KÉM/282 langokk17em Chemistry and physics of flames

KÖR-2/73 Generation of air pollution in combustion systems

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2024

Topics 1

- 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 2

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:
Analysis of kinetic reaction mechanisms in the autumn semesters

Combustion Science

an interdisciplinary science

chemistry	physical chemistry	reaction kinetics thermodynamics transport phenomena	gas kinetics
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

J. Warnatz, U. Maas, R.W. Dibble: Combustion
Physical and Chemical Fundamentals,
Modeling and Simulation, Experiments, Pollutant Formation
Springer, Berlin, 1996, 2005, 2008

I. Glassman, R.A. Yetter, N.G. Glumac: Combustion
5th edition, Academic, 2014

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

W.C. Gardiner: Combustion Chemistry
1st edition 1985, 2nd edition 1999

S.R. Turns
An introduction to combustion.
Concepts and applications
3rd edition, McGraw-Hill, Boston, 2011

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 earth cold
fire **water**
hot air 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

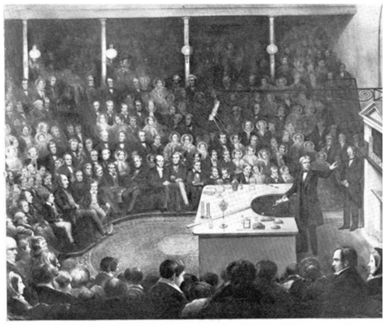
Lomonosov

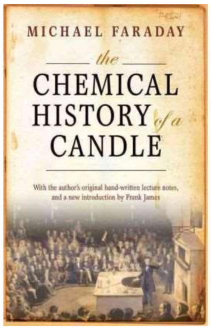
Lavoisier

the original apparatus of Lavoisier

The experiments of Faraday

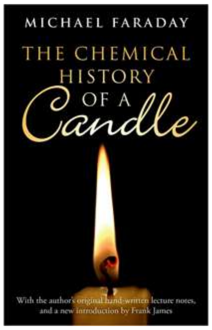
1861 Michael Faraday: The Chemical History of a Candle





MICHAEL FARADAY
the
CHEMICAL
HISTORY of a
CANDLE

With the author's original hand-written lecture notes, and a new introduction by Frank James



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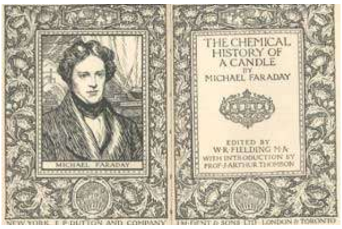
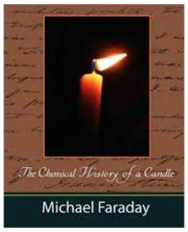


MICHAEL FARADAY

THE CHEMICAL
HISTORY OF
A CANDLE
BY
MICHAEL FARADAY

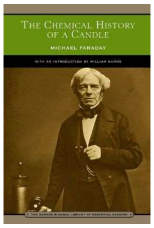
EDITED BY
W·R·FIELDING M·A·
WITH INTRODUCTION BY
PROF·J·ARTHUR THOMSON

NEW YORK E.P. DUTTON AND COMPANY J.M. DENT & SONS LTD LONDON & TORONTO



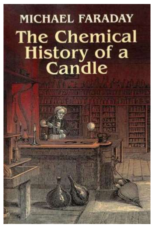
The Chemical History of a Candle

Michael Faraday



THE CHEMICAL HISTORY
OF A CANDLE
MICHAEL FARADAY
WITH AN INTRODUCTION BY WILLIAM BURNS

THE BARNES & NOBLE LIBRARY OF ESSENTIAL READING



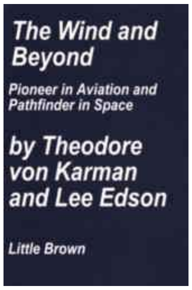
MICHAEL FARADAY
The Chemical
History of a
Candle

Modern combustion science

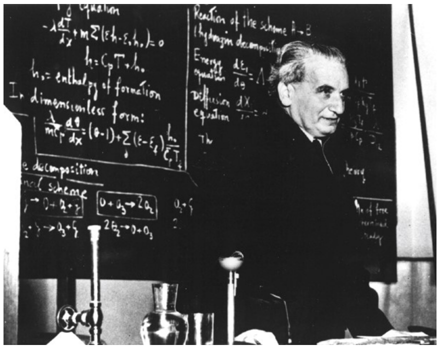
Theodore von Kármán

~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



The Wind and Beyond
Pioneer in Aviation and Pathfinder in Space
by Theodore von Karman and Lee Edson
Little Brown



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 journals:

Combustion and Flame	(Elsevier, IF= 4.4)
Proc. Combust. Inst.	(Elsevier, IF= 3.4)

Hungarian Section of the Combustion Institute
„Magyar Égéstudományi Bizottság”

Further combustion journals:

Combustion Science and Technology	(Taylor & Francis, IF= 1.6)
Combustion Theory and Modelling	(Taylor & Francis, IF= 1.7)
Fuel	(Elsevier, IF= 5.1)
Energy	(Elsevier, IF= 5.5)
Energy & Fuels	(ACS, IF= 3.0)
International Journal of Hydrogen Energy	(Elsevier, IF= 4.1)
Combustion, Explosion, and Shock Waves	(Springer, IF 0.4)
Progress in Energy and Combustion Science	(Elsevier, IF: 26.5)

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*
2018	37th Symposium	*Dublin, Ireland*
2020	38th Symposium	Adelaide, Australia
2022	39th Symposium	*Vancouver, Canada*
2024	40th Symposium	Milano, Italy

Topic 1: Basic notions of combustion science

What is combustion and what is a flame?

Typical combustion reactions. Main types of flames.

Features of laminar / turbulent and premixed / non-premixed flames.

The Hindenburg disaster.

Equivalence ratio.

Definition and typical magnitude of laminar flame velocity.

The change of laminar flame velocity with equivalence ratio, pressure and initial temperature.

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

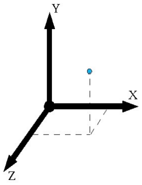
Several typical combustion reactions:

combustion of methane	$CH_4 + 2\ O_2 = CO_2 + 2\ H_2O$
hydrogen-chlorine flame	$H_2 + Cl_2 = 2\ HCl$
termite reaction	$2\ Al + Fe_2O_3 = 2\ Fe + Al_2O_3$

flame: high temperature reaction front

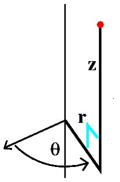
The geometry of flames

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

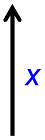


3D flame: *e.g.* a bonfire
T and **c** are the functions of three spatial coordinates (x,y,z)

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 <u>open</u> air inlet:
Complete mixing of air and natural gas in the long metal tube.
Blue premixed flame on the top of the tube.

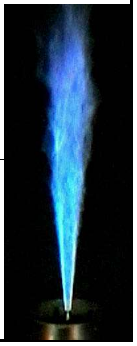
Bunsen burner with <u>closed</u> air inlet:
there is natural gas only in the tube.
Yellow non-premixed flame on the top of the tube.

Similar to a candle flame!

Main flame types

	premixed	non-premixed
laminar flame	gas stove flame Bunsen burner with blue flame	candle Bunsen burner with yellow flame
turbulent flame	petrol engine with carburator	gas turbine rocket engine (H_2+O_2 or kerosene+O_2) Diesel engine

Main flame types

	premixed	non-premixed
laminar flame		
turbulent flame		

Main flame types 2

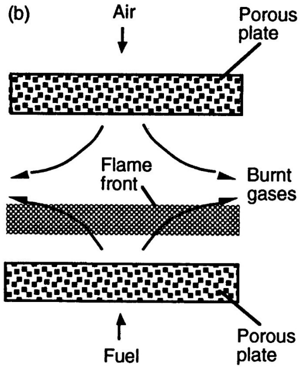
premixed flame
mixing and then burning;
it is safe only in small scale; not used in the industry

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!

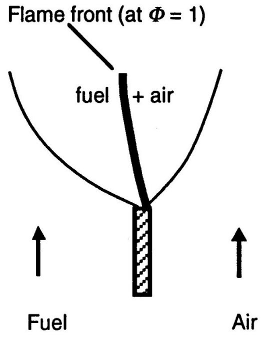
Laminar non-premixed flame/diffusion flame

counterflow geometry



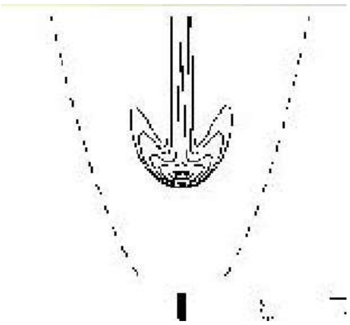
Laminar non-premixed flame/diffusion flame

coflow geometry



triple flame or tulip flame

premixed flame on the two sides
with $\varphi<1$ and $\varphi>1$.
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

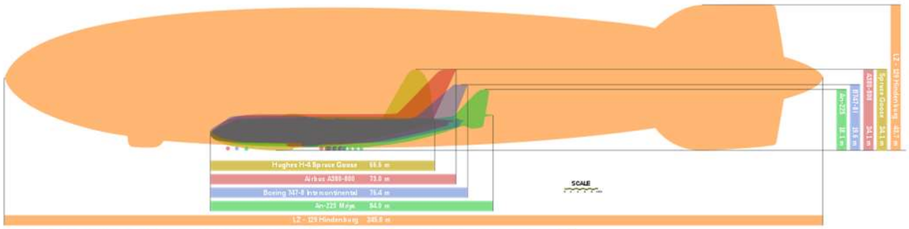
63 flights
17 Atlantic Ocean crossings

72 passengers
61 staff

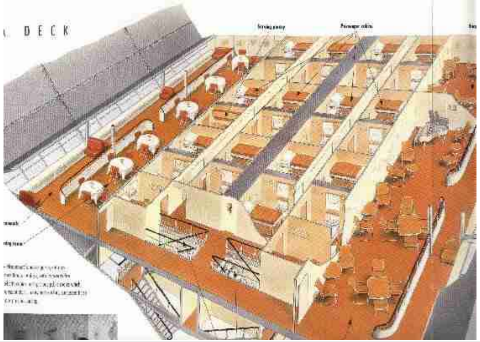
Inside the airship:

passenger quarters, dining room,
lounge, writing room,
washrooms,
a smoking lounge

Airship Hindenburg



The largest areal transport vehicle ever built:
245 meter length, 41 meter diameter



The Hindenburg disaster

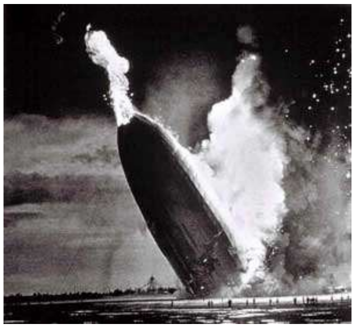
burning of Airship Hindenburg
3 May, 1937 at 19:25

200.000 m^3 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 m^3 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 passangers and the staff had 20 seconds to set themselves free and run away.

Equivalence ratio

fuel lean flame
CH_4+O_2 mixture → CO_2 + H_2O + (O_2 remains)
$\varphi<1;\ \lambda>1$

stoichiometric flame
CH_4+O_2 mixture → CO_2+H_2O
$\varphi=1;\ \lambda=1$

fuel rich flame
CH_4+O_2 mixture → CO_2+H_2O + (CH_4 remains)
$\varphi>1;\ \lambda<1$

In fact, no methane remains, because at high temperature methane decomposes to hydrogen and olefins!

Stoichiometric ratios:

$H_2 + 0.5\ O_2 \rightarrow H_2O$
$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$

$$\varphi = \frac{n_{fuel}/n_{oxidizer}}{(n_{fuel}/n_{oxidizer})_{stoichiometric}}$$

λ : air equivalence ratio (see „λ sensor”)
φ : fuel equivalence ratio $\varphi = 1/\lambda$

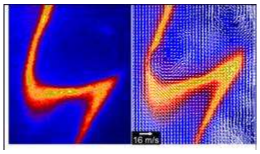
laminar burning velocity, v_L [m/s]

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

1 infinitely large, adiabatic ⇒ no heat loss

2 planar ⇒ 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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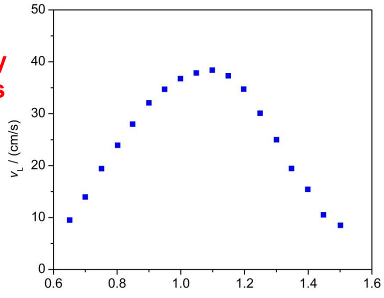
laminar burning velocity 2

CH_4/air, $\varphi = 1$, $p = 1$ atm, $T_0 = 300$ K, $v_L = 35.7$ cm/s

measured flame velocity of methane–air mixtures as a function of φ

it has a maximum at $\varphi = 1.1$



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

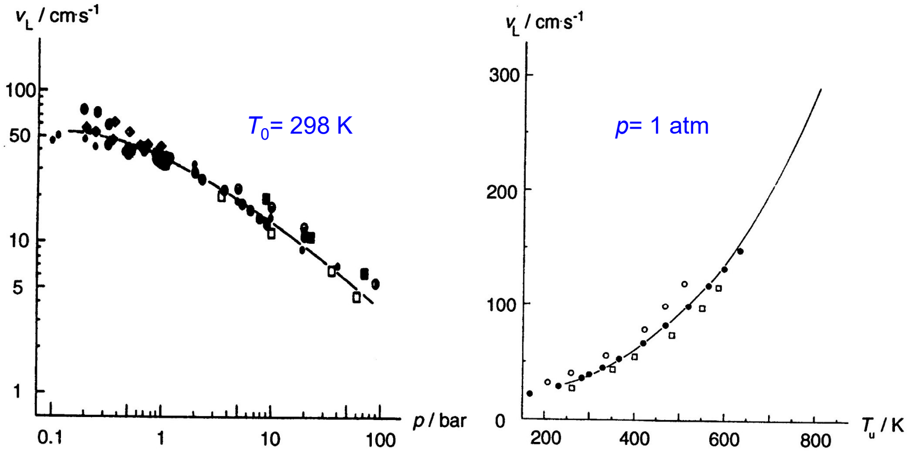
Below the lower flammable limit and above the upper flammable limit there is no deflagration.
Also called „flammability limits” or „explosive limits”.

Other typical flame speeds:
hydrocarbon/air and alcohol/air mixtures at p=1 atm, T_0= 300 K
typically 20–50 cm/s (that is 0.7 – 1.8 km/h)
H_2/air, $\varphi = 1$, $p = 1$ atm, $T_0 = 300$ K, $v_L = 200$ cm/s

laminar burning velocity 3

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 $H+O_2=OH+O$, $O+H_2=OH+H$ are faster

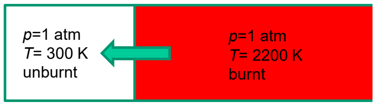


flame velocity of stoichiometric methane-air flame at various *p* and *T*

laminar burning velocity vs. laminar flame velocity

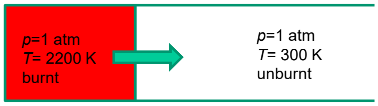
ethane−air combustion: $C_2H_6 + 3.5\ O_2 + 13.17\ N_2 = 2\ CO_2 + 3\ H_2O + 13.17\ N_2$
$O_2 : N_2 = 0.21 : 0.79$

Increase of the number of moles from 1.0 + 3.5 + 13.17 = 17.67 moles to
2.0 + 3.0 + 13.17 = 18.17 moles.



laminar burning velocity
p= 1 atm, T_0= 300 K
v_L = 38 cm/s

(assume that on the wall there is no heat loss and no radical loss)



actual laminar flame velocity
p= 1 atm, T_0= 300 K
$v_F = (n_2/n_1)\times(T_2/T_1)\times V_L.$
= (18.17/17.67)×(2200/300)×38 cm/s
= 287 cm/s

The hot gas pushes out the flame front!
(assume that on the wall there is no heat loss and no radical loss)

FLOX: Flameless Oxidation

Related methods:

FLOX	FLameless OXidation
MILD combustion	Moderate or Intense Low-oxygen Dilution

FLOX requirements:
- the fuel and oxidiser gas streams are heated above the ignition temperature
- very fast mixing
- overall lean equivalence ratio

MILD requirements:
- oxidiser gas stream is heated above the ignition temperature
- highly diluted oxidizer: *e.g.* 3% O_2 in N_2
- overall lean equivalence ratio

features:
- fast oxidation without flames, almost homogeneous gas mixture
- low final temperature
- low NOx and soot formation
- „one of the best new technologies for clean and efficient combustion"

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?

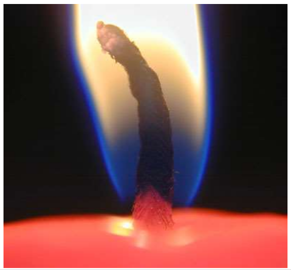
The shape of the flame at normal gravity (1 g) and
in microgravity.

Investigation of flames at zero gravity or microgravity.

A close look at a candle

The flame of the candle melts the paraffin vax
a small cup is formed, which contains melted wax.
The remaining solid wax forms the wall of the cup.
Wrong candle: the paraffin vax 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 vax 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 (φ=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.

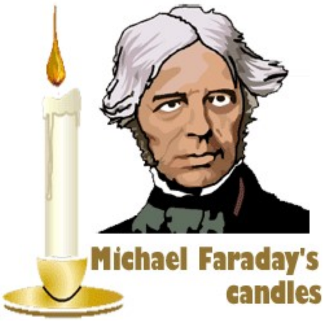
Inside the candle flame
the gas mixture is fuel rich (φ>1).

Outside the candle flame
the gas mixture is fuel lean (φ<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.

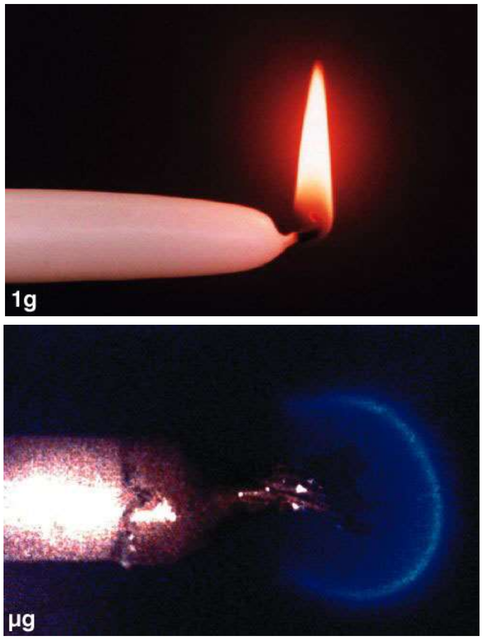
The fast airflow at the side of the flame:

- 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.

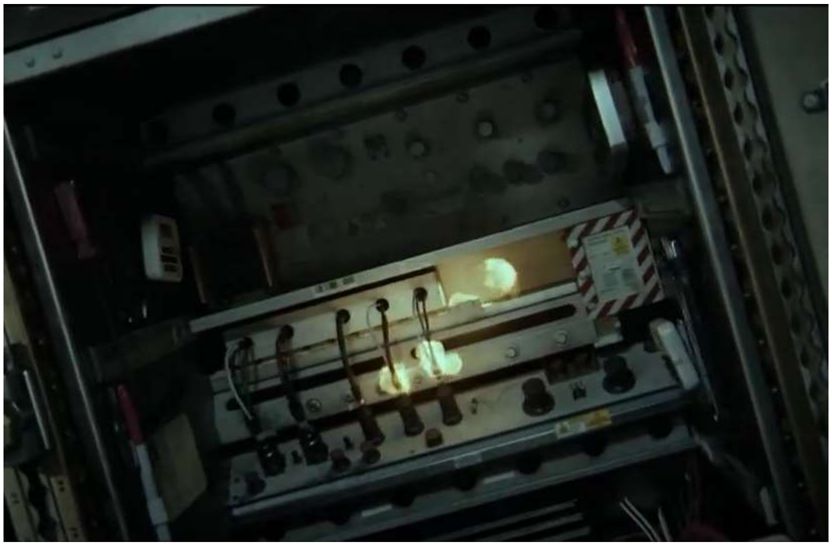
- Diffusion is the only means of transport (for both O_2 and the products)
- Low reaction speed, the flame is colder
- the flame has spherical shape, not droplet shape

Candle flame at zero gravity



A candle flame in
microgravity.

Zero gravity in the reel space



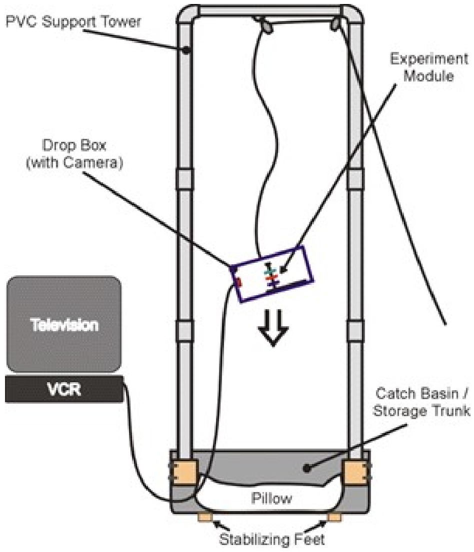
fire aboard the International Space Station

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 $H+O_2 \rightarrow$ 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:

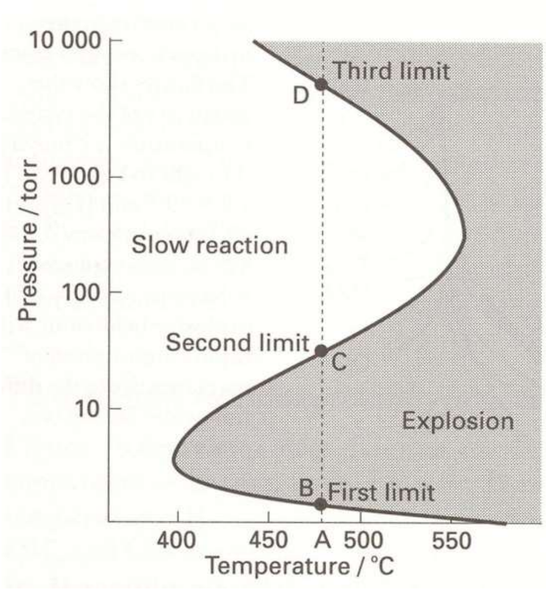
- Ó Conaire *et al.* (Galway, 2004)
- Konnov (Lund, 2008)
- Hong *et al.* (Stanford, 2011)
- Burke *et al.* (Princeton, 2012)
- Keromnes *et al.* (Galway, 2013)
- Sánches and Williams (San Diego, 2014)
- Varga *et al.* (Budapest, 2016)
- Konnov (Lund, 2019)

Why is it important?

- „the fuel of the future" , „hydrogen economy", „carbon-free energetics"
- practical fuel (rocket fuel / satellite launchers)
- industrial safety (H_2 generation in a nuclear accident, Fukushima)
- **the core reactions of the oxidation of hydrocarbons**

Explosion of a hydrogen-oxygen mixture

$2 H_2 + O_2 = 2 H_2O$



1	$H_2 + O_2 \rightarrow .H + .HO_2$	chain initiation
2	$.H + O_2 \rightarrow .OH + :O$	chain branching
3	$.OH + H_2 \rightarrow .H + H_2O$	chain continuation
4	$:O + H_2 \rightarrow .OH + .H$	chain branching
5	$.H + O_2 + M \rightarrow .HO_2 + M$	chain termination*
6	$.HO_2 + H_2 \rightarrow .H + H_2O_2$	chain initiation*
7	$2\ .HO_2 \rightarrow H_2O_2 + O_2$	chain termination
8	$H_2O_2 + M \rightarrow 2\ .OH + M$	chain initiation
9	$.H \rightarrow$ wall	chain termination
10	$.HO_2 \rightarrow$ wall	chain termination

1	$H_2 + O_2 \rightarrow .H + .HO_2$	chain initiation
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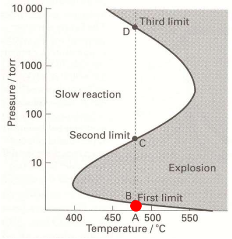
6	$.HO_2 + H_2 \rightarrow .H + H_2O_2$	chain initiation*
7	$2\ .HO_2 \rightarrow H_2O_2 + O_2$	chain termination
8	$H_2O_2 + M \rightarrow 2\ .OH + M$	chain initiation
9	$.H \rightarrow$ wall	chain termination
10	$.HO_2 \rightarrow$ wall	chain termination

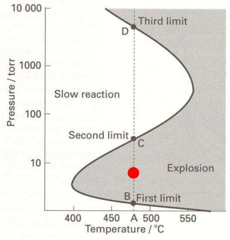


below the 1st explosion limit:

chain termination reaction 9 removes the H radicals
(radical loss on the wall)

→ no explosion

1	$H_2 + O_2 \rightarrow .H + .HO_2$	chain initiation
2	$.H + O_2 \rightarrow .OH + :O$	chain branching
3	$.OH + H_2 \rightarrow .H + H_2O$	chain continuation
4	$:O + H_2 \rightarrow .OH + .H$	chain branching
5	$.H + O_2 + M \rightarrow .HO_2 + M$	chain termination*
6	$.HO_2 + H_2 \rightarrow .H + H_2O_2$	chain initiation*
7	$2\ .HO_2 \rightarrow H_2O_2 + O_2$	chain termination
8	$H_2O_2 + M \rightarrow 2\ .OH + M$	chain initiation
9	$.H \rightarrow$ wall	chain termination
10	$.HO_2 \rightarrow$ wall	chain termination



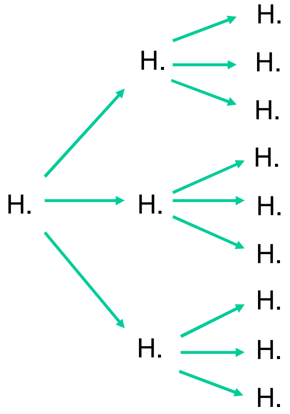
between explosion limits 1 and 2:

2-3-4 chain branching steps

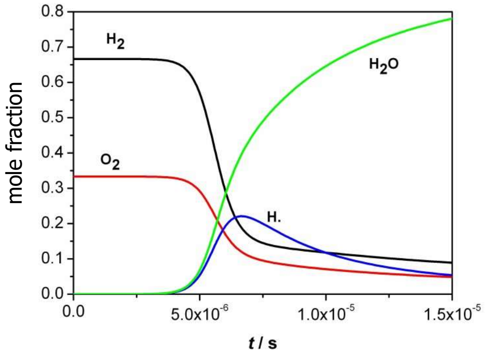
2 $H + O_2 \rightarrow .OH + :O$
3 $.OH + H_2 \rightarrow .H + H_2O$
4 $:O + H_2 \rightarrow .H + .OH$
3 $.OH + H_2 \rightarrow .H + H_2O$
+

$$.H + O_2 + 3\ H_2 \rightarrow \mathbf{3}\ .H + 2\ H_2O$$

→ explosion

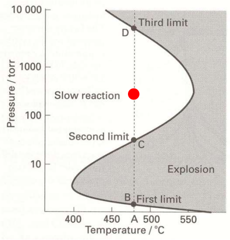


Hydrogen-oxygen explosion between limits 1 and 2



H atom is a very reactive intermediate
its concentration first increases quickly + starts to decay
when the concentrations of H_2 and O_2 decreases
concentration of H_2O: saturation curve

1	$H_2 + O_2 \rightarrow .H + .HO_2$	chain initiation
2	$.H + O_2 \rightarrow .OH + :O$	chain branching
3	$.OH + H_2 \rightarrow .H + H_2O$	chain continuation
4	$:O + H_2 \rightarrow .OH + .H$	chain branching
5	$.H + O_2 + M \rightarrow .HO_2 + M$	chain termination*
6	$.HO_2 + H_2 \rightarrow .H + H_2O_2$	chain initiation*
7	$2\ .HO_2 \rightarrow H_2O_2 + O_2$	chain termination
8	$H_2O_2 + M \rightarrow 2\ .OH + M$	chain initiation
9	$.H \rightarrow$ wall	chain termination
10	$.HO_2 \rightarrow$ wall	chain termination

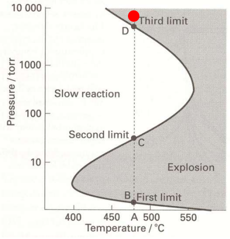


between explosion limits 2 and 3:

5	$.H + O_2 + M \rightarrow .HO_2 + M$	chain termination*
10	$.HO_2 \rightarrow$ wall	chain termination

→ no explosion

M any species present
at the hydrogen/air explosion it is mainly N_2 O_2 H_2
but can be any other species (*e.g.* .H $.HO_2$ .OH)



1	$H_2 + O_2 \rightarrow .H + .HO_2$	chain initiation
2	$.H + O_2 \rightarrow .OH + :O$	chain branching
3	$.OH + H_2 \rightarrow .H + H_2O$	chain continuation
4	$:O + H_2 \rightarrow .OH + .H$	chain branching
5	$.H + O_2 + M \rightarrow .HO_2 + M$	chain termination*
6	$.HO_2 + H_2 \rightarrow .H + H_2O_2$	chain initiation*
7	$2\ .HO_2 \rightarrow H_2O_2 + O_2$	chain termination
8	$H_2O_2 + M \rightarrow 2\ .OH + M$	chain initiation
9	$.H \rightarrow$ wall	chain termination
10	$.HO_2 \rightarrow$ wall	chain termination

above explosion limit 3

- high pressure ⇒ reaction step 5 produces much $.HO_2$
- reaction step 6 converts $.HO_2$ to H_2O_2
- at high pressure the decomposition of H_2O_2 is fast (reaction 8) and it produces highly reactive OH radicals

→ **Explosion**

the chain branching reaction sequence
(rates of reactions 5 and 8 linearly increase with pressure!):

$$.H \xrightarrow{5} .HO_2 \xrightarrow{6} H_2O_2 \xrightarrow{8} 2\ OH \xrightarrow{3} 2\ H$$

Effect of the heterogeneous reactions

9	$.H \rightarrow$ wall	chain termination
10	$.HO_2 \rightarrow$ wall	chain termination

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 ε:
ratio (collisions resulting in adsorption) / (all collisions)

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

Calculation of the rate coefficients of reactions 9 and 10:

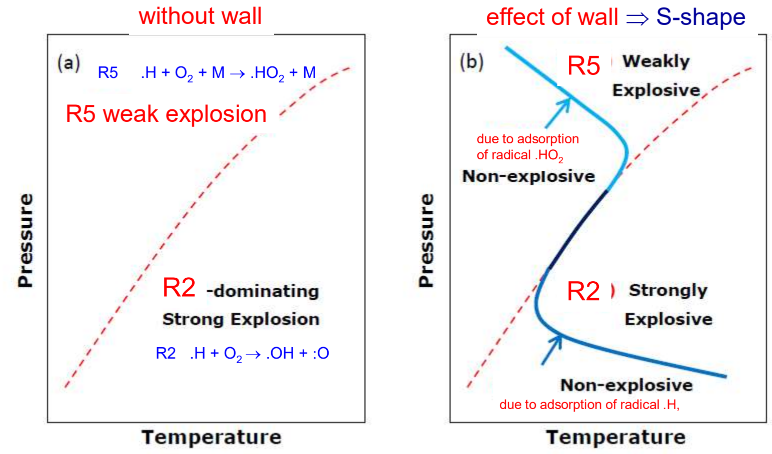
$$k = \frac{1}{4} \varepsilon \bar{v} \frac{S}{V}$$

where

S surface of the vessel
V volume of the vessel
$\bar{v}$ average flying velocity of the radical

$$\bar{v} = \sqrt{\frac{8 k_B T}{\pi m}}$$

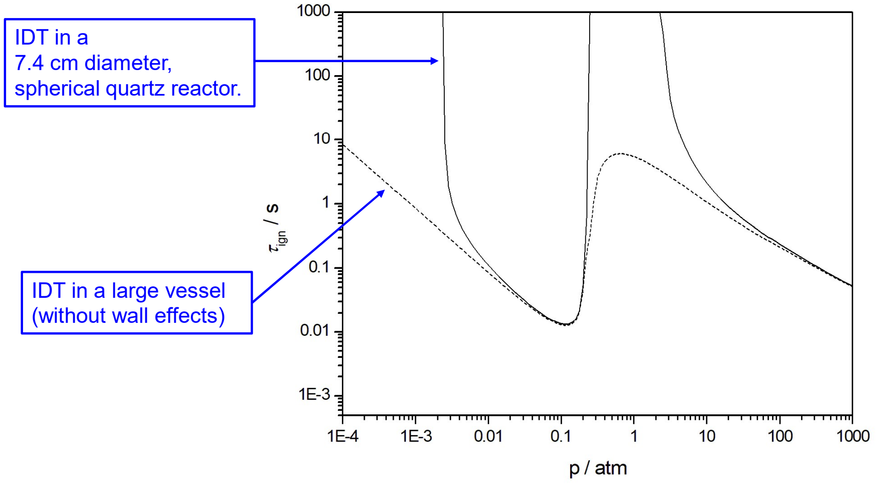
Effect of the heterogeneous reactions 2



The dashed line corresponds to pressure where [M] = 2 k_2/k_5
(R2 .H + O_2 → .OH + :O R5 .H + O_2 + M → .HO_2 + M)

The wall reactions result in the non-explosive regions!
lower non-explosive region (below limit 1): **adsorption of radical H**
upper non-explosive region (between limits 2 and 3): **adsorption of radical .HO_2**

Simulated ignition delay times



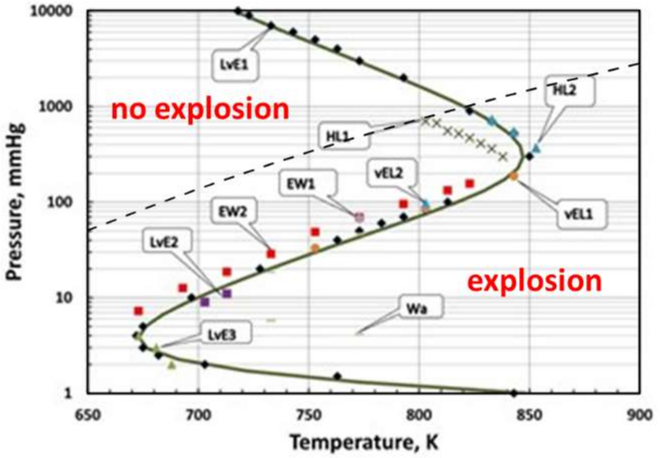
IDT in a
7.4 cm diameter,
spherical quartz reactor.

IDT in a large vessel
(without wall effects)

Calculated ignition delay times (IDTs) of a stoichiometric hydrogen–air mixture at 800 K initial temperature as a function of pressure.
using homogeneous, isochoric, adiabatic simulations.

Valkó et al. *Proc. Combust. Inst.*, **36** (2017) 681–689.

Comparison with the measurements



The dashed line corresponds to pressure where [M] = 2 k_2/k_5
(R2 .H + $O_2 \rightarrow$ .OH + :O R5 .H + O_2 + M $\rightarrow$ .HO_2 + M)

The dots are various measurements.

---

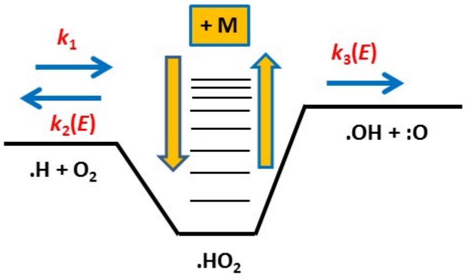
between limits 1 and 3

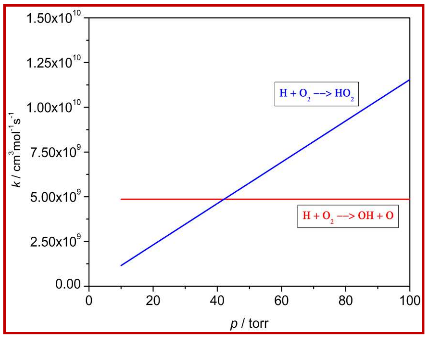
the key of explosion / no explosion behaviour
the HO_2 reaction system

at temperature 650 K

below about 40 torr R2 .H + $O_2 \rightarrow$ .OH + :O → explosion

above about 40 torr R5 .H + O_2 + M $\rightarrow$ .HO_2 + M → **NO** explosion





.H + $O_2 \rightarrow$ .HO_2*

low pressure: .HO_2*→ .H + O_2 or .HO_2*→ .OH + :O → explosion

high pressure: .HO_2*→ .HO_2 (stabilization) → **NO explosion**

Third body collision efficiency

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

Its role is the removal of the extra energy of the excited species (here: radical $.HO_2^*$) 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 collison)

N_2 it can store the energy also in rotational and vibrational modes
(in plain English: N_2 molecule goes faster after collison +
faster rotations and more excited vibrations)

H_2O many rotational and vibrational modes
+ the energy levels are close to those of radical $.HO_2^*$

typical relative collision efficiencies (Burke *et al.*, 2012):
$m(He)= 0.8$ $m(N_2)= 1.0$ $m(O_2)= 0.78$ $m(H_2)= 2.0$ $m(H_2O)= 14.0$

Dependence of explosion / no explosion on the composition of gas mixture

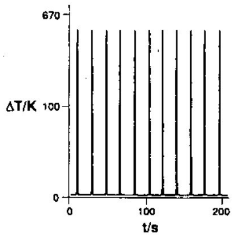
Investigation at *T*, *p* where the rates of reactions R2 and R5 are similar

R2 $.H + O_2 \rightarrow .OH + :O$ r_2= intermediate
R5 $.H + O_2 + M \rightarrow .HO_2 + M$ $M=H_2, O_2$ r_5= slow ($m \approx 1$) → **explosion**

R2 $.H + O_2 \rightarrow .OH + :O$ r_2= intermediate (no change)
R5 $.H + O_2 + M \rightarrow .HO_2 + M$ $M= H_2O$ r_5= 14 × faster → **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 $m \approx 1$

after the explosion high $[H_2O]$ in the chamber and the average collision efficiency $m \approx 14$
it prevents the explosion until the inflowing gases remove water.



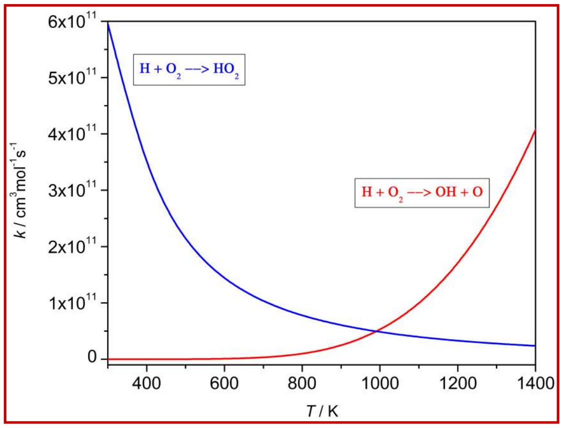
⇒ **a series of explosions**
Tomlin *et al.*, *Combust.Flame*, **91**, 107-130(1992)

Hydrogen-air flame

at pressure 1 bar:

above about 900 K .H + O_2 → .OH + :O → chain reaction

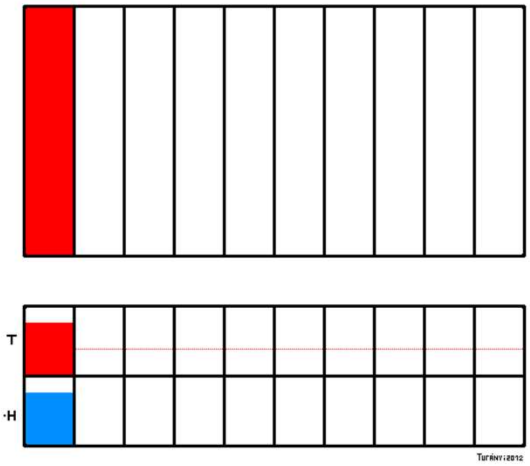
below about 900 K .H + O_2 + M → $.HO_2$ + M → **NO** chain reaction



cold gas .H arrives: .H + O_2 + M → $.HO_2$ + M → **NO** explosion

hot gas .H arrives: .H + O_2 → .OH + :O → **explosion**

Propagation of hydrogen–air flame



.H transport to cold mixture : R5 .H + O_2 + M → $.HO_2$ + M → **NO explosion**

.H transport to hot mixture : R2 .H + O_2 → .OH + :O → **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?

Combustion of wet carbon monoxide

dry CO: no combustion
wet CO (CO + O_2 + H_2O / H_2 / 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 H_2 is produced: **synthesis gas**

water-gas shift reaction, WGS:
$CO + H_2O = CO_2 + H_2$ changing the CO/H_2 ratio
electricity production in gas turbines and internal combustion engines
clean, well controllable, efficient

technologies combating global warming:

synthesis gas from biomass (CO_2 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 CO_2 capture

Combustion of wet CO 2

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

$CO + .OH \rightarrow CO_2 + .H$ This is the main heat producing step
MAIN SOURCE OF HEAT IN ALL HYDROCARBON FLAMES!!!

important CO reactions:

$CO + .OH = CO_2 + .H$	at high temperature and low pressure
$CO + .HO_2 = CO_2 + .OH$	at low temperature (T<1300 K), and high pressure
$CO + O_2 = CO_2 + :O$	

other, less important reaction:
$CO + O + M = CO_2 + M$

H + CO + M = HCO +M **HCO formation and consumption**
$H + HCO = H_2 + CO$
HCO + O = CO + OH
$HCO + O = CO_2 + H$
HCO + OH = CO + H2O
$HCO + O_2 = CO + HO_2$

Combustion of methane

$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$ the overall reaction

The mechanism:

1. production of radical CH_3

$CH_4 + O_2 \rightarrow .CH_3 + .HO_2$ homogeneous explosion
$CH_4 + M \rightarrow .CH_3 + .H + M$ homogeneous explosion

$CH_4 + .H \rightarrow .CH_3 + H_2$ in a flame front
$CH_4 + .OH \rightarrow .CH_3 + H_2O$ in a flame front

2. production of formaldehyde from $.CH_3$

$.CH_3 + O_2 \rightarrow CH_3O. + :O$
$CH_3O. + M \rightarrow CH_2O + .H + M$

$.CH_3 + :O \rightarrow CH_2O + .H$

---

3. production of .HCO from CH_2O

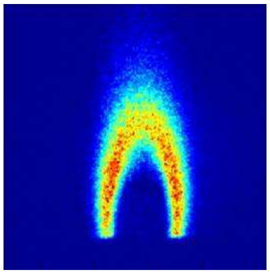
$CH_2O + .H \rightarrow .HCO + H_2$
$CH_2O + .OH \rightarrow .HCO + H_2O$

4. production of CO from .HCO

$HCO + .H \rightarrow CO + H_2$
$HCO + M \rightarrow CO + .H + M$
$HCO + O_2 \rightarrow CO + .HO_2$

5. production of CO_2 from CO

$CO + OH \rightarrow CO_2 + H$



measuring
OH concentration
in methane flame

The radicals to these reactions are provided by the H_2/O_2 reaction system.

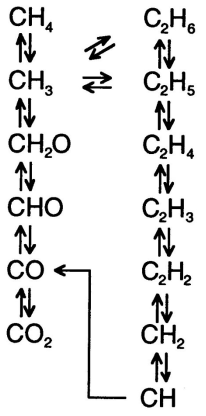
6. production of C_2H_6 :

$2\ CH_3 \rightarrow C_2H_6$

C1 chain:
$CH_4 \rightarrow .CH_3 \rightarrow CH_2O \rightarrow .HCO \rightarrow CO \rightarrow CO_2$

C2 chain:
$C_2H_6 \rightarrow .C_2H_5 \rightarrow C_2H_4 \rightarrow .C_2H_3 \rightarrow C_2H_2 \rightarrow CO$

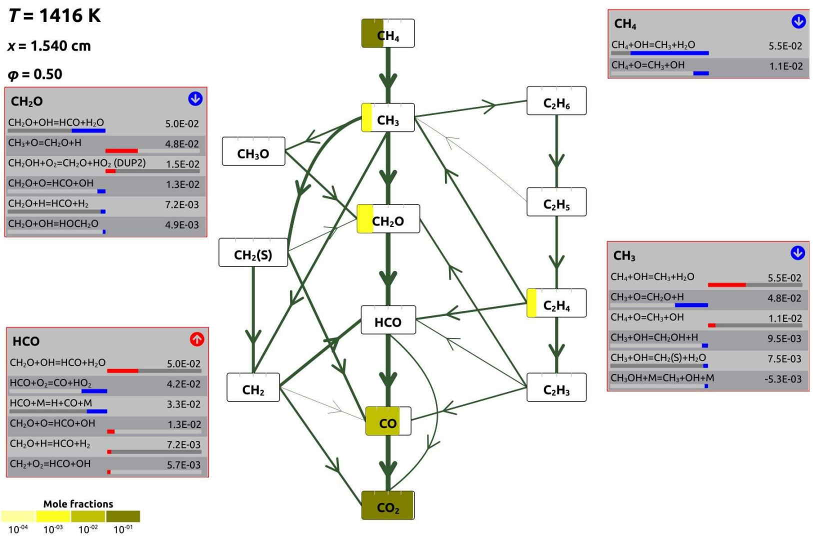
each step is a hydrogen abstraction by
a small radical (.H, :O, .OH)
Every second product is a radical.



a detailed CH_4 combustion mechanism:
37 species and ~350 irreversible reactions
also describes ethane combustion

lean methane combustion	C1 chain + (C2 chain)
stoichiometric methane combustion	C1 chain + C2 chain
rich methane combustion	(C1 chain) + C2 chain

Lean (φ=0.5) methane flame



***T* = 1416 K**

***x* = 1.540 cm**

φ = 0.50

CH_2O	
$CH_2O+OH=HCO+H_2O$	5.0E-02
$CH_3+O=CH_2O+H$	4.8E-02
$CH_2OH+O_2=CH_2O+HO_2$ (DUP2)	1.5E-02
$CH_2O+O=HCO+OH$	1.3E-02
$CH_2O+H=HCO+H_2$	7.2E-03
$CH_2O+OH=HOCH_2O$	4.9E-03

HCO	
$CH_2O+OH=HCO+H_2O$	5.0E-02
$HCO+O_2=CO+HO_2$	4.2E-02
HCO+M=H+CO+M	3.3E-02
$CH_2O+O=HCO+OH$	1.3E-02
$CH_2O+H=HCO+H_2$	7.2E-03
$CH_2+O_2=HCO+OH$	5.7E-03

CH_4	
$CH_4+OH=CH_3+H_2O$	5.5E-02
$CH_4+O=CH_3+OH$	1.1E-02

CH_3	
$CH_4+OH=CH_3+H_2O$	5.5E-02
$CH_3+O=CH_2O+H$	4.8E-02
$CH_4+O=CH_3+OH$	1.1E-02
$CH_3+OH=CH_2OH+H$	9.5E-03
$CH_3+OH=CH_2(S)+H_2O$	7.5E-03
$CH_3OH+M=CH_3+OH+M$	-5.3E-03

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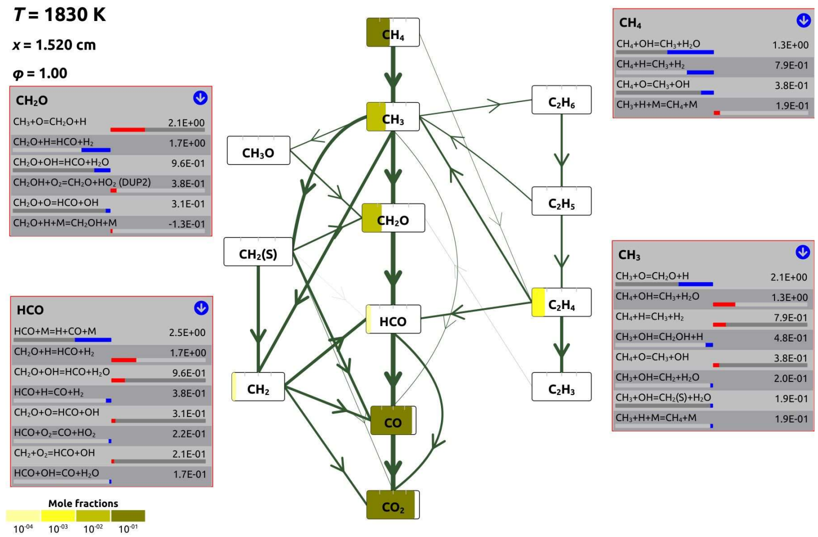
Stoichiometric (φ=1.0) methane flame



T = 1830 K

x = 1.520 cm

φ = 1.00

CH_2O	↓
$CH_3+O=CH_2O+H$	2.1E+00
$CH_2O+H=HCO+H_2$	1.7E+00
$CH_2O+OH=HCO+H_2O$	9.6E-01
$CH_2OH+O_2=CH_2O+HO_2$ (DUP2)	3.8E-01
$CH_2O+O=HCO+OH$	3.1E-01
$CH_2O+H+M=CH_2OH+M$	-1.3E-01

HCO	↓
$HCO+M=H+CO+M$	2.5E+00
$CH_2O+H=HCO+H_2$	1.7E+00
$CH_2O+OH=HCO+H_2O$	9.6E-01
$HCO+H=CO+H_2$	3.8E-01
$CH_2O+O=HCO+OH$	3.1E-01
$HCO+O_2=CO+HO_2$	2.2E-01
$CH_2+O_2=HCO+OH$	2.1E-01
$HCO+OH=CO+H_2O$	1.7E-01

CH_4	↓
$CH_4+OH=CH_3+H_2O$	1.3E+00
$CH_4+H=CH_3+H_2$	7.9E-01
$CH_4+O=CH_3+OH$	3.8E-01
$CH_3+H+M=CH_4+M$	1.9E-01

CH_3	↓
$CH_3+O=CH_2O+H$	2.1E+00
$CH_4+OH=CH_3+H_2O$	1.3E+00
$CH_4+H=CH_3+H_2$	7.9E-01
$CH_3+OH=CH_2OH+H$	4.8E-01
$CH_4+O=CH_3+OH$	3.8E-01
$CH_3+OH=CH_2+H_2O$	2.0E-01
$CH_3+OH=CH_2(S)+H_2O$	1.9E-01
$CH_3+H+M=CH_4+M$	1.9E-01

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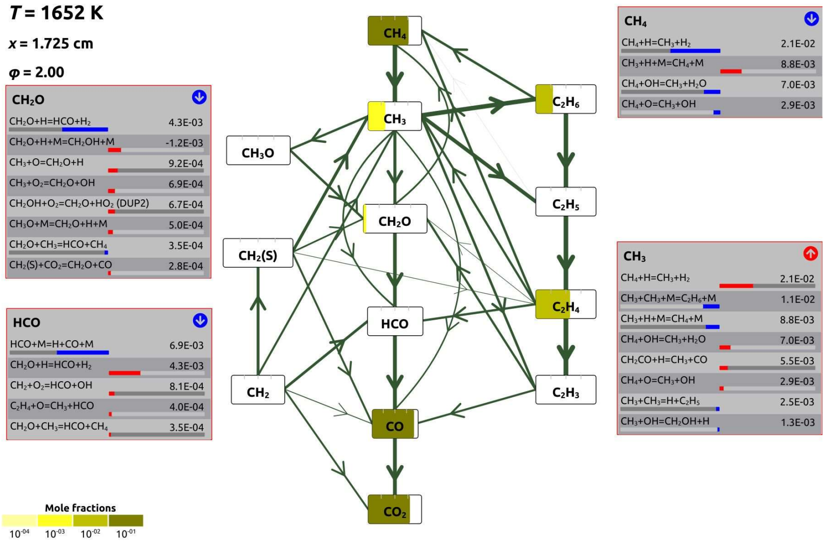
Rich (φ=2.0) methane flame



T = 1652 K

x = 1.725 cm

φ = 2.00

CH_2O	↓
$CH_2O+H=HCO+H_2$	4.3E-03
$CH_2O+H+M=CH_2OH+M$	-1.2E-03
$CH_3+O=CH_2O+H$	9.2E-04
$CH_3+O_2=CH_2O+OH$	6.9E-04
$CH_2OH+O_2=CH_2O+HO_2$ (DUP2)	6.7E-04
$CH_3O+M=CH_2O+H+M$	5.0E-04
$CH_2O+CH_3=HCO+CH_4$	3.5E-04
$CH_2(S)+CO_2=CH_2O+CO$	2.8E-04

HCO	↓
$HCO+M=H+CO+M$	6.9E-03
$CH_2O+H=HCO+H_2$	4.3E-03
$CH_2+O_2=HCO+OH$	8.1E-04
$C_2H_4+O=CH_3+HCO$	4.0E-04
$CH_2O+CH_3=HCO+CH_4$	3.5E-04

CH_4	↓
$CH_4+H=CH_3+H_2$	2.1E-02
$CH_3+H+M=CH_4+M$	8.8E-03
$CH_4+OH=CH_3+H_2O$	7.0E-03
$CH_4+O=CH_3+OH$	2.9E-03

CH_3	↑
$CH_4+H=CH_3+H_2$	2.1E-02
$CH_3+CH_3+M=C_2H_6+M$	1.1E-02
$CH_3+H+M=CH_4+M$	8.8E-03
$CH_4+OH=CH_3+H_2O$	7.0E-03
$CH_2CO+H=CH_3+CO$	5.5E-03
$CH_4+O=CH_3+OH$	2.9E-03
$CH_3+CH_3=H+C_2H_5$	2.5E-03
$CH_3+OH=CH_2OH+H$	1.3E-03

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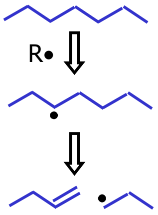
High-temperature combustion of alkanes



alkane

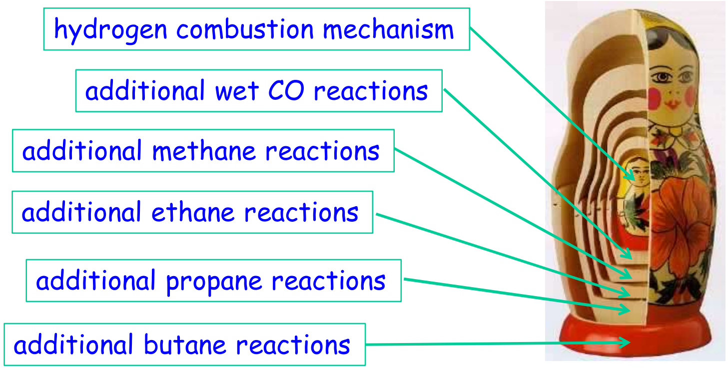
alkyl radicals

alkene +
small radical

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

High temperature hydrocarbon combustion
does not depend strongly on the structure of the hydrocarbon!

High-temperature combustion of hydrogen – wet CO – hydrocarbons



hydrogen combustion mechanism

additional wet CO reactions

additional methane reactions

additional ethane reactions

additional propane reactions

additional butane reactions

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 present is 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.)

The colour of a dragon flame

Daenerys' dragon	dragon of the Night King
nonpremixed flame	premixed flame
yellow	blue
radiation from soot particles	emission from CH radicals

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.

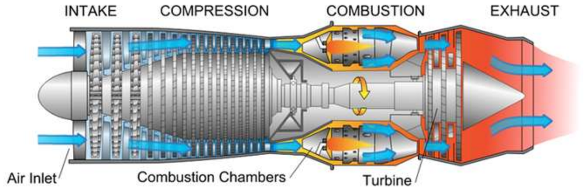
What is knocking?

Determination of the knocking properties of fuels.
RON, MON and PON.

Two main types of internal combustion engines

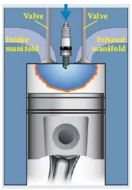
Gas turbines (first gas turbines: 1932)
- continous combustion
- continous rotation („rotary engines”)
- high power, high efficiency

Main applications:
- airplanes
- power stations



Reciprocating engines (e.g. Otto-engine (1876))

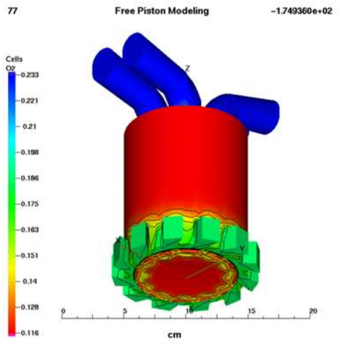
- combustion in a cylinder
- piston is moving up and down
- two main types:
- Spark ignition engine (SI) /gasoline engine/
- Compression ignition engine (CI) /Diesel engine/



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 CO_2 emission.



4 Valves

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)

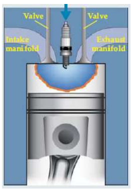
(3) Experiments with an engine prototype

Otto-engine ↔ Diesel-engine

Otto-engine (1876) Nicolaus Otto (1832-1891)

high fuel consumption
high power per unit cylinder volume

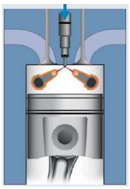
- electric spark + spread of a premixed flame
- nearly stoichiometric fuel-air ratio
- the compression is lower than optimal, to avoid knocking
- much NO is produced (to be removed by the catalyst)



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)

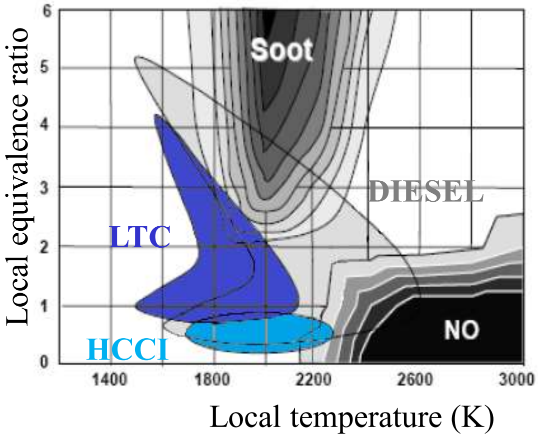


None of these engine types are optimal.
Which is the engine that combines the advantages of both engines above?

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

HCCI:
homogeneous charge
compression ignition

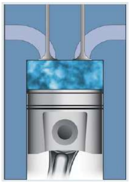
HCCI: Homogeneous Charge Compression Ignition engine

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 $\Rightarrow$ few NO, few soot



Several companies
have experimental engines

Mercedes F700 concept car (2007)

„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_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.

Mazda 3 with Skyactiv-X Compression-Ignition Gas Engine

first mass produced HCCI car

30% less fuel consumption

autumn of 2018

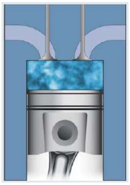
compression ignition + spark plug as a combustion control

SPCCI = Spark Plug Controlled Compression Ignition

Skyactiv-X uses extremely lean fuel mixtures like an HCCI engine
- mixes air and fuel during the intake stroke (very lean)
- injects a secondary fuel before the power stroke
  and ignites it using the spark plug
- the flame created spreads out and down while also raising the cylinder pressure high enough - along with the compression from the piston - to combust the lean primary air/fuel mixture.

RCCI: Reactivity Controlled Compression Ignition engine

a given fuel is optimal only at a given engine speed
(measured in rotation per minute (rpm))
- it is not optimal at lower or higher engine speeds
- assistance of spark ignition is needed at very low or very high speeds



A possible solution: using two fuels
pure fuel A is optimal at very high speed
pure fuel B is optimal at very low speed

The engine receives a mixture of A and B at intermediate speed

The on board computer controls the appropriate mixing of the two fuels according to the actual engine speed.

Problem: filling two different fuels is needed to two separate tanks.

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.

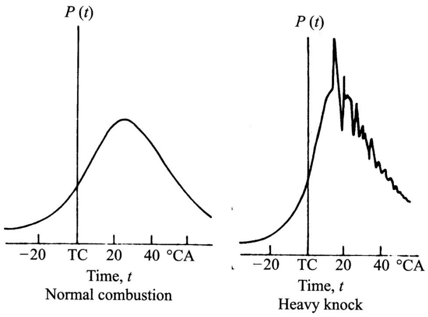
Using homogeneous charge, the mixture should be stoichiometric.

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

Engine knocking

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

BUT: it is limited by knocking



Normal combustion

Heavy knock

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

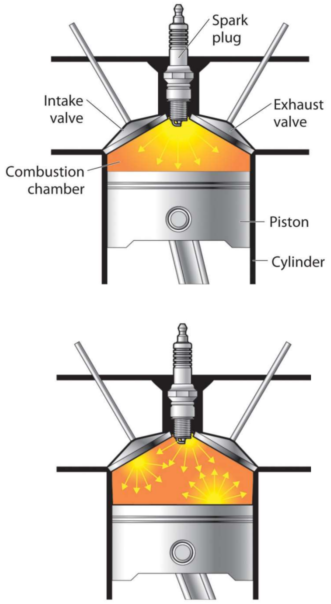
Engine knocking 2

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

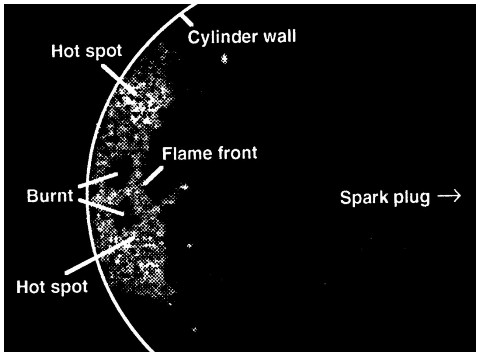


Engine knocking 3

BUT: at some locations temperature, pressure and fuel concentration is different: hot spots
hot spots may start a new flame front

→ pressure induced flame propogation
OR
→ **detonation waves**

consequences:
⇒ higher pressure earlier
⇒ pressure oscillations



Engine knocking 4

The consequence of knocking:
- lower power
- demaged 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

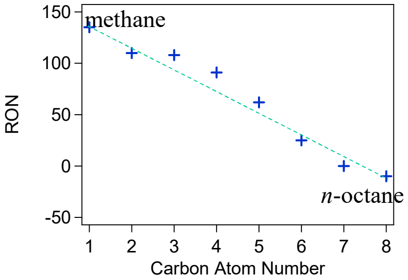
100 = 100% *iso*-octane
0 = 100% *n*-heptane

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
speed 600 RPM
inlet mixture temperature: 52 °C
ignition timing: 13° bTDC

RON of the various compounds

Fuel	RON
n-hexadecane	< -30
n-octane	-10
n-heptane	**0**
diesel fuel	15–25
n-hexane	25
n-pentane	62
n-butane	91
EuroSuper	95
iso-octane	**100**
benzene	101
ethane	108
propane	110
toluene	111
ethanol	129
methanol	133
methane	135



For **n-alkanes**: RON decreases with the size of the molecule.
→ The smaller, the more difficult the ignition.

Octane number 2

MON: motor octane number
speed 900 RPM
inlet mixture temperature: 149 °C
ignition timing: 19-26° bTDC

- MON is measured at more realistic conditions
- MON is lower than RON by 8-12

S = RON – MON called „fuel sensitivity”

even more realistic octane number:
„octane number” in Brazil, Canada, and the United States:

PON (Posted Octane Number or Pump Octane Number) =
= Anti-Knock Index (AKI) = „(R+M)/2 method” = (RON+MON) /2

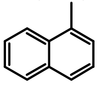
„EuroSuper" or "Regular unleaded" in Europe:
RON= 95 MON= 85 PON=AKI= 90

Cetane number

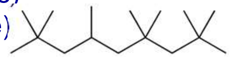
<u>characterization of a Diesel oil</u>: ignition time is the same than with a

% composition of a *n*-cetane (*n*-$C_{16}H_{34}$) –

1-methylnaphthalene mixture



100 = 100% *n*-cetane
0 = 100% 1-methylnaphthalene ($C_{11}H_{10}$) (expensive)
15 = 100% isocetane (2,2,4,4,6,8,8-heptamethylnonane)



In a given diesel engine,
higher cetane fuel ⇒ shorter ignition delay period

European Union standard EN 590: minimum cetane number = 51
Premium diesel fuels CN > 60

USA minimum cetane number = 40 (typical values 42-45)

biodiesel from vegetable oil: cetane number 46-52
animal-fat based biodiesels: cetane number 56-60

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 $.HO_2/H_2O_2$ 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 $H+O_2 \rightarrow O+OH$
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).

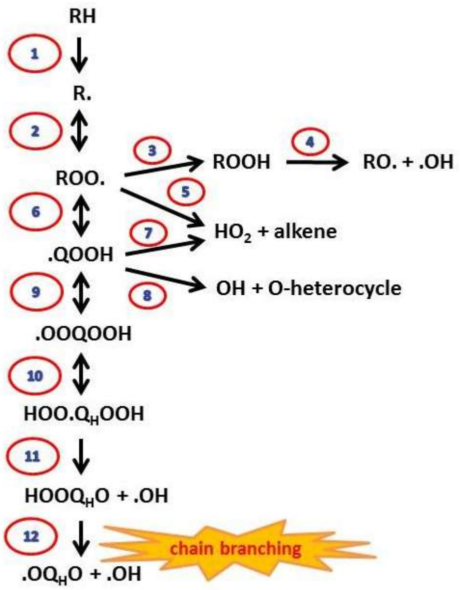
Hydrocarbons (ethane and above) can be oxidized at low-temperature in chain reaction.

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

J. Zádor, C. A. Taatjes and R. X. Fernandes,
"Kinetics of elementary reactions in low-temperature autoignition chemistry"
Progress in Energy and Combustion Science , **37**, 371-421 (2011).

The chemistry of low-temp HC oxidation



(1) *initiation*

This is a very slow reaction in propene/air mixtures:

$CH_3CH_2CH_3 + O_2 \rightarrow CH_3CH_2CH_2. + .HO_2$

Faster reaction in the presence of .OH

$CH_3CH_2CH_3 + .OH \rightarrow CH_3CH_2CH_2. + H_2O$

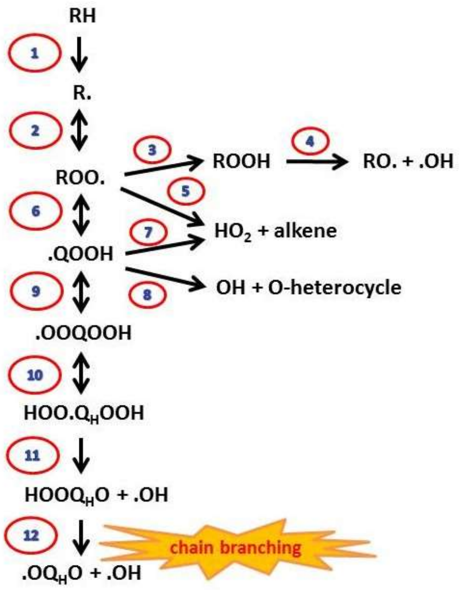
(2) *production of alkylperoxy radicals*

$CH_3CH_2CH_2. + O_2 \rightarrow CH_3CH_2CH_2OO.$

(3) *production of alkylhydroperoxide*

$CH_3CH_2CH_2OO. + .HO_2 \rightarrow CH_3CH_2CH_2OOH + O_2$

The chemistry of low-temp HC oxidation 2



(4) *decomposition of the alkylhydroperoxide*

$CH_3CH_2CH_2OOH \rightarrow CH_3CH_2CH_2O. + .OH$

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

(5) *generation of* HO_2 *radical + alkene*

$CH_3CH_2CH_2OO. \rightarrow .HO_2 + CH_3CH{=}CH_2$

(6)

intramolecular hydrogen atom abstraction

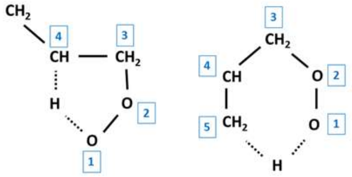
the most important step of the reaction chain OO. group acquires a hydrogen atom of the hydrocarbon chain

step (6): intramolecular hydrogen atom abstraction

The chemical reaction in 1D:

$CH_3CH_2CH_2OO. = \overset{5}{.CH_2}\overset{4}{CH_2}\overset{3}{CH_2}\overset{2}{O}\overset{1}{OH}$ or $CH_3CH_2CH_2OO. \rightarrow \overset{5}{CH_3}\overset{4}{\underset{.}{C}}H\overset{3}{CH_2}\overset{2}{O}\overset{1}{OH}$

The chemical reaction in 2D:



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

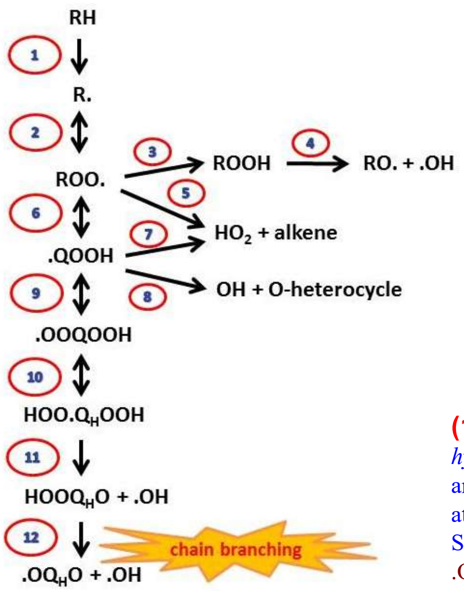
1,3-hydrogen atom transfer **rare event**

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 a*lkyl-hydroperoxy* radical

$.CHCH_2CH_2OOH \rightarrow .HO_2 + CH_3CH{=}CH_2$ (7)

$.CHCH_2CH_2OOH \rightarrow .OH + \text{oxetane}$ (8)

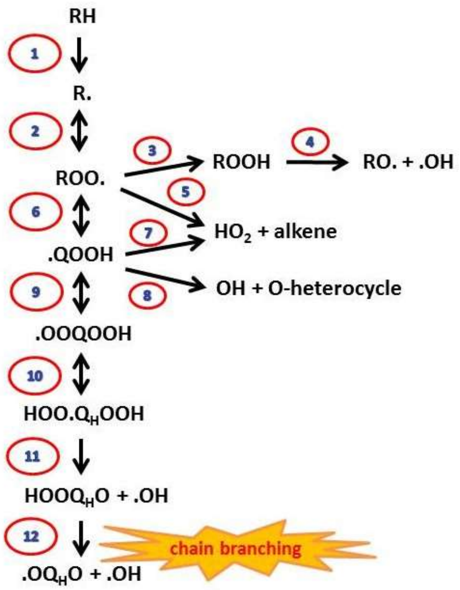
(7) $.HO_2$ product: deceleration
(8) .OH product: acceleration

(9) *alkyl-hydroperoxy radical* + O_2

$.CHCH_2CH_2OOH + O_2 \rightarrow .OOCHCH_2CH_2OOH$

(10) *second intramolecular hydrogen atom abstraction*
another .OO group is also able to get another H-atom from the hydrocarbon chain.
Similar to reaction (6).
$.OOCH_2CH_2CH_2OOH \rightarrow OOCH_2CH_{2.}CHOOH$

The chemistry of low-temp HC oxidation 4



(11) *generation of OH-radical*:

$HOOCH_2CH_2CHOOH \rightarrow$
$HOOCH_2CH_2CHO + .OH$

(12) *generation of a second OH-radical*:

$HOOCH_2CH_2CHO \rightarrow .OCH_2CH_2CHO + .OH$

Steps (11) and (12) produce 2 OH

Summary of steps (1) – (12) :
step (1): consumption of 1 OH
steps (1)-(12) : production of 2 OH

⇒ branching chain reaction

⇒ hydrocarbon–air mixtures may explode below 900 K !

The $.HO_2/H_2O_2$ explosion route

Another chain branching mechanism above about 1000 K

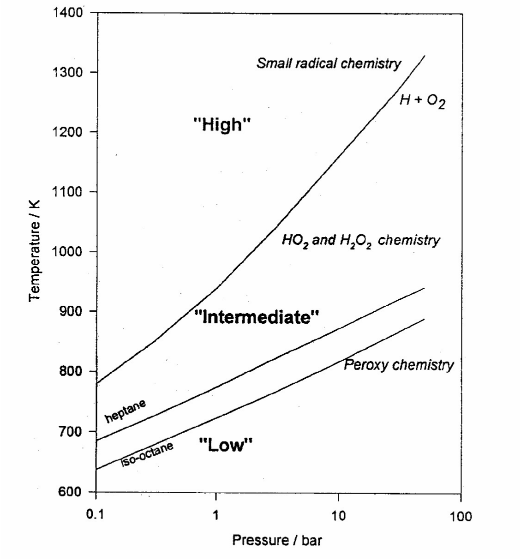
$.HO_2 + RH \rightarrow H_2O_2 + .R$
$H_2O_2 + M \rightarrow 2\ .OH + M$ (chain branching)
$.OH + H_2 \rightarrow H_2O + H.$
$.H + O_2 + M \rightarrow .HO_2 + M$

effect of the first two reactions:
$.HO_2 \rightarrow 2\ .OH$

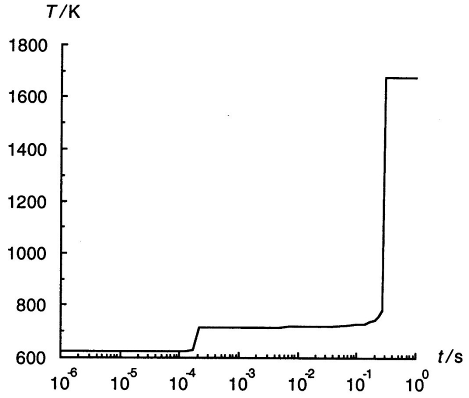
effect of the last two reactions:
$2\ .OH \rightarrow 2\ .HO_2$

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

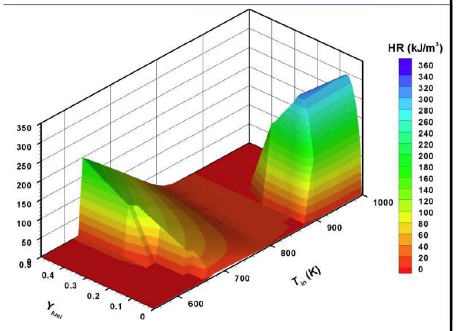
Hydrocarbon oxidation: changes with temperature and pressure



Low-temperature hydrocarbon oxidation: two-step ignition



two stage ignition



heat production in a *n*-heptane-air mixture

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.

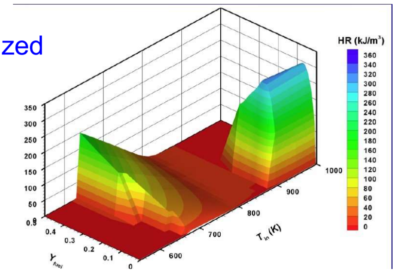
the cool flame is frequently oscillating

T < 700 °C

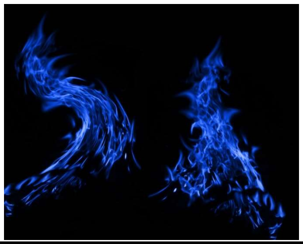
Discovery:
1810 Sir Humphry Davy
(„the flame did not burn his finger”)

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

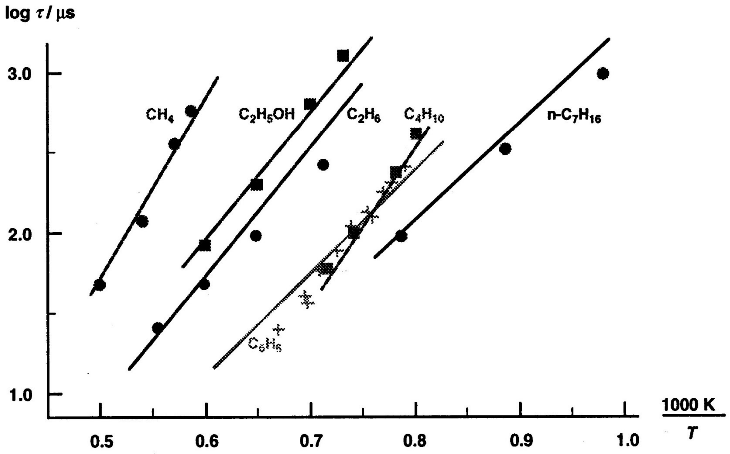
The coolest cool flame: 80 °C
diethylether–air flame at pressure 300 torr
pale bluish colour from CH_2O^* emission



heat production in a
n-heptane-air mixture

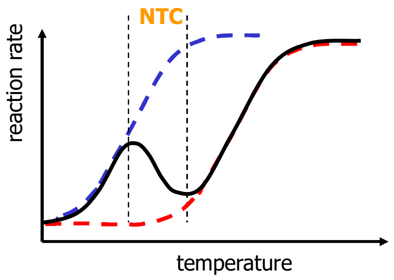


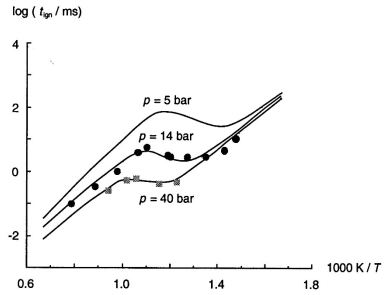
High temperature hydrocarbon ignition



Alkane ignition: log(τ) – 1/*T* follows a line

Low-temperature hydrocarbon oxidation NTC ignition





negative temperature
coefficient (NTC) ignition

adiabatic ignition of n-heptane-air mixture
ignition time *vs.* temperature
T_0= 625K - 1250K, p = 15 atm

The reason is the generation of peroxide radicals
in equilibrium reactions: X. + $O_2 \rightarrow .XO_2$
small increase of the temperature ⇒ the equilibrium is shifted to the left
slows down the low-temperature chain branching reaction

Topic 7. Production of nitrogen oxides in combustion

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:

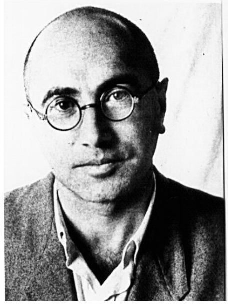
CO_2	greenhouse gas
CO	poisoning
SO_2	acid rain
NO_x	harmful products:
NO, NO_2	causing photochemical smog and acid rain in the troposphere decomposes O_3 in the stratosphere
N_2O	greenhouse gas

Five ways of NOx production

1) thermal NO or Zeldovich-NO
2) prompt NO or Fenimore-NO
3) NO generated via N_2O
4) NO generated via NNH
5) NO generated from fuel-bounded nitrogen

Source of most reaction schemes:
Peter Glarborg, James A. Miller, Branko Ruscic, Stephen J. Klippenstein:
Modeling nitrogen chemistry in combustion
Progress in Energy and Combustion Science , **67**, 31-68 (2018).

Thermal NO



suggested by Y. B. Zeldovich in 1946

(1) $O + N_2 \rightleftarrows NO + N$
(2) $N + O_2 \rightleftarrows NO + O$
(3) $N + OH \rightleftarrows NO + H$

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

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

Zeldovich Y B: The oxidation of nitrogen in combustion and explosions.
Acta Physicochem USSR, **21**, 577–628 (1946).

Thermal NO 2

Thermal NO production requires:

- high temperature T>1900 K,
  because the activation energy of reaction step 1 is high
  (1) $O + N_2 = NO + N$ E_1=314 kJ/mol
- long residence time (slow reaction)
- high [O]
  (these conditions are present in the post-flame region)

Experimental study:

- hydrogen flame
- wet CO flame

Prompt NO 1

discovered by C.P. Fenimore, 1971
observation: much NO can be produced in methane flames
cannot be explained with the Zeldovich mechanism

Fenimore C P. Formation of nitric oxide in premixed hydrocarbon flames. *Proc.Combust. Inst.* **13**,373–380 (1971)

$N_2 \rightarrow NO$ catalysed by radical CH

<u>features:</u>
important in fuel rich flames, due to the high [CH]
$\varphi < 1.2$ (to prevent reburning)

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

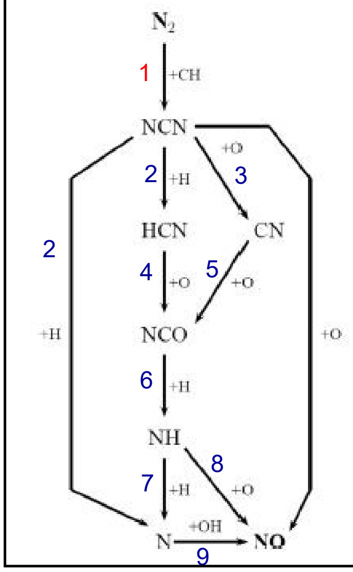
<u>most important reaction:</u> $CH + N_2 = NCN + H$
Klippenstein et al., 1999,
Moskaleva and Lin, 2000

of secondary importance $C + N_2 = NCN$

Prompt NO 2

formation of radical CH; transformation of N_2; interconversion of N species

$CH_3 + OH = CH_2 + H_2O$
$CH_3 + H = CH_2 + H_2$
$CH_2 + OH = CH + H_2O$
$CH_2 + H = CH + H_2$



1 $CH+N_2 \rightleftarrows NCN+H$

2 $NCN+H \rightleftarrows HCN+N$
3 $NCN+O \rightleftarrows CN+NO$

4 $HCN+O \rightleftarrows NCO+H$
5 $CN+O \rightleftarrows NCO$

6 $NCO+H \rightleftarrows NH+CO$

7 $NH+H \rightleftarrows N+H_2$
8 $NH+O \rightleftarrows NO+H$
9 $N+OH \rightleftarrows NO+H$

NO production via N_2O

Malte P, Pratt D T. Measurements of atomic oxygen and nitrogen oxides in jet-stirred combustion. *Proc.Combust.Inst.***15**,1061–1070 (1975)

N_2O production from N_2

$N_2 + O + M \rightleftarrows N_2O + M$

NO production from N_2O

$N_2O + O \rightleftarrows 2\,NO$

$N_2O + H \rightleftarrows NO + NH$

N_2 back conversion

$N_2O + O \rightleftarrows N_2 + O_2$

$N_2O + H \rightleftarrows N_2 + OH$

features:

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

- termolecular reactions:
  their rate increases linearly with pressure

NO production via NNH

Important reactions:

in the first reaction steps, NH and NNH are produced from N_2

$N_2 + H \rightleftarrows NH + N$

$N_2 + OH \rightleftarrows NH + NO$

$NNH \rightleftarrows N_2 + H$

$NNH + O \rightleftarrows NO + NH$

$N_2 + H \rightleftarrows NNH$

$N_2 + OH \rightleftarrows NNH + O$

$N_2 + H_2 \rightleftarrows NNH + H$

$N_2 + H_2O \rightleftarrows NNH + OH$

feature:

important in lean and low-temperature flames

(⇒ thermal NO and prompt NO routes are slow) and

at low pressure

(at high pressure the „via N_2O” route is fast).

NO production from fuel N

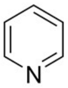
The nitrogen of NO may also come from the fuel
It is especially important at coal combustion.

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

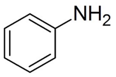
heterocyclic compounds → HCN → NO
→ HNCO → NO

example: pyridine

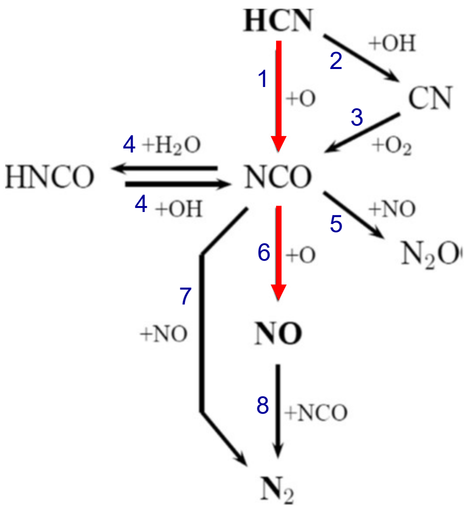


amines → NH_3 → NO

example: aniline



NO production from HCN



1 $HCN+O \rightarrow NCO+H$
2 $HCN+OH \rightarrow CN+H_2O$
3 $CN+O_2 \rightarrow CN+H_2O$

4 $NCO+H_2O \rightleftarrows HNCO+OH$

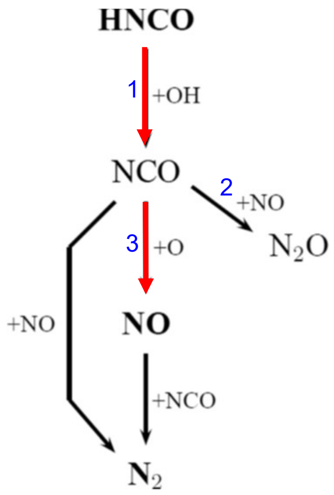
5 $NCO+NO \rightarrow N_2O+CO$

6 $NCO+O \rightarrow NO+CO$

7 $NO+NCO \rightarrow N_2+CO_2$

8 $NO+NCO \rightarrow N_2+H_2O$

NO production from HNCO (isocyanic acid)

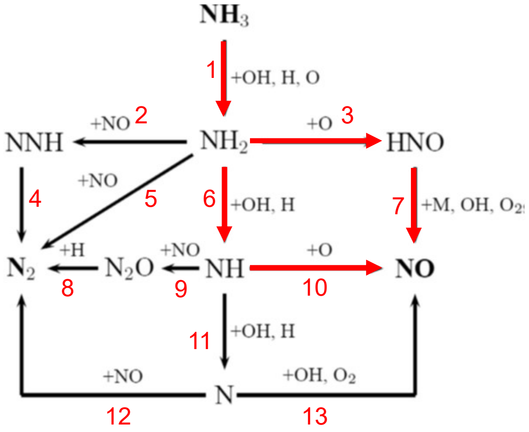


1 $HNCO+OH = NCO+H_2O$

2 $NCO+NO = N_2O+CO$

3 $NCO+O = NO+CO$

NO production from NH_3



1a $NH_3+OH = NH_2+H_2O$
1b $NH_3+H = NH_2+H_2$
1c $NH_3+O = NH_2+OH$

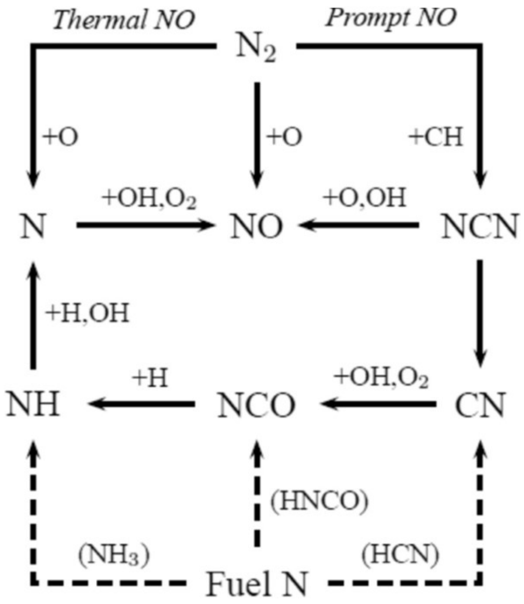
2 $NH_2+NO = NNH+OH$
3 $NH_2+O = HNO+H$
4 $NNH = N_2+H$
5 $NH_2+NO = N_2+H_2O$
6a $NH_2+OH = NH+H_2O$
6b $NH_2+H = NH+OH$

7a $HNO+M = NO+H+M$
7b $HNO+OH = NO+H_2O$
7c $HNO+O_2 = NO+HO_2$
8 $N_2O+H = N_2+OH$

9 $NH+NO = N_2O+H$
10 $NH+O = NO+H$
11a $NH+OH = N+H_2O$
11b $NH+H = N+ H_2$

12 $N+NO = N_2+O$
13a $N+OH = NO+H$
13b $N+O_2 = NO+O$

Summary of NO production in combustion



Topic 8. Methods for decreasing NO emission

Primarily and secondary methods and their features.

The chemistry of staged combustion and reburn.

Selective catalytic reduction.

The Thermal DeNOx process and its chemical kinetics.

The NOxOut process and the usage of AdBlue.

NO removal methods

1 primary methods combustion modification

- staged combustion - fuel staging
- air staging
- reburning

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

2 aftertreatment of the exhaust gas

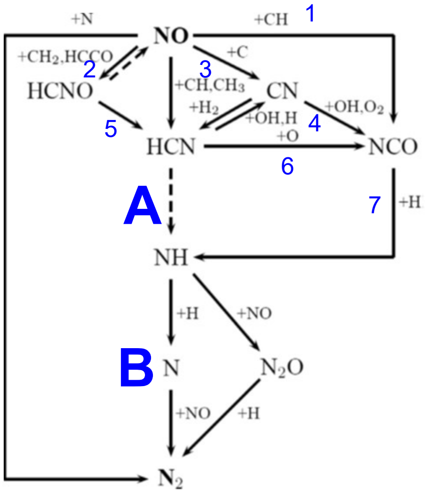
NO removal without the modification of the furnace
selective heterogeneous catalytic reduction (*e.g.* car catalyst)

selective catalytic reduction (homogeneous catalysis)

— Thermal De NO_X	– using NH_3
— RapReNOx	– using cyanuric acid, $(HOCN)_3$
— NOxOut (AdBlue)	– using urea, $H_2N\text{-}CO\text{-}NH_2$

Chemistry of staged combustion / reburn

the fuel rich flame has a reduction capacity
→ NO is reduced to N_2



1 $NO+CH = NCO+H$
2 $NO+CH_2 = HCNO+H$
3 $NO+C = CN+O$

4 $CN+OH = NCO+H$
5 $HCNO+H = HCN+OH$
6 $HCN+O = NCO+OH$

7 $NCO+H = NH+CO$

process A:
see the HCN → NH
transformation scheme

process B:
see the $NH_3 \rightarrow NH$
reaction scheme

Chemistry of staged combustion 2

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

solution:

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

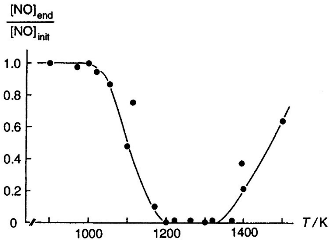
Wendt J O L, Sternling C V, Matovich M A: Reduction of sulfur trioxide and nitrogen oxides by secondary fuel injection, *Proc. Combust. Inst.* **14**, 897–904 (1973)

Thermal DeNOx (using NH_3)

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_2O_2 : temperature window moves downwards
its width remains identical

+H_2O : 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 DeNOx 1

NH_3 + .OH = $.NH_2$ + H_2O
$.NH_2$ + NO = .NNH + .OH
.NNH + NO = N_2 + HNO
HNO + M = .H + NO + M
.H + O_2 = .OH + :O
:O + H_2O = 2 .OH
+______________________

$NH_3 + NO + O_2 \rightarrow N_2 + 3\ .OH$

this is the overall equation of the Thermal DeNO$_X$ method

Chemistry of Thermal DeNOx 2

Chain terminating reactions:

$NH_2 + NO \rightarrow N_2 + H_2O$ (removes NO, but chain terminating!)
$NH_2 + NHO \rightarrow NH_3 + NO$
$OH + HNO \rightarrow H_2O + NO$

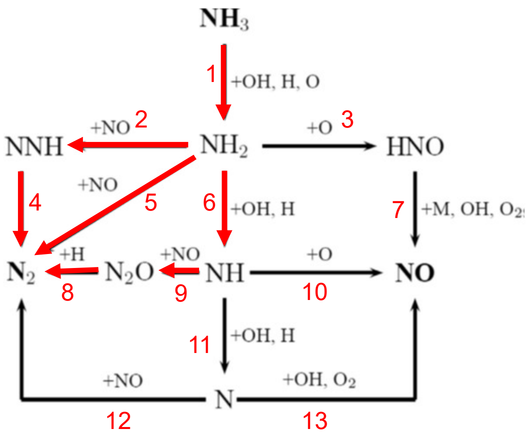
low temperature ($T < 1100$ K)
→ the chain terminating reactions above are fast

high temperature ($T > 1400$ K)
→ oxidation of NH_3 to NO

without water:
$NH_3+O \rightarrow NH_2+OH$ (instead of $H_2O+O \rightarrow 2OH$ chain branching)
less OH is produced

much ammonia is present:
$NH_3+H \rightarrow NH_2+H_2$ (instead of $O_2+H \rightarrow OH+O$ chain branching)

NO removal using NH_3



1a $NH_3+OH = NH_2+H_2O$
1b $NH_3+H = NH_2+H_2$
1c $NH_3+O = NH_2+OH$

2 $NH_2+NO = NNH+OH$
3 $NH_2+O = HNO+H$
4 $NNH = N_2+H$
5 $NH_2+NO = N_2+H_2O$
6a $NH_2+OH = NH+H_2O$
6b $NH_2+H = NH+OH$

7a $HNO+M = NO+H+M$
7b $HNO+OH = NO+H_2O$
7c $HNO+O_2 = NO+HO_2$
8 $N_2O+H = N_2+OH$

9 $NH+NO = N_2O+H$
10 $NH+O = NO+H$
11a $NH+OH = N+H_2O$
11b $NH+H = N+ H_2$

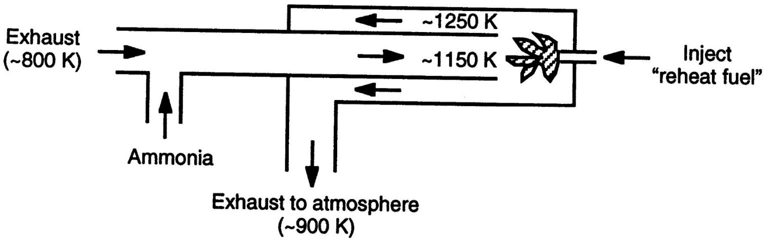
12 $N+NO = N_2+O$
13a $N+OH = NO+H$
13b $N+O_2 = NO+O$

Thermal DeNOx

This is the most practical exhaust gas treating method.

Relatively cheap.

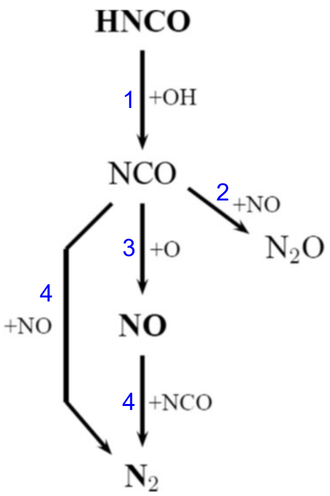
The temperature of the exhaust gas should be in the good temperature interval.



RapReNOx using cyanuric acid (HOCN)$_3$

$(HOCN)_3 \rightarrow 3\ HNCO$ (isocyanic acid) reaction is quick at high temperature

NO removal using HNCO (isocyanic acid)



1 $HNCO+OH = NCO+H_2O$

2 $NCO+NO = N_2O+CO$
3 $NCO+O = NO+CO$

4 $NCO+NO = N_2+CO_2$

NOxOut using urea (NH$_2$)$_2$CO AdBlue

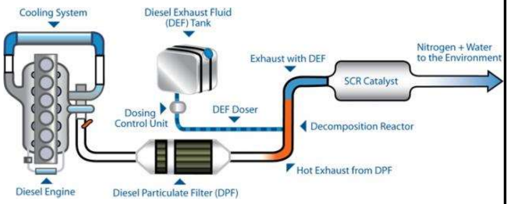
Diesel Exhaust Fluid (DEF)
also known as AdBlue® or AUS 32

carbamide (also called urea)
solution of 32,5% in distilled water

Carbamide decomposes at the high temperature (above 250 °C) of the exhaust gas
$(NH_2)_2CO \rightarrow NH_3 + HNCO$

NH_3 removes NO:
see the Thermal DeNOx process.

HNCO (isocyanic acid) removes NO:
see the RapReNOx process.



AdBlue consumption: 3-4% (Euro 4) or 5-7% (Euro 5) of Diesel oil consumption

Muzio L J, Arand J K, Teixeira D P: Gas phase decomposition of nitric oxide in combustion products. *Proc. Combust. Inst.*, **16**, 199–208 (1977).

Topic 9. Soot

Advantages and disadvantages of soot formation.

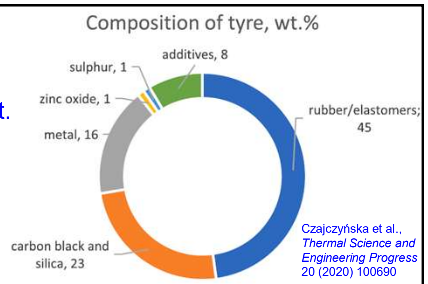
The process of soot formation. PAH.

The HACA mechanism.

Soot and the global warming.

Soot

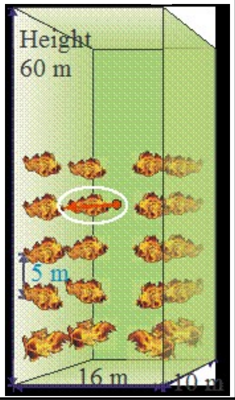
„Carbon black" is an important industrial product.
- a component of black paints
- 20% of the mass of car tyres is soot



Czajczyńska et al., *Thermal Science and Engineering Progress* 20 (2020) 100690

Fig. 1. Composition of typical passenger car tyre

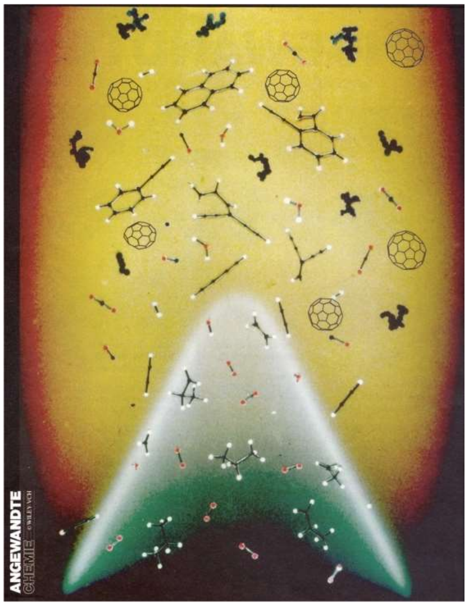
- „black body radiation": soot is an important intermediate
- soot is the source of the yellow light of the candle
- soot improves the heat transfer in furnaces
  furnaces: generation of soot and then complete burnout



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

$CH + C_2H_2 \rightarrow H_2CCCH$ (propargyl radical)
$2\ H_2CCCH \rightarrow$ benzene
benzene $\rightarrow \rightarrow \rightarrow$ PAH

PAH: polycyclic aromatic hydrocarbon

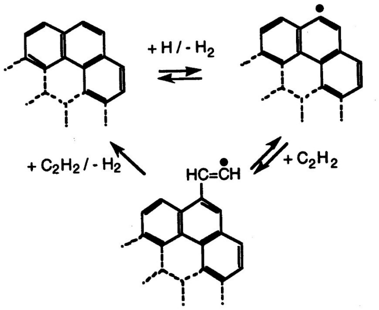
Route to soot formation 2

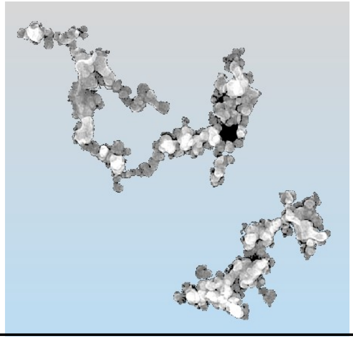
production of PAHs is gas phase chemical reactions:
the chemistry is not very clear.

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



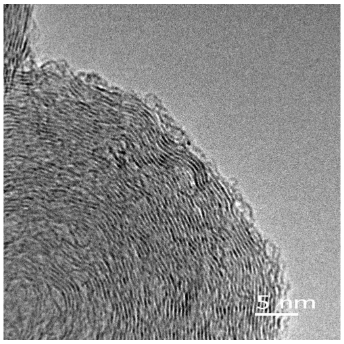


Route to soot formation 3

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."

http://bit.ly/11vqZFX
Journal of Geophysical Research: Atmospheres, 15 January 2013

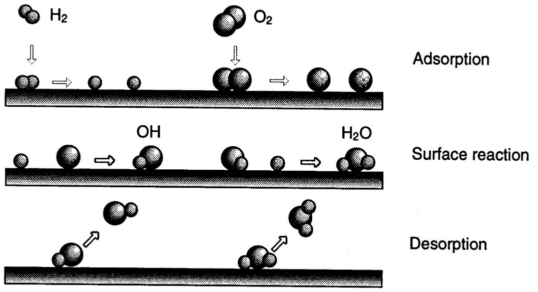
NATURE: Soot a major contributor to climate change, 15 January 2013

Shindell, D. et al. Science 335, 183–189 (2012).

Topic 10. Heterogeneous ignition and combustion

- Sticking coefficient and surface coverage.
- What is happening with the H_2 and O_2 molecules on a Pt surface?
- $H_2/O_2/Pt$ 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 H_2 ?
- Why is the heterogeneous ignition temperature decreasing by increasing the concentration of CH_4 or C_2H_6 ?
- Applications of heterogeneous combustion
- Three-way car catalysts.

Heterogeneous reaction of H_2 and O_2 on a Pt surface



important quantitative measures:

ε 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

θ 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

Heterogeneous ignition and combustion

Species H_2 and O_2 are adsorbed on an originally clean Pt surface.
H_2 has a higher sticking coefficient ⇒ 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 ⇒ 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
  ⇒ immediate reaction

Increasing temperature: more H_2 is desorbed
⇒ the rate limiting step is the desorption of H_2

after a threshold temperature
(„heterogeneous ignition temperature")

⇒ **HETEROGENEOUS IGNITION**

Heterogeneous ignition and combustion 2

HETEROGENEOUS IGNITION

- sudden temperature jump
  all adsorbed H_2 and O_2 are immediatelly reacted
  almost empty surface
- the rate limiting step is the diffusion to the surface

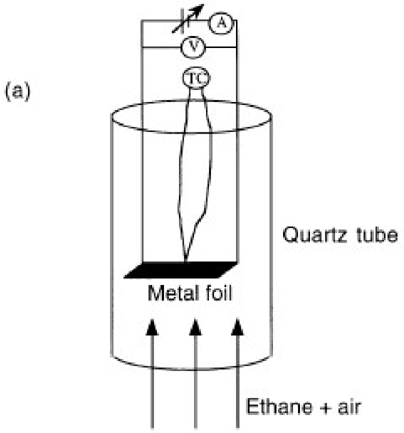
STEADY FAST SURFACE REACTION

Increasing the temperature further
may start a homogeneous flame front.

HOMOGENEOUS IGNITION

Experimental study of heterogeneous ignition

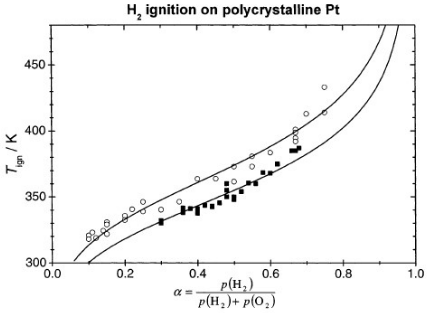
Experimental arrangements:
stagnation point flow (SPF) above a plate
wire in flow

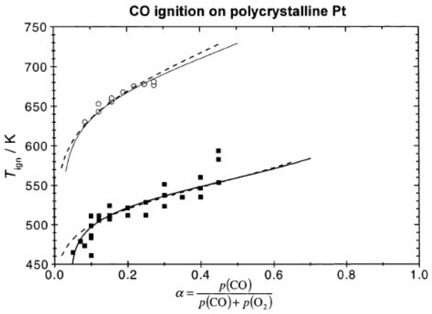


The three roles of platinum plate or wire:

- catalytic surface
- temperature measurement
  (measurement of resistance)
- electric heater

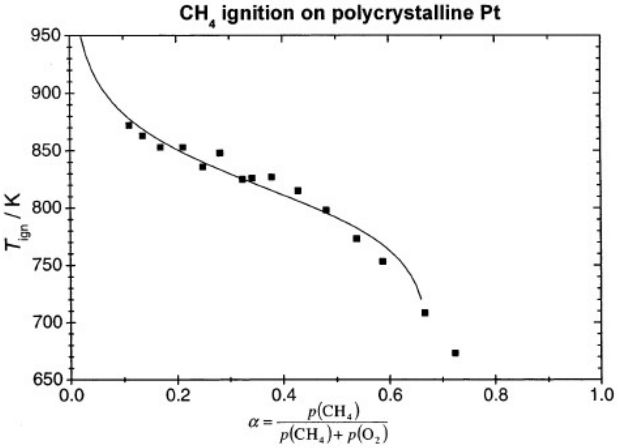
Change of heterogeneous ignition temperature by increasing the H_2, CO, C_2H_4 concentration





The ignition temperature increases (that is the <u>reactivity decreases</u>) by increasing the concentration of the fuel, if it attaches more to the surface than O_2 (examples: H_2, CO, C_2H_4)

Change of heterogeneous ignition temperature by increasing the CH_4 or C_2H_6 concentration

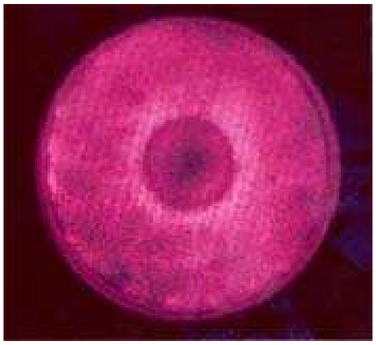


The ignition temperature decreases (that is the <u>reactivity increases</u>) by increasing the concentration of the fuel, if it attaches less to the surface than O_2 (examples: CH_4, C_2H_6)

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)



Selective heterogeneous catalytic reduction

basic application: catalysts in cars CO → CO_2: NO→ N_2

requirements:
- well defined, nearly stoichiometric λ ($\varphi=\lambda=1$)
  λ-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 → $CO_2 + H_2O$

2 CO → CO_2

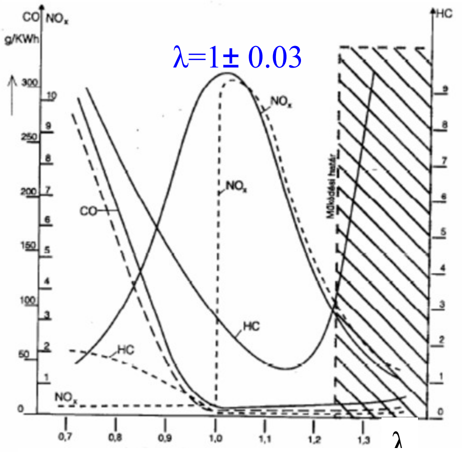
Reductive reactions with Rh catalyst:

3 NO → N_2

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$

$$2\,C_2H_6 + 7\,O_2 \longrightarrow 4\,CO_2 + 6\,H_2O$$

$$2\,NO + 2\,CO \longrightarrow N_2 + 2\,CO_2$$



composition of the exhaust gas

------ after the catalyst

—— before the catalyst

See you in 2 weeks ...