Princeton Combustion Summer School 2023

Combustion Theory, Modeling and Applications

Heinz Pitsch
Institut für Technische Verbrennung
RWTH Aachen University

Combustion Applications

Mobility & Transport

Power Generation

Industry & Household

Combustion Applications

Mobility & Transport

Power Generation
Combustion is omnipresent! But causes emissions of:
- Harmful pollutants
- Greenhouse gases

Design challenge:
- Combustion extremely complex, multi-scale & multi-physics
- Devices usually big and high power
- Measurement difficult

Analysis, understanding, and computational engineering very important.

Combustion research started many years ago

- Why is combustion science still important?
- Why is combustion science interesting?

EIA’s International Energy Outlook 2021

World Energy Consumption
- Increase of renewable energy by factor 2.5
- However, fossil fuels projected to remain primary source of energy
- Almost 70% of energy consumption by fossil fuels

World Energy Consumption $[10^{15} \text{ Btu}]$

Quelle: EIA’s International Energy Outlook, 2021
EIA's International Energy Outlook 2021

World Energy Consumption
- Increase of renewable energy by factor 2.5
- However, fossil fuels projected to remain primary source of energy
- Almost 70% of energy consumption by fossil fuels

Large numbers
- 120 million tons daily CO₂ emissions in 2040
  → 13 kg daily per person
- 10 billion liter daily fuel consumption
  → 1.3 liter daily liquid fuel use

World Energy Outlook 2019

World Primary Energy Demand
- Different scenarios
  - Current policies
  - Stated policies
  - Sustainable Development
- Even in sustainable development scenario, fossil fuels still play important role

Oil consumption in the transport sector
- Significant growth:
  - 120% increase in truck traffic
  - 200% increase in air traffic
- Increased traffic must be offset by improved efficiency and alternative propulsion technologies

Clean combustion extremely important!
World Energy Demand in Mtoe by Fuel & Sector in 2040

GHG emissions can be reduced by considering:
1. Energy use
2. Primary energy
3. Conversion process

Mitigation of GHG Emissions

Primary Energy and Conversion Process

Opportunities:
- Cleaner fuels, e.g., natural gas
  - Almost 50% lower specific carbon emissions compared with coal
- Biofuels
  - Cluster of Excellence The Fuel Science Center
- Carbon-free fossil fuel combustion
  - CCS, CCU (SFB Oxyflame)
- Renewable electricity
  - Storage
    - E-fuels
    - Ammonia
    - Hydrogen

Opportunities:
- Electrification, but
  - Electrical power has to be from renewable sources
- Also, not all relevant applications can be electrified, i.e.
  - Industrial processes requiring high process temperatures
  - Applications requiring high energy densities

Requirement for Energy Storage

Electricity generation from different sources in December 2019 in Germany

Maximum power requirement (dashed line)
Requirement for Energy Storage

- Classified wind development potential index

Development potential resulting from spatial multi-criteria decision analysis techniques accounting for both resource potential and development feasibility

Renewable energy needs to be stored over time and transported over long distances!

Requirement for Energy Storage

- Energy storage
  - Chemical energy storage, e.g. H₂, NH₃, CH₄, OME, bio-hybrid fuels
  - Reconversion becomes important
    - Fuel cells for electricity
    - Thermo-chemical energy conversion for electricity or heat
  - Advantages of thermo-chemical energy conversion
    - Continuous energy transition without the need for step changes
    - Possible for both power and high-temperature heat
    - Possible for all sectors
    - High efficiencies possible at large scale
    - Proven technology

Requirement for Energy Storage

- Reduction of Greenhouse Gas Emissions
  - Different technologies for CO₂ avoidance, e.g.
    - Hydrogen economy
    - CO₂-sequestration (Carbon Capture and Storage, CCS)
    - Bio-fuels

Particularly important
- Increase in efficiency
- Chemical energy storage

Combustion theory very important!
What is Combustion?

- What is the difference between combustion and fuel oxidation in a fuel cell?

- In contrast to isothermal chemically reacting flows
  - Heat release induces temperature increase
  - Thereby combustion is self accelerating

- Important
  - Each chemical or physical process has associated time scale

- Interaction of flow (transport) and chemistry
  - Laminar and turbulent combustion
  - New dimensionless groups (similar to Reynolds number)
    - Damköhler number, Karlovitz number, ...

Combustion Applications: Examples

- Premixed combustion
  - Spark-ignition engine
  - Premixed

- Non-premixed combustion
  - Diesel engine
  - Aircraft engine

Aim of this Course

- Develop understanding of combustion processes from physical and chemical perspectives

- Fundamentals:
  - Thermodynamics
  - (Kinetics see parallel course)
  - Fluid mechanics
  - Heat and mass transfer

- Applications:
  - Reciprocating engines
  - Gas turbines
  - Furnaces
  - Industrial burners

Course Overview

- Part I: Fundamentals and Laminar Flames

- Part II: Turbulent Combustion

CEFRIC Summer School
Princeton
June 28th - July 2nd, 2010
Norbert Peters³
RWTH Aachen University
Princeton Combustion Summer School 2023

Fundamentals and Mass Balances of Combustion Systems

Heinz Pitsch
Institut für Technische Verbrennung
RWTH Aachen University

The final state (after very long time) of a homogeneous system is governed by the classical laws of thermodynamics!

Prerequisites:
- Definitions of concentrations and thermodynamic variables
- Mass and energy balances for multicomponent systems
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

 Definitions, Equation of State, Mass Balance

- Definitions, Equation of State, and Mass Balance
- Elementary and Global Reactions
- Coupling Functions
- Stoichiometry
- Mixture Fraction
- Burke-Schumann Solution

Course Overview

Mass fraction

- Mass $m_i$ of all molecules of species $i$ is related to its number of moles by
  $$m_i = W_i n_i, \quad i = 1, 2, \ldots, k$$
  where $W_i$ is the molecular weight of species $i$
- Total mass of all molecules in the mixture:
  $$m = \sum_{i=1}^{k} m_i$$
- Mass fraction of species $i$:
  $$Y_i = \frac{m_i}{m}, \quad i = 1, 2, \ldots, k$$
- Mean molecular weight $W$:
  $$W = \sum_{i=1}^{k} W_i X_i = \left( \sum_{i=1}^{k} \frac{Y_i}{W_i} \right)^{-1}$$
- Mass fraction and mole fraction:
  $$Y_i = \frac{W_i}{W} X_i$$

Definitions, Equation of State, Mass Balance

- In chemical reactions, mass and chemical elements are conserved
- Combustion always involves multiple species
- Mole Fraction
  - Multi-component system with $k$ different chemical species
  - Mole: $6.0236 \cdot 10^{23}$ molecules defined as one mole $\rightarrow$ Avogadro number $N_A$
  - Number of moles of species $i$:
    $$n_i = \sum_{i=1}^{k} n_i$$
  - Total number of moles:
    $$n_p = \sum_{i=1}^{k} n_i$$
  - Mole fraction of species $i$:
    $$X_i = \frac{n_i}{n_p}, \quad i = 1, 2, \ldots, k$$

Element mass fractions

- Element mass fractions are very useful in combustion
  - Mass of the species changes due to chemical reactions, but mass of the elements is conserved
  - Number of atoms of element $j$ in a molecule of species $i$:
    $$a_{ij}$$
  - Mass of all atoms $j$ in the system:
    $$m_j = \sum_{i=1}^{k} \frac{a_{ij} W_i}{W_i} n_i, \quad j = 1, 2, \ldots, k_e$$
  where $k_e$ is the total number of elements in the system, $W_j$ is molecular weight of element $j$
The mass fraction of elements

- Mass fraction of element $j$ is then

$$z_j = \frac{m_j}{m} = \sum_{i=1}^{k} \frac{a_{ij}W_j}{W_i}Y_i = \frac{W_j}{W} \sum_{i=1}^{k} a_{ij}X_i, \quad j = 1, 2, \ldots, k$$

- From definitions above it follows

$$\sum_{i=1}^{k} X_i = 1, \quad \sum_{i=1}^{k} Y_i = 1, \quad \sum_{j=1}^{k} Z_j = 1$$

The partial molar density (concentration)

- Number of moles per volume $V$ or partial molar density, the concentration:

$$[X_i] = \frac{n_i}{V}, \quad i = 1, 2, \ldots, k$$

- Total molar density of the system is then

$$\frac{n_s}{V} = \sum_{i=1}^{k} [X_i]$$

The Partial Density

- Density and partial density are defined

$$\rho = \frac{m}{V}, \quad \rho_i = \frac{m_i}{V} = \rho Y_i, \quad i = 1, 2, \ldots, k$$

- Partial molar density is related to partial density and mass fraction by

$$[X_i] = \frac{\rho_i}{W_i} = \frac{\rho Y_i}{W_i}, \quad i = 1, 2, \ldots, k$$

(relation often important for evaluation of reaction rates)

The ideal gas thermal equation of state

- In most combustion systems, thermally ideal gas law is valid

- Even for high pressure combustion this is a sufficiently accurate approximation, because the temperatures are typically also very high

- In mixture of ideal gases, molecules of species $i$ exert on the surrounding walls of the vessel the partial pressure

$$p_i = \frac{n_iRT}{V} = [X_i]RT = \frac{\rho Y_iRT}{W_i}, \quad i = 1, 2, \ldots, k$$

- Universal gas constant equal to

$$R = 8.3143 \text{ J/mol/K} = 82.05 \text{ atm cm}^3/\text{mol/K}$$
Dalton’s law

- For an ideal gas the total pressure is equal to the sum of the partial pressures

\[ p = \sum_{i=1}^{k} p_i = \sum_{i=1}^{k} n_i \frac{RT}{V} = \rho RT \]

- From this follows

\[ p_i = pX_i, \quad i = 1, 2, \ldots, k \]

- And for the volume

\[ V = n_i \frac{RT}{p_i} = n_i \frac{RT}{\rho} \]

---

*Example: Methane/Air Mixture

- Known: CH₄-air mixture: 5 mass percent CH₄, 95 mass percent air
  - Air: 21% (volume fraction) O₂, 79% N₂ (approximately)

- Unknown: Mole fractions and element mass fractions

- Solution:
  - Molar masses:
    - MO₂ = 32 g/mol, MN₂ = 28 g/mol, MCH₄ = 16 g/mol
  - Mass fractions in the air:
    - \( Y_{i} = \frac{M_{i}}{M} \)
  - In the mixture:
    - \( Y_{O₂} = 0.95 \), \( Y_{N₂} = 0.05 \)
  - Mean molar mass:
    - \( M = \frac{3}{\sum_{i=1}^{3} \frac{M_{i}}{Y_{i}}} = 27.5 \text{ g/mol} \)

---

Course Overview

Part I: Fundamentals and Laminar Flames

- Introduction
  - Definitions, Equation of State, Mass Balance
- 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
- Elementary and Global Reactions
- Coupling Functions
- Stoichiometry
- Mixture Fraction
- Burke-Schumann Solution
**Elementary and Global Reactions**

- Distinction between elementary reactions and global reactions important!

- Elementary reactions
  - Describe actual micro-process of chemical reaction
  - Only take place, if collisions between reactants take place
  - Reaction velocities can be determined experimentally or theoretically

- Global reactions
  - Conversion of educts to products
  - Ratios of amounts of substance
  - Does not represent a chemical micro-process
  - Temporal process of the reaction cannot be given

---

**Elementary Reactions**

- Observe the conservation of elements
- Chemical changes due to collisions of components
- Transition from educts to products symbolized by arrow

- Example: Bimolecular elementary reaction
  \[ \text{H}_2 + \text{O}_2 \rightarrow \text{OH}^0 + \text{O}^0 \]

- Elementary reactions also proceed backwards:
  \[ \text{H}_2^0 + \text{O}_2 \rightarrow \text{OH}^0 + \text{O}^0 \]

- Often symbolized by a double arrow:
  \[ \text{H}_2^0 + \text{O}_2 \leftrightarrow \text{OH}^0 + \text{O}^0 \]

---

**Global reactions**

- Conservation of elements
- Global ratios of amounts of substance
- Do not take place on atomic scale
- Global balance of a variety of elementary reactions
- Equality sign for global reactions
- Example for global reaction: \[ 2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O} \]
  means that 2 mol H\(_2\) react with 1 mol O\(_2\), yielding 2 mol H\(_2\)O

---

**Global reactions**

- Multiples of the equation are also valid:
  \[ \text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O} \]
  - This does not hold for elementary reactions!

- Multiplication of the equation of the global reaction by the molar masses
  → Mass balance during combustion

- Example: Combustion of H\(_2\) using the foregoing equation
  \[ 2\text{g H}_2 + 16\text{g O}_2 = 18\text{g H}_2\text{O} \]
**Global reactions**

- Stoichiometric coefficient of reactants $i$: $\nu_i$
- Stoichiometric coefficient of products $i$: $\nu_i''$
  - Example: $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$ \[ \nu_{\text{CH}_4} = 1, \quad \nu_{\text{H}_2\text{O}} = 2 \]

- Stoichiometric coefficient of a component $i$: $\kappa_i := \nu_i'' - \nu_i$
  - Example: $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$
  \[ \nu_{\text{CH}_4} = -1, \quad \nu_{\text{H}_2\text{O}} = 2 \]

- Rate of change for reactants negative

**Note:**
- Stoichiometric coefficients $\nu_i$ of reactants are negative!
- $\nu_i''$ are defined to be positive!

---

**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

- Definitions, Equation of State, Mass Balance
- Elementary and Global Reactions
- Coupling Functions
- Stoichiometry
- Mixture Fraction
- Burke-Schumann Solution

---

**Global reactions**

**Formulation of global reactions:**

- Combustion of hydrocarbon fuel or oxygenated hydrocarbon
  \[ \nu_{\text{H}_2\text{B}} + \nu_{\text{O}_2} = \nu_{\text{CO}_2} + \nu_{\text{H}_2\text{O}} \]

- Atoms in the fuel: Carbon, hydrogen and oxygen
  - Number of atoms in the fuel $a_{\text{BC}}, a_{\text{BH}}, a_{\text{BO}}$

- Stoichiometric coefficients of the global reaction are derived from $\nu_i$

- Balances of atoms
  - C: $\nu_i'\text{O}_2 = a_{\text{BC}} \nu_i'$
  - H: $\nu_i'\text{H}_2 = a_{\text{BH}} \nu_i'$
  - O: $\nu_i'\text{O}_2 + \nu_i'\text{H}_2\text{O} = a_{\text{BO}} \nu_i'/2$

- Example: $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$
  \[ a_{\text{BC}} = 1, \quad a_{\text{BH}} = 4, \quad a_{\text{BO}} = 0, \quad \nu_i' = 1 \]

---

**Coupling Functions**

**Example: Global reaction**

\[ 4 \text{H}_2 + 2\text{O}_2 = 4\text{H}_2\text{O} \]

- Consider conversion of 8 molecules of $\text{H}_2$
  - How many moles of $\text{O}_2$ have been converted?
  - Reaction has taken place how many times?

- In equations:
  - Global reaction, e.g.:
    \[ \nu_1' \text{F} + \nu_2' \text{O} = \nu_3' \text{P} \]
  - Concentration rate of change
    \[ \frac{dC_i}{dt} = \nu_i \omega \quad \text{with} \quad C_i = \frac{n_i}{V} \]
    or
    \[ \frac{dn_i/n_i}{dt} = \omega V \]

  - Change of mole number divided by stoichiometric coefficient $d n_i/\nu_i$ same for all species
Coupling functions

- It follows
  \[
  \frac{dn_i}{n_i} = \frac{dn_1}{n_1}, \quad \frac{dm_i}{m_i} = \frac{dm_1}{m_1}, \quad \frac{dY_i}{Y_i} = \frac{dY_1}{Y_1} \quad (i = 1, 2, ..., n)
  \]

- Integrating, e.g. for fuel and oxygen from the unburnt state

  \[
  \frac{Y_{O_2} - Y_{O_2,u}}{\nu_{O_2} M_{O_2}} = \frac{Y_B - Y_{B,u}}{\nu_B M_B}
  \]

- For one-step global reaction, only one species is independent
- Similar coupling function exists with temperature

Coupling functions – Example H₂

Coupling function:

\[
\frac{Y_{O_2} - Y_{O_2,u}}{\nu_{O_2} M_{O_2}} = \frac{Y_B - Y_{B,u}}{\nu_B M_B} \quad \Leftrightarrow \quad \Delta Y_{O_2} = \nu \Delta Y_B
\]

Example:
A closed system contains H₂ and O₂. Through combustion reactions, 1 kg H₂ is consumed. What mass of O₂ has been converted? How much air is needed?

1. Multiply coupling function by total mass

   \[
   \Delta m_{O_2} = \nu \Delta m_B
   \]

2. Determination of \( \nu \):

   \[
   \frac{H_2 + \frac{1}{2} O_2 = H_2O}{\nu = \frac{0.5 \cdot 32g/mol}{2g/mol} = 8}
   \]

   \( \Delta m_{O_2} = 8 \cdot 1kg = 8kg \)

   \( \Rightarrow \text{For burning 1kg H}_2, 8kg \times 76.7/23.3 = 26.3 \text{ kg of air is needed} \)

Coupling functions – Example Gasoline

Example: How much CO₂ is formed when burning 1 liter of gasoline?

Assumptions: Density of liquid gasoline is roughly 0.75 kg/l
Gasoline can be approximated by iso-octane

1. Starting point: One-step global reaction \( \text{C}_8\text{H}_{18} + 12.5 \text{ O}_2 = 8 \text{ CO}_2 + 9 \text{ H}_2\text{O} \)

2. Coupling function between fuel and CO₂

   \[
   \frac{dm_B}{\nu B M_B} = \frac{dm_{CO_2}}{\nu_{CO_2} M_{CO_2}}
   \]

3. Integrations leads to

   \[
   \Delta m_{CO_2} = \frac{\nu_{CO_2} M_{CO_2}}{\nu_B M_B} (-\Delta m_B)
   \]

   \( \Rightarrow \) During combustion of 1 liter Gasoline, 2.3 kg CO₂ are produced

   \( \Rightarrow \) Under standard conditions, this is roughly 1.3 m³ CO₂

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

- Definitions, Equation of State, Mass Balance
- Elementary and Global Reactions
- Coupling Functions
- Stoichiometry
- Mixture Fraction
- Burke-Schumann Solution
**Stoichiometry**

- **Stoichiometric:**
  - Fuel-to-oxygen ratio such that both are entirely consumed when combustion to CO$_2$ and H$_2$O is completed.

- For example:
  - Global reaction describing combustion of a single component hydrocarbon fuel C$_m$H$_n$ (subscript F for fuel): $v_F^C_mH_n + v_F^O_2O_2 = v_F^CO_2CO_2 + v_F^H_2H_2C$
  - Stoichiometric coefficients are $v_F = 1$, $v_O_2 = m + \frac{n}{4}$, $v_F^CO_2 = m$, $v_F^H_2O_2 = \frac{n}{2}$

  where $v_F = 1$ may be chosen arbitrarily to unity.

**Stoichiometric Mass Ratio**

- **Mole number ratio for stoichiometric condition**
  \[
  \frac{n_{O_2,m}}{n_{F,m}} = \frac{v_F^O_2}{v_F^F}
  \]

  or in terms of mass fractions

  \[
  \frac{Y_{O_2,m}}{Y_{F,m}} = \frac{v_F^O_2W_O_2}{v_F^FW_F} = \nu
  \]

  where $\nu$ is called the stoichiometric mass ratio.

- **Typical values:** Methane: $\nu = 4$; n-dodecane: $\nu = 3.5$
- If mass ratio equals $\nu$
  - Fuel and oxidizer are both consumed when combustion is completed.

---

**Stoichiometric Mass Ratio**

- This is consistent with coupling function, since

  \[
  \frac{Y_{O_2} - Y_{O_2,m}}{v_F^O_2W_O_2} = \frac{Y_F - Y_{F,m}}{v_F^FW_F}
  \]

  leads to

  \[
  \nu Y_F - Y_{O_2} = \nu Y_{F,m} - Y_{O_2,m}
  \]

- **Complete consumption of fuel and oxygen**

  \[
  Y_F = Y_{O_2} = 0
  \]

  leads to

  \[
  \frac{Y_{O_2,m}}{Y_{F,m}} = \frac{v_F^O_2W_O_2}{v_F^FW_F} = \nu
  \]

**Extra: Minimum oxygen requirement**

- **Minimum oxygen requirement (molar):** $\alpha_{\text{min}}$
  - Fuel/air mole number ratio before combustion at stoichiometric conditions
  - Ratio of the stoichiometric coefficients

  \[
  \alpha_{\text{min},m} = \frac{n_{O_2,m}}{n_{B,m}} = \frac{X_{O_2,m}}{X_{B,m}} = \frac{v_F^O_2}{v_B^O_2}
  \]

- **Minimum oxygen requirement (mass):** $\alpha_{\text{min}}$

  \[
  \alpha_{\text{min}} = \frac{m_{O_2,m}}{m_{B,m}} = \frac{X_{O_2,m}}{X_{B,m}} = \frac{M_{O_2}}{M_B} = \frac{v_F^O_2M_{O_2}}{v_B^O_2M_B} = \nu
  \]
**Extra: Minimum air requirement**

- Minimum air requirement:
  - Mass of air per mass of fuel in complete combustion

\[ \ell_{\text{min}} \]

- Relation between minimum oxygen and minimum air requirement:

\[ \ell_{\text{min}} = \frac{\alpha_{\text{min}}}{Y_{O_2,\text{luft}}}, \quad \ell_{\text{min},m} = \frac{\alpha_{\text{min},m}}{X_{O_2,\text{luft}}} \rightarrow \ell_{\text{min}} = \alpha_{\text{min}}, \quad \ell_{\text{min},m} = \alpha_{\text{min},m} \]

with:
- Mass fraction \( Y_{O_2,\text{luft}} = 0.232 \)
- Mole fraction \( X_{O_2,\text{luft}} = 0.21 \)

---

**The Equivalence Ratio**

- The equivalence ratio is the ratio of fuel to oxidizer ratio in the unburnt to that of a stoichiometric mixture

\[ \phi = \frac{Y_{F,\text{luft}}/Y_{O_2,\text{luft}}}{(Y_{F,\text{luft}}/Y_{O_2,\text{luft}})_s} = \nu Y_{F,\text{luft}} / Y_{O_2,\text{luft}} \]

- Can be written also in terms of
  - Fuel to air ratio
  - Mole fractions
  - Stoichiometric mass ratio \( \nu \) obtained from global reaction

---

**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
- Definitions, Equation of State, Mass Balance
- Elementary and Global Reactions
- Coupling Functions
- Stoichiometry
- Mixture Fraction
- Burke-Schumann Solution

---

**The Mixture Fraction**

- Equivalence ratio important parameter in combustion
- Mixture fraction quantifies local fuel-air ratio in non-premixed combustion

- Consider two separate feed streams of
  - Fuel
  - Oxidizer (air, pure oxygen)

- Streams mix and burn

- Fuel stream
  - Often consists of one component only
  - In general does not contain oxidizer
- Oxidizer stream
  - Generally does not contain fuel
The mixture fraction

In the following:
- Fuel stream: Subscript 1
- Oxidizer stream: Subscript 2

Definition mixture fraction
- Mass fraction of the fuel stream in the mixture:
  \[ z = \frac{m_1}{m_1 + m_2} \]
  where \( m_1 \) and \( m_2 \) are the local mass originating from the individual streams
- Mixture fraction always between zero and one
  - Fuel stream: \( Z = 1 \)
  - Oxidizer stream: \( Z = 0 \)

The mixture fraction

- Mass fraction of fuel in the fuel stream: \( Y_{B,1} \)
- Mass fraction of oxygen in the oxidizer stream: \( Y_{O_2,2} \)

Two-stream system before combustion:
- Divide \( m_{B,1} = Y_{B,1} m_1 \) for stream 1 by total mass
- Mixture fraction linear with fuel mass
  \[ Y_{B,a} = Y_{B,1} Z \]
  \[ Y_{O_2,a} = Y_{O_2,2} (1 - Z) \]
- Insert into coupling function:
  \[ z = \frac{\nu Y_B - Y_{O_2} + Y_{O_2,2}}{\nu Y_{B,1} + Y_{O_2,2}} \]

*Mixture fraction definition by Bilger*

- Consider elements C, H, O in combustion of a \( C_m H_n \) fuel with oxygen or air
  \[ \nu C_m H_n + \nu_{O_2} O_2 = \text{Products} \]
- Changes in elements
  \[ \frac{d n_C}{\nu F_{mW_C}} = \frac{d n_H}{\nu F_{mW_H}} = \frac{d n_O}{2 \nu W_{O_2}} \]
  or in terms of element mass fraction
  \[ \frac{d Z_C}{\nu F_{mW_C}} = \frac{d Z_H}{\nu F_{mW_H}} = \frac{d Z_O}{\nu W_{O_2}} \]
- Coupling function:
  \[ \beta = \frac{Z_C}{\nu F_{mW_C}} + \frac{Z_H}{\nu F_{mW_H}} - \frac{2 Z_O}{\nu W_{O_2}} \]
  \( \beta \) should not change by chemical reactions
**Mixture fraction definition by Bilger**

- Normalizing this such that $Z = 1$ in the fuel stream and $Z = 0$ in the oxidizer stream, one obtains Bilger's definition

$$Z = \frac{\beta - \beta_2}{\beta_1 - \beta_2}$$

or

$$Z = \frac{Z_T/(mW_T) + Z_{H_i}/(mW_{H_i}) + 2(Y_{O_2,u} - Z_T)/(Y_{O_2}/W_{O_2})}{Z_{C_i,1}/(mW_{C_i}) + Z_{H_i,1}/(mW_{H_i}) + 2Y_{O_2,u}/(Y_{O_2}/W_{O_2})}$$

- Because elements are conserved during combustion, element mass fractions calculated from

$$Z_j = \frac{m_j}{m} = \sum_{i=1}^k \frac{a_{ij}W_j}{W_i} Y_i = \frac{W_j}{W} \sum_{i=1}^k a_{ij}X_i, \quad j = 1, 2, \ldots, k_e,$$

do not change

---

**The equivalence ratio**

- This relation is also valid for multicomponent fuels (see exercise below)

- It illustrates that the mixture fraction is simply another expression for the local equivalence ratio

**Exercise:**

- The element mass fractions $Z_{H,F}, Z_{C,F}$ of a mixture of hydrocarbons and its mean molecular weight $W$ are assumed to be known

- Determine its stoichiometric mixture fraction in air

- Hint: $Z_{H,F} = nW_{H}/W$, $Z_{C,F} = mW_{C}/W$

---

**Relation of mixture fraction with equivalence ratio**

- Fuel-air equivalence ratio

$$\phi = \frac{Y_{F,u}/Y_{O_2,u}}{(Y_{F,u}/Y_{O_2,u})_{st}} = \frac{\nu Y_{F,u}}{Y_{O_2,u}}$$

- Introducing $Y_{F,u} = Y_{F,1}Z$ and $Y_{O_2,u} = Y_{O_2,2}(1 - Z)$

leads with

$$\frac{\nu Y_{F,1}}{Y_{O_2,2}} = \frac{1 - Z_{st}}{Z_{st}}$$

to a unique relation between the equivalence ratio and the mixture fraction

$$\phi = \frac{Z}{1 - Z} \frac{1 - Z_{st}}{Z_{st}}$$

---

**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

- Definitions, Equation of State, Mass Balance

- Elementary and Global Reactions

- Coupling Functions

- Stoichiometry

- Mixture Fraction

- Burke-Schumann Solution
**Burke-Schumann Solution**

- Diffusion Flame Structure at complete conversion
- Profiles of $Y_z$ and $Y_{O_2}$ in the unburnt gas

![Graph showing Burke-Schumann Solution](image)

**Diffusion Flame Structure at Complete Conversion**

- Stoichiometric composition
  
  $$Z_{st} = \frac{Y_{O_2,2}}{\nu Y_{F,1} + Y_{O_2,2}}$$

- If $Z < Z_{st}$, fuel is deficient $Y_{F,b} = \zeta$
  - Mixture is fuel lean
  - Combustion terminates when all fuel is consumed:
    (burnt gas, subscript $b$)
    $$Z = \frac{\nu Y_{F} - Y_{O_2} + Y_{O_2,2}}{\nu Y_{F,1} + Y_{O_2,2}}$$
    - Remaining oxygen mass fraction in the burnt gas is calculated from
    $$Y_{O_2,b} = Y_{O_2,2} (1 - \frac{Z}{Z_{st}}), \ Z \leq Z_{st}$$

**Diffusion Flame Structure at Complete Conversion**

- If $Z > Z_{st}$, oxygen is deficient
  - Mixture is fuel rich

- Combustion then terminates when all the oxygen is consumed: $Y_{O_2,b} = \zeta$

  Leading to
  $$Y_{F,b} = Y_{F,1} \frac{Z - Z_{st}}{1 - Z_{st}}, \ Z \geq Z_{st}$$

**Diffusion Flame Structure at Complete Conversion**

- For hydrocarbon fuel $C_nH_m$, the element mass fractions in the unburnt mixture are
  $$Z_C = \frac{W_C}{W_F} Y_{F,b}, \ Z_H = \frac{W_H}{W_F} Y_{F,b}, \ Z_O = Y_{O_2,b}$$

- For the burnt gas, these are for the hydrocarbon fuel considered above
  $$Z_C = \frac{W_C}{W_F} Y_{F,b} + \frac{W_C}{W_{CO_2}} Y_{CO_2,b}$$
  $$Z_H = \frac{W_H}{W_F} Y_{F,b} + 2 \frac{W_{H_2O}}{W_{CO_2}} Y_{H_2O,b}$$
  $$Z_O = \frac{W_O}{W_{O_2}} Y_{O_2,b} + 2 \frac{W_{CO_2}}{W_{CO_2}} Y_{CO_2,b} + \frac{W_O}{W_{H_2O}} Y_{H_2O,b}$$

- Elements are conserved, hence $Z_{st} = Z_b$
Diffusion Flame Structure at Complete Conversion

\[ Y_{F, a} = Y_{F, 1} Z \quad \text{and} \quad Y_{F, b} = 0 \quad \text{for} \quad Z \leq Z_{st} \]

and

\[ Z = \frac{\nu Y_F - Y_{O_2} + Y_{O_2, 2}}{\nu Y_{F, 1} + Y_{O_2, 2}} \quad Z \geq Z_{st} \]

to piecewise linear relations of the product mass fractions in terms of \( Z \):

- \( Z \leq Z_{st} \): \[ Y_{CO_2, h} = Y_{CO_2, h}' Z_{st} \quad Y_{H_2O, h} = Y_{H_2O, h}' Z_{st} \]
- \( Z \geq Z_{st} \): \[ Y_{CO_2, h} = Y_{CO_2, h}' Z_{st} + \frac{Z}{1 - Z_{st}} \quad Y_{H_2O, h} = Y_{H_2O, h}' \frac{1 - Z_{st}}{1 - Z} \]

where

\[ Y_{CO_2, h}' = Y_{F, 1} Z_{st} - m_{CO_2} \]

Profiles in the burning mixture

Burke-Schumann Solution:

- Infinitely fast, irreversible chemistry

Summary

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

- Definitions, Equation of State, Mass Balance
- Elementary and Global Reactions
- Coupling Functions
- Stoichiometry
- Mixture Fraction
- Burke-Schumann Solution
Thermodynamics, Flame Temperature and Equilibrium

Heinz Pitsch
Institut für Technische Verbrennung
RWTH Aachen University

Thermodynamic Quantities

First law of thermodynamics - balance between different forms of energy

- Change of specific internal energy: \( du \)
- Specific work due to volumetric changes: \( \delta w = -p\delta v \), \( v = 1/\rho \)
- Specific heat transfer from the surroundings: \( \delta q \)

- Related quantities
  - Specific enthalpy (general definition): \( h = u + pv \)
  - Specific enthalpy for an ideal gas: \( h = u + \frac{RT}{M} \)

  - Energy balance for a closed system:
    \[ du = \delta q + \delta w \]

Multicomponent system

- Specific internal energy and specific enthalpy of mixtures
  \[ u = \sum_{i=1}^{k} Y_i u_i, \quad h = \sum_{i=1}^{k} Y_i h_i \]

- Relation between internal energy and enthalpy of single species
  \[ h_i = u_i + \frac{RT}{M_i}, \quad i = 1, 2, \ldots, k \]
**Multicomponent system**

- Ideal gas
  
  \[ u \text{ and } h \text{ only function of temperature} \]
  
  \[ h_i(T) = u_i(T) + \frac{R T}{M_i} i = 1, 2, \ldots, k \]

- If \( c_p \) is specific heat at constant pressure and \( h_{\text{ref}} \) is reference enthalpy at reference temperature \( T_{\text{ref}} \), temperature dependence of partial specific enthalpy is given by
  
  \[ h_i = h_{\text{ref}} + \int_{T_{\text{ref}}}^{T} c_p \, dT, \quad i = 1, 2, \ldots, k \]

- Reference temperature may be arbitrarily chosen, most frequently used:
  
  \[ T_{\text{ref}} = 0 \text{ K or } T_{\text{ref}} = 298.15 \text{ K} \]

**Determination of Caloric Properties**

- Temperature dependence of molar enthalpy, molar entropy, and molar specific heat may be calculated from polynomials

- Reference enthalpies of \( \text{H}_2, \text{O}_2, \text{N}_2 \) and solid carbon \( \text{C}_s \) were chosen as zero, because they represent the chemical elements

  \[
  \begin{align*}
  \frac{c_p}{R} &= a_1 + a_2 \frac{T}{K} + a_3 \left( \frac{T}{K} \right)^2 + a_4 \left( \frac{T}{K} \right)^3 + a_5 \left( \frac{T}{K} \right)^4 \\
  \frac{h_m}{RT} &= a_1 + a_2 \frac{T}{K} + a_3 \left( \frac{T}{K} \right)^2 + a_4 \left( \frac{T}{K} \right)^3 + a_5 \left( \frac{T}{K} \right)^4 \frac{K}{T} + a_6 \\
  \frac{s_m}{R} &= a_1 \ln(T/K) + a_2 T/K + a_3 \left( \frac{T}{K} \right)^2 + a_4 \left( \frac{T}{K} \right)^3 \frac{K}{T} + a_5 \left( \frac{T}{K} \right)^4 \frac{K}{T} + a_7 \frac{R}{T}
  \end{align*}
  \]

- Constants \( a_j \) for each species \( i \) are listed in tables

**Multicomponent system**

- Partial molar enthalpy \( h_{i,m} \) is
  
  \[ h_{i,m} = M_i h_i \quad i = 1, 2, \ldots, k \]

  and its temperature dependence is
  
  \[ h_{i,m} = h_{i,m,\text{ref}} + \int_{T_{\text{ref}}}^{T} c_{p,i,m} \, dT \quad i = 1, 2, \ldots, k \]

  where the molar specific heat at constant pressure is
  
  \[ c_{p,i,m} = M_i c_{p,i} \quad i = 1, 2, \ldots, k \]

- In a multicomponent system, the specific specific heat at constant pressure of the mixture is
  
  \[ c_p = \sum_{i=1}^{n} Y_i c_{p,i} \quad c_{p,m} = \sum_{i=1}^{n} X_i c_{p,i,m} \]

**Determination of Caloric Properties**

- Temperature dependence of molar enthalpy, molar entropy, and molar specific heat may be calculated from polynomials

- Reference enthalpies of \( \text{H}_2, \text{O}_2, \text{N}_2 \) and solid carbon \( \text{C}_s \) were chosen as zero, because they represent the chemical elements

  \[
  \begin{align*}
  \frac{c_p}{R} &= a_1 + a_2 \frac{T}{K} + a_3 \left( \frac{T}{K} \right)^2 + a_4 \left( \frac{T}{K} \right)^3 + a_5 \left( \frac{T}{K} \right)^4 \\
  \frac{h_m}{RT} &= a_1 + a_2 \frac{T}{K} + a_3 \left( \frac{T}{K} \right)^2 + a_4 \left( \frac{T}{K} \right)^3 + a_5 \left( \frac{T}{K} \right)^4 \frac{K}{T} + a_6 \\
  \frac{s_m}{R} &= a_1 \ln(T/K) + a_2 T/K + a_3 \left( \frac{T}{K} \right)^2 + a_4 \left( \frac{T}{K} \right)^3 \frac{K}{T} + a_5 \left( \frac{T}{K} \right)^4 \frac{K}{T} + a_7 \frac{R}{T}
  \end{align*}
  \]

- Constants \( a_j \) for each species \( i \) are listed in tables

**Determination of Caloric Properties**

- Temperature dependence of molar enthalpy, molar entropy, and molar specific heat may be calculated from polynomials

- Reference enthalpies of \( \text{H}_2, \text{O}_2, \text{N}_2 \) and solid carbon \( \text{C}_s \) were chosen as zero, because they represent the chemical elements

  \[
  \begin{align*}
  \frac{c_p}{R} &= a_1 + a_2 \frac{T}{K} + a_3 \left( \frac{T}{K} \right)^2 + a_4 \left( \frac{T}{K} \right)^3 + a_5 \left( \frac{T}{K} \right)^4 \\
  \frac{h_m}{RT} &= a_1 + a_2 \frac{T}{K} + a_3 \left( \frac{T}{K} \right)^2 + a_4 \left( \frac{T}{K} \right)^3 + a_5 \left( \frac{T}{K} \right)^4 \frac{K}{T} + a_6 \\
  \frac{s_m}{R} &= a_1 \ln(T/K) + a_2 T/K + a_3 \left( \frac{T}{K} \right)^2 + a_4 \left( \frac{T}{K} \right)^3 \frac{K}{T} + a_5 \left( \frac{T}{K} \right)^4 \frac{K}{T} + a_7 \frac{R}{T}
  \end{align*}
  \]

- Constants \( a_j \) for each species \( i \) are listed in tables

**Determination of Caloric Properties**

- Temperature dependence of molar enthalpy, molar entropy, and molar specific heat may be calculated from polynomials

- Reference enthalpies of \( \text{H}_2, \text{O}_2, \text{N}_2 \) and solid carbon \( \text{C}_s \) were chosen as zero, because they represent the chemical elements

  \[
  \begin{align*}
  \frac{c_p}{R} &= a_1 + a_2 \frac{T}{K} + a_3 \left( \frac{T}{K} \right)^2 + a_4 \left( \frac{T}{K} \right)^3 + a_5 \left( \frac{T}{K} \right)^4 \\
  \frac{h_m}{RT} &= a_1 + a_2 \frac{T}{K} + a_3 \left( \frac{T}{K} \right)^2 + a_4 \left( \frac{T}{K} \right)^3 + a_5 \left( \frac{T}{K} \right)^4 \frac{K}{T} + a_6 \\
  \frac{s_m}{R} &= a_1 \ln(T/K) + a_2 T/K + a_3 \left( \frac{T}{K} \right)^2 + a_4 \left( \frac{T}{K} \right)^3 \frac{K}{T} + a_5 \left( \frac{T}{K} \right)^4 \frac{K}{T} + a_7 \frac{R}{T}
  \end{align*}
  \]

- Constants \( a_j \) for each species \( i \) are listed in tables

**Determination of Caloric Properties**

- Temperature dependence of molar enthalpy, molar entropy, and molar specific heat may be calculated from polynomials

- Reference enthalpies of \( \text{H}_2, \text{O}_2, \text{N}_2 \) and solid carbon \( \text{C}_s \) were chosen as zero, because they represent the chemical elements

  \[
  \begin{align*}
  \frac{c_p}{R} &= a_1 + a_2 \frac{T}{K} + a_3 \left( \frac{T}{K} \right)^2 + a_4 \left( \frac{T}{K} \right)^3 + a_5 \left( \frac{T}{K} \right)^4 \\
  \frac{h_m}{RT} &= a_1 + a_2 \frac{T}{K} + a_3 \left( \frac{T}{K} \right)^2 + a_4 \left( \frac{T}{K} \right)^3 + a_5 \left( \frac{T}{K} \right)^4 \frac{K}{T} + a_6 \\
  \frac{s_m}{R} &= a_1 \ln(T/K) + a_2 T/K + a_3 \left( \frac{T}{K} \right)^2 + a_4 \left( \frac{T}{K} \right)^3 \frac{K}{T} + a_5 \left( \frac{T}{K} \right)^4 \frac{K}{T} + a_7 \frac{R}{T}
  \end{align*}
  \]

- Constants \( a_j \) for each species \( i \) are listed in tables
Reaction Enthalpy

- First law of thermodynamics for a system at constant pressure \((dp = 0)\)
  
  - From first law follows
    \[ du = dq + dq \]
    \[ dh = du + vdp + pdv = dq + vdp = dq \]
  
  - Heat release during combustion \((dp = 0)\) given by reaction enthalpy:
    \[ \Delta h_m = \sum \nu_i h_i,m \]
  
  - Stoichiometric coefficients:
    - Example: \(\text{CO} + 3 \text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}\)
  
  - Reaction enthalpy:
    \[ \Delta h_m = h_{\text{CH}_4,m} + h_{\text{H}_2\text{O},m} - h_{\text{CO},m} - 3h_{\text{H}_2,m} \]

List of enthalpies of formation

<table>
<thead>
<tr>
<th>(i)</th>
<th>(M_i [\text{kg/kmol}])</th>
<th>(h_i,m,\text{ref} [\text{kJ/mol}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H(_2)</td>
<td>2.016</td>
</tr>
<tr>
<td>2</td>
<td>H(_2)O</td>
<td>18.016</td>
</tr>
<tr>
<td>3</td>
<td>H(_2)O</td>
<td>34.016</td>
</tr>
<tr>
<td>4</td>
<td>NO</td>
<td>30.008</td>
</tr>
<tr>
<td>5</td>
<td>NO(_2)</td>
<td>46.008</td>
</tr>
<tr>
<td>6</td>
<td>N(_2)</td>
<td>28.016</td>
</tr>
<tr>
<td>7</td>
<td>N(_2)O</td>
<td>44.016</td>
</tr>
<tr>
<td>8</td>
<td>O</td>
<td>16.000</td>
</tr>
<tr>
<td>9</td>
<td>O(_2)</td>
<td>32.000</td>
</tr>
<tr>
<td>10</td>
<td>O(_3)</td>
<td>48.000</td>
</tr>
</tbody>
</table>

Reference temperature: \(T_{\text{ref}} = 298, 15 \text{ K}\)

Reaction Enthalpy

- Assumption that reaction occurs at \(T = T_{\text{ref}}\), then
  \[ h_{i,m} = h_{i,m,\text{ref}} + \int_{T_{\text{ref}}}^{T} c_{p,i} dT = h_{i,m,\text{ref}} \quad i = 1,2, \ldots, k \]

- Example \(\text{CH}_4\): \(\text{C(s)} + 2\text{H}_2(g) = \text{CH}_4(g)\)
  \[ \Delta h_{\text{CH}_4,m} = h_{\text{CH}_4,m,\text{ref}} - h_{\text{C},m,\text{ref}} - 2h_{\text{H}_2,m,\text{ref}} = h_{\text{CH}_4,m,\text{ref}} \]

- Example \(\text{CO}_2\): \(\text{C(s)} + \frac{1}{2}\text{O}_2(g) = \text{CO}_2(g)\)
  \[ \Delta h_{\text{CO}_2,m} = h_{\text{CO}_2,m,\text{ref}} \]

- Example \(\text{H}_2\text{O}\): \(\frac{1}{2}\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) = \text{H}_2\text{O}(g)\)
  \[ \Delta h_{\text{H}_2\text{O},m} = h_{\text{H}_2\text{O},m,\text{ref}} \]

- \(h_{i,m,\text{ref}}\) is the chemical energy of a species with respect to \(\text{H}_2(g), \text{O}_2(g), \text{N}_2(g), \text{C(s)}\)

Classification of reactions:
- Exothermic reaction: \(\Delta h_m < 0\)
- Endothermic reaction: \(\Delta h_m > 0\)

Lower heating value (LHV)

\[ \text{LHV} = \frac{-\Delta h_m}{M_{\text{fuel}}} \]

Higher heating value (HHV)

\[ \text{HHV} = \frac{-\Delta h_m}{M_{\text{fuel}}} + \frac{M_{\text{H}_2\text{O}}}{2M_{\text{fuel}}} \cdot Z_{\text{fuel}} \cdot R = \frac{-\Delta h_m}{M_{\text{fuel}}} + 8.937 \cdot Z_{\text{fuel}} \cdot R \cdot 2442 \text{ kJ/kg} \]

- For \(\text{CH}_4\): HHV is ~10% larger than LHV
Example: Condensing Boiler

Floor standing condensing boilers

The GB312 is available in the following kW outputs:
- 90kW
- 120kW
- 160kW
- 200kW
- 240kW
- 280kW

Quick links
> Contact us
> Sales Managers
> CAD drawings
> Manuals
> Enquiry form
> Discontinued product

Enhanced Capital Allowance (ECA)

Servicing and maintenance
The GB312 is designed to make servicing and maintenance as straightforward as possible. All parts can be accessed from the front and the burners can be accessed without having to disturb the gas connection. The boiler is equipped with SAFe digital ignition technology and a Buderus Energy Management System (EMS).

Performance and design
The GB312 is a high performance, compact condensing boiler which provides an efficiency of up to 108% (NVC). It can be fitted individually or as part of a 2 boiler cascade kit and is especially well suited to medium-large buildings and office blocks.

For a powerful floor standing condensing boiler it is very compact, lightweight and easy to install. The boiler is whisper quiet, even when running at full output.

Features
- Controls
- Key technologies

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

Flame Temperature at Complete Conversion

- First law of thermodynamics for an adiabatic system at constant pressure (dq = 0, dp = 0) with only reversible work (dw = -pdv)

- From first law $du = dq + dw = -pdv$

  with $dh = du + pdv + vdp$

  follows $dh = C$

- Integrated from the unburnt $(u)$ to burnt $(b)$ gives $h_u = h_l$

  or $\sum_{i=1}^{k} Y_{i,u} h_{i,u} = \sum_{i=1}^{k} Y_{i,b} h_{i,b}$

- With $\sum_{i=1}^{k} Y_{i,u} h_{i,u} = \sum_{i=1}^{k} Y_{i,b} h_{i,b}$

  and

  $h_i = h_{i,ref} + \int_{T_{ref}}^{T} \epsilon_{i,u} \omega \, dT$

  follows

  $\sum_{i=1}^{k} (Y_{i,u} - Y_{i,b}) h_{i,ref} = \int_{T_{ref}}^{T_b} \epsilon_{i,bu} \omega \, dT$

  - Specific heats to be calculated with the mass fractions of the burnt and unburnt gases

    $\epsilon_{i,b} = \sum_{i=1}^{k} Y_{i,b} \epsilon_{i,bu}(T)$, $\epsilon_{i,u} = \sum_{i=1}^{k} Y_{i,u} \epsilon_{i,bu}(T)$.
Flame Temperature at Complete Conversion

- For a one-step global reaction, the left hand side of
  \[ \sum_{i=1}^{k} (Y_{a,i} - Y_{b,i})h_{i,ref} = \int_{T_{ref}}^{T_f} c_p \partial T - \int_{T_{ref}}^{T_f} c_p \partial T \]

may be calculated by integrating coupling function

\[ \frac{dY}{\nu_i M_i} = \frac{dY}{\nu_1 M_1} \quad (i = 1, 2, \ldots, n) \]

which gives

\[ Y_{a,i} - Y_{b,i} = (Y_{a,i} - Y_{b,i}) \frac{\nu_i M_i}{\nu_1 M_1} \quad i = 1, 2, \ldots, k. \]

and finally

\[ \sum_{i=1}^{k} (Y_{a,i} - Y_{b,i})h_{i,ref} = \frac{(Y_{a,i} - Y_{b,i})}{\nu_i M_i} \sum_{i=1}^{k} \nu_i M_i h_{i,ref} \]

\[ / \times h_{i,ref} / \]

Flame Temperature at Complete Conversion

- Definition: Heat of combustion

\[ Q = - \sum_{i=1}^{k} \nu_i M_i h_i = - \sum_{i=1}^{k} \nu_i h_{i,m} \]

Heat of combustion changes very little with temperature

- Often set to:

\[ Q_{ref} = - \sum_{i=1}^{k} \nu_i h_{i,m,ref} \]

- Simplification: \( T_0 = T_{ref} \) and assume \( c_{p,b} \) approximately constant

  - For combustion in air, nitrogen is dominant in calculating \( c_{p,b} \)
  - Value of \( c_{p,b} \) somewhat larger for \( CO_2 \); somewhat smaller for \( O_2 \), while that for \( H_2O \) is twice as large

- Approximation for specific heat of burnt gas for lean and stoichiometric mixtures \( c_p = 1.40 \text{ kJ/kg/K} \)

Flame Temperature at Complete Conversion

- For a rich mixture

\[ Y_{a,i} - Y_{b,i} = (Y_{a,i} - Y_{b,i}) \frac{\nu_i M_i}{\nu_F M_F} \quad i = 1, 2, \ldots, k. \]

should be replaced by

\[ Y_{a,i} - Y_{b,i} = (Y_{a,i} - Y_{b,i}) \frac{\nu_i M_i}{\nu_F M_F} \quad i = 1, 2, \ldots, k. \]

- One obtains similarly for complete consumption of the oxygen \( (Y_{O_2,b} = 0) \)

\[ T_b - T_a = \frac{Q_{ref} Y_{O_2,b}}{c_p \nu_F M_F} \]

\[ \rightarrow \text{Coupling function between fuel mass fraction and temperature!} \]

- With \( \nu_i = \nu_1 \) follows

\[ T_b - T_a = \frac{Q_{ref} Y_{O_2,b}}{c_p \nu_F M_F} \]
Flame Temperature at Complete Conversion

- Flame Temperature for stoichiometric CH$_4$/air combustion at $T_u = 298$ K:
  
  \[ C_H_4 + 2O_2 = CO_2 + 2H_2O \]

  \[ Q_{ref} = -(h_{CO_2,m} + 2h_{H_2O,m} - h_{C_H_4,m}) = 802.3 \text{ kJ/kg} \]

- Further Quantities:
  \[ Y_{F,u} = 0.0548 \quad c_p = 1.4 \text{ kJ/kg} \quad M_F = 0.016 \text{ kg/mol} \]

- Flame Temperature
  \[ T_b - T_u = \frac{Q_{ref}Y_{F,u}}{c_pM_F} \quad T_b = 2261K \]

- Determination of flame temperature from detailed thermodata models (no assumption for $c_p$)
  \[ T_b = 2225K \quad \Delta T_b = 36K \]

Flame Temperature at Complete Conversion

- Equations
  \[ T_b - T_u = \frac{Q_{ref}Y_{F,u}}{c_pM_F} \quad \text{and} \quad T_b - T_u = \frac{Q_{ref}Y_{O_2,u}}{c_pM_F} \]

  may be expressed in terms of the mixture fraction

- Introducing
  \[ Y_{F,u} = Y_{F,Z} \quad \text{and} \quad Y_{O_2,u} = Y_{O_2,Z}(1 - Z) \]

  and specifying the temperature of the unburnt mixture by

  \[ T_u(Z) = T_2 - Z(T_2 - T_1) \]

  where

  - $T_2$ is the temperature of the oxidizer stream and $T_1$ that of the fuel stream
  - $c_p$ assumed to be constant

Burke-Schumann Solution: Infinitely fast, irreversible one-step chemistry
**Flame Temperature at Complete Conversion**

- Table shows values for combustion of pure fuels ($Y_{f1} = 1$) in air ($Y_{O2,2} = 0.232$) with $T_{uo} = 300$ K and $C_p = 1.4$ kJ/kg/K
  - stoichiometric mixture fraction
  - stoichiometric flame temperatures for some hydrocarbon-air mixtures

<table>
<thead>
<tr>
<th>Fuel</th>
<th>$Z_{st}$</th>
<th>$T_{st}$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>0.05496</td>
<td>2263.3</td>
</tr>
<tr>
<td>C2H6</td>
<td>0.05864</td>
<td>2288.8</td>
</tr>
<tr>
<td>C2H4</td>
<td>0.06349</td>
<td>2438.5</td>
</tr>
<tr>
<td>C2H2</td>
<td>0.07021</td>
<td>2686.7</td>
</tr>
<tr>
<td>C3H0</td>
<td>0.06010</td>
<td>2289.7</td>
</tr>
</tbody>
</table>

**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

- Thermodynamic quantities
- Flame temperature at complete conversion
- Chemical equilibrium

**Chemical Equilibrium**

- Assumption of complete combustion is approximation, because it disregards the possibility of dissociation of combustion products
- More general formulation is assumption of chemical equilibrium
  - Complete combustion then represents limit of infinitely large equilibrium constant (see below)
- Chemical equilibrium and complete combustion are valid in the limit of infinitely fast reaction rates only, which is often invalid in combustion systems

Importance of kinetics!
Entropy and Molar Entropy

- Partial molar entropy $s_{i,m}$ of chemical species in a mixture of ideal gases depends on partial pressure

$$s_{i,m} = s_{i,m}^0 - R \ln \frac{P_i}{P_0} \quad i = 1, 2, \ldots, k$$

where $p_0 = 1$ atm and

$$s_{i,m}^0 = s_{i,m,ref}^0 + \int_{T_{ref}}^{T} \frac{\rho_{i,m}}{T} dT \quad i = 1, 2, \ldots, k$$

depends only on temperature.

- Values for the reference entropy $s_{i,m,ref}$ are listed in tables.

Entropy and Chemical Potential

Gibbs Free Energy

- Gibbs Free Energy:

$$G = H - TS$$

Part of energy that can be converted to work.

- For mixtures with molar Gibbs Free Energy $g_{i,m}$

$$G = \sum_{i=1}^{n} n_i g_{i,m}$$

- Equilibrium, when Gibbs Free Energy reaches minimum, i.e. $dG = 0$

- Gibbs equation for $G = G(p, T, n_i)$

$$dG = V dp - SdT + \sum_{i=1}^{n} n_i d\mu_i$$

Chemical Potential and Partial Molar Gibbs Free Energy

- From Gibbs equation

$$dG = V dp - SdT + \sum_{i=1}^{n} \mu_i dn_i$$

and total differential of $G = G(p, T, n_i)$

$$dG = \left. \frac{\partial G}{\partial p} \right|_{T, \{n_i\}} dp + \left. \frac{\partial G}{\partial T} \right|_{p, \{n_i\}} dT + \sum_{i=1}^{n} \left. \frac{\partial G}{\partial n_i} \right|_{T, \{n_{i, \neq i}\}} dn_i$$

follows

$$\left. \frac{\partial G}{\partial n_i} \right|_{T, \{n_{i, \neq i}\}} = \mu_i$$

- Since

$$G = \sum_{i=1}^{n} n_i \mu_i$$

Chemical potential is equal to partial molar Gibbs free energy.

Chemical Potential and the Law of Mass Action

- Chemical potential

$$\mu_i = h_{i,m} - Ts_{i,m} = \mu_i^0(T) + RT \ln \frac{P_i}{P_0} \quad i = 1, 2, \ldots, k$$

where

$$\mu_i^0 = h_{i,m,ref} - T s_{i,m,ref} + \int_{T_{ref}}^{T} \frac{\rho_{i,m}}{T} dT - \int_{T_{ref}}^{T} \frac{\rho_{i,m,ref}}{T} dT \quad i = 1, 2, \ldots, k$$

is chemical potential at 1 atm.

- Chemical equilibrium: From $dG = 0$

$$\sum_{i=1}^{n} n_i \mu_i = \sum_{i=1}^{n} n_i \frac{dn_i}{n_i} = 0$$

- With coupling function, $dn_i/n_i$ same for all species

$$\frac{dn_i}{n_i} \sum_{i=1}^{n} n_i \mu_i = 0 \quad \Rightarrow \quad \sum_{i=1}^{k} \nu_i \mu_i = 0, \quad i = 1, 2, \ldots, r.$$
Chemical Potential and the Law of Mass Action

- Using \( \mu_i = \mu_{i,m} - T s_{i,m} = \mu_i^0(T) + RT \ln \frac{P_i}{P_0} \) \( i = 1, 2, \ldots, k \),
in
  \[
  \sum_{i=1}^{k} \nu_i \mu_i = 0, \quad i = 1, 2, \ldots, r
  \]
leads to

  \[
  - \sum_{i=1}^{k} \nu_i \mu_i^0 = RT \ln \sum_{i=1}^{k} \left( \frac{P_i}{P_0} \right)^{\nu_i}, \quad i = 1, 2, \ldots, r.
  \]

- Defining the equilibrium constant \( K_p \) by

  \[
  RT \ln K_p = - \sum_{i=1}^{k} \nu_i \mu_i^0, \quad i = 1, 2, \ldots, r
  \]
leads to

  \[
  \prod_{i=1}^{k} \left( \frac{P_i}{P_0} \right)^{\nu_i} = K_p(T), \quad i = 1, 2, \ldots, r.
  \]

Composition

\[ \rightarrow \] Depends only on thermodynamics, not on composition

Chemical potential and the Law of Mass Action

- Law of mass action using \( K_p \)

  \[
  \prod_{i=1}^{k} \left( \frac{P_i}{P_0} \right)^{\nu_i} = K_p(T), \quad i = 1, 2, \ldots, r.
  \]

- With the ideal gas law \( p_i = C_i RT \)

  follows

  \[
  \prod_{i=1}^{k} C_i^{\nu_i} \left( \frac{RT}{P_0} \right)^{\sum_{i=1}^{k} \nu_i} = K_p(T)
  \]

- Law of mass action using \( K_C \)

  \[
  \prod_{i=1}^{k} C_i^{\nu_i} = \frac{K_p(T)}{\left( \frac{RT}{P_0} \right)^{\sum_{i=1}^{k} \nu_i}} = K_C(T).
  \]

Chemical potential and the Law of Mass Action

- The law of mass action

  \[
  \prod_{i=1}^{r} \left( \frac{P_i}{P_0} \right)^{\nu_i} = K_p(T), \quad i = 1, 2, \ldots, r.
  \]

\( \rightarrow \) \( K_p \) only depends on temperature

- Examples:
  1. \( A + B = C + D \)

\[
K_p(T) = \frac{P_C \cdot P_D}{P_A \cdot P_B} = \frac{X_C \cdot X_D}{X_A \cdot X_B}
\]

\( \rightarrow \) \( K_p \) determines composition as a function of temperature: \( \{X_i\} = f(T) \)

  2. \( A + B = C \)

\[
K_p(T) = \frac{P_C}{P_A \cdot P_B} = \frac{X_C}{X_A \cdot X_B}
\]

\( \rightarrow \) \( K_p \) determines composition as a function of temperature and pressure: \( \{X_i\} = f(T, p) \)

Chemical potential and the Law of Mass Action

- Equilibrium for elementary reaction: \( \nu_A A + \nu_B B = \nu_C C + \nu_D D \)

\[
K_C(T) = \frac{C_C^{\nu_C}}{C_A^{\nu_A} C_B^{\nu_B}}
\]

\( \rightarrow \) \( K_C \) only depends on temperature

- Rate of change

\[
\frac{dC_A}{dt} = \nu_A (k_f(C_A^{\nu_A} C_B^{\nu_B} - k_r(C_C^{\nu_C} C_D^{\nu_D})) = 0
\]

\[
(k_f(C_A^{\nu_A} C_B^{\nu_B}))_{eq} = (k_r(C_C^{\nu_C} C_D^{\nu_D}))_{eq}
\]

- For rate coefficients follows

\[
\frac{k_f(T)}{k_r(T)} = K_C(T) \quad \text{with} \quad K_C(T) = \frac{C_C^{\nu_C} C_D^{\nu_D}}{C_A^{\nu_A} C_B^{\nu_B}} \quad \text{and} \quad K_C(T) = K_C(T) \cdot \left( \frac{P_0}{RT} \right)^{\nu_i}
\]

\( \rightarrow \) Equilibrium constant determines ratio of forward and reverse rate

This is usually used to determine reverse from forward rate
### Chemical potential and the law of mass action

- Equilibrium constants for three reactions:

\[
\begin{align*}
K_{pk}(T) &= \exp \left( -\frac{\sum \nu_i \mu_i^\theta}{RT} \right) \\

\text{With:} \\
\mu_i^\theta &= \frac{h_{m,ref}^\theta}{RT} - \frac{S_{m,ref}^\theta}{R} + \int c_{p,i}dT + \int \frac{C_{p,i}}{R}dT
\end{align*}
\]

It follows for constant \( c_{p,i} \):

\[
K_i(T) = \exp \left( -\frac{\sum \nu_i h_{m,ref}^\theta}{RT} \right) \exp \left( \sum \nu_i S_{m,ref}^\theta/R \right) \exp \left( \sum \frac{\nu_i C_{p,i}}{K} \ln T \right)
\]

#### Approximation for Equilibrium Constants

- Approximation:

\[
K_p(T) = B_p T^m \exp \left( -\frac{\Delta h_{m,ref}}{RT} \right)
\]

#### Approximation of Equilibrium Constants

- Approximate calculation of equilibrium constants \( K_{pk}(T) \) from the chemical potentials with:
  - Enthalpies of formation
  - Entropies of formation
  - Specific heats

- Approximation
  - Neglect temperature dependence of specific heats

**With**

- \( B_p = \exp \left( \sum \nu_i \sigma_i \right) \)
- \( n_p = \sum \nu_i \tau_i \)
- \( \Delta h_{m,ref} = \sum \nu_i h_{m,ref} \)
- \( K_p = B_p T^m \exp \left( -\frac{\Delta h_{m,ref}}{RT} \right) \)
### Properties for gases at $T_{\text{ref}} = 298.15$ K

<table>
<thead>
<tr>
<th></th>
<th>$M_i$ [kg/kmol]</th>
<th>$h_{\text{c,i,ref}}$ [kJ/mol]</th>
<th>$s_{\text{c,i,ref}}$ [kJ/mol K]</th>
<th>$\gamma_A$</th>
<th>$\gamma_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>1,008</td>
<td>217,986</td>
<td>114,470</td>
<td>-1.2261</td>
</tr>
<tr>
<td>2</td>
<td>HNO</td>
<td>31,016</td>
<td>99,579</td>
<td>220,438</td>
<td>-1.0110</td>
</tr>
<tr>
<td>3</td>
<td>OH</td>
<td>17,008</td>
<td>39,463</td>
<td>183,367</td>
<td>3,3965</td>
</tr>
<tr>
<td>4</td>
<td>HO$_2$</td>
<td>33,008</td>
<td>20,920</td>
<td>227,358</td>
<td>-1,510</td>
</tr>
<tr>
<td>5</td>
<td>H$_2$</td>
<td>2,016</td>
<td>0,000</td>
<td>130,423</td>
<td>-2,4889</td>
</tr>
<tr>
<td>6</td>
<td>H$_2$O</td>
<td>18,016</td>
<td>-241,826</td>
<td>188,493</td>
<td>-1,6437</td>
</tr>
<tr>
<td>7</td>
<td>H$_2$O$_2$</td>
<td>34,016</td>
<td>-136,105</td>
<td>233,178</td>
<td>-8,4782</td>
</tr>
<tr>
<td>8</td>
<td>N</td>
<td>14,008</td>
<td>472,645</td>
<td>153,054</td>
<td>5,8661</td>
</tr>
<tr>
<td>9</td>
<td>NO</td>
<td>30,008</td>
<td>90,290</td>
<td>210,442</td>
<td>5,3476</td>
</tr>
<tr>
<td>10</td>
<td>NO$_2$</td>
<td>46,008</td>
<td>33,095</td>
<td>239,785</td>
<td>-1,1988</td>
</tr>
<tr>
<td>11</td>
<td>N$_2$</td>
<td>28,016</td>
<td>0,000</td>
<td>191,300</td>
<td>3,6670</td>
</tr>
<tr>
<td>12</td>
<td>N$_2$O</td>
<td>44,016</td>
<td>82,048</td>
<td>219,777</td>
<td>-5,3523</td>
</tr>
</tbody>
</table>

### Properties for gases at $T_{\text{ref}} = 298.15$ K

<table>
<thead>
<tr>
<th></th>
<th>$M_i$ [kg/kmol]</th>
<th>$h_{\text{c,i,ref}}$ [kJ/mol]</th>
<th>$s_{\text{c,i,ref}}$ [kJ/mol K]</th>
<th>$\gamma_A$</th>
<th>$\gamma_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>O</td>
<td>16,000</td>
<td>249,194</td>
<td>160,728</td>
<td>6,8561</td>
</tr>
<tr>
<td>14</td>
<td>O$_2$</td>
<td>32,000</td>
<td>0,000</td>
<td>204,848</td>
<td>4,1730</td>
</tr>
<tr>
<td>15</td>
<td>O$_3$</td>
<td>48,000</td>
<td>142,674</td>
<td>238,216</td>
<td>-3,3620</td>
</tr>
<tr>
<td>16</td>
<td>NH</td>
<td>15,016</td>
<td>331,372</td>
<td>180,949</td>
<td>3,0865</td>
</tr>
<tr>
<td>17</td>
<td>NH$_2$</td>
<td>16,024</td>
<td>168,615</td>
<td>188,522</td>
<td>-1,9835</td>
</tr>
<tr>
<td>18</td>
<td>NH$_2$O</td>
<td>17,032</td>
<td>-46,191</td>
<td>192,137</td>
<td>-8,2828</td>
</tr>
<tr>
<td>19</td>
<td>N$_2$H$_4$</td>
<td>30,032</td>
<td>212,965</td>
<td>218,362</td>
<td>-8,9795</td>
</tr>
<tr>
<td>20</td>
<td>N$_2$H$_3$</td>
<td>31,040</td>
<td>153,971</td>
<td>228,513</td>
<td>-17,5062</td>
</tr>
<tr>
<td>21</td>
<td>N$_2$H$_4$</td>
<td>32,048</td>
<td>95,186</td>
<td>236,651</td>
<td>-25,3189</td>
</tr>
<tr>
<td>22</td>
<td>C</td>
<td>12,011</td>
<td>715,003</td>
<td>157,853</td>
<td>6,4461</td>
</tr>
<tr>
<td>23</td>
<td>CH</td>
<td>13,019</td>
<td>594,128</td>
<td>182,723</td>
<td>2,4421</td>
</tr>
<tr>
<td>24</td>
<td>HCN</td>
<td>27,027</td>
<td>130,540</td>
<td>201,631</td>
<td>-5,3642</td>
</tr>
</tbody>
</table>
Properties for gases at $T_{ref} = 298.15$ K

<table>
<thead>
<tr>
<th>$M_i$ [kg/kmol]</th>
<th>$h_{i,ref}$ [kJ/mol]</th>
<th>$s_{i,ref}$ [kJ/mol K]</th>
<th>$\pi_A$</th>
<th>$\pi_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>49 $\text{C}<em>4\text{H}</em>{10}$</td>
<td>58,124</td>
<td>-134,516</td>
<td>304,850</td>
<td>-86,8641</td>
</tr>
<tr>
<td>50 $\text{C}<em>5\text{H}</em>{12}$</td>
<td>70,135</td>
<td>-35,941</td>
<td>325,281</td>
<td>-96,9383</td>
</tr>
<tr>
<td>51 $\text{C}<em>6\text{H}</em>{12}$</td>
<td>72,151</td>
<td>-160,247</td>
<td>332,858</td>
<td>-110,1702</td>
</tr>
<tr>
<td>52 $\text{C}<em>7\text{H}</em>{12}$</td>
<td>84,152</td>
<td>-59,622</td>
<td>350,087</td>
<td>-123,2381</td>
</tr>
<tr>
<td>53 $\text{C}<em>8\text{H}</em>{14}$</td>
<td>86,178</td>
<td>-185,560</td>
<td>380,497</td>
<td>-137,3228</td>
</tr>
<tr>
<td>54 $\text{C}<em>9\text{H}</em>{14}$</td>
<td>98,189</td>
<td>-72,132</td>
<td>389,217</td>
<td>-147,4583</td>
</tr>
<tr>
<td>55 $\text{C}<em>{10}\text{H}</em>{16}$</td>
<td>100,205</td>
<td>-197,652</td>
<td>404,773</td>
<td>-162,6188</td>
</tr>
<tr>
<td>56 $\text{C}<em>{11}\text{H}</em>{16}$</td>
<td>112,216</td>
<td>-135,821</td>
<td>418,705</td>
<td>-173,7077</td>
</tr>
<tr>
<td>57 $\text{C}<em>{12}\text{H}</em>{16}$</td>
<td>114,232</td>
<td>-223,676</td>
<td>430,826</td>
<td>-191,8158</td>
</tr>
<tr>
<td>58 $\text{C}_2\text{H}_2\text{O}$</td>
<td>44,054</td>
<td>-51,003</td>
<td>243,044</td>
<td>-34,3705</td>
</tr>
<tr>
<td>59 $\text{HNO}_3$</td>
<td>63,016</td>
<td>-134,306</td>
<td>266,425</td>
<td>-19,5553</td>
</tr>
<tr>
<td>60 He</td>
<td>4,003</td>
<td>0,000</td>
<td>125,800</td>
<td></td>
</tr>
</tbody>
</table>

*Example 1: Equilibrium Calculation of the NO-air system

- Calculation of the equilibrium concentration [ppm] of NO in air
  - Temperatures up to 1500 K
  - $p = p_0 = 1$ atm

- Global reaction:
  $$\text{N}_2 + \text{O}_2 = 2\text{NO}$$

<table>
<thead>
<tr>
<th>$\pi_A$</th>
<th>$\pi_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N}_2$</td>
<td>3,6670</td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>4,1730</td>
</tr>
<tr>
<td>NO</td>
<td>5,3476</td>
</tr>
</tbody>
</table>

Law of mass action:

$$K_p(T) = 17,38 \exp\left(-\frac{21719}{T/K}\right)$$

- Assumption: $X_{O_2} = 0.21$, $X_{N_2} = 0.79$ (air) unchanged

$$v_{NO}^2 = p_{N_2}p_{O_2}K_p(T) = p^2X_{N_2}X_{O_2}K_p(T)$$

$$X_{NO} = \frac{p_{NO}}{p} = 1.7(T/K)^{0.0124}\exp\left(-\frac{10860}{(T/K)}\right)$$
**Example 2: Equilibrium Calculation of the H₂-air system**

Using the law of mass action one obtains for the reaction \( 2 \text{H}_2 + \text{O}_2 = 2 \text{H}_2\text{O} \)
the relation between partial pressures

\[
\rho_{\text{H}_2\text{O}}^2 \rho_{\text{O}_2} = \rho_{\text{H}_2}^2 \rho_{\text{O}_2}
\]

was approximated using

\[
K_{pl} = 0.0835 T^{-1.3565} \exp(58171/T)
\]

and the values for

\[
K_{pl} = B_{pl} T^{\gamma_i} \exp \left( \frac{Q_i}{RT} \right), \quad i = 1, 2, \ldots, r.
\]

from the Janaf-Table

\[
B_{pl} = \exp \left( \sum_{i=1}^{3} \nu_{pl} \Gamma_i \right), \quad \nu_{pl} = \sum_{i=1}^{3} \nu_{pl,i}, \quad i = 1, 2, \ldots, r.
\]

**Result: Equilibrium Calculation of the NO-air system**

**Result:**

\[
X_{NO} = \frac{p_{NO}}{p} = 1.7(T/K)^{0.0124} \exp \left( -\frac{10860}{T/K} \right)
\]

<table>
<thead>
<tr>
<th>( T ) [K]</th>
<th>( X_{NO} )</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>3.52 \cdot 10^{-16}</td>
<td>3.52 \cdot 10^{-10}</td>
</tr>
<tr>
<td>600</td>
<td>2.55 \cdot 10^{-8}</td>
<td>2.55 \cdot 10^{-2}</td>
</tr>
<tr>
<td>1000</td>
<td>3.57 \cdot 10^{-5}</td>
<td>35.7</td>
</tr>
<tr>
<td>1500</td>
<td>1.22 \cdot 10^{-3}</td>
<td>1220</td>
</tr>
</tbody>
</table>

1 ppv = \( 10^{-6} \) parts per million (volume fraction)

\[
Y_i = \frac{M_{NO}}{M_i} X_i = \frac{28}{28.8} X_i \approx X_i
\]

\[X_{NO} = 1.7 \; T^{0.0124} \exp(-10860/T)\]

**Result: Equilibrium Calculation of the NO-air system**

**Mole fraction of NO in equilibrium:**

- Equilibrium values for \( T = 2000 \) K and \( T = 400 \) K differ by 10 orders of magnitude
- High temperatures during combustion lead to high NO-concentration
- NO is retained to a large extent if gas is cooled down rapidly

**Example 2: Equilibrium Calculation of the H₂-air system**

Introducing the definition

\[
\Gamma_i = \frac{Y_i}{M_i}, \quad i = 1, 2, \ldots, k
\]

the partial pressures

\[
p_i = p X_i, \quad i = 1, 2, \ldots, k
\]

are written with as

\[
p_i = p X_i = p M_i Y_i = p M \Gamma_i, \quad i = 1, 2, \ldots, k
\]

where the mean molecular weight is

\[M = (\Gamma_{\text{H}_2} + \Gamma_{\text{O}_2} + \Gamma_{\text{H}_2\text{O}} + \Gamma_{\text{H}_2})^{-1}\]
**Example 2: Equilibrium Calculation of the H₂-air system**

- The element mass fractions of the unburnt mixture are

\[ Z_H = Y_{H_2} z, \quad Z_O = Y_{O_2} (1-z), \quad Z_H = Y_{H_2O} (1-z) \]

- These are equal to those in the equilibrium gas where

\[ \frac{Z_H}{M_H} = 2\Gamma_{H_2O,b} + 2\Gamma_{H_2O,A} \]
\[ \frac{Z_O}{M_O} = 2\Gamma_{O_2,b} + \Gamma_{H_2O,A} \]

while \( Z_u \) remains unchanged.

**Example 2: Equilibrium Calculation of the H₂-air system**

- These equations lead to the following nonlinear equation for \( \Gamma_{H_2O,b} \)

\[
f(\Gamma_{H_2O,b}) = (\Gamma_{H_2O,b} - \frac{Z_H}{2M_H})^2 \left( \frac{Z_O}{M_O} - \Gamma_{H_2O,b} \right) - \Gamma_{H_2O,b}^2 \left( \frac{Z_H}{M_H} + \frac{Z_O}{M_O} + 2\Gamma_N - \Gamma_{H_2O,b} \right) = 0
\]

**Example 2: Equilibrium Calculation of the H₂-air system**

- Equation has one root between \( \Gamma_{H_2O,b} = 0 \) and the maximum values

\( \Gamma_{H_2O,b} = \frac{Z_H}{2M_H} \) and \( \Gamma_{H_2O,b} = \frac{Z_O}{M_O} \)

which correspond to complete combustion for lean and rich conditions in the limit

\( \Gamma_{p1} \rightarrow \infty \)

- The solution, which is a function of the temperature, may be found by successively bracketing the solution within this range

- The temperature is then calculated by employing a Newton iteration on

\[ h_u = h_i \]

leading to

\[ f_x(T) = h_u - \sum_{i=1}^{k} Y_{i,b} h_{i,ref} - \int_{T_{ref}}^{T} C_x(T) \]
Result: Equilibrium Calculation of the H₂-air system

- Equilibrium mass fractions of H₂, O₂, and H₂O for p = 1 bar and p = 10 bar and different temperatures

\[ 2 \text{H}_2 + \text{O}_2 = 2 \text{H}_2\text{O} \]

<table>
<thead>
<tr>
<th>T [K]</th>
<th>p [bar]</th>
<th>Y_H₂</th>
<th>Y_O₂</th>
<th>Y_H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>1</td>
<td>0.0096</td>
<td>0.0049</td>
<td>0.9945</td>
</tr>
<tr>
<td>3000</td>
<td>1</td>
<td>0.0112</td>
<td>0.1364</td>
<td>0.8484</td>
</tr>
<tr>
<td>4000</td>
<td>1</td>
<td>0.0653</td>
<td>0.5180</td>
<td>0.4167</td>
</tr>
<tr>
<td>2000</td>
<td>10</td>
<td>0.0002</td>
<td>0.0022</td>
<td>0.9974</td>
</tr>
<tr>
<td>3000</td>
<td>10</td>
<td>0.0084</td>
<td>0.0664</td>
<td>0.9252</td>
</tr>
<tr>
<td>4000</td>
<td>10</td>
<td>0.0394</td>
<td>0.3127</td>
<td>0.6478</td>
</tr>
</tbody>
</table>

- \( T \uparrow \rightarrow Y_{\text{H}_2\text{O}} \)
- \( p \uparrow \rightarrow Y_{\text{H}_2\text{O}} \)

Conclusion: Pressure and temperature dependency of the equilibrium constant

- Temperature dependence

\[ K_p = H_p T^v \exp \left( \frac{-\Delta h_{\text{m.ref}}}{RT} \right) \]

- Exothermic reactions: \( \Delta h_{\text{m.ref}} < 0 \rightarrow \frac{dK_p}{dT} < 0 \)
- Equilibrium is shifted towards educts with increasing temperature

- Pressure dependence

\[ \prod_{i=1}^{n} \left( \frac{p_i}{p_0} \right)^{v_i} = K_p(T) \]

- Less dissociation at higher pressure
- Le Chatelier’s Principle

Equilibrium tries to counteract the imposed changes in temperature and pressure!

Summary

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

- Thermodynamic quantities
- Flame temperature at complete conversion
- Chemical equilibrium
Balance Equations

- A time-independent control volume $V$ for a balance quality $F(t)$
- The scalar product between the surface flux $\sigma_f(x,t)$ and the normal vector $n$ determines the outflow through the surface $A$, a source $s_f$, the rate of production of $F(t)$
- Let us consider a general quantity per unit volume $f(x, t)$. Its integral over the finite volume $V$, with the time-independent boundary $A$ is given by

$$ F(t) = \int_V f(x, t) dV $$

Balance Equations

- The temporal change of $F$

$$ \frac{\partial F}{\partial t} = \int_V \frac{\partial f}{\partial t} dV $$

is then due to the following three effects:

1. by the flux $f_f$ across the boundary $A$. This flux may be due to convection or molecular transport.

2. By integration over the boundary $A$ we obtain the net contribution

$$ - \int_A \phi_f \cdot n \, dA, $$

which is negative, if the normal vector is assumed to direct outwards.
Balance Equations

2. by a local source $s_f$ within the volume. This is an essential production of partial mass by chemical reactions. Integrating the source term over the volume leads to

$$\int_V \sigma_f \, dV$$

3. by an external induced source $s_f$. Examples are the gravitational force or thermal radiation. Integration of $s_f$ over the volume yields

$$\int_V s_f \, dV$$

We therefore have the balance equation

$$\frac{\partial f}{\partial t} = \text{div} \phi_f + \sigma_f + s_f$$

Changing the integral over the boundary $A$ into a volume integral using Gauss' theorem

$$\int_A \phi_f \cdot n \, dA = \int_V \text{div} \phi_f \, dV$$

and realizing that the balance must be independent of the volume, we obtain the general balance equation in differential form

$$\frac{\partial f}{\partial t} = -\text{div} \phi_f + \sigma_f + s_f$$

Mass Balance

Set the partial mass per unit volume $\rho_i = \rho Y_i = f$.

The partial mass flux across the boundary is $\rho_i v_i = \phi_i$, where $v_i$ is called the diffusion velocity.

Summation over all components yields the mass flow $\rho v = \sum_{i=1}^{k} \rho_i v_i$, where $v$ is the mass average velocity.

The difference between $v_i$ defines the diffusion flux $v_i - v = \frac{\dot{\mathbf{j}}_i}{\rho_i}$, where the sum satisfies

$$\sum_{i=1}^{k} \dot{\mathbf{j}}_i = 0$$
Mass Balance

- Introducing the total derivative of a quantity $A$
  \[
  \frac{DA}{Dt} = \frac{\partial A}{\partial t} + v \cdot \text{grad} \ A
  \]
  a combination with the continuity equation yields
  \[
  \frac{\rho}{\rho} \frac{DA}{Dt} = \frac{\partial (\rho A)}{\partial t} + \text{div} (\rho v A).
  \]

- Then \( \frac{\partial \rho}{\partial t} = -\text{div}(\rho v) + \dot{m}_i, \) \( i = 1, 2, \ldots, k. \) using \( v_i - v = \frac{j_i}{\rho_i} \)
  may also be written
  \[
  \frac{\rho}{\rho} \frac{DY_i}{Dt} = -\text{div} j_i + \dot{m}_i, \quad i = 1, 2, \ldots, k.
  \]

Momentum Balance

- Set the momentum per unit volume \( p v = f. \)
- The momentum flux is the sum of the convective momentum in flow \( p v v \)
  and the stress tensor
  \[
  P = p I + \tau
  \]
  where \( I \) is the unit tensor and \( \tau \) is the viscous stress tensor.
- Therefore \( p v v + P = \phi_f. \)
- There is no local source of momentum, but the gravitational force from outside
  \[ s_f = \rho g \]
  where \( g \) denotes the constant of gravity.

Kinetic Energy Balance

- The scalar product of the momentum equation
  \[
  \frac{\partial (\rho v)}{\partial t} = -\text{div} (\rho v v + P) + \rho g
  \]
  or with \( \frac{\rho}{\rho} \frac{DA}{Dt} = \frac{\partial (\rho A)}{\partial t} + \text{div} (\rho v A) \) for \( A = v \)
  we obtain
  \[
  \frac{\rho}{\rho} \frac{Dv}{Dt} = -\text{grad} p - \text{div} \tau + \rho g.
  \]
Potential Energy Balance

- The gravitational force may be written as the derivative of the time-independent potential

\[ g = -\nabla \psi, \quad \frac{\partial \psi}{\partial t} = 0 \]

- Then with the continuity equation

\[ \frac{\partial \rho}{\partial t} = -\text{div}(\rho \mathbf{v}) \]

the balance for the potential energy is

\[ \frac{\partial (\rho \psi)}{\partial t} = -\text{div}(\rho \mathbf{v} \psi) - \rho g \cdot \mathbf{v}. \]

Total and Internal Energy and Enthalpy Balance

- The first law of thermodynamics states that the total energy must be conserved, such that the local source \( \sigma_f = 0 \).

- We set \( \rho e = f \), where the total energy per unit mass is

\[ e = u + \frac{1}{2} v^2 + \psi. \]

- This defines the internal energy introduced in

\[ du + \rho d\mathbf{v} = dh - v dp = \delta q + \delta w_R \]

Total and Internal Energy and Enthalpy Balance

- The total energy flux \( \phi_f \equiv \mathbf{j}_e \) is

\[ \mathbf{j}_e = \rho e \mathbf{v} + \mathbf{P} \cdot \mathbf{v} + \mathbf{j}_q \]

which defines the total heat flux \( \mathbf{j}_q \).

- The externally induced source due to radiation is \( \dot{q}_R = s_f \).

- Then the total energy balance

\[ \frac{\partial (\rho e)}{\partial t} = -\text{div} \mathbf{j}_e + \dot{q}_R \]

may be used to derive an equation for the internal energy

\[ \frac{\partial (\rho u)}{\partial t} = -\text{div} (\rho vu + j_q) - P : \nabla \mathbf{v} + \dot{q}_R \]

illustrating the equivalence with the first law introduced in a global thermodynamic balance.
Total and Internal Energy and Enthalpy Balance

- With the enthalpy \( h = u + p/\rho \) the energy balance equation can be formulated for the enthalpy

\[
\frac{\rho}{\rho} \frac{Dh}{D\tau} = \frac{Dp}{Dt} = -\text{div} \ j_q + \tau : \text{grad} \ v + \dot{q} R.
\]

Transport Processes

- In its most general form Newton's law states that the viscous stress tensor is proportional to the symmetric, trace-free part of the velocity gradient

\[
\tau = -\mu \left[ \text{grad} \ v - \frac{\text{div} \ v}{3} I \right]^\text{sym}
\]

- Here the suffix \( ^\text{sym} \) denotes that only the symmetric part is taken and the second term in the brackets subtracts the trace elements from the tensor.

- Newton's law thereby defines the dynamic viscosity.

Transport Processes

- Similarly Fick's law states that the diffusion flux is proportional to the concentration gradient.

- Due to thermodiffusion it is also proportional to the temperature gradient.

- The most general form for multicomponent diffusion is written as

\[
\dot{j}_i = \frac{W_i}{W} \sum_{j=1}^{k} \rho D_{ij} W_j \text{grad} X_j \frac{DF_{ji}}{T} \text{grad} T, \quad i = 1, 2, \ldots, k
\]

- For most combustion processes thermodiffusion can safely be neglected.

- For a binary mixture Fick's law reduces to

\[
\dot{j}_i = -\rho D_{ij} \text{grad} Y_i
\]

where \( D_{ij} = D_{ji} \) is the binary diffusion coefficient.

- A generalization for an effective diffusion coefficient \( D_i \) to be used for the minor species is

\[
D_i = \frac{\sum_{i=1}^{k} X_i}{\sum_{j=1}^{k} \frac{X_j}{D_{ij}}} \sum_{j=1}^{k} \frac{X_j}{D_{ij}}
\]
Transport Processes

- Note that the use of \( \dot{j}_i = -\rho D_i \text{grad} Y_i, \quad D_i = D_{i,N_2} \)
  \[ \sum_{i=1}^{k} \dot{j}_i = 0. \]
  does not satisfy the condition.

- Finally, Fourier's law of thermal conductivity states that the heat flux should be proportional to the negative temperature gradient.

- The heat flux \( \dot{j}_q \) includes the effect of partial enthalpy transport by diffusion and is written
  \[ \dot{j}_q = -\lambda \text{grad} T + \sum_{i=1}^{k} h_i \dot{j}_i \]
  which defines the thermal conductivity \( \lambda \).

Different Forms of the Energy Equation

- We start from the enthalpy equation
  \[ \rho \frac{Dh}{Dt} = D\rho + \text{div} \dot{j}_q + \tau : \text{grad} \dot{v} + \dot{q}_R. \]
  and neglect in the following the viscous dissipation term and the radiative heat transfer term.

- Then, differentiating \( h = \sum_{i=1}^{k} Y_i h_i \) yields
  \[ dh = c_p dT + \sum_{i=1}^{k} h_i dY_i, \]
  where \( c_p \) is the heat capacity at constant pressure of the mixture.

Transport Processes

- In Fourier's law
  \[ \dot{j}_q = -\lambda \text{grad} T + \sum_{i=1}^{k} h_i \dot{j}_i \]
  the Dufour heat flux has been neglected.

- Transport coefficients for single components can be calculated on the basis of the theory of rarefied gases.

Different Forms of the Energy Equation

- We can write the heat flux as
  \[ \dot{j}_q = -\frac{\lambda}{c_p} \text{grad} h + \sum_{i=1}^{k} h_i \left( \dot{j}_i + \frac{\lambda}{c_p} \text{grad} Y_i \right) \]

- If the diffusion flux can be approximated by
  \[ \dot{j}_i = -\rho D_{ij} \text{grad} Y_i = -\rho D_i \text{grad} Y_i \]
  with an effective diffusion coefficient \( D_i \), we introduce the Lewis number
  \[ \text{Le}_i = \frac{\lambda}{\rho c_p D_i} \]
  and write the last term as
  \[ \sum_{i=1}^{k} h_i \left( \dot{j}_i + \frac{\lambda}{c_p} \text{grad} Y_i \right) = \sum_{i=1}^{k} h_i \left( 1 - \frac{1}{\text{Le}_i} \right) \frac{\lambda}{c_p} \text{grad} Y_i \]
  This term vanishes if the Lewis numbers of all species can be assumed equal to unity.
Different Forms of the Energy Equation

- This is an interesting approximation because it leads to the following form of the enthalpy
  \[ \frac{\partial h}{\partial t} + \text{div} \left( \frac{\lambda}{c_p} \text{grad} h \right) = 0. \]

- If the \( p = \text{const} \) as it is approximately the case in all applications except in reciprocating engines, the enthalpy equation would be very much simplified.

- The assumption \( \text{Le} = 1 \) for all species is not justified in many combustion applications.

- In fact, deviations from that assumption lead to a number of interesting phenomena that have been studied recently in the context of flame stability and the response of flames to external disturbances.

- We will address these questions in some of the lectures below.

\[ \text{Different Forms of the Energy Equation} \]

- Another important form of the energy equation is that in terms of the temperature.

\[ \frac{\partial h}{\partial t} = c_p \frac{dT}{dt} + \sum_{i=1}^{k} h_i \frac{dY_i}{dt}, \]

and

\[ \rho \frac{\partial Y_i}{\partial t} = -\text{div} \, j_i + m_i, \quad i = 1, 2, \ldots, k. \]

the total derivative of the enthalpy can be written as

\[ \frac{\partial h}{\partial t} = \rho c_p \frac{dT}{dt} + \sum_{i=1}^{k} (-\text{div} \, j_i + m_i) h_i. \]

- Then with
  \[ j_q = -\lambda \text{grad} T + \sum_{i=1}^{k} h_i j_i, \]

the enthalpy equation

\[ \frac{\partial h}{\partial t} = \frac{\partial p}{\partial t} - \text{div} \, j_q + \rho c_p \text{grad} \, v + q_R, \]

without the second last term yields the temperature equation

\[ \rho c_p \frac{\partial T}{\partial t} + \text{div} \left( \lambda \text{grad} T \right) - \sum_{i=1}^{k} c_p h_i \text{grad} \, T - \sum_{i=1}^{k} m_i h_i + q_R \]

- Here the last term describes the temperature change due to chemical reactions.

\[ \text{Different Forms of the Energy Equation} \]

- It may be written as
  \[ -\sum_{i=1}^{k} \tilde{m}_i h_i = -\sum_{i=1}^{k} \sum_{l=1}^{r} \nu_{i l} W_i h_{l q l} = \sum_{i=1}^{r} Q_{i q l} \]

where the definition
  \[ a_l = -\sum_{i=1}^{k} \nu_{i l} W_i h_i = -\sum_{i=1}^{k} \nu_{i l} H_i \]

has been used for each reaction.

- The second term on the right hand side may be neglected, if one assumes that all specific heats \( c_{pi} \) are equal.

- This assumption is very often justified since this term does not contribute as much to the change of temperature as the other terms in the equation, in particular the chemical source term.
If one also assumes that spatial gradients of \( c_p \) may be neglected for the same reason, the temperature equation takes the form

\[
\rho \frac{DT}{Dt} = \frac{1}{c_p} \frac{Dp}{Dt} + \text{div}\left( \frac{\lambda}{c_p} \text{grad} T \right) + \sum_{i=1}^{r} Q_i \frac{\omega_i}{c_p} + \frac{\dot{q}_R}{c_p}.
\]

For a constant pressure it is very similar to the equation for the mass fraction \( Y_i \) with an equal diffusion coefficient \( D = \frac{\lambda}{\rho c_p} \) for all reactive species and a spatially constant Lewis number may be written as

\[
\rho \frac{DY_i}{Dt} = \frac{1}{\text{Le}_i} \text{div}\left( \frac{\lambda}{c_p} \text{grad} Y_i \right) + W_i \sum_{i=1}^{r} \nu_{ij} \omega_i.
\]

For flame calculations a sufficiently accurate approximation for the transport properties is [Smooke]

\[
\frac{\lambda}{c_p} = 2.58 \cdot 10^{-4} \frac{g}{\text{cm sec} \left( \frac{T}{298 \text{ K}} \right)}^{0.7},
\]

a constant Prandtl number \( \text{Pr} = \frac{\mu c_p}{\lambda} = 0.75 \), and constant Lewis numbers \( \text{Le}_i = \frac{\lambda}{\rho c_p D_i} \).

Lewis numbers of some reacting species occurring in methane-air flames

\[
\begin{array}{cccccccccc}
\text{CH}_4 & \text{O}_2 & \text{H}_2\text{O} & \text{CO}_2 & \text{H} & \text{O} & \text{OH} & \text{HO}_2 \\
0.97 & 1.11 & 0.83 & 1.39 & 0.18 & 0.70 & 0.73 & 1.10 \\
\hline
\text{H}_2 & \text{CO} & \text{H}_2\text{O}_2 & \text{HCO} & \text{CH}_2\text{O} & \text{CH}_3 & \text{CH}_3\text{O} \\
0.3 & 1.10 & 1.12 & 1.27 & 1.28 & 1.00 & 1.30 \\
\end{array}
\]

For \( \text{Le}=1 \) the species transport equation and the temperature equation are easily combined to obtain the enthalpy equation.

Since the use of \( \frac{\rho}{c_p} \frac{DY_i}{Dt} = \frac{1}{\text{Le}_i} \text{div}\left( \frac{\lambda}{c_p} \text{grad} Y_i \right) + W_i \sum_{i=1}^{r} \nu_{ij} \omega_i \)
and

\[
\frac{\rho}{c_p} \frac{DY_i}{Dt} = \frac{1}{\text{Le}_i} \text{div}\left( \frac{\lambda}{c_p} \text{grad} Y_i \right) + W_i \sum_{i=1}^{r} \nu_{ij} \omega_i
\]

does not require the \( \text{Le}=1 \) assumption, this formulation is often used when non-unity Lewis number effects are to be analyzed.

A first approximation for other hydrocarbon species can be based on the assumption that the binary diffusion coefficients of species \( i \) with respect to nitrogen is approximately proportional to

\[
D_i \sim \left( \frac{W_i + W_{N_2}}{2W_i W_{N_2}} \right)^{1/2}
\]

Then the ratio of its Lewis number to that of methane is

\[
\frac{\text{Le}_i}{\text{Le}_{\text{CH}_4}} = \left( \frac{W_i}{W_{\text{CH}_4} + W_{N_2}} \right)^{1/2}
\]
Balance Equations for Element Mass Fractions

- Summation of the balance equations for the mass fractions
\[ \rho \frac{D Y_i}{Dt} = - \text{div} \, j_i + \dot{m}_i, \quad i = 1, 2, \ldots, k \]
according to
\[ Z_j = \frac{m_j}{m} = \sum_{i=1}^{k} \frac{a_{ij} W_j Y_i}{W_i} = \frac{W_j}{W} \sum_{i=1}^{k} a_{ij} X_i, \quad j = 1, 2, \ldots, k_e, \]
leads to the balance equations for \( Z_j \):
\[ \rho \frac{D Z_j}{Dt} = - \text{div} \sum_{i=1}^{k} a_{ij} W_j j_i. \]

- Here the summation over the chemical source terms vanishes
\[ W_j \sum_{i=1}^{k} \sum_{l=1}^{r} a_{ij} \nu_l w_l = W_j \sum_{l=1}^{r} w_l \sum_{i=1}^{k} a_{ij} \nu_l = 0 \]
since the last sum vanishes for each reaction.

A similar equation may be derived for the mixture fraction \( Z \).

Since \( Z \) is defined according to
\[ Z = \frac{m_1}{m_1 + m_2} \]
as the mass fraction of the fuel stream, it represents the sum of element mass fractions contained in the fuel stream.

The mass fraction of the fuel is the sum of the element mass fractions
\[ Y_{F,u} = \sum_{j=1}^{k_e} Z_{j,F}, \]
where
\[ Z_{j,F} = a_{F,j} W_j Y_{F,u}. \]

With \( Y_{F,u} = Y_{F,1} Z \) the mixture fraction may therefore be expressed as a sum of element mass fractions
\[ Z = \sum_{i=1}^{k_e} \frac{Z_{i,F}}{Y_{F,1}}. \]

Then, with the assumption of \( L_e=1 \), a summation over
\[ \rho \frac{D Z_j}{Dt} = \text{div} \left( \frac{\lambda}{c_p} \text{grad} Z_j \right) \]
leads to a balance equation for the mixture fraction
\[ \rho \frac{D Z}{Dt} = \text{div} \left( \frac{\lambda}{c_p} \text{grad} Z \right). \]
Balance Equations for Element Mass Fractions

- For a one-step reaction with the reaction rate \( w \) this equation can also be derived using
  \[
  Z = \frac{\nu F - Y_{O_2} + Y_{O_2,2}}{\nu F,1 + Y_{O_2,2}}
  \]

  and
  \[
  \rho \frac{DY_i}{Dt} = \frac{1}{Le} \text{div} \left( \lambda \text{grad} Y_i \right) + W_i \sum_{j=1}^{p} \nu_j \omega_j
  \]

  for \( Y_f \) and \( Y_{O_2} \) with \( Le = L_{O_2} = 1 \) as
  \[
  \rho \frac{DY_F}{Dt} = \text{div} \left( \lambda \text{grad} Y_F \right) - \nu F W F \omega
  \]
  \[
  \rho \frac{DY_{O_2}}{Dt} = \text{div} \left( \lambda \text{grad} Y_{O_2} \right) - \nu'O_{2} W_{O_2} \omega.
  \]

For constant pressure the enthalpy equation has the same form as
\[
\rho \frac{Dh}{Dt} = \frac{Dp}{Dt} + \text{div} \left( \lambda \text{grad} h \right)
\]
has the same form as
\[
\rho \frac{DZ}{Dt} = \text{div} \left( \lambda \text{grad} Z \right).
\]
and a coupling relation between the enthalpy and the mixture fraction may be derived
\[
h = h_2 + Z(h_1 - h_2)
\]
where \( h_1 \) is the enthalpy of the fuel stream and \( h_2 \) that of the oxidizer stream.

Similarly, using
\[
\rho \frac{DZ_j}{Dt} = \text{div} \left( \lambda \text{grad} Z_j \right)
\]
and
\[
\rho \frac{DZ}{Dt} = \text{div} \left( \lambda \text{grad} Z \right).
\]
the element mass fractions may be expressed in terms of the mixture fraction
\[
Z_j = Z_{j,2} + Z(Z_{j,1} - Z_{j,2}),
\]
where \( Z_{j,1} \) and \( Z_{j,2} \) are the element mass fractions in the fuel and oxidizer stream.
Balance Equations for Element Mass Fractions

- It should be noted that the coupling relations

\[ h = h_2 + Z(h_1 - h_2) \]

and

\[ Z_j = Z_{j,2} + Z(Z_{j,1} - Z_{j,2}) \]

required a two feed system with equivalent boundary conditions for the enthalpy and the mass fractions.

- A practical example is a single jet as fuel stream with co-flowing air as oxidizer stream into an open atmosphere, such that zero gradient boundary conditions apply everywhere except at the input streams.

- Once the mixture fraction field has been obtained by numerical solution of

\[ \rho \frac{DZ}{Dt} = \text{div} \left( \frac{\lambda}{c_p} \text{grad} Z \right) \]

the adiabatic flame temperature may be calculated using the methods of lecture 2 as a local function of \( Z \).
Laminar Premixed Flames: Kinematics and Burning Velocity

Heinz Pitsch
Institut für Technische Verbrennung
RWTH Aachen University

Princeton Combustion Summer School 2023

Laminar Premixed Flames

- Premixed combustion used in combustion devices when high heat release rates are desired
  - Small devices
  - Low residence times
- Examples:
  - SI engine
  - Stationary gas turbines
- Advantage → Lean combustion possible
  - Smoke-free combustion
  - Low NOₓ
- Disadvantage: Danger of
  - Explosions
  - Combustion instabilities
  → Large-scale industrial furnaces and aircraft engines are typically non-premixed

Premixed Flames

- Premixed flame: Blue or blue-green by chemiluminescence of excited radicals, such as C₂O and CH₂
- Diffusion flames: Yellow due to soot radiation

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
  - Flame structure
  - Laminar diffusion flames
  - FlameMaster flame calculator

Part II: Turbulent Flames
- Introduction
- Kinematic balance for steady oblique flames
- Laminar burning velocity
- Field equation for the flame position
- Flame stretch and curvature
- Thermo-diffusive flame instability
- Hydrodynamic flame instability
Flame Structure of Premixed Laminar Flames

- Fuel and oxidizer are **convected** from upstream with the burning velocity $s_L$
- Fuel and air **diffuse** into the reaction zone
- Mixture **heated up** by heat conduction from the burnt gases
- Fuel consumption, radical production, and oxidation when **inner layer temperature** is reached
- Increase temperature and gradients
- Fuel is entirely depleted
- Remaining oxygen is **convected** downstream

Premixed Flame in a Bunsen Burner

- Fuel enters the Bunsen tube with **high momentum** through a small orifice
- High momentum → **underpressure** into Bunsen tube
- Premixing of fuel and air in the Bunsen tube
- At tube exit: **homogeneous, premixed fuel/air mixture**, which can and should(!) be ignited

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

Kinematic Balance for Steady Oblique Flame

- In steady state, flame forms **Bunsen cone**
- Velocity component normal to flame front is locally equal to the **propagation velocity of the flame front**
- **Burning velocity**
Kinematic Balance for Steady Oblique Flame

- Laminar burning velocity $s_{u,\text{b}}$:
  
  Velocity of the flame normal to the flame front and relative to the unburnt mixture (index 'u')

- Can principally be experimentally determined with the Bunsen burner

- Need to measure
  - Velocity of mixture at Bunsen tube exit
  - Bunsen cone angle $\alpha$

Splitting of the tube exit velocity in components normal and tangential to the flame

Kinematic balance yields relation unburnt gas velocity and flame propagation velocity

For laminar flows:

\[ s_{L,u} = v_{n,u} = v_u \sin \alpha \]

Burning Velocity at the Flame Tip

- Tip of the Bunsen cone
  - Symmetry line
  - Burning velocity equal to velocity in unburnt mixture
  - Here: Burning velocity = normal component, tangential component = 0

→ Burning velocity at the tip by a factor $1/\sin(\alpha)$ larger than burning velocity through oblique part of the cone

- Flame front:
  - Large temperature increase
  - Pressure almost constant
  → Density decreases drastically

- Mass balance normal to the flame front:
  \[ (\rho v_U)_n = (\rho v_U)_b \quad \Rightarrow \quad v_{n,b} = v_{n,U} \frac{p_U}{p_b} \]

- Normal velocity component increases through flame front
  \[ v_{n,b} = v_{n,b} \]

- Momentum balance in tangential direction:
  → Deflection of the streamlines away from the flame

\[ \text{Laminar Bunsen Flame} \quad \text{(Mungal et al.)} \]
Burning velocity at the flame tip

- **Explanation:** Strong curvature of the flame front at the tip

  → Increased preheating
    - In addition to heat conduction normal to the flame front preheating by the lateral parts of the flame front

- **Effect of non-unity Lewis numbers**
  → Explanation of difference between lean hydrogen and lean hydrocarbon flames

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

Measuring the laminar burning velocity

- **Spherical constant volume combustion vessel**
  - Principle
    - Flame initiated by a central spark
    - Spherical propagation of a flame
    - Measurements of radial flame propagation velocity \( \frac{dr_f}{dt} \)

  - Kinematic relation for flame displacement speed
    \[
    \frac{dr_f}{dt} = v_f + \sigma_L \frac{dr_f}{dt}.
    \]

  - Flame front position and displacement speed are unsteady
  - Pressure increase negligible as long as volume of burnt mixture small relative to total volume
  - Influence of curvature

Spherical constant volume combustion vessel
*Flame front velocity in a spherical combustion vessel*

- Velocity relative to flame front is the burning velocity
  - Different in burnt and unburnt region
- From kinematic relation
  \[
  \frac{dr_f}{dt} = v_u + s_{L,u}
  \]
  - Velocity on the unburnt side (relative to the flame front)
  \[
  v_u - \frac{dr_f}{dt}
  \]
- Burnt side of the front
  \[
  v_b - \frac{dr_f}{dt}
  \]
- Spherical propagation: Due to symmetry, flow velocity in the burnt gas is zero
  \[
  v_b = 0
  \]
- Mass balance yields:
  \[
  \rho_u (v_u - \frac{dr_f}{dt}) = \rho_b (v_b - \frac{dr_f}{dt}) = \rho_b (-\frac{dr_f}{dt})
  \]

---

**Relation between*** \( s_{L,u} \) ***and*** \( s_{L,b} \) **

- Burning velocity \( s_{L,u} \) defined with respect to the unburnt mixture
- Another burning velocity \( s_{L,b} \) can be defined with respect to the burnt mixture
- Continuity yields the relation: 
  \[
  s_{L,b} = \frac{\rho_u}{\rho_b} s_{L,u}
  \]
- In the following, we will usually consider the burning velocity with respect to the unburnt \( s_L = s_{L,u} \)

---

**Flat Flame Burner and Flame Structure**

- One-dimensional flame
- Stabilization by heat losses to burner
  - In theory, velocity could be increased until heat losses vanish, then
    - Unstretched
    - \( u_u = s_L \)
- Analysis of flame structure of flat flames
  - Measurements of temperature and species concentration profiles

*From mass balance and kinematic relation follows

\[
\frac{dr_f}{dt} = \frac{\rho_u - \rho_b}{\rho_b} v_u = v_u + s_{L,u}
\]

- Flow velocity on the unburnt side of the front
  \[
  v_u = \frac{\rho_u - \rho_b}{\rho_b} s_{L,u}
  \]
  → Flow of unburnt mixture induced by expansion of gases behind flame front

- Measurements of the flame front velocity \( dr_f/dt \)
  → Burning velocity \( s_{L,u} \):
  \[
  s_{L,u} = \frac{\rho_u}{\rho_b} \frac{dr_f}{dt}
  \]
The general case with multi-step chemical kinetics

- Laminar burning velocity $s_l$ can be calculated by solving governing conservation equations for the overall mass, species, and temperature (low Mach limit)

- Continuity
  \[
  \frac{d(\rho u)}{dx} = 0
  \]

- Species
  \[
  \rho u \frac{dY_i}{dx} = \frac{d\dot{m}_i}{dx} + \dot{m}_i
  \]

- Energy
  \[
  \frac{\rho u c_p}{dx} \frac{dT}{dx} = \frac{d}{dx} \left( \lambda \frac{dT}{dx} \right) - \sum_{i=1}^{k} \dot{q}_{hi} - \sum_{i=1}^{k} \dot{q}_{ji} \frac{dT}{dx} + \frac{dp}{dx}
  \]

Continuity equation may be integrated once to yield
\[
\rho u = \rho u(t)
\]

- Burning velocity is eigenvalue, which must be determined as part of the solution

- System of equations may be solved numerically with
  - Appropriate upstream boundary conditions
  - Zero gradient boundary conditions downstream

Laminar Burning Velocity

Example: Burning velocities of premixed methane-air flames

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Equivalence Ratio</th>
<th>Pressure</th>
<th>Temperature</th>
<th>Experimental Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane/air</td>
<td></td>
<td>1 atm</td>
<td>300 K</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methane/air</td>
<td></td>
<td>1 atm</td>
<td>373 K</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Example: Burning velocities for different fuels

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Equivalence Ratio</th>
<th>Pressure</th>
<th>Temperature</th>
<th>Experimental Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane/air</td>
<td></td>
<td>1 atm</td>
<td>300 K</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methane/air</td>
<td></td>
<td>1 atm</td>
<td>373 K</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen/air</td>
<td></td>
<td>1 atm</td>
<td>300 K</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen/air</td>
<td></td>
<td>1 atm</td>
<td>373 K</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Heptane/air</td>
<td></td>
<td>1 atm</td>
<td>373 K</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Heptane/air</td>
<td></td>
<td>1 atm</td>
<td>373 K</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Heptane/air</td>
<td></td>
<td>1 atm</td>
<td>373 K</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Heptane/air</td>
<td></td>
<td>1 atm</td>
<td>373 K</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Error band (present study)
- Aramco 2.0
- GRI 3.0
- ITV Base
- Updated mech.
- Pitsch & Peters [1]
Laminar Burning Velocity

Example: Effect of pressure and preheat temperature on burning velocities of iso-octane

\[ s_b \text{ decreases with increasing pressure but increases with increasing preheat temperature} \]

Laminar Burning Velocity

- Burning velocity is fundamental property of a premixed flame
- Can be used to determine flame dynamics
- Depends on thermo-chemical parameters of the premixed gas ahead of flame only
  - Defined for flat undisturbed flame
  - Curvature must be taken into account

Next

- We will first calculate flame shapes
- Then we will consider external influences that locally change the burning velocity and discuss the response of the flame to these disturbances

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
- Introduction
- Kinematic balance for steady oblique flames
- Laminar burning velocity
- Field equation for the flame position
- Flame stretch and curvature
- Thermo-diffusive flame instability
- Hydrodynamic flame instability

A Field Equation Describing the Flame Position

- Kinematic relation \( \frac{dx_f}{dt} = v + s_L n \) between \( \frac{dx_f}{dt} = v + s_L n \)
  - Displacement velocity
  - Flow velocity
  - Burning velocity
- May be generalized by introducing vector \( n \) normal to the flame
  \[ \frac{dx_f}{dt} = v + s_L n, \]
  where \( x_f \) is the vector describing the flame position, \( dx_f/dt \) the flame propagation velocity, \( v \) the velocity vector
A Field Equation Describing the Flame Position

- Introduce level set function $G(x,t)$ as scalar field such that $G(x,t) = G_0$ represents the flame surface.
- Normal vector can be expressed in terms of level set function $n = -\frac{\nabla G}{|\nabla G|}$ defined to point towards the unburnt mixture.
- Flame contour $G(x,t) = G_0$ divides physical field into two regions, where $G > G_0$ is the region of burnt gas and $G < G_0$ that of the unburnt mixture.

Differentiating $G(x,t) = G_0$ with respect to $t$ at $G = G_0$ gives
\[ \frac{\partial G}{\partial t} + \nabla G \cdot \frac{\partial x}{\partial t} |_{G = G_0} = 0. \]

Introducing $\frac{dx_f}{dt} = v + s_L n.$ leads to
\[ \frac{\partial G}{\partial t} + v \cdot \nabla G = -s_L n \cdot \nabla G. \]

Level set equation for the propagating flame follows using $n = -\frac{\nabla G}{|\nabla G|}$
\[ \frac{\partial G}{\partial t} + v \cdot \nabla G = s_L |\nabla G|. \]

Burning velocity $s_L$ is defined w.r.t. the unburnt mixture.
Flow velocity $v$ defined as conditioned velocity field in unburnt mixture ahead of flame.

For a constant value of $s_L$, the solution of
\[ \frac{\partial G}{\partial t} + v \cdot \nabla G = s_L |\nabla G| \]
is non-unique, and cusps will form where different parts of the flame intersect.
Even an originally smooth undulated front in a quiescent flow will form cusps and eventually become flatter with time.
This is called Huygens' principle.

Exercise: Slot Burner

- A closed form solution of the G-equation
\[ \frac{\partial G}{\partial t} + v \cdot \nabla G = s_L |\nabla G| \]
can be obtained for the case of a slot burner with a constant exit velocity $u$ for premixed combustion.
- This is the two-dimensional planar version of the axisymmetric Bunsen burner.
- The G-equation takes the form
\[ u \frac{\partial G}{\partial x} = s_L \sqrt{(\frac{\partial G}{\partial x})^2 + (\frac{\partial G}{\partial y})^2}. \]
Exercise: Slot Burner

With the ansatz \( G = x + F(y) \)
and \( G_y = 0 \) one obtains
\[
 u = s_L \sqrt{1 + \left( \frac{\partial F}{\partial y} \right)^2}
\]
leading to
\[
 F = \sqrt{\frac{u^2 - s_L^2}{s_L^2}} |y| + \text{const.}
\]

As the flame is attached at \( x = 0, y = \pm b/2 \), where \( G = 0 \),
this leads to the solution
\[
 G = \sqrt{\frac{u^2 - s_L^2}{s_L^2}} \left( |y| - \frac{b}{2} \right) + x.
\]

Exercise: Slot Burner

The flame tip lies with \( y = 0, G = 0 \) at
\[
 x_{F,0} = \frac{b}{2} \sqrt{\frac{u^2 - s_L^2}{s_L^2}}
\]
and the flame angle \( \alpha \) is given by
\[
 \tan \alpha = \frac{b}{2x_{F,0}} = \sqrt{\frac{u^2 - s_L^2}{s_L^2}}.
\]

With \( \tan^2 \alpha = \sin^2 \alpha \left( 1 - \sin^2 \alpha \right) \), it follows
\[
 \sin \alpha = \frac{s_L}{u}
\]
which is equivalent to
\[
 s_L, k = v_B, k = v_B \sin \alpha.
\]

This solution shows a cusp at the flame tip \( x = x_{F,0}, y = 0 \). In order to obtain a
rounded flame tip, one has to take modifications of the burning velocity due to
flame curvature into account. This leads to the concept of flame stretch.

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

- Introduction
- Kinematic balance for steady oblique flames
- Laminar burning velocity
- Field equation for the flame position
- Flame stretch and curvature
- Thermo-diffusive flame instability
- Hydrodynamic flame instability

Flame stretch

- Flame stretch consists of two contributions:
  - Flame curvature
  - Flow divergence or strain

- For one-step large activation energy reaction and with the assumption of constant properties, the burning velocity \( s_L \) is modified by these two effects as
  \[
  s_L = s_L^0 - s_L^0 \mathcal{L} n + \mathcal{L} n \cdot \nabla v \cdot n.
  \]
- \( s_L^0 \) is the burning velocity for an unstretched flame
- \( \mathcal{L} \) is the Markstein length
**Flame stretch**

- The flame curvature $\kappa$ is defined as
  \[
  \kappa = \nabla \cdot \nu = -\nabla \cdot \left( \frac{\nabla G}{\left| \nabla G \right|} \right)
  \]
  which may be transformed as
  \[
  \kappa = -\frac{\nabla^2 G + \nabla \cdot (\nu \cdot \nabla G)}{\left| \nabla G \right|}
  \]

- Markstein length $\mathcal{L}$ is of same order of magnitude and proportional to laminar flame thickness $\ell_F$.

- Ratio $\ell_F/\mathcal{L}$ is called Markstein number.

**Markstein length**

- With assumptions:
  - One-step reaction with a large activation energy
  - Constant transport properties and heat capacity $c_p$
  - Markstein length with respect to the unburnt mixture

  \[
  \mathcal{L}_u = \frac{s_v - \mathcal{L}_b}{2} \left( \frac{\gamma}{\gamma - 1} \right) \frac{\ln(1 + s_v)}{s_v}
  \]

- Determined experimentally
- Determined by asymptotic analysis

**Example: Effect of Flame Curvature**

- We want to explore the influence of curvature on the burning velocity for the case of a spherical propagating flame

  \[
  \frac{dr(t)}{dt} = s_{L,b}
  \]
  where $r(t)$ is the radial flame position

  - The burning velocity is then $s_{L,b}$ and the Markstein length is that with respect to the burnt gas $\mathcal{L}_b$.

  - Here, we assume $\mathcal{L}_b > 0$ to avoid complications associated with thermo-diffusive instabilities.
*Example: Effect of Flame Curvature*

- In a spherical coordinate system, the G-equation reads
  \[
  \frac{\partial G}{\partial t} = s_L \frac{\partial G}{\partial r} + 2 \frac{\partial G}{\partial \theta} \frac{\partial}{\partial \theta}
  \]
  where the entire term in round brackets represents the curvature in spherical coordinates
  \[G = r_f(t) - r\]
- We introduce the ansatz
  \[
  \frac{\partial r_f}{\partial t} = s_L \left( 1 - \frac{2 \mathcal{L}_b}{r_f} \right)
  \]
  to obtain at the flame front \[r_f = r_f(0) + \int_0^t \frac{\partial r_f}{\partial t} \, dt\]
  This equation may also be found in Clavin (1985)

This equation reduces to \[\frac{\partial r_f}{\partial t} = 0\] for \[s_L \mathcal{L}_b = 0\].
- It may be integrated to obtain
  \[
  s_L = \int_0^t \frac{\partial r_f}{\partial t} \, dt = \frac{r_f(t) - r_f(0)}{1 - \frac{2 \mathcal{L}_b}{r_f(0)}}
  \]
  where the initial radius at \(t=0\) is denoted by \(r_f(0)\)
- This expression has no meaningful solutions for \[s_L \mathcal{L}_b < 2 \mathcal{L}_b\], indicating that there needs to be a minimum initial flame kernel for flame propagation to take off
- It should be recalled that \[\mathcal{L}_b \ll 1\] is only valid if the product

- For curvature corrections are important at early times only

### Effects of curvature and strain on laminar burning velocity

Curvature Effect on Laminar Burning Velocity from Experiments and Theory

Strain Effect on Laminar Burning Velocity from Numerical Simulations

Lean Hydrogen/Air Flame (\(L_e < 1\))

Lean Propane/Air Flame (\(L_e > 1\))
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

- Introduction
- Kinematic balance for steady oblique flames
- Laminar burning velocity
- Field equation for the flame position
- Flame stretch and curvature
- Thermo-diffusive flame instability
- Hydrodynamic flame instability

Flame Instabilities: Thermo-diffusive instability

Effect of Curvature

\[ \frac{\partial n}{\partial t} = \frac{\partial}{\partial x} \left[ L_K \frac{\partial n}{\partial x} - L_S \right] \]

Effect of stretch

Unburnt

Burnt

Unstretched laminar burning velocity

Example: Thermo-diffusive instability

Thermo-diffusive instability for lean hydrogen flame

Literature Review: Characteristic flame patterns

Large-scale DNS

<table>
<thead>
<tr>
<th>Fuel</th>
<th>( \text{H}_2/\text{air} ) with ( \phi = 0.4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanism</td>
<td>Finite rate chemistry (Hong et al., Combust Flame 158 (2011))</td>
</tr>
<tr>
<td>Physical time</td>
<td>173 ( \tau_{\text{Laminar}} ) (120,000 time steps)</td>
</tr>
<tr>
<td>CPUh</td>
<td>0.88 Mio</td>
</tr>
<tr>
<td>Domain</td>
<td>0.14m x 0.56m (grid: 2048 x 8192 points)</td>
</tr>
</tbody>
</table>

Experiment

<table>
<thead>
<tr>
<th>Fuel</th>
<th>12.7% ( \text{H}_2 ), 7.90% ( \text{O}_2 ), 79.4% ( \text{N}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Configuration</td>
<td>Hele-Shaw cell</td>
</tr>
<tr>
<td>Width</td>
<td>0.4m</td>
</tr>
</tbody>
</table>

Example: Thermo-diffusive Instability in Turbulent Hydrogen Flame

DNS of hydrogen/air flame: Tu = 298K, \( p = 1 \) bar, \( \phi = 0.4 \), Re = 11,000, Ka = 16

Flame Instabilities: Hydrodynamic Instability

Illustration starting with a slightly undulated flame

- Consider positive curvature
  - convex into unburnt
- Streamline deflection causes converging streamlines in burnt gas region
  - locally higher pressure
- This leads to diverging streamlines in unburnt region
  - local deceleration ahead of flame front, hence \( s_L > u_L \)
  - similarly local flow acceleration for negative curvature, hence \( s_L < u_L \)

Initial perturbation will grow!
**Flame Instabilities: Hydrodynamic Instability**

- Analysis can be performed with following simplifications:
  - Viscosity, gravity and compressibility in the burnt and unburnt gas are neglected.
  - Density is discontinuous at the flame front.
  - The influence of the flame curvature on the burning velocity is retained, flame stretch due to flow divergence is neglected.

- Analysis results in dispersion relation:
  \[ \sigma = \frac{s_L S_F k}{1 + r} \left\{ \sqrt{1 + k^2 \mathcal{L}^2} - \frac{2k^2}{r} \left[ 1 - \frac{r^2}{r^2} \right] \right\} \]

  where \( \sigma \) is the non-dimensional growth rate of the perturbation, \( r \) is density ratio and \( k \) the wave number.

  Perturbation grows exponentially in time only below a certain wavenumber:
  \[ k^* = \left( r - 1 \right) / \left( 2 \mathcal{L} \right). \]

- Without influence of curvature (\( \mathcal{L} = 0 \)), flame is unconditionally unstable.

- For perturbations at wave numbers \( \kappa > \kappa^* \), a planar flame with positive Markstein number is unconditionally stable.

- Influence of front curvature on burning velocity.

**Details of the Analysis for Hydrodynamic Instability**

- The burning velocity is given by:
  \[ s_L = s_L^0 \left( 1 + \kappa \mathcal{L} \right) \]

- Reference values for length, time, density, pressure:
  \[ \ell_F, \quad \ell_L/s_{L,0}, \quad \rho_s, \quad \rho_u s_{L,0}^2 \]

- Introduce the density rate:
  \[ r = \rho_u / \rho_s < 1 \]

- Dimensionless variables:
  \[ u^* = u/s_{L,0}, \quad v^* = v/s_{L,0}, \quad p^* = p / \rho_u s_{L,0}^2, \quad x^* = x/\ell_F, \quad y^* = y/\ell_F, \quad \tau^* = \tau / \ell_F/s_{L,0} \]
The non-dimensional governing equations are then
(with the asterisks removed)

\[ \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \]
\[ \frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial x} \]
\[ \frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial y} \]

where \( \rho_+ = 1 \) and \( \rho = r \) in the unburnt and burnt mixture respectively.

If \( G \) is a measure of the distance to the flame front, the \( G \)-field is described by:

\[ G = x - F(y, t) \]

Due to the discontinuity in density at the flame front, the Euler equations
are only valid on either side of the front, but do not hold across it.

Therefore jump conditions for mass and momentum conservation across the discontinuity
are introduced [Williams85, p. 16]:

\[ (r - 1) \frac{dx}{dt} |_{G=G_0} = n \cdot (r v_+ - v_-) \]
\[ (r u_+ - u_-) \frac{dx}{dt} |_{G=G_0} = n \cdot (r u_+ v_+ - v_- (p_+ - p_-)) \]

The subscripts + and - refer to the burnt and the unburnt gas and denote the properties
immediately downstream and upstream of the flame front.

With equations

\[ n = -\frac{\nabla G}{|\nabla G|} \quad \frac{\partial G}{\partial t} - |\nabla G| \ n \cdot \frac{\partial x}{\partial t} |_{G=G_0} = 0 \]

the normal vector \( n \) and the normal propagation velocity then are

\[ n = (-1, \frac{\partial F}{\partial y}) / \sqrt{1 + \left(\frac{\partial F}{\partial y}\right)^2}, \quad n \cdot \frac{dx}{dt} |_{G=G_0} = \frac{\partial F}{\partial t} / \sqrt{1 + \left(\frac{\partial F}{\partial y}\right)^2} \]

In terms of the \( u \) and \( v \) components the jump conditions read

\[ (r - 1) \frac{\partial F}{\partial t} = ru_+ - u_- - \frac{\partial F}{\partial y} (rv_+ - v_-) \]
\[ (r u_+ - u_-) \frac{\partial F}{\partial t} = ru_+ (u_+ - \frac{\partial F}{\partial y} v_+) - u_- (u_- - \frac{\partial F}{\partial y} v_-) + p_+ - p_- \]
\[ (r v_+ - v_-) \frac{\partial F}{\partial t} = rv_+ (v_+ - \frac{\partial F}{\partial y} v_+) - v_- (v_- - \frac{\partial F}{\partial y} v_-) - \frac{\partial F}{\partial y} (p_+ - p_-) \]

Under the assumption of small perturbations of the front, with \( \varepsilon << 1 \) the
unknowns are expanded as

\[ u = U + \varepsilon u, \quad v = \varepsilon v \]
\[ p = p + \varepsilon p, \quad F = \varepsilon f \]
**Details of the Analysis for Hydrodynamic Instability**

- Jump conditions to leading order
  \[ U_+ = 1, \quad P_+ = 0 \]
  \[ U_- = \frac{1}{r}, \quad P_- = \frac{r - 1}{r} \]
  and to first order
  \[ (r - 1) \frac{\partial f}{\partial r} = ru_+ - u_- \]
  \[ 0 = 2(u_+ - u_-) + p_+ - p_- \]
  \[ 0 = 1 - r \frac{\partial f}{\partial \eta} \]
  where the leading order mass flux has been set equal to one:
  \[ \bar{m} = r\bar{U}_+ = \bar{U}_- = 1 \]

With the coordinate transformation \( x = \xi + F(\eta, \tau), \quad y = \eta, \quad t = \tau \)
we fix the discontinuity at \( x = 0 \).

To first order the equations for the perturbed quantities on both sides of the flame front now read

\[ \frac{\partial u}{\partial \xi} + \frac{\partial u}{\partial \eta} = 0 \]
\[ \frac{\partial v}{\partial \xi} + \frac{U}{\partial \xi} \frac{\partial u}{\partial \xi} + \frac{1}{\rho} \frac{\partial \rho}{\partial \xi} = 0 \]

where \( \rho = 1 \) for \( \xi < 0 \) (unburnt gas) and \( \rho = r \) for \( \xi > 0 \) (burnt gas) is to be used.

In case of instability perturbations which are initially periodic in the h-direction and vanish for \( x \to \pm \infty \) would increase with time.

Since the system is linear, the solution may be written as

\[ w = \begin{pmatrix} u \\ v \\ \rho \end{pmatrix} = w_0 \exp(\alpha \xi) \exp(\sigma \tau - i\kappa \eta) \]

where \( \sigma \) is the non-dimensional growth rate, \( \chi \) the non-dimensional wave number and \( i \) the imaginary unit.

Introducing this into the first order equations the linear system may be written as

\[ A \cdot w = 0 \]

The matrix \( A \) is given by

\[ A = \begin{pmatrix} \alpha - i\kappa & 0 & 0 \\ \sigma + aU & 0 & a/\rho \\ 0 & \sigma + aU & -i\kappa/\rho \end{pmatrix} \]

The eigenvalues of \( A \) are obtained by setting \( \det(A) = 0 \).

This leads to the characteristic equation

\[ \det(A) = \frac{1}{\rho} (\kappa^2 - a^2) (\sigma + aU) = 0 \]

Here again \( U = 1/r, \rho = r \) for \( \xi > 0 \) and \( U = 1, \rho = 1 \) for \( \xi < 0 \).

There are three solutions to the characteristic equation for the eigenvalues \( \alpha_j, j = 1,2,3 \).

Positive values of \( \alpha_j \) satisfy the upstream (\( \xi < 0 \)) and negative values the downstream (\( \xi > 0 \)) boundary conditions of the Euler equations.
In terms of the original unknowns $u, v$ and the solution is now

$$
\begin{align*}
\xi > 0 : & \quad \begin{pmatrix} u \\ v \end{pmatrix} = \left( a \begin{pmatrix} 1 \\ \frac{1}{k} \end{pmatrix} \exp(-r \sigma \xi) + b \begin{pmatrix} 1 \\ -1 + \frac{r \sigma}{k} \end{pmatrix} \exp(-k \xi) \right) \exp(\sigma \tau - i k \eta), \\
\xi < 0 : & \quad \begin{pmatrix} u \\ v \end{pmatrix} = \left( c \begin{pmatrix} 1 \\ -1 - \frac{\sigma}{k} \end{pmatrix} \exp(k \xi + \sigma \tau - i k \eta) \right).
\end{align*}
$$

For the perturbation $f(\eta, t)$ the form

$$f = \tilde{f} \exp(\sigma \tau - i k \eta)$$

will be introduced.

This leads to first order to

\begin{align*}
\frac{\partial f}{\partial \tau} - \frac{\partial^2 f}{\partial \eta^2} & = \tilde{f} \exp(\sigma \tau - i k \eta), \\
\frac{\partial f}{\partial \tau} - \frac{\partial^2 f}{\partial \eta^2} & = \frac{\partial f}{\partial \tau} + \frac{\partial^2 f}{\partial \eta^2} - \frac{1}{r} \frac{\partial f}{\partial \eta}.
\end{align*}

The jump conditions can be written as

\begin{align*}
(r - 1) \frac{\partial f}{\partial \tau} & = r u_+ - u_- \\
0 & = 2(u_+ - u_-) + p_+ - p_- \\
0 & = v_+ - v_- + \frac{1 - r}{r} \frac{\partial f}{\partial \eta}.
\end{align*}

\begin{align*}
(r - 1) \sigma f & = r(a + b) - c \\
0 & = 2a + b(1 + \frac{\sigma}{k}) + c(\frac{\sigma}{k} - 1) \\
\frac{1 - r}{r} k f & = a \frac{\sigma}{k} + b + c.
\end{align*}
Details of the Analysis for Hydrodynamic Instability

The system
\[ u_+ = \frac{\partial f}{\partial r} - \frac{\partial^2 f}{\partial \eta^2} r \]
then reads
\[ c = f(\sigma + k^2 \mathcal{L}) \]
\[ a + b = f(\sigma + \frac{k^2 \mathcal{L}}{r}) \]

Since equation
\[ (r-1)\sigma f = r(a+b) - c \]
is linear dependent from equations
\[ c = f(\sigma + k^2 \mathcal{L}) \]
\[ a + b = f(\sigma + \frac{k^2 \mathcal{L}}{r}) \]
it is dropped and the equations
\[ 0 = 2a + b(1 + r\mathcal{L}^2) + c(\frac{r}{k} - 1) \]
\[ \frac{1-r}{r} k\sigma = -a \mathcal{L} + b + c \]
remain for the determination of a, b, c and σ(k).

Dividing all equations by \( k \mathcal{L} \) one obtains four equations for
\[ \hat{a} = a/(k \mathcal{L}), \quad \hat{b} = b/(k \mathcal{L}), \quad \hat{c} = c/(k \mathcal{L}), \quad \hat{\varphi} = \sigma/k \]
The elimination of the first three unknown yields the equation
\[ \hat{\varphi}^2(1+r) + \hat{\varphi}(1+r) + \frac{2k \mathcal{L}}{r} + \frac{1-r}{r} = 0 \]
The solution may be written in terms of dimensional quantities as
\[ \sigma = \frac{\text{Obst}}{1+r} \left\{ \frac{1 + k^2 \mathcal{L}^2 - \frac{2k \mathcal{L}}{r} - \frac{1}{r} - (1 + k \mathcal{L})}{r} \right\} \]
Here only the positive root has been taken, since it refers to possible solutions with exponential growing amplitudes.

The relation
\[ \sigma = \frac{\text{Obst}}{1+r} \left( \frac{1 + k^2 \mathcal{L}^2 - \frac{2k \mathcal{L}}{r} - \frac{1}{r} - (1 + k \mathcal{L})}{r} \right) \]
is the dispersion relation which shows that the perturbation \( f \) grows exponentially in time only for a certain wavenumber range \( 0 < k < k^* \).

Here \( k^* \) is the wave number of which \( j = 0 \) in
\[ \hat{\varphi}^2(1+r) + 2\hat{\varphi}(1+k \mathcal{L}) + \frac{2k \mathcal{L}}{r} + \frac{r-1}{r} = 0 \]
which leads to
\[ k^* = (r-1)/(2 \mathcal{L}) \]
Exercise

- Under the assumption of a constant burning velocity $s_L = s_{L0}$, the linear stability analysis leads to the following dispersion relation:

$$\sigma = \frac{s_{L0} k}{1 + r} \left\{ \sqrt{1 + 1 - \frac{r^2}{r}} - 1 \right\}.$$

- Validate this expression by inserting $L = 0$:

$$\sigma = \frac{s_{L0} k}{1 + r} \left\{ \sqrt{1 + k^2 L^2} - \frac{2k L}{r} + \frac{1 - r^2}{r} - (1 + k L) \right\}.$$

- What is the physical meaning of this result?
- What effect has the front curvature on the flame front stability?

Exercise

- The front curvature has a stabilizing effect on the flame front stability.

- As it is shown in the last section, the linear stability analysis for a burning velocity with the curvature effect retained leads to instability of the front only for the wave number range:

$$0 < k < k^* = \frac{(r - 1)}{(2L)}.$$

whereas the front is stable to all perturbations with $k > k^*$.

Exercise

- The dispersion relation for constant burning velocity $s_L = s_{L0}$:

$$\sigma = \frac{s_{L0} k}{1 + r} \left\{ \sqrt{1 + 1 - \frac{r^2}{r}} - 1 \right\}.$$

shows that the perturbation $F$ grows exponentially in time for all wave numbers.

- The growth $g$ is proportional to the wave number $k$ and always positive since the density rate $r$ is less than unity.

- This means that a plane flame front with constant burning velocity is unstable to any perturbation.

Summary

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
- Introduction
- Kinematic balance for steady oblique flames
- Laminar burning velocity
- Field equation for the flame position
- Flame stretch and curvature
- Thermo-diffusive flame instability
- Hydrodynamic flame instability
**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 solvable form of the governing equations
- This theory is the origin of a development, which placed combustion science on a mathematical basis
Thermal Flame Theory

Flame front (lean mixture):
- Complete fuel conversion
- Excess oxygen remains
- Temperature rises from the initial value $T_i$ to the adiabatic flame temperature $T_b$
- The area around the flame front is divided in three zones by Zeldovich and Frank-Kamenetski:
  - Preheat zone
  - Reaction zone
  - Equilibrium zone

Preheat Zone
- Chemically inert
- 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

Reaction Zone
- Transition at position $x_i$ and temperature $T_i$
- Chemical reactions

Simplification:
- Global reaction equation
  $$\nu_F F + \nu_{O_2} O_2 \rightarrow \nu_P P$$
- Reaction rate
  $$\omega = \frac{\nu_F \rho F \rho_{O_2} \rho_{O_2} \exp \left(-\frac{E}{RT}\right)}{W_F \rho_{O_2}}$$

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

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:
$$Y_F = \frac{\nu_F \rho F \rho_{F} (T - T_b) + Y_{F,b}}{Q}$$
$$Y_{O_2} = \frac{\nu_{O_2} \rho_{O_2} \rho_{O_2} (T - T_b) + Y_{O_2,b}}{Q}$$
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:
  \[ \rho \frac{D}{Dx} \rho \frac{dV}{dx} \Rightarrow \rho \frac{d}{dx} \left( \rho \frac{dL}{dx} \right) \]

- 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:
  \[ \rho \frac{D}{Dx} \rho \frac{dV}{dx} \Rightarrow \rho \frac{d}{dx} \left( \rho \frac{dL}{dx} \right) \]

Thermal Flame Theory

- Only one differential equation. Temperature equation in $x$-direction
  \[ \frac{d}{dx} \left( \frac{\lambda}{c_p} \frac{dT}{dx} \right) - \frac{Q}{c_p} \omega \]

- 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

- Preheat zone assumption yields
  \[ \rho \frac{d}{dx} \left( \lambda \frac{dT}{dx} \right) - \frac{Q}{c_p} \omega \]

- Integration of the simplified differential equation in the preheat zone $x = -\infty$

- For the first derivative, with boundary conditions at $x = -\infty$

\[ \frac{dT}{dx} = \frac{\Delta H}{\lambda} (T - T_u) \]

At $x = -\infty$:
\[ \frac{d}{dx} \left( \frac{\lambda}{c_p} \frac{dT}{dx} \right) = \frac{\Delta H}{\lambda} \frac{d}{dx} (T - T_u) \]

Thermal Flame Theory

- Reaction zone assumption yields
  \[ \frac{d}{dx} \left( \frac{\lambda}{c_p} \frac{dT}{dx} \right) - \frac{Q}{c_p} \omega \]

- Heat conduction term can be substituted by

\[ \frac{d}{dx} \left( \frac{\lambda}{c_p} \frac{dT}{dx} \right) = \frac{d}{dx} \left( \frac{\lambda}{c_p} \frac{dT}{dx} \right) = c_p \frac{d}{dx} \left( \frac{\lambda}{c_p} \frac{dT}{dx} \right) \]

- The differential equation then becomes

\[ \frac{d}{dx} \left( \frac{\lambda}{c_p} \frac{dT}{dx} \right) = \frac{(-\Delta H)\lambda}{c_p} \frac{d}{dx} (T - T_u) \]
Thermal Flame Theory

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

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

At \( x = x_i \):

\[
\frac{dT^R}{dx}_{x_i} = \frac{2(-\Delta H)}{\lambda^2} \int_{T_i}^{T_n} \lambda w(T) dT.
\]

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

\[
\frac{dT^V}{dx}_{x_i} = \frac{dT^R}{dx}_{x_i},
\]

- 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

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

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

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

\( \square \) Even for high \( E/(RT_b^2) \) order of magnitude is one

- In the reaction zone: material properties assumed constant

- Reaction becomes

\[
\omega = B \rho Y_b \exp \left( \frac{E}{RT_b} \right) \exp \left( -\frac{E}{RT_b} \right) \left[ \Theta + \right. \frac{\nu T^2}{\Delta H} \left. \left( 1 - \Theta + \Theta^2 \right) \exp \Theta \right]
\]

\( \int_{T_i}^{T_n} \lambda w(T) dT = \lambda w(T) \text{d}T \int_{T_i}^{T_n} \lambda w(T) dT \)

\[
= \frac{\lambda w(T) M_O}{\Delta H} \exp \left( \frac{E}{RT_b} \right) \left[ \frac{\nu T^2}{\Delta H} + \frac{\nu T^2}{\Delta H} \left( 1 - \Theta + \Theta^2 \right) \exp \Theta \right]
\]
**Thermal Flame Theory**

- **Integral:**
  \[
  \int_{T_i}^{T_b} \frac{\lambda \omega dT}{T} = \frac{\lambda R T^2}{E} \int_{\Theta_i}^{\Theta_b} \omega(\Theta) d\Theta
  \]
  \[
  = \frac{\lambda R T^2}{E} \exp \left( \frac{E}{R T_b} \right) \left[ \left( \frac{v_1 Y_{O_2,b}}{M_{O_2}} + \frac{v_2 Y_{E,b}}{M_p} \right) (1 + (\Theta - 1) \exp(\Theta)) + 2 \frac{v_2 Y_{O_2,b} R T^2}{(\Delta H) E} \left( 1 - \frac{1}{2} \Theta + \Theta^2 \right) \exp(\Theta) \right]
  \]

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

- **Substitution of \( \Theta \) by \( \Theta_i \) in integration limits

  → Assumption: Reaction zone also valid in the preheat zone

**Thermal Flame Theory**

- **Equating the expressions**

  \[
  \frac{dT}{dx}^V = \frac{c_p \rho S_k}{\lambda_b} (T_b - T_a)
  \]

  \[
  \left. \frac{dT}{dx} \right|_{x_i}^{T_b} = \frac{\left( -\Delta H \right)}{\lambda_b} \int_{T_i}^{T_b} \lambda w(T) dT
  \]

  leads to

  \[
  \phi_{hL} = \frac{1}{2 c_p \rho S_k} \frac{\left( -\Delta H \right)}{\lambda_b} \int_{T_i}^{T_b} \lambda w(T) dT
  \]

  with

  \[
  S = \frac{\gamma_1 Y_{O_2,b}}{M_{O_2}} + \frac{\gamma_2 Y_{E,b}}{M_p} + 2 \frac{\gamma_2 Y_{O_2,b} R T^2}{(\Delta H) E}
  \]

  → **S-Term depends on equivalence ratio \( \phi \)**
  - Lean mixture → \( Y_{E,b} \approx 0 \)
  - Rich mixture → \( Y_{O_2,b} \approx 0 \)
  - Stoichiometric mixture → \( Y_{O_2,b} \approx Y_{E,b} \approx 0 \)
  → **Approximation**
  \[
  S = \frac{\gamma_2 Y_{O_2,b} R T^2}{(\Delta H) E} \text{ for } \phi < 1
  \]
  \[
  S = \frac{\gamma_2 Y_{O_2,b} R T^2}{(\Delta H) E} \text{ for } \phi > 1
  \]
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

Part II: Thermochemical Flame Structure
- Thermal flame theory
- Flame thickness and flame time
- Burning velocity s_f: Eigenvalue, results from solution of one-dimensional balance equation
- Assumptions:
  - One step reaction → Only one chemical time scale
  - Le = 1, thermal diffusivity \( a = \lambda / (\rho c_p) \) equal to mass diffusivity D
  - Use analytic solution to determine relevant time and length scales

Diffusivity and Chemical Time Scale
- Chemical time scale:
  \( t_c = \frac{\rho_0 E^2(T_h - T_a)^2}{2B \rho_0 (RT_h^2)^2 S \exp\left(\frac{E}{RT_h}\right)} \)
  For lean mixtures
- Time scale of global reaction: \( \nu_B B + \nu_O O_2 \rightarrow \text{Produkte} \)
- Square of Zeldovich-Number appears \( Z = \frac{E(T_h - T_a)}{RT_h^2} \)
  \( Z \) is order 10
  \( t_c \) determined not only by chemistry, but also by flame structure

Flame Time \( t_F \)
- Time, during which the flame front moves by one flame thickness
- Comparison:
  \( \frac{t_F}{s_L} = \frac{D}{s_L} = \frac{\lambda_h}{c_D \rho a s_L} \)
- \( t_c = \frac{D}{s_L} \)
  \( t_F = \frac{t_c}{s_L} = t_F \)
Flame Thickness

- Definition of flame thickness: \[ l_F = \frac{D}{\dot{s}_L} = \frac{\lambda_b}{c_p \rho_b s^*_L} \]

- 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

  ![Graphical determination of flame thickness](image)

- From analysis
  - Replace LHS of \( \frac{dT}{dx} = \frac{c_p \rho_b s^*_L}{\lambda} (T - T_u) \)
  - \( (T_b - T_u)/l_F \)
  - and evaluate RHS at \( T = T_b \) yields \( l_F = \frac{\lambda_b}{c_p \rho_b s^*_L} \)

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

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

Understanding Combustion Chemistry

- Initiation reaction (Production of chain carriers from stable components)
  \[ CH_4 + M \rightarrow CH_3^* + H^0 + M \quad \text{oder} \quad H_2 + O_2 \rightarrow OH^0 + OH^\circ \]

- Chain propagation reaction (No change in number of radicals)
  \[ CH_4 + H^0 \rightarrow CH_3^* + H_2 \]

- Chain branching reaction (Increase in number of radicals)
  \[ H_2 + O^\circ \rightarrow OH^0 + H^0 \]

- Chain breaking reaction (Decrease in number of radicals)
  \[ H^0 + H^0 + M \rightarrow H_2 + M \quad \text{oder} \quad H^0 + O^\circ + M \rightarrow OH^0 + M \]
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 \( \text{H}, \text{OH}, \text{O} \), and for radical-poor situations also \( \text{HO}_2 \)

One more rule:
6. \( \text{O} \)-radical counts twice! Reason: Fast Shuffle Reactions

Chemical mechanism for methane oxidation

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Reaktion</th>
<th>( \beta )</th>
<th>( n )</th>
<th>( E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3</td>
<td>( 1 \text{ H}_2\text{O}_2 )-Bildung und -Verbrauch</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>( \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 )</td>
<td>2.50E+11</td>
<td>0,00</td>
<td>-5,30</td>
</tr>
<tr>
<td>12</td>
<td>( \text{OH} + \text{O}^+ \rightarrow \text{HO}_2 + \text{M}^- )</td>
<td>3.25E+22</td>
<td>-2,00</td>
<td>0,00</td>
</tr>
<tr>
<td>13</td>
<td>( \text{H}_2\text{O}_2 + \text{M}^- \rightarrow \text{OH}^+ + \text{OH}^- + \text{M}^0 )</td>
<td>1.68E+24</td>
<td>-2,00</td>
<td>202,29</td>
</tr>
<tr>
<td>14</td>
<td>( \text{HO}_2 + \text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{M}^- )</td>
<td>1.05E+13</td>
<td>0,00</td>
<td>15,00</td>
</tr>
<tr>
<td>146</td>
<td>( \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{M}^- )</td>
<td>1.15E+12</td>
<td>0,00</td>
<td>85,88</td>
</tr>
<tr>
<td>1.4</td>
<td>( \text{H}^+ + \text{H}^+ + \text{M}^- \rightarrow \text{H}_2 + \text{O}_2^- )</td>
<td>1.80E+19</td>
<td>-1,00</td>
<td>0,00</td>
</tr>
<tr>
<td>16</td>
<td>( \text{OH}^- + \text{H}^+ + \text{M}^- \rightarrow \text{H}_2\text{O} + \text{M}^0 )</td>
<td>2.70E+22</td>
<td>-3,00</td>
<td>0,00</td>
</tr>
<tr>
<td>17</td>
<td>( \text{O}^- + \text{O}^- + \text{M}^- \rightarrow \text{O}_2 + \text{M}^0 )</td>
<td>2.50E+17</td>
<td>-1,00</td>
<td>0,00</td>
</tr>
</tbody>
</table>

Chemical mechanism for methane oxidation

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Reaktion</th>
<th>( \beta )</th>
<th>( n )</th>
<th>( E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.1</td>
<td>( 2 \text{ H}_2\text{O}_2 )-Kettenreaktionen</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>( \text{H}^+ + \text{O}_2 \rightarrow \text{OH} + \text{O} )</td>
<td>2.00E+14</td>
<td>0,00</td>
<td>75,30</td>
</tr>
<tr>
<td>18</td>
<td>( \text{OH}^- + \text{O}_2 \rightarrow \text{O}_2^- + \text{H} )</td>
<td>1.56E+13</td>
<td>0,00</td>
<td>3,52</td>
</tr>
<tr>
<td>27</td>
<td>( \text{O}^+ + \text{H}_2 \rightarrow \text{OH} + \text{H}^- )</td>
<td>5.00E+04</td>
<td>2,07</td>
<td>26,30</td>
</tr>
<tr>
<td>26</td>
<td>( \text{OH}^- + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{O} )</td>
<td>2.22E+04</td>
<td>2,07</td>
<td>18,29</td>
</tr>
<tr>
<td>37</td>
<td>( \text{OH}^- + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}^- )</td>
<td>1.00E+08</td>
<td>1,60</td>
<td>13,80</td>
</tr>
<tr>
<td>35</td>
<td>( \text{H}_2\text{O} + \text{H}^- \rightarrow \text{H}_2\text{O}_2^- + \text{H} )</td>
<td>4.31E+08</td>
<td>1,60</td>
<td>78,46</td>
</tr>
<tr>
<td>44</td>
<td>( \text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O} )</td>
<td>1.50E+09</td>
<td>1,14</td>
<td>0,42</td>
</tr>
<tr>
<td>45</td>
<td>( \text{H}_2\text{O} + \text{O}^+ \rightarrow \text{H}_2\text{O}_2 + \text{O} )</td>
<td>1.47E+10</td>
<td>1,14</td>
<td>71,09</td>
</tr>
</tbody>
</table>

Chemical mechanism for methane oxidation

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Reaktion</th>
<th>( \beta )</th>
<th>( n )</th>
<th>( E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.2</td>
<td>( 2 \text{ HO}_2 )-Bildung und -Verbrauch</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>( \text{H}^+ + \text{O}_2 + \text{M}^- \rightarrow \text{HO}_2 + \text{M}^- )</td>
<td>2.30E+18</td>
<td>-0,80</td>
<td>0,00</td>
</tr>
<tr>
<td>58</td>
<td>( \text{HO}_2 + \text{M}^- \rightarrow \text{H}^+ + \text{O}^- + \text{M}^0 )</td>
<td>3.10E+18</td>
<td>-0,80</td>
<td>195,39</td>
</tr>
<tr>
<td>6</td>
<td>( \text{H}^+ + \text{HO}_2 \rightarrow \text{O}^- + \text{H}_2\text{O} + \text{M}^- )</td>
<td>1.50E+14</td>
<td>0,00</td>
<td>4,70</td>
</tr>
<tr>
<td>7</td>
<td>( \text{HO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 )</td>
<td>2.50E+13</td>
<td>0,00</td>
<td>2,90</td>
</tr>
<tr>
<td>8</td>
<td>( \text{OH}^- + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 )</td>
<td>6.00E+13</td>
<td>0,00</td>
<td>0,00</td>
</tr>
<tr>
<td>9</td>
<td>( \text{HO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 )</td>
<td>3.00E+13</td>
<td>0,00</td>
<td>7,20</td>
</tr>
<tr>
<td>10</td>
<td>( \text{HO}_2 + \text{O}^- \rightarrow \text{H}_2\text{O} + \text{O} )</td>
<td>1.80E+13</td>
<td>0,00</td>
<td>1,70</td>
</tr>
</tbody>
</table>

Chemical mechanism for methane oxidation

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Reaktion</th>
<th>( \beta )</th>
<th>( n )</th>
<th>( E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.1</td>
<td>( \text{CO}/\text{CO}_2 )-Mechanismen</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>187</td>
<td>( \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} )</td>
<td>4.40E+06</td>
<td>1,50</td>
<td>-3,10</td>
</tr>
<tr>
<td>186</td>
<td>( \text{CO} + \text{H}_2 \rightarrow \text{CO}_2 + \text{H} )</td>
<td>4.05E+08</td>
<td>1,50</td>
<td>89,76</td>
</tr>
<tr>
<td>19</td>
<td>( \text{CH}_2 + \text{O} \rightarrow \text{CHO} + \text{O} )</td>
<td>3.00E+13</td>
<td>0,00</td>
<td>0,00</td>
</tr>
<tr>
<td>20</td>
<td>( \text{CO}_2 + \text{CH} \rightarrow \text{CH}_2 + \text{O} )</td>
<td>3.40E+12</td>
<td>0,00</td>
<td>2,90</td>
</tr>
<tr>
<td>13.2</td>
<td>( \text{CHO}^- )-Verbrauch</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>( \text{CHO}^- + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} )</td>
<td>2.00E+14</td>
<td>0,00</td>
<td>0,00</td>
</tr>
<tr>
<td>22</td>
<td>( \text{CHO}^- + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} )</td>
<td>1.00E+14</td>
<td>0,00</td>
<td>0,00</td>
</tr>
<tr>
<td>23</td>
<td>( \text{CHO}^- + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2 )</td>
<td>3.00E+12</td>
<td>0,00</td>
<td>0,00</td>
</tr>
<tr>
<td>24</td>
<td>( \text{CHO}^- + \text{M}^- \rightarrow \text{CO} + \text{M}^- )</td>
<td>7.10E+14</td>
<td>0,00</td>
<td>70,30</td>
</tr>
<tr>
<td>245</td>
<td>( \text{CO} + \text{H}_2 \rightarrow \text{CHO} + \text{M}^- )</td>
<td>1.13E+15</td>
<td>0,00</td>
<td>9,97</td>
</tr>
</tbody>
</table>
### Chemical mechanism for methane oxidation

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Reaktion</th>
<th>$n$</th>
<th>$\beta$</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25/1</td>
<td>$\text{CH}_4 + \text{O}^\circ$ $\rightarrow$ $\text{CH}_3 + \text{H}_2$</td>
<td>6,40E+09</td>
<td>1,50</td>
<td>1,40</td>
</tr>
<tr>
<td>25/2</td>
<td>$\text{CH}_4 + \text{H}_2$ $\rightarrow$ $\text{CH}_3 + \text{H}_2$</td>
<td>5,83E+09</td>
<td>1,50</td>
<td>13,08</td>
</tr>
<tr>
<td>26/1</td>
<td>$\text{CH}_4 + \text{O}^\circ$ $\rightarrow$ $\text{CO} + \text{H}_2$</td>
<td>8,00E+13</td>
<td>0,00</td>
<td>3,00</td>
</tr>
<tr>
<td>26/2</td>
<td>$\text{CH}_4 + \text{O}^\circ$ $\rightarrow$ $\text{CO} + \text{H}_2$</td>
<td>6,50E+12</td>
<td>0,00</td>
<td>6,30</td>
</tr>
</tbody>
</table>

### Chemical mechanism for methane oxidation

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Reaktion</th>
<th>$n$</th>
<th>$\beta$</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>33/1</td>
<td>$\text{CH}_4 + \text{H}_2$ $\rightarrow$ $\text{CH}_3 + \text{H}_2$</td>
<td>1,83E+14</td>
<td>0,00</td>
<td>63,00</td>
</tr>
<tr>
<td>34/1</td>
<td>$\text{CH}_4 + \text{H}_2$ $\rightarrow$ $\text{CH}_3 + \text{H}_2$</td>
<td>3,65E+13</td>
<td>0,00</td>
<td>44,33</td>
</tr>
<tr>
<td>35/1</td>
<td>$\text{CH}_4 + \text{H}_2$ $\rightarrow$ $\text{CH}_3 + \text{H}_2$</td>
<td>2,12E+14</td>
<td>0,00</td>
<td>63,00</td>
</tr>
<tr>
<td>36/1</td>
<td>$\text{CH}_4 + \text{H}_2$ $\rightarrow$ $\text{CH}_3 + \text{H}_2$</td>
<td>6,29E+13</td>
<td>-1,00</td>
<td>0,00</td>
</tr>
<tr>
<td>37/1</td>
<td>$\text{CH}_4 + \text{H}_2$ $\rightarrow$ $\text{CH}_3 + \text{H}_2$</td>
<td>7,00E+13</td>
<td>0,00</td>
<td>63,00</td>
</tr>
<tr>
<td>38/1</td>
<td>$\text{CH}_4 + \text{H}_2$ $\rightarrow$ $\text{CH}_3 + \text{H}_2$</td>
<td>3,61E+13</td>
<td>0,00</td>
<td>44,33</td>
</tr>
</tbody>
</table>

### Chemical mechanism for methane oxidation

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Reaktion</th>
<th>$n$</th>
<th>$\beta$</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>43/1</td>
<td>$\text{CH}_4 + \text{H}_2$ $\rightarrow$ $\text{CH}_3 + \text{H}_2$</td>
<td>1,10E+13</td>
<td>0,00</td>
<td>17,00</td>
</tr>
<tr>
<td>44/1</td>
<td>$\text{CH}_4 + \text{H}_2$ $\rightarrow$ $\text{CH}_3 + \text{H}_2$</td>
<td>5,27E+13</td>
<td>0,00</td>
<td>31,99</td>
</tr>
</tbody>
</table>

### Chemical mechanism for methane oxidation

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Reaktion</th>
<th>$n$</th>
<th>$\beta$</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>49/1</td>
<td>$\text{CH}_4 + \text{H}_2$ $\rightarrow$ $\text{CH}_3 + \text{H}_2$</td>
<td>3,00E+13</td>
<td>0,00</td>
<td>0,00</td>
</tr>
<tr>
<td>50/1</td>
<td>$\text{CH}_4 + \text{H}_2$ $\rightarrow$ $\text{CH}_3 + \text{H}_2$</td>
<td>5,40E+11</td>
<td>0,00</td>
<td>0,00</td>
</tr>
<tr>
<td>51/1</td>
<td>$\text{CH}_4 + \text{H}_2$ $\rightarrow$ $\text{CH}_3 + \text{H}_2$</td>
<td>2,00E+14</td>
<td>0,00</td>
<td>1,00</td>
</tr>
<tr>
<td>52/1</td>
<td>$\text{CH}_4 + \text{H}_2$ $\rightarrow$ $\text{CH}_3 + \text{H}_2$</td>
<td>1,05E+14</td>
<td>0,00</td>
<td>3,39</td>
</tr>
</tbody>
</table>
### Chemical mechanism for methane oxidation

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Reaktion</th>
<th>( B ) in mol cm(^{-3}) s</th>
<th>( n )</th>
<th>( E ) in kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.7 C(_2)H(_5)-Verbrauch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>C(_2)H(_5) + H(_2) \rightarrow C(_2)H(_4) + H(_3) &amp; 5.400E+02 &amp; 3.50 &amp; 21.80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>C(_2)H(_6) + O(_2) \rightarrow C(_2)H(_5) + OH(_2) &amp; 3.000E+07 &amp; 2.00 &amp; 21.40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>61</td>
<td>C(_2)H(_4) + OH(_2) \rightarrow C(_2)H(_3) + H(_2)O &amp; 6.300E+06 &amp; 2.00 &amp; 27.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.1 C(_2)H(_5)-Verbrauch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>62</td>
<td>C(_2)H(_5) + O(_2) \rightarrow CH(_2)O + CH(_3)O &amp; 6.000E+12 &amp; 0.00 &amp; 0.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>63</td>
<td>C(_2)H(_5) + O(_2) \rightarrow C(_2)H(_4) + CO &amp; 3.800E+13 &amp; 0.00 &amp; 0.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>64</td>
<td>C(_2)H(_5) + OH \rightarrow C(_2)H(_4) + H(_2)O &amp; 5.000E+14 &amp; 0.00 &amp; 370.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>C(_2)H(_5) + OH \rightarrow C(_2)H(_4) + HO &amp; 1.700E+13 &amp; 0.00 &amp; 19.88</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.2 C(_2)H(_5)-Verbrauch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>66</td>
<td>C(_2)H(_4) + O(_2) \rightarrow C(_2)H(_3) + CH(_2)O &amp; 1.000E+12 &amp; 0.00 &amp; 0.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>67</td>
<td>C(_2)H(_4) + O(_2) \rightarrow C(_2)H(_3) + CH(_3)O &amp; 1.000E+12 &amp; 0.00 &amp; 0.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>C(_2)H(_4) + OH \rightarrow C(_2)H(_3) + H(_2)O &amp; 1.000E+12 &amp; 0.00 &amp; 0.00</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ C_{H_2} = 6.5C_{CH_4} + 6.5C_{C_2H_4} + 1.5C_{CO_2} + 0.75C_{CO} + 0.4C_{O_2} + 0.4C_H + 1.0C_{H_2} \]

### Flame structure from multi-step chemical kinetics

- Structure of an unstretched premixed methane/air flame at standard conditions from numerical simulations
Flame structure from multi-step chemical kinetics

- 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.

The Four-Step Model for Methane-Air Flames

- Systematically reduced mechanism using quasi steady state approximations.

- Non steady state components
  - Stable components $\text{CH}_4, \text{O}_2, \text{H}_2\text{O}, \text{CO}_2, \text{H}_2, \text{CO}$
  - $H^-$-radical
    - Representing effect of radicals on flame structure
    - Competition between chain branching and chain breaking
    - Typically H-radical because of its importance in main radical reactions

$$
\begin{align*}
1f & : H^o + O_2 \rightarrow OH^o + O^o \\
5f & : H^o + O_2 + M' \rightarrow HO_2 + M'
\end{align*}
$$

The cross-over (inner layer) temperature

- Most important chain branching and chain breaking reactions hydrogen and hydrocarbon combustion:
  - $1f: H^o + O_2 \rightarrow OH^o + O^o$
  - $5f: H^o + O_2 + M' \rightarrow HO_2 + M'$

- Competition of $1f$ and $5f$ leads to

$$
\frac{\omega_1}{\omega_5} = \frac{k_2 C_O C_{H}}{k_2 C_O C_{H} C_M} = \frac{k_2}{k_5 C_M}
$$

Cross-over temperature $T^0$ (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

$$
\begin{align*}
1 & : H^o + O_2 \rightarrow OH^o + O^o \\
2 & : O^o + H_2 \rightarrow OH^o + H^o \\
3 & : OH^o + H_2 \rightarrow H_2O + H^o
\end{align*}
$$

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

$$
\begin{align*}
5 & : H^o + O_2 + M \rightarrow HO_2 + M \\
7 & : H^o + HO_2 \rightarrow H_2 + O_2 \\
\end{align*}
$$
The Four-Step Model for Methane-Air Flames

- **Global reaction I** with the rate of reaction 38f describes fuel consumption
  
  \[
  \begin{align*}
  38f : & \quad CH_4 + H^+ \rightarrow CH_3 + H_2 \\
  35 : & \quad CH_3 + O^+ \rightarrow CH_2O + H^+ \\
  29 : & \quad CH_2O + H^+ \rightarrow CHO^+ + H_2 \\
  24f : & \quad CHO^+ + M \rightarrow CO + H^+ + M \\
  26 : & \quad H^+ + OH^- \rightarrow O^- + H_2 \\
  36 : & \quad H^+ + H_2O \rightarrow OH^- + H_2 
  \end{align*}
  \]

  \[ T : \quad CH_4 + 2H^+ + H_2O \rightarrow CO + 4H_2. \]

- Radical consuming because of CH₃ consumption reaction

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

  \[
  \begin{align*}
  18f : & \quad CO + OH^- \rightarrow CO_2 + H^+ \\
  36 : & \quad H_2O + H^+ \rightarrow H_2 + OH^- \\
  II : & \quad CO + H_2O \rightarrow CO_2 + H_2 
  \end{align*}
  \]

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

  \[ 2 \: O + H_2 \rightarrow OH + H \]
  \[ 3 \: OH + H_2 \rightarrow H_2O + H \]

  \[
  \begin{align*}
  [O] &= \frac{[H][OH]}{K_2[H_2]} \\
  [OH] &= \frac{[H_2O][H]}{K_3[H_2]} 
  \end{align*}
  \]

  where \( K_2 \) and \( K_3 \) are the equilibrium constants of reactions 2 and 3, respectively.

---

The Four-Step Model for Methane-Air Flames

- Four-step model for methane flames is in summary

  - Principal rates governing global reactions are

    \[
    \begin{align*}
    \omega_I &= \omega_{11}, \quad \omega_{II} = \omega_{19} \\
    \omega_{III} &= \omega_{25}, \quad \omega_{IV} = \omega_{11}
    \end{align*}
    \]

  - These correspond to elementary reactions

    \[
    \begin{align*}
    11 & \quad CH_4 + H \rightarrow CH_3 + H_2 \\
    9 & \quad CO + OH \rightarrow CO_2 + H \\
    5 & \quad H + O_2 + M \rightarrow HO_2 + M \\
    1 & \quad H + O_2 \rightarrow OH + O
    \end{align*}
    \]

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

    \[
    \begin{align*}
    \omega_I &= \kappa_{11}[CH_4][H] \\
    \omega_{II} &= \kappa_{25} \frac{[M]}{K_3[H_2]} \left( [CO][H_2O] - \frac{1}{K_{II}} [CO_2][H_2] \right) \\
    \omega_{III} &= \kappa_{25} [H][O_2][M] \\
    \omega_{IV} &= \kappa_{25} \frac{[H]}{[H_2]^3} \left( [O_2][H_2O]^3 - \frac{1}{K_{IV}} [H]^2[H_2O]^2 \right)
    \end{align*}
    \]

  - Equilibrium constants are given as:

    \[
    \begin{align*}
    K_3 &= 0.216 \ exp(7658/T) \\
    K_{II} &= 0.035 \ exp(3652/T) \\
    K_{IV} &= 1.48 \ exp(6133/T).
    \end{align*}
    \]
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 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
  
  \[
  \begin{align*}
  \text{I} & : \text{CH}_4 + 2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 4\text{H}_2 \\
  \text{II} & : \text{CO} + \text{H}_2 \rightleftharpoons \text{CO}_2 + \text{H}_2 \\
  \text{III} & : \text{H} + \text{H} + \text{M} \rightleftharpoons \text{H}_2 + \text{M} \\
  \text{IV} & : \text{O}_2 + 3\text{H}_2 \rightleftharpoons 2\text{H} + 2\text{H}_2\text{O}
  \end{align*}
  \]

- Adding reaction IV to I and III leads to the three steps
  
  \[
  \begin{align*}
  \text{I'} & : \text{CH}_4 + \text{O}_2 = \text{CO} + \text{H}_2 + \text{H}_2\text{O} \\
  \text{II'} & : \text{CO} + \text{H}_2 = \text{CO}_2 + \text{H}_2 \\
  \text{III'} & : \text{O}_2 + 2\text{H}_2 = 2\text{H}_2\text{O}
  \end{align*}
  \]

- Determine [H] from the steady state equation for H
- Taking H balance in four-step mechanism and setting H steady state leads to

  \[
  L(\Pi) = -\omega_1 - \omega_{\Pi II} + \omega_{IV} = 0
  \]

  This leads to

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

  where \([H_{eq}]\) based on partial equilibrium of reaction IV

  \[
  [H_{eq}] = k_{IV}^{-1/2}[\text{O}_2]^{1/2}[\text{H}_2]^{3/2}/[\text{H}_2\text{O}].
  \]

- The equation

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

  has three interesting consequences

  1. At temperatures above 1400 K, second term in brackets small while ratio \(k_{11} / k_1 \gg 1 \)
     \(\Rightarrow \) \([\text{CH}_2]/[\text{O}_2]\) must be much smaller than unity, if [H] is to remain real

  2. Equation cannot be valid in the preheat zone where second term is large

  3. It also follows that [H] vanishes in the preheat zone, which is therefore chemically inert
Flame Structure based on the four-step mechanism

Course Overview

Part I: Fundamentals and Laminar Flames
- Introduction
- Fundamentals and mass balances of combustion systems
- 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 Asymptotic Structure of Stoichiometric Methane-Air Flames

Asymptotic Analysis based on Two-Step Mechanism
- Further simplification couples CO and $H_2$
  leading to two-step mechanism
  \[ I' \quad CH_4 + O_2 = \frac{1}{2}(H_2 + nCO) + \frac{3}{2}H_2O + \frac{1}{2}CO_2 \]
  \[ III' \quad O_2 + \frac{1}{2}(H_2 + nCO) = \frac{1}{2}H_2O + \frac{1}{2}CO_2 \]
- It contains three layers
  1. A chemically inert preheat zone of order $I'$ upstream
  2. A thin inner layer of order $d$ in which the fuel is consumed and the intermediates $H_2$ and CO are formed according to the global step $I''$
  3. A thin oxidation layer of order $e$ downstream where $H_2$ and CO are oxidized according to global step $III''$

*Details of the Asymptotic Analysis*

- At first the inner layer shall be analyzed
  - We will denote quantities at the inner layer with a subscript $0$ but the inner layer temperature as $T_0$
  - In this layer all concentrations except that of the fuel, which is depleted, may be assumed constant to leading order
**Details of the Asymptotic Analysis**

- **Introducing**
  
  \[ [H] = [H_{eq}] \]

  into

  \[ \omega_1 = k_{11}[\text{CH}_4][H] \]

  leads to

  \[ \omega_1 = D_{\omega 1} x_{\text{CH}_4} \left(1 - \frac{x_{\text{CH}_4}}{\delta} \right)^{1/2} \]

  where the Damköhler number is

  \[ D_{\omega 1} = \frac{\rho^2 Y_{\text{CH}_4} \lambda_0 \left(K_{IV} X_{\text{O}_2} X_{\text{H}_2} \right)^{1/2}}{\rho^2 x_{\text{H}_2} \gamma_0 X_{\text{H}_2} Lc \text{CH}_4 k_{11}(T^0)} \]

**Details of the Asymptotic Analysis**

- **The small parameter** \( \delta \) **was defined as**

  \[ \delta = \frac{k_1(T^0)X_{\text{O}_2}X_{\text{H}_2}}{k_{11}(T^0)Lc \text{CH}_4} \]

- **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** \( X_{\text{O}_2} \) **in the inner layer** \( X_{\text{O}_2} < 1 \), \( \delta \approx 0.1 \) **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**

  \[ \delta = \frac{k_1(T^0)X_{\text{O}_2}X_{\text{H}_2}}{k_{11}(T^0)Lc \text{CH}_4} \]

  \[ \omega_1 = D_{\omega 1} x_{\text{CH}_4} \left(1 - \frac{x_{\text{CH}_4}}{\delta} \right)^{1/2} \]

  the term in parenthesis that \( x_{\text{O}_2} \) **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** \( x_{\text{O}_2} \) **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**

  \[ \frac{d^2 y}{d\zeta^2} = -\omega_1 \]

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

  \[ \frac{d^2 y}{d\zeta^2} = (\delta^2 D_{\omega 1})y(1 - y)^{1/2} \].
The downstream boundary condition of this equation is

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

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

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

which leads to the expansion \( x_{CH_4} \approx -x \) around \( x = 0 \)

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

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

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

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

With the boundary conditions

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

and

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

the equation

\[ \frac{d^2y}{d\zeta^2} = (\delta^2Da_1)y(1-y)^{1/2} \]

can be integrated once to obtain the eigenvalue

\[ \delta^2Da_1 = \frac{15}{8} \]
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:

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

One may use the coupling relations:

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

$$\frac{\partial^2}{\partial z^2}[(1 + \alpha)\eta x_{H_2} + 2x_{CH_4} + x_{H_2}O] = 0,$$

$$\frac{\partial^2}{\partial z^2}[(1 + \alpha)\eta x_{CH_4} + x_{CO}] = 0,$$

$$\frac{\partial^2}{\partial z^2}[(1 + \alpha)\eta x_{H_2} + x_{H_2}O + x_{CH_4} + x_{CO} + 7] = 0$$

to show that the downstream boundary conditions are satisfied by:

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

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 $D_{III}$ and will finally determine the pressure dependence of the burning velocity.
**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

\[
\eta = \frac{2\alpha z}{c}
\]

- The downstream boundary condition of equation

\[
\frac{d^2z}{d\eta^2} = (e^4D_3M)^2 \eta
\]

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

\[
\frac{dx_{H_2}}{dx} \bigg|_{0-} - \frac{dx_{H_2}}{dx} \bigg|_{0+} = 1 + \alpha \left( \frac{dx_{H_2}}{dx} \bigg|_{0-} - \frac{dx_{H_2}}{dx} \bigg|_{0+} \right)
\]

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

\[
\frac{dx_{H_2}}{dx} \bigg|_{0-} < < \frac{dx_{H_2}}{dx} \bigg|_{0+}
\]

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

that the upstream boundary condition of

\[
\frac{d^2z}{d\eta^2} = (e^4D_3M)^2 \eta
\]

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 \( \eta_0 = 2^{1/4} \) at \( \eta = 0 \)

**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

\[
\frac{dx_{H_2}}{dx} \bigg|_{0-} - \frac{dx_{H_2}}{dx} \bigg|_{0+} = 1 + \alpha \left( \frac{dx_{H_2}}{dx} \bigg|_{0-} - \frac{dx_{H_2}}{dx} \bigg|_{0+} \right)
\]

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 \( \eta = \zeta \)

may now be used in

\[
\dot{r}_{H_2} = \frac{e x}{(1 + \alpha) \phi}
\]

and

\[
\omega_{\text{III}} = 2\eta D_{\text{III}} z^3
\]

to determine the quantities required in

\[
D_{\text{II}} = \frac{\rho_0}{\rho_0^{1/2}} \frac{Y_{\text{CH}_4} n_0}{w_{\text{CH}_4} n_{0_0}} \frac{(K_{\text{IV}} \lambda_{\text{O}_2})^{1/2}}{X_{\text{H}_2}} L_{\text{CH}_4} k_{11}(T_0)
\]

and thereby the burning velocity \( s_L \)

---

**An Analytic Expression for the Burning Velocity**

- By dividing

\[
D_{\text{II}} = \frac{\rho_0^{1/2} Y_{\text{CH}_4} n_0}{\rho_0^{1/2} W_{\text{CH}_4} n_{0_0}} \frac{(K_{\text{IV}} \lambda_{\text{O}_2})^{1/2}}{X_{\text{H}_2}} L_{\text{CH}_4} k_{11}(T_0)
\]

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

\[
\frac{k^2(T_0)}{k_{11}(T_0) k_0(T_0) / (K/10^0)} = 1.5 \frac{L_{\text{CH}_4}}{L_{\text{O}_2}}
\]

- 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**

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

\[
k_0^2 = \frac{8}{15 k_{11} q^2 X_{\text{H}_2} W_{\text{CH}_4} n_{0_0}} \frac{L_{\text{CH}_4}^2 L_{\text{O}_2}^2}{L_{\text{CH}_4}^2} (1 + \alpha_0) \frac{K_{\text{IV}}(T_0)}{1/2 \sqrt{2} (T_b - T_0) \sqrt{2} (T_b - T_0)}
\]

where

\[
z_0 = 2^{1/4} \at \eta = 0 \quad \omega_{\text{III}} = 2\eta D_{\text{III}} z^3
\]

were used to relate \( \zeta \) to the difference between \( T_b \) and \( T_0 \)

\[
\zeta = \frac{T_b - T_0}{T_b - T_0}
\]
Results of the Asymptotic Analysis

- Asymptotic Analysis leads to analytic expression for laminar burning velocity

\[
\tilde{s}_L = \frac{8}{15} \frac{k_1^2}{k_1(T_0)} \frac{1}{Y_{\text{CH}_4}} \frac{1}{1 + \alpha_0} \frac{1}{1 + \alpha_0} K_{\text{CH}_4}(T_0) \left( \frac{T_b - T_0}{T_0} \right)^4 \frac{1}{T_0} \left( \frac{T_b}{T_0} - 1 \right)^3
\]

- Pressure obtained from

\[
k_1(T_0) \frac{k_1(T_0)}{k_1(T_0)} E(T) = 1.5 Y_{\text{CH}_4} L_{\text{LO}}
\]

- Undiluted stoichiometric methane flame with
  - \( T_0 = 300 \text{ K} \)
  - \( p = 1 \text{ atm} \)

  \( s_L = 54 \text{ cm/s} \)

- Further consequence of equation

\[
\tilde{s}_L = \frac{8}{15} \frac{k_1^2}{k_1(T_0)} \frac{1}{Y_{\text{CH}_4}} \frac{1}{1 + \alpha_0} \frac{1}{1 + \alpha_0} K_{\text{CH}_4}(T_0) \left( \frac{T_b - T_0}{T_0} \right)^4 \frac{1}{T_0} \left( \frac{T_b}{T_0} - 1 \right)^3
\]

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

\[ s_L = 54 \text{ cm/s} \]

Results of the Asymptotic Analysis

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

\[
\tilde{s}_L = \frac{8}{15} \frac{k_1^2}{k_1(T_0)} \frac{1}{Y_{\text{CH}_4}} \frac{1}{1 + \alpha_0} \frac{1}{1 + \alpha_0} K_{\text{CH}_4}(T_0) \left( \frac{T_b - T_0}{T_0} \right)^4 \frac{1}{T_0} \left( \frac{T_b}{T_0} - 1 \right)^3
\]

and

\[
\frac{k_1^2(T_0)}{k_1(T_0) E(T_0)} = 1.5 \rho Y_{\text{CH}_4} L_{\text{LO}}
\]

- Reaction:
  11. \( \text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2 \)
  9. \( \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \)
  5. \( \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \)
  1. \( \text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O} \)

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

- Using the burning velocity expression from the thermal flame theory

\[
\rho \tilde{s}_L = \frac{2 - B \rho k_1 T_b \rho R T_0^4}{\rho E(T_b) S} \exp \left( \frac{E}{R T_b} \right) S
\]

\[
S = \frac{\rho Y_{\text{CH}_4}}{M_{\text{CH}_4}} + \frac{\rho Y_{\text{O}_2}}{M_{\text{O}_2}} + 2 \frac{\rho Y_{\text{H}_2}}{M_{\text{H}_2}} \frac{R T_0^2}{(-\Delta H)}
\]

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

- Applying this form to burning velocity from 2-step mechanism
  \[
  s^2 = \frac{8 \lambda_0}{15 k_{11} \sigma} \frac{T_0}{W_{CH_4}} \left( \frac{1}{\varepsilon_0} - 1 \right) \frac{1}{\lambda_{CH_4} \sigma} \left( 1 + 2 \right) \left( \frac{T_0}{T_b} \right) \left( \frac{T_b}{T_0} \right)^4
  \]

  with \( T^0 \) fixed leads to
  \[
  \frac{d \ln s^2}{d \ln T_b} = \frac{4 T_b}{T_b - T_0} - \frac{4 T_b}{T_0 - T_b}
  \]

- Since the second of the terms is much smaller then the first,
  \[
  s^2 = \frac{8 \lambda_0}{15 k_{11} \sigma} \frac{T_0}{W_{CH_4}} \left( \frac{1}{\varepsilon_0} - 1 \right) \frac{1}{\lambda_{CH_4} \sigma} \left( 1 + 2 \right) \left( \frac{T_0}{T_b} \right) \left( \frac{T_b}{T_0} \right)^4
  \]

  with \( T^0 \) fixed leads to
  \[
  \frac{d \ln s^2}{d \ln T_b} = \frac{4 T_b}{T_b - T_0} - \frac{4 T_b}{T_0 - T_b}
  \]

  Therefore the Zeldovich number introduced in the previous lecture may be expressed as
  \[
  Z_e = \frac{E(T_b - T_u)}{RT_b^2} = \frac{4}{\varepsilon_0}
  \]

Course Overview

Part I: Fundamentals and Laminar Flames
- 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

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

- 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
- 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

\[ s_L = \frac{Y_{CH_4} \lambda_0}{15 k_{\text{eff}} q H_2O W_{CH_4} \eta_0} \left( \frac{1}{T_0} \right)^{\frac{1}{a}} \frac{1}{\left( 1 + \alpha \theta \right)^n} \left( \frac{K_N}{T_0} \right)^{1/2} \frac{\left( T_b - T_0 \right)^4}{T_0^2} \left( T_b - T_a \right)^n \]

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

\[ s_L = Y_{CH_4} P_m A(T_0) \left( \frac{T_b}{T_0} \right)^{\frac{1}{n}} \left( T_b - T_0 \right)^n \]

with

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

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

Analytic Approximations of Burning Velocities for Lean Hydrocarbon Flames

- Data set of 197, 223, 252, 248, and 215 premixed flames for \( CH_4, C_2H_6, C_2H_4, C_2H_2 \) and \( C_3H_8 \), in the range between

  - \( p = 1 \) atm and 40 atm,
  - \( T_u \) between 298 K and 800 K
  - \( \phi = 0.4 \) and 1.0

<table>
<thead>
<tr>
<th>Brennstoff</th>
<th>( B ) [bar]</th>
<th>( E ) [k]</th>
<th>( F ) [cm/s]</th>
<th>( G ) [k]</th>
<th>( m )</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>3.1557 × 10⁸</td>
<td>23873.0</td>
<td>2.21760 × 10⁴</td>
<td>-6444.27</td>
<td>0.565175</td>
<td>2.5158</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>5.6834 × 10⁹</td>
<td>13444.4</td>
<td>3.77466 × 10⁴</td>
<td>1032.36</td>
<td>0.007619</td>
<td>2.5874</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>3.7036 × 10⁹</td>
<td>14368.7</td>
<td>9.07890 × 10⁴</td>
<td>263.23</td>
<td>0.771333</td>
<td>2.3998</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>4.3203 × 10⁹</td>
<td>18859.0</td>
<td>1.90041 × 10⁵</td>
<td>-506.97</td>
<td>0.431345</td>
<td>2.1804</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>2.2501 × 10⁹</td>
<td>17223.5</td>
<td>1.72489 × 10⁵</td>
<td>-1324.78</td>
<td>0.582214</td>
<td>2.3970</td>
</tr>
<tr>
<td>CH₂OH</td>
<td>2.1100 × 10⁹</td>
<td>17657.5</td>
<td>9.99057 × 10⁴</td>
<td>1088.85</td>
<td>0.91</td>
<td>2.263</td>
</tr>
<tr>
<td>i-C₂H₆</td>
<td>1.7000 × 10⁹</td>
<td>17508.0</td>
<td>7.95600 × 10⁴</td>
<td>912.00</td>
<td>0.52</td>
<td>2.30</td>
</tr>
<tr>
<td>n-C₂H₆</td>
<td>3.8600 × 10⁹</td>
<td>20906.0</td>
<td>2.92600 × 10⁴</td>
<td>-25.60</td>
<td>0.5578</td>
<td>2.5214</td>
</tr>
</tbody>
</table>

Analytic Approximations of Burning Velocities for Lean Hydrocarbon Flames

- Adiabatic flame temperature

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

<table>
<thead>
<tr>
<th>Brennstoff</th>
<th>( a )</th>
<th>( b [k] )</th>
<th>( c [k] )</th>
<th>( d [k] )</th>
<th>( e [k] )</th>
<th>( E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0.627</td>
<td>1270.15</td>
<td>-2449.9</td>
<td>6776</td>
<td>-3556</td>
<td>0.91</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>0.52</td>
<td>1646.0</td>
<td>-2965.0</td>
<td>8187</td>
<td>-4160</td>
<td>1.68</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>0.44</td>
<td>602.0</td>
<td>890.0</td>
<td>2686</td>
<td>-1891</td>
<td>1.21</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.526</td>
<td>1437.0</td>
<td>-2967.0</td>
<td>7538</td>
<td>-3873</td>
<td>1.32</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>0.53</td>
<td>1434.0</td>
<td>-2952.0</td>
<td>7518</td>
<td>-3056</td>
<td>1.63</td>
</tr>
<tr>
<td>C₂H₂OH</td>
<td>0.77</td>
<td>1260.0</td>
<td>-2449.0</td>
<td>6797</td>
<td>-3594</td>
<td>1.68</td>
</tr>
<tr>
<td>i-C₂H₆</td>
<td>0.49</td>
<td>756.7</td>
<td>-277.8</td>
<td>4269</td>
<td>-2642</td>
<td>2.056</td>
</tr>
<tr>
<td>n-C₂H₆</td>
<td>0.61</td>
<td>936.0</td>
<td>-1127.0</td>
<td>5326</td>
<td>-3044</td>
<td>2.565</td>
</tr>
</tbody>
</table>

Compared to a detailed model, generally good agreement is observed except for rich conditions.
Analytic Approximations of Burning Velocities for Lean CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{3}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}, and C\textsubscript{3}H\textsubscript{8} Flames

Comparison of approximation with detailed model

- Variation in pressure
  → Generally good agreement

Example

- From the approximation \( s_L = Y_F^{0.2}A(\gamma^0)_{T_0}^{T_0} \frac{P}{P_0} \left( T_b - T_0 \right)^n \)

  calculate in comparison with

  \[
  \rho u_L = \sqrt{\frac{2 \rho_0 \lambda_R R^2 T_b^4}{c_0(T_b - T_u)^3 \varepsilon}} \exp \left( \frac{E}{RT_b} \right) S
  \]

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

  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

  \[
  \rho u_L = \sqrt{\frac{2 B \rho_0 \lambda_R R^2 T_b^4}{c_0(T_b - T_u)^3 \varepsilon}} \exp \left( \frac{E}{RT_b} \right) S
  \]

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

  approximately as

  \[
  \rho u_L = \text{const} \exp \left( -\frac{E}{RT_b} \right)
  \]

  and logarithmizes this expression:

  \[
  2 \ln \rho u_L = \ln \text{const} - \frac{E}{RT_b}
  \]

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

Solution

- This leads to

  \[
  \frac{E}{R} = -2 \frac{d \ln \rho u_L}{\sigma(1/T_b)} = 2 T_b \frac{d}{d T_b} \left( \ln \rho u_L \right)
  \]

- Using this

  \[
  s_L = Y_F^{0.2}A(\gamma^0)_{T_0}^{T_0} \frac{P}{P_0} \left( T_b - T_0 \right)^n
  \]

  for \( \rho u_L = \text{const} \), it follows

  \[
  2 T_b \frac{d}{d T_b} \left( \ln \rho u_L \right) = 2 n T_b \frac{T_b - T_0}{T_b - T_u} - 2 n T_b
  \]

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

  \[
  Z_e = n \frac{T_b - T_0}{T_b - T_u} - 1
  \]
Here, following

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

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

\[ T_b(z) = T_u(z) + \frac{Q_{ref} Y_F z}{c_p \rho F}, \quad z \leq z_{st} \]

\[ T_u(z) = T_u(z) + \frac{Q_{ref} Y_O z}{c_p \rho O} (1 - z), \quad z \geq z_{st} \]

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.

**Artificial Neural Network as Alternative Burning Velocity Model**

- **ANN**
  - Input layer: 3 neurons
  - Hidden layer: 100 neurons
  - Output layer: 1 neuron
  - Sklearn Multilayer Perceptron Regressor with \( \tanh \) activation function

- Data from unstretched premixed flame simulations
  - Pressure: 1-120 bar
  - Temperature: 300-1200K
  - Equivalence ratio: 0.5-2.0
  - Total 34515 data points (80% training, 20% testing)

**Solution**

- Gülser model:

\[ \dot{V}_f = \frac{Q_{ref} Y_F}{P_{ref}} \left( \frac{P}{P_{ref}} \right)^t \left( 1 - \nu V_{f_{id}} \right) \]

- Asymptotic model:

\[ \dot{V}_f = \frac{P_{ref} Q_{ref} Y_F}{\nu} \exp \left( \frac{Q_{ref} Y_F}{P_{ref}} \right) \left( \frac{P}{P_{ref}} \right) \left( \frac{P}{P_{ref}} \right) \]

- Validation of detailed model
  - Training with data from unstretched premixed flame (UPF) calculations in FlameMaster using well validated chemical mechanisms
  - ITV Mechanism: 79 species, 1055 reactions
  - Example: Methane/air flames at 300 K and 1 bar

**Comparison for few cases**
ANN Model for Laminar Burning Velocity

Quantitative Structure-Property Relationship

Application to oxygenated fuel candidates

- 1,3-Dioxolane & 1,3-dioxane with highest predicted LBVs
- Up to 50% increase over gasoline, up to 20% increase over ethanol

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 a 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
  $\rightarrow$ Corresponds to $T_0$ in the approximation equation:

$$ s_L = Y_L^0 A(T^0)^n \exp \left( \frac{T^0}{T_L} \left( \frac{T^0}{T_R} - \frac{T_L}{T_R} \right) \right) $$

- $T^0$: "cross-over" temperature between chain termination and chain branching
  $\rightarrow$ kinetically determined
**Kinetically determined lean flammability limit**

- Starting point: Approximation equation:
  \[ s_L = Y_F^{P_0} A(T_0^0) \frac{T_b}{T_0 - T_b} \]
  \[ A(T_0^0) = F \exp(-G/T_0) \times \frac{F}{\ln(q_0/F)} \]

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

  - \( T_0^0 \) depends on pressure but not on fuel mass fraction \( T_b \)
  - Approaching lean flammability limit by decreasing fuel mass fraction in the mixture \( T_b \) decreases

- If fuel mass fraction too low:
  - Inner „cross-over“- temperature \( T_b \) is not reached
  - No chain branching
  - Extinction

**Flammability limit from coupling function**

- Coupling function yields a relation for \( Y_F \)
  \( Y_F = \frac{T_b}{T_0 - T_b} \)

  - With \( T_0 = T_b, T_0 \) and complete combustion \( Y_F = 0 \) follows
  \[ (Y_F)_L = \frac{(T_0 - T_b)\rho_F^0 W_F}{Q_{ref}} \]

- Simplify with coupling function for stoichiometric mixture
  - Mass fraction of the fuel at the lean flammability limit compared to the stoichiometric mixture
  \[ (Y_F)_L = \frac{T_0 - T_b}{T_0 - T_b} Y_F \]

- Example: Methane-air-flame
  - \( T_0 = 300 \text{ K}, p = 1 \text{ bar} \)
  - \( T_0 = 1219 \text{ K}, T_0 = 2229 \text{ K} \)
  - Corresponds to \( \phi = 0.46 \)

**Flammability limits of real flames**

- Real situations:
  - Flame extinction occurs sooner

- Iterative calculation of the limit \( Y_F \) from \( s_L \)

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

- \( T_0 = T_b \); Lower value of mole fraction

- Kinetically determined

**Theoretical explanation of the lean flammability limit**

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

- Exponential dependence of the laminar burning velocity on the temperature in the burned mixture:

  \[ \rho_s = \frac{B_{ref} \sqrt{T_b R^2 T_b}}{\sqrt{(T_0 - T_b) \rho^0}} \exp \left( -\frac{E}{RT_b} \right) S \]

  - 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
Summary

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
Princeton Combustion Summer School 2023

Laminar Premixed Flames: Flame Structure

Heinz Pitsch
Institut für Technische Verbrennung
RWTH Aachen University

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

Part II: Turbulent Flames
- Introduction
- Turbulence and combustion
- Turbulent premixed flames
- Turbulent diffusion flames
- Flamelet models
- Flamelet-to-turbulence interactions
- Flame stability

Laminar diffusion flames
- Separate feeding of fuel and oxidizer into the combustion chamber
  - Diesel engine
  - Jet engine
- In the combustion chamber:
  - Mixing and combustion simultaneously
- Mixing: Convection and diffusion
  - On a molecular level → (locally) stoichiometric mixture
- Simple example for a diffusion flame:
  - Candle flame
    - Paraffin vaporizes at the wick → diffuses into the surrounding air
    - Simultaneously: Air flows towards the flame due to free convection and forms a mixture with the vaporized paraffin

Candle flame
- In a first approximation, combustion takes place at locations, where the concentrations of oxygen and fuel prevail in stoichiometric conditions.
Comparison of laminar premixed and diffusion flames

- Structure of a premixed flame (schematic)
- Structure of a diffusion flame (schematic)

Soot in candle flames

- Soot particles
  - Formation in fuel rich regions of the flame
  - Transported to lean regions through the surface of stoichiometric mixture
  - Combustion of the soot particles in reaction zone

- Sooting flame: Residence time of the soot particles in reaction zone and high temperatures too short to burn all particles

Time Scales

- For many technical combustion systems
  - Characteristic times of chemical reactions much smaller than transport

- Limit of fast chemical reactions

  - Mixing is the slowest and therefore rate determining process

  - “mixed = burnt”

- Not valid for pollutants

The mixture fraction

- Mixture fraction:
  \[ Z = \frac{\nu Y_B - Y_{O_2} - Y_{O_2,2}}{\nu Y_{B,1} + Y_{O_2,2}} \]

- Stoichiometric mixture fraction:
  \[ Z_{st} = \frac{Y_{O_2,2}}{\nu Y_{F,1} + Y_{O_2,2}} \]

- Relation with equivalence ratio
  \[ \phi = \frac{Z (1 - Z_{st})}{1 - Z} \]

  - Pure oxidizer \((\phi = 0)\):
    \[ Z = 0 \]

  - Pure fuel \((\phi = \infty)\):
    \[ Z = 1 \]
**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

**Counterflow Diffusion flame**
- One-dimensional similarity solution
- Used for
  - Studying flame structure
  - Studying chemistry in diffusion flames
  - Study interaction of flow and chemistry
- Strain appears as parameter → Da

\[
Da = \frac{t_F}{t_c}
\]

**Counterflow diffusion flame: Governing Equations**
- Continuity
  \[
  \frac{\partial}{\partial y} (\rho V) + \frac{1}{x} \frac{\partial}{\partial x} (\rho x U) = 0
  \]
- \( \text{X - Momentum} \)
  \[
  \rho U \frac{\partial U}{\partial x} + \rho V \frac{\partial U}{\partial y} = - \frac{\partial P}{\partial x} + \frac{1}{x} \frac{\partial}{\partial x} \left( x \mu \frac{\partial U}{\partial x} \right) + \frac{\partial}{\partial y} \left( \frac{\partial U}{\partial y} \right) - \frac{U}{x^2}
  \]
  \[
  + \frac{\partial U}{\partial x} \frac{\partial \mu}{\partial x} + \frac{\partial V}{\partial x} \frac{\partial \mu}{\partial y}
  \]
- Energy
  \[
  \rho U c_p \frac{dT}{dx} + \rho V c_p \frac{dT}{dy} = \frac{1}{x} \frac{\partial}{\partial x} \left( x \lambda \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( \lambda \frac{\partial T}{\partial y} \right) - \sum_{i=1}^{N} h_i \dot{m}_i
  \]
  \[
  - \sum_{i=1}^{N} c_{p,i} j_i \dot{y} \frac{dt}{dy} - \sum_{i=1}^{N} c_{p,i} j_i \dot{x} \frac{dt}{dx}
  \]

**Counterflow diffusion flame: Similarity solution**
- Three assumptions reduce systems of equation to 1D
  1. Radial velocity varies linearly with distance from centerline
  2. Similarity assumption
  3. Mass fractions and temperature have no radial dependence close to centerline
**Counterflow diffusion flame: Similarity solution**

- This results in
  \[
  \frac{d}{dy} (\rho V) + 2\rho G = 0
  \]
  \[
  \rho G^2 + \rho V \frac{dG}{dy} = P' + \frac{d}{dy} \left( \mu \frac{dG}{dy} \right)
  \]
  \[
  \rho V c_p \frac{dT}{dy} = \frac{d}{dy} \left( k \frac{dT}{dy} \right) - \sum_{i=1}^{N} h_i \dot{m}_i - \sum_{i=1}^{N} c_{p,i} \dot{\bar{m}}_i \frac{dT}{dy}
  \]
  with boundary conditions
  \[
  y \to 0 : V = V_{\text{nozzle}}, \quad G = (dU/dx)_{y=0}, \quad y=0, \quad T = T_0
  \]
  \[
  y \to L : V = -V_{\text{nozzle}}, \quad G = (dU/dx)_{y=L}, \quad y=L, \quad T = T_0
  \]

- Alternatively, potential flow boundary conditions can be used at \( y \to \pm \infty \) instead of nozzles

- 1D similarity solution can be derived with definition of strain rate
  \[
  \frac{a}{(\rho \mu_{\text{ref}})} \int_{0}^{\eta} \frac{d}{dy} f(dy)
  \]
  the similarity coordinate \( \eta \)
  \[
  \eta = \left[ \frac{a}{(\rho \mu_{\text{ref}})} \right]^{1/2} \int_{0}^{y} \rho(dy)
  \]
  the non-dimensional stream function \( f \) defined by
  \[
  \rho a = \sqrt{(\rho \mu_{\text{ref}})} (0, \frac{\partial f}{\partial y})
  \]
  and the Chapman-Rubesin parameter
  \[
  C = \frac{(\rho \mu)}{(\rho \mu_{\text{ref}})}
  \]

*Counterflow diffusion flame: Similarity solution*

- Potential flow similarity solution
  \[
  \frac{d^2 f}{d\eta^2} + \frac{\rho_{\infty}}{\rho} \left( \frac{df}{d\eta} \right)^2 + \frac{d}{d\eta} \left( c_p \frac{d^2 f}{d\eta^2} \right) = 0
  \]
  \[
  \frac{dy}{d\eta} = \frac{1}{\sqrt{(\rho \mu_{\text{ref}})}} \frac{d}{d\eta} \left( \rho V_{\infty} \right) + \frac{\dot{m}_i}{\rho a} = 0, \quad i = 1, 2, \ldots, N
  \]
  \[
  f \frac{dT}{d\eta} + \frac{1}{c_p (\rho \mu_{\text{ref}})} \frac{d}{d\eta} \left( \rho \frac{dT}{d\eta} \right) - \frac{1}{\sqrt{(\rho \mu_{\text{ref}})}} \frac{d}{d\eta} \left( \rho V_{\infty} \right) - \frac{1}{c_p (\rho \mu_{\text{ref}})} \sum_{i=1}^{N} \dot{m}_i h_i - \frac{1}{c_p (\rho \mu_{\text{ref}})} \sum_{i=1}^{N} q_i = 0
  \]

- With Dirichlet boundary conditions for mass fractions and temperature
  \[
  \eta \to \pm \infty : \frac{d}{d\eta} \left[ \frac{\rho_{\infty}}{\rho} \right] = 0
  \]
  \[
  \eta = 0 : f = 0
  \]
  \[
  \eta \to \pm \infty : \frac{df}{d\eta} = 1
  \]
  and where the velocities are obtained from
  \[
  a = a \frac{\partial f}{\partial \eta} \quad \rho a = -\sqrt{(\rho \mu_{\text{ref}})} \frac{df}{d\eta} \]

*Structure of non-premixed laminar flames*

**Temperature for methane/air counterflow diffusion flames**

- Methane/air Counterflow Diffusion Flames
  - \( a = 0.04 \text{ cm/s} \)
  - \( a = 0.05 \text{ cm/s} \)
  - \( a = 0.06 \text{ cm/s} \)

- Methane/air Counterflow Diffusion Flames
  - \( a = 0.04 \text{ cm/s} \)
  - \( a = 0.05 \text{ cm/s} \)
  - \( a = 0.06 \text{ cm/s} \)
Institute for Combustion Technology | Heinz Pitsch

**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
- Counterflow diffusion flame
- Flamelet structure of diffusion flames
- Single droplet combustion

**Theoretical description of diffusion flames**

- Assumption of fast chemical reactions considers no details of chemical kinetics
  - Predicts only global properties, e.g. flame length
- If characteristic timescales of the flow and the reaction are of same order of magnitude:
  - Chemical reaction processes have to be considered explicitly
  - Liftoff and extinction of diffusion flames
  - Formation of pollutants
- Flamelet formulation for non-premixed combustion
  - Mixture fraction as independent coordinate
  - Asymptotic approximation in the limit of sufficiently fast chemistry leads to one-dimensional equations for reaction zone

**Assumptions:** Equal diffusivities of chemical species and temperature

\[ \text{Le}_i = \lambda / (\rho_\text{f} D_i) = 1, \quad i = 1, 2, \ldots, k \quad \Rightarrow \quad D = \lambda / (\rho_\text{f}) \]

- The balance equation for mixture fraction, temperature and species read

\[
\begin{align*}
\frac{\partial \phi_i}{\partial t} + \rho_0 \frac{\partial \phi_i}{\partial x_\alpha} \frac{\partial \mu_i}{\partial x_\alpha} &= 0 \\
\frac{\partial T}{\partial t} + \rho_0 \frac{\partial T}{\partial x_\alpha} &= \sum_{i=1}^{k} m_i \left( \frac{\partial T}{\partial x_\alpha} \right) + \frac{1}{c_p} \frac{\partial p}{\partial t} \\
\frac{\partial y_i}{\partial t} + \rho_0 \frac{\partial y_i}{\partial x_\alpha} &= \sum_{i=1}^{k} m_i \left( \frac{\partial y_i}{\partial x_\alpha} \right)
\end{align*}
\]

- **Low Mach number limit**
  - Zero spatial pressure gradients
  - Temporal pressure change is retained

1 For formulation for non-unity Lewis numbers see Pitsch, Peters, Combust. Flame 1998
Consider surface of stoichiometric mixture: \( Z(x_0, t) = Z_{st} \)

- Reaction zone confined to thin layer around this surface

Locally introduce an orthogonal coordinate system \( x_1, x_2, x_3 \) attached to the surface of stoichiometric mixture

- \( x_1 \) points normal to the surface \( Z_{st} \), \( x_2 \) and \( x_3 \) lie within the surface

Replace coordinate \( x_1 \) by mixture fraction \( Z \) and \( x_2, x_3 \) and \( t \) by \( Z_2 = x_2, Z_3 = x_3, t = t \)

Transformation of temperature and species mass fraction equations \( \psi_j \):

\[
\frac{\partial \psi_j}{\partial t} + \frac{\partial \psi_j}{\partial Z} = \frac{1}{2} \frac{\partial^2 \psi_j}{\partial Z^2}
\]

Example: Temperature \( T \)

\[
\frac{\partial T}{\partial t} = \frac{1}{\rho D} \frac{\partial^2 T}{\partial Z^2}
\]

Analogous for \( x_j \)

**Flamelet Equations**

- Resulting equation

Local change

\[
\text{Describes mixing: } \frac{\partial (\rho D)}{\partial Z} \int^Z_{-Z} \frac{\partial^2 T}{\partial Z^2} = \omega
\]

- If flamelet is thin in \( Z \)-direction, changes in \( Z \)-direction are much larger than along the stoichiometric surface and the leading term is

\[
\left( \frac{\partial Z}{\partial x_j} \right)^2 \frac{\partial^2 T}{\partial Z^2}
\]

is dominating term of the spatial derivatives

- All other terms containing spatial derivatives can be neglected to leading order

\( \partial T \partial t \) is important if very rapid changes, such as extinction, occur

**Flamelet structure of a diffusion flame**

- Transformation of temperature and species mass fraction equations \( \psi_j \):

\[
x_1, x_2, x_3, t \rightarrow Z(x_1, x_2, x_3, t), Z_2, Z_3, t \text{ (where } Z_2 = x_2, Z_3 = x_3, t = t \text{)}
\]

\[
\psi(x_1, x_2, x_3, t) \rightarrow \psi(Z(x_1, x_2, x_3, t), Z_2, Z_3, t)
\]

- Example: Temperature \( T \)

\[
\frac{\partial T}{\partial t} = \frac{1}{\rho D} \frac{\partial^2 T}{\partial Z^2}
\]

Here

\[
\chi_{st} = 2 D \left( \frac{\partial Z}{\partial x_j} \right)^2
\]

is the instantaneous scalar dissipation rate at stoichiometric conditions

- Dimension \( 1/s \) → Inverse of characteristic diffusion time

- Depends on \( t \) and \( Z \) and acts as an external parameter, representing the flow and the mixture field

- In the limit \( \chi_{st} \rightarrow 0 \), equations for the homogeneous reactor are obtained
Example

- DNS of Non-Premixed Combustion in Isotropic Turbulence

- Temperature (color)
- Stoichiometric mixture fraction (line)

Steady solutions of the Flamelet equation: The S-Shaped Curve

- Burning flamelet correspond to the upper branch of the S-shaped curve

- If $\chi_{st}$ is increased, the curve is traversed to the left until $\chi_q$ is reached, beyond which value only the lower, nonreacting branch exists

- Thus at $\chi_{st} = \chi_q$ the quenching of the diffusion flamelet occurs

Structure of non-premixed laminar flames

Temperature and CH Profiles for Different Scalar Dissipation Rates

LES of Sandia Flame D with Lagrangian Flamelet Model

Curvature corresponds to source term:

$$-\rho \chi_{st} \frac{\partial^2 T}{\partial Z^2} = \sum \zeta$$
Scalar dissipation rate from analytic solution

- Counterflow diffusion flames
  - Often used
  - Represent one-dimensional diffusion flame structure

- Flame embedded between two potential flows, if
  - Flow velocities of both streams are sufficiently large and removed from stagnation plane

---

**The Planar Counterflow Diffusion Flame**

Flow equations and boundary conditions

- Prescribing the potential flow velocity gradient in the oxidizer stream

\[ a = \frac{\partial v_{\infty}}{\partial y} \]

the velocities and the mixture fraction are

\[ y \to \infty : \quad v_{\infty} = -ay, \quad u_{\infty} = ax, \quad Z = 0 \]

- Equal stagnation point pressure for both streams requires that the velocities in the fuel stream are

\[ y \to -\infty : \quad v_{-\infty} = -\sqrt{\frac{\rho_{\infty}}{\rho_{-\infty}}} ay, \quad u_{-\infty} = \frac{\rho_{\infty}}{\rho_{-\infty}} ax, \quad Z = 1. \]

---

**Example: Analysis of the Counterflow Diffusion Flame**

Introducing the similarity transformation

\[ \eta = \left( \frac{a}{(\rho \mu)_{\infty}} \right)^{1/2} \int_0^y \rho \, dy, \quad \xi = x \]

one obtains the system of ordinary differential equations

\[ f' = \frac{\eta}{\int_0^\eta \rho \, dy} \]

\[ \frac{\partial}{\partial \eta} \left( C \frac{\partial f'}{\partial \eta} \right) + \frac{\partial f'}{\partial \eta} + \frac{\rho_{\infty}}{\rho} - f'^2 = 0 \]

\[ \frac{\partial}{\partial \eta} \left( \frac{C}{\rho} \frac{\partial Z}{\partial \eta} \right) + f' \frac{\rho Z}{\rho \eta} = 0 \]

- in terms of the non-dimensional stream function

\[ f = \frac{\rho \mu}{(\rho \mu)_{\infty} a} \]

and the normalized tangential velocity

\[ f' = \frac{u}{ax} \]
**Example: Analysis of the Counterflow Diffusion Flame**

- Furthermore the Chapman-Rubens parameter $C$ and the Schmidt number $Sc$ are defined

  $$C = \frac{\rho_1}{(\rho\mu)_\infty}, \quad Sc = \frac{\mu}{\rho D}$$

- The boundary equations are

  \begin{align*}
  \eta = +\infty: & \quad f' = 1, \quad Z = 0 \\
  \eta = -\infty: & \quad f' = \sqrt{\rho w_\infty/\rho}, \quad Z = 1
  \end{align*}

- An integral of the $Z$-equation is obtained as where the integral $I(\eta)$ is defined as

  $$Z = \frac{1}{2} I(\infty) - I(\eta)$$

  $$I(\eta) = \frac{\eta}{C} \exp\left\{ - \int_0^\eta \frac{\eta Sc}{C d\eta} \right\} d\eta$$

**Example: Analysis of the Counterflow Diffusion Flame**

- For constant properties $\rho = \rho_\infty, \quad C = 1 \quad f = \eta$ satisfies

  $$\frac{\partial}{\partial \eta} \left( \frac{\partial f'}{\partial \eta} \right) + f' \frac{\partial f'}{\partial \eta} + \frac{\rho_\infty}{\rho} f' - \frac{f'^2}{c} = \lambda$$

  and

  $$Z = \frac{1}{2} \text{erfc}\left( \frac{\eta}{\sqrt{2}} \right)$$

- The instantaneous scalar dissipation rate is here

  $$\chi = 2D \left( \frac{\partial Z}{\partial \eta} \right)^2 = 2 \left( \frac{C}{Sc} \right) \left( \frac{\partial Z}{\partial \eta} \right)^2$$

  where

  $$\eta = \left( \frac{a}{(\rho\mu)_\infty} \right)^{1/2} \int_0^\eta \rho d\eta, \quad \xi = x$$

  and

  $$C = \frac{\rho_\infty}{(\rho\mu)_\infty}, \quad Sc = \frac{\mu}{\rho D}$$

  have been used

**Example: Analysis of the Counterflow Diffusion Flame**

- When the scalar dissipation rate is evaluated with the assumptions that led to

  one obtains

  $$Z = \frac{1}{2} \text{erfc}\left( \frac{\eta}{\sqrt{2}} \right)$$

  $$\chi = \frac{a}{\pi} \exp\left[ - \eta^2 (Z) \right] = \frac{a}{\pi} \exp\left[ -2(\text{erfc}^{-1} (2Z))^2 \right]$$

- For small $Z$ one obtains with l’Hospital’s rule

  $$\frac{dZ}{d\eta} = -\frac{1}{2} \frac{df}{d\eta} \left( \frac{Z}{I(\infty)} - I(\eta) \right) = -\frac{Sc}{C} f Z.$$

- Therefore, in terms of the velocity gradient $a$ the scalar dissipation rate becomes

  $$\chi = 2a f^2 Z^2$$

  showing that $\chi$ increases as $Z^2$ for small $Z$

**Example: Analysis of the Counterflow Diffusion Flame**

- Mixture fraction field described as

  $$Z = \frac{1}{2} \text{erfc}\left( \frac{\eta}{\sqrt{2}} \right)$$

- From this follows scalar dissipation rate as

  $$\chi = \frac{a}{\pi} \exp\left[ - \eta^2 (Z) \right] = \frac{a}{\pi} \exp\left[ -2(\text{erfc}^{-1} (2Z))^2 \right]$$

- This provides

  - Relation between strain rate and scalar dissipation rate
  - Mixture fraction dependence of scalar dissipation rate, often used in solving flamelet equations
Flame Structure of Methane-Air Diffusion Flames

- Classical Linan one-step model with a large activation energy is able to predict important features such as extinction, but for small values of $Z_{st}$, it predicts the leakage of fuel through the reaction zone.

- However, experiments of methane flames, on the contrary, show leakage of oxygen rather than of fuel through the reaction zone.

Flame Structure of Methane-Air Diffusion Flames

- An asymptotic analysis by Seshadri (1988) based on the four-step model shows a close correspondence between the different layers identified in the premixed methane flame and those in the diffusion flame.

Flame Structure of Methane-Air Diffusion Flames

- Simulation results using detailed chemistry.

- Fuel leakage not observed.

- Oxygen leakage increases as extinction is approached.

Flame Structure of Methane-Air Diffusion Flames

- Outer structure of diffusion flame is classical Burke-Schumann structure governed by the overall one-step reaction

$$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$$

with the flame sheet positioned at $Z = Z_{st}$.

- Inner structure consists of thin $\text{H}_2 - \text{CO}$ oxidation layer of thickness of order $\varepsilon$ toward the lean side and a thin inner layer of thickness of order $\delta$ slightly toward the rich side of $Z = Z_{st}$.

- Beyond this layer, rich side is chemically inert, because all radicals are consumed by the fuel.
Diffusion Flame Structure of Methane-Air Flames

Results from numerical Simulation of Methane/Air diffusion flame

- The comparison of the diffusion flame structure with that of a premixed flame shows that
  - Rich part of the diffusion flame corresponds to the upstream preheat zone of the premixed flame
  - Lean part corresponds to the downstream oxidation layer
  - The maximum temperature corresponds to the inner layer temperature of the asymptotic structure

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
- Introduction
- Counterflow diffusion flame
- Flamelet structure of diffusion flames
- Single droplet combustion

*Spray Combustion: Gas Turbine Combustion Chamber

Quelle: C. Edwards, Stanford University
**Modeling Multiphase Flows**

- **Euler-Lagrange Approach**
  - Fluid phase: continuum ➔ Navier-Stokes Equations
  - Dispersed phase is solved by tracking a large number of particles
  - The dispersed phase can exchange momentum, mass, and energy with the fluid phase

- **Euler-Euler Approach**
  - All phases: Eulerian description
  - Conservation equation for each phase
  - One phase per volume element ➔ Volume Fraction
  - Phase-phase interaction
  - Surface-tracking technique applied to a fixed Eulerian mesh

**Dispersed Phase: Droplets**

- Lagrangian frame of reference
- Droplets
  - Diameter (evaporation)
  - Temperature (heat transfer)
  - Deformation (aerodynamic forces)
  - Collision, breakup, ...
- Source terms along droplet trajectories
- Stochastic approaches:
  - Monte Carlo method
  - Stochastic Parcel method

**Lagrangian Description: Balance equations**

- Mass balance (single droplet)
  \[ \frac{Dm_0}{Dt} = \frac{1}{1-Y_0} \left[ \frac{\partial}{\partial \theta} (p) - Y_0 (\partial Y_0/\partial \theta) \right] \]

- Balance of energy (single droplet)
  \[ m_0 \frac{DT_0}{Dt} = \Delta H(T_0) + \frac{D}{Dt} [m_0 (\partial T_0/\partial \theta)] \]

- Momentum balance (single droplet)
  \[ \frac{D}{Dt} (m_0 u_i) = \sum_{j} F_{ij} \]
  - \( F_{ij} \): Drag
  - \( F_{ij} \): Weight/buoyant force
  - ... Pressure/virtual/Magnus forces, ...

**Coupling Between the Discrete and Continuous Phases**

- Mass
  \[ \dot{\hat{\omega}}_m = \frac{1}{V_{cell}} \sum_k \hat{N} \left[ m_0^k - n_0^k \right] \]

- Momentum
  \[ \dot{\hat{\omega}}_m = \frac{1}{V_{cell}} \sum_k \hat{N} \left[ (m_0 u_i) - \dot{m}_0 u_i \right] \]

- Energy
  \[ \dot{\hat{\omega}}_E = \frac{1}{V_{cell}} \sum_k \hat{N} \left[ m_0^k (T_0 - T_0) - n_0^k (T_0 + T_0) \right] \]

Coupling Between the Discrete and Continuous Phases

- Continuous phase impacts the discrete phase (one-way coupling)
- Effect of the discrete phase trajectories on the continuum (source terms, two-way coupling)
- Interaction within the discrete phase: particle/particle (four-way coupling)
**Single Droplet Combustion**

- **Multiphase combustion**
  - phase change during combustion process:
    - **Liquid → gas phase**

- **Theoretical description:** Single Droplet Combustion
  - **Aim:** Mass burning rate $\frac{dm}{dt}$ as function of
    - Chemical properties of droplet and surrounding: mixture fraction $Z$
    - Thermodynamical properties: Temperature $T$, density $\rho$, pressure $p$
    - Droplet size and shape: diameter $d$

- **Assumptions**
  - Small droplets which follow the flow very closely
  - Velocity difference between the droplet and the surrounding fuel is **zero**
  - Quiescent surrounding
  - Spherically symmetric droplet
  - Neglect buoyant forces
  - Fuel and oxidizer fully separated → Combustion where the surface of stoichiometric mixture surrounds the single droplet → **Diffusion flame**
  - Evaporation and combustion process: **quasi-steady**

- **Expected temperature and mixture fraction profiles:**
**Single Droplet Combustion**

- Quasi stationary evaporation and combustion of a spherically symmetric droplet in Quiescent surrounding
  - One step reaction with fast chemistry
  - $L_e = 1$

**Balance equations:**
- Momentum equation: $p$ = const.
- Conservation of mass: $\rho u_r = const.$
- Temperature

- Mixture Fraction

$$\rho u_r \frac{d T}{dr} = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \rho D \frac{dT}{dr} \right) + \frac{(-\Delta h_v)}{c_p}$$

$$\rho u_r \frac{d Z}{dr} = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \rho D \frac{dZ}{dr} \right)$$

**Temperature boundary condition**
- Gas phase
- Liquid phase

**Mixture Fraction boundary condition**
- Difference between the mixture fraction within the droplet and that in the gas phase at the droplet surface

**Temperature BC:**
- Enthalpy of evaporation $h_v$
- Temperature within the droplet $T_i = const.$
- $T_i$ is boiling temperature $T_i = T_i(p)$

- Mixture Fraction BC:
  - Difference between the mixture fraction within the droplet and that in the gas of 1 inside the droplet surface
From the equations for temperature and mixture fraction it follows in transformed coordinates:

\[
\frac{d\theta}{d\eta} = \frac{d^2T}{dr^2} + \frac{\rho}{\rho_0} \frac{dZ}{dr} = \frac{\rho}{\rho_0} \frac{d^2\zeta}{dr^2}
\]

Transformed BCS

\[
\zeta = \eta_0 = \frac{\eta}{\eta_0}, \quad T_R = T_0, \quad Z_R = Z_0
\]

Solution of the mixture fraction

\[
Z = \eta
\]

Temperature solution where \( Z = \eta \)

\[
\rho \left( \frac{d\theta}{d\eta} \right)^2 \frac{d^2T}{d\eta^2} = \frac{\rho}{\rho_0} \frac{d^2Z}{dr^2} = \zeta
\]

We consider the Burke-Schumann-solution

- \( T_2 \): Temperature in the surrounding
- \( T_0 \): Temperature at droplet surface
**Single Droplet Combustion**

- At fuel rich side

\[ T_0(Z) = T_1(Z) + \frac{(-\Delta h_f)Y_{O_2}(1 - Z)}{c_p \rho_c M_{O_2}} \]

\[ T_u(Z) = T_2 + T_1(Z) \]

- Problem:
  - Temperature \( T_1 \) not known
  - Needed to determine \( T_u(Z) \) in the unburnt mixture

- From BC and follows

\[ T_1(Z) = \frac{T_0(Z) - T_u(Z)}{1 - Z} \]

- \( T_1 \) is a hypothetical temperature corresponding to the fuel if one considers the droplet as a point source of gaseous fuel

**Result:** Non-dimensional mass burning rate

- From \( \xi = -\ln(1 - \eta) \)

\[ T(Z) = \frac{T_1 + (T_2 - T_1)Z}{1 + \xi} + \frac{(-\Delta h_f)Y_{O_2}(1 - Z)}{c_p \rho_c M_{O_2}} \]

follows

\[ \xi = \ln\left(1 + \frac{c_p(T_2 - T_1) + \frac{(-\Delta h_f)Y_{O_2}}{c_p \rho_c M_{O_2}}}{h}\right) \]

- RHS is not a function of the droplet radius

- With \( \rho D = (\rho D)_{\text{ref}} = \text{const.} \) and

\[ \eta = 4\pi(\rho D)_{\text{ref}} c_r R \]

**Mass burning rate:**

\[ m = 4\pi(\rho D)_{\text{ref}} c_r R \]

- Mass burning rate is proportional to \( R \)

**Assumptions:**

- Quasi stationary diffusion flame surrounding the droplet
- Constant temperature \( T_1 \) within the droplet
**Burnout Time**

It is possible to determine the time needed to burn a droplet with initial radius $R$.

\[ \dot{m} = - \frac{d}{dt} \left( \frac{4}{3} \pi R^3 \dot{R} \right) = - \rho \pi R^2 \dot{R} \]

- With $\dot{m} = 4\pi (\rho D)_{ref} \dot{R}$, integration yields

\[ t_b = \frac{\rho L}{8\pi (\rho D)_{ref}} \]

- Burnout time:

This is called $d^2$-law of droplet combustion.

- It represents a very good first approximation for the droplet combustion time and has often been confirmed by experiments.

---

**Radius of the surrounding diffusion flame**

- We want to calculate the radial position of the surrounding flame:
  - From $\rho D = (\rho D)_{ref}$ = const, \[ \int \right = \frac{\dot{m}}{4\pi} (\rho D^{2})^{-1} \] \[ \omega = \frac{\dot{m}}{4\pi (\rho D)_{ref}} = \frac{\dot{m}}{\rho L} \]
  - With $\eta = 1 - \exp(-\zeta)$ and $Z = \eta$
  - $1 - Z_\omega = \exp(-\zeta_\omega)$

- Flame radius

- For sufficiently small values of $Z_\omega$, the denominator may be approximated by $Z_\omega$ itself showing that ratio $r_\omega/R$ may take quite large values.

---

**Single Droplet Combustion**

Heptane drop in 741 K ambient air

*Single Droplet Combustion*

**Introduction**

- Fundamentals and Laminar Flames
  - Laminar premixed flames: Kinematics and burning velocity
  - Laminar diffusion flames
  - FlameMaster flame calculator

**Summary**

**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 diffusion flames
- FlameMaster flame calculator