The chemistry and physics of flames

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Topics of the first lecture series

• characterization and history of combustion science
• basic books, scientific journals and conferences
• basic notions

The chemistry of gas phase combustion:
• combustion of hydrogen, CO, CH$_4$ and other alkanes
• internal combustion engines
• hydrocarbon oxidation at low temperatures
• formation of NO$_x$ in flames
• NOx removal methods
• soot
• heterogeneous ignition and combustion
Topics of the second lecture series

Quantitative simulation of combustion

- detailed reaction mechanisms
- measurement of ignition time and flame velocity
- methods for the detection of radicals (LIF, RF, MS)
- measurement of the rate coefficients of elementary gas phase reactions using shock tube, flash photolysis and discharge flow
- chemical kinetics databases
- development of reaction mechanisms
- solving balance equations for the simulation of flames

related special course:
Reakciómechanizmusok vizsgálata
(Analysis of kinetic reaction mechanisms) in the autumn semesters

Combustion Science
an interdisciplinary science

chemistry  physical chemistry  reaction kinetics  gas kinetics
thermodynamics  transport phenomena

physics  fluid dynamics (CFD: Computational Fluid Dynamics)

math  numerical methods
analytical solution of equations

engineering science

The chemistry part: combustion chemistry

F.A. Williams: Combustion theory  mainly physics
“Numerical combustion” conferences  mainly math
I. Glassman: Combustion  mainly chemistry
some basic books


I. Glassman, R.A. Yetter: Combustion

F.A. Williams: Combustion theory
Benjamin, Menlo Park, 1984

W.C. Gardiner: Combustion Chemistry

S.R. Turns
An introduction to combustion.
Concepts and applications

M.J. Pilling – P.W. Seakins:
Reaction kinetics, Oxford Univ. Press, 1995

The history of combustion science

in ancient Greece according to Aristotle:
fire is one of the „classical elements“ with features hot and dry

dry fire hot
earth water air

cold wet

The fifth element according to Aristotle: aether

consequence of the Greek theory:
The classical elements can be transformed by changing their features
gold: earth with much fire content

middle ages: all types of „earthes“ (minerals, metals) were heated to increase their fire content
Phlogiston theory

First stated in 1667 by Johann Joachim Becher:

a fire-like element called phlogiston, contained within combustible bodies, is released during combustion.

**Problem:**
Metals gained mass when they were oxidized
⇒ phlogiston must have negative mass.

Discovery of oxygen

18th century

Lomonosov  Lavoisier  the original apparatus of Lavoisier
The experiments of Faraday

1861  Michael Faraday: The Chemical History of a Candle

Modern combustion science

~1930 → A new interdisciplinary science:
invented by Theodore von Kármán
(born in Budapest as „Kármán Tódor“ (1881 –1963)

his main idea:
engineering science = applied physics

Modern reaction kinetics based on elementary reactions and radicals,
founded by

Hinshelwood, Norrish, Porter
Semyonov, Zeldovich,
Frank-Kamenetskii
The international organization of combustion science

The Combustion Institute, Pittsburgh

own journal: Combustion and Flame

Hungarian Section of The Combustion Institute
„Magyar Égéstudományi Bizottság“

Further combustion journals:

Combustion Science and Technology
Combustion Theory and Modelling
Fuel
Energy

International Symposium on Combustion

since 1949, in every second year

1990 23rd Symposium Orleans, France
1992 24th Symposium Sydney, Australia
1994 25th Symposium Irvine, USA
1996 26th Symposium Naples, Italy
1998 27th Symposium Boulder, USA
2000 28th Symposium Edinburgh, UK
2002 29th Symposium Sapporo, Japan
2004 30th Symposium Chicago, USA
2006 31st Symposium Heidelberg, Germany
2008 32nd Symposium Montreal, Canada
2010 33rd Symposium Beijing, China
2012 34th Symposium Warsaw, Poland
2014 35th Symposium San Francisco, USA
2016 36th Symposium Seoul, South Korea

Proceedings of the Combustion Institute
(single volume of about 1200 pages, published in every 2nd year)
What is combustion?

Everyone knows what combustion is, but a generally accepted definition does not exist.

A possible definition:
Combustion is chemical transformation with significant heat release.

Wrong definitions of combustion:
- reaction of oxygen with a fuel
- reaction of gases accompanied with light emission

Several typical combustion reactions:

- combustion of methane: \( \text{CH}_4 + 2 \text{O}_2 = \text{CO}_2 + 2 \text{H}_2\text{O} \)
- hydrogen-chlorine flame: \( \text{H}_2 + \text{Cl}_2 = 2 \text{HCl} \)
- termite reaction: \( 2 \text{Al} + \text{Fe}_2\text{O}_3 = 2 \text{Fe} + \text{Al}_2\text{O}_3 \)

flame: high temperature reaction front
The geometry of flames

non-stationary flame (changes in time) ⇔ stationary flame
  = constant $T$ and $c$ at a given location for a long time

3D flame: e.g. a bonfire
$T$ and $c$ are the functions of three spatial coordinates
$(x,y,z)$

2D flame: candle, Bunsen burner
$T$ and $c$ are the functions of two spatial coordinates
$(r$ and $z)$

1D flame: flat flame
$T$ and $c$ is a function of the height $(x)$ above the mesh

0D combustion: not a flame, spatially homogeneous

A close look at a Bunsen burner

No combustion below the flame cone:
there is a small gap between the flame and the metal tube.
REASON:
quenching of radicals on the metal surface.

Bunsen burner with open air inlet:
Complete mixing of air and natural gas in the long metal tube.
Blue premixed flame on the top of the tube.

Bunsen burner with closed air inlet:
there is natural gas only in the tube.
Yellow non-premixed flame on the top of the tube.

Similar to a candle flame!
## Main flame types

<table>
<thead>
<tr>
<th></th>
<th>premixed</th>
<th>non-premixed</th>
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</thead>
<tbody>
<tr>
<td>laminar flame</td>
<td>gas stove flame</td>
<td>candle</td>
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<tr>
<td></td>
<td>Bunsen burner</td>
<td>Bunsen burner</td>
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<tr>
<td></td>
<td>with blue flame</td>
<td>with yellow flame</td>
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<tr>
<td>turbulent flame</td>
<td>petrol engine</td>
<td>gas turbine</td>
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<td>with carburator</td>
<td>rocket engine</td>
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<td></td>
<td></td>
<td>(H₂+O₂ or kerosene+O₂)</td>
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<td>Diesel engine</td>
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## Main flame types

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<td>![Image of laminar flame]</td>
<td>![Image of Bunsen burner with blue flame]</td>
</tr>
<tr>
<td>turbulent flame</td>
<td>![Image of petrol engine with carburator]</td>
<td>![Image of gas turbine rocket engine]</td>
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</table>
Main flame types 2

**premixed flame**
mixing and then burning;
it is safe only in small scale; not used in the industry

**non-premixed flame** (old usage: diffusion flame)
mixing and burning simultaneously;
safe, because the combustible mixture is generated locally

**laminar flame**
the total heat production is small
BUT large heat production in some points!

**turbulent flame**
large fuel consumption, large total heat production
BUT small heat production in each point!

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Laminar non-premixed flame/diffusion flame

counterflow geometry

![Counterflow geometry diagram](image)
Laminar non-premixed flame/diffusion flame

coflow geometry

triple flame or tulip flame

premixed flame on the two sides with $\phi < 1$ and $\phi > 1$.
non-premixed flame in the middle

Airship Hindenburg

A very successful airship

135 km/h cruising speed
112 metric ton load
completed: 4 March, 1936

63 flights
17 Atlantic Ocean crossings
72 passengers
61 staff

Inside the airship:

passenger quarters, dining room, lounge, writing room, washrooms, a smoking lounge
The largest areal transport vehicle ever built:
245 meter length, 41 meter diameter

Airship Hindenburg

The Hindenburg disaster

burning of Airship Hindenburg
3 May, 1937 at 19:25
200,000 m³ hydrogen was burnt in 34 seconds
97 people were aboard
62 people survived !!!
How is it possible ???
The Hindenburg disaster 2

burning of Airship Hindenburg
3 May, 1937 at 19:25
200.000 m³ hydrogen was burnt
in 34 seconds
97 people were aboard
62 people survived !!!
How is it possible ???

It was a non-premixed hydrogen–air flame.
The flame was only on the top of the balloon initially.
The passengers and the staff had 20 seconds to
set themselves free and run away.

Equivalence ratio

fuel lean flame
\[ \text{CH}_4 + \text{O}_2 \text{ mixture } \rightarrow \text{CO}_2 + \text{H}_2\text{O} + (\text{O}_2 \text{ remains}) \]
\( \varphi < 1; \lambda > 1 \)

stoichiometric flame
\[ \text{CH}_4 + \text{O}_2 \text{ mixture } \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]
\( \varphi = 1; \lambda = 1 \)

fuel rich flame
\[ \text{CH}_4 + \text{O}_2 \text{ mixture } \rightarrow \text{CO}_2 + \text{H}_2\text{O} + (\text{CH}_4 \text{ remains}) \]
\( \varphi > 1; \lambda < 1 \) In fact, no methane remains, because
at high temperature methane decomposes
to hydrogen and olefins!

Stoichiometric ratios:
\[ \varphi = \frac{n_{\text{fuel}}/n_{\text{oxidizer}}}{(n_{\text{fuel}}/n_{\text{oxidizer}})_{\text{stoichiometric}}} \]

\( \lambda \): air equivalence ratio (see „\( \lambda \) sensor“)
\( \varphi \): fuel equivalence ratio \( \varphi = 1/\lambda \)
laminar burning velocity, laminar flame velocity \( v_L \) [m/s]

Travelling speed of a laminar flame front, if it is infinitely large, adiabatic, planar, and without stretch (flow in perpendicular direction).

1. infinitely large, adiabatic \( \Rightarrow \) no heat loss
2. planar \( \Rightarrow \) curved flame front has a different speed concave: faster convex: slower
3. stretch (cross flow) changes the flame velocity

laminar flame velocity is a physical constant, at a given gas composition, initial temperature and pressure

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laminar flame velocity

\( \text{CH}_4/\text{air}, \phi = 1, p = 1 \text{ atm}, T_0 = 300 \text{ K}, v_L = 35.7 \text{ cm/s} \)

measured flame velocity of methane–air mixtures as a function of \( \phi \)

it has a maximum at \( \phi = 1.1 \)

lower flammable limit (LFL) upper flammable limit (UFL)

Below the lower flammable limit and above the upper flammable limit there is no deflagration. Also called „flammability limits“ or „explosive limits“.

Other typical flame speeds:

hydrocarbon/air and alcohol/air mixtures at \( p = 1 \text{ atm}, T_0 = 300 \text{ K} \) typically 20–50 cm/s (that is 0.7 – 1.8 km/h)

\( \text{H}_2/\text{air}, \phi = 1, p = 1 \text{ atm}, T_0 = 300 \text{ K}, v_L = 200 \text{ cm/s} \)
increasing pressure: $v_L$ decreases  
**REASON:** $H+O_2+M=HO_2+M$ is faster

increasing temperature: $v_L$ increases  
**REASON:** $H+O_2+M=HO_2+M$ is slower  
reactions $H+O_2=OH+O$, $O+H=OH+H$ are faster

**Topic 2. The flame of a candle**

The chemistry and physics of a candle flame.

Evaporation and pyrolysis of the paraffin.

The change of equivalence ratio inside the candle flame.

Why is the candle flame yellow?

The shape of the flame at normal gravity (1 g) and in microgravity.

Investigation of flames at zero gravity or microgravity.
A close look at a candle

The flame of the candle melts the paraffin wax
a small cup is formed, which contains melted wax.
The remaining solid wax forms the wall of the cup.

Wrong candle: the paraffin wax is flowing away
and remains unburnt.

Due to capillary action, the candle wick is drawing ("wicking") the melted wax up to the flame. The paraffin is consumed, the flame is moving downwards, melting more paraffin. The top of the wick is burnt in the upper part of the flame.

Wrong candle: The wick cannot transport the melted paraffin.
The wick remains unburnt.

Paraffin wax is evaporating on the top of the wick
The paraffin is decomposed and olefins are formed.

Combustion of olefins (ethenes) in the flame.
The unburnt olefins are inside the flame.
Air is flowing outside upwards, due to the density difference. Oxygen is transported to the flame by diffusion and small eddies.

Where is the location of combustion in a candle flame?

In the case of hydrocarbons, the nearly stoichiometric ($\phi=1.1$) premixed flame has the largest burning velocity (largest flame speed).

In a non-premixed flame the equivalence ratio is continuously changing with the location.

Inside the candle flame
the gas mixture is fuel rich ($\phi>1$).

Outside the candle flame
the gas mixture is fuel lean ($\phi<1$).

The flame front inside the candle flame is where the gas mixture is nearly stoichiometric.

No oxygen inside the flame front.
Why has the candle flame a droplet shape?

The side of the flame is heating up air. The hot air has a lower density than the surrounding cold air. The hot air is rising up fast.

The fast airflow at the side of the flame:

• creates the droplet shape of the flame
• is transporting $O_2$ to the flame
• removes reaction products $CO_2$ and $H_2O$
• makes small eddies, making transport more effective

At zero gravity there is also density difference between the cold and hot gases, but there is no buoyancy.

• Diffusion is the only means of transport (for both $O_2$ and the products)
• Low reaction speed, the flame is colder
• the flame has spherical shape, not droplet shape

Candle flame at zero gravity

A candle flame in microgravity.
Zero gravity in the reel space

Fire aboard the International Space Station

Zero gravity in the real space

FSDC:
Fiber-Supported Droplet Combustion
burning of methanol droplets,
fixed by glass fibers
Zero gravity aboard an airplane

Zero gravity on Earth
Topic 3. The combustion of hydrogen

The overall chemical equation and the 12-step mechanism.
The change of explosion limits with temperature and pressure.
Explanation to the explosion limits.
The effect of heterogeneous reactions.
The change of the branching ratio of reaction step $\text{H} + \text{O}_2 \rightarrow$ with pressure, temperature and gas composition.
Spread of the hydrogen – air flame.

Combustion of hydrogen

„The oxidation of hydrogen is the most studied oxidation process, and even the fine details of its mechanism are well known.”

A.B. Nalbandjan – V.V. Vojevodszkij
The mechanism of the oxidation and combustion of hydrogen
Izd. Acad. Nauk., Moscow, Leningrad, 1949

New mechanism in almost every year:
Ó Conaire et al. (Galway, 2004)
Konnov (Lund, 2008)
Hong et al. (Stanford, 2011)
Burke et al. (Princeton, 2012)
Keromnes et al. (Galway, 2013)
Sánchez and Williams (San Diego, 2014)

Why is it important?
„the fuel of the future“, „hydrogen economy“, „carbon-free energetics“
practical fuel (rocket fuel / satellite launchers)
industrial safety (H₂ generation in a nuclear accident, Fukushima)
the core reactions of the oxidation of hydrocarbons
Explosion of a hydrogen-oxygen mixture

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

1. \( \text{H}_2 + \text{O}_2 \rightarrow \cdot\text{H} + \cdot\text{HO}_2 \) chain initiation
2. \( \cdot\text{H} + \text{O}_2 \rightarrow \cdot\text{OH} + \cdot\text{O} \) chain branching
3. \( \cdot\text{OH} + \text{H}_2 \rightarrow \cdot\text{H} + \text{H}_2\text{O} \) chain continuation
4. \( \cdot\text{O} + \text{H}_2 \rightarrow \cdot\text{OH} + \cdot\text{H} \) chain branching
5. \( \text{H} + \text{O}_2 + \text{M} \rightarrow \cdot\text{HO}_2 + \text{M} \) chain termination*
6. \( \cdot\text{H} \rightarrow \text{wall} \) chain termination
7. \( \cdot\text{O} \rightarrow \text{wall} \) chain termination
8. \( \cdot\text{OH} \rightarrow \text{wall} \) chain termination
9. \( \cdot\text{HO}_2 + \text{H}_2 \rightarrow \cdot\text{H} + \text{H}_2\text{O}_2 \) chain initiation*
10. \( 2 \cdot\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \) chain termination
11. \( \text{H}_2\text{O}_2 + \text{M} \rightarrow 2 \cdot\text{OH} + \text{M} \) chain initiation
12. \( \cdot\text{HO}_2 \rightarrow \text{wall} \) chain termination
below the 1st explosion limit:

chain termination reactions 6, 7, 8 remove the radicals
(radical loss on the wall)

→ no explosion
Hydrogen-oxygen explosion between limits 1 and 2

H atom is a very reactive intermediate, its concentration first increases quickly and starts to decay when the concentrations of H₂ and O₂ decreases. Concentration of H₂O: saturation curve.

\[ H + O \rightarrow H + O_2 \]  
\[ .H + O \rightarrow .OH + :O \]  
\[ .OH + H → .H + H₂O \]  
\[ .O + H₂ → .OH + .H \]  
\[ .H + O₂ + M → .HO₂ + M \] chain termination*  
\[ .H → wall \] chain termination  
\[ .O → wall \] chain termination  
\[ .OH → wall \] chain termination  
\[ .HO₂ + H₂ → H₂O₂ + O₂ \] chain termination  
\[ H₂O₂ + M → 2 .OH + M \] chain initiation  
\[ .HO₂ → wall \] chain termination

between explosion limits 2 and 3:

\[ .H + O₂ + M → .HO₂ + M \] chain termination*  
\[ 2 .HO₂ → H₂O₂ + O₂ \] chain termination  
\[ .HO₂ → wall \] chain termination

→ no explosion

M any species present  
at the hydrogen/air explosion it is mainly \( N₂ \), \( O₂ \), \( H₂ \) (e.g. \( H \), \( .HO₂ \), \( .OH \)).
above explosion limit 3

high pressure \( \Rightarrow \) reaction step 5 produces much .HO

Reaction steps 9 and 10 convert .HO to H\(_2\)O

At high pressure the decomposition of H\(_2\)O\(_2\) is fast (reaction 11) and it produces much highly reactive OH radicals

\( \rightarrow \) explosion

Effect of the heterogeneous reactions

radicals collide to the wall and might get adsorbed.

The typical sticking coefficient is \( \varepsilon = 10^{-5} - 10^{-2} \) (glass or quartz wall)

sticking coefficient \( \varepsilon \):

ratio of collisions resulting in adsorption and all collisions

\( \Rightarrow \varepsilon = 10^{-3} \) sticking coefficient means that 1 radical is adsorbed out of 1000 radicals colliding to the wall

Calculation of the rate coefficients of reactions 6, 7, 8, 12:

\[
k = \frac{1}{4} \varepsilon \overline{V} \frac{S}{V}
\]

where

- \( S \) surface of the vessel
- \( V \) volume of the vessel
- \( \overline{V} \) average flying velocity of the radical

\[
\overline{V} = \sqrt{\frac{8k_BT}{\pi m}}
\]
Effect of the heterogeneous reactions 2

The dashed line corresponds to pressure where 
\[ [M] = 2 \frac{k_d}{k_0} \]

(R2 \[ \cdot H + O_2 \rightarrow \cdot OH + :O \])
(R5 \[ \cdot H + O_2 + M \rightarrow \cdot HO_2 + M \])

The wall reactions result in the non-explosive regions!
lower non-explosive region (below limit 1): adsorption of radicals H, :O, \cdot OH
upper non-explosive region (between limits 2 and 3): adsorption of radical \cdot HO_2

Hydrogen-air flame

at pressure 1 bar:
above about 900 K \[ \cdot H + O_2 \rightarrow \cdot OH + :O \] → chain reaction
below about 900 K \[ \cdot H + O_2 + M \rightarrow \cdot HO_2 + M \] → NO chain reaction

cold gas \( \cdot H \) arrives: \[ \cdot H + O_2 + M \rightarrow \cdot HO_2 + M \] → NO explosion
hot gas \( \cdot H \) arrives: \[ \cdot H + O_2 \rightarrow \cdot OH + :O \] → explosion
the key of explosion / no explosion behaviour
the HO₂ reaction system

at temperature 650 K
below about 40 torr  \( \text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O} \) \( \rightarrow \) explosion
above about 40 torr  \( \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \) \( \rightarrow \) NO explosion

\[ \text{H} + \text{O}_2 \rightarrow \text{HO}_2^* \]
low pressure:  \( \text{HO}_2^* \rightarrow \text{H} + \text{O}_2 \) or \( \text{HO}_2^* \rightarrow \text{OH} + \text{O} \) \( \rightarrow \) explosion
high pressure:  \( \text{HO}_2^* \rightarrow \text{HO}_2 \) (stabilization) \( \rightarrow \) NO explosion

Third body collision efficiency

M can be any species present (molecule, radical, atom)

It role is the removal of the extra energy of the excited species (here: radical \( \text{HO}_2^* \)) via a collision

Energy removal effectivity depends on the modes where M can store the energy

He it can store the energy only in translational mode
(in plain English: Helium atom goes faster after collision)

\( \text{N}_2 \) it can store the energy also in rotational and vibrational modes
(in plain English: \( \text{N}_2 \) molecule goes faster after collision + faster rotations and excited vibrations)

\( \text{H}_2\text{O} \) many rotational and vibrational modes
+ the energy levels are close to those of radical \( \text{HO}_2^* \)

typical relative collision efficiencies (Burke et al., 2012):
\( m(\text{He}) = 0.8 \quad m(\text{N}_2) = 1.0 \quad m(\text{O}_2) = 0.78 \quad m(\text{H}_2) = 2.0 \quad m(\text{H}_2\text{O}) = 14.0 \)
Dependence of explosion / no explosion on the composition of gas mixture

Investigation at $T$, $p$ where the rates of reactions $R2$ and $R5$ are similar

$$R2 \cdot H + O_2 \rightarrow \cdot OH + :O \quad r_2 = \text{intermediate}$$

$$R5 \cdot H + O_2 + M \rightarrow \cdot HO_2 + M \quad M=H_2/O_2 \quad r_5 = \text{slow ($m=1$)} \rightarrow \text{explosion}$$

$$R2 \cdot H + O_2 \rightarrow \cdot OH + :O \quad r_2 = \text{intermediate (no change)}$$

$$R5 \cdot H + O_2 + M \rightarrow \cdot HO_2 + M \quad M=H_2O \quad r_5 = 14 \times \text{faster} \rightarrow \text{NO EXPLOSION}$$

- hydrogen and oxygen gas inflow to a reactor
- setting of temperature and pressure: conditions of explosion
- before the explosion: $H_2/O_2$ mixture, average collision efficiency $m=1$

after the explosion high $[H_2O]$ in the chamber and the average collision efficiency $m=14$

it prevents the explosion until the inflowing gases remove water.

$\Rightarrow$ a series of explosions

Tomlin et al., Combust.Flame, 91, 107-130(1992)

$p$ and $T$ dependence of the hydrogen-air system between limits 1 and 3

fixed temperature, increasing pressure
$R5$ becomes more important than $R2$: explosive mixture $\rightarrow$ non-explosive

fixed pressure, increasing temperature
$R2$ becomes more important than $R5$: non-explosive $\rightarrow$ explosive mixture

at atmospheric pressure ($p=1$ atm)
the threshold temperature is about 900 K:

above 900 K mixtures of air with hydrogen / wet CO / organics explodes due to reaction $R2 \cdot OH + H_2 \rightarrow \cdot HO_2^* \rightarrow \cdot H + H_2O$

below 900 K hydrogen, wet CO: no reaction
hydrocarbons, oxygenates: „low temperature oxidation”, „cool flames”
Propagation of hydrogen–air flame

\[ \text{.H transport to cold mixture:} \quad \text{R5} \quad \text{.H + O}_2 + \text{M} \rightarrow \text{.HO}_2 + \text{M} \rightarrow \text{NO explosion} \]

\[ \text{.H transport to hot mixture:} \quad \text{R2} \quad \text{.H + O}_2 \rightarrow \text{.OH + .O} \rightarrow \text{explosion} \]

Methanol – air flame

video with original speed and then 5x slower
Topic 4. Combustion of wet CO, methane and other alkanes

The significance of syngas in environmental protection.

Reaction steps of wet CO combustion.

C1 and C2 reaction chains of methane combustion.

The reaction steps of the C1 and C2 chains.

Combustion of higher alkanes (ethane, propane, buthane).

Why is the flame of hydrocarbons blue?

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Combustion of wet carbon monoxide

dry CO: no combustion

wet CO (CO + O₂ + H₂O / H₂ / organics) combustion

Large amount of coal is available (e.g. in China), but the direct combustion produces large amount of pollution

Exposing burning coal to water vapour, mixture of CO and H₂ is produced: synthesis gas

water-gas shift reaction, WGS:

CO + H₂O = CO₂ + H₂ changing the CO/H₂ ratio

electricity production in gas turbines and internal combustion engines clean, well controllable, efficient

Technologies combating global warming:

synthesis gas from biomass (CO₂ neutral technology!)

IGCC-CCS technology: integrated gasification combined cycle + carbon capture and storage

Combined Cycle Gas Turbine (CCGT) (60% efficiency) the heat of a gas turbine is used in a steam turbine

Oxy-fuel combustion: combustion with pure oxygen, easier CO₂ capture
Combustion of wet CO 2

Mechanism of wet CO combustion:
H/O reactions ⇒ almost equilibrium state of H/O/OH radicals
and then:

\[ \text{CO} + \cdot \text{OH} \rightarrow \text{CO}_2 + \cdot \text{H} \]

This is the main heat producing step
MAIN SOURCE OF HEAT IN ALL HYDROCARBON FLAMES!!!

Important CO reactions:
- \[ \text{CO} + \cdot \text{OH} = \text{CO}_2 + \cdot \text{H} \] at high temperature and low pressure
- \[ \text{CO} + \cdot \text{HO}_2 = \text{CO}_2 + \cdot \text{OH} \] at low temperature (T<1300 K), and high pressure
- \[ \text{CO} + \text{O}_2 = \text{CO}_2 + \cdot \text{O} \]

Other, less important reaction:
- \[ \text{CO} + \text{O} + \text{M} = \text{CO}_2 + \text{M} \]
- \[ \text{H} + \text{CO} + \text{M} = \text{HCO} + \text{M} \] HCO formation and consumption
- \[ \text{H} + \text{HCO} = \text{H}_2 + \text{CO} \]
- \[ \text{HCO} + \text{O} = \text{CO} + \text{OH} \]
- \[ \text{HCO} + \text{O}_2 = \text{CO} + \text{HO}_2 \]
- \[ \text{HCO} + \cdot \text{O} = \text{CO} + \cdot \text{H} \]
- \[ \text{HCO} + \text{OH} = \text{CO} + \text{H}_2\text{O} \]

Combustion of methane

\[ \text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \]

The overall reaction

The mechanism:

1. Production of radical \( \text{CH}_3 \)

- \[ \text{CH}_4 + \text{O}_2 \rightarrow \cdot \text{CH}_3 + \cdot \text{HO}_2 \] homogeneous explosion
- \[ \text{CH}_4 + \text{M} \rightarrow \cdot \text{CH}_3 + \cdot \text{H} + \text{M} \] homogeneous explosion

- \[ \text{CH}_4 + \cdot \text{H} \rightarrow \cdot \text{CH}_3 + \text{H}_2 \] in a flame front
- \[ \text{CH}_4 + \cdot \text{OH} \rightarrow \cdot \text{CH}_3 + \text{H}_2\text{O} \] in a flame front

2. Production of formaldehyde from \( \text{CH}_3 \)

- \[ \cdot \text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}. + \cdot \text{O} \]
- \[ \text{CH}_3\text{O}. + \text{M} \rightarrow \text{CH}_2\text{O} + \cdot \text{H} + \text{M} \]
- \[ \cdot \text{CH}_3 + \cdot \text{O} \rightarrow \text{CH}_2\text{O} + \cdot \text{H} \]
3. production of .HCO from CH\(_2\)O

\[
\text{CH}_2\text{O} + .H \rightarrow .\text{HCO} + \text{H}_2 \\
\text{CH}_2\text{O} + .\text{OH} \rightarrow .\text{HCO} + \text{H}_2\text{O}
\]

4. production of CO from .HCO

\[
\text{HCO} + .H \rightarrow \text{CO} + \text{H}_2 \\
\text{HCO} + \text{M} \rightarrow \text{CO} + .H + \text{M} \\
\text{HCO} + \text{O}_2 \rightarrow \text{CO} + .\text{HO}_2
\]

5. production of CO\(_2\) from CO

\[
\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}
\]

The radicals to these reactions are provided by the H\(_2\)/O\(_2\) reaction system.

6. production of C\(_2\)H\(_6\):

\[
2 \text{CH}_3 \rightarrow \text{C}_2\text{H}_6
\]
Combustion of methane

stoichiometric methane-air flame

rich methane-air flame

Methane combustion – main reaction pathways

lean ($\phi = 0.7$) methane-air flame
High-temperature combustion of alkanes

\[ R\cdot \xrightarrow{\text{alkane}} \text{alkyl radicals} \]
\[ \xrightarrow{\text{alkene} + \text{small radical}} \]

High-temperature combustion:
- reactions between oxygen-containing radicals (\( :O, .OH, .HO_2, \ldots \))
- other small radicals (\( .H, .CH_3, .C_2H_3, \ldots \))
- small molecules (\( e.g. C_2H_4 \) and \( C_2H_2 \))

High-temperature combustion of hydrogen – wet CO – hydrocarbons

The core of all high-temperature (T > about 900 K) combustion is the hydrogen combustion mechanism. Adding other reactions, the combustion of other fuels can be described.
The colour of a flame

The hydrogen–oxygen flame is colourless („invisible”), because none of the species causes it to be coloured.

The premixed methane–air flame is pale blue:
radical CH becomes electronically excited by collisions.
It radiates a pale blue light when returns to ground state.

The candle flame and the non-premixed methane–air flame is yellow:
The alkane molecules are decomposed (pyrolysed) in the hot oxygen-free gas. Olefins and radicals are formed.
The chemical reactions of these species make small soot particles.
The soot particles emit yellow light at 1200 K. („black body radiation”)

Outside the flame front there is high oxygen concentration and high temperature.
The soot particles are completely burnt. (⇔ wrong sooting candles.)

Topic 5. Internal combustion engines

The operation of Otto- and Diesel-engines
HCCI-engine, stratified charge engines.

The advantages and disadvantages of the various types.
The aspect of environmental protection.

Change of pressure in the cylinder of a petrol engine during normal operation and knocking.

What is knocking?

Determination of the knocking properties of fuels.
The principles of car engine development

The aim is much smaller fuel consumption, because
- fuel is getting more and more expensive
- combating global warming by reducing the CO₂ emission.

The steps of optimization:
1. A basic idea
2. Detailed computational model of the planned engine:
   - accurate simulation of both the chemical processes (combustion) and physical processes (gas flows, heat transfer, mechanics)
3. Experiments with an engine prototype

Otto-engine ↔ Diesel-engine

**Otto-engine (1876)**
- Nicolaus Otto (1832-1891)
- high fuel consumption
- high power per unit cylinder volume
- electric spark + spread of a premixed flame
- nearly stoichiometric fuel-air ratio
- the compression is lower than optimal, to avoid knocking
- much NO is produced (to be removed by the catalyst)

**Diesel-engine (1893)**
- Rudolf Diesel (1858-1913)
- low fuel consumption
- low power for unit cylinder volume
- hot air generated by compression + Diesel oil injection
- fuel rich combustion, diffusion flame
- the compression is higher than optimal, to ensure ignition
- much soot is produced (to be removed by the filter)

None of these engine types are optimal.
Which is the engine that combines the advantages of both engines above?
HCCI: Homogeneous Charge Compression Ignition engine

petrol-air mixture in the cylinder, compressed by a piston

the mixture is ignited by the compression heat
(like in the Diesel-engine)

very precise ignition timing is needed, controlled by
the chemistry and the valves

low temperature ⇒ few NO, few soot

Several companies (*e.g.* Honda and General Motors)
have experimental engines

The only HCCI car on the street:
Mercedes-Benz: prototype F700

---

Mercedes F700

„DiesOtto“ engine

4 cylinders
1.8 liter total cylinder volume
petrol injection

its power is equivalent to those of the
3.5 liter V6 petrol engine of the
Mercedes S-class

fuel consumption 5.3 liter/ 100 km = 44.38 MPG (US) = 53.30 MPG (UK)
127 gramm CO\textsubscript{2} / km

very low NOx and soot emission

The fuel-air mixture is usually ignited by the compression, but
spark ignition is used at idle speed and at very high rotational speed.
Stratified charge engines

1. compression of the air
2. fuel injection near the top dead centre
3. several fuel inlets for making a non-homogeneous fuel-air mixture

stoichiometric mixture near the spark plug: stable flame spread
fuel lean mixture far from the spark plug: reduced possibility of knocking, less remaining hydrocarbon and CO, less NOx is produced.

Using homogeneous charge, the mixture should be stoichiometric.

The advantages of stratified charge:
• high compression ratio without knocking
• the total equivalence ratio is fuel lean
• low NOx, hydrocarbon and soot emission

Map for the operation of engines

fuel droplets are burning in the Diesel-engines:
high local $\varphi \Rightarrow$ soot formation

petrol engines:
high temperature and nearly $\varphi = 1 \Rightarrow$ NOx formation

LTC: low-temperature combustion
Engine knocking

the power a petrol engine
can be increased
by increasing the compression ratio

BUT: it is limited by knocking

pressure in the cylinder vs. crank angle
for a normally working and a knocking engine

Karl Benz and his wife, Bertha Ringer
with car Benz Victoria of 1893

Engine knocking 2

normal operation:
ignition before the top dead centre (TDC)
using a spark plug.

spread of a flame front in the mixture
→ pressure maximum after the TDC
smooth pressure function,
max. pressure is about 60 atm

ignition timing
BTDC: before top dead centre
(for example 5°±1°/900 BTDC)

knocking:
explosion of the gas and therefore
→ pressure maximum before the TDC
sharp pressure peaks
max. pressure is about 80 atm
BUT: at some locations temperature, pressure and fuel concentration is different: hot spots
hot spots may start a new flame front

→ pressure induced flame propagation
OR
→ detonation waves

consequences:
⇒ higher pressure earlier
⇒ pressure oscillations

Engine knocking 3

Engine knocking 4

The consequence of knocking:
• lower power
• damaged engine due to higher pressure and faster pressure rise

Avoiding knocking at a fixed compression ratio:
• a different design of the engine
• using higher octane number fuel
Octane number

Characterization of petrol: (since about 1930)

% composition of a \( n \)-heptane – iso-octane (2,2,4-trimethylpentane) mixture

\[
\begin{align*}
100 &= 100\% \text{ iso-octane} \\
0 &= 100\% \text{ } \text{n-heptane}
\end{align*}
\]

The knocking ability of a fuel is compared to the knocking of a \( n \)-heptane – iso-octane mixture in a standard single cylinder engine. The octane number can be negative or higher than 100!

"octane number" in Europe, Australia, and New Zealand:
RON: research octane number
inversion of knocking at 600 RPM

"octane number" in Brazil, Canada, and the United States:
PON (Pump Octane Number) = Anti-Knock Index (AKI) = (RON+MON) /2
MON: motor octane number (lower than RON by 8-10)
investigation of knocking at 900 RPM (+ more realistic engine conditions)

---

Topic 6. Low-temperature hydrocarbon oxidation

Chain branching mechanism below 900 K.

The reaction steps of low temperature propane oxidation.

The characteristic features of intramolecular hydrogen abstraction.

Why does the knocking depend on the structure of the fuel molecule?

The \( \cdot \text{HO}_2/\text{H}_2\text{O}_2 \) explosion route.

Two stage ignition, negative temperature coefficient (NTC) ignition and cool flames.
Low-temperature hydrocarbon oxidation

At high temperature the main chain branching reaction is H + O₂ → O + OH but it is too slow at low temperature.

Hydrogen, wet CO, and methane at low temperature:
no oxidation in chain reaction
The threshold temperature is about 900 K (depends on pressure).

Hydrocarbons (ethane and above) can be oxidized at low-temperature in chain reaction.

This is the basis of a series of industrially important notions:
- ignition of fuel in a Diesel engine
- knocking of petrol engines
- industrial safety (e.g. safety of oil rigs, crude oil processing)

A series of interesting phenomena:
- cool flames
- two-step ignition


The chemistry of low-temp HC oxidation

1. \[ \text{RH} \rightarrow \text{R} \]
2. \[ \text{ROO} \leftrightarrow \text{ROOH} \]
3. \[ \text{ROOH} \rightarrow \text{RO} + \text{OH} \]
4. \[ \text{HO}_2 + \text{alkene} \]
5. \[ \text{OH} + \text{O-hetercycle} \]
6. \[ \text{HOO}_2 \text{O}_2 \]
7. \[ \text{HOO}_2 \text{O} + \text{OH} \]
8. \[ \text{OO}_2 \text{O} + \text{OH} \]

(1) initiation
This is a very slow reaction in propene/air mixtures:
\[ \text{CH}_3\text{CH}_2\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2. + \text{HO}_2 \]

Faster reaction in the presence of \text{.OH}:
\[ \text{CH}_3\text{CH}_2\text{CH}_3 + \text{.OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2. + \text{H}_2\text{O} \]

(2) production of alkylperoxy radicals
\[ \text{CH}_3\text{CH}_2\text{CH}_2. + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OO} \]

(3) production of alkylhydroperoxide
\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{OO} + \text{.HO}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OOH} + \text{O}_2 \]
The chemistry of low-temp HC oxidation 2

(4) decomposition of the alkylhydroperoxide
\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{OOH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{O} + .\text{OH} \]

reaction (3)+(4): the less reactive .HO_2 radical is converted to high reactivity.OH radical!

(5) generation of HO_2 radical + alkene
\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{OO} \rightarrow .\text{HO}_2 + \text{CH}_3\text{CH} = \text{CH}_2 \]

(6) intramolecular hydrogen atom abstraction

the most important step of the reaction chain

OO. group acquires a hydrogen atom of the hydrocarbon chain

---

step (6): intramolecular hydrogen atom abstraction

The chemical reaction in 1D:
\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{OO} \rightarrow \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2\text{OOH} \]

or
\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{OO} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \]

The chemical reaction in 2D:

1,5-hydrogen atom transfer and 1,4-hydrogen atom transfer: frequent

1,3-hydrogen atom transfer: rare event

1,\( n \)-hydrogen atom transfer \((n > 5)\): rare event

Reason:
1,3-hydrogen atom transfer = 4-membered ring = large ring strain energy

1,\( n \)-hydrogen atom transfer \((n > 5)\) = low probability to meet a hydrogen atom that belongs to a far carbon atom
The chemistry of low-temp HC oxidation 3

(7) - (8) decomposition of the alkyl-hydroperoxy radical

\[ \text{CHCH}_2\text{CH}_2\text{OOH} \rightarrow \text{HO}_2 + \text{CH}_2\text{=CH}_2 \]  \( (7) \)

\[ \text{CHCH}_2\text{CH}_2\text{OOH} \rightarrow \text{OH} + \text{oxetane} \]  \( (8) \)

(7) \text{HO}_2 product: deceleration
(8) \text{OH} product: acceleration

(9) alkyl-hydroperoxy radical + \text{O}_2

\[ \text{CHCH}_2\text{CH}_2\text{OOH} + \text{O}_2 \]

\[ \text{OOCHCH}_2\text{OOH} \]

(10) second intramolecular hydrogen atom abstraction

another \text{OO} group is also able to get another H-atom from the hydrocarbon chain.
Similar to reaction (6).

\[ \text{OOCH}_2\text{CH}_2\text{OOH} \]

\[ \text{HOOCH}_2\text{CH}_2\text{CHOOH} \]

The chemistry of low-temp HC oxidation 4

(11) generation of \text{OH-radical:}

\[ \text{HOOCH}_2\text{CH}_2\text{CHO} \rightarrow \text{HOOCH}_2\text{CH}_2\text{CHO} + \text{.OH} \]

(12) generation of a second \text{OH-radical:}

\[ \text{HOOCH}_2\text{CH}_2\text{CHO} \rightarrow \text{OCH}_2\text{CH}_2\text{CHO} + \text{.OH} \]

Steps (11) and (12) produce 2 \text{OH}

Summary of steps (1) - (12):
step (1): consumption of 1 \text{OH}
steps (1)-(12): production of 2 \text{OH}

⇒ branching chain reaction
⇒ hydrocarbon–air mixtures may explode below 900 K!
Another chain branching mechanism above about 1000 K

\[ \text{.HO}_2 \text{ + RH} \rightarrow \text{H}_2\text{O}_2 \text{ + .R} \]
\[ \text{H}_2\text{O}_2 \text{ + M} \rightarrow 2 \text{ .OH + M} \] (chain branching)
\[ \text{.OH + H}_2 \rightarrow \text{H}_2\text{O + H.} \]
\[ \text{.H + O}_2 \text{ + M} \rightarrow \text{.HO}_2 \text{ + M} \]

effect of the first two reactions:
\[ \text{.HO}_2 \rightarrow 2 \text{ .OH} \]

effect of the last two reactions:
\[ 2 \text{ .OH} \rightarrow 2 \text{ .HO}_2 \]

(These are the 3rd explosion limit reactions of the H/O system.)

Hydrocarbon oxidation:
changes with temperature and pressure
Low-temperature hydrocarbon oxidation: two-step ignition

$n$-heptane–air mixture; adiabatic ignition
measured temperature – time curve
$T_0 = 625$ K, $p = 15$ atm

Cool flames

If heat is removed from the reacting mixture in a proper way, then the flame can be stabilized near the lower heat generating peak.

the cool flame is frequently oscillating

$T < 700$ °C

Discovery:
1810 Sir Humphry Davy
(„the flame did not burn his finger“)

term „cool flame“
1929 Harry Julius Emeléus
recorded the emission IR spectrum of the flame

The coolest cool flame: 80 °C
diethylether–air flame at pressure 300 torr
pale bluish colour from CH$_2$O* emission
High temperature hydrocarbon ignition

Alkane ignition: $\log(\tau) - 1/T$ follows a line

Low-temperature hydrocarbon oxidation

NTC ignition

The reason is the generation of peroxide radicals in equilibrium reactions: $X. + O_2 \rightleftharpoons XO_2$

Small increase of the temperature $\Rightarrow$ the equilibrium is shifted to the left, slows down the low-temperature chain branching reaction
Pollutant formation during combustion

The main routes of NO formation:
• thermal NO or Zeldovich-NO
• prompt NO or Fenimore-NO
• NO generated via $N_2O$
• NO generated via NNH
• NO generated from fuel-bounded nitrogen

The chemistry of the various routes and their features.

Pollutant formation during combustion

Water is the only environmentally friendly combustion product:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>greenhouse gas</td>
</tr>
<tr>
<td>CO</td>
<td>poisoning</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>acid rain</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>harmful products:</td>
</tr>
<tr>
<td>NO, NO$_2$</td>
<td>causing photochemical smog and acid rain in the troposphere decomposes $O_3$ in the stratosphere</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>greenhouse gas</td>
</tr>
</tbody>
</table>
Five ways of NOx production

1) thermal NO or Zeldovich-NO

2) prompt NO or Fenimore-NO

3) NO generated via N₂O

4) NO generated via NNH

5) NO generated from fuel-bounded nitrogen

Thermal NO

suggested by Y. B. Zeldovich, 1946

\[
\begin{align*}
(1) \quad & O + N_2 = NO + N \\
(2) \quad & N + O_2 = NO + O \\
(3) \quad & N + OH = NO + H
\end{align*}
\]

N atom reacts extremely fast, therefore the quasi-steady-state approximation (QSSA) is applicable:

\[
\frac{d[NO]}{dt} = 2k_1[O][N_2]
\]
Thermal NO 2

Thermal NO production requires:

- high temperature $T>1900$ K, because the activation energy of reaction step 1 is high
  \[ (1) \quad \text{O} + \text{N}_2 = \text{NO} + \text{N} \quad E_1=314 \text{ kJ/mol} \]

- long residence time (slow reaction)
- high $[\text{O}]$
  (these conditions are present in the post-flame region)

Experimental study:

- hydrogen flame
- wet CO flame

Thermal NO 3

Calculation:

- using a detailed reaction mechanism, calculated „accurate“ $T$, $[\text{O}]$, $[\text{OH}]$

- $T$, $\text{H}_2$, $\text{O}_2$ measured, $[\text{O}]$, $[\text{OH}]$ calculated using QSSA

WRONG APPROACH:

assuming that the $[\text{O}]$ corresponds to the thermodynamic equilibrium:
  10x wrong (higher) value
Prompt NO 1

discovered by C.P. Fenimore, 1979

observation: much NO can be produced in methane flames
cannot be explained with the Zeldovich mechanism

$\text{N}_2 \rightarrow \text{NO catalysed by radical CH}$

features:
important in fuel rich flames, due to the high [CH]

important only at not very high temperatures (T~1000K),
because at high temperature thermal NO production is faster

most important reaction:

$\text{CH} + \text{N}_2 = \text{NCN} + \text{H}$  (Moskaleva, Lin, Smith, 2000-)

Prompt NO 2

origin of radical CH

$\text{CH}_3 + \text{OH} = \text{CH}_2 + \text{H}_2\text{O}$
$\text{CH}_3 + \text{H} = \text{CH}_2 + \text{H}_2$
$\text{CH}_2 + \text{OH} = \text{CH} + \text{H}_2\text{O}$
$\text{CH}_2 + \text{H} = \text{CH} + \text{H}_2$

transformation of HCN, N and NH

$\text{CH} \quad \text{O} \quad \text{H} \quad \text{OH}$
$\text{N}_2 \quad \rightarrow \quad \text{NCN} \quad \rightarrow \quad \text{NCO} \quad \rightarrow \quad \text{NH} \quad \rightarrow \quad \text{N} \quad \rightarrow \quad \text{NO}$

$\text{CH}+\text{N}_2 = \text{NCN}+\text{H}$
$\text{NCN}+\text{O} \rightarrow \text{NCO}+\text{N}$
$\text{NCO}+\text{H} \rightarrow \text{NH}+\text{CO}$
$\text{NH}+\text{H} \rightarrow \text{N}+\text{H}_2$
$\text{N}+\text{OH} \rightarrow \text{NO}+\text{H}$
**NO production via \( \text{N}_2\text{O} \)**

**important reactions:**

\( \text{N}_2\text{O} \) production from \( \text{N}_2 \)
- \( \text{N}_2 + \text{O} + \text{M} = \text{N}_2\text{O} + \text{M} \)
- \( \text{N}_2 + \text{OH (+M)} = \text{N}_2\text{O} + \text{H (+M)} \)
- \( \text{N}_2 + \text{HO}_2 (+\text{M}) = \text{N}_2\text{O} + \text{OH (+M)} \)
- \( \text{N}_2 + \text{O}_2 (+\text{M}) = \text{N}_2\text{O} + \text{O (+M)} \)

\( \text{N}_2\text{O} \) production from \( \text{N}_2\text{O} \)
- \( \text{N}_2\text{O} + \text{O} = 2 \text{ NO} \)
- \( \text{N}_2\text{O} + \text{H} = \text{NO} + \text{NH} \)

**features:**

- important in lean and low temperature flames
  (at such conditions thermal NO and prompt NO is not important).

- termolecular reactions:
  their rate increases linearly with pressure

---

**NO production via \( \text{NNH} \)**

**Important reactions:**
in the first reaction steps, \( \text{NH} \) and \( \text{NNH} \) are produced from \( \text{N}_2 \)

\( \text{N}_2 + \text{H} = \text{NH} + \text{N} \)
\( \text{N}_2 + \text{OH} = \text{NH} + \text{NO} \)

\( \text{N}_2 + \text{H} = \text{NNH} \)
\( \text{N}_2 + \text{OH} = \text{NNH} + \text{O} \)
\( \text{N}_2 + \text{H}_2 = \text{NNH} + \text{H} \)
\( \text{N}_2 + \text{H}_2\text{O} = \text{NNH} + \text{OH} \)

**feature:**

important in lean and low-temperature flames

\( \Rightarrow \) thermal NO and prompt NO routes are slow) and
at low pressure (at high pressure the „via \( \text{N}_2\text{O} \)“ route is fast).
The nitrogen of NO may also come from the fuel. It is especially important at coal combustion.

natural gas: no fuel nitrogen
coal: 0.5-2 w% N (coal has also high H content)

The transformation (fuel-N → NO) depends on:
- conditions of combustion (temperature and stoichiometry)
- concentration of N-compound

NO production from fuel N

heterocyclic compounds → HCN → NO
amines → NH₃ → NO

reactions of transformation:

\[
\begin{align*}
\text{NH}_3 + \text{H} &= \text{NH}_2 + \text{H}_2 \\
\text{NH}_4 + \text{OH} &= \text{NH}_3 + \text{H}_2 \text{O} \\
\text{NH}_3 + \text{O} &= \text{NH}_2 + \text{OH} \\
\text{NH}_2 + \text{O} &= \text{HNO} + \text{H} \\
\text{HNO} + \text{M} &= \text{NO} + \text{H} + \text{M} \\
\text{HNO} + \text{OH} &= \text{NO} + \text{H}_2 \text{O} \\
\text{HNO} + \text{NH}_2 &= \text{NO} + \text{NH}_3 \\
\text{N} + \text{OH} &= \text{NO} + \text{H} \\
\text{N} + \text{NO} &= \text{N}_2 + \text{O} \\
\text{NH} + \text{NO} &= \text{N}_2 \text{O} + \text{H} \\
\text{N}_2 \text{O} + \text{H} &= \text{N}_2 + \text{OH}
\end{align*}
\]
Topic 8. Methods for decreasing NO emission

Primarily and secondary methods and their features.
The chemistry of staged combustion.
Selective heterogeneous catalytic reduction.
The Thermal DeNOx process and its chemical kinetics.
The usage of AdBlue.

NO removal methods

**Primary methods:** combustion modification
- staged combustion
- fuel staging
- air staging
- reburning

**Primary methods:**
*usually extensive modification of the furnace is needed*
→ these principles are mainly used at the design of new furnaces

**NO removal without the modification of the furnace:**
→ aftertreatment of the exhaust gas
Aftertreatment of combustor exhaust products

selective heterogeneous catalytic reduction

selective catalytic reduction

— Thermal De NO\textsubscript{X}

— AdBlue

Chemistry of staged combustion

the fuel rich flame has a reduction capacity

→ NO is reduced to N\textsubscript{2}

main reactions:

\[ \text{CH}_2 + \text{NO} = \text{HCNO} + \text{H} \]
\[ \text{CH} + \text{NO} = \text{HCN} + \text{O} \]
\[ \text{C} + \text{NO} = \text{CN} + \text{O} \]

and then CN → N\textsubscript{2}

\[ \begin{align*}
\text{H}_2 & \quad \text{O} \quad \text{H} \quad \text{H} \quad \text{NO} \\
\text{CN} & \rightarrow \text{HCN} \rightarrow \text{NCO} \rightarrow \text{NH} \rightarrow \text{N} \rightarrow \text{N}_2 \\
& \quad \text{H} \quad \uparrow \text{H} \\
& \quad \text{HNCO} \rightarrow \text{NH}_2
\end{align*} \]
Chemistry of staged combustion 2

**problem:** if $\phi >> 1 \rightarrow$ the furnace has a low efficiency

**solution:**

first phase: fuel rich stage $\phi = 1.4$

NO reduction to N$_2$ (including the NO of fuel origin)

second phase: air stage
(complete fuel conversion, high efficiency, but here the temperature is low)

reburning: adding fuel to the exhaust gas

Selective heterogeneous catalytic reduction

basic application: catalysts in cars CO $\rightarrow$ CO$_2$: NO $\rightarrow$ N$_2$

**requirements:**
- well defined, nearly stoichiometric $\lambda$ ( $\phi = \lambda = 1$ )
  $\lambda$-sensor electronic feedback control
- gas without particles

- advantage: simple operation, long lifetime
- disadvantage: does not work in power stations, clogging
Car catalysts

„three way” catalyst ($T > 600$ K)

Oxidative reactions
with Pt and Pd catalysts:
1. organics $\rightarrow$ CO$_2$ + H$_2$O
2. CO $\rightarrow$ CO$_2$

Reductive reactions
with Rh catalyst:
3. NO $\rightarrow$ N$_2$

Thermal De NOX

NH$_3$ is added to the exhaust gas

features:
- works in a narrow temperature window around $T=1250$ K
  ($1100$ K $< T < 1400$ K)

+ H$_2$ or
+H$_2$O$_2$: temperature window moves downwards
  its width remains identical

+H$_2$O: temperature window moves upwards
  its width remains identical

- SO$_2$: white powder appears (fouling)

- much extra O$_2$ should be present

- increasing [NH$_3$] with fixed [O$_2$]: lower efficiency
Chemistry of Thermal De NOX 1

$$\text{NH}_3 + .\text{OH} = .\text{NH}_2 + \text{H}_2\text{O}$$

$$\text{.NH}_2 + \text{NO} = .\text{NNH} + .\text{OH}$$

$$\text{.NNH} + \text{NO} = \text{N}_2 + \text{HNO}$$

$$\text{HNO} + \text{M} = .\text{H} + \text{NO} + \text{M}$$

$$\text{.H} + \text{O}_2 = .\text{OH} + :\text{O}$$

$$:\text{O} + \text{H}_2\text{O} = 2 .\text{OH}$$

$$\text{NH}_3 + \text{NO} + \text{O}_2 \rightarrow \text{N}_2 + 3 .\text{OH}$$

This is the overall equation of the Thermal DeNO\textsubscript{X} method.

Chemistry of Thermal DeNO\textsubscript{X} 2

Chain terminating reactions:

$$\text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O}$$ (removes NO, but chain terminating!)

$$\text{NH}_2 + \text{NHO} \rightarrow \text{NH}_3 + \text{NO}$$

$$\text{OH} + \text{HNO} \rightarrow \text{H}_2\text{O} + \text{NO}$$

Low temperature ($T < 1100 \text{ K}$)

$\rightarrow$ the chain terminating reactions above are fast

High temperature ($T > 1400 \text{ K}$)

$\rightarrow$ oxidation of NH\textsubscript{3} to NO

Without water:

$$\text{NH}_3 + \text{O} \rightarrow \text{NH}_2 + \text{OH}$$ (instead of $\text{H}_2\text{O} + \text{O} \rightarrow 2\text{OH}$ chain branching)

Less OH is produced

Much ammonia is present:

$$\text{NH}_3 + \text{H} \rightarrow \text{NH}_2 + \text{H}_2$$ (instead of $\text{O}_2 + \text{H} \rightarrow \text{OH} + \text{O}$ chain branching)
**Thermal DeNOx**

This is the most practical exhaust gas treating method

Relatively cheap.

The temperature of the exhaust gas should be in the good temp. interval.

**AdBlue**

AdBlue: 32,5% carbamide in distilled water

Carbamide decomposes at high temp:

\[(NH_2)_2CO + H_2O \rightarrow 2 NH_3 + CO_2\]

The obtained NH\(_3\) removes NO with the same chemical reactions as at the Thermal DeNOx process.

AdBlue consumption:

- 3-4% (Euro 4)
- 5-7% (Euro 5)

of Diesel oil consumption
Topic 9. Soot

Advantages and disadvantages of soot formation.

The process of soot formation. PAH.

The HACA mechanism.

Soot and the global warming.

Soot

„Carbon black” is an important industrial product.
• a component of black paints
• 60% of the mass of car tyres is soot

• „black body radiation”: soot is an important intermediate
• soot is the source of the yellow light of the candle
• soot improves the heat transfer in furnaces
  furnaces: generation of soot and then complete burnout

Heavy pollutant:
main sources are the old Diesel engines

• carcinogen (may cause cancer)
• may absorb PAHs, which are also carcinogen
• reactions with NOx increase the carcinogen activity
Soot 2.

Route to soot formation

Step 1: production of small hydrocarbon species

in fuel rich hydrocarbon flames:
high $[C_2H_2]$ and $[.CH]$
(see the earlier chemical equations)

Step 2 : production of soot precursors

$CH + C_2H_2 \rightarrow H_2 CCCH$ (propargyl radical)
$2 H_2 CCCH \rightarrow$ benzene
benzene $\rightarrow \rightarrow \rightarrow$ PAH

PAH: polycyclic aromatic hydrocarbon
Route to soot formation 2

Production of PAHs is gas phase chemical reactions:
the chemistry is not very clear.

One of the theories: “HACA mechanism”

Hydrogen abstraction ACetylene Addition

- the mass of the molecules and radicals is continuously increasing
- these become solid above about 2000 Dalton

Route to soot formation 3

Step 3: increasing the size of young soot

This a gas phase – solid phase heterogeneous reaction.
The size of the solid particles is increasing by chemical reactions till about size 20 nm

fresh soot: C : H = 1 : 1

Step 4: ageing of soot

soot particles are aggregating to form larger particles
at the exit from the flame C : H = 10 : 1

sooting of premixed flames:
naphthalene > benzene > paraffins > olefins > acetylene
Soot and the global warming

„The contribution of soot to global warming is much higher than previously thought. The 'black carbon' is the second only to carbon dioxide in terms of its warming impact on the current climate.”

„Black carbon’s impact on the climate is larger than that of methane and roughly two-thirds that of carbon dioxide.”

„A study published in Science last year estimated that aggressive action on black carbon and methane could cut the rate of warming in half within the next 40 years”

“Reducing black carbon gives you immediate cooling.”


NATURE: Soot a major contributor to climate change, 15 January 2013


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Topic 10. Heterogeneous ignition and combustion

• Sticking coefficient and surface coverage.
• What is happening with the H₂ and O₂ molecules on a Pt surface?
• H₂/O₂/Pt reaction: the shift from slow surface reaction to gas phase flame propagation by increasing the temperature.
• Experimental investigation of heterogeneous ignition.
• Why is the heterogeneous ignition temperature increasing by increasing the concentration of CO or H₂?
• Why is the heterogeneous ignition temperature decreasing by increasing the concentration of CH₄ or C₂H₆?
• Applications of heterogeneous combustion.
Heterogeneous reaction of $H_2$ and $O_2$ on a Pt surface

**Important quantitative measures:**

- **$\varepsilon$** sticking coefficient (dynamic measure)
  - the ratio of the number of the adsorbed ("sticked") species and the number of species hitting the surface ($0 \leq \varepsilon \leq 1$)
  - $\varepsilon = 1$ means that all species stick

- **$\theta$** surface coverage (static measure)
  - the ratio of the number of adsorbed species and the number of species corresponding to full coverage ($0 \leq \theta \leq 1$)
  - $\theta = 1$ means full coverage

Species $H_2$ and $O_2$ are adsorbed on an originally clean Pt surface. $H_2$ has a higher sticking coefficient $\Rightarrow$ higher $H_2$ initial surface concentration. **Surface reaction:** the originally lower surface concentration $O_2$ is fully reacted, the empty sites are mainly covered with $H_2$ $\Rightarrow$ soon the whole surface is covered by $H_2$. ("poisoning the surface with the fuel")

**Slow stationary reaction:**
- if an $H_2$ is desorbed and if the empty side is filled with $O_2$
  $\Rightarrow$ immediate reaction

Increasing temperature: more $H_2$ is desorbed $\Rightarrow$ the rate limiting step is the desorption of $H_2$

**After a threshold temperature**
("heterogeneous ignition temperature")

$\Rightarrow$ **Heterogeneous ignition and combustion**

Increasing temperature: more $H_2$ is desorbed $\Rightarrow$ the rate limiting step is the desorption of $H_2$
Heterogeneous ignition and combustion 2

HETEROGENEOUS IGNITION

- sudden temperature jump
  all adsorbed $\text{H}_2$ and $\text{O}_2$ are immediately reacted
  almost empty surface
- the rate limiting step is the diffusion to the surface

STEADY FAST SURFACE REACTION

Increasing the temperature further
may start a homogeneous flame front.

HOMOGENEOUS IGNITION

Experimental study of heterogeneous ignition

Experimental arrangements:
  stagnation point flow (SPF) above a plate
  wire in flow

The three roles of platinum plate or wire:

- catalytic surface
- temperature measurement (measurement of resistance)
- electric heater
Change of heterogeneous ignition temperature by increasing the H₂, CO, C₂H₄ concentration

The ignition temperature increases (that is the reactivity decreases) by increasing the concentration of the fuel, if it attaches more to the surface than O₂ (examples: H₂, CO, C₂H₄)

Change of heterogeneous ignition temperature by increasing the CH₄ or C₂H₆ concentration

The ignition temperature decreases (that is the reactivity increases) by increasing the concentration of the fuel, if it attaches less to the surface than O₂ (examples: CH₄, C₂H₆)
Applications of heterogeneous combustion

stabilization of ultra lean combustion

radiant burner:
catalytic reaction on a surface:
low power, low temperature, low NOx emission
(applied e.g. on construction sites)

Car catalysts

The Catalytic Converter

Modeling
- A single channel of the monolith is considered
- 2D axis symmetric flow field
- Steady-state laminar flow
See you next week ...