KÉM/282 langokk17em Chemistry and physics of flames

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

PART 2

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Quantitative description and modelling of combustion systems

Modelling of combustion systems is important in the practice:

- **design** of new engines, furnaces, burners
- **development** of existing installations
- **control** of the operation of an equipment

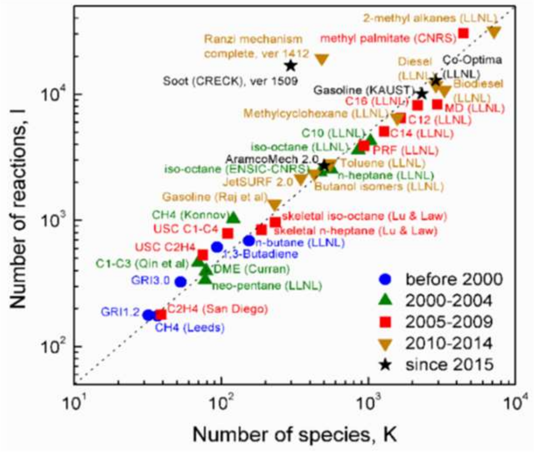
Combustion systems are described by detailed reaction mechanisms

For each reaction step, we have to know the following:

- stoichiometric information (Which are the reactants and the products?)
- value of the rate coefficient k
  as a function of temperature, pressure and mixture composition

Reaction mechanisms are getting larger

The reaction mechanisms are getting larger, because
– increasing chemical knowledge
– faster computers with larger memory are available



F.N. Egolfopoulos, N. Hansen, Y. Ju, K. Kohse-Höinghaus, C.K. Law, F. Qi,
Prog. Energy Combust. Sci. **43** (2014) 36–67.

Detailed reaction mechanisms:
many reaction steps and many parameters

hydrogen combustion	30 reaction steps
natural gas combustion	300 reaction steps
petrol combustion	3000 reaction steps
Diesel oil combustion	15000 reaction steps

This is a skeleton 12-step hydrogen combustion mechanism:

1	$H_2 + O_2 \rightarrow .H + .HO_2$	$k_1(T)$
2	$.H + O_2 \rightarrow .OH + :O$	$k_2(T)$
3	$.OH + H_2 \rightarrow .H + H_2O$	$k_3(T)$
4	$:O + H_2 \rightarrow .OH + .H$	$k_4(T)$
5	$.H + O_2 + M \rightarrow .HO_2 + M$	$k_5(T, p)$
6	$.H \rightarrow$ wall	$k_6(T)$
7	$:O \rightarrow$ wall	$k_7(T)$
8	$.OH \rightarrow$ wall	$k_8(T)$
9	$.HO_2 + H_2 \rightarrow .H + H_2O_2$	$k_9(T)$
10	$2\ .HO_2 \rightarrow H_2O_2 + O_2$	$k_{10}(T)$
11	$H_2O_2 + M \rightarrow 2\ .OH + M$	$k_{11}(T, p)$
12	$.HO_2 \rightarrow$ wall	$k_{12}(T)$

$k(T, p)$ temperature-dependence: 3-parameter Arrhenius-equation
pressure-dependence: several more parameters

Further parameters to each species: thermodynamical data, diffusion coefficients, viscosity

Topic 11. Reaction kinetics and thermodynamic data in a detailed combustion mechanism

- Temperature dependence of the thermodynamic data
- Temperature dependence of the rate coefficient:
  Arrhenius equation and the extended Arrhenius equation
- Pressure dependence of the rate coefficients:
  unimolecular decomposition and
  complex-forming bimolecular reactions
  Lindemann model, Troe parameterization
  The shape of the fall-off curve
- Concentration units and their features.
- Calculation of temperature change in homogeneous reaction mixtures.
- CHEMKIN simulation codes and
  the CHEMKIN mechanism format

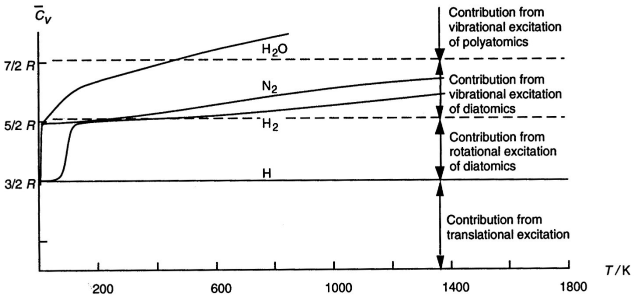
Temperature dependence of thermodynamic data

NASA polynomials

$$\frac{H^{\theta}}{RT} = a_1 + \frac{a_2}{2}T + \frac{a_3}{3}T^2 + \frac{a_4}{4}T^3 + \frac{a_5}{5}T^4 + \frac{a_6}{T}$$

$$\frac{c_p}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

$$\frac{S^{\theta}}{R} = a_1 \ln T + a_2 T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4 + a_7$$



Temperature dependence of rate coefficient *k*

Described by the Arrhenius equation:

$$k = A\exp\left(-\frac{E_a}{RT}\right) \qquad \ln k = \ln A - \frac{E_a}{RT}$$

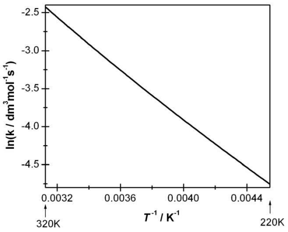
A preexponential factor
Ea activation energy

If the rate coefficient k is measured at several T temperatures and

ln *k* is plotted as a function of 1/*T*

the data fit to a line, if the (original) Arrhenius equation is valid
slope is $m = -E_a/R$ ⇒ determination of E_a

Arrhenius plot:

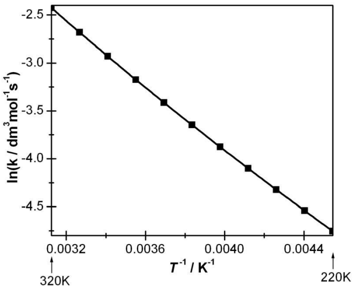


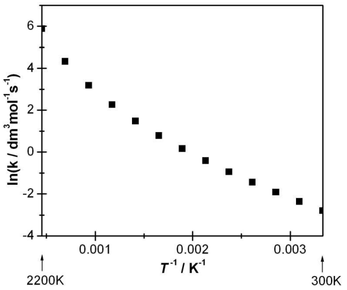
Example: reaction $CH_4 + OH \rightarrow CH_3 + H_2O$

- the most important methane consuming reaction step in the troposphere
- one of the most important steps at methane combustion

Arrhenius plot between 220 K (– 53 °C) and 320 K (+ 47 °C)

Arrhenius plot between 300 K (27 °C) and 2200 K (≈1930 °C)





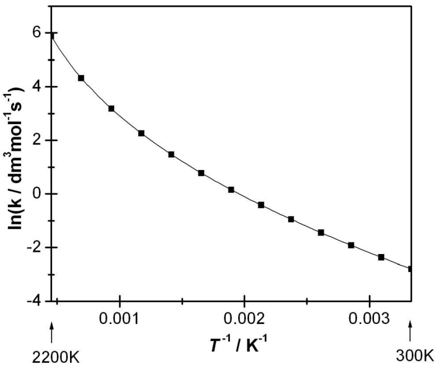
the Arrhenius equation is usually very accurate in a small (few times 10 K) temperature range. (solution phase and atmospheric chemistry)

the original Arrhenius equation is usually not applicable in a wide temperature range (combustion and pyrolytic systems)

Temperature dependence of the rate coefficient *2*

$$k = BT^{n}\,\mathrm{e}^{-\frac{C}{RT}}$$

extended Arrhenius equation



Important!
If $n \neq 0$. then $A \neq B$ and $E_a \neq C$

General definition of activation energy:

$$E_a = -R\frac{\partial \ln k}{\partial (1/T)}$$

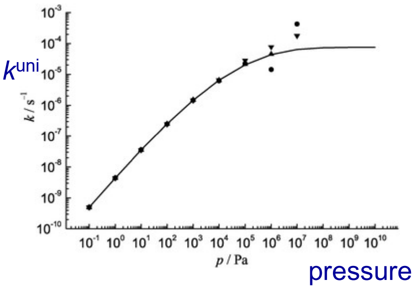
Pressure dependence of the rate coefficients 1

unimolecular decomposition

decomposition or isomerization of a species

A + M = P + M

A	reactant
P	product
M	colliding partner for energy transfer



low pressure	2nd order decay of A
high pressure	1st order decay of A

„pseudo first order” rate coefficient:

high pressure limit:	$k^{\mathrm{uni}} = k_\infty$
low pressure limit:	$k^{\mathrm{uni}} = k_0\,[\mathrm{M}]$

The temperature dependences of k_0 and k_∞ are described independently by extended Arrhenus equations:

$$k_0 = A_0 T^{n_0} \exp\left(\frac{-E_0}{RT}\right) \qquad k_\infty = A_\infty T^{n_\infty} \exp\left(\frac{-E_\infty}{RT}\right)$$

Lindemann – Hinshelwood model

$$\begin{array}{lll} A + M & \rightarrow A^* + M & k_1 \\ A^* + M & \rightarrow A + M & k_2 \\ A^* & \rightarrow P & k_3 \end{array} \qquad k_{\mathrm{uni}} = \frac{k_3 k_1 [M]}{k_2 [M] + k_3}$$

high pressure: [M] $\rightarrow \infty$ $\quad k_{\mathrm{uni}} \approx \frac{k_3 k_1}{k_2}$ $\quad k_\infty = \frac{k_3 k_1}{k_2}$

low pressure: [M] ≈ 0 $\quad k_{\mathrm{uni}} \approx k_1 [M]$ $\quad k_0 = k_1$

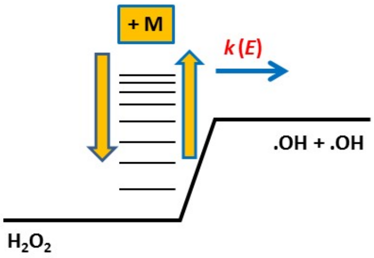
unimolecular decomposition rates:

k^{uni}	„pseudo first order" rate coefficient (s^{-1})
k_∞	high pressure limit (first order) rate coefficient (s^{-1})
k_0	low pressure limit (second order) rate coefficient ($mol^{-1}\ dm^3\ s^{-1}$)

Refined Lindemann – Hinshelwood model of unimolecular reactions

sample reaction: $H_2O_2 + M \rightarrow H_2O_2^* + M \rightarrow .OH + .OH + M$

- instead of assuming a single excited species, $H_2O_2^*$ exists in a range of different rovibrationally excited states.
- the rate of the decompostion step increases with the increasing rovibrational energy of $H_2O_2^*$



low pressure:
- the rate limiting is the collision with M
- the overall decomposition rate is proportional with pressure

high pressure:
- the rate limiting is the decomposition of $H_2O_2^*$
- the overall decomposition rate is independent of pressure

$H_2O_2 \rightarrow .OH + .OH$ $\qquad$ 2nd order at low pressure, 1st order at high pressure

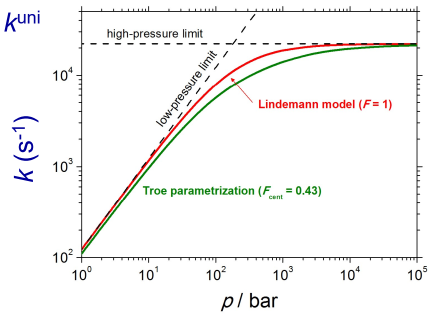
Unimolecular decomposition: calculation of the rate coefficient at an intermediate pressure

$$k = k_\infty \left(\frac{P_r}{1 + P_r} \right) F$$

$$P_r = \frac{k_0 [\mathrm{M}]}{k_\infty}$$

P_r reduced pressure
F controls the shape
of the $k(p)$ curve

H_2O_2 (+M) → .OH + .OH (+M)



in the Lindemann model F = 1

F can be defined as a function of pressure and temperature
(*e.g.* using Troe parameterization):

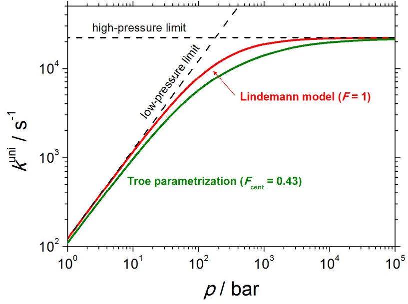
$$\log F = \log F_{\mathrm{cent}} \left[1 + \left[\frac{\log P_r + c}{n - d(\log P_r + c)} \right]^2 \right]^{-1}$$

$c = -0.4 - 0.67 \log F_{\mathrm{cent}}$
$n = -0.75 - 1.271 \log F_{\mathrm{cent}}$
$d = 0.14$

$$F_{cent} = (1 - \alpha) \exp\left(-\frac{T}{T^{***}} \right) + \alpha \exp\left(-\frac{T}{T^{*}} \right) + \exp\left(-\frac{T^{**}}{T} \right)$$

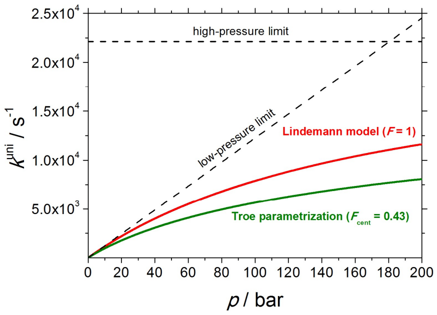
Reaction H_2O_2 (+M) → .OH + .OH (+M)

lg k^{uni} – lg p plot



***T* = 1000 K**

k^{uni} – p plot



source of data: J. Troe, *Combustion and Flame* **158,** 594–601 (2011)

Collision efficiency parameters

M — any species present in the mixture
BUT some species are more effective colliders

good collider: removes much energy from the excited species in each collision

Which are the good colliders?
- species with similar energy levels to those of the excited species
- large molecules with many energy levels

poor collider: *e.g.* noble gases:
no rotational or vibrational energy levels
only the translational mode can be excited

calculation of the effective concentration of M:

m_i: collision efficiency parameter

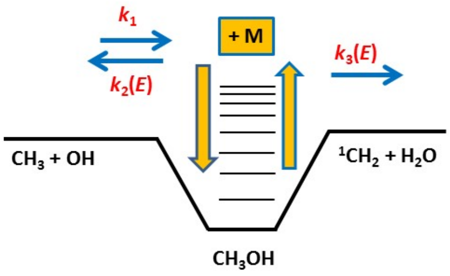
$$[M] = \sum_i m_{y_i} [Y_i]$$

calculation for reaction **H_2O_2 (+M) → .OH + .OH (+M):**

$[M] = 5[H_2O] + 5.13[H_2O_2] + 0.8[O_2] + 2.47[H_2] + 1.87[CO] + 1.07[CO_2] + 0.67[Ar] + 0.43[He] + [\text{all others}]$

Pressure dependence of the rate coefficients 2
complex-forming bimolecular reactions

sample reaction: $CH_3 + OH\ (+ M) \rightarrow CH_3OH^* \rightarrow CH_3OH\ (+ M)$
$\rightarrow {}^1CH_2 + H_2O\ (+ M)$



low pressure:
mainly CH_3OH^* decomposition to $^1CH_2 + H_2O$
($^1CH_2$ = singlet CH_2 = electronically excited CH_2)

high pressure:
mainly CH_3OH^* stabilization, giving CH_3OH

$CH_3 + OH \rightarrow CH_3OH$	3rd order at low pressure, 2nd order at high pressure
$CH_3 + OH \rightarrow {}^1CH_2 + H_2O$	3rd order at low pressure, 2nd order at high pressure

Formation of the stabilization product

$$k^{\mathrm{bi}} = k_\infty \left(\frac{P_r}{1+P_r} \right) F$$

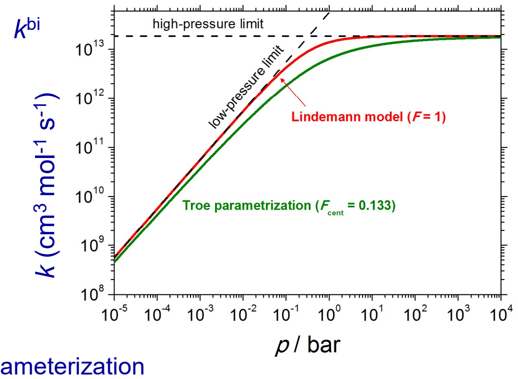
$$P_r = \frac{k_0 [\mathrm{M}]}{k_\infty}$$

P_r reduced pressure
F controls the shape of the
$k(p)$ curve

in the Lindemann model $F = 1$

$F(p,T)$ can be defined by *e.g.* Troe parameterization

$\mathrm{CH_3 + OH\ (+\ M) \rightarrow CH_3OH\ (+\ M)}$



k^{bi} „pseudo second order” rate coefficient
at low pressure: $k^{\mathrm{bi}} = k_0\,[\mathrm{M}]$
at high pressure: $k^{\mathrm{bi}} = k_\infty$

Formation of the decomposition products

$$k^{\mathrm{tri}} = k_0 \left(\frac{1}{1+P_r} \right) F$$

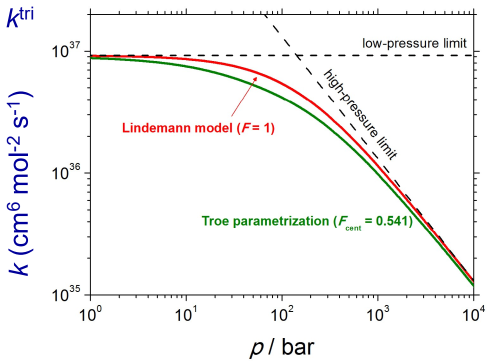
$$P_r = \frac{k_0 [\mathrm{M}]}{k_\infty}$$

P_r reduced pressure
F controls the shape of the
$k(p)$ curve

in the Lindemann model $F = 1$

$F(p,T)$ can be defined by *e.g.* Troe parameterization

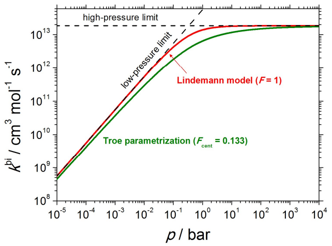
$\mathrm{CH_3 + OH\ (+M) \rightarrow {}^1CH_2 + H_2O\ (+M)}$



k^{tri} „pseudo third order” rate coefficient
at low pressure: $k^{\mathrm{tri}} = k_0$
at high pressure: $k^{\mathrm{tri}} = k_\infty\,/\,[\mathrm{M}]$

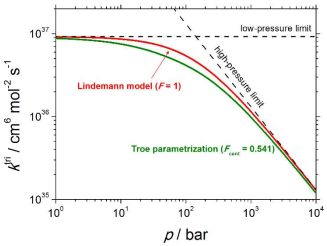
Reaction $CH_3 + OH \rightarrow$ products

$CH_3 + OH\ (+M) \rightarrow CH_3OH\ (+M)$

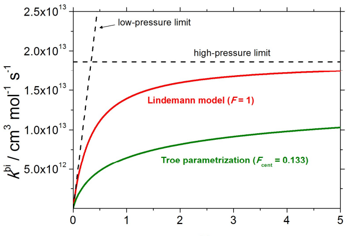


lg k^{bi} – lg p plot

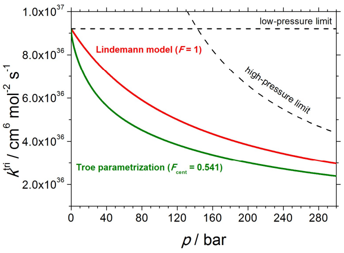
$CH_3 + OH\ (+M) \rightarrow {}^1CH_2 + H_2O\ (+M)$



lg k^{tri} – lg p plot



k^{bi} – p plot



k^{tri} – p plot

T = 1000 K

source of data: R. De Avillez Pereira *et al. J. Phys. Chem. A*, **101**, 9681–9693 (1997)

Units of concentration 1

$$c_i = \frac{n_i}{V}$$

molar concentration *e.g.* [mol/dm^3], [molecule/cm^3]
amount of matter / volume
the favourite of chemists

pro:
- has to be present in the rate equations
- clearly shows the molar ratio of the reactants

con:
gas temperature increases & no chemical reaction → molar concentration changes

$$x_i = \frac{n_i}{n}$$

mole fraction
the other favourite of chemists

pro:
- shows the molar ratio of the reactants
- gas temperature increases & no chemical reaction → the mole fraction does not change

con:
cannot be used in rate equations

Units of concentration 2

$$w_i = \frac{m_i}{m}$$

mass fraction
the favourite of physicists
representative of concentrations in balance equations

pro: linked to a conserved quantity (mass)
present in the balance equations

con: does not show the molar ratios

Conversions:

$$w_i = \frac{M_i n_i}{\sum_j M_j n} \qquad x_i = \frac{w_i}{M_i}\overline{M}$$

where $\overline{M} = \frac{m}{n}$ is the mean molar mass

pV=nRT the ideal gas law is well applicable in combustion systems due to the high temperature

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Simulation of spatially homogeneous systems

calculation of concentration changes
(solution of the kinetic system of differential equations) :

$$\frac{\mathrm{d}\mathbf{Y}}{\mathrm{d}t} = \mathbf{f}(\mathbf{Y},\mathbf{p}) \qquad \mathbf{Y}(t_0) = \mathbf{Y}_0$$

calculation of temperature changes in an adiabatic system:

rate of reaction step *i*
⇓

$$C_p \frac{\mathrm{d}T}{\mathrm{d}t} = \sum_{i=1}^{N_R} \Delta_r H_i^{\ominus} r_i \qquad T(t_0) = T_0$$

heat capacity of the mixture ⇑

⇑ standard reaction enthalpy
of reaction step *i*

CHEMKIN simulation codes

www.reactiondesign.com

CHEMKIN → CHEMKIN -II → CHEMKIN 3 → CHEMKIN 4 → CHEMKIN PRO

CHEMKIN (1975–)	classified code
CHEMKIN-II (1986–)	classified code, then freeware
since CHEMKIN 3 (1996–)	commercial code

CHEMKIN-II simulation codes:

SENKIN	spatially homogeneous reactions
PREMIX	laminar premixed flames
SHOCK	shock tube simulations
PSR	perfectly stirred reactor simulations

Options of SENKIN:

adiabatic system, constant *p* pressure
adiabatic system, constant *V* volume
adiabatic system, *V*(*t*) function
closed system, constant *p*, *T*
closed system, constant *V*, *T*
closed system, *p*(*t*) and *T*(*t*) function

CHEMKIN format of mechanisms

```
ELEMENTS  H  O  N  AR  END
SPECIES
H2    O2   H2O   H2O2   H   O   OH   HO2   N2     AR
END
THERMO ALL
  300.000  1000.000  5000.000
H2                  H   2    0    0    0G    300.00   5000.00 1000.00    0 1
 2.99142300E+00 7.00064400E-04-5.63382900E-08-9.23157800E-12 1.58275200E-15    2
-8.35034000E+02-1.35511000E+00 3.29812400E+00 8.24944200E-04-8.14301500E-07    3
-9.47543400E-11 4.13487200E-13-1.01252100E+03-3.29409400E+00                   4
O2                  O   2    0    0    0G    300.00   5000.00 1000.00    0 1
 3.69757800E+00 6.13519700E-04-1.25884200E-07 1.77528100E-11-1.13643500E-15    2
-1.23393000E+03 3.18916600E+00 3.21293600E+00 1.12748600E-03-5.75615000E-07    3
 1.31287700E-09-8.76855400E-13-1.00524900E+03 6.03473800E+00                   4
H2O                 H   2O   1    0    0G    300.00   5000.00 1000.00    0 1
 2.67214600E+00 3.05629300E-03-8.73026000E-07 1.20099600E-10-6.39161800E-15    2
-2.98992                                                                       3
 6.968581
H2O2
 4.573167                                                                      2
-1.800696                                                                      3
-4.625806
H                   H   1    0    0    0G    300.00   5000.00 1000.00    0 1
 2.50000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00    2
 2.54716300E+04-4.60117600E-01 2.50000000E+00 0.00000000E+00 0.00000000E+00    3
 0.00000000E+00 0.00000000E+00 2.54716300E+04-4.60117600E-01                   4
…
```

for each species, the description of the temperature dependence of H, S and c_p
NASA polynomials: 2×7 parameters

CHEMKIN format of mechanisms

```
REACTIONS   MOLES  KJOULES/MOLE
H2+O              => OH+H             5.120E+04   2.67     26.27
OH+H              => H2+O             3.534E+04   2.62     18.95
H2+OH              => H2O+H             1.020E+08   1.60
H2O+H              => H2+OH             4.520E+08   1.60
O2+H+M              => HO2+M              2.100E+18   -.80       .00
 N2/0.67/ O2/0.4/ H2O/0./ AR/0.28/
HO2+M              => O2+H+M             1.159E+20  -1.26    211.41
                                                      .00    -8.73
HO2+H2O              => O2+H+H2O              3.801E+17   -.46    202.68
O2+H              => OH+O             9.756E+13   .00     62.11
OH+O              => O2+H             1.450E+13   .00      2.94
H2O2+O              => OH+HO2             6.620E+11   .00     16.63
OH+HO2              => H2O2+O             4.073E+08   .72     77.51
H2O2+OH              => H2O+HO2              7.830E+12   .00      5.57
H2O+HO2              => H2O2+OH              4.744E+11   .45    140.59
H2O2(+M)              => 2OH(+M)              3.000E+14   .00    202.87
 N2/0.4/ O2/0.4/ H2O/6.5/ AR/0.35/
   LOW /  3.000E+17    .00     190.40 /
   TROE /     1.0000      1.00      1.00   1040.00 /
2OH(+M)              => H2O2(+M)              7.230E+13   -.37      .00
 N2/0.4/ O2/0.4/ H2O/6.5/ AR/0.35/
   LOW /  5.530E+19    .76        .00 /
   TROE /     1.0000      1.00      1.00   1040.00 /
...
...
END
```

Arrhenius parameters *A, n, E*

3rd body collision efficiencies

Arrhenius parameters of k_0

Troe-parameters for the desciption of *p*-dependence

Direct and indirect measurements

Direct measurements:

- separate experiment for each elementary reaction step
- the aim is the determination of the rate coefficient of a single reaction step at a given temperature, pressure and bath gas

Indirect measurements:
can be interpreted only with the simulation of a detailed reaction mechanism

- flame velocity measurements
- ignition delay time measurements
- concentration measurements in reactors

The traditional way of the development detailed reaction mechanisms:

Setting up and parameterization of a detailed reaction mechanism on the basis of direct measurements and theoretical calculations.
testing (or „validation”) of the mechanism on indirect measurements

Topic 12. Indirect measurements 1: Measurement of ignition delay time and concentrations

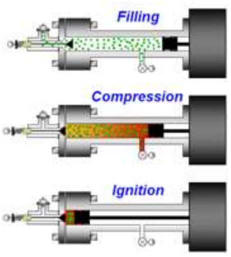
Measurement of ignition delay times
in shock tubes and rapid compression machines
The limitations of the measurements.

Measurement of concentrations coupled with
the following types of reactors
- perfectly stirred reactor (PSR)
- tubular reactor
- shock tube

Rapid compression machine (RCM)

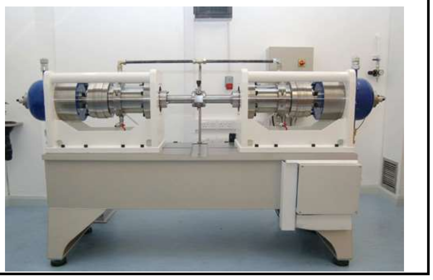
a cylinder is filled with a fuel–air mixture and it is compressed with a piston

nearly adiabatic conditions
temperature increases due to compression heat, leading to homogeneous explosion



traditional single piston RCM

twin piston RCM



Measurement of ignition delay time using RCM

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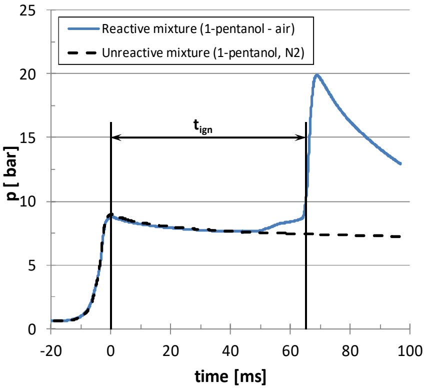
Experiment with an inert mixture:
(*e.g.* alcohol + N_2)
- compression (about 16 ms)
  temperature increases due to compression heat
- slow cooling of the mixture

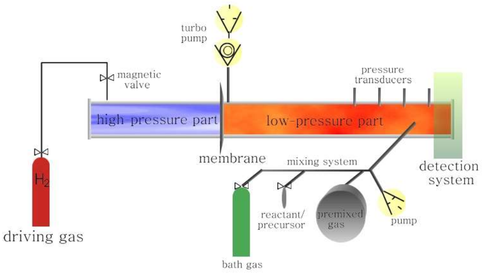
Experiment with a reactive mixture:
(e.g. alcohol + air)
- compression (about 16 ms)
  temperature increases due to compression heat
- slow cooling of the mixture and then ignition occurs (about 65 ms)

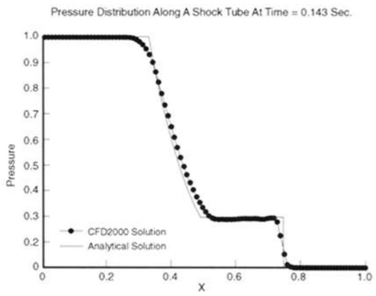
$\Rightarrow t_{ign}$ ignition delay time
ignition time, time-to-ignition



pressure is measured
as a function of time
typical shortest measured ignition time
is about 1 ms

Shock tube





rupture of the membrane
$\Rightarrow$ shock wave propagation in the
low pressure driven section

in the front of the shock wave the low-*p* gas
- gets compressed
- pressure and temperature is increased

can be incident shockwave OR
reflected shockwave when the shock wave is refflected from the back wall

Measuring ignition delay time with a shock tube

data of a high-pressure shock tube
in Galway, Ireland

- pressure resistent stainless steel tube
- 3.0 m high-pressure driver section
- 5.7 m low-pressure driven section
- internal diameter 63.5 mm
- maximal initial tube temperature 200°C
- maximal pressure 500 bar

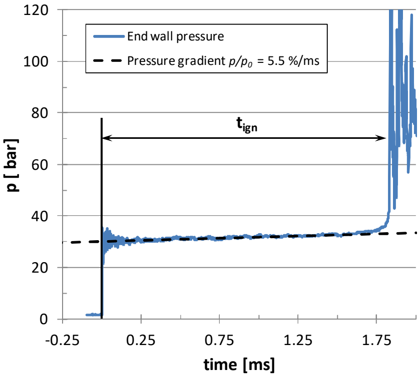
Measured pressure change at the back wall:

first pressure jump:
arrival of the shock wave to the back wall

the shock wave gets reflected from the wall

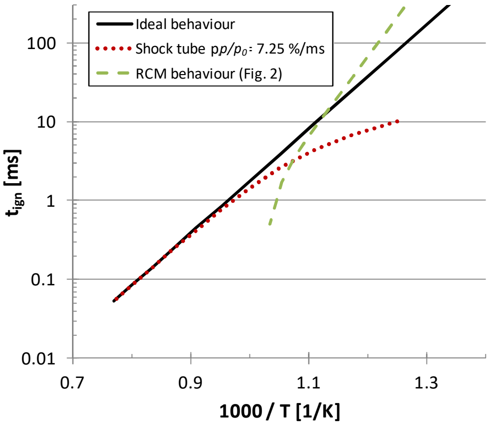
second pressure jump:
ignition of the reactive mixture

⇒ determination of ignition delay time t_{ign}



Measuring ignition delay time: limitations of RCMs and shock tubes

shock tube:	realistic result below about 1 ms
RCM:	good for long (t > 10 ms) ignition delay times short times: correction is needed on the basis of measured pressure



Perfectly stirred reactor (PSR) + measured outlet concentrations

perfectly stirred reactor (PSR)
also called
jet stirred reactor (JSR)

The nozzles create jets
the glass sphere is placed in a thermostate

fuel and oxidizer inlet

the gas is mixed by the gas jets + slow reaction:
spatially homogeneous mixture, assuming „perfect mixing"

the composition of the outlet gas is analysed using
gas chromatograph (GC) or
high pressure liquid chromatograph (HPLC) or
Fourier-transformed Infra-Red spectroscopy (FT-IR)

tubular reactor + measured outlet concentrations

tubular reactor
(also called: plug flow reactor, PFR)

slow, plug flow transport
of the reacting mixture
diffusion along the tube can be neglected

in the laboratory:
glass or quartz tube heated
by electric cartridges from the outside

concentration of the outlet gas is measured
by GC, HPLC or FT-IR.

shock wave + measured concentrations

shock wave experiment

the velocity of the shock wave is measured using a series of pressure transducers along the tube:
calculated temperature

the composition of the gas mixture after the reaction is analysed (GC, HPLC)

Topic 13. Indirect measurements 2: Measuring the laminar flame velocity

1. flame propagation in a tube
2. flame cone method
3. outwardly propagating spherical flame
4. twinflame method
5. heat flux burner method

Measuring laminar flame velocity 1
propagation of a flame in a tube

It is not easy to measure laminar flame velocity:
the practically most important flame is the
methane/air flame at conditions p= 1 atm and T_c= 298.15 K
Its reported laminar flame velocity changed
42 cm/s ⇒ 35.7 ± 0.5 cm/s in 15 years

A simple laboratory experiment:

Long tube, one side closed, other side open.
Filled up with the fuel/air mixture, ignited on the open side.

Propagation of the flame front is measured with
a series of thermocouples, mounted on the side of the wall.

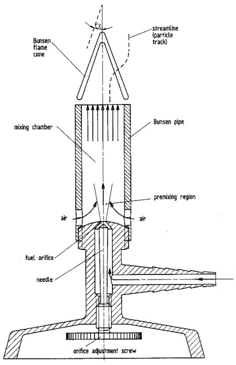
Very nice experiment, but the measured flame velocity is
too slow due to the significant wall effect.

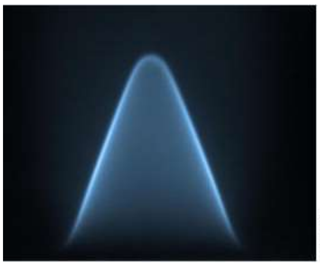
Measuring laminar flame velocity 2
flame cone method

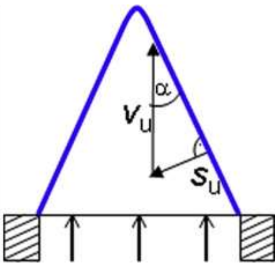
angle α between the cone of a Bunsen-flame and
the horizontal direction is measured

v_u outlet gas velocity. It is assumed to be uniform
(independent of the distance from the centre of the tube)

$$v_L = v_u \sin \alpha$$



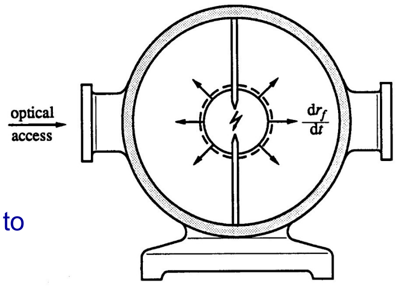




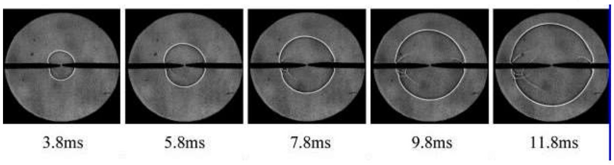
Kick *et al.*, An experimental and modeling study of
burning velocities of possible future synthetic jet fuels
Energy, **43**, 111-123(2012)

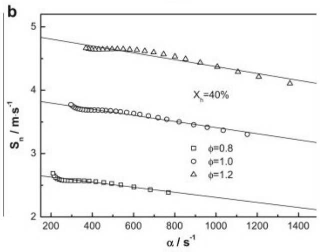
Measuring laminar flame velocity 3
outwardly propagating spherical flame

A sphere is filled with the gas mixture ignition with an electric spark in the centre of the sphere.



continous decrease of curvature and stretch
⇒ the flame slows down
⇒ flame velocity is the extrapolated velocity to a planar flame





Zhang *et al.*, Experimental determination of laminar burning velocities... ,
Int. J. of Hydrogen Energy, **36**, 13194-13206(2011)

Measuring laminar flame velocity 4
counterflow twinflame method

Two opposing, symmetrical burners

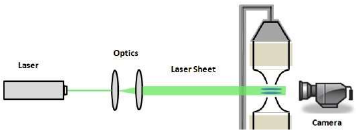
inner ring:
flow of premixed fuel/air mixture
forming a premixed flame after ignition.

outer concentric ring
flow of nitrogen,
to seal the flame from the air

the flame is in interaction with another flame:
no heat loss, no losses of radicals

C.M. Vagelopoulos, F.N. Egolfopoulos, C.K. Law:
Further considerations on the determination of laminar flame speeds with the counterflow twin-flame technique, *Proc. Combust. Inst.*, **25**,1341-1347(1994)
http://www.forbrf.lth.se/english/research/combustion_chemistry/facilities/counterflow_burner_rig/

Measuring laminar flame velocity 4
counterflow twinflame method



Measuring the axiali gas velocity using
digital particle image velocimetry (DPIV)

The „particles”:
silicon oil droplets (∅ 0.3 μm)

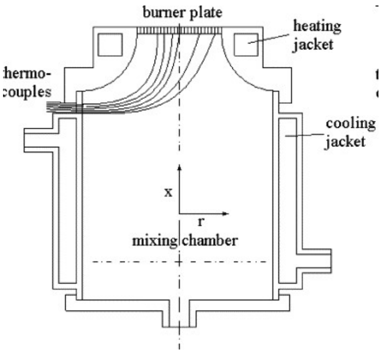
Possible problems:
- temperature of the upper burner is higher
- the flame is not perfectly cylindrical
- DPIV provides a range of gas velocities

New version:
single flame with nitrogen counterflow

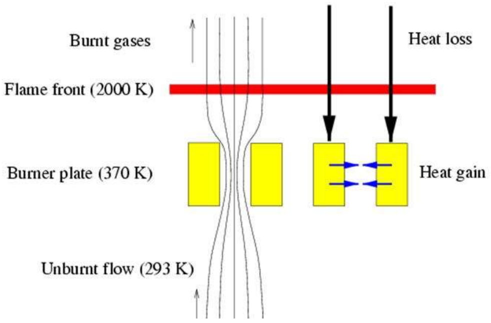
P. S. Veloo *et al.*: *Combustion and Flame* **157** (2010) 1989–2004

Measuring laminar flame velocity 5
heat flux burner method

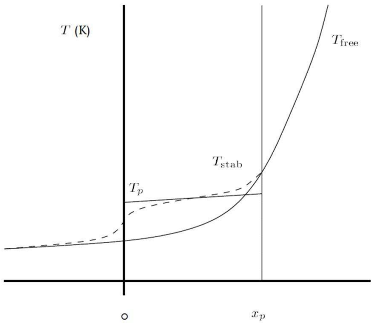
The brass block of the burner is heated with flow of hot water through the heating jacket till there is
no heat exchange between the flame and the burner.
At this condition, the flow velocity of the gas is measured.



heat flux burner method 2



temperature profile in the gas



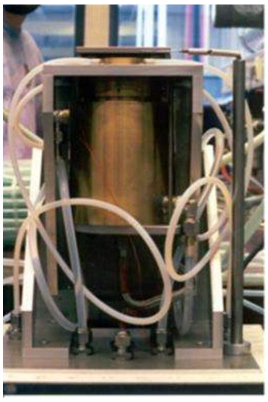
heat loss: ↓ ↓

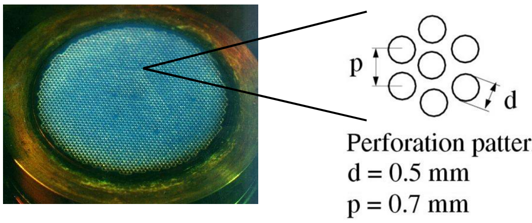
heat gain: → →

___	freely propagating flame	T_{free}
---	burner stabilized flame	T_{stab}
	temp. of burner grid	T_p

From the presentation of Prof. Dr. L.P.H. de Goey (Warsaw, 2012).

heat flux burner method 3



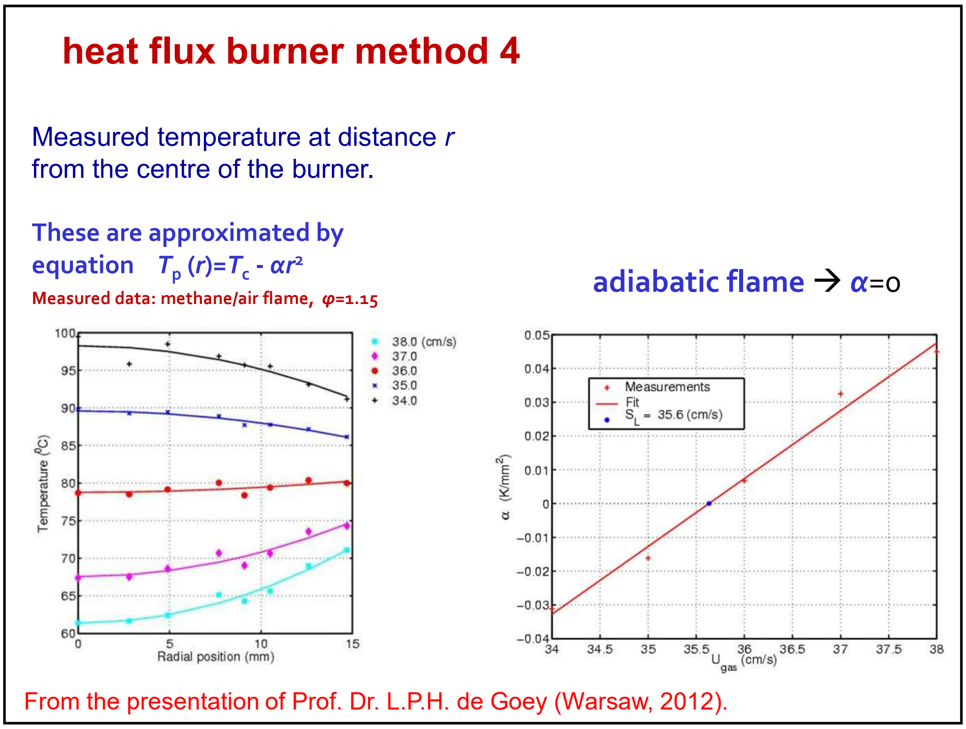


Perforation pattern :
d = 0.5 mm
p = 0.7 mm

a) Small holes are needed, not to object the gas flow

b) Good heat transfer is needed to get an adiabatic flame

From the presentation of Prof. Dr. L.P.H. de Goey (Warsaw, 2012).



heat flux burner method 4

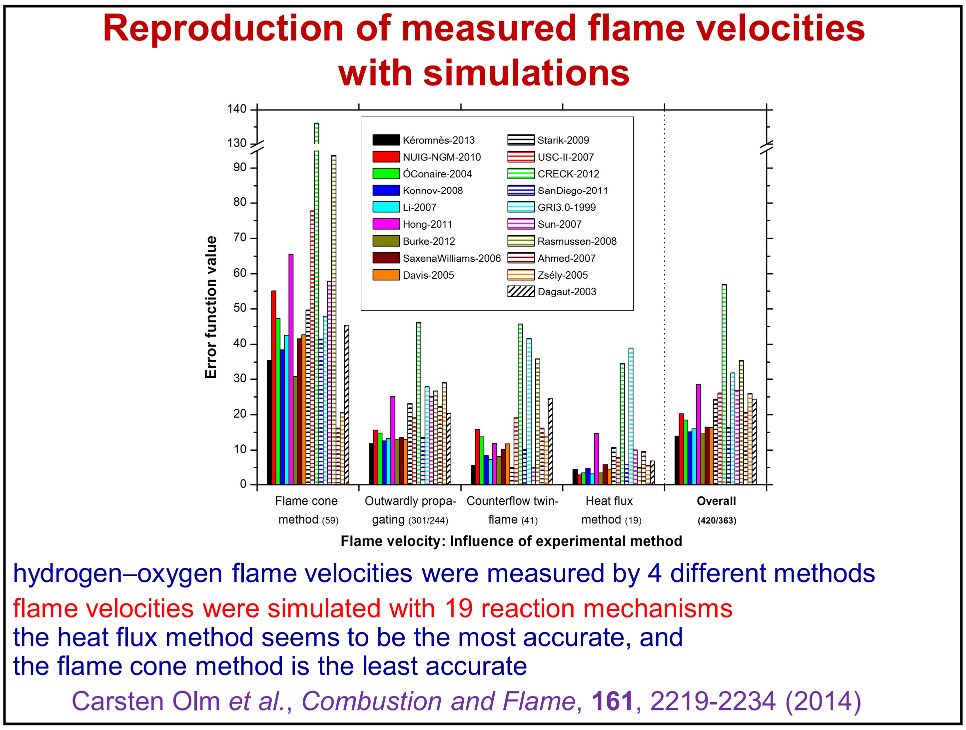
Measured temperature at distance *r* from the centre of the burner.

These are approximated by equation $T_p(r) = T_c - \alpha r^2$

Measured data: methane/air flame, $\varphi = 1.15$

adiabatic flame → $\alpha = 0$

From the presentation of Prof. Dr. L.P.H. de Goey (Warsaw, 2012).



Reproduction of measured flame velocities with simulations

hydrogen–oxygen flame velocities were measured by 4 different methods
flame velocities were simulated with 19 reaction mechanisms
the heat flux method seems to be the most accurate, and
the flame cone method is the least accurate

Carsten Olm *et al.*, *Combustion and Flame*, **161**, 2219-2234 (2014)

Topic 14. Direct measurements 1:
Using lasers for the production and detection of radicals

Why are the radical–molecule and radical–radical reactions so important?

The principles of lasers. Common lasers used in gas kinetics: excimer laser, Nd-YAG laser, dye laser.

Applications of lasers for
generating radicals and
measuring the concentrations of radicals
with laser induced fluorescence (LIF).

Measuring light intensity with a photomultiplier.

Why are the reactions of radicals important?

species in a reactive gas mixtures

molecules:	A	low reactivity, usually high concentration
radicals:	B.	high reactivity, usually low concentration

A+A reactions:	very slow
A+B. reactions:	fast
B.+B. reactions:	fast (provided that the concentrations are large enough) $r = k\,[.B_1]\,[.B_2]$

The most frequently studied elementary reactions: A+B. and B.+B.

Example: explosion of stoichiometric hydrogen/air mixtures

Reactive mixture contains 4 molecules (H_2, O_2, H_2O, H_2O_2) and
4 radicals (.H :O .OH .HO_2);
28 important (irreversible) reaction steps:

reaction of type A+A	3	(chain initiation reactions) **in the reverse order these are radical-radical reactions!**
reaction of type A+B.	11	(chain continuation reactions)
reaction of type B.+B.	14	(can be chain branching/continuation/termination)

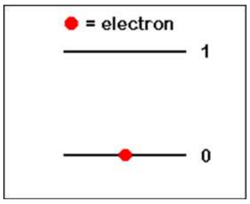
Measurement of the rate coefficients of elementary gas phase reactions

Ingredients for the measurement of the rate coefficients of
A+B. and B.+B. type elementary reactions:

- generation of radicals in the gas mixture
  (methods: high temperature (shock tube), flash (laser or conventional), microwave discharge
- measurement of radical concentrations
  (resonance fluorescence **RF**,
  laser induced fluorescence **LIF**,
  light absorption, mass spectrometric detection **MS**
- determination of the rate coefficient
  by fitting a function to the measured radical concentrations

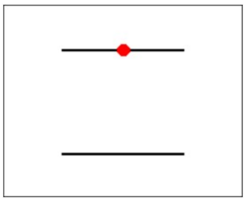
---

Lasers 1



light absorption and
then emission

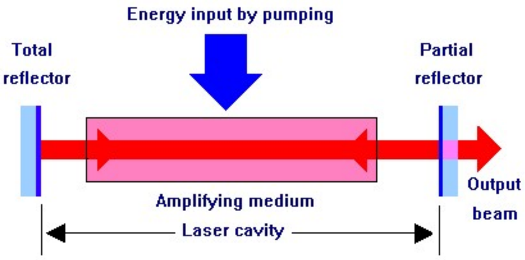
$$A + h\nu \rightarrow A^*$$
$$A^* \rightarrow A + h\nu$$

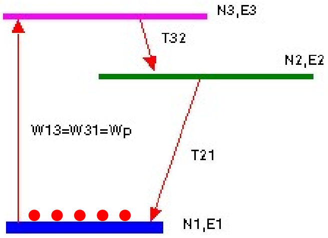


light absorption and
then stimulated emission

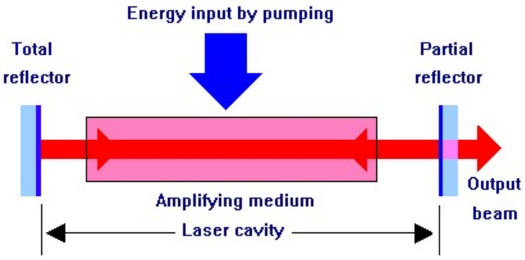
$$A + h\nu \rightarrow A^*$$
$$A^* + h\nu \rightarrow A + 2\,h\nu$$

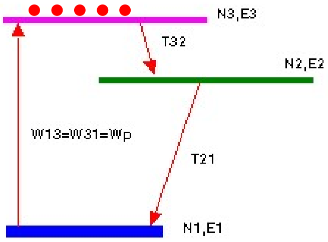
Lasers 2



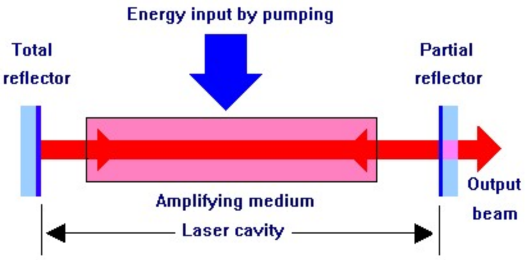


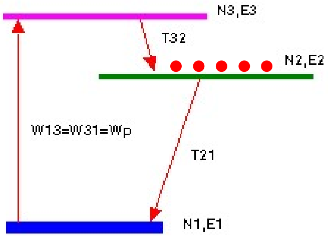
Lasers 2





Lasers 2



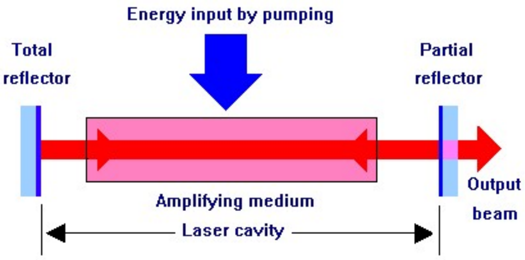


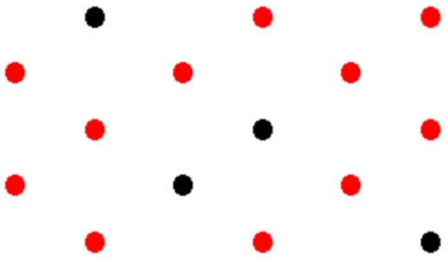
population inversion

the particles get stuck on
a high energy level,
waiting for a stimulated emission

<u>important</u>: the medium should not absorb the laser light.

Lasers 3



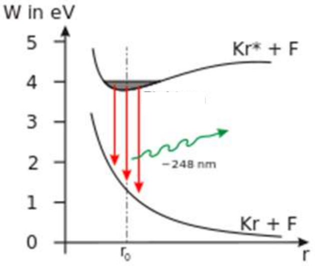


● = excited atom

START

Excimer laser

gas mixture	excimer	λ
$Ar/F_2/He$	ArF	193 nm
Kr/HCl/He	KrCl	222 nm
$Kr/F_2/He$	KrF	248 nm
Xe/HCl/He	XeCl	308 nm
$Xe/F_2/He$	XeF	351 nm



high voltage electric discharge in a noble gas – halogen gas mixture:

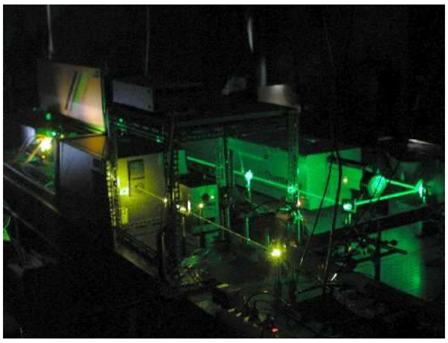
formation of an excited noble gas–halogen compound, *e.g.*

ArF* , KrF* , KrCl*

these do exist in excited state only.
Emission of an UV photon + dissociation.

There is no ground state ArF species
⇒ it cannot absorb laser light.

Nd-YAG laser



	laser light / λ	
Nd-YAG original	1064 nm	IR
doubled	532 nm	green
doubled	266 nm	UV

Nd:YAG neodymium-doped yttrium aluminum garnet $Nd{:}Y_3Al_5O_{12}$

Ions Nd^{3+} and Y^{3+} have similar size, a part of the Y^{3+} ions is replaced by Nd^{3+} ions. (about 1 mol% neodymium content)

Excitation: light of flash lamp or diode laser.
can be a continuous or pulsed laser
most of the emitted light is 1064 nm infrared (IR)

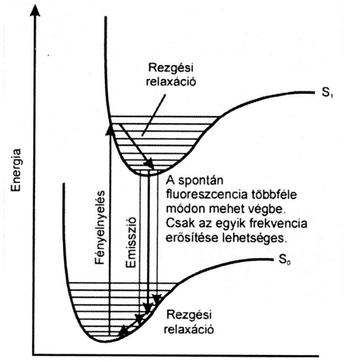
Dye lasers

The laser active medium is fluorescent organic molecules in a solvent (*e.g.* methanol)

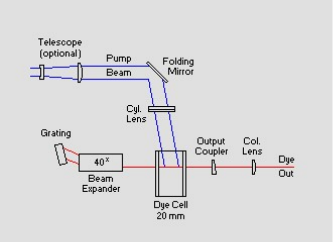
Light is emitted at several frequencies,
but only one frequency is amplified
via stimulated emission.

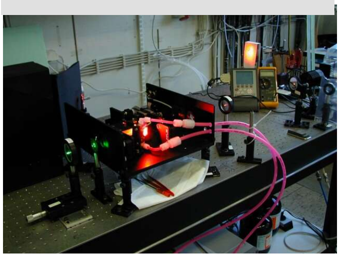
\+ wide light frequency range can be covered with the approriate selection of the laser dye.

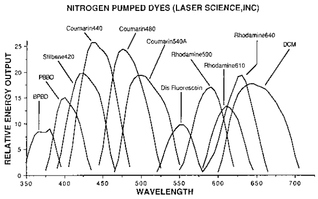
– Not really monochromatic; low light intensity



A spontán fluoreszcencia többféle módon mehet végbe. Csak az egyik frekvencia erősítése lehetséges.







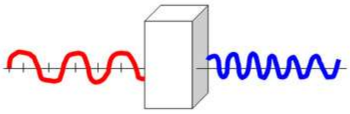
Application of lasers for the generation of radicals

Several molecules get decomposed exposed to UV light
and radicals are generated:
for example: $CH_3COCH_3 \rightarrow 2\ .CH_3 + CO$

A part of the lasers emit UV flash: *e.g.* excimer laser

The light of other lasers can be converted to UV flash
by frequency doubling (tripling)

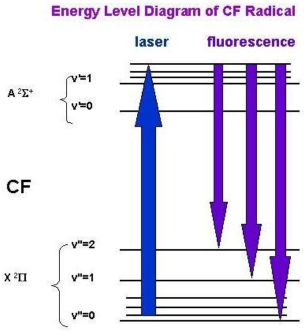
Nd-YAG original 1064 nm (IR)
doubled 532 nm (green),
twice doubled 266 nm (UV)



Measuring radical concentrations using
Laser induced fluorescence (LIF)

Light with exact wavelength
needed for the excitation of radicals
is emitted by dye laser.
The exciting light is coming from one direction,
the light is emitted to all directions
⇒ measurement at a right angle.

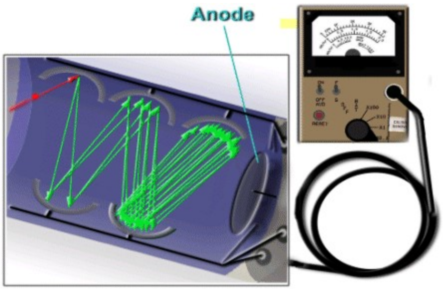
The intensity of light is measured emitted by
the radical when it is returning to ground state.
The intensity of measured light is
proportional to the concentration of the radical.



Features:

- can be applied for many radicals
- expensive: needed fast electronics + dye laser
  + dye laser pumping laser
- good quality signal with low scatterl

Measuring light with a photomultiplier



measurement of very low intensity light:
photomultiplier (PM)

Even a single photon can be detected!

vacuum in the glass tube
quartz window on one side
series of metallic plates,
with a voltage difference (*e.g.* 100 V)

the incident photon generates an electron.
the **electron** is accelerated towards the next metallic plate
and generates **2 electrons**
after each metallic plate the number of **electrons** is increasing,
resulting in a voltage jump.
can be used for single-photon counting or
the measurement of light intensity.

Topic 15. Direct measurements 2: Slow flow reactor with pulsed laser photolysis (PLP) and laser induced fluorescence (LIF) detection

Direct measurement with
pulsed laser photolysis (PLP) radical generation and
laser induced fluorescence (LIF) radical detection.

The layout of the PLP-LIF apparatus.
Application for a given elementary reaction.

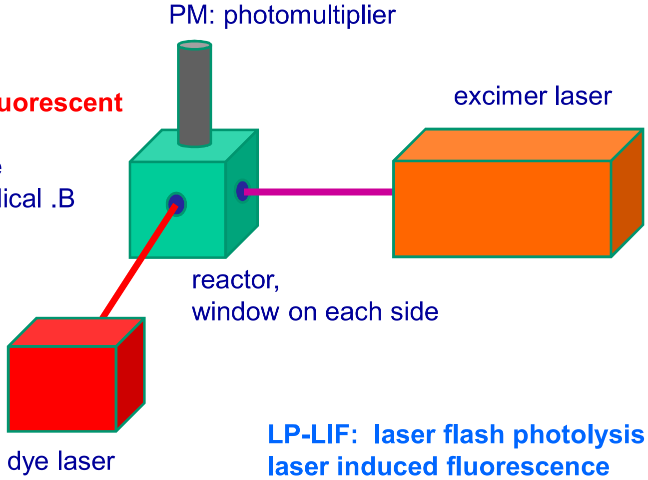
Features of the PLP-LIF method.

PLP-LIF: laser flash photolysis + laser induced fluorescence

1) **generation of radicals with excimer laser UV flash**
production of radical .B

2) ***x* μs later:**
dye laser flash
+ measuring the fluorescent light with PM
determination of the concentration of radical .B

3) measuring the [.B] – time curve by changing the delay time (*x* μs) between the two laser flashes



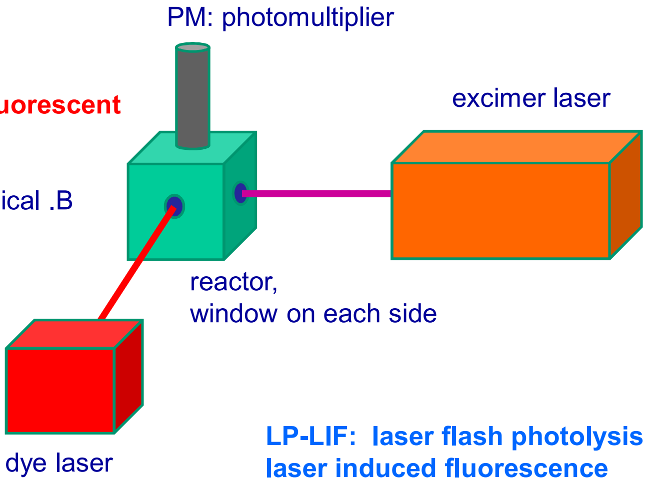
LP-LIF: laser flash photolysis – laser induced fluorescence

PLP-LIF: laser flash photolysis + laser induced fluorescence

1) **generation of radicals with excimer laser UV flash**
production of radical .B

2) ***x* μs later:**
dye laser flash
+ measuring the fluorescent light with PM
determination of the concentration of radical .B

3) measuring the [.B] – time curve by changing the delay time (*x* μs) between the two laser flashes



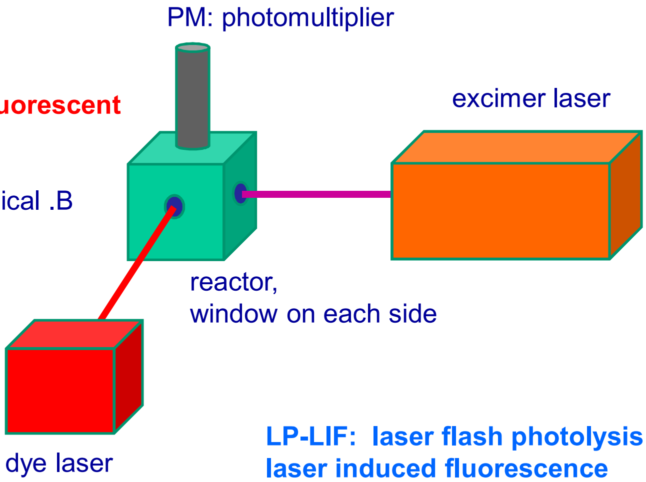
LP-LIF: laser flash photolysis – laser induced fluorescence

PLP-LIF: laser flash photolysis + laser induced fluorescence

1) **generation of radicals with excimer laser UV flash**
production of radical .B

2) ***x* μs later:**
dye laser flash
+ measuring the fluorescent light with PM
determination of the concentration of radical .B

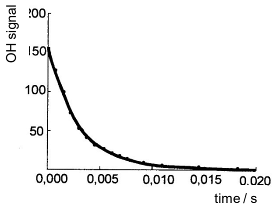
3) measuring the [.B] – time curve by changing the delay time (*x* μs) between the two laser flashes



LP-LIF: laser flash photolysis – laser induced fluorescence

PLP-LIF sample reaction: $C_2H_6 + OH \rightarrow C_2H_5 + H_2O$

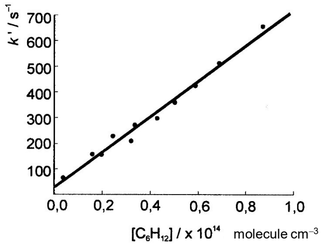
Gas mixture is flowing slowly through the reactor:	mixture of C_2H_6 and HNO_3 in Ar bath gas
light used for photolysis:	ArF excimer laser, UV flash of 193 nm
source of .OH radicals:	$HNO_3 \rightarrow .OH + NO_2$
the reaction:	$C_2H_6 + OH \rightarrow C_2H_5 + H_2O$



⇐ measuring relative OH concentration using LIF

the fluorescence light is proportional to the radical concentration: it is easy to measure relative radical concentration changes.

⇒ measurement at pseudo-first order conditions using large C_2H_6 concentration,
the decay of [OH] follows first order kinetics.



Features of the PLP-LIF method

	typical	extreme
temperature range	**300-500 K**	200 K - 1000 K (-73°C - 730°C)
pressure range	**10-760 torr**	3 torr - 20 atm

advantages:

- using proper laser light and precursor: very clean radical source
  (example: generation of OH from HNO_3)
- no side reactions
- several thousands of repetitions (2-10 Hz laser flash frequency)
  (slow flow of the gas mixture: renewal of gas composition)
- good accuracy (*k* determiniation with ~10% (1σ) accuracy)

disadvantages:

- best applicable in temperature range *T*= 300-500 K
- requires real time data processing
- the time scale is 1 μs – 1 ms; all reactions should be shifted to this range
- some radicals cannot be measured (*e.g.* alkyl radicals)

Topic 16. Direct measurements 3: Methods for the measurement of radical concentrations

laser induced fluorescence (LIF)

resonance fluorescence (RF)

atomic resonance absorption spectroscopy (ARAS)

light absorption

mass spectrometry

synchrotron vacuum ultraviolet
photoionization mass spectrometry (SVUV-PIMS)

Further direct methods for the measurement of rate coefficients of gas phase reactions

The starting point can be the PLP-LIF method. Possible changes:

Application of other methods to measure the radical concentrations

laser induced fluorescence (LIF),
resonance fluorescence (RF), ARAS
light absorption, mass spectrometry, syncrotron radiation

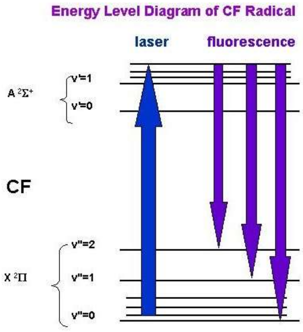
Application of other methods for the generation of radicals

conventional flash photolysis, pulsed laser photolysis (PLP)
microwave discharge, shock tube

Using lasers for the measurement of radical concentrations:
Laser Induced Fluorescence (LIF)

Light of the dye laser that is applicable
for the excitation of a radical.

The light is measured that is emitted
when the radical returns to its ground state.
The intensity of the measured emitted light
is proportional to the concentration of the radical
⇒ **measuring radical concentrations**



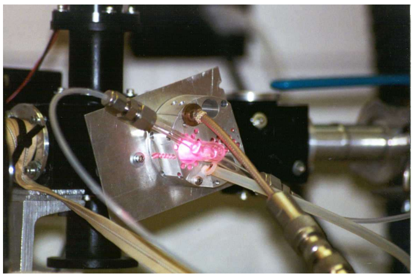
features:

- applicable for several radicals
- expensive: needed a dye laser and a driver laser + electronics
- excellent signal with low scatter

Resonance fluorescence (RF)

The source of light
needed for the detection of the radical:

decomposition of the appropriate molecule
(*e.g.* H_2O, H_2, NH_3, Br_2)
in microwave discharge +
light emission of the obtained
excited radical

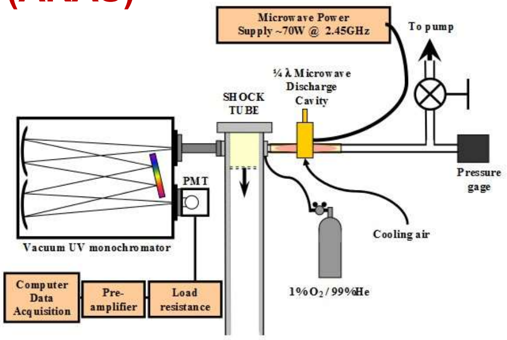


Features:

- continous emission of light, but with some fluctuations
- applicable for a few radicals only: OH, H, NH, Br
- simple and cheap
- the signal has slightly higher scatter (compared to the LIF)

Atomic Resonance Absorption Spectroscopy (ARAS)

source of light:
the corresponding element
(H_2, O_2, Br_2) in He
+ microwave discharge
(*e.g.* „H-lamp”)

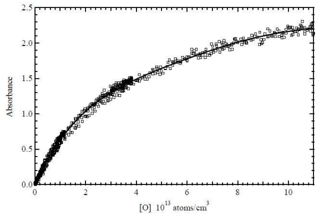


Radiation of

H-atom / O-atom (etc.) goes through the gas mixture +

monochromator +

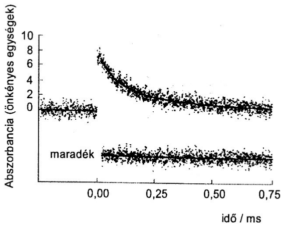
light absorption is measured by photomultiplier (PM)



Shock tube measurements of CH_3+O_2 kinetics
and the heat of formation of the OH radical.
John Thomas Herbon, Report TSD-153,
June 2004, Stanford University

O-ARAS calibration curve

Measurement of concentration changes with light absorption



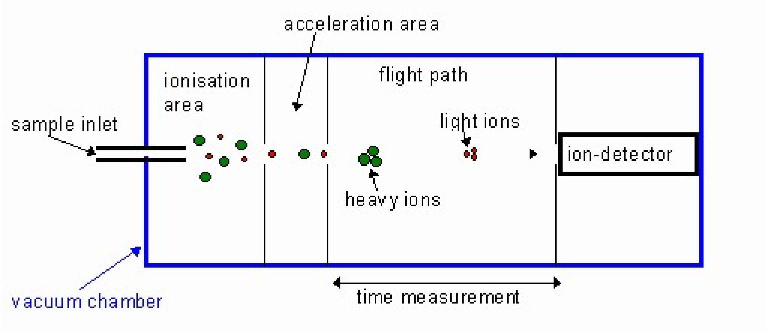
Example 1: IR light absorption + FT-IR method

Example 2: electric arc, a narrow UV frequency range is cut +
measurement of the UV light absorption

Features:

- applicable for radicals (*e.g.* CH_3) that cannot be measured with RF or LIF
- applicable at high radical concentrations only

Mass spectrometry



sampling the reactor by sucking through a small hole

Features:

good for all kinds of species

two basic solutions:

- sampling a stationary system
- opening a valve with high frequency

following quickly changing concentrations

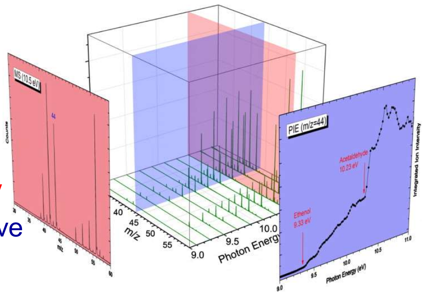
Synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS)

Synchrotron emits radiation in a very wide range, including vacuum UV.
The wavelength can be tuned.
It is used for the ionization of the radicals/molecules in the gas mixture.

2D spectrum:

- **scanning according to species mass**
- **scanning according to ionization energy**

New possibilities in qualitative and quantitative analysis of gas mixtures.



Taatjes CA, Hansen N, Osborn DL, Kohse-Höinghaus K, Cool TA, Westmoreland PR. "Imaging" combustion chemistry via multiplexed synchrotron-photoionization mass spectrometry. *Phys Chem Chem Phys.*, **10,** 20-34(2008)

Z. Zhou, H. Guo, F. Qi: Recent developments in synchrotron vacuum ultraviolet photoionization coupled to mass spectrometry, *Trends in Analytical Chemistry*, **30**,1400–1409(2011)

Topic 17. Direct measurements 4:
Methods for the generation of radicals

traditional flash photolysis

pulsed laser photolysis (PLP)

discharge flow

shock tube

Further direct methods for the measurement of rate coefficients of gas phase reactions

The starting point is the PLP-LIF method. Possible changes:

Application of other methods to measure the radical concentrations

laser induced fluorescence (LIF),
resonance fluorescence (RF), ARAS
light absorption, mass spectrometry, syncrotron radiation

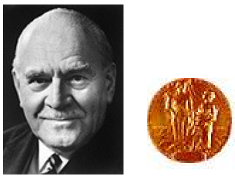
Application of other methods for the generation of radicals

conventional flash photolysis, pulsed laser photolysis (PLP)
microwave discharge, shock tube

Conventional pulsed photolysis

Generation of radicals from a precursor by flash light

⇒ Ronald George Wreyford Norrish and Sir George Porter,
Nobel Prize,1967



Norrish 1897-1978

Porter 1920-2002

Light source: photographic flash lamp

duration: 1 ms

shortest kinetic timescale: about 100 ms

(it should be much shorter,
than the duration of the flash)

Pulsed Laser Photolysis (PLP)

former name: Laser Flash photolysis (LF)

Several molecules decompose when exposed to UV light and radicals are generated:

example: $CH_3COCH_3 \rightarrow 2\ .CH_3 + CO$

UV laser flash (excimer laser or Nd-YAG laser + 2x frequency doubling)

typical flashing time: 1 ns (10^{-9} s)

⇒ shortest time scale of concentration changes: about 100 ns

Discharge flow experiment

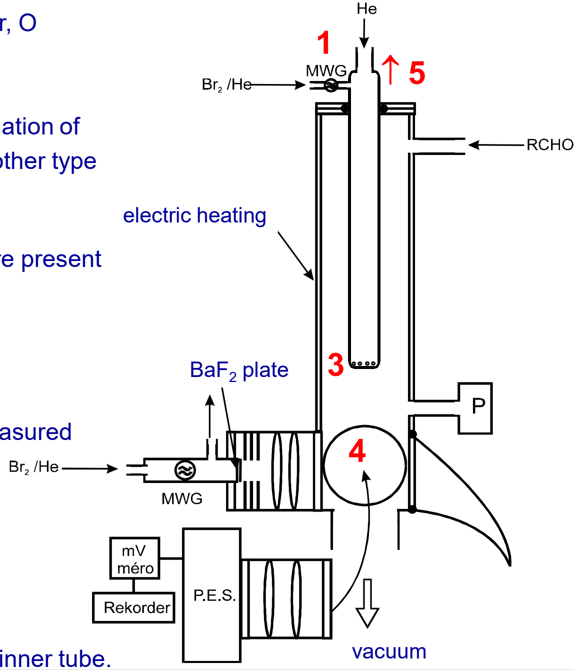
1. Generation of radicals H, Cl, Br, O
   in a microwave discharge

2. Optional quantitative transformation of
   one type of radicals to another type
   „radical titration”

3. The radical and the reactant are present
   in two fast gas flows, located
   in concentric tubes.
   The two flows are then mixed.

4. Radical concentrations are measured
   at a given distance
   at stationary conditions.

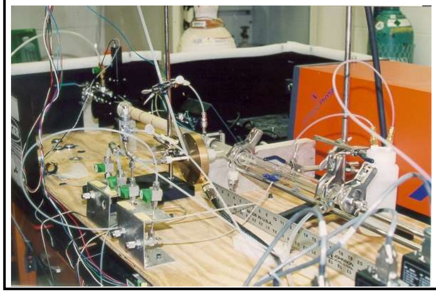
5. The distance between
   the locations of mixing and
   concentration measurement
   is changed by moving out the inner tube.



Discharge flow experiments: two typical chemical kinetic systems

Generation of the radical in discharge: $H_2 \rightarrow 2\ .H$
Generation of another radical: $.H + NO_2 \rightarrow .OH + NO$
The reaction investigated: $.OH + C_5H_{12} \rightarrow .C_5H_{11} + H_2O$

Generation of the radical in discharge: $Cl_2 \rightarrow 2\ Cl.$
Generation of another radical: $.Cl + C_2H_6 \rightarrow HCl + .C_2H_5$
The reaction investigated: $.C_2H_5 + O_2 \rightarrow C_2H_5O_2$
$\searrow C_2H_4 + HO_2$



Discharge flow: advantages and disadvantages

typical temperature range: 300 K – 500 K (max: 200 K – 1000 K)
similarly to the flash photolysis methods
the mixing time should be much shorter than the reaction time
magnitude of rate coefficients: similar to those of LP-LIF

+ advantages:

stationary system: simple, slow electronics is applicable
mass spectrometry (MS) is well applicable
radical titration: several types of radicals can be produced

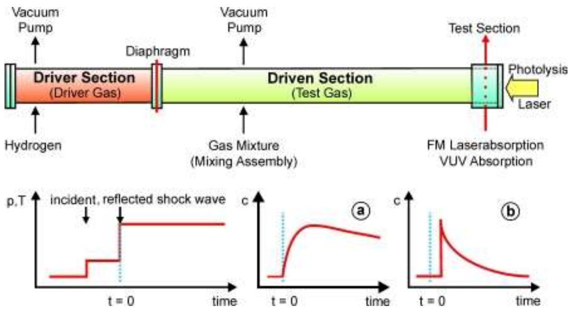
- disadvantages:

applicable only in pressure range *p* = 1-10 torr
high pressure → consumption of too much gas
→ plug flow at low *p* only
possible wall reactions.
how to avoid: (1) ageing of the wall; (2) Teflon coating
checking: changing the diameter of the wall
the experimental error is slightly higher than those of LP-LIF

Shock tube

Composition of gas mixture:
- reactant
- precursor
- diluent

- shock wave suddenly produces hot gas mixture
- sudden decomposition of the precursor
- the radical reacts with the reactant



⇑
another setup:
shock wave
produces high *T*

radical is produced
by laser flash

investigation of reaction C+NO → CNO

reactant NO
precursor C_3O_2
at high temperature: $C_3O_2 \rightarrow C + 2\,CO$
$C + NO \rightarrow CNO$

Shock tube: advantages and disadvanteges

+ advantage: *T* and *p* domain
that cannot be reached using any other method
typical temperature range: 1000–3500 K

- disadvantages:

- Due to the high temperature,
usually there are many simultaneous reactions

  the measured data are fitted using an assumed kinetic mechanism
  → the error of the other rate coefficients have an effect on the determined rate coefficient
- one shot – one measurement
poor *S/N* ratio (Signal/Noise ratio)
(S/*N* could be improved by many similar measurements)
- expensive to operate

Summary of direct methods

the experiment is carried out at conditions that allows the determination of the rate coefficient of a single elementary reaction
The elementary reaction is always a radical-molecule or radical-radical reaction.

Methods have to be selected for the:
1) generation of radicals
2) measurement of radical concentrations
Any combination of the two methods is possible!

Methods for the measurement of radical concentrations:
laser induced fluorescence (LIF),
resonance fluorescence (RF), ARAS
light absorption, mass spectrometry, synchrotron (SVUV-PIMS)

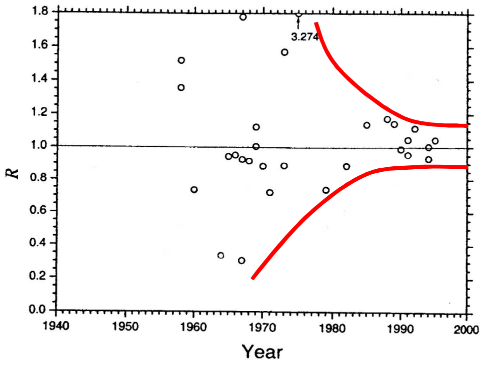
Methods for the generation of radicals
traditional flash photolysis, pulsed laser photolysis (PLP)
microwave discharge, high temperature (shock tube)

Topic 18. Uncertainty of data

Uncertainty of data used in combustion modelling.
Why is the quantitative modelling of combustion systems possible?
Multichannel reactions.
NIST Chemical Kinetics Database.
Uncertainty of rate parameters,
uncertainty of the enthalpies of formation,
typical uncertainty of experimental data.

Few reaction rate coefficients are known

the chemical kinetics of about 300 reaction steps is known
(with accuracy of about ± 30%)
although in a combustion mechanism several hundred/thousand
reaction steps are present



rate coefficient of reaction H + $O_2 \rightarrow OH + O$ *vs.* year of measurement

Why is the quantitative modelling of combustion systems possible?

- **many common reactions**
  there are many common reactions
  in the combustion mechanisms of
  basic fuels; these rate coefficents are known
- **chemical compounds with similar structures**
  if the rate coefficent is known for a given compound
  the rate coefficient for a similar compound can be estimated
- **Only a small fraction of the rate parameters determine the simulation results**
  (these parameters can be identified with sensitivity analysis)

Features of reaction kinetics data

☹ many measurements only near 300 K
(atmospheric chemistry measurements,
easier to measure at room temperature,
less data at high temperature)

☹ The rate coefficients of radical recombination reactions
(*e.g.* $2\ CH_3 + M \leftrightarrow C_2H_6 + M$)
may depend on the the pressure and bath gas,
but usually few data are available for the
p and third body dependence

☹ multichannel reactions
only the rate coefficient of the overall reaction is known
for many reactions
(sum of the rate coefficients of the individual channels)
frequently the individual rate coefficients / branching ratios are not known

Multichannel reactions

example:

$H+HO_2 \rightarrow 2\,OH$ (chain branching!)
$\rightarrow H_2+O_2$ (chain termination!)
$\rightarrow H_2O+O$ (chain branching, due to the later reaction $O + H_2 \rightarrow OH + H$)

The change of branching ratio with temperature have a high influence on the rate of overall reaction

„energy barrier is not discriminative at high temperature”

low temperature:
the channel with the lowest activation energy is fast

high temperature:
no simple rule for the preferred channels

Source of chemical kinetic data

measured and calculated chemical kinetic data → journal publications

data compilation → books. data bases.
e.g. **NIST database**
www.nist.gov

data evaluation → review articles
reevaluation and comparison of several articles evaluated/recommended data

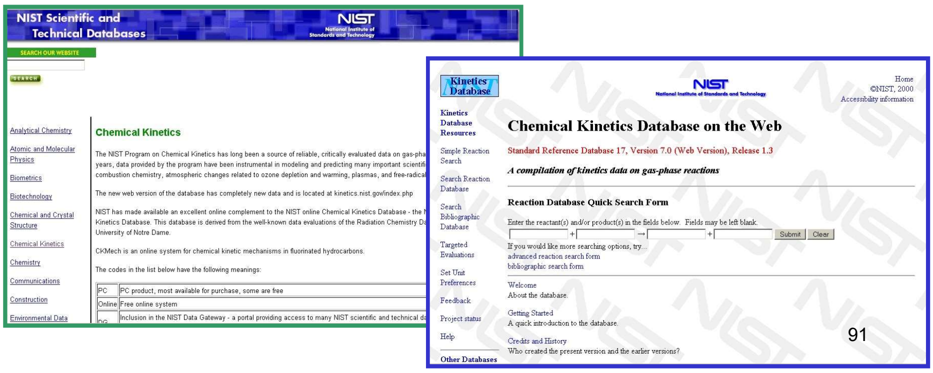
NIST Chemical Kinetics Database

www.nist.gov

⇒ Databases ⇒ Chemical Kinetics

⇒ NIST Chemical Kinetics Online (http://kinetics.nist.gov/kinetics/)

NIST Chemical Kinetics Database	11.700 gas phase reactions
	38.000 data entry
	12.000 referenced articles



Chemical Kinetics

The NIST Program on Chemical Kinetics has long been a source of reliable, critically evaluated data on gas-pha years, data provided by the program have been instrumental in modeling and predicting many important scientifi combustion chemistry, atmospheric changes related to ozone depletion and warming, plasmas, and free-radical

The new web version of the database has completely new data and is located at kinetics.nist.gov/index.php

NIST has made available an excellent online complement to the NIST online Chemical Kinetics Database - the N Kinetics Database. This database is derived from the well-known data evaluations of the Radiation Chemistry Da University of Notre Dame.

CKMech is an online system for chemical kinetic mechanisms in fluorinated hydrocarbons.

The codes in the list below have the following meanings:

PC	PC product, most available for purchase, some are free
Online	Free online system
DG	Inclusion in the NIST Data Gateway - a portal providing access to many NIST scientific and technical da

Chemical Kinetics Database on the Web

Standard Reference Database 17, Version 7.0 (Web Version), Release 1.3

A compilation of kinetics data on gas-phase reactions

Reaction Database Quick Search Form

Enter the reactant(s) and/or product(s) in the fields below. Fields may be left blank.

___ + ___ → ___ + ___

If you would like more searching options, try...
advanced reaction search form
bibliographic search form

Welcome
About the database.

Getting Started
A quick introduction to the database.

Credits and History
Who created the present version and the earlier versions?

NIST Databases 2

Author(s): Gierczak. T.; Talukdar. R.K.; Herndon. S.C.; Vaghjiani. G.L. Ravishankara. A.R.
Title: Rate coefficients for the reactions of hydroxyl radicals with methane and deuterated methanes
Journal: J. Phys. Chem. A:
Volume: 101
Page(s): 3125 - 3134
Year: 1997
Reference type: Journal article
Squib: 1997GIE/TAL3125-3134

Reaction: $CH4 + \cdot OH \rightarrow \cdot CH3 + H2O$
Reaction order: 2
Temperature: 196 - 420 K
Pressure: 0.13 Bar
Rate expression: $1.76\text{x}10^{-13}$ (cm^3/molecule s) $(T/298\ K)^{2.82}\ e^{-1.96\ (\pm 0.02\ \text{kcal/mole})/RT}$
Bath gas: He
Data type: Absolute value measured directly
Excitation technique: Flash photolysis (laser or conventional)
Analytical technique: Laser induced fluorescence

Using thermodynamic data in combustion simulations

ΔH_f ⇒ calculation of heat production in a reacting mixture
→ calculation of temperature changes
⇒ calculation of $\Delta_r G^0$

c_p ⇒ calculation of temperature changes

ΔS ⇒ calculation of $\Delta G = \Delta H - T\Delta S$
→ calculation of the equilibrium constant
→ calculation of the rate coefficient of reverse reactions

Uncertainty of thermodynamic data

c_p and ΔS can be calculated from the IR spectrum
using methods of statistical thermodynamics

ΔH_f - can be computed
(for small molecules only; not easy)
- can be determined experimentally by
- measuring the equilibrium constant of a reaction
  → reaction enthalpy → enthalpy of formation
- measuring ionization energy by mass spectrometry

Uncertainty of thermodynamic data 2

typical uncertainty of ΔH_f (1σ):

molecules and small radicals: 0.1-0.5 kJ/mole
e.g. CO= 0.17 kJ/mol, CH_4= 0.4 kJ/mol, CH_3=0.4 kJ/mole

large radicals: 1.0 – 5.0 kJ/mole
e.g. HO_2= 3.35 kJ/mol, CH_2OH= 4.2 kJ/mole

less known radicals: 8-10 kJ/mole
e.g. $HCCO$= 8.8 kJ/mol, CH_2HCO= 9.2 kJ/mole

Uncertainty of thermodynamic data 3

Question: Reaction enthalpy is changed by 1 kJ mole^{-1}
What is the consequence on the calculated equilibrium constant?

Answer: $\Delta_r H$ is changed by 1 kJ mol^{-1}
$\Delta_r S$ is assumed to be accurate ⇒

$\Delta_r G = \Delta_r H - T\,\Delta_r S$ ⇒ $\Delta_r G$ is also changed by 1 kJ mole^{-1}

$-\Delta_r G = RT \ln K$

$-\Delta_r G - (-\Delta_r G') = 1\ \text{kJ mol}^{-1} = RT \ln K - RT \ln K' = RT \ln (K/K')$

$1000\ \text{J mole}^{-1} = 8.3145\ \text{J mole}^{-1}\ \text{K}^{-1} \times 2000\ \text{K}\ \ln (K/K')$

$K/K' = 1.062$

1 kJ mole^{-1} change in $\Delta_r H$ ⇒ 6.2% change of K

Uncertainty of direct and indirect measurements

direct measurement:
determination of the rate coefficient of a single elementary reaction
at a given temperature, pressure, and bath gas

the rate coefficients are published

very high quality data uncertainty (3σ) factor of 1.3 ±10 % (1σ)
typical data uncertainty (3σ) factor of 3.0 ±44 % (1σ)

(high level) theoretical determinations:
TST/master equation calculations
typical uncertainty (3σ): factor of 3 (main channels)
factor of 10 (minor channels)
see: Goldsmith *et al. PCI*. 2013; Prager *et al. PCI*. 2013

indirect measurements:
simulation with a detailed mechanism is needed for the interpretation
ignition delay times: good 1 σ uncertainty: 10%
flame velocities: good 1 σ uncertainty: 1 cm/s (hydrocarbon flames)

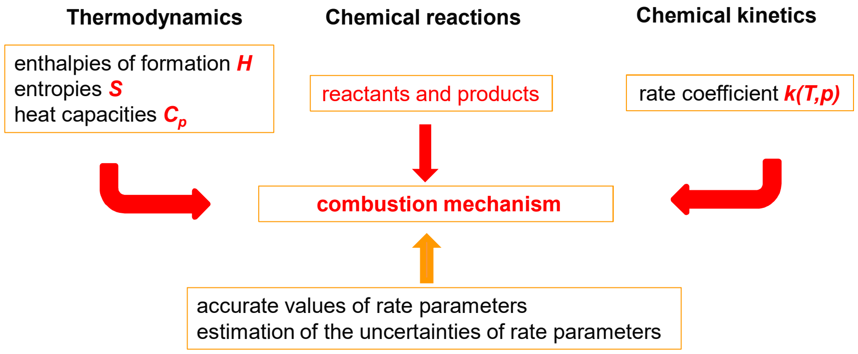
Topic 19. Validation of detailed reaction mechanisms

- comparison of experimental data and simulation results on plots
- definition of the error function values *E*
- comparison based on *E* values according to measurement categories
- change of *E* values in ranges of temperature, pressure, equivalence ratio, and dilution
- using stacked plots
- ReSpecTh Information Site
- RKD data format

Validation of chemical kinetics models

Applications of detailed chemical kinetics models:

- Design and development of an equipment (engines, gas turbines, burners)
- Real time control of the operation of an equipment
- Regulations on polluted emissions



Thermodynamics

enthalpies of formation ***H***
entropies ***S***
heat capacities C_p

Chemical reactions

reactants and products

Chemical kinetics

rate coefficient ***k(T,p)***

combustion mechanism

accurate values of rate parameters
estimation of the uncertainties of rate parameters

Development of large mechanisms

Large amount of experimental data has been published

- Direct measurements of rate coefficients
- Indirect measurements
  1. Ignition delay time (shock tube, rapid compression machine)
  2. Laminar burning velocity
  3. Concentration measurements
     in i.e. flow reactors, jet-stirred reactors, shock tubes

These data are not easily available:

- The data were published as dots in figures
- The experimental conditions were described in the text

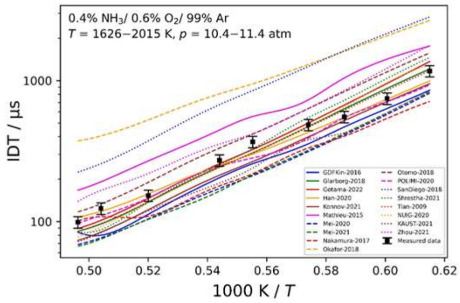
Much human work is needed for validating the trial mechanisms!

Word ‚validation' is misleading (maybe testing should be used instead).
Even if there is a good agreement between the simulation results and the indirect experimental data, it is not a proof that all parameters (*or even any of them*) are accurate: see compensation effects, fitting parameters to wrong data.

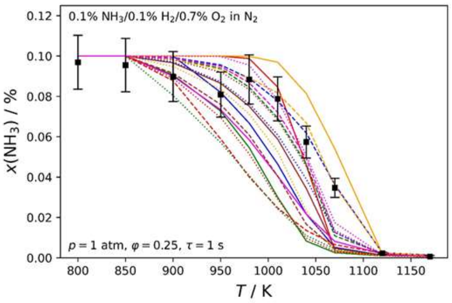
Mechanism testing and comparison

- The investigated models have very different performances. *Selected examples*:

ST-IDT measurements by Mathieu et al. [1]



JSR-conc measurements by Zhang et al. [2]



A quantitative method is needed to assess the goodness of mechanisms on a large set of data!

[1] O. Mathieu and E. L. Petersen, *Combust. Flame* 162 (2015) 554–570.
[2] X. Zhang et al., *Combust. Flame* 234 (2021) 111653.

The mean squared error function value

The error function value E can be calculated by the following equations:

$$E_{ij} = \left(\frac{Y_{ij}^{sim} - Y_{ij}^{exp}}{\boxed{\sigma\left(Y_{ij}^{exp}\right)}}\right)^2 \text{ by point} \rightarrow E_i = \frac{1}{N_i}\sum_{j=1}^{N_i} E_{ij} \text{ by dataset} \rightarrow E_{xml} = \sum_{i\in xml} \frac{1}{M_i} E_i \text{ by xml}$$

$$\downarrow$$

$$Y_{ij} = \begin{cases} y_{ij} & if\ \sigma\left(y_{ij}^{\text{exp}}\right) \approx \text{constant} \\ \ln y_{ij} & if\ \sigma\left(\ln y_{ij}^{\text{exp}}\right) \approx \text{constant} \end{cases}$$

$$E = \frac{1}{N_{xml}} \sum_{i=1}^{N} \frac{1}{N_i} \frac{1}{M_i} \sum_{j=1}^{N_i} E_{ij} \quad \textbf{by mechanism}$$

$$\sigma_{ij} = \sqrt{\sigma_{exp,ij}{}^2 + \sigma_{stat,i}{}^2}$$

$\sigma_{exp,ij}$: experimental uncertainty (as reported)

$\sigma_{stat,i}$: statistical error obtaining from Minimal Spline fit [1]

N_i : the number of included data points in the *i*-th dataset
M_i : the number of included datasets in the XML file
N_{xml} : the number of XML files

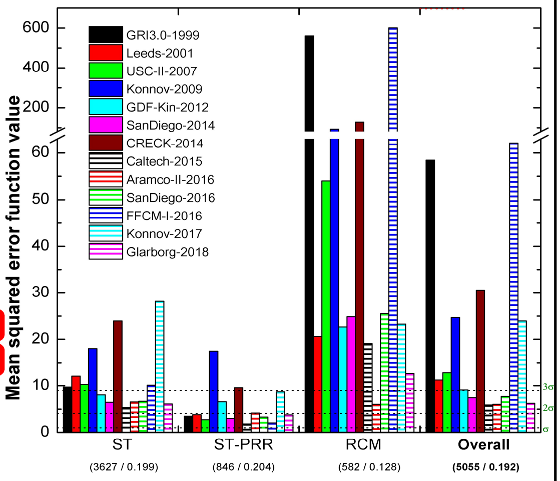
Error type:
- absolute value: ppm - Conc; cm/s - LBV
- relative value: % - IDT, Conc, LBV
- universal value: IDT, LBV, Conc
- pointwise values for one dataset: LBV

1. T. Nagy, Minimal Spline Fit - Model-free least squares fitting with Akima Splines, available from: ***respect.hu***.

Sample results – methane IDT

using *E* value tables and bars

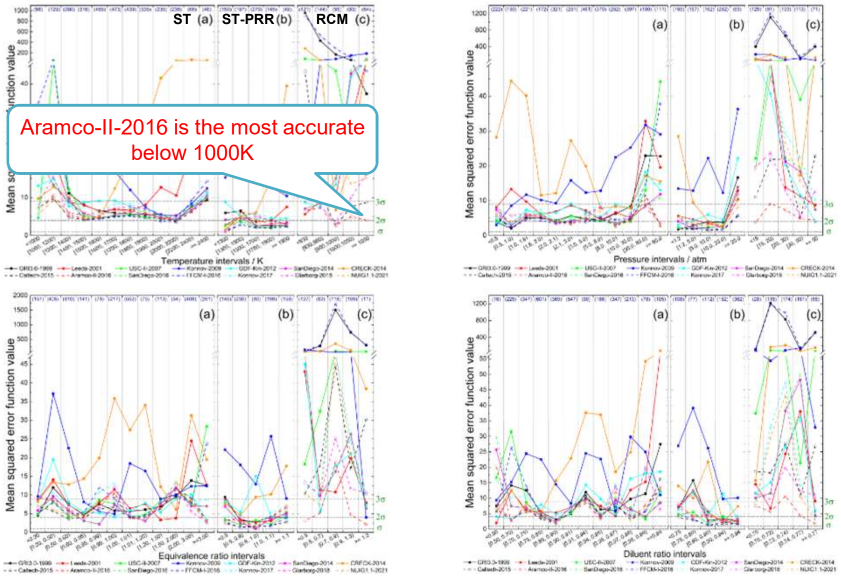
No	Mechanisms ID	Mean squared error function values			
		ST	ST-PRR	RCM	Overall
1	GRI30-1999	9.70	3.46	560.42	58.44
2	Leeds-2001	12.03	3.82	20.62	11.21
3	USC-II-2007	10.26	2.73	54.03	12.77
4	Konnov-2009	18.02	17.45	92.95	24.71
5	GDF-Kin-2012	8.06	6.57	22.65	9.09
6	SanDiego-2014	6.46	3.02	24.85	7.45
7	CRECK-2014	23.96	9.60	127.64	30.57
8	Caltech-2015	5.33	1.85	19.10	5.90
9	Aramco-II-2016	6.54	4.18	6.03	6.03
10	SanDiego-2016	6.68	3.29	25.52	7.73
11	FFCM-I-2016	10.10	2.06	600.87	62.12
12	Konnov-2017	28.17	8.73	23.25	23.94
13	Glarborg-2018	6.11	3.80	12.61	6.25



Ignition delay time: Influence of experimental method

Sample results 2 – methane IDT

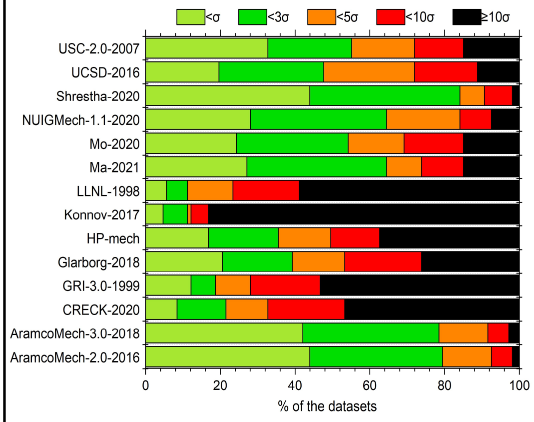
Change of *E* with temperature, pressure, φ and dilution



Aramco-II-2016 is the most accurate below 1000K

Sample results 3 – ethane IDT

using stacked plots



Stacked bar plot of the frequencies for IDT-ST simulations

If some of the mechanisms have very poor performance or there are meny failed simulations

⇒ using stacked plots is recommended

The investigated systems

We have carried out mechanism validation studies for the combustion of the following fuels:

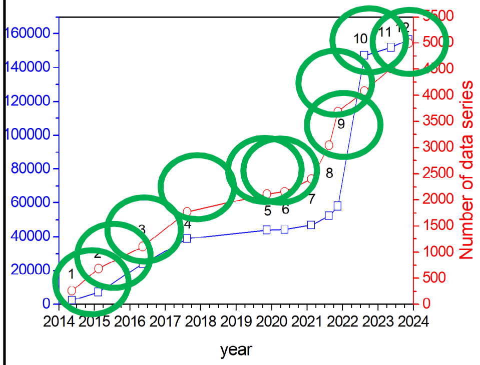
- our aim was to collect all indirect experimental data for the combustion of the selected fuel

- almost all mechanisms published in the last 20 years were tested (20-30 mechanisms for each fuel)

- hydrogen	Olm et al., *Combust. Flame* (2014)
- syngas	Olm et al., *Combust. Flame* (2015)
- ethanol	Olm et al., *Int.J.Chem.Kinet.* (2016)
- methanol and formaldehyde	Olm et al., *Combust. Flame* (2017)
- $H_2/O_2/NOx$ combustion	Kovács et al., *Fuel* (2020)
- ammonia combustion 1	Kawka et al., *Z. Phys. Chem.* (2020)
- methanol/NOx combustion	Kovács et al., *Int.J.Chem.Kinet.* (2021)
- methane ignition delay time	Zhang et al., *Energy&Fuels* (2021)
- methane laminar burning velocity	Zhang et al., *Combust. Flame* (2022)
- butanol	Bolla et al., *Energy&Fuels* (2022)
- ammonia combustion 2	Szanthoffer et al., *AECS* (2023)
- ethylene combustion	Su et al., *Combust. Flame* (2023)

All collected experimental data are freely available from the ReSpecTh.hu web site.

http://respecth.hu/ Information Site



Combustion data in the ReSpecTh web site.

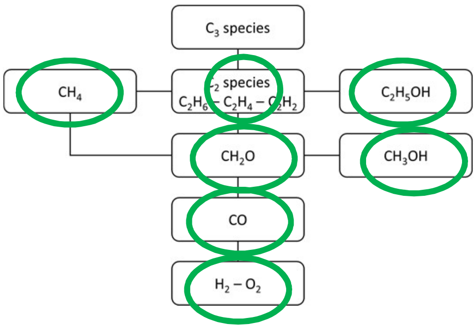
(1) hydrogen, (2) syngas, (3) ethanol,

(4) methanol and formaldehyde, (5) $NO_x/H_2/O_2$,

(6) NH_3, (7) methanol/NO_x,

(8) methane (IDT data), (9) methane (LBV data),

(10) butanol, (11) NH_3 again, (12) ethylene



Hierarchical relationship among the
combustion mechanisms of various fuels.
C. K. Westbrook, F. L. Dryer,
Prog Energy Combust Sci 10 (1984) 1–57.

Additional combustion systems:

(i) $NO_x/H_2/O_2$, (ii) methanol/NO_x, (iii) NH_3,

(iv) butanol

All data and software have been published

ReSpecTh Information System http://respecth.hu/

- **Database** of combustion experimental data
  RKD 2.4 format XML files
  (now 156,296 data points in 3463 data files)

- **Optima++ framework**: (multiplatform: Windows or Linux)
  - testing a mechanism against many datasets
  - calculation of error function value *E*
  - simulation packages
    OpenSMOKE++, **FlameMaster, Zero-RK** or **Cantera**

- **Codes for mechanism analysis, reduction and optimization:**
  (*e.g.* MinimalSplineFit, KINAL, KINALC, GUI-HDMR, MECHMOD,
  outgen, SEM, UBAC)

M. Papp,T. Varga, Á. Busai, I.Gy. Zsély, T. Nagy, T.Turányi Optima++ v2,1
A general C++ framework for performing combustion simulations and mechanism optimization (2022)

RKD-data format v. 2.5

We started to work with the PrIMe XML data format, but found some problems:

- not standalone:
  references to PrIMe web site database of literature and species
- several types of experiments could not be encoded

Some features of Respecth Kinetics Dataformat (RKD) v.2.5

- definition of the uncertainty of data points individually
- distinguishing published and derived information
- DOI of the referred (experimental) paper is stored
- bibliography data encoded using BIBTeX format
- identification of species with CAS, InChI and SMILES
- DOI numbers were requested for these XML data files

Using everywhere publicly available references and formats (DOI, CAS, InChI, SMILES, BIB TeX)

Topic 20. Reactive flows and the simulation of flames

Reactive flows.
The properties of a flow and
the effects that change these properties.
Computational Fluid Dynamics (CFD).
Simplifying assumptions for the description of 1D flames.
The general 1D balance equation for conserved property *E*.
The meaning and dimension of each quantity.

The simplifying assumptions of Frank-Kamenetskii.
The two-variate equation and its conversion to a single variate differential equation.
Lewis number. Dependence of the flame velocity on the diffusion constant and the rate of the chemical reaction.

Reactive flow

The first sentence of each course in reaction kinetics:
„Assume that the system is spatially homogenous."

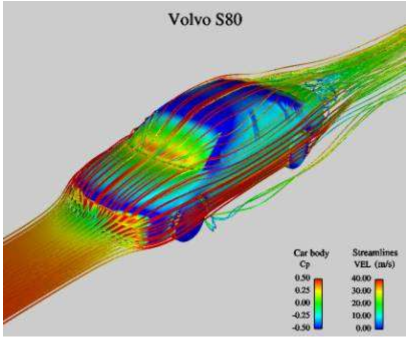
The real world: spatially (3D) inhomogeneous system + chemical reactions

The following properties are changing in space and time:

pressure p
density ρ
temperature T
gas flow velocity $\mathbf{v}=(v_1,v_2,v_3)$
the concentrations of the species $\mathbf{c}=(c_1,\ldots,c_n)$

The effects that change the properties

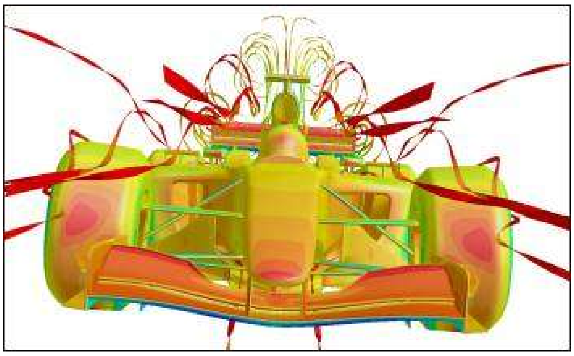
- convection
- chemical reaction
- radiation
- molecular transport
  - diffusion
  - heat conductivity
  - viscosity



Description of reactive flows

based on the laws of the conservation of mass, momentum and energy

conserved properties :
m, *I* ,*E*, amount of matter („number of moles") of each element
the form of equations: balance equations / conservation equations



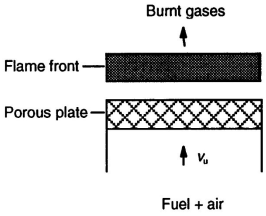
Description of reactive flows 2

fluid dynamics / computational fluid dynamics (CFD)
probably the largest sink of CPU time in the world.
(meteorology, design of cars and airplanes, flow of air in public buildings)

What we need: CFD + chemistry

The basic ideas will be demonstrated on the simplest (1D) flame:
laminar premixed flat flame

experimental setup: flat burner



Simplifying assumptions for the description of 1D flames

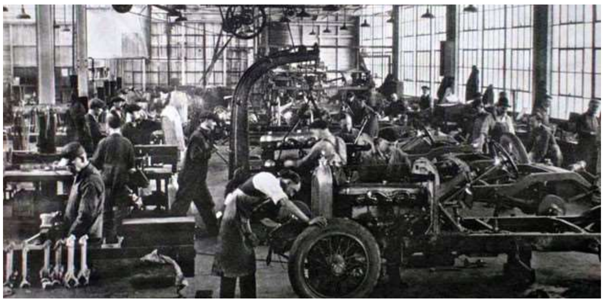
- the ideal gas law can be applied $pV = nRT$ **OK**
- the effect of external forces (*e.g.* gravity) is negligible **OK**
- the system is spatially continuous =
  the mean free paths of then molecules is much shorter
  than the width of the flame **OK**
- pressure is constant →
  fluctuations in space and time are negligible
  (↔ **flame diagnostics from the noise**)
- the energy of motion of the gas flow is negligible
  compared to the chemical energy release
  (↔ **modelling detonation waves**)

Simplifying assumptions 2

- the radiative heat transfer is negligible
  (↔ **IR radiation of CO_2 molecules and soot**)
- local thermal equilibrium is valid
  (↔ **modelling non-thermal plasmas,**
  ↔ **modelling ultrafast systems**)
- the flame is stationary
  (The equations contain time, but the aim is
  obtaining the stationary solution
  by solving the system till long simulation times
  ($t \to \infty$))

Balance of screws in a car factory

Assume that
we have a car factory:



This factory uses large amount of screws.
The screws are produced in the factory,
but we can also sell / buy screws:

change of the number of screws inside the walls of the factory =

export/import through the gates + production/consumption

General 1D balance equation
for conserved variable *E*

$$\frac{\partial W}{\partial t} + \frac{\partial J}{\partial z} = Q$$

change in time | export/import | production/consumption

		dimension
E	conserved property	[e]
z	spatial coordinate	[length]
t	time	[time]
W	density of *E*	[e/volume]
J	flux of *E* (also called „flux density”)	[e/(area*time)]
Q	source or sink of *E*	[e/(volume*time)]

Conserved properties

$$\frac{\partial W}{\partial t}+\frac{\partial J}{\partial z}=Q$$

1 Conserved property: total mass

W	total mass density	ρ	[kg/m^3]
J	density × flow velocity	$J = \rho v$	[kg/m^{2}s]
Q	always zero, because the total mass is not changed in chemical systems		

The corresponding balance equation is the continuity equation

$$\frac{\partial \rho}{\partial t}+\frac{\partial(\rho v)}{\partial z}=0$$

Further conserved properties considered:

2 mass m_i of species i

3 enthalpy *h* of the mixture

see the Appendix (at the end of the slides) for the full derivation

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The obtained balance equations

Equation for the mass fractions of each species:

$$\rho\frac{\partial w_i}{\partial t}=\frac{\partial}{\partial z}\left(D_i\rho\frac{\partial w_i}{\partial z}\right)\quad-\rho v\frac{\partial w_i}{\partial z}\quad+r_i$$

change in time — diffusion — convection — chemistry

Equation for the calculation of temperature:

$$\rho c_p\frac{\partial T}{\partial t}=\frac{\partial}{\partial z}\left(\lambda\frac{\partial T}{\partial z}\right)-\left(\rho v c_p+\sum_i j_i c_{p,i}\right)\frac{\partial T}{\partial z}-\sum_i h_i r_i$$

change in time — diffusion — convection — chemistry

The common form of the two types of equations:

$$\frac{\partial Y}{\partial t}=\frac{\partial}{\partial z}\left(A\frac{\partial Y}{\partial z}\right)+B\frac{\partial Y}{\partial z}+C$$

Analytical description of 1D laminar flames

The obtained equations can be solved numerically.

For a 20-species mechanism about 5 minutes are needed to get a solution on a modern PC. There is no exact analytical solution. (analytical = the solution is given as an explicit function)

BUT: Zeldovich and Frank-Kamenetskii suggested an approximate analytical solution (1938)

Yakov B. Zeldovich, Andrei Sakharov and David A. Frank-Kamenetskii in town Sarov, 1950s

see also: **http://garfield.chem.elte.hu/combustion/Frank-Kamenetskii/DAFK.htm**

Analytical description of 1D laminar flames: simplifying assumptions

1) The chemical changes can be represented by a single fuel (F) to product (P) overall reaction, and its temperature dependence can be described by a single Arrhenius expression:

$F \rightarrow P$ $\qquad$ $k = A \exp(-E/RT)$

rate: $r = -\rho\, w_F\, k = -\rho\, w_F\, A \exp(-E/RT)$

(2) The following quantities do not change with distance:

λ	heat conductivity
c_p	specific heat capacity
ρD	product of density and diffusion constant

(3) Enthalpy transported by species diffusion can be neglected.

The 2-variate description of 1D flames

Using the simplifications above we get two similar equations:

equation for the mass fraction of the fuel:

$$D\frac{\partial^2 w_F}{\partial z^2} - v\frac{\partial w_F}{\partial z} - w_F \qquad A\exp\left(-\frac{E}{RT}\right) = 0$$

equation for the temperature:

$$\alpha\frac{\partial^2 T}{\partial z^2} - v\frac{\partial T}{\partial z} - w_F\frac{h_p - h_F}{c_p}A\exp\left(-\frac{E}{RT}\right) = 0$$

where α is the thermal diffusivity constant: $\alpha = \frac{\lambda}{\rho c_p}$

Joining the two equations

Two equations are too many!
More simplifying assumptions:

(1) $D = \alpha$

This is largely true for most species (experimental observation).

Le= α/D Lewis number (usually close to 1)

(2) $\delta = T_b - T = \frac{h_P - h_F}{c_p} w_F$

T_b temperature of the burnt mixture
T temperature at a given location z

IDEA: the origin of all heat is the burning of the fuel. Decrease of w_F can be converted to heat production knowing the reaction enthalpy ($h_P - h_F$), while the heat production can be converted to T change by knowing the heat capacity c_p

The unified equation: $$\alpha\frac{\mathrm{d}^2\delta}{dz^2} - v\frac{d\delta}{dz} - \delta\, A\exp\left(-\frac{E}{R(T_b - \delta)}\right) = 0$$

This is not a partial differential equation, but
a second order ordinary differential equation !

The solution of the combined equation

$$\alpha \frac{\mathrm{d}^2 \delta}{d z^2} - v \frac{d \delta}{d z} - \delta\, A \exp\left(- \frac{E}{R(T_b - \delta)} \right) = 0$$

Can be solved using a Taylor expansion of the exponential term.

MATH: the error of the expansion is small if *E* large.

CHEMISTRY: the reaction rate has to be much faster at higher temperature

Frank-Kamenetskii showed that the condition of stationary solution is

$$v = v_L = \sqrt{\frac{\alpha}{\tau}}$$

v_L	laminar flame velocity
α	thermal diffusivity constant
τ	characteristic time of reaction

Assuming a first order consuming reaction of F, the characteristic time is the reciprocal of the rate coefficient at the burnt temperature

$$\tau = \frac{1}{k} = \frac{1}{A \exp\left(- \frac{E}{R T_b} \right)}$$

Analytically calculated flame velocity

Therefore, the flame velocity can be calculated as:

$$v_L = \sqrt{\alpha\, k}$$

This means that the flame is travelling fast, if we have a
large diffusion constant (fast diffusion) and
large rate coefficient (fast chemical reaction)

This is in good accordance with
our previous picture on flame propogation:
diffusion of radicals and heating up the cold gas layer
are both needed.

Thank you
for your kind attention
during the whole course!

Appendix

Derivation of the balance equations for a
1D („flat”), stationary, laminar flame,
based on the following book:

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

General 1D balance equation for conserved variable *E*

$$\underbrace{\frac{\partial W}{\partial t}}_{\text{change in time}} + \underbrace{\frac{\partial J}{\partial z}}_{\text{export/import}} = \underbrace{Q}_{\text{production/consumption}}$$

		dimension
E	conserved property	[e]
z	spatial koordinate	[length]
t	time	[time]
W	density of *E*	[e/volume]
J	flux of *E* (also called „flux density”)	[e/(area*time)]
Q	source or sink of *E*	[e/(volume*time)]

1 Conserved property: total mass

$$\frac{\partial W}{\partial t} + \frac{\partial J}{\partial z} = Q$$

W	total mass density	ρ	[kg/m^3]
J	density × flow velocity (the flow velocity is the travelling speed of the mass center)	$J = \rho v$	[kg/m^{2}s]
Q	always zero, because the total mass is not changed in chemical systems		

The corresponding balance equation:

$$\frac{\partial \rho}{\partial t} + \frac{\partial (\rho v)}{\partial z} = 0$$

continuity equation

2 Conserved property: mass m_i of species i

$$\frac{\partial W}{\partial t} + \frac{\partial J}{\partial z} = Q$$

W partial density ρ_i of species *i* [kg/m^3]

where m_i mass of species *i*

w_i mass fraction of species *i*

J partial density × flow velocity

$J = \rho_i v_i = w_i \rho v_i$ [kg/m^{2}s]

where v_i is the speed of species *i*

Q $r_i = M_i \left(\frac{\partial c_i}{\partial t} \right)_{reakcio}$

where M_i is the molar mass of species *i* [kg/mol]

$\frac{\partial c_i}{\partial t}$ chemical molar production rate of species *i* [mol/m^{3}s]

r_i chemical production rate of species *i* in mass unit [kg/m^{3}s]

balance equation for the mass of species *i* :

$$\frac{\partial(\rho w_i)}{\partial t} + \frac{\partial(\rho w_i v_i)}{\partial z} = r_i$$

Simplification of the balance equation for w_i

Original equation:

$$\frac{\partial(\rho w_i)}{\partial t} + \frac{\partial(\rho w_i v_i)}{\partial z} = r_i$$

$v_i = v + V_i$

v_i speed of the mass centre of speces *i*

v speed of the mass centre of the whole gas mixture

V_i speed of diffusion of species *i* compared to the mass centre of the gas mixture

$$\frac{\partial(\rho w_i)}{\partial t} + \frac{\partial(\rho w_i v)}{\partial z} + \frac{\partial(\rho w_i V_i)}{\partial z} = r_i \qquad (*)$$

differentiating a product function:

(uv)'=uv'+u'v or $\frac{\partial(uv)}{\partial x} = u\frac{\partial v}{\partial x} + v\frac{\partial u}{\partial x}$

$$\underbrace{w_i \frac{\partial \rho}{\partial t} + \rho \frac{\partial w_i}{\partial t}}_{(1)} + \rho v \frac{\partial w_i}{\partial z} + \underbrace{w_i \frac{\partial(\rho v)}{\partial z}}_{(2)} + \underbrace{\frac{\partial(\rho w_i V_i)}{\partial z}}_{(3)} = r_i$$

$$w_i\frac{\partial\rho}{\partial t}+\rho\frac{\partial w_i}{\partial t}+\rho v\frac{\partial w_i}{\partial z}+w_i\frac{\partial(\rho v)}{\partial z}+\frac{\partial(\rho w_i V_i)}{\partial z}=r_i$$

(1) (2) (3)

According to the continuity equation (1)+(2)=0, since $\frac{\partial\rho}{\partial t}+\frac{\partial(\rho v)}{\partial z}=0$

term (3) is a simplified way: $w_i\frac{\partial\rho}{\partial t}+w_i\frac{\partial(\rho v)}{\partial z}=0$

whre j_i is the diffusion flux of species *i*
compared to the mass centre of the gas mixture $j_i=\rho w_i V_i=\rho_i V_i$

The simplified form: $\frac{\partial(\rho w_i V_i)}{\partial z}=\frac{\partial j_i}{\partial z}$

$$\rho\frac{\partial w_i}{\partial t}+\rho v\frac{\partial w_i}{\partial z}+\frac{\partial j_i}{\partial z}=r_i$$

---

3 Conserved property: enthalpy *h* of the mixture

$$\frac{\partial W}{\partial t}+\frac{\partial J}{\partial z}=Q$$

W enthalpy for volume unit [J/m^3]

$$\sum_i\rho_i h_i=\sum_i\rho w_i h_i$$

where
h_i enthalpy of species *i*
w_i mass fraction of species *i*
ρ_i partial density of of species *i*

J flux of enthalpy =
= flux of heat + enthalpy carried with species

$$j_q+\sum_i\rho_i v_i h_i=j_q+\sum_i\rho v_i w_i h_i$$ [J/m^{2}s]

where j_i is the flux of heat:
enthalpy transport due to the temperature gradient

Q 0 (zero) due to the law of energy conservation

The balance equation: $\sum_i\frac{\partial(\rho w_i h_i)}{\partial t}+\sum_i\frac{\partial(\rho v w_i h_i)}{\partial z}+\sum_i\frac{\partial(\rho V_i w_i h_i)}{\partial z}+\frac{\partial j_q}{\partial z}=0$

(1) (2) (3) (4)

$$\sum_i \frac{\partial(\rho w_i h_i)}{\partial t} + \sum_i \frac{\partial(\rho v w_i h_i)}{\partial z} + \sum_i \frac{\partial(\rho V_i w_i h_i)}{\partial z} + \frac{\partial j_q}{\partial z} = 0$$

(1) (2) (3) (4)

(1)+(2)= $$\sum_i \left(\rho w_i \frac{\partial h_i}{\partial t} + h_i \frac{\partial(\rho w_i)}{\partial t} \right) + \sum_i \left(\rho v w_i \frac{\partial h_i}{\partial z} + h_i \frac{\partial(\rho v w_i)}{\partial z} \right) =$$

(a) (b) (c) (d)

$$\rho v \sum_i w_i \frac{\partial h_i}{\partial z} + \rho \sum_i w_i \frac{\partial h_i}{\partial t} + \sum_i h_i \left[\frac{\partial(\rho v w_i)}{\partial z} + \frac{\partial(\rho w_i)}{\partial t} \right] =$$

(c) (a) (d) (b)

equation (*) shows that $$\frac{\partial(\rho v w_i)}{\partial z} + \frac{\partial(\rho w_i)}{\partial t} = r_i - \frac{\partial(\rho w_i V_i)}{\partial z}$$

by inserting it: $$\rho v \sum_i w_i \frac{\partial h_i}{\partial z} + \rho \sum_i w_i \frac{\partial h_i}{\partial t} + \sum_i h_i r_i - \sum_i h_i \frac{\partial(\rho w_i V_i)}{\partial z}$$

$$\sum_i \frac{\partial(\rho w_i h_i)}{\partial t} + \sum_i \frac{\partial(\rho v w_i h_i)}{\partial z} + \sum_i \frac{\partial(\rho V_i w_i h_i)}{\partial z} + \frac{\partial j_q}{\partial z} = 0$$

(1) (2) (3) (4)

(1)+(2) transformed = $$\rho v \sum_i w_i \frac{\partial h_i}{\partial z} + \rho \sum_i w_i \frac{\partial h_i}{\partial t} + \sum_i h_i r_i - \sum_i h_i \frac{\partial(\rho w_i V_i)}{\partial z}$$

(3) transformed = $$\sum_i \frac{\partial(\rho V_i w_i h_i)}{\partial z} = \sum_i \rho V_i w_i \frac{\partial h_i}{\partial z} + \sum_i h_i \frac{\partial(\rho V_i w_i)}{\partial z}$$

sum of terms (1)+(2) transformed + term (3). transformed + term (4) =

$$\rho v \sum_i w_i \frac{\partial h_i}{\partial z} + \rho \sum_i w_i \frac{\partial h_i}{\partial t} + \sum_i h_i r_i + \sum_i j_i \frac{\partial h_i}{\partial z} + \frac{\partial j_q}{\partial z} = 0$$

Calculation of fluxes

j_q	heat flux	Fourier's law	$j_q = -\lambda \dfrac{\partial T}{\partial z}$	[J m^{-2}s^{-1}]
		λ is the heat conductivity constant		
j_q	species flux	Fick's 1st law	$j_i = -D_i \dfrac{\partial c_i}{\partial z}$	[mol m^{-2}s^{-1}]
		D_i is the diffusion constant of species i		

if the concentration is given in mass fraction,
Fick's 1st law is the following:

$$j_i = -D_i\, \rho \frac{\partial w_i}{\partial z}$$

Equations for the description of 1D flames

We should like to get the following variables as a function of distance (z)

temperature T, pressure p,
gas flow velocity v (compared to the flame front),

density ρ, and mass fractions $w_1, \ldots, w_{n-1}$
OR
partial densities $\rho_1, \ldots, \rho_n$

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho v)}{\partial z} = 0 \quad + \quad \frac{\partial \rho}{\partial t} = 0 \quad \Rightarrow \quad \frac{\partial(\rho v)}{\partial z} = 0$$

continuity equation — stationary system — mass flux ρv does not change with z

if p is constant and equal to the external pressure
(it was one of the initial assuptions)

ρ can be calculated in each point from T, p and composition
v can be calculated in each point from density ρ

System of equations for the mass fractions

From the balance equation for the mass of each species:

$$\rho \frac{\partial w_i}{\partial t} + \rho v \frac{\partial w_i}{\partial z} + \frac{\partial j_i}{\partial z} = r_i$$

Using Fick’s first law, flux j_i can be calculated:

$$\rho \frac{\partial w_i}{\partial t} = \frac{\partial}{\partial z}\left(D_i \rho \frac{\partial w_i}{\partial z} \right) \qquad - \rho v \frac{\partial w_i}{\partial z} \qquad + r_i$$

change
in time

diffusion

convection

chemistry

$$\frac{\partial Y}{\partial t} = \frac{\partial}{\partial z}\left(A \frac{\partial Y}{\partial z} \right) + B \frac{\partial Y}{\partial z} + C$$

System of equations for the temperature

balance equation for the enthalpy:

$$\rho v \sum_i w_i \frac{\partial h_i}{\partial z} + \rho \sum_i w_i \frac{\partial h_i}{\partial t} + \sum_i h_i r_i + \sum_i j_i \frac{\partial h_i}{\partial z} + \frac{\partial j_q}{\partial z} = 0$$

(1) (2) (3) (4) (5)

Knowing the temperature gradient is needed for the calculation of the flux, therefore calculation of temperature changes is needed.

enthalpy change → temperature change: $\mathrm{d}\, h_i = c_{p,i}\, \mathrm{d}\, T$

the specific heat capacity of the mixture $c_p = \sum_i w_i\, c_{p,i}$

the modified equation:

(2) (5) (1) (4) (3)

$$\rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial z}\left(\lambda \frac{\partial T}{\partial z} \right) - \left(\rho v c_p + \sum_i j_i\, c_{p,i} \right) \frac{\partial T}{\partial z} - \sum_i h_i r_i$$

change
in time

diffusion

convection

chemistry