

# Laminar Premixed Flames: Flame Structure

CEFRC Combustion Summer School

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# Course Overview

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## 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
  - **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
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# Thermal Flame Theory

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The first theoretical treatment of stationary one dimensional flames:

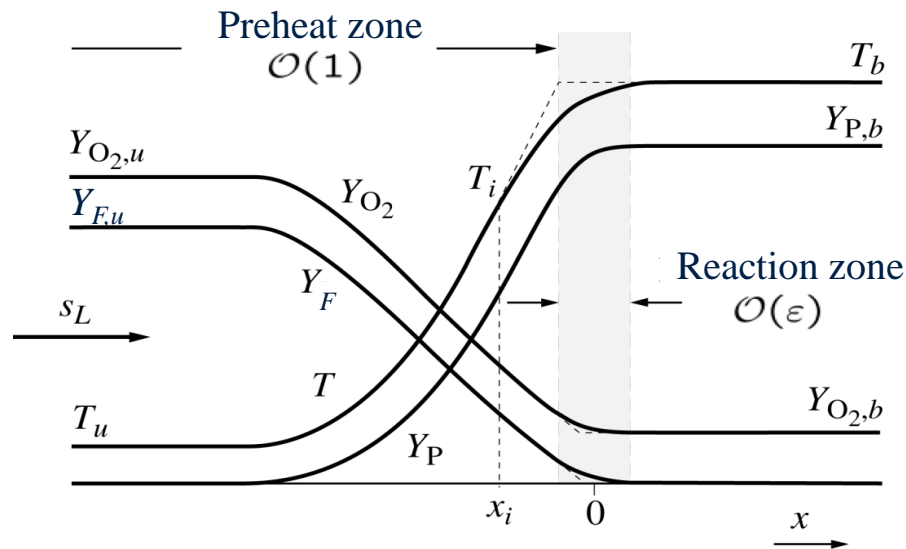
Thermal Flame Theory of Zeldovich and Frank-Kamenetzki (1938)

- 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

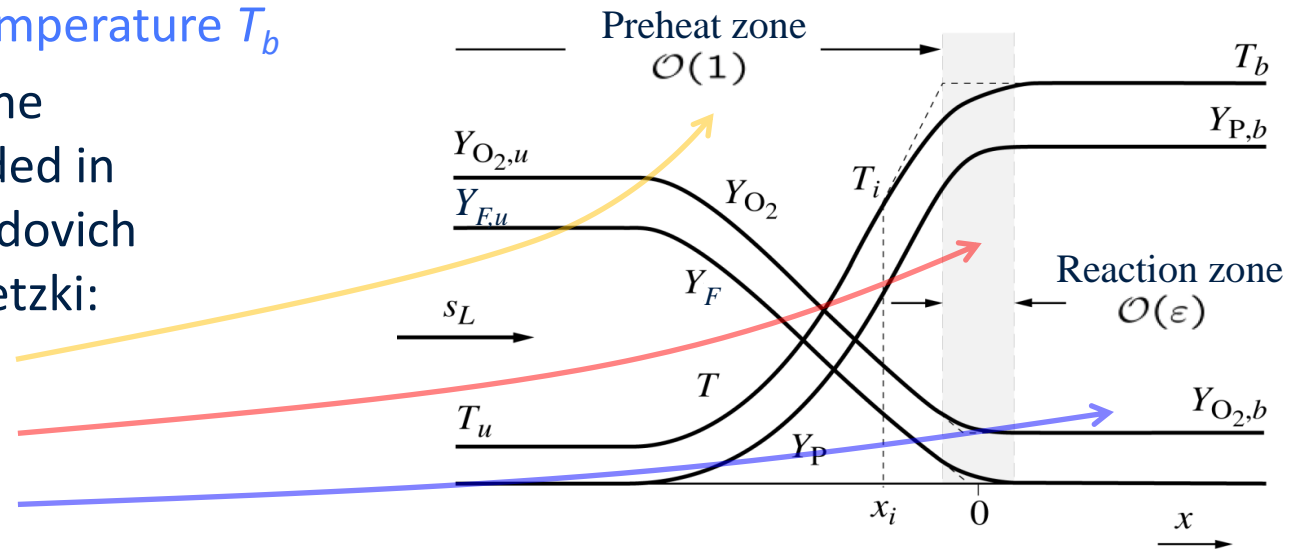


# Thermal Flame Theory

Flame front (lean mixture):

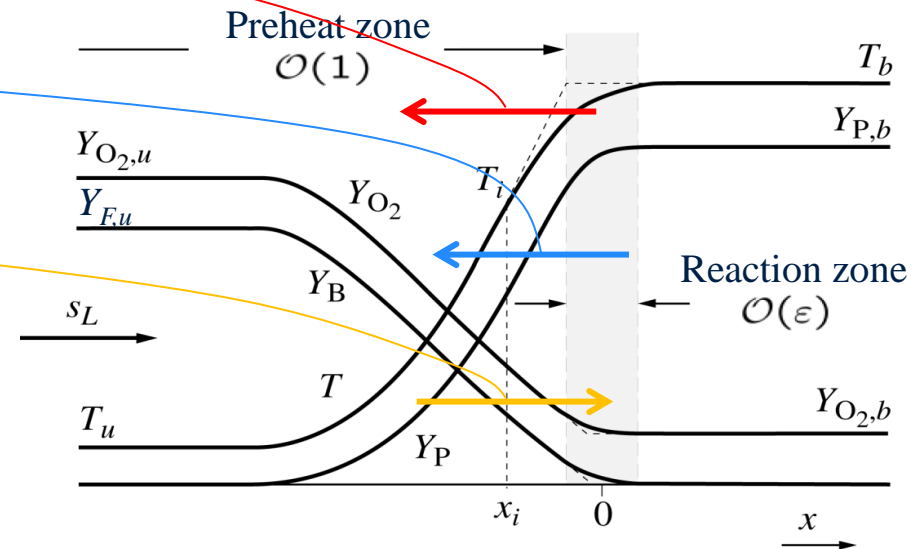
- Complete fuel conversion
- Excess oxygen remains
- Temperature rises from the initial value  $T_u$  to the **adiabatic flame temperature  $T_b$**
- The area around the flame front is divided in **three zones** by Zeldovich and Frank-Kamenetzki:

- Preheat zone
- Reaction zone
- Equilibrium zone



# Thermal Flame Theory

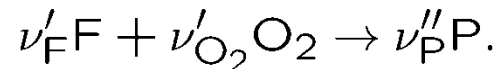
- **Heat conduction** out of reaction zone  
 → Mixture in the **preheat zone** is **continuously heated**
- **Diffusion** of combustion products back into the **unburnt mixture**
- **Diffusion** of reactants (fuel and oxygen), **into the reaction zone**
- Transition
  - Position  $x_i$
  - Temperature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



# Thermal Flame Theory

- Simplification:

- Global reaction equation



- Reaction rate

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

- 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

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- Further simplifications:
  - Specific heat capacity 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

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- 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

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- 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:
  - Preheat zone,  $T < T_i$ : no reactions:  $\omega = 0$
  - 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  $x = -\infty$

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

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

- Second assumption yields

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

- Heat conduction term can be substituted by

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

- The differential equation then becomes

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

# Thermal Flame Theory

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

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

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

- 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  $\rightarrow$  Eigenvalue  $\rightarrow$  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

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

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:

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



# Thermal Flame Theory

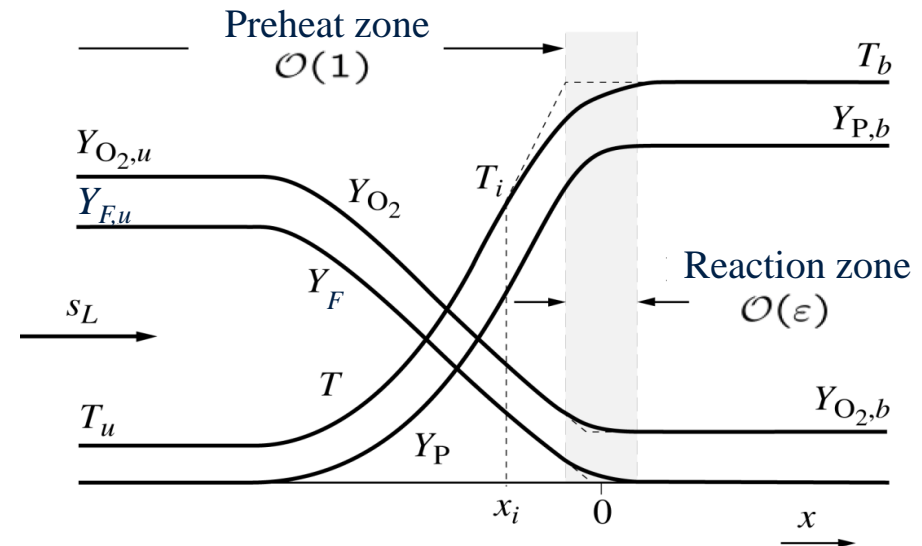
- Integral: 
$$\int_{T_i}^{T_b} \lambda \omega dT = \lambda_b \frac{\mathcal{R} T_b^2}{E} \int_{\Theta_i}^0 w(\Theta) d\Theta$$

$$= \frac{\lambda_b B \rho_b^2 c_p \mathcal{R}^2 T_b^4}{(-\Delta H) E} \exp\left(-\frac{E}{\mathcal{R} T_b}\right) \left[ \left( \frac{\nu'_F Y_{O_2,b}}{M_{O_2}} + \frac{\nu'_{O_2} Y_{F,b}}{M_F} \right) (1 + (\Theta_i - 1) \exp \Theta_i) \right.$$

$$\left. + 2 \frac{\nu'_{O_2} \nu'_F c_p \mathcal{R} T_b^2}{(-\Delta H) E} \left( 1 - \left( 1 - \Theta_i + \frac{\Theta_i^2}{2} \right) \exp \Theta_i \right) \right]$$

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

- **Substitution of  $\theta_i$  by  $\theta_u$**   
 → 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  $T_b$
- $\theta_u$  has a high negative values for high activation energies
- In terms, which include  $\exp(\theta_u)$ ,  $\theta_u$  can be replaced by  $-\infty$   
 → Terms disappear

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

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

# Thermal Flame Theory

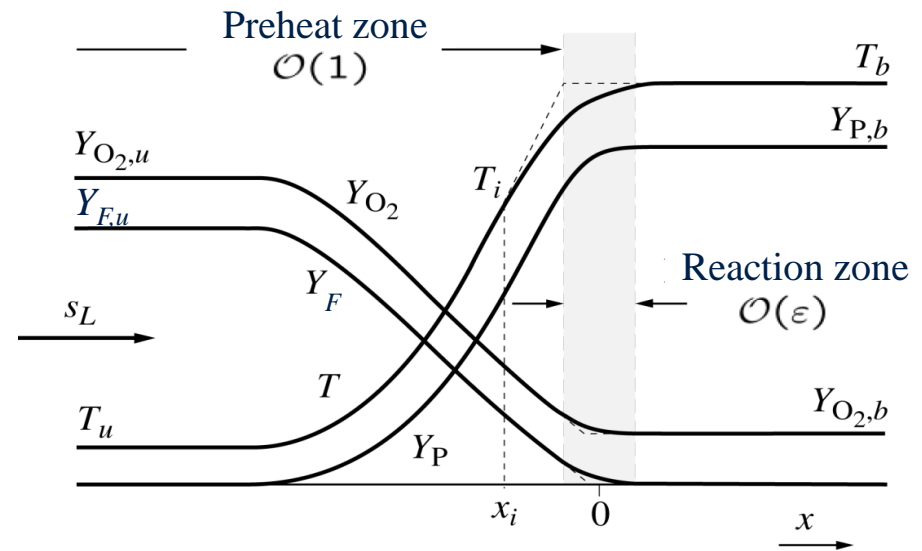
Preheat zone:

- Replacing  $T_i$  by  $T_b$  and  $\lambda_i$  by  $\lambda_b$

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

- 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  $\phi$** :
  - 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  $\rightarrow Y_{O_2,b} \approx Y_{B,b} \approx 0$

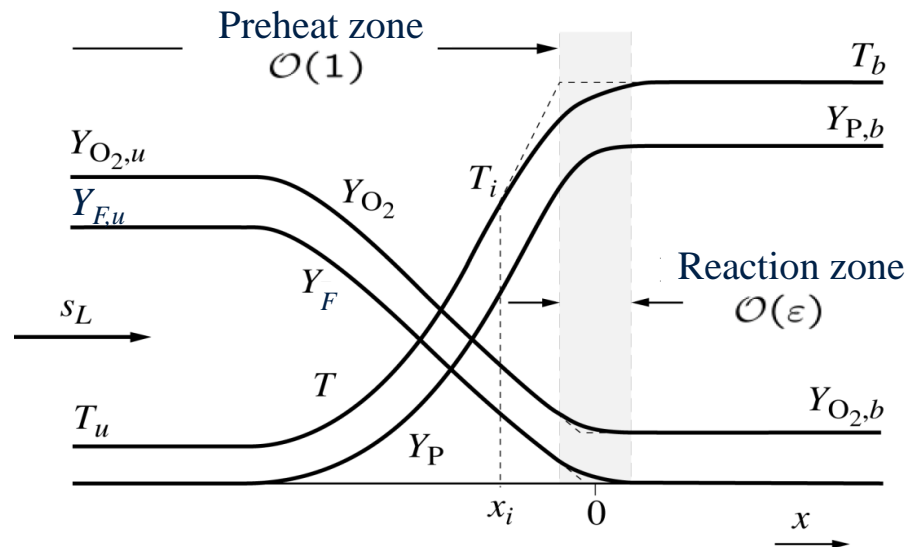
$$\rho_u s_L = \sqrt{2 \frac{B \rho_b^2 \lambda_b \mathcal{R}^2 T_b^4}{c_p (T_b - T_u)^2 E^2} \exp\left(-\frac{E}{\mathcal{R} T_b}\right) S}$$
$$S = \frac{\nu'_F Y_{O_2,b}}{M_{O_2}} + \frac{\nu'_{O_2} Y_{F,b}}{M_F} + \frac{2 \nu'_{O_2} \nu'_F c_p \mathcal{R} T_b^2}{(-\Delta H) E}$$

- 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)

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

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

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:

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

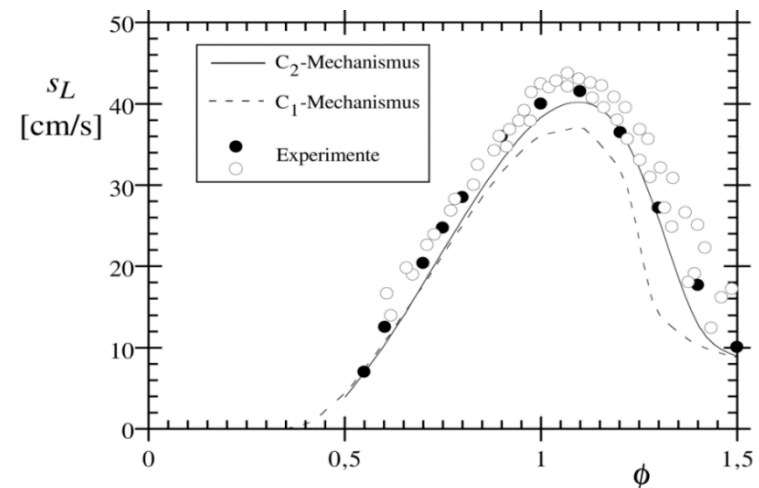
- Very rich/very lean mixture: reaction of first order

- 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
- Determined by  $\rho = \rho_u$  by  $\lambda = \lambda_b$

$$D = \frac{\lambda_b}{\rho_u c_p},$$

- Chemical time scale:

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

- One or both of the reactants are consumed in the reaction zone
- Square of Zeldovich-Number appears

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

# Chemical Time Scale

- Ze is of the order of 10

→ Chemical time scale  $t_c$  by two orders of magnitude larger than the chemical time scale which (apart from the density ratio  $\rho_u/\rho_b$ ) results from the reaction rate, e.g. for very lean mixtures  $\phi_u \ll 1$ , as the inverse of

$$B \frac{\rho Y_{O_2}}{M_{O_2}} \exp\left(\frac{-E}{RT}\right) \quad \text{bei} \quad T = T_b, \rho = \rho_b, Y_{O_2} = Y_{O_2,b}$$

- $t_c$  not determined by chemistry alone, additional influence of flame structure
- Definition of flame thickness:

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

# Flame Time $t_F$

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

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

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

$$l_F = \frac{D}{s_L} = \frac{\lambda_b}{c_p \rho u s_L}$$

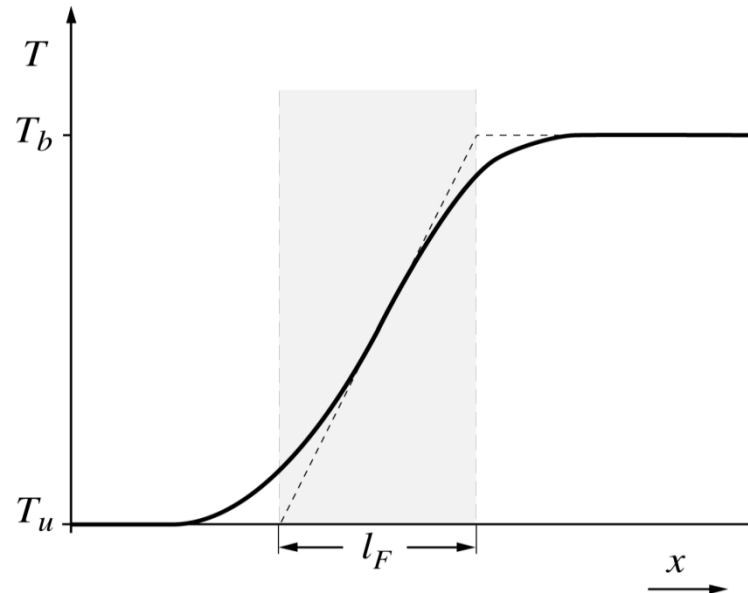
$$t_F = \frac{l_F}{s_L}$$

- $t_c$  is the flame time:

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

# Flame Thickness

- 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



# Flame Thickness

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- In

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

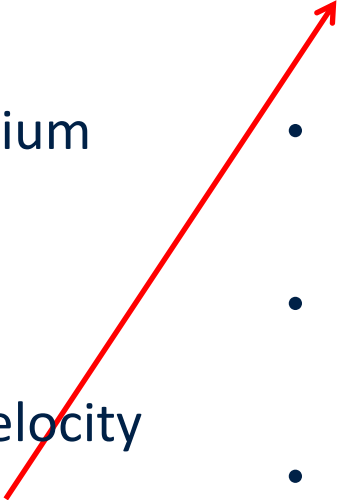
replacment of the left hand side by  $(T_b - T_u)/l_F$  and evaluation of the right hand side at  $T = T_b$  yields:

$$l_F = \frac{\lambda_b}{c_p \rho u s_L}$$

# Course Overview

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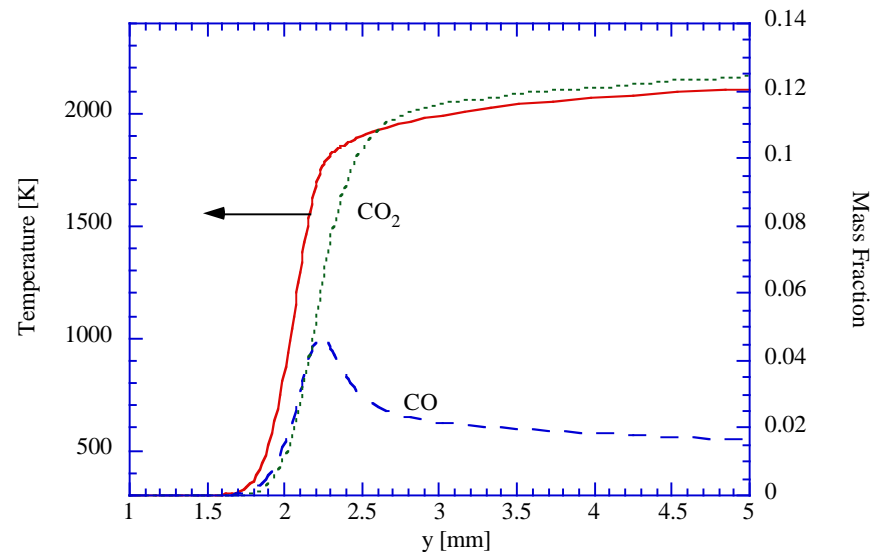
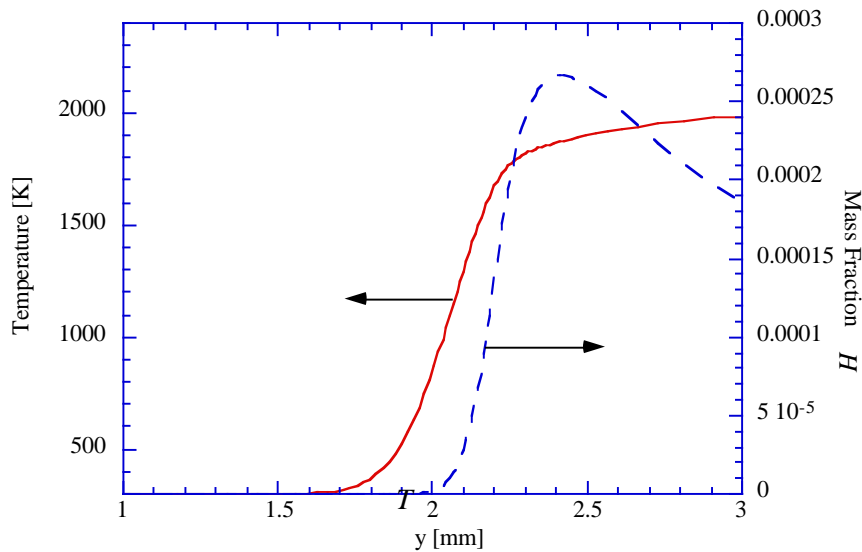
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- Asymptotic description of premixed flames based on an assumed **one-step reaction**
  - Basic understanding of the flame structure when a **large sensitivity to temperature** was built into the model
- **There is no chemical basis for the one-step 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

- 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  $\text{CH}_4$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CO}$
  - $\text{H}^\circ$ -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

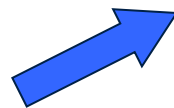
- Most important chain branching and chain breaking reactions hydrogen and hydrocarbon combustion



- Competition of 1f and 5f leads to

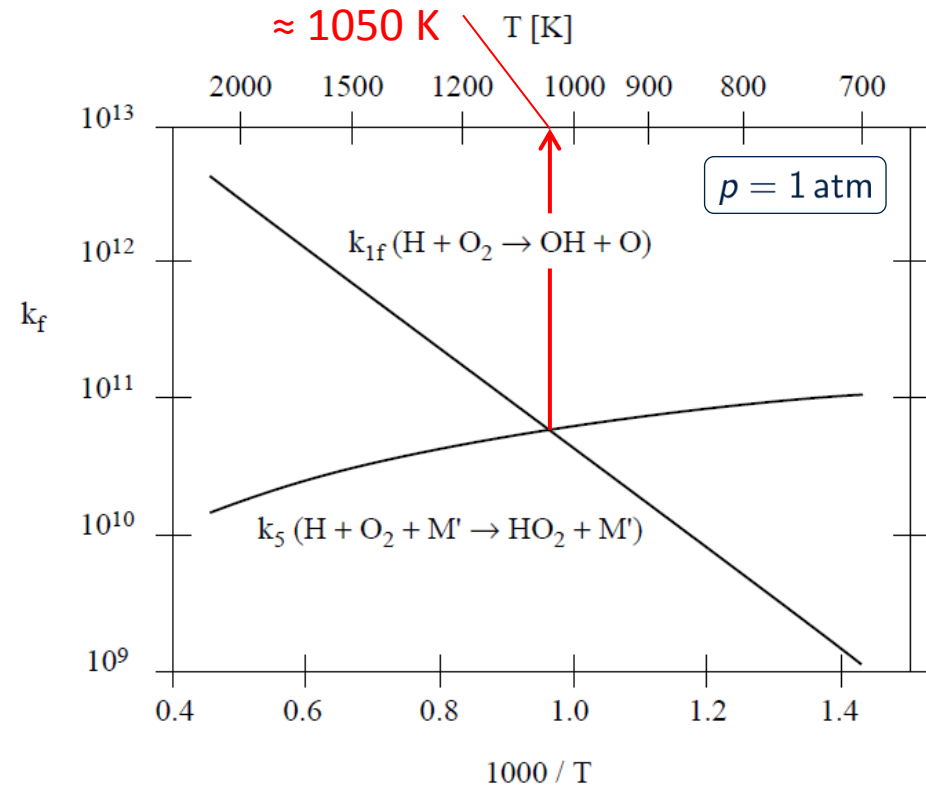
$$\frac{\omega_1}{\omega_5} = \frac{k_1 C_{\text{O}_2} C_{\text{H}}}{k_5 C_{\text{O}_2} C_{\text{H}} C_{\text{M}}} = \frac{k_1}{k_5 C_{\text{M}}}$$

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



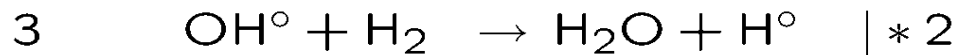
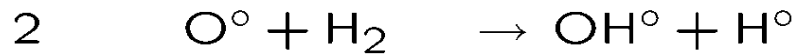
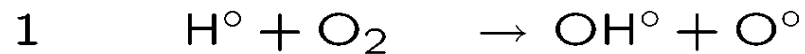
**Cross-over temperature  $T^0$**   
(aka: Inner layer temperature)

- $T < T^0$ : 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**

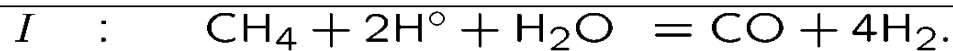
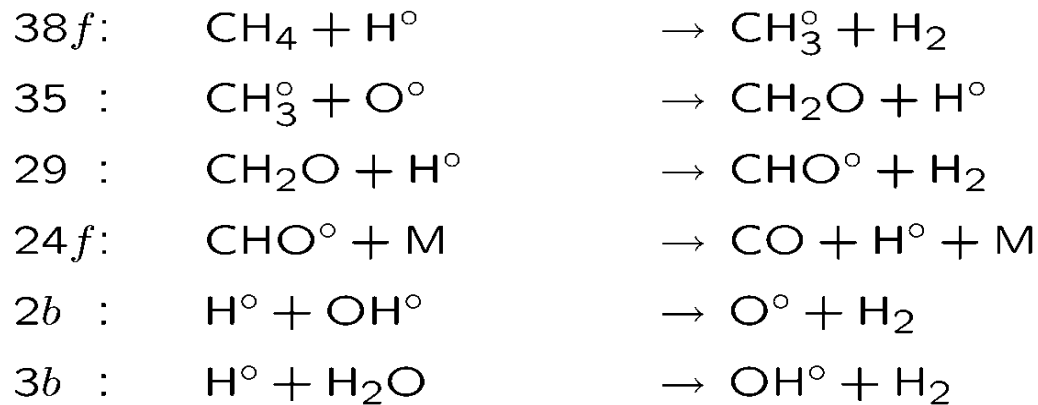


- Global **reaction IV** with the rate of reaction 5f describes **chain breaking**



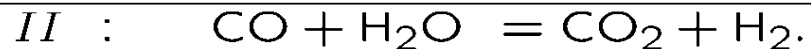
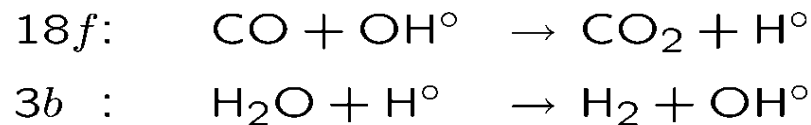
# The Four-Step Model for Methane-Air Flames

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



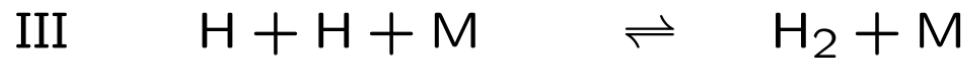
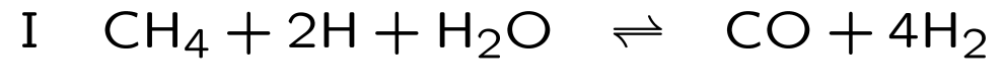
Radical consuming because of  $\text{CH}_3$  consumption reaction

- 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





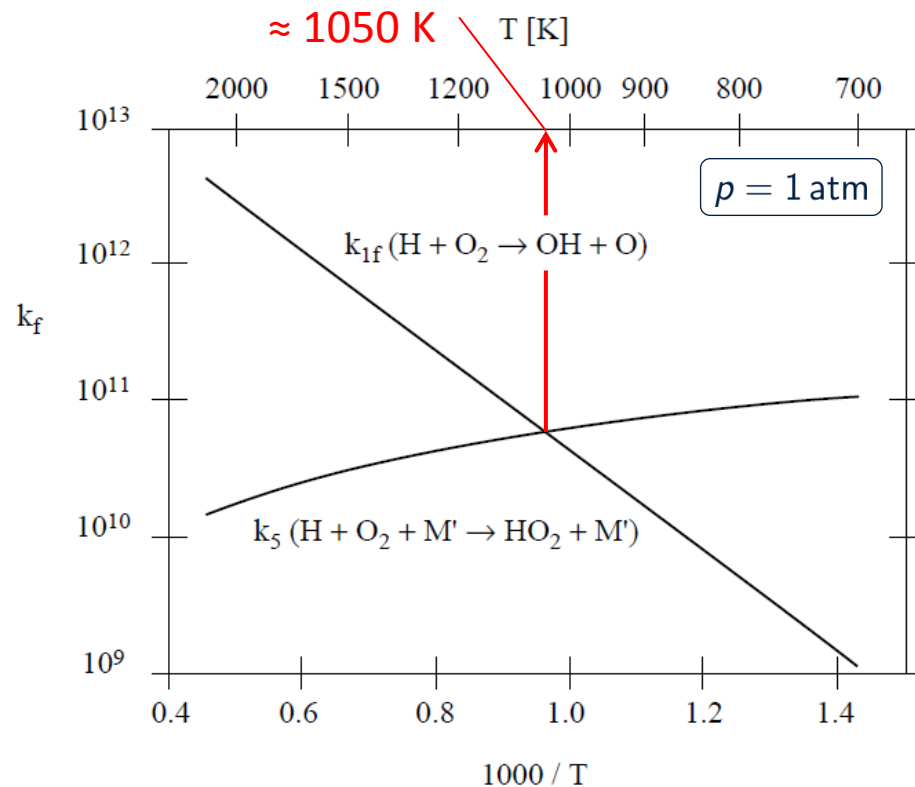
# The Four-Step Model for Methane-Air Flames

- 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



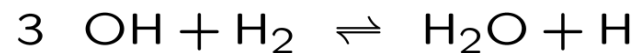
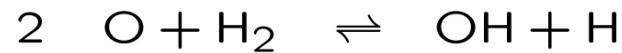
Inner layer Temperature  $T^0$

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

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

# 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:

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

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

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

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

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:

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

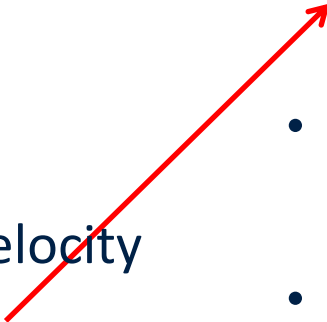
$$K_{\text{II}} = 0.035 \exp(3652/T)$$

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

# Course Overview

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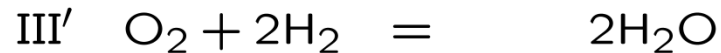
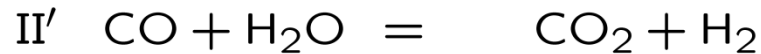
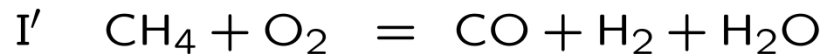
## Part I: Fundamentals and Laminar Flames

- 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
  - 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

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- 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

# 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

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

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 Three-Step Model for Methane-Air Flames

- The equation

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

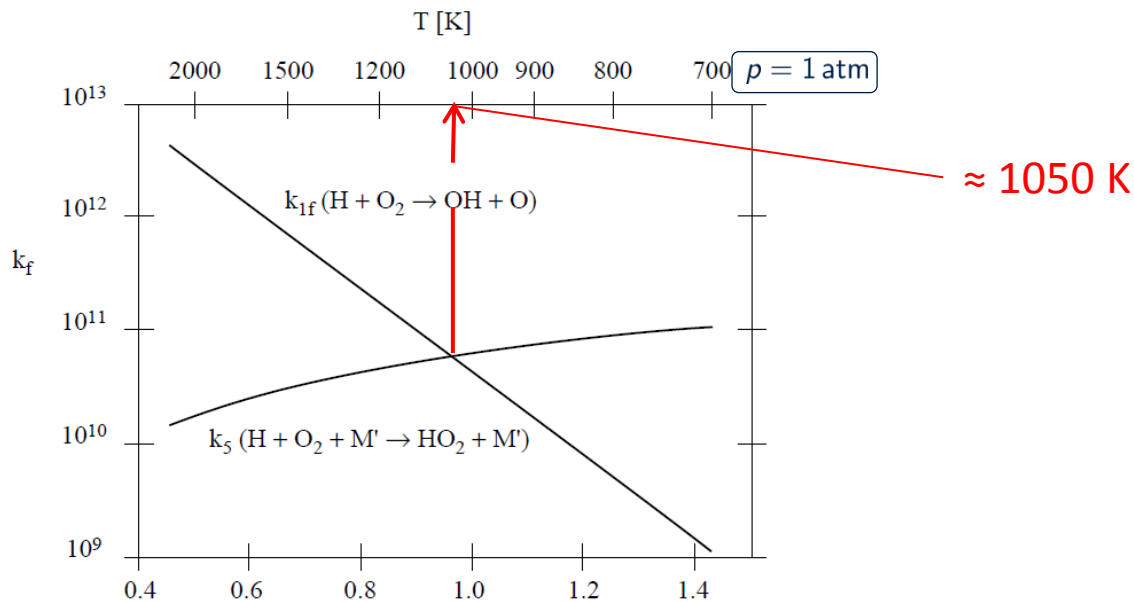
shows an interesting structure

- 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

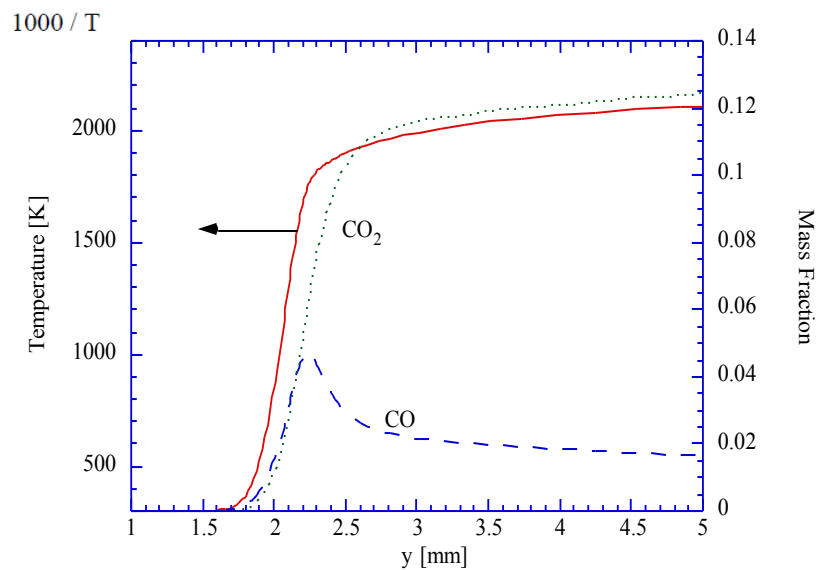
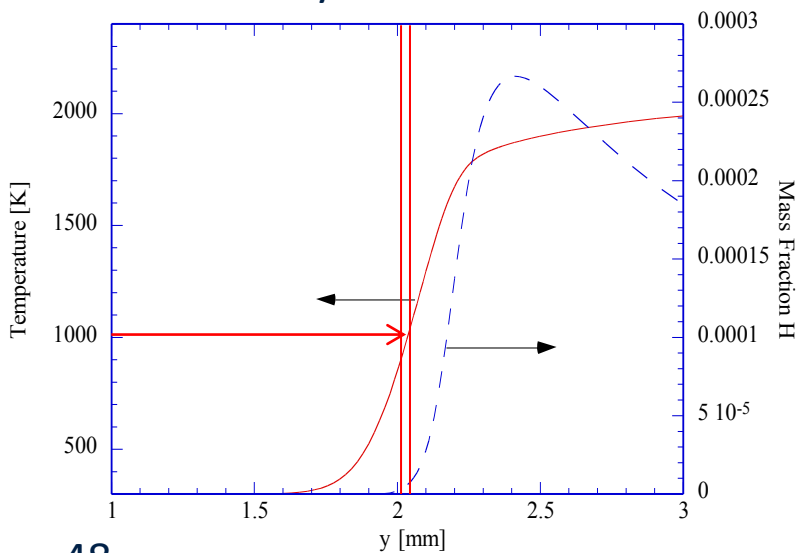
➔  $[CH_4]/[O_2]$  must be **much smaller than unity**, if [H] is to remain real

- 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





# Course Overview

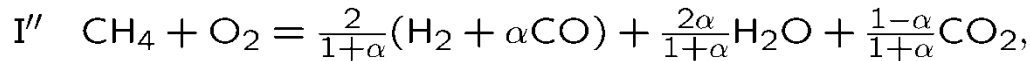
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## Part I: Fundamentals and Laminar Flames

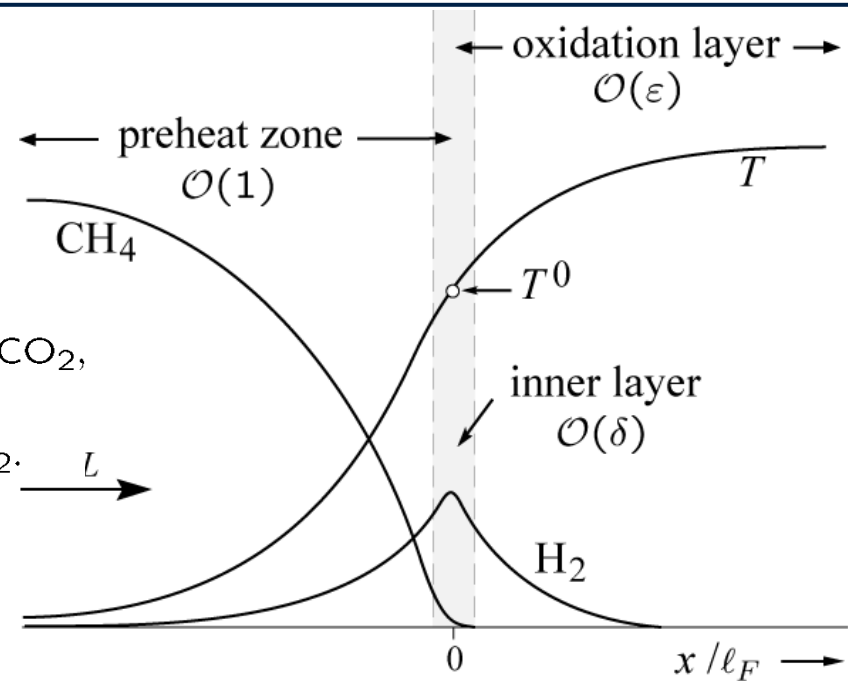
- Introduction
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- Three-step model for methane-air flames
- **Asymptotic structure of stoichiometric methane-air flames**
- Analytic expression for the burning velocity of methane and other hydrocarbon flames
- Flammability limits

# The Asymptotic Structure of Stoichiometric Methane-Air Flames

- Further simplification couples CO and H<sub>2</sub> leading to **two-step mechanism**

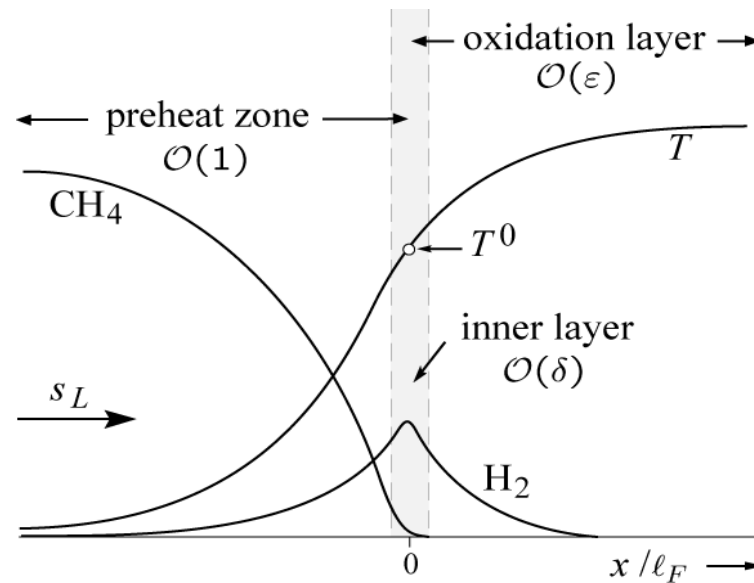


- It contains three layers
  1. A chemically inert preheat zone of order 1 upstream
  2. A thin inner layer of order  $\delta$  in which the fuel is consumed and the intermediates H<sub>2</sub> and CO are formed according to the global step I''
  3. A thin oxidation layer of order  $\varepsilon$  downstream where H<sub>2</sub> 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

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

## \*Details of the Asymptotic Analysis

---

- The small parameter  $\delta$  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  $\delta$  is small, since  $\omega_1$  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 parenthesis that  $x_{CH_4}$  must not exceed the value of  $\delta$

- 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  $x_{\text{CH}_4}$  is then of order  $\delta$  and one may introduce the scaling

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

and the stretched variable

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

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

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

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

## \*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  $x_{\text{H}_2}$  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

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

## \*Details of the Asymptotic Analysis

- In these expansions  $\varepsilon$  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

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

## \*Details of the Asymptotic Analysis

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- 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  $\varepsilon$  is smaller than unity but typically larger than  $\delta$

## \*Details of the Asymptotic Analysis

- Even though  $\delta$  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



## \*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

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

- Since the thickness of the preheat zone is of order 1 and that of the oxidation layer of order  $\varepsilon$  the upstream slope of the  $H_2$  concentration can be neglected compared to the downstream slope

$$\frac{dx_{H_2}}{dx} \Big|_{0+} \ll \frac{dx_{H_2}}{dx} \Big|_{0-}$$

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

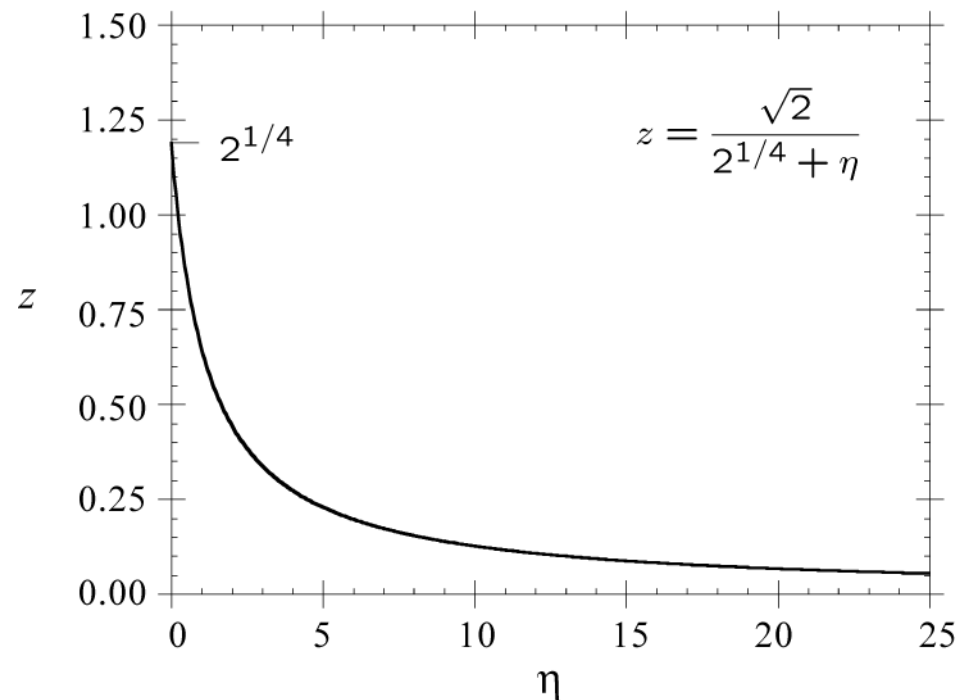
$$\frac{dz}{d\eta} = -1 \quad \text{at} \quad \eta = 0$$

Then the solution is

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

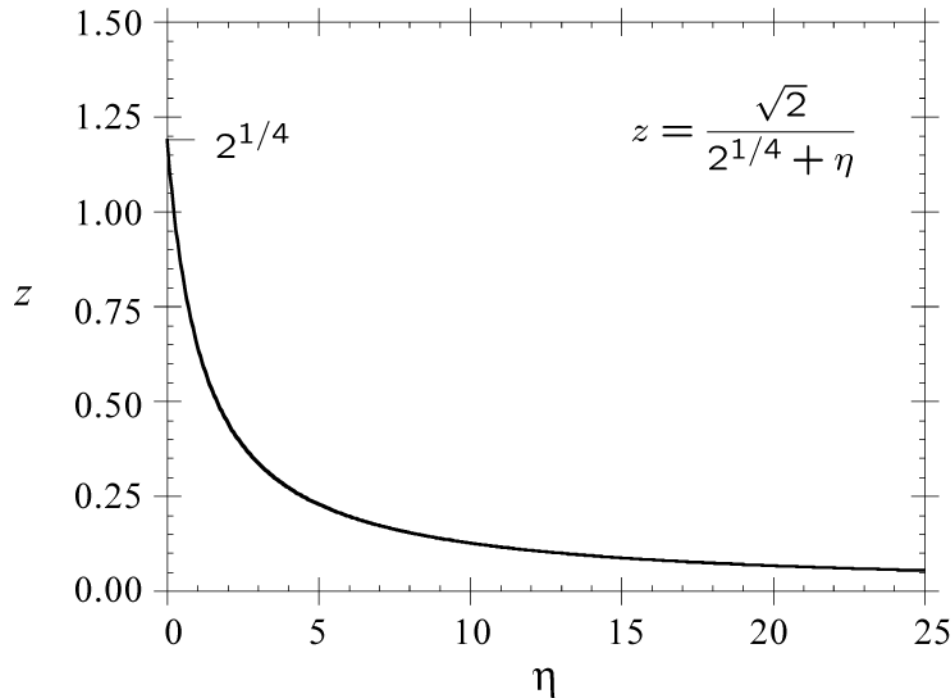
with

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



## \*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

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

and thereby the burning velocity  $s_L$

## \*An Analytic Expression for the Burning Velocity

- By dividing

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

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

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

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

were used to relate  $\varepsilon$  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

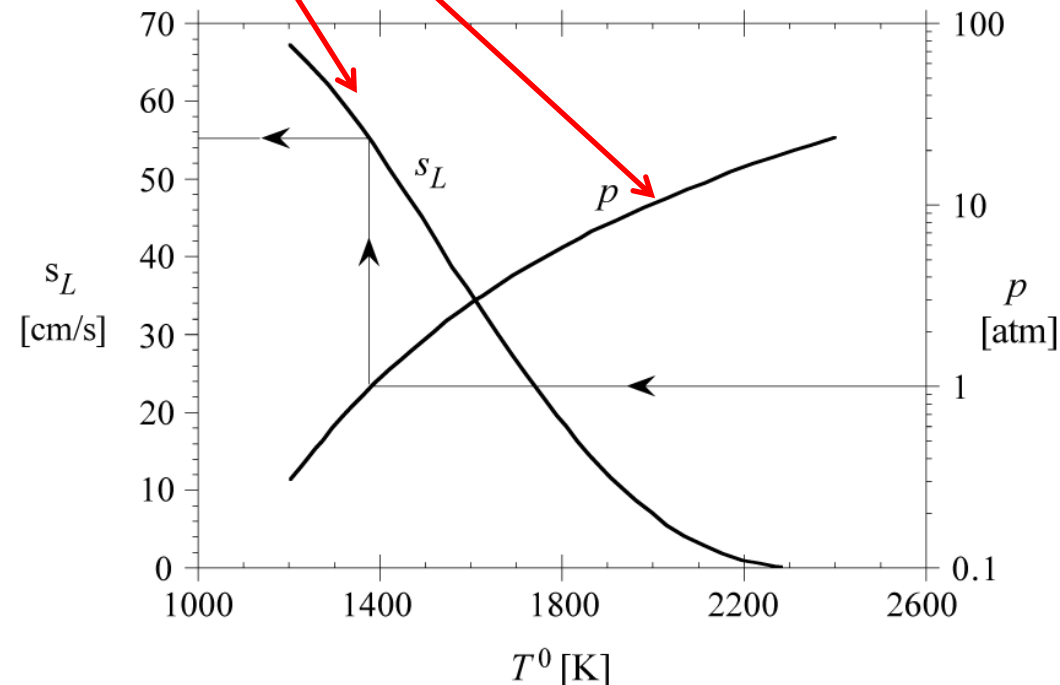
Asymptotic Analysis leads to analytic expression for laminar burning velocity

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

- 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**





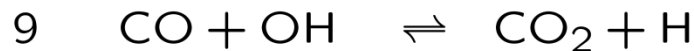
# Results of the Asymptotic Analysis

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

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



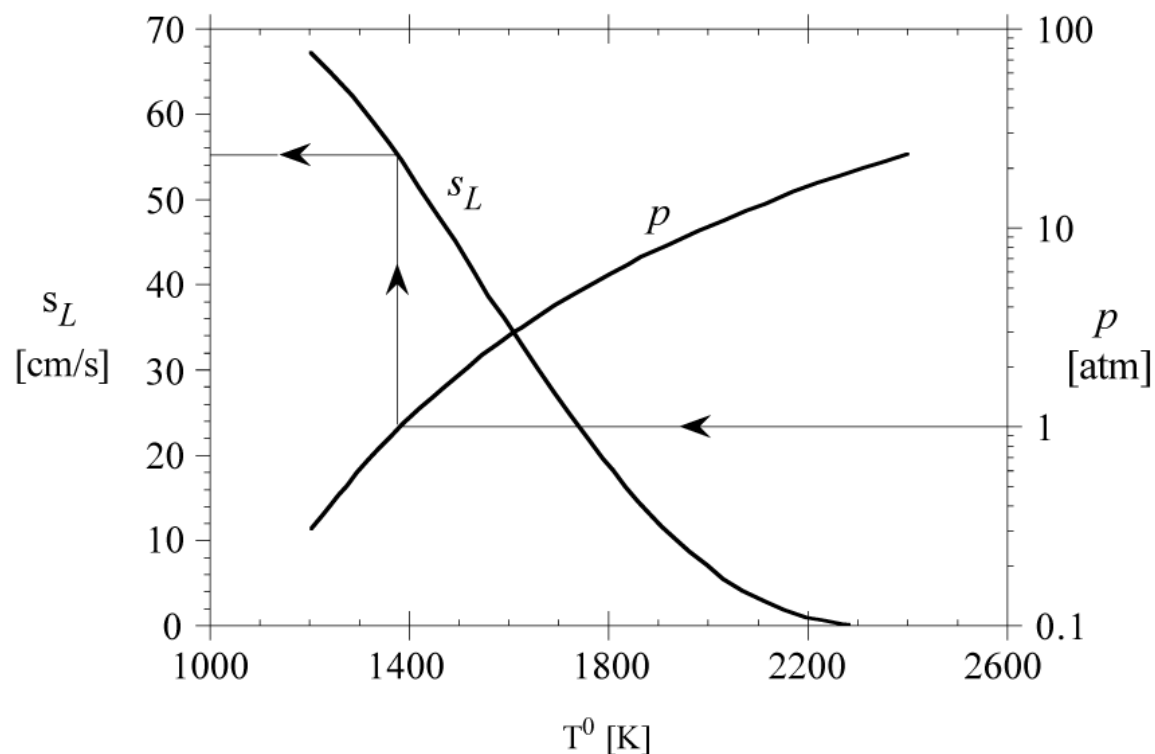
# Results of the Asymptotic Analysis

- 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



# Results of the Asymptotic Analysis

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- 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 ratio 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

## \*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

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

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  $\varepsilon$  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

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

# Relation to the Activation Energy of the One-step Model

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- 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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- Laminar premixed flames: Flame structure
- Laminar diffusion flames
- 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: Analytic Approximations of Burning Velocities for Lean CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, and C<sub>3</sub>H<sub>8</sub> Flames



- 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

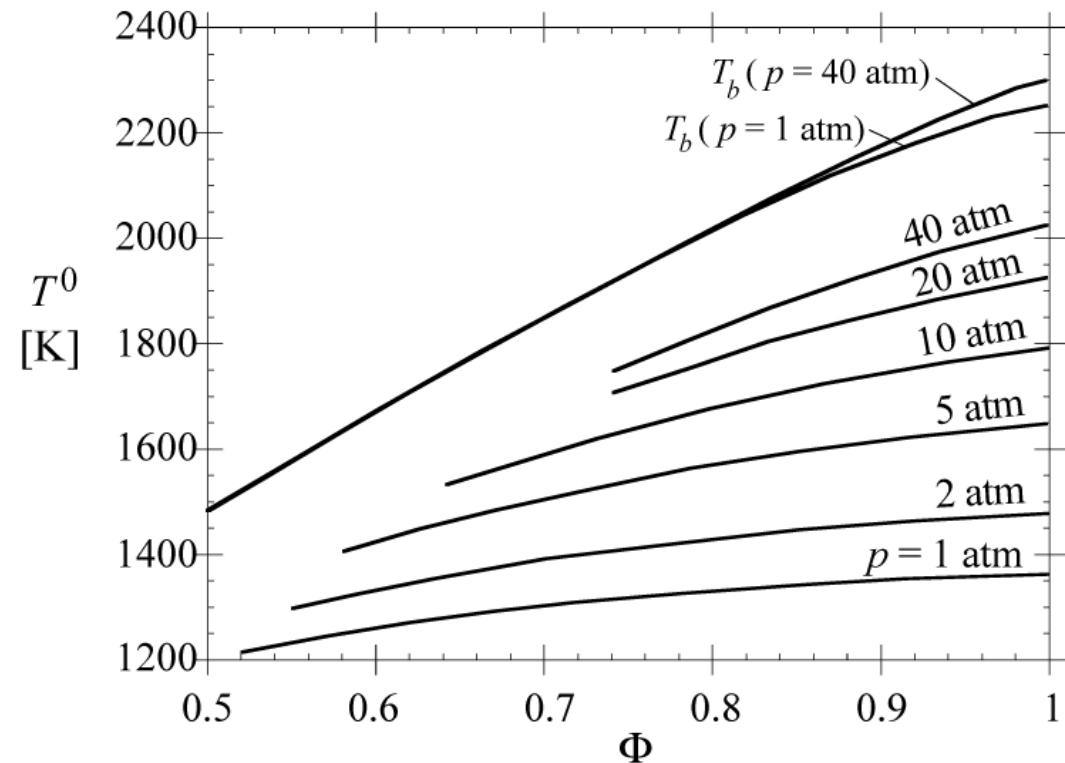
$$s_L = Y_{F,u}^m A(T^0) \frac{T_u}{T^0} \left( \frac{T_b - T^0}{T_b - T_u} \right)^n \quad \text{and} \quad p = P(T^0)$$

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

# Analytic Approximations of Burning Velocities for Lean $\text{CH}_4$ , $\text{C}_2\text{H}_6$ , $\text{C}_2\text{H}_4$ , $\text{C}_2\text{H}_2$ , and $\text{C}_3\text{H}_8$ 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



# Analytic Approximations of Burning Velocities for Lean CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, and C<sub>3</sub>H<sub>8</sub> Flames



- 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  $P(T^0)$  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)
- Basis of approximation was a data set of 197, 223, 252, 248, and 215 premixed flames for CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> and C<sub>3</sub>H<sub>8</sub>, 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]	$m$	$n$
$\text{CH}_4$	3.1557e8	23873.0	22.176	-6444.27	0.565175	2.5158
$\text{C}_2\text{H}_2$	56834.0	11344.4	37746.6	1032.36	0.907619	2.5874
$\text{C}_2\text{H}_4$	3.7036e5	14368.7	9978.9	263.23	0.771333	2.3998
$\text{C}_2\text{H}_6$	4.3203e6	18859.0	1900.41	-506.973	0.431345	2.1804
$\text{C}_3\text{H}_8$	2.2502e6	17223.5	1274.89	-1324.78	0.582214	2.3970

- The approximation was surprisingly the best for  $\text{C}_2\text{H}_2$ , yielding a standard deviation for  $s_L$  of 2.3%, followed by  $\text{C}_2\text{H}_4$  with 3.2%,  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$  with 6.2%, and  $\text{CH}_4$  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  $\text{CH}_4$  and  $\text{C}_3\text{H}_8$ , but close to unity for  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$
- This suggests that the **asymptotic model for these flames should differ from the one for  $\text{CH}_4$  in some important details**
- The exponent  $m$  lies around 2.5 and thereby sufficiently close to 2 for all fuels

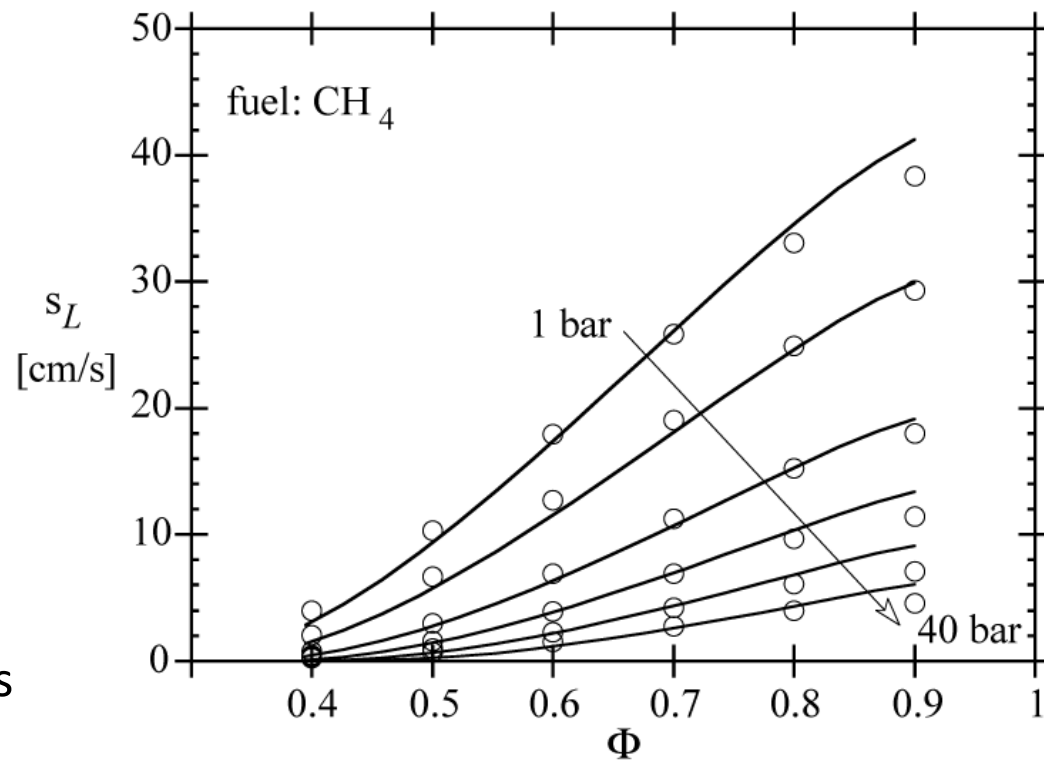
# Analytic Approximations of Burning Velocities for Lean $\text{CH}_4$ , $\text{C}_2\text{H}_6$ , $\text{C}_2\text{H}_4$ , $\text{C}_2\text{H}_2$ , and $\text{C}_3\text{H}_8$ Flames

- 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 derivations from the numerical computations occur around  $\phi = 1$

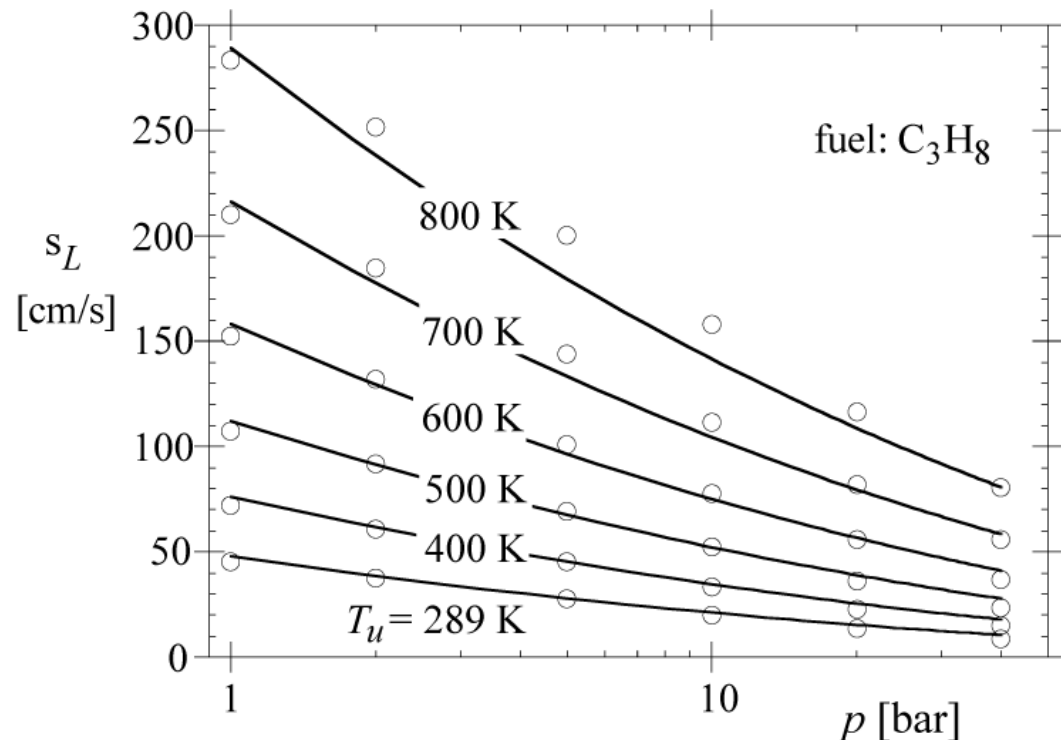


# Analytic Approximations of Burning Velocities for Lean $\text{CH}_4$ , $\text{C}_2\text{H}_6$ , $\text{C}_2\text{H}_4$ , $\text{C}_2\text{H}_2$ , and $\text{C}_3\text{H}_8$ Flames

- Burning velocities for methane calculated from

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

- 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



# 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  $1/T_b$

# 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

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

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

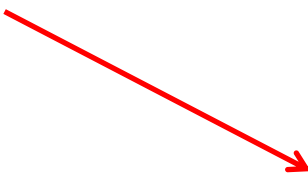
depends both on  $T_u$  and on the fuel-air ratio  $\phi = 1/\lambda$

- 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

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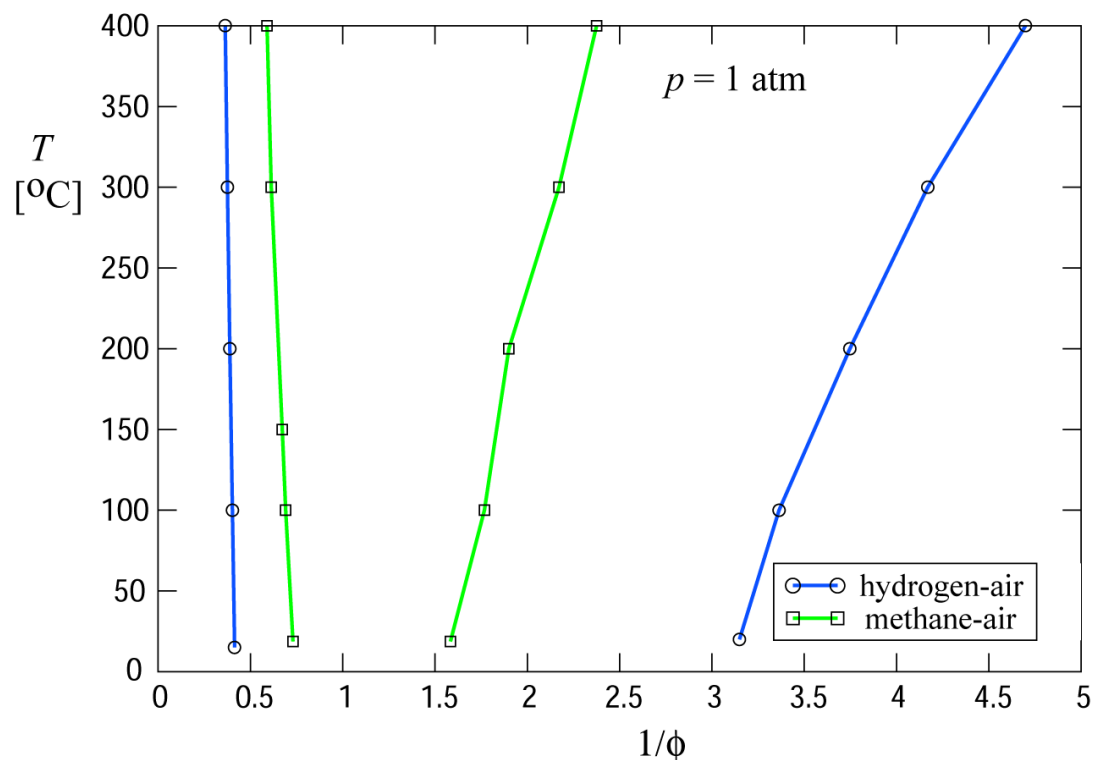
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- 

# 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



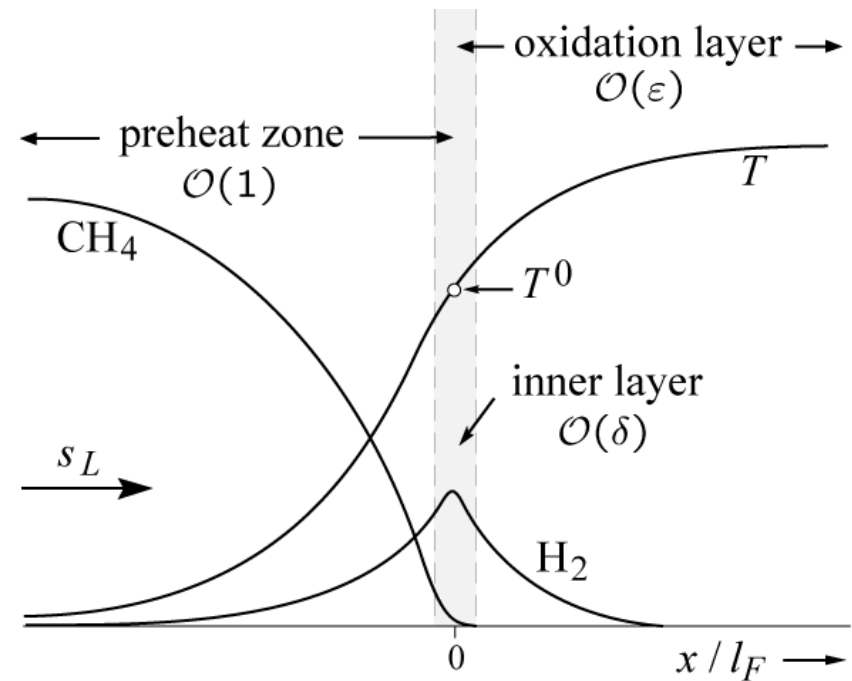
- This shows that hydrogen leakage may cause greater safety hazards than, for instance, hydrocarbons, which have flammability limits close to those of methane

# 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:  $A(T_0) = F \exp(-G/T_0)$ ,  $T_0 = -\frac{F}{\ln(p/B)}$ .  
→  $T_0$  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
- 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  $Y_{F,u}$ :  $(Y_{F,u})_{l.l.} = \frac{(T^0 - T_u)c_p\nu'_F W_F}{Q_{ref}}$ 
  - with  $T_b = T^0$
  - complete combustion ( $Y_{F,b} = 0$ )
- Eliminate values of the mass fraction with coupling equation 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:  $(Y_{F,u})_{l.l.} = 0.476 Y_{F,u,st}$ 
  - $T_u = 300\text{ K}$ ,  $p = 1\text{ bar}$
  - $T^0 = 1219\text{ K}$ ,  $T_{st} = 2229\text{ K}$
  - Corresponds to  $\lambda = 2,16$

→ Upper value for the lean flammability limit



# Flammability limits of real flames

- Real situations:  
→ Flame extinction occurs sooner

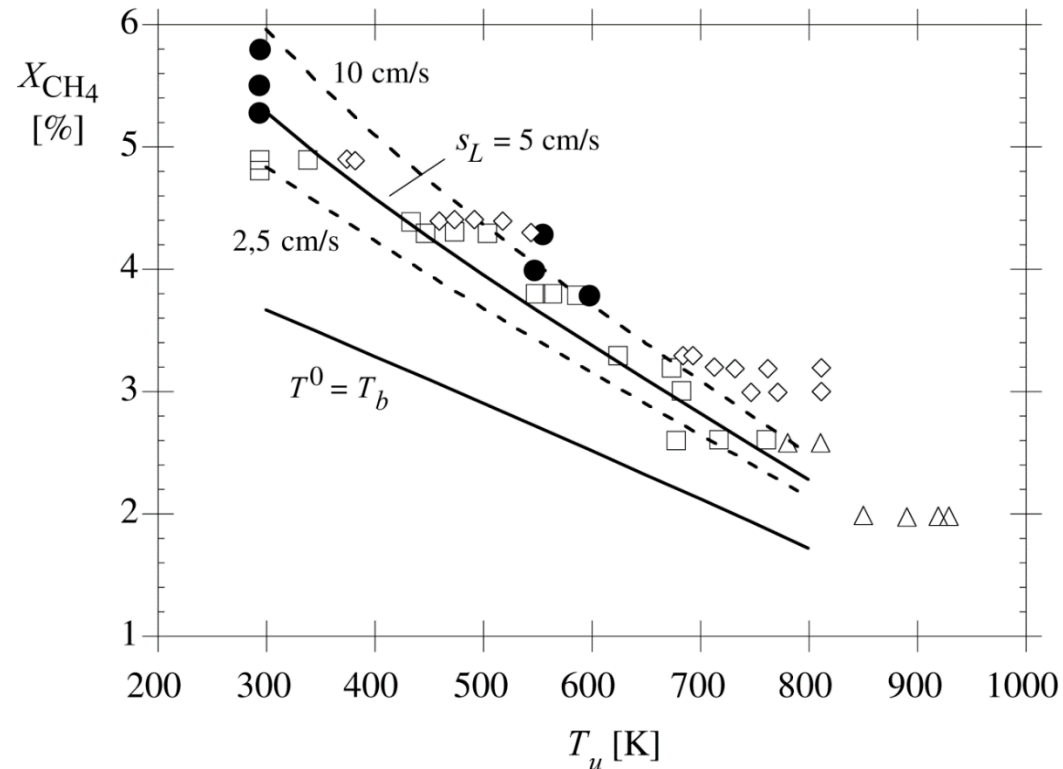
$$(Y_{F,u})_{l.l.} = \frac{T^0 - T_u}{T_{st} - T_u} Y_{F,u,st}$$

- 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 the mole fraction

→ Kinetically determined



# Theoretical explanation of the lean flammability limit

- **Thermal Flame Theory**: No flammability limit
- Exponential dependence 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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