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
    \[ \nu'_F F + \nu'_O_2 O_2 \rightarrow \nu''_P P. \]
  – Reaction rate
    \[ \omega = B \frac{\rho Y_F \rho Y_{O_2}}{W_F W_{O_2}} \exp \left( \frac{-E}{RT} \right) \]

• Behind the flame front:
  – No chemical conversion \rightarrow 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 $Le = 1$
  $\rightarrow$ Enthalpy is constant

• Coupling functions between the concentrations and the temperatures:

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

\[
Y_{O_2} = -\frac{\nu'_F W_{O_2} c_p}{Q} (T - T_b) + Y_{O_2,b}
\]
Thermal Flame Theory

• Momentum equation, limit of small Mach-Numbers $\rightarrow$ 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 \( x = -\infty \)

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

At \( x = x_i : \quad \left. \frac{dT}{dx} \right|_{x_i} = \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

\[
\frac{d}{dx} \left( \frac{\lambda}{c_P} \frac{dT}{dx} \right) = \frac{dT}{dx} \frac{d}{dT} \left( \frac{\lambda}{c_P} \frac{dT}{dx} \right) = c_P \frac{1}{\lambda} \frac{d}{2dT} \left( \frac{\lambda}{c_P} \frac{dT}{dx} \right)^2
\]

• The differential equation then becomes

\[
\frac{1}{2} \frac{d}{dT} \left( \frac{\lambda}{c_P} \frac{dT}{dx} \right)^2 = -\frac{(-\Delta H)}{c_P^2} \frac{\lambda}{w(T)}
\]
Thermal Flame Theory

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

\[
\frac{dT}{dx} = \sqrt{2 \frac{(-\Delta H)}{\lambda^2} \int_{T_i}^{T_b} \lambda w(T) \,dT}.
\]

At \( x = x_i \):

\[
\left. \frac{dT}{dx} \right|_x^R = \sqrt{2 \frac{(-\Delta H)}{\lambda^2} \int_{T_i}^{T_b} \lambda w(T) \,dT}.
\]

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

\[
\left. \frac{dT}{dx} \right|_x^V = \left. \frac{dT}{dx} \right|_x^R.
\]

- 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

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

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

\[
- \frac{E}{RT} = - \frac{E}{RT_b} + \frac{E(T - T_b)}{RT_b^2}
\]
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

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

• Integration yields:

\[
\int_{T_i}^{T_b} \lambda \omega dT = \lambda_b \frac{R T_b^2}{E} \int_{\Theta_i}^{0} w(\Theta) d\Theta
\]

\[
= \frac{\lambda_b B \rho^2_b c_p R^2 T_b^4}{(-\Delta H)E} \exp \left( - \frac{E}{RT_b} \right) \left[ \left( \frac{\nu'_F Y_{O_2,b}}{M_{O_2}} + \frac{\nu'_O Y_{F,b}}{M_F} \right) (1 + (\Theta_i - 1) \exp \Theta_i) \right]
\]

\[
+ 2 \frac{\nu'_O \nu'_F c_p R T_b^2}{(-\Delta H)E} \left( 1 - \left( 1 - \Theta_i + \frac{\Theta_i^2}{2} \right) \exp \Theta_i \right)
\]
Thermal Flame Theory

- **Integral:**
  \[
  \int_{T_i}^{T_b} \lambda \omega dT = \lambda_b \frac{RT_b^2}{E} \int_0^\Theta w(\Theta) d\Theta
  \]

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

- **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.
  $\Rightarrow$ 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 $-\infty$.
  $\Rightarrow$ Terms disappear.

\[
\int_{T_i}^{T_b} \lambda w dT = \lambda_b \frac{RT_b^2}{E} \int_{\Theta_i}^0 w(\Theta) d\Theta
\]

\[
= \frac{\lambda_b B \rho_b^2 c_p R^2 T_b^4}{(-\Delta H)E} \exp \left( -\frac{E}{RT_b} \right) \left[ \left( \frac{\nu'_B Y_{O_2,b}}{M_{O_2}} + \frac{\nu'_O Y_{B,b}}{M_B} \right) \left( 1 + (\Theta_i - 1) \exp \Theta_i \right) \right]
\]

\[
+ 2 \frac{\nu'_O \nu'_B c_p R T_b^2}{(-\Delta H)E} \left( 1 - \left( 1 - \Theta_i + \frac{\Theta_i^2}{2} \right) \exp \Theta_i \right).
\]

At $x = x_i$:

\[
\left. \frac{dT}{dx} \right|_{x_i}^R = \sqrt{2 \frac{(-\Delta H)}{\lambda^2}} \int_{T_i}^{T_b} \lambda w(T) dT.
\]
Thermal Flame Theory

Preheat zone:

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

$$\frac{dT}{dx}
\bigg|_{x_i}^P = \frac{c_p \rho u s_L}{\lambda_b} (T_b - T_u)$$

- 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

\[
\frac{dT}{dx} \bigg|_{x_i}^V = \frac{c_p \rho u S_L}{\lambda_b} (T_b - T_u) \quad \frac{dT}{dx} \bigg|_{x_i}^R = \sqrt{2 \frac{(-\Delta H)}{\lambda^2}} \int_{T_i}^{T_b} \lambda \, w(T) \, dT
\]

leads to:

\[
\rho u S_L = \sqrt{2 \frac{B \rho_b^2 \lambda_b R^2 T_b^4}{c_p(T_b - T_u)^2 E^2}} \exp \left( -\frac{E}{\mathcal{RT}_b} \right) S
\]

with

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

• 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 \( \rightarrow \) \( Y_{O_2,b} \approx Y_{B,b} \approx 0 \)
Thermal Flame Theory

\[ \rho u^s_L = \sqrt{2 \frac{B \rho_b^2 \lambda_b R^2 T_b^4}{c_p (T_b - T_u)^2 E^2}} \exp \left( -\frac{E}{RT_b} \right) S \]

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

- In a stoichiometric mixture, the last term is dominant
  \[ \rightarrow \text{ Approximation:} \]

\[ S = \begin{cases} 
\frac{\nu'_F Y_{O_2,b}}{M_{O_2}} & \text{für } \phi \ll 1, \\
\frac{2 \nu'_O \nu'_F c_p R T_b^2}{(-\Delta H) E} & \text{für } \phi = 1, \\
\frac{\nu'_O Y_{F,b}}{M_F} & \text{für } \phi \gg 1.
\end{cases} \]
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 → Integral between $T = -\infty$ und $T = T_b$
- When using the solution from the preheat zone, $T_i$ is set equal to $T_b$. 

![Diagram of Thermal Flame Theory](image)
Thermal Flame Theory (Summary)

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

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

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

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

• 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
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- 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
Flame Thickness and Flame Time

• Thermal flame theory:

\[
\rho u s_L = \sqrt{\frac{2B\rho_b^2\lambda_b R^2 T_b^4}{c_p(T_b - T_u)^2 E^2}} \exp \left( -\frac{E}{RT_b} \right) S
\]

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

• Burning velocity \( s_L \): Eigenvalue, results from the solution of the one-dimensional balance equation

• Assumptions:
  – One step reaction \( \rightarrow \) 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
  \[ s_L = \sqrt{\frac{D}{t_C}} \]
  \[ l_F = \sqrt{D \cdot t_C} \]
  \[ t_F = \frac{l_F}{s_L} = t_C \]
- Chemical time scale:
  \[ t_c = \frac{\rho_u E^2 (T_b - T_u)^2}{2 B \rho_b^2 (RT_b)^2 S} \exp \left( \frac{E}{R T_b} \right) \]
  \[ = \frac{1}{2} \cdot \frac{\rho_u}{\rho_b} \cdot Z e^2 \cdot \left[ \nu'_B B \left( \frac{\rho_b Y_{O_2,b}}{M_{O_2}} \right) \exp \left( - \frac{E}{R T_b} \right) \right]^{-1} \]
  Time scale of global reaction: \( \nu'_B B + \nu'_O_2 O_2 \rightarrow \text{Produkte} \)
- Square of Zeldovich-Number appears
  \[ Ze = \frac{E(T_b - T_u)}{R T_b^2} \]
  Ze is order 10

\( t_c \) 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:

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

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

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

- $t_c$ 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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Flame structure analysis using multi-step chemistry

- 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)
  \[ \text{CH}_4 + \text{M} \rightarrow \text{CH}_3^\circ + \text{H}^\circ + \text{M} \quad \text{oder} \quad \text{H}_2 + \text{O}_2 \rightarrow \text{OH}^\circ + \text{OH}^\circ \]

- Chain propagation reaction (No change in number of radicals)
  \[ \text{CH}_4 + \text{H}^\circ \rightarrow \text{CH}_3^\circ + \text{H}_2 \]

- Chain branching reaction (Increase in number of radicals)

- Chain breaking reaction (Decrease in number of radicals)
  \[ \text{H}^\circ + \text{H}^\circ + \text{M} \rightarrow \text{H}_2 + \text{M} \quad \text{oder} \quad \text{H}^\circ + \text{O}^\circ + \text{M} \rightarrow \text{OH}^\circ + \text{M} \]
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 $H^o$, $OH^o$, $O^o$, and for radical-poor situations also $HO_2^o$

One more rule:

6. **O-radical counts twice!**
## Chemical mechanism for methane oxidation

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Reaktion</th>
<th>$B$</th>
<th>$n$</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>in mol, cm$^3$, s</td>
<td></td>
<td>kJ/mol</td>
</tr>
<tr>
<td>1.1 H$_2$/O$_2$-Kettenreaktionen</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1f</td>
<td>$\text{H}^\circ + \text{O}_2 \rightarrow \text{OH}^\circ + \text{O}^\circ$</td>
<td>2,000E+14</td>
<td>0,00</td>
<td>70,30</td>
</tr>
<tr>
<td>1b</td>
<td>$\text{OH}^\circ + \text{O}^\circ \rightarrow \text{O}_2 + \text{H}^\circ$</td>
<td>1,568E+13</td>
<td>0,00</td>
<td>3,52</td>
</tr>
<tr>
<td>2f</td>
<td>$\text{O}^\circ + \text{H}_2 \rightarrow \text{OH}^\circ + \text{H}^\circ$</td>
<td>5,060E+04</td>
<td>2,67</td>
<td>26,30</td>
</tr>
<tr>
<td>2b</td>
<td>$\text{OH}^\circ + \text{H}^\circ \rightarrow \text{H}_2 + \text{O}^\circ$</td>
<td>2,222E+04</td>
<td>2,67</td>
<td>18,29</td>
</tr>
<tr>
<td>3f</td>
<td>$\text{OH}^\circ + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}^\circ$</td>
<td>1,000E+08</td>
<td>1,60</td>
<td>13,80</td>
</tr>
<tr>
<td>3b</td>
<td>$\text{H}_2\text{O} + \text{H}^\circ \rightarrow \text{H}_2 + \text{OH}^\circ$</td>
<td>4,312E+08</td>
<td>1,60</td>
<td>76,46</td>
</tr>
<tr>
<td>4f</td>
<td>$\text{OH}^\circ + \text{OH}^\circ \rightarrow \text{H}_2\text{O} + \text{O}^\circ$</td>
<td>1,500E+09</td>
<td>1,14</td>
<td>0,42</td>
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<td>$\text{H}_2\text{O} + \text{O}^\circ \rightarrow \text{OH}^\circ + \text{OH}^\circ$</td>
<td>1,473E+10</td>
<td>1,14</td>
<td>71,09</td>
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<tr>
<td>1.2 HO$_2$°-Bildung und -Verbrauch</td>
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<td></td>
</tr>
<tr>
<td>5f</td>
<td>$\text{H}^\circ + \text{O}_2 + \text{M}' \rightarrow \text{HO}_2^\circ + \text{M}'$</td>
<td>2,300E+18</td>
<td>-0,80</td>
<td>0,00</td>
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<tr>
<td>5b</td>
<td>$\text{HO}_2^\circ + \text{M}' \rightarrow \text{H}^\circ + \text{O}_2 + \text{M}'$</td>
<td>3,190E+18</td>
<td>-0,80</td>
<td>195,39</td>
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<td>6</td>
<td>$\text{H}^\circ + \text{HO}_2^\circ \rightarrow \text{OH}^\circ + \text{OH}^\circ$</td>
<td>1,500E+14</td>
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<td>7</td>
<td>$\text{HO}_2^\circ + \text{H}^\circ \rightarrow \text{H}_2 + \text{O}_2$</td>
<td>2,500E+13</td>
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<td>8</td>
<td>$\text{OH}^\circ + \text{HO}_2^\circ \rightarrow \text{H}_2\text{O} + \text{O}_2$</td>
<td>6,000E+13</td>
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<td>9</td>
<td>$\text{HO}_2^\circ + \text{H}^\circ \rightarrow \text{H}_2\text{O} + \text{O}^\circ$</td>
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<td>10</td>
<td>$\text{HO}_2^\circ + \text{O}^\circ \rightarrow \text{OH}^\circ + \text{O}_2$</td>
<td>1,800E+13</td>
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<td>-1,70</td>
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### Chemical mechanism for methane oxidation

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Reaktion</th>
<th>( B )</th>
<th>( n )</th>
<th>( E )</th>
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<td><strong>H₂O₂-Bildung und -Verbrauch</strong></td>
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<td>11</td>
<td>( \text{HO}_2^\circ + \text{HO}_2^\circ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 )</td>
<td>2.500E+11</td>
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<td>12f</td>
<td>( \text{OH}^\circ + \text{OH}^\circ + \text{M}' \rightarrow \text{H}_2\text{O}_2 + \text{M}' )</td>
<td>3.250E+22</td>
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<td>12b</td>
<td>( \text{H}_2\text{O}_2 + \text{M}' \rightarrow \text{OH}^\circ + \text{OH}^\circ + \text{M}' )</td>
<td>1.692E+24</td>
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<td>13</td>
<td>( \text{H}_2\text{O}_2 + \text{H}^\circ \rightarrow \text{H}_2\text{O} + \text{OH}^\circ )</td>
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<td>( \text{H}_2\text{O}_2 + \text{H}^\circ \rightarrow \text{H}_2 + \text{HO}_2^\circ )</td>
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<td>( \text{H}_2 + \text{HO}_2^\circ \rightarrow \text{H}_2\text{O}_2 + \text{H}^\circ )</td>
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<td><strong>Rekombinationsreaktionen</strong></td>
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<td>15</td>
<td>( \text{H}^\circ + \text{H}^\circ + \text{M}' \rightarrow \text{H}_2 + \text{M}' )</td>
<td>1.800E+18</td>
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<td>16</td>
<td>( \text{OH}^\circ + \text{H}^\circ + \text{M}' \rightarrow \text{H}_2\text{O} + \text{M}' )</td>
<td>2.200E+22</td>
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<tr>
<td>17</td>
<td>( \text{O}^\circ + \text{O}^\circ + \text{M}' \rightarrow \text{O}_2 + \text{M}' )</td>
<td>2.900E+17</td>
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## Chemical mechanism for methane oxidation

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<td>2. CO/CO$_2$-Mechanismus</td>
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<tr>
<td>18$f$</td>
<td>CO + OH$^\circ$ → CO$_2$ + H$^\circ$</td>
<td>4,400E+06</td>
<td>1,50</td>
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<td>18$b$</td>
<td>CO$_2$ + H$^\circ$ → CO + OH$^\circ$</td>
<td>4,956E+08</td>
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<td>3.1 CH$^\circ$-Verbrauch</td>
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<td>19</td>
<td>CH$^\circ$ + O$_2$ → CHO$^\circ$ + O$^\circ$</td>
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<td>20</td>
<td>CO$_2$ + CH$^\circ$ → CHO$^\circ$ + CO</td>
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<td>3.2 CHO$^\circ$-Verbrauch</td>
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<td>21</td>
<td>CHO$^\circ$ + H$^\circ$ → CO + H$_2$</td>
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<td>22</td>
<td>CHO$^\circ$ + OH$^\circ$ → CO + H$_2$O</td>
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<td>23</td>
<td>CHO$^\circ$ + O$_2$ → CO + H$_2$O$_2$</td>
<td>3,000E+12</td>
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<td>24$f$</td>
<td>CHO$^\circ$ + M$'$ → CO + H$^\circ$ + M$'$</td>
<td>7,100E+14</td>
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<td>24$b$</td>
<td>CO + H$^\circ$ + M$'$ → CHO$^\circ$ + M$'$</td>
<td>1,136E+15</td>
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Chemical mechanism for methane oxidation

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<td>25$f$</td>
<td>CH₂⁺⁺ + H⁻⁻ → CH⁺⁺ + H₂</td>
<td>8,400E+09</td>
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<td>1,40</td>
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<td>25$b$</td>
<td>CH⁺⁺ + H₂ → CH⁺⁺ + H⁻⁻</td>
<td>5,830E+09</td>
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<td>13,08</td>
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<td>26</td>
<td>CH₂⁺⁺ + O⁻⁻ → CO + H⁺⁻ + H⁻⁻</td>
<td>8,000E+13</td>
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<tr>
<td>27</td>
<td>CH₂⁺⁺ + O₂ → CO + OH⁺⁻ + H⁻⁻</td>
<td>6,500E+12</td>
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<tr>
<td>28</td>
<td>CH₂⁺⁺ + O₂ → CO₂ + H⁺⁻ + H⁻⁻</td>
<td>6,500E+12</td>
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<td>3.4 CH₂O-Verbrauch</td>
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<td>29</td>
<td>CH₂O + H⁻⁻ → CHO⁺⁻ + H₂</td>
<td>2,500E+13</td>
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<td>30</td>
<td>CH₂O + O⁻⁻ → CHO⁺⁻ + OH⁻⁻</td>
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<td>31</td>
<td>CH₂O + OH⁻⁻ → CHO⁺⁻ + H₂O</td>
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<td>32</td>
<td>CH₂O + M' → CHO⁺⁻ + H⁺⁻ + M'</td>
<td>1,400E+17</td>
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Chemical mechanism for methane oxidation

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<td>kJ/mol</td>
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<td>3.5 CH$_3^\circ$-Verbrauch</td>
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<tr>
<td>33f</td>
<td>CH$_3^\circ$ + H$^\circ$ → CH$_2^\circ$ + H$_2$</td>
<td>1,800E+14</td>
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<td>63,00</td>
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<td>33b</td>
<td>CH$_2^\circ$ + H$^\circ$ → CH$_3^\circ$ + H$^\circ$</td>
<td>3,680E+13</td>
<td>0,00</td>
<td>44,30</td>
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<tr>
<td>34</td>
<td>CH$_3^\circ$ + H$^\circ$ + (M) → CH$_4$ + (M)</td>
<td>$k_\infty$</td>
<td>0,00</td>
<td>44,30</td>
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<tr>
<td></td>
<td>k$_0$</td>
<td>6,257E+23</td>
<td>-1,80</td>
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<td>35</td>
<td>CH$_3^\circ$ + O$^\circ$ → CH$_2$O + H$^\circ$</td>
<td>7,000E+13</td>
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<td>0,00</td>
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<tr>
<td>36</td>
<td>CH$_3^\circ$ + CH$_3^\circ$ + (M) → C$_2$H$_6$ + (M)</td>
<td>$k_\infty$</td>
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<td>k$_0$</td>
<td>3,613E+13</td>
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<td>37</td>
<td>CH$_3^\circ$ + O$_2$ → CH$_2$O + OH$^\circ$</td>
<td>1,270E+41</td>
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<td>37,40</td>
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<td>38f</td>
<td>CH$_4$ + H$^\circ$ → CH$_3^\circ$ + H$_2$</td>
<td>2,200E+04</td>
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<td>36,60</td>
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<td>38b</td>
<td>CH$_3^\circ$ + H$_2$ → CH$_4$ + H$^\circ$</td>
<td>8,391E+02</td>
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<td>34,56</td>
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<td>39</td>
<td>CH$_4$ + O$^\circ$ → CH$_3^\circ$ + OH$^\circ$</td>
<td>1,200E+07</td>
<td>2,10</td>
<td>31,90</td>
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<td>40f</td>
<td>CH$_4$ + OH$^\circ$ → CH$_3^\circ$ + H$_2$O</td>
<td>1,600E+06</td>
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<td>10,30</td>
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<td>40b</td>
<td>CH$_3^\circ$ + H$_2$O → CH$_4$ + OH$^\circ$</td>
<td>2,631E+05</td>
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4.1 C$_2$H-Verbrauch

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<td>kJ/mol</td>
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<td>41f</td>
<td>C$_2$H + H$_2$ → C$_2$H$_2$ + H$^\circ$</td>
<td>1,100E+13</td>
<td>0,00</td>
<td>12,00</td>
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<tr>
<td>41b</td>
<td>C$_2$H$_2$ + H$^\circ$ → C$_2$H + H$_2$</td>
<td>5,270E+13</td>
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<td>119,95</td>
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<td>42</td>
<td>C$_2$H + O$_2$ → CHCO$^\circ$ + O$^\circ$</td>
<td>5,000E+13</td>
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<td>6,30</td>
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### 4.2 CHCO°-Verbrauch

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<td>43f</td>
<td>CHCO° + H° → CH₂ + CO</td>
<td>3,000E+13</td>
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<td>43b</td>
<td>CH₂ + CO  → CHCO° + H°</td>
<td>2,361E+12</td>
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<td>-29,39</td>
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<tr>
<td>44</td>
<td>CHCO° + O° → CO + CO + H°</td>
<td>1,000E+14</td>
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### 4.3 C₂H₂-Verbrauch

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<td>45</td>
<td>C₂H₂ + O° → CH₂ + CO</td>
<td>4,100E+08</td>
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<td>46</td>
<td>C₂H₂ + O° → CHCO° + H°</td>
<td>4,300E+14</td>
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<td>50,70</td>
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<tr>
<td>47f</td>
<td>C₂H₂ + OH° → C₂H + H₂O</td>
<td>1,000E+13</td>
<td>0,00</td>
<td>29,30</td>
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<tr>
<td>47b</td>
<td>C₂H + H₂O → C₂H₂ + OH°</td>
<td>9,000E+12</td>
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<td>-15,98</td>
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<td>48</td>
<td>C₂H₂ + CH° → C₃H₃</td>
<td>2,100E+14</td>
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### 4.4 C₂H₃-Verbrauch

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<td>49</td>
<td>C₂H₃ + H° → C₂H₂ + H₂</td>
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<tr>
<td>50</td>
<td>C₂H₃ + O₂ → C₂H₂ + HO₂°</td>
<td>5,400E+11</td>
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<td>0,00</td>
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</table>
| 51f | C₂H₃ + (M) → C₂H₂ + H° + (M) | 2,000E+14 | 0,00 | 166,29| $k_\infty$
| 51b | C₂H₂ + H° → C₂H₃ | 1,053E+14 | 0,00 | 3,39  | $k_\infty$
## Chemical mechanism for methane oxidation

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<td>52f</td>
<td>$\mathrm{C}_2\mathrm{H}_4 + H^o \rightarrow \mathrm{C}_2\mathrm{H}_3^o + H_2$</td>
<td>1,500E+14</td>
<td>0,00</td>
<td>42,70</td>
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<td>52b</td>
<td>$\mathrm{C}_2\mathrm{H}_3^o + H_2 \rightarrow \mathrm{C}_2\mathrm{H}_4 + H^o$</td>
<td>9,605E+12</td>
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<td>53</td>
<td>$\mathrm{C}_2\mathrm{H}_4 + O^o \rightarrow \mathrm{CH}_3^o + \mathrm{CO} + H^o$</td>
<td>1,600E+09</td>
<td>1,20</td>
<td>3,10</td>
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<td>54f</td>
<td>$\mathrm{C}_2\mathrm{H}_4 + \mathrm{OH}^o \rightarrow \mathrm{C}_2\mathrm{H}_3^o + \mathrm{H}_2\mathrm{O}$</td>
<td>3,000E+13</td>
<td>0,00</td>
<td>12,60</td>
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<tr>
<td>54b</td>
<td>$\mathrm{C}_2\mathrm{H}_3^o + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{C}_2\mathrm{H}_4 + \mathrm{OH}^o$</td>
<td>8,283E+12</td>
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<td>65,20</td>
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<td>55</td>
<td>$\mathrm{C}_2\mathrm{H}_4 + M' \rightarrow \mathrm{C}_2\mathrm{H}_2 + \mathrm{H}_2 + M'$</td>
<td>2,500E+17</td>
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### 4.6 $\mathrm{C}_2\mathrm{H}_5^o$-Verbrauch

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<td>56f</td>
<td>$\mathrm{C}_2\mathrm{H}_5^o + H^o \rightarrow \mathrm{CH}_3^o + \mathrm{CH}_3^o$</td>
<td>3,000E+13</td>
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<tr>
<td>56b</td>
<td>$\mathrm{CH}_3^o + \mathrm{CH}_3^o \rightarrow \mathrm{C}_2\mathrm{H}_5^o + H^o$</td>
<td>3,547E+12</td>
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<td>$\mathrm{C}_2\mathrm{H}_5^o + \mathrm{O}_2 \rightarrow \mathrm{C}_2\mathrm{H}_4 + \mathrm{HO}_2^o$</td>
<td>2,000E+12</td>
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<td>20,90</td>
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<tr>
<td>58f</td>
<td>$\mathrm{C}_2\mathrm{H}_5^o + (M) \rightarrow \mathrm{C}_2\mathrm{H}_4 + H^o + (M)$</td>
<td>2,000E+13</td>
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<td>166,00</td>
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<tr>
<td></td>
<td></td>
<td>1,000E+17</td>
<td>0,00</td>
<td>130,00</td>
</tr>
<tr>
<td>58b</td>
<td>$\mathrm{C}_2\mathrm{H}_4 + H^o \rightarrow \mathrm{C}_2\mathrm{H}_5^o$</td>
<td>3,189E+13</td>
<td>0,00</td>
<td>12,61</td>
</tr>
</tbody>
</table>
## Chemical mechanism for methane oxidation

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Reaktion</th>
<th>(B)</th>
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<tbody>
<tr>
<td></td>
<td>in mol, cm(^3), s</td>
<td>kJ/mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.7</td>
<td>C(_2)H(_6)-Verbrauch</td>
<td></td>
<td></td>
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<tr>
<td>59</td>
<td>C(_2)H(_6) + H(^\circ) \rightarrow C(_2)H(_5)^\circ + H(_2)</td>
<td>5,400E+02</td>
<td>3.50</td>
<td>21,80</td>
</tr>
<tr>
<td>60</td>
<td>C(_2)H(_6) + O(^\circ) \rightarrow C(_2)H(_5)^\circ + OH(^\circ)</td>
<td>3,000E+07</td>
<td>2.00</td>
<td>21,40</td>
</tr>
<tr>
<td>61</td>
<td>C(_2)H(_6) + OH(^\circ) \rightarrow C(_2)H(_5)^\circ + H(_2)O</td>
<td>6,300E+06</td>
<td>2.00</td>
<td>2,70</td>
</tr>
<tr>
<td>5.1</td>
<td>C(_3)H(_3)-Verbrauch</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>62</td>
<td>C(_3)H(_3)^\circ + O(_2) \rightarrow CHCHO(^\circ) + CH(_2)O</td>
<td>6,000E+12</td>
<td>0,00</td>
<td>0,00</td>
</tr>
<tr>
<td>63</td>
<td>C(_3)H(_3)^\circ + O(^\circ) \rightarrow C(_2)H(_2)^\circ + CO</td>
<td>3,800E+13</td>
<td>0,00</td>
<td>0,00</td>
</tr>
<tr>
<td>64f</td>
<td>C(_3)H(_4) \rightarrow C(_3)H(_3)^\circ + H(^\circ)</td>
<td>5,000E+14</td>
<td>0,00</td>
<td>370,00</td>
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<tr>
<td>64b</td>
<td>C(_3)H(_3)^\circ + H(^\circ) \rightarrow C(_3)H(_4)</td>
<td>1,700E+13</td>
<td>0,00</td>
<td>19,88</td>
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<tr>
<td>5.2</td>
<td>C(_3)H(_4)-Verbrauch</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>C(_3)H(_4) + O(^\circ) \rightarrow C(_2)H(_2) + CH(_2)O</td>
<td>1,000E+12</td>
<td>0,00</td>
<td>0,00</td>
</tr>
<tr>
<td>66</td>
<td>C(_3)H(_4) + O(_2) \rightarrow C(_2)H(_3)^\circ + CHO(^\circ)</td>
<td>1,000E+12</td>
<td>0,00</td>
<td>0,00</td>
</tr>
<tr>
<td>67</td>
<td>C(_3)H(_4) + OH(^\circ) \rightarrow C(_2)H(_3)^\circ + CH(_2)O</td>
<td>1,000E+12</td>
<td>0,00</td>
<td>0,00</td>
</tr>
<tr>
<td>68</td>
<td>C(_3)H(_4) + OH(^\circ) \rightarrow C(_2)H(_4) + CHO(^\circ)</td>
<td>1,000E+12</td>
<td>0,00</td>
<td>0,00</td>
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<td></td>
<td></td>
<td>in mol, cm³, s</td>
<td></td>
<td>kJ/mol</td>
</tr>
<tr>
<td>5.3</td>
<td>$\text{C}_3\text{H}_6^o$-Verbrauch</td>
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<tr>
<td>69$f$</td>
<td>$\text{C}_3\text{H}_5^o \rightarrow \text{C}_3\text{H}_4 + \text{H}^o$</td>
<td>3,980E+13</td>
<td>0,00</td>
<td>293,10</td>
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<tr>
<td>69$b$</td>
<td>$\text{C}_3\text{H}_4 + \text{H}^o \rightarrow \text{C}_3\text{H}_5^o$</td>
<td>1,267E+13</td>
<td>0,00</td>
<td>32,48</td>
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<tr>
<td>70</td>
<td>$\text{C}_3\text{H}_5^o + \text{H}^o \rightarrow \text{C}_3\text{H}_4 + \text{H}_2$</td>
<td>1,000E+13</td>
<td>0,00</td>
<td>0,00</td>
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<tr>
<td>5.4</td>
<td>$\text{C}_3\text{H}_6$-Verbrauch</td>
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<tr>
<td>71$f$</td>
<td>$\text{C}_3\text{H}_6 \rightarrow \text{C}_2\text{H}_3^o + \text{CH}_3^o$</td>
<td>3,150E+15</td>
<td>0,00</td>
<td>359,30</td>
</tr>
<tr>
<td>71$b$</td>
<td>$\text{C}_2\text{H}_3^o + \text{CH}_3^o \rightarrow \text{C}_3\text{H}_6$</td>
<td>2,511E+12</td>
<td>0,00</td>
<td>-34,69</td>
</tr>
<tr>
<td>72</td>
<td>$\text{C}_3\text{H}_6 + \text{H}^o \rightarrow \text{C}_3\text{H}_5^o + \text{H}_2$</td>
<td>5,000E+12</td>
<td>0,00</td>
<td>6,30</td>
</tr>
<tr>
<td>5.5</td>
<td>$\text{C}_3\text{H}_7^o$-Verbrauch</td>
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<td></td>
</tr>
<tr>
<td>73</td>
<td>$n - \text{C}_3\text{H}_7^o \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3^o$</td>
<td>9,600E+13</td>
<td>0,00</td>
<td>129,80</td>
</tr>
<tr>
<td>74$f$</td>
<td>$n - \text{C}_3\text{H}_7^o \rightarrow \text{C}_3\text{H}_6 + \text{H}^o$</td>
<td>1,250E+14</td>
<td>0,00</td>
<td>154,90</td>
</tr>
<tr>
<td>74$b$</td>
<td>$\text{C}_3\text{H}_6 + \text{H}^o \rightarrow n - \text{C}_3\text{H}_7^o$</td>
<td>4,609E+14</td>
<td>0,00</td>
<td>21,49</td>
</tr>
<tr>
<td>75</td>
<td>$i - \text{C}_3\text{H}_7^o \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3^o$</td>
<td>6,300E+13</td>
<td>0,00</td>
<td>154,50</td>
</tr>
<tr>
<td>76</td>
<td>$i - \text{C}_3\text{H}_7^o + \text{O}_2 \rightarrow \text{C}_3\text{H}_6 + \text{HO}_2^+$</td>
<td>1,000E+12</td>
<td>0,00</td>
<td>20,90</td>
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<tr>
<td>77</td>
<td>$\text{C}_3\text{H}_8 + \text{H}^\circ \rightarrow n - \text{C}_3\text{H}_7^\circ + \text{H}_2$</td>
<td>$1,300\text{E}+14$</td>
<td>0,00</td>
<td>40,60</td>
</tr>
<tr>
<td>78</td>
<td>$\text{C}_3\text{H}_8 + \text{H}^\circ \rightarrow i - \text{C}_3\text{H}_7^\circ + \text{H}_2$</td>
<td>$1,000\text{E}+14$</td>
<td>0,00</td>
<td>34,90</td>
</tr>
<tr>
<td>79</td>
<td>$\text{C}_3\text{H}_8 + \text{O}^\circ \rightarrow n - \text{C}_3\text{H}_7^\circ + \text{OH}^\circ$</td>
<td>$3,000\text{E}+13$</td>
<td>0,00</td>
<td>24,10</td>
</tr>
<tr>
<td>80</td>
<td>$\text{C}_3\text{H}_8 + \text{O}^\circ \rightarrow i - \text{C}_3\text{H}_7^\circ + \text{OH}^\circ$</td>
<td>$2,600\text{E}+13$</td>
<td>0,00</td>
<td>18,70</td>
</tr>
<tr>
<td>81</td>
<td>$\text{C}_3\text{H}_8 + \text{OH}^\circ \rightarrow n - \text{C}_3\text{H}_7^\circ + \text{H}_2\text{O}$</td>
<td>$3,700\text{E}+12$</td>
<td>0,00</td>
<td>6,90</td>
</tr>
<tr>
<td>82</td>
<td>$\text{C}_3\text{H}_8 + \text{OH}^\circ \rightarrow i - \text{C}_3\text{H}_7^\circ + \text{H}_2\text{O}$</td>
<td>$2,800\text{E}+12$</td>
<td>0,00</td>
<td>3,60</td>
</tr>
</tbody>
</table>

$$C_{M'} = 6,5 \cdot C_{\text{CH}_4} + 6,5 \cdot C_{\text{H}_2\text{O}} + 1,5 \cdot C_{\text{CO}_2} + 0,75 \cdot C_{\text{CO}} + 0,4 \cdot C_{\text{O}_2} + 0,4 \cdot C_{\text{N}_2} + 1,0 \cdot C_{\text{sonstige}}$$
Flame structure from multi-step chemical kinetics

- 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 $\text{C}_2\text{H}_6$, $\text{C}_2\text{H}_4$, $\text{C}_2\text{H}_2$ and $\text{C}_3\text{H}_8$ 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$_2$O, CO$_2$, H$_2$, CO
  - 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

\[
1 f \quad \text{H}^\circ + \text{O}_2 \rightarrow \text{OH}^\circ + \text{O}^\circ
\]
\[
5 f \quad \text{H}^\circ + \text{O}_2 + M' \rightarrow \text{HO}_2 + M'
\]
The cross-over (inner layer) temperature

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

\[ 1f \quad H^\circ + O_2 \rightarrow OH^\circ + O^\circ \]
\[ 5f \quad H^\circ + O_2 + M' \rightarrow HO_2^\circ + M' \]

- Competition of 1f and 5f leads to

\[ \frac{\omega_1}{\omega_5} = \frac{k_1 C_{O_2} C_H}{k_5 C_{O_2} C_H C_M} = \frac{k_1}{k_5 C_M} \]

\[ \frac{\omega_1}{\omega_5} \bigg|_{T^0} = \frac{k_1 (T^0) R T^0}{k_5 (T^0) p} \equiv 1 \]

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

1. $H^\circ + O_2 \rightarrow OH^\circ + O^\circ$
2. $O^\circ + H_2 \rightarrow OH^\circ + H^\circ$
3. $OH^\circ + H_2 \rightarrow H_2O + H^\circ$ | $\times 2$

$$III. \quad O_2 + 3H_2 = 2H_2O + 2H^\circ$$

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

5. $H^\circ + O_2 + M \rightarrow HO_2^o + M$
7. $H^\circ + HO_2^o \rightarrow H_2 + O_2$

$$IV. \quad H^\circ + H^\circ + M = H_2 + M$$
The Four-Step Model for Methane-Air Flames

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

\[
38f: \quad \text{CH}_4 + \text{H}^\circ \rightarrow \text{CH}_3^\circ + \text{H}_2
\]
\[
35 : \quad \text{CH}_3^\circ + \text{O}^\circ \rightarrow \text{CH}_2\text{O} + \text{H}^\circ
\]
\[
29 : \quad \text{CH}_2\text{O} + \text{H}^\circ \rightarrow \text{CHO}^\circ + \text{H}_2
\]
\[
24f: \quad \text{CHO}^\circ + \text{M} \rightarrow \text{CO} + \text{H}^\circ + \text{M}
\]
\[
2b : \quad \text{H}^\circ + \text{OH}^\circ \rightarrow \text{O}^\circ + \text{H}_2
\]
\[
3b : \quad \text{H}^\circ + \text{H}_2\text{O} \rightarrow \text{OH}^\circ + \text{H}_2
\]
\[
\boxed{I : \quad \text{CH}_4 + 2\text{H}^\circ + \text{H}_2\text{O} = \text{CO} + 4\text{H}_2.}
\]

Radical consuming because of CH\textsubscript{3} consumption reaction

- Global reaction // with the rate of reaction 18f describes CO oxidation (water gas shift reaction)

\[
18f: \quad \text{CO} + \text{OH}^\circ \rightarrow \text{CO}_2 + \text{H}^\circ
\]
\[
3b : \quad \text{H}_2\text{O} + \text{H}^\circ \rightarrow \text{H}_2 + \text{OH}^\circ
\]
\[
\boxed{II : \quad \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2.}
\]
The four-step model for methane flames is in summary:

1. $\text{CH}_4 + 2\text{H} + \text{H}_2\text{O} \Leftrightarrow \text{CO} + 4\text{H}_2$
2. $\text{CO} + \text{H}_2\text{O} \Leftrightarrow \text{CO}_2 + \text{H}_2$
3. $\text{H} + \text{H} + \text{M} \Leftrightarrow \text{H}_2 + \text{M}$
4. $\text{O}_2 + 3\text{H}_2 \Leftrightarrow 2\text{H} + 2\text{H}_2\text{O}$
The Four-Step Model for Methane-Air Flames

- The principal rates governing these global reactions are

\[
\omega_1 = \omega_{11}, \quad \omega_{11} = \omega_9 \\
\omega_{III} = \omega_5, \quad \omega_{IV} = \omega_1
\]

- They correspond to the elementary reactions

\[
\begin{align*}
11 & \quad \text{CH}_4 + \text{H} \quad \rightarrow \quad \text{CH}_3 + \text{H}_2 \\
9 & \quad \text{CO} + \text{OH} \quad \Rightarrow \quad \text{CO}_2 + \text{H} \\
5 & \quad \text{H} + \text{O}_2 + \text{M} \quad \rightarrow \quad \text{HO}_2 + \text{M} \\
1 & \quad \text{H} + \text{O}_2 \quad \Leftrightarrow \quad \text{OH} + \text{O}
\end{align*}
\]

Inner layer Temperature \( T^0 \)

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

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

\[
\begin{align*}
2 & \quad \text{O} + \text{H}_2 \quad \Leftrightarrow \quad \text{OH} + \text{H} \\
3 & \quad \text{OH} + \text{H}_2 \quad \Leftrightarrow \quad \text{H}_2\text{O} + \text{H}
\end{align*}
\]

\[
[\text{O}] = \frac{[\text{H}][\text{OH}]}{K_2[\text{H}_2]} \\
[\text{OH}] = \frac{[\text{H}_2\text{O}][\text{H}]}{K_3[\text{H}_2]}
\]

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:

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

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

• Equilibrium constants are given as:

\[
\begin{align*}
K_3 &= 0.216 \exp(7658/T) \\
K_{II} &= 0.035 \exp(3652/T) \\
K_{IV} &= 1.48 \exp(6133/T).
\end{align*}
\]
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

\[
\begin{align*}
\text{I} & : \text{CH}_4 + 2\text{H} + \text{H}_2\text{O} & \rightleftharpoons & \text{CO} + 4\text{H}_2 \\
\text{II} & : \text{CO} + \text{H}_2\text{O} & \rightleftharpoons & \text{CO}_2 + \text{H}_2 \\
\text{III} & : \text{H} + \text{H} + \text{M} & \rightleftharpoons & \text{H}_2 + \text{M} \\
\text{IV} & : \text{O}_2 + 3\text{H}_2 & \rightleftharpoons & 2\text{H} + 2\text{H}_2\text{O}
\end{align*}
\]

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

\[
\begin{align*}
\text{I}' & : \text{CH}_4 + \text{O}_2 & = & \text{CO} + \text{H}_2 + \text{H}_2\text{O} \\
\text{II}' & : \text{CO} + \text{H}_2\text{O} & = & \text{CO}_2 + \text{H}_2 \\
\text{III}' & : \text{O}_2 + 2\text{H}_2 & = & 2\text{H}_2\text{O}
\end{align*}
\]
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

\[
\omega_I + \omega_{III} = \omega_{IV}
\]

- This leads to

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

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

$\approx 1050 \text{ K}$
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The Asymptotic Structure of Stoichiometric Methane-Air Flames

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

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

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

- It contains three layers:
  1. A chemically inert preheat zone of order 1 upstream.
  2. A thin inner layer of order δ in which the fuel is consumed and the intermediates H₂ and CO are formed according to the global step I''.
  3. 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

\[ \text{Da}_I = \frac{\rho_0^2 Y_{\text{CH}_4} u \lambda_0 (K_{IV} X_{\text{O}_2} X_{\text{H}_2}^3)^{1/2}}{\rho_{u s_L}^2 W_{\text{CH}_4} c_{p0} X_{\text{H}_2O} \text{Le}_{\text{CH}_4} k_{11}(T^0)} \]
**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

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

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

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
• 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

$$\frac{d^2 y}{d\zeta^2} = (\delta^2 \text{Da}_I)y(1 - y)^{1/2}$$
• The downstream boundary condition of this equation is

\[ y = 0 \quad \text{as} \quad \zeta \to +\infty \]

since reaction 1 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

\[ x_{CH_4} = 1 - \exp(Le_{CH_4}x) \]

which leads to the expansion \( x_{CH_4} = -x \) 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**

\[ y = 0 \quad \text{as} \quad \zeta \to +\infty \]

- In this layer the steady state approximation for the H-radical breaks down

- This layer occurs at \( y = 1, \zeta = -1 \) in terms of the inner layer variables

- Since the fuel is not consumed in this radical layer the slope of the fuel concentration is continuous and matching across this layer leads to

\[ y = 1, \quad \frac{dy}{d\zeta} = -1 \quad \text{at} \quad \zeta = -1. \]
With the boundary conditions

\[ y = 0 \quad \text{as} \quad \zeta \to +\infty \]

and

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

the equation

\[ \frac{d^2y}{d\zeta^2} = (\delta^2 Da_I)y(1 - y)^{1/2} \]

can be integrated once to obtain the eigenvalue

\[ \delta^2 Da_I = \frac{15}{8} \]
Details of the Asymptotic Analysis

- With

\[ \delta^2 D_{\alpha I} = \frac{15}{8} \]

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 \( x_{CH_4} = 0 \) 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:

\[
\begin{align*}
\frac{d^2}{dx^2}[(1 + \alpha)x_{H_2} + 4x_{CH_4} - 2x_{O_2}] &= 0, \\
\frac{d^2}{dx^2}[x_{H_2} + 2x_{CH_4} + x_{H_2O}] &= 0, \\
\frac{d^2}{dx^2}[x_{H_2} + x_{CH_4} + x_{CO_2}] &= 0, \\
\frac{d^2}{dx^2}[(q_{H_2} + \alpha q_{CO})x_{H_2} + x_{CH_4} + T] &= 0
\end{align*}
\]

To show that the downstream boundary conditions are satisfied by:

\[
x_{O_2} = \frac{\varepsilon z}{2q}, \quad T = 1 - \varepsilon z
\]
*Details of the Asymptotic Analysis

• In these expansions $\varepsilon$ is the small parameter related to the thickness of the oxidation layer.

• Introducing

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

into

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

leads to

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

where the Damköhler number of reaction III is defined as

$$\text{Da}_{\text{III}} = \frac{\rho_0^2 \frac{Y_{\text{CH}_4}u}{\rho_{u}s^2 L} \lambda_0 \left( \frac{K_{\text{IV}} \text{Le}_2^3 \text{Le}_2^3}{25(1 + \alpha)^3} \right)^{1/2} k_5[\text{M}]}{q^4 X_{\text{H}_2\text{O}}}.$$
The concentration of the third body in reaction 5 may be determined approximately by using the third body efficiencies evaluated at the burnt gas conditions.

This leads to

\[ [M] = \frac{1.6p}{RT} \]

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 \( \omega_1 = 0 \) 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

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

- This suggests the definition

  \[
  \varepsilon = Da^{-1/4}_{III}
  \]

- 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

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

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

  since reaction III is irreversible

- The upstream boundary condition must be determined from jump conditions across the inner layer
• Since the fuel is depleted and H\textsubscript{2} is formed in the inner layer following reaction II', the stoichiometry of this reaction also determines the change of slopes of the H\textsubscript{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 \(\epsilon\) the upstream slope of the H\textsubscript{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 \( x_{H2} = \frac{\varepsilon z}{(1 + \alpha)q} \) 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 $\eta \to \infty$

\[ z = \frac{\sqrt{2}}{2^{1/4} + \eta} \]

- This may explain why in numerically and experimentally obtained concentration and temperature profiles the downstream conditions are approached only very far behind the flame
An Analytic Expression for the Burning Velocity

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

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

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

  to determine the quantities required in
  \[
  \text{Da}_I = \frac{\rho_0^2 Y_{\text{CH}_4 u} \lambda_0}{\rho_u s_L^2 W_{\text{CH}_4} c_{p0}} \frac{(K_{\text{IV}} X_{\text{O}_2} X_{\text{H}_2}^3)_0^{1/2}}{X_{\text{H}_2O}} \text{Le}_{\text{CH}_4} k_{11}(T^0).
  \]

  and thereby the burning velocity \( s_L \)
An Analytic Expression for the Burning Velocity

- By dividing

\[ Da_I = \frac{\rho_0^2 Y_{CH_4u} \lambda_0 (K_1 V X_{O_2} X_{H_2}^3)_0^{1/2}}{\rho_u s_L^2 W_{CH_4} c_{p0} X_{H_2O}} \frac{Le_{CH_4} k_{11}(T^0)}{Le_{O_2}} \]

by

\[ \eta = \frac{2qx}{\varepsilon} \]

one can eliminate \( s_L \) and obtain a relation of the form

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

- Here the universal gas constant must be used as \( R = 82.05 \text{ atm cm}^3/\text{mol/K} \) 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.
After some algebraic manipulations the expression for the burning velocity reads

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

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

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

\[ s_L^2 = \frac{8}{15} \frac{k_1^2}{k_{11}} \frac{1}{q^4 X_{H_2O}} \frac{Y_{CH_4,u}}{W_{CH_4}} \frac{\lambda_0}{c_p} \left( \frac{LeO_2^5 LeH_2^3 K_{IV}(T^0)}{LeCH_4 2^5 (1 + \alpha_0)^3} \right) \frac{1/2 T_u^2 (T_b - T^0)^4}{T_0^2 (T_b - T_u)^4} \]

- Pressure obtained from

- Undiluted stoichiometric methane flame with
  - \( T_u = 300 \text{ K} \)
  - \( p = 1 \text{ atm} \)

\[ s_L = 54 \text{ cm/s} \]
Results of the Asymptotic Analysis

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

\[ s^2_L = \frac{8}{15} \frac{k_1^2}{k_{11}} \frac{1}{q^4 X_{H_2O}} \frac{Y_{\text{CH}_4,u}}{W_{\text{CH}_4}} \frac{\lambda_0}{c_{p_0}} \left( \frac{\text{Le}_{O_2}^5 \text{Le}_{H_2}^3 K_{IV}(T^0)}{\text{Le}_{\text{CH}_4} 2^5 (1 + \alpha_0)^3} \right)^{1/2} \frac{T_u^2}{T_0^2} \frac{(T_b - T^0)^4}{(T_b - T_u)^4} \]

and

\[ \frac{k_1^2(T^0)}{k_{11}(T^0)k_5(T^0)/(\mathcal{R}/T^0)} = 1.5p \frac{\text{Le}_{\text{CH}_4}}{\text{Le}_{O_2}} \]

11 \hspace{1cm} \text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2

9 \hspace{1cm} \text{CO} + \text{OH} \Leftrightarrow \text{CO}_2 + \text{H}

5 \hspace{1cm} \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}

1 \hspace{1cm} \text{H} + \text{O}_2 \Leftrightarrow \text{OH} + \text{O}
Results of the Asymptotic Analysis

- Further consequence of equation

\[
\frac{s_L^2}{L} = \frac{8}{15k_{11}} \frac{k_1^2}{q^4X_{H_2O}} \frac{Y_{CH_4,u}}{W_{CH_4}} \frac{\lambda_0}{c_p_0} \left( \frac{Le_{O_2}^5 Le_{H_2}^3 K_{IV}(T^0)}{Le_{CH_4} 2^5(1 + \alpha_0)^3} \right) \frac{1/2 T_u^2(T_b - T^0)^4}{T_0^2(T_b - T_u)^4}
\]

is that the burning velocity vanishes as \( T^0 \) reaches \( T_b \)

- With \( T_b = 2320 \text{ K} \), \( T^0 \) reaches \( T_b \) when the pressure is larger than approximately 20 atm
• Using the burning velocity expression from the thermal flame theory

\[ \rho_u S_L = \sqrt{2 \frac{B \rho_b^2 \lambda_b R^2 T_b^4}{c_p(T_b - T_u)^2 E^2}} \exp \left( -\frac{E}{RT_b} \right) S \]

\[ S = \frac{\nu'_\text{CH}_4 Y_{\text{O}_2,b}}{M_{\text{O}_2}} + \frac{\nu'_\text{O}_2 Y_{\text{CH}_4,b}}{M_{\text{CH}_4}} + \frac{2 \nu'_\text{O}_2 \nu'_\text{CH}_4 c_p R T_b^2}{(-\Delta H) E}, \]

one may plot the burning velocity in an Arrhenius diagram over \( 1/T_b \).
Then in the limit of a large activation energy, the slope in this diagram is given by

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

Applying this form to burning velocity from 2-step mechanism

\[
s_L^2 = 8 \frac{k_1^2}{15 k_{11} q^4 X_{H_2O}} \frac{1}{W_{CH_4}} \frac{Y_{CH_4,u} \lambda_0}{c_{p_0}} \left( \frac{Le_{O_2}^5 Le_{H_2}^3 K_{IV}(T^0)}{Le_{CH_4} 2^5 (1 + \alpha_0)^3} \right)^{1/2} \frac{T_u^2 (T_b - T^0)}{T_0^2 (T_b - T_u)^4}
\]

with \( T^0 \) fixed leads to

\[
\frac{d \ln s_L^2}{d \ln T_b} = \frac{4T_b}{T_b - T^0} - \frac{4T_b}{T_b - T_u}
\]
Since the second of the terms is much smaller than the first,

\[ \varepsilon z_0 = \frac{T_b - T_0}{T_b - T_u} \]

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

\[ \frac{E}{RT_b} = \frac{4T_b}{T_b - T_u \varepsilon z_0} \]

Therefore the Zeldovich number

\[ Z_e = \frac{E(T_b - T_u)}{RT_b^2} \]

introduced in the previous lecture may be expressed as

\[ Z_e = \frac{E(T_b - T_u)}{RT_b^2} = \frac{4}{\varepsilon z_0} \]
Relation to the Activation Energy of the One-step Model

• 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
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: Analytic Approximations of Burning Velocities
for Lean Hydrocarbon Flames

- Burning velocity expression

\[ s_L^2 = \frac{8}{15} \frac{k_1^2}{k_{11}} \frac{1}{q^4 X_{H_2O}} \frac{Y_{CH_4,u}}{W_{CH_4}} c_{p_0} \left( \frac{\text{Le}_{O_2}^5 \text{Le}_{H_2}^3 K_{IV}(T^0)}{\text{Le}_{CH_4} 2^5 (1 + \alpha_0)^3} \right)^{1/2} \frac{T_u^2 (T_b - T^0)^4}{T_0^2 (T_b - T_u)^4} \]

\[ \frac{k_1^2(T^0)}{k_{11}(T^0) k_5(T^0)/(R/T^0)} = 1.5 p \frac{\text{Le}_{CH_4}}{\text{Le}_{O_2}} \]

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$_2$H$_6$, C$_2$H$_4$, C$_2$H$_2$ and C$_3$H$_8$, in the range between
  - $p = 1$ atm and 40 atm,
  - $T_u$ between 298 K and 800 K
  - $\phi = 0.4$ and 1.0

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Göttgens et al. (1992)

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Analytic Approximations of Burning Velocities for Lean Hydrocarbon Flames

- Adiabatic flame temperature

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

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<td>-277,8</td>
<td>4269</td>
<td>-2642</td>
<td>2.056</td>
</tr>
<tr>
<td>i-C₈H₁₈</td>
<td>0.61</td>
<td>936,0</td>
<td>-1127,0</td>
<td>5326</td>
<td>-3044</td>
<td>2.55</td>
</tr>
</tbody>
</table>
Analytic Approximations of Burning Velocities for Lean CH$_4$, C$_2$H$_6$, C$_2$H$_4$, C$_2$H$_2$, and C$_3$H$_8$ Flames

- Burning velocities for methane calculated from

\[ s_L = Y_{F_{u}}^{m}A(T^{0}) \frac{T_u}{T^{0}} \left( \frac{T_b - T^0}{T_b - T_u} \right)^n \]

and

\[ p = P(T^{0}) \]

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 CH$_4$, C$_2$H$_6$, C$_2$H$_4$, C$_2$H$_2$, and C$_3$H$_8$ Flames

- Burning velocities for methane calculated from

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

- 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

\[ \rho_{u,s_L} = \sqrt{\frac{2B \rho_b^2 \lambda_b R^2 T_b^4}{c_p(T_b - T_u)^2 E^2} \exp \left( \frac{-E}{RT_b} \right) S} \]

\[ S = \frac{\nu'_F Y_{O_2,b}}{M_{O_2}} + \frac{\nu'_O Y_{F,b}}{M_F} + \frac{2 \nu'_O \nu'_F c_p RT_b^2}{(-\Delta H)E} \]

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

\[
\rho_{uS_L} = \sqrt{2 \frac{B \rho_b^2 \lambda_b R^2 T_b^4}{c_p (T_b - T_u)^2 E^2}} \exp \left( -\frac{E}{RT_b} \right) S
\]

\[
S = \frac{v'_F Y_{O_2,b}}{M_{O_2}} + \frac{v'_O_2 Y_{F,b}}{M_F} + \frac{2 v'_O_2 v'_F c_p R T_b^2}{(-\Delta H) E}.
\]

approximately as

\[(\rho_{uS_L})^2 = \text{const} \exp(-E/RT_b)\]

and logarithmizes this expression:

\[
2 \ln(\rho_{uS_L}) = \ln(\text{const}) - \frac{E}{RT_b},
\]

one can determine the activation energy by differentiation with respect to \(1/T_b\).
Solution

- This leads to
  \[ \frac{E}{R} = -2 \frac{d \ln(\rho_u s_L)}{d(1/T_b)} = 2T_b^2 \frac{d}{dT_b} \left( \ln(\rho_u s_L) \right) \]

- 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

\[ 2T_b^2 \frac{d}{dT_b} \left( \ln(\rho_u s_L) \right) = \frac{2nT_b}{T_b - T_0} - \frac{2nT_b}{T_b - T_u} \]

- Therefore one obtains for the Zeldovich number \( Z_e \)

\[ Z_e = n \left( \frac{T_b - T_u}{T_b - T_0} - 1 \right) \]
Solution

• 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:

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

- $T^0$: „cross-over“-temperature between chain termination and chain branching
  - kinetically determined
Kinetically determined lean flammability limit

- Approximation equation:
  \[ s_L = Y_{F_0}^m A(T_0) \frac{T_u}{T_0} \left( \frac{T_b - T_0}{T_b - T_u} \right)^n \]

  \( \rightarrow T_b = T_0 \): Burning velocity = 0

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

  \( \rightarrow T_0 \) depends on pressure but not on the fuel mass fraction

- Condition \( T_b = T_0 \): Decreasing the fuel mass fraction in the mixture \( \rightarrow T_b \) 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 $Y_{F,u}$:
  \[ (Y_{F,u})_{l.l.} = \frac{(T^0 - T_u) c_p \nu_F W_F}{Q_{ref}} \]
  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:
  - $T_u = 300 \, K$, $p = 1 \, \text{bar}$
  - $T^0 = 1219 \, K$, $T_{st} = 2229 \, K$
  - Corresponds to $\phi = 0.46$

\[ \Rightarrow \] Approximation for the lean flammability limit
Flammability limits of real flames

- Real situations:
  → Flame extinction occurs sooner

- 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

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

  \[
  \rho_w s_L = \sqrt{2 \frac{B \rho_b^2 \lambda_b R^2 T_b^4}{c_p(T_b - T_u)^2 E^2}} \exp \left( - \frac{E}{RT_b} \right) S
  \]

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

  - 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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