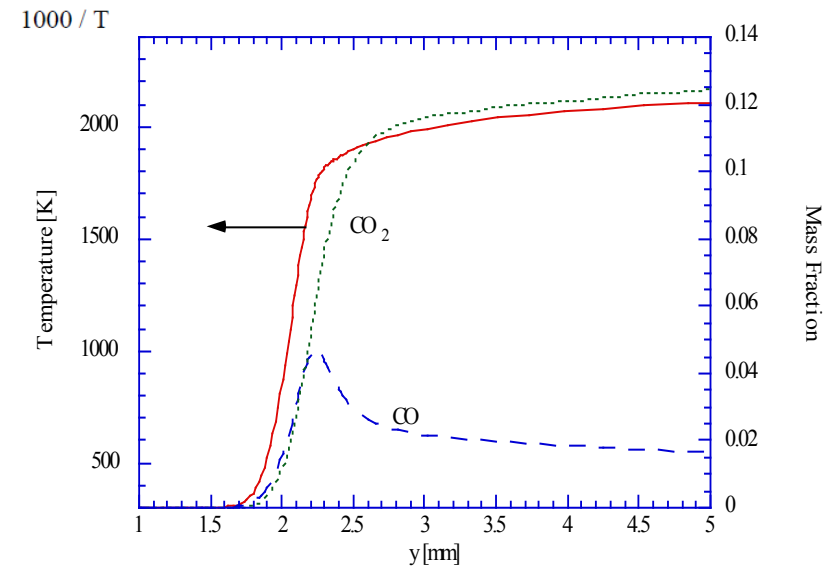
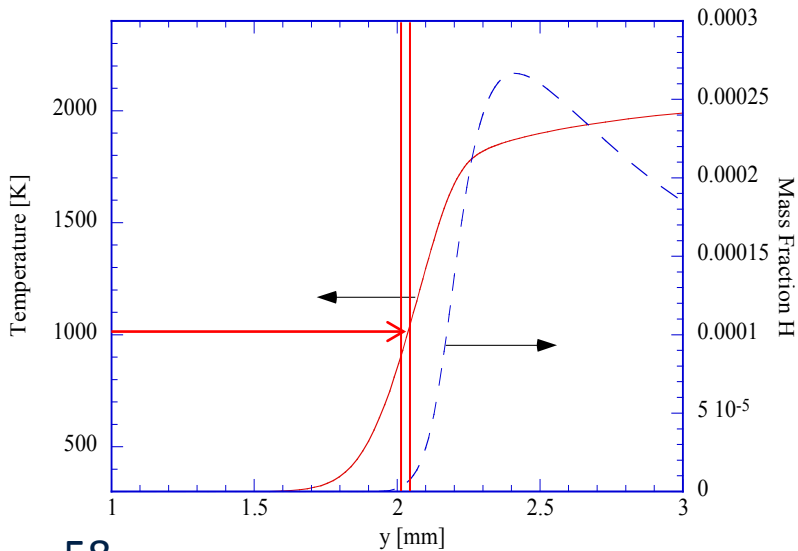
➡ $[CH_4]/[O_2]$ must be much smaller than unity, if $[H]$ is to remain real

- Equation cannot be valid in the preheat zone where second term is large
- It also follows that $[H]$ vanishes in the preheat zone, which is therefore chemically inert

Flame Structure based on the four-step mechanism



Results from
detailed chemistry

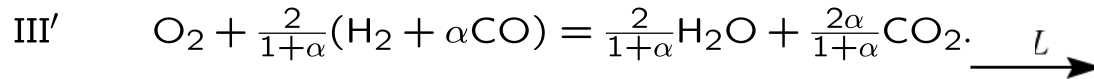
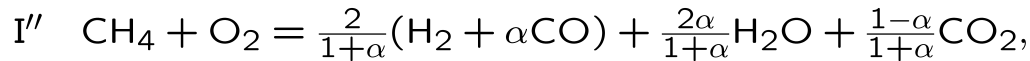


Part I: Fundamentals and Laminar Flames

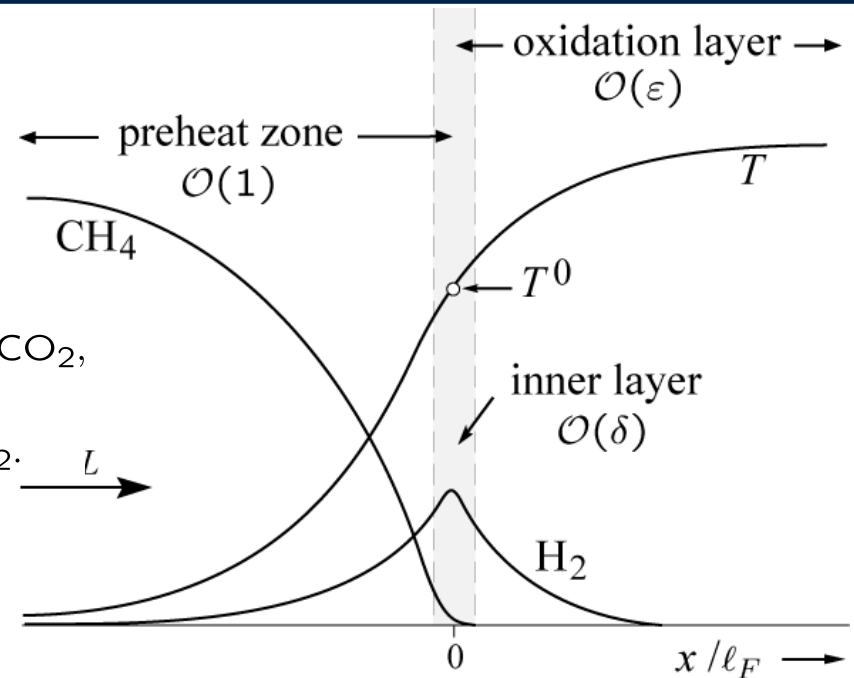
- Introduction
- Fundamentals and mass balances of combustion systems
- Thermodynamics, flame temperature, and equilibrium
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The Asymptotic Structure of Stoichiometric Methane-Air Flames

- Further simplification couples CO and H₂ leading to **two-step mechanism**

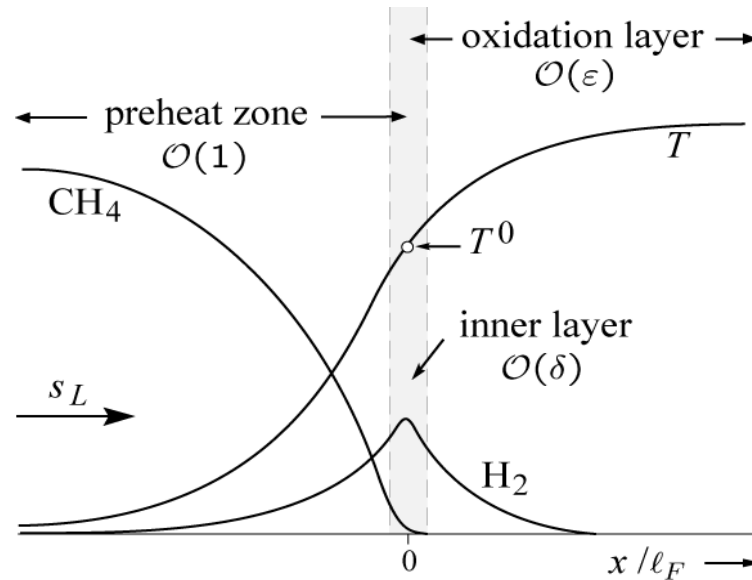


- It contains three layers
 - A chemically inert preheat zone of order 1 upstream
 - A thin inner layer of order δ in which the fuel is consumed and the intermediates H₂ and CO are formed according to the global step I''
 - A thin oxidation layer of order ε downstream where H₂ and CO are oxidized according 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

*Details of the Asymptotic Analysis

- 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

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

*Details of the Asymptotic Analysis

- The small parameter δ was defined as

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

- It denotes the ratio of the rate coefficients of reaction I and II
- It hence 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

*Details of the Asymptotic Analysis

- If δ is small, since ω_I 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 parenthesis 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

*Details of the Asymptotic Analysis

- 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

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

*Details of the Asymptotic Analysis

- 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 $x = 0$

*Details of the Asymptotic Analysis

- 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

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

*Details of the Asymptotic Analysis

- 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

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

*Details of the Asymptotic Analysis

- 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 $\omega_I = 0$
- The temperature varies only slowly in this layer and since the activation energy of k_5 is small, temperature variations may be neglected

*Details of the Asymptotic Analysis

- 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

$$x_{H_2} = \frac{\varepsilon z}{(1 + \alpha)q}$$

- One may use the coupling relations

$$\frac{d^2}{dx^2}[(1 + \alpha)x_{H_2} + 4x_{CH_4} - 2x_{O_2}] = 0,$$

$$\frac{d^2}{dx^2}[x_{H_2} + 2x_{CH_4} + x_{H_2O}] = 0,$$

$$\frac{d^2}{dx^2}[x_{H_2} + x_{CH_4} + x_{CO_2}] = 0,$$

$$\frac{d^2}{dx^2}[(q_{H_2} + \alpha q_{CO})x_{H_2} + x_{CH_4} + T] = 0$$

to show that the downstream boundary conditions are satisfied by

$$x_{O_2} = \varepsilon z / 2q, \quad T = 1 - \varepsilon z$$

*Details of the Asymptotic Analysis

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

- Introducing $x_{H_2} = \frac{\varepsilon z}{(1 + \alpha)q}$ and $\omega_{III} = 2qDa_{III}\varepsilon^3 z^3$

into

$$\omega_{III} = k_5[H][O_2][M]$$

leads to

$$\omega_{III} = 2qDa_{III}\varepsilon^3 z^3$$

where the Damköhler number of reaction III is defined as

$$Da_{III} = \frac{\rho_0^2}{\rho_u^2 s_L^2} \frac{Y_{CH_4 u}}{W_{CH_4}} \frac{\lambda_0}{c_{p0}} \left(\frac{K_{IV} Le_{O_2}^3 Le_{H_2}^3}{2^5 (1 + \alpha)^3} \right)^{1/2} \frac{k_5[M]}{q^4 X_{H_2O}}.$$

*Details of the Asymptotic Analysis

- 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.

*Details of the Asymptotic Analysis

- 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

*Details of the Asymptotic Analysis

- 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 $\frac{d^2 z}{d\eta^2} = (\varepsilon^4 \text{Da}_{\text{III}}) z^3$

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

*Details of the Asymptotic Analysis

- Since the fuel is depleted and H_2 is formed in the inner layer following reaction I'', the stoichiometry of this reaction also determines the change of slopes of the H_2 in comparison of those of the fuel
- This is written as

$$\left. \frac{dx_{CH_4}}{dx} \right|_{0-} - \left. \frac{dx_{CH_4}}{dx} \right|_{0+} = \frac{1 + \alpha}{2} \left(\left. \frac{dx_{H_2}}{dx} \right|_{0-} - \left. \frac{dx_{H_2}}{dx} \right|_{0+} \right)$$

- 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 H_2 concentration can be neglected compared to the downstream slope

$$\left. \frac{dx_{H_2}}{dx} \right|_{0+} \ll \left. \frac{dx_{H_2}}{dx} \right|_{0-}$$

*Details of the Asymptotic Analysis

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

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

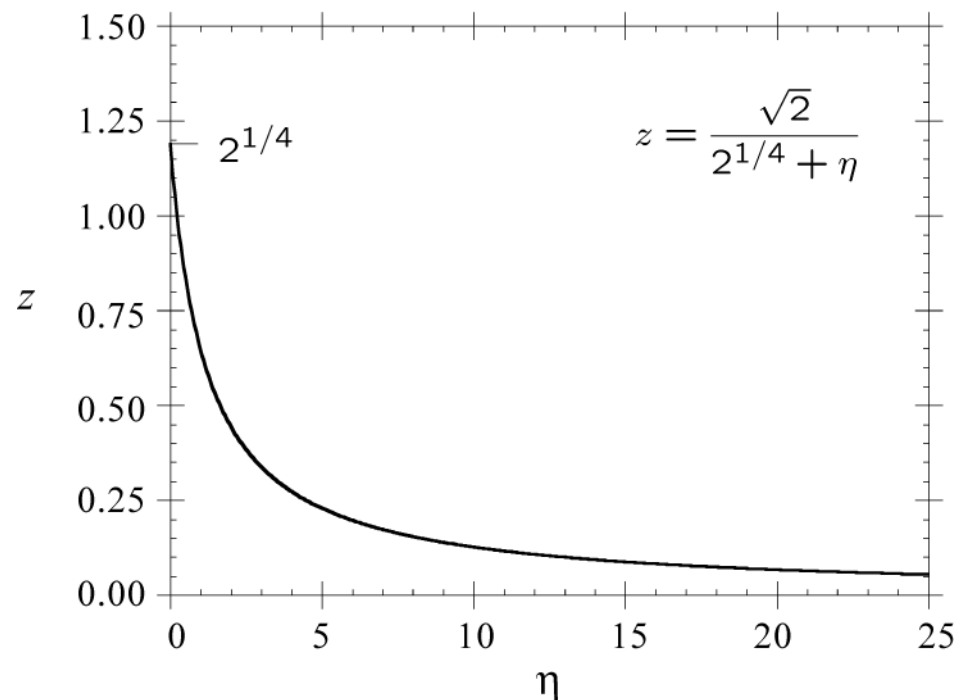
$$\frac{dz}{d\eta} = -1 \quad \text{at} \quad \eta = 0$$

Then the solution is

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

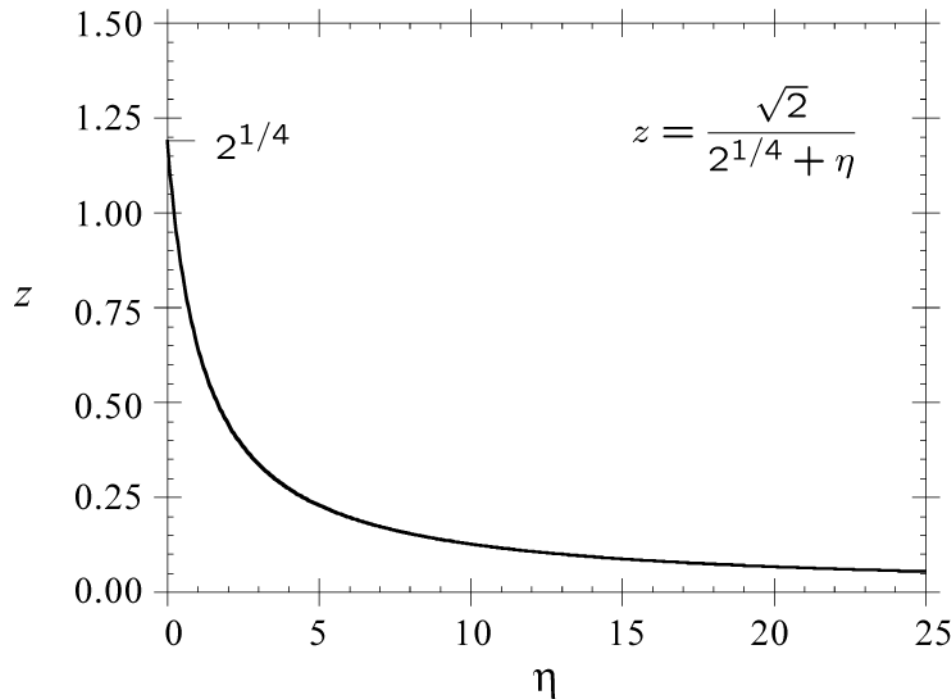
with

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



*Details of the Asymptotic Analysis

- 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 $x_{H_2} = \frac{\varepsilon z}{(1 + \alpha)q}$

and $\omega_{III} = 2qDa_{III}\varepsilon^3 z^3$

to determine the quantities required in

$$Da_I = \frac{\rho_0^2}{\rho_u^2 s_L^2} \frac{Y_{CH_4} u}{W_{CH_4} c_{p0}} \frac{\lambda_0 (K_{IV} X_{O_2} X_{H_2}^3)_0^{1/2}}{X_{H_2O}} Le_{CH_4} k_{11}(T^0).$$

and thereby the burning velocity s_L

*An Analytic Expression for the Burning Velocity

- By dividing

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

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

*An Analytic Expression for the Burning Velocity

- The equation

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

shows that with the rate coefficients fixed, 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

*An Analytic Expression for the Burning Velocity

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

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

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

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

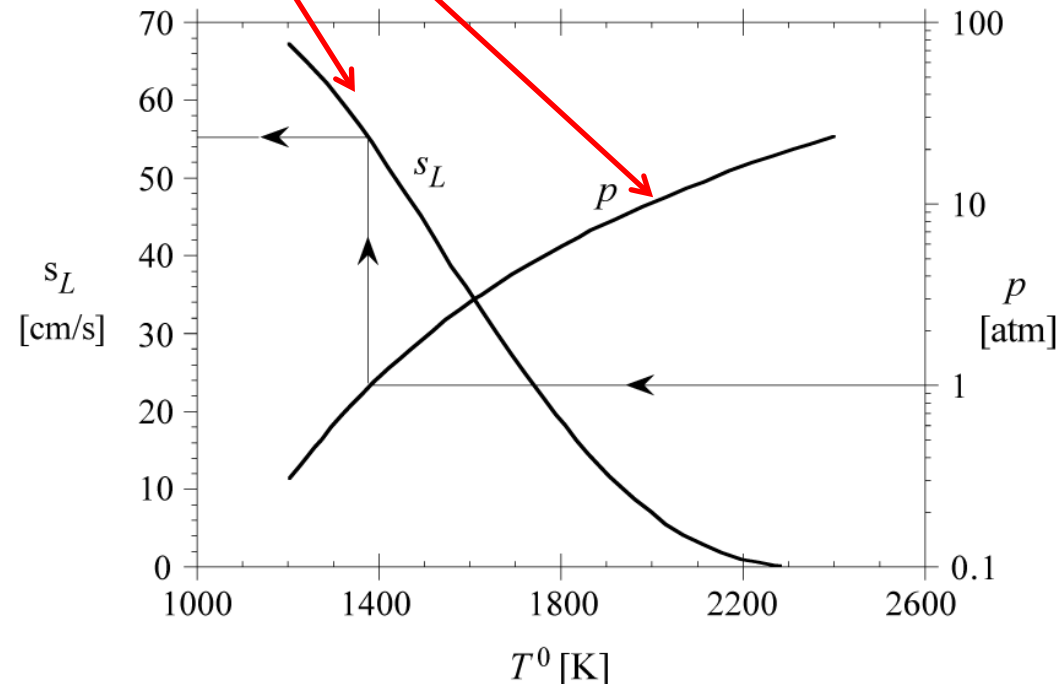
Results of the Asymptotic Analysis

Asymptotic Analysis leads to analytic expression for laminar burning velocity

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

- Pressure obtained from
- Undiluted stoichiometric methane flame with
 - $T_u = 300$ K
 - $p = 1$ atm

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



→ $s_L = 54$ cm/s

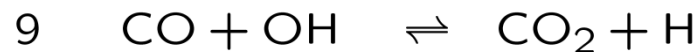
Results of the Asymptotic Analysis

- Only rates of **reactions 1, 5, and 11** influence the burning velocity in the approximation

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

and

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



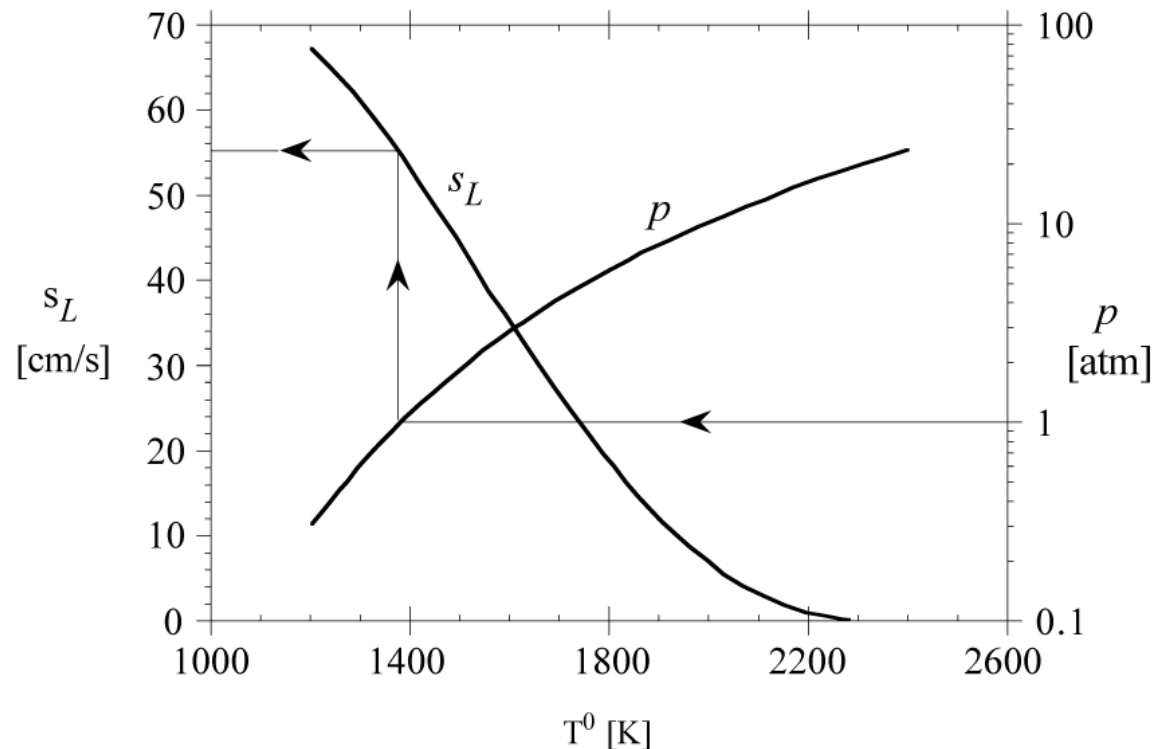
Results of the Asymptotic Analysis

- Further consequence of equation

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

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



*Detail: Relation to the Activation Energy of the One-step Model

- Using the burning velocity expression from the [thermal flame theory](#)

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

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

*Detail: Relation to the Activation Energy of the One-step Model

- 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 burning velocity from 2-step mechanism

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

with T^0 fixed leads to

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

*Detail: Relation to the Activation Energy of the One-step Model

- 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

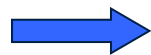
$$\frac{E}{RT_b} = \frac{4T_b}{T_b - T_u} \frac{1}{\varepsilon z_0}$$

- 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

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

- One-step model
 - Reaction zone thickness was of order of the inverse Zeldovich number
- Two-step model for methane flames
 - Oxidation layer thickness of order of the inverse Zeldovich number

 Oxidation layer plays similar role in hydrocarbon flames as reaction zone in one-step asymptotics

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- 

Application: Analytic Approximations of Burning Velocities for Lean Hydrocarbon Flames

- Burning velocity expression

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

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

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

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

with

$$A(T_0) = F \exp(-G/T_0), \quad T_0 = -\frac{E}{\ln(p/B)}.$$

- Parameters m, n, B, E, F, G are fuel specific determined using fits with numerical data

Analytic Approximations of Burning Velocities for Lean Hydrocarbon Flames

- 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
 - $p = 1 \text{ atm}$ and 40 atm ,
 - T_u between 298 K and 800 K
 - $\phi = 0.4$ and 1.0

Brennstoff	B [bar]	E [K]	F [cm/s]	G [K]	m	n
CH_4	$3,1557 \times 10^8$	23873,0	$2,21760 \times 10^1$	-6444,27	0,565175	2,5158
C_2H_2	$5,6834 \times 10^4$	11344,4	$3,77466 \times 10^4$	1032,36	0,907619	2,5874
C_2H_4	$3,7036 \times 10^5$	14368,7	$9,97890 \times 10^3$	263,23	0,771333	2,3998
C_2H_6	$4,3203 \times 10^6$	18859,0	$1,90041 \times 10^3$	-506,97	0,431345	2,1804
C_3H_8	$2,2501 \times 10^6$	17223,5	$1,27489 \times 10^3$	-1324,78	0,582214	2,3970
CH_3OH	$2,1100 \times 10^6$	17657,5	$9,99557 \times 10^3$	1088,85	0,91	2,263
$n\text{-C}_7\text{H}_{16}$	$1,7000 \times 10^6$	17508,0	$7,95600 \times 10^3$	912,00	0,52	2,30
$i\text{-C}_8\text{H}_{18}$	$3,8000 \times 10^7$	20906,0	$2,92600 \times 10^3$	-25,60	0,5578	2,5214

Göttgens et al. (1992)

- Adiabatic flame temperature

$$T_b = a T_u + b + c \phi + d \phi^2 + e \phi^3$$

Brennstoff	a	b [K]	c [K]	d [K]	e [K]	Le
CH ₄	0,627	1270,15	-2449,0	6776	-3556	0,91
C ₂ H ₂	0,52	1646,0	-2965,0	8187	-4160	1,68
C ₂ H ₄	0,44	602,0	880,0	2686	-1891	1,21
C ₂ H ₆	0,526	1437,0	-2967,0	7538	-3873	1,32
C ₃ H ₈	0,53	1434,0	-2952,0	7518	-3856	1,63
CH ₃ OH	0,77	1260,0	-2449,0	6797	-3594	1,68
<i>n</i> -C ₇ H ₁₆	0,49	758,7	-277,8	4269	-2642	2,056
<i>i</i> -C ₈ H ₁₈	0,61	936,0	-1127,0	5326	-3044	2,55

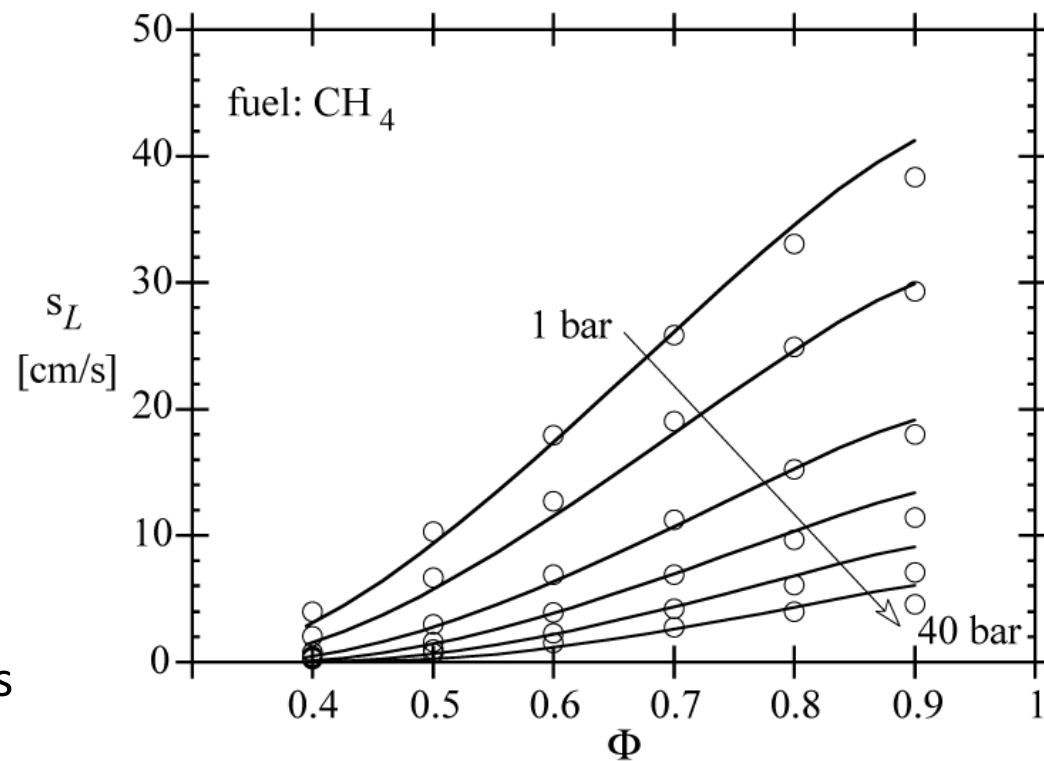
Analytic Approximations of Burning Velocities for Lean CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , and C_3H_8 Flames

- 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 $\phi = 1$

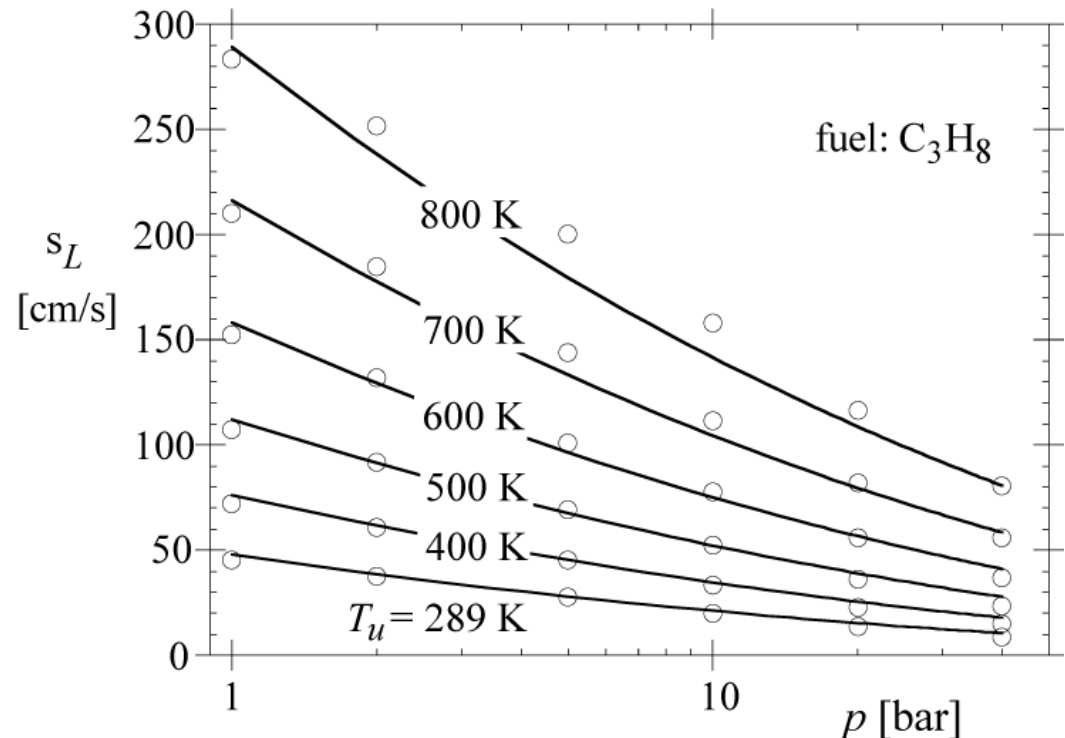


Analytic Approximations of Burning Velocities for Lean CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , and C_3H_8 Flames

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- 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

$$\rho_u s_L = \sqrt{2 \frac{B \rho_b^2 \lambda_b \mathcal{R}^2 T_b^4}{c_p (T_b - T_u)^2 E^2} \exp \left(-\frac{E}{\mathcal{R} T_b} \right) S}$$

$$S = \frac{\nu'_F Y_{O_2,b}}{M_{O_2}} + \frac{\nu'_{O_2} Y_{F,b}}{M_F} + \frac{2 \nu'_{O_2} \nu'_F c_p \mathcal{R} T_b^2}{(-\Delta H) E}$$

the activation energy that 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

- 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 $1/T_b$

Solution

- 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

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

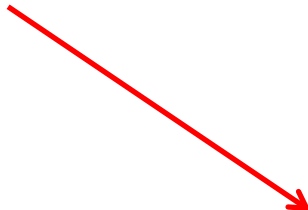
$$T_b(Z) = T_u(Z) + \frac{Q_{\text{ref}} Y_{O_2,2}}{c_p \nu'_{O_2} W_{O_2}} (1 - Z) \quad Z \geq Z_{st}$$

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

Course Overview

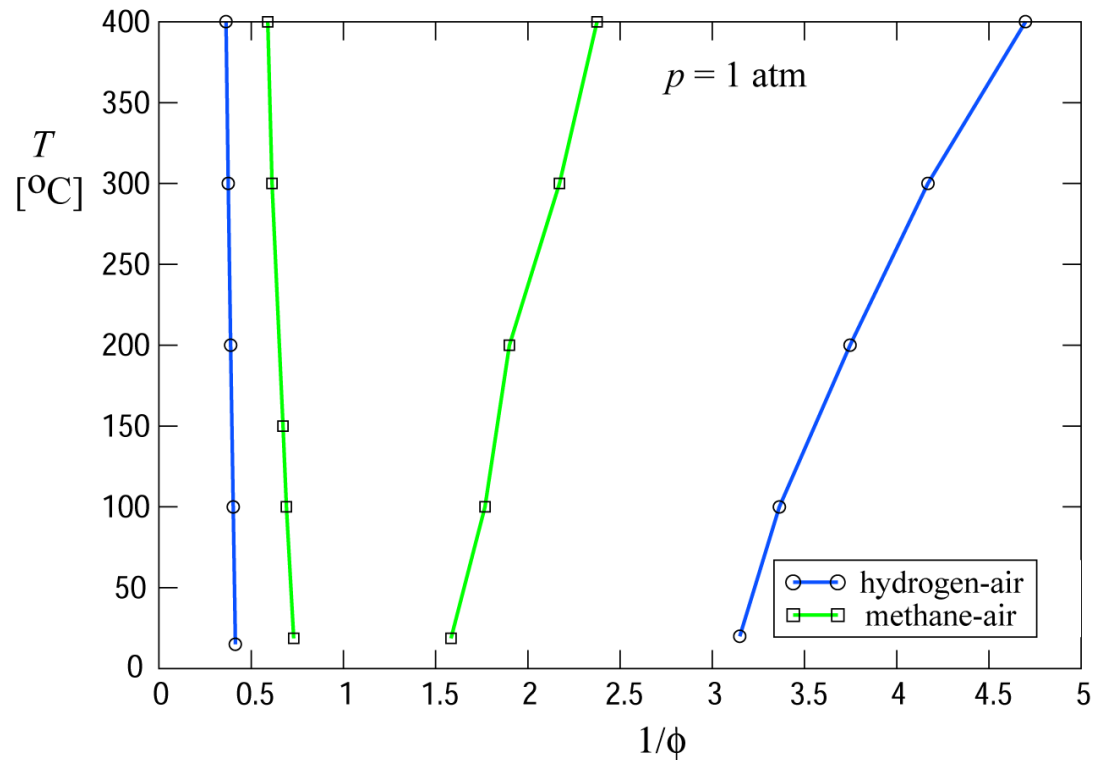
Part I: Fundamentals and Laminar Flames

- Introduction
 - Fundamentals and mass balances of combustion systems
 - Thermodynamics, flame temperature, and equilibrium
 - Governing equations
 - Laminar premixed flames: Kinematics and burning velocity
 - Laminar premixed flames: Flame structure
 - Laminar diffusion flames
 - FlameMaster flame calculator
 - Thermal flame theory
 - Flame thickness and flame time
 - Four-step model for methane-air flames
 - Three-step model for methane-air flames
 - Asymptotic structure of stoichiometric methane-air flames
 - Analytic expression for the burning velocity of methane and other hydrocarbon flames
 - Flammability limits
- 

Application: Flammability limits

- Lean and rich flammability limits are function of temperature and pressure

- For lean mixtures (RHS of the diagram), flammability limits of hydrogen extend to much larger values than for methane



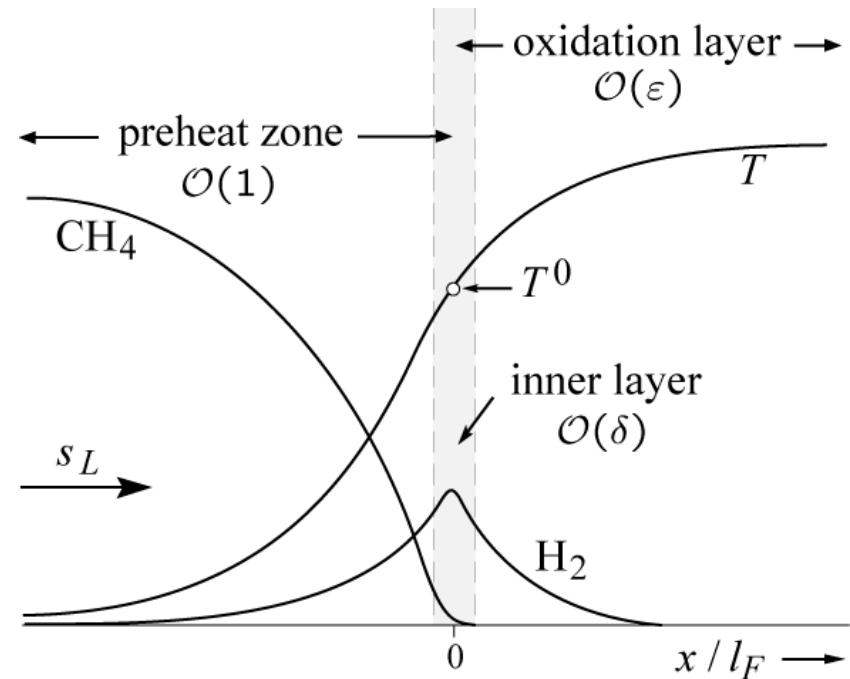
- This shows that hydrogen leakage may cause greater safety hazards than, for instance, hydrocarbons, which have flammability limits close to those of methane

Kinetically determined flammability limit

- Temperature T^0 of the inner layer
 → Corresponds to T_0 in the approximation equation:

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

- T^0 : „cross-over“-temperature between chain termination and chain branching
 → kinetically determined



Kinetically determined lean flammability limit

- Approximation equation:

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

→ $T_b = T_0$: Burning velocity = 0

- From approximation of the coefficients: $A(T_0) = F \exp(-G/T_0)$, $T_0 = -\frac{E}{\ln(p/B)}$.

→ T_0 depends on pressure but not on the fuel mass fraction

- Condition $T_b = T_0$: Decreasing the fuel mass fraction in the mixture → T_b decreases
- Corresponds to approaching the lean flammability limit
- If fuel mass fraction too low:
 - Inner „cross-over“- temperature T_0 is not reached
 - No chain branching
 - Extinction

Flammability limit from coupling function

- Coupling function yields a relation for $Y_{F,u}$: $(Y_{F,u})_{l.l.} = \frac{(T^0 - T_u)c_p\nu'_F W_F}{Q_{\text{ref}}}$
 - with $T_b = T^0$
 - complete combustion ($Y_{F,b} = 0$)
- Simplify with coupling function for stoichiometric mixture
 - Mass fraction of the fuel at the lean flammability limit compared to the stoichiometric mixture

$$(Y_{F,u})_{l.l.} = \frac{T^0 - T_u}{T_{st} - T_u} Y_{F,u,st}$$

- Example: Methane-air-flame:

- $T_u = 300 \text{ K}$, $p = 1 \text{ bar}$
- $T^0 = 1219 \text{ K}$, $T_{st} = 2229 \text{ K}$
- Corresponds to $\phi = 0.46$

$$(Y_{F,u})_{l.l.} = 0.476 Y_{F,u,st}$$

→ Approximation for the lean flammability limit

Flammability limits of real flames

- Real situations:
→ Flame extinction occurs sooner

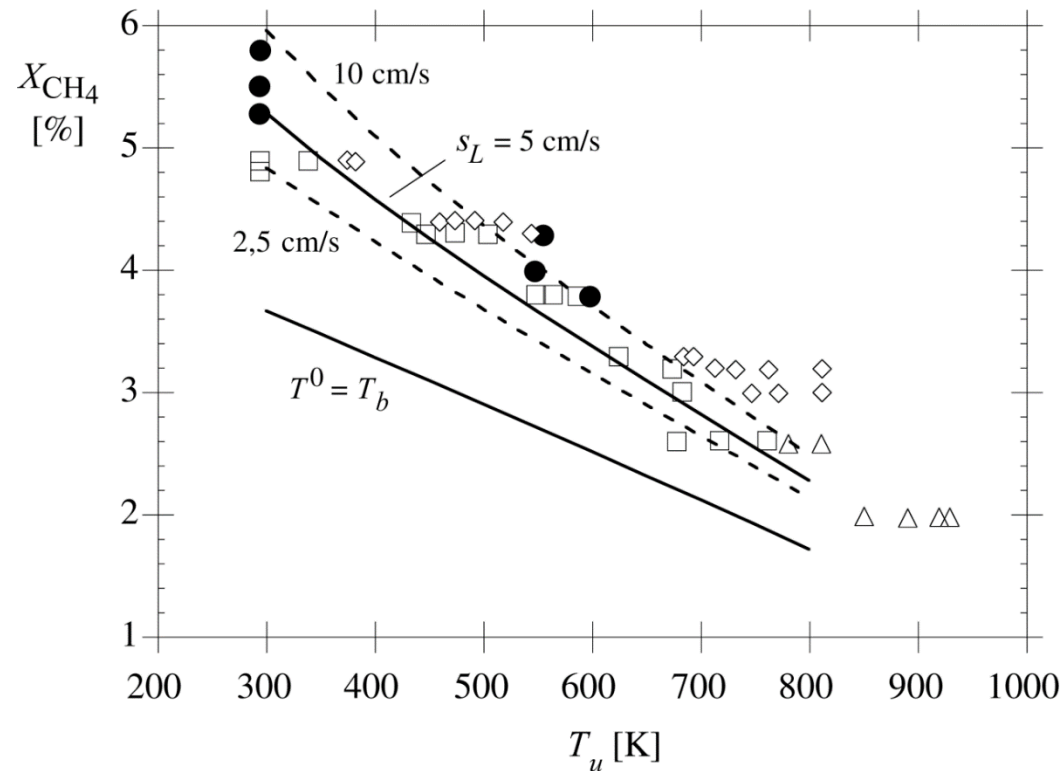
$$(Y_{F,u})_{l.l.} = \frac{T^0 - T_u}{T_{st} - T_u} Y_{F,u,st}$$

- Iterative calculation of the limit
 $Y_{B,u}$ from s_L

- Increasing temperature
 - Mole fraction decreases
 - Region of flammable mixture broadens

- $T^0 = T_b$: Lower value of mole fraction

→ Kinetically determined



Theoretical explanation of the lean flammability limit

- **Thermal Flame Theory**: No flammability limit
- Exponential dependance of the laminar burning velocity on the temperature in the burned mixture:

$$\rho_u s_L = \sqrt{2 \frac{B \rho_b^2 \lambda_b \mathcal{R}^2 T_b^4}{c_p (T_b - T_u)^2 E^2} \exp\left(-\frac{E}{\mathcal{R} T_b}\right) S}$$

$$S = \frac{\nu'_F Y_{O_2,b}}{M_{O_2}} + \frac{\nu'_{O_2} Y_{F,b}}{M_F} + \frac{2 \nu'_{O_2} \nu'_F c_p \mathcal{R} T_b^2}{(-\Delta H) E}.$$

- **Laminar burning velocity** takes very low values with **decreasing T_b** but will never become zero
- Flame propagation can be disrupted due to **heat loss effects**

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