Reaction kinetics modelling

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Recommended special courses of Tamás Turányi

Chemistry and Physics of Flames (in English)

- combustion chemistry
- experimental methods for the investigation of combustion reactions
- experimental determination of gas-phase rate coefficients
- physics of flame spread

Analysis of Kinetic Reaction Mechanisms (in English)

- reaction kinetics modelling
- sensitivity analysis
- uncertainty analysis
- time scale analysis
- mechanism reduction

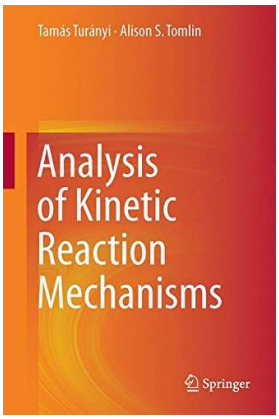
Analysis of kinetic reaction mechanisms – the book

Tamás Turányi and Alison S. Tomlin:

Analysis of kinetic reaction mechanisms

Springer, 2014

(with 1025 references)



Web page:
http://garfield.chem.elte.hu/Turanyi/KineticReactionMechanisms.html

- table of contents
- download the chapters
- references
- typos found

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Practical applications of reaction kinetics

- **modelling atmospheric chemical processes**
  - forecast of air pollution (weather forecast is needed!)
  - determination of emission limits
- **modelling of ignition and combustion**
  - modelling power stations, furnaces, engines
  - improving efficiency
  - elaboration of methods for the decrease of pollutant emission
- **process engineering; modelling of chemical engineering processes**
  - considering efficiency and the aspects of environment protection
- **systems biology: modelling biochemical processes within living organisms**
  - metabolic networks (*e.g.* medical drug decomposition in the body)
  - molecular signal transfer
  - modelling the cell cycle
- **non-chemical models using reaction kinetic formalism**
  - predator-prey models
  - description of ecological systems

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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

Equivalence ratio

fuel lean combustion
CH_4+O_2 mixture → CO_2 + H_2O + (O_2 remains)
φ<1; λ>1

stoichiometric combustion
CH_4+O_2 mixture → CO_2+H_2O
φ=1; λ=1

fuel rich combustion
CH_4+O_2 mixture → CO_2+H_2O + (CH_4 remains)
φ>1; λ<1

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

Stoichiometric ratios:

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

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

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

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 ⇓

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

heat capacity of the mixture ⇑

⇑ standard reaction enthalpy of reaction step i

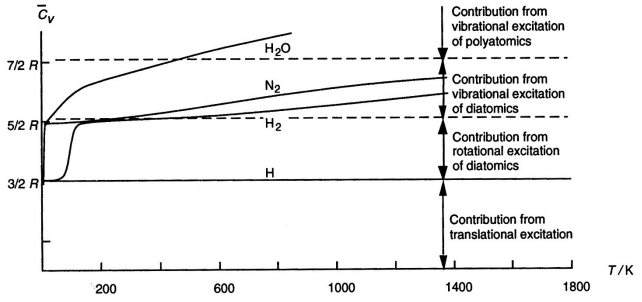
Temperature dependence of thermodynamic data

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*

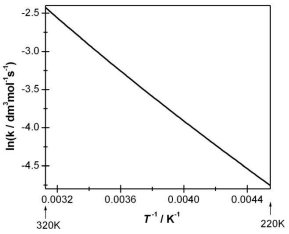
Described by the Arrhenius equation:

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

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 $m = -E_a/R$ $\Rightarrow$ determination of E_a

Arrhenius plot:



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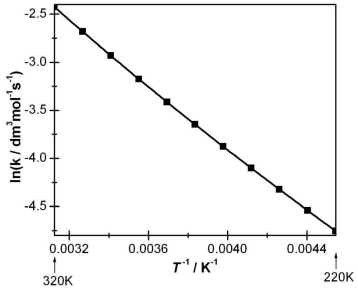
Example: reaction $CH_4 + OH \rightarrow CH_3 + H_2O$

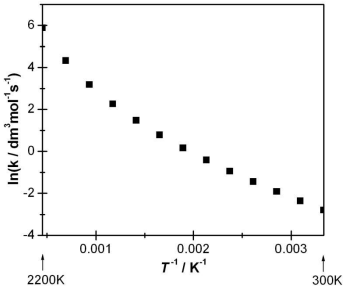
- the most important methane consuming reaction step in the troposphere
- one of the most important steps at methane combustion

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



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

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



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

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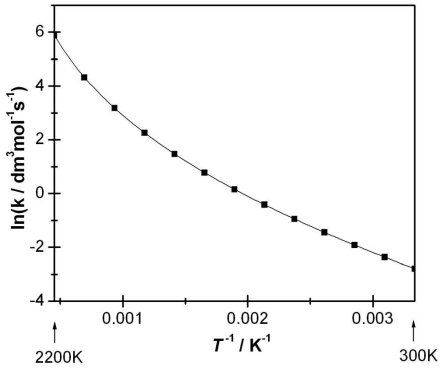
Temperature dependence of the rate coefficient *2*

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

extended Arrhenius equation



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

General definition of activation energy:

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

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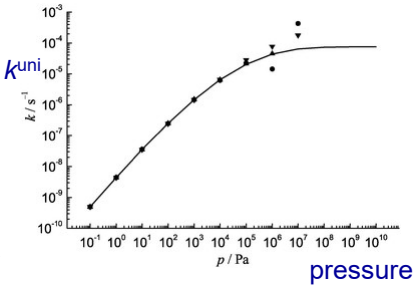
Pressure dependence of the rate coefficients 1

unimolecular decomposition

decomposition or isomerization of a species

A + M = P + M

A reactant
P product
M colliding partner for energy transfer



pressure

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: $k^{\mathrm{uni}} = k_0$ [M]

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

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

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Lindemann – Hinshelwood model

A + M	$\rightarrow$ A* + M	k_1
A* + M	$\rightarrow$ A + M	k_2
A*	$\rightarrow$ P	k_3

$$k_{uni} = \frac{k_3 k_1 [M]}{k_2 [M] + k_3}$$

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

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

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 ($mol^{-1}\ dm^3\ s^{-1}$)

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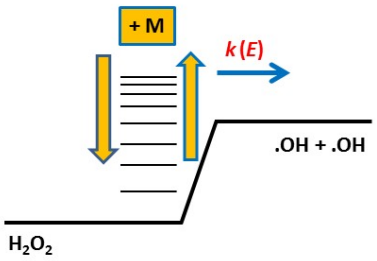
Refined Lindemann – Hinshelwood model of unimolecular reactions

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 $\quad$ 2nd order at low pressure, 1st order at high pressure

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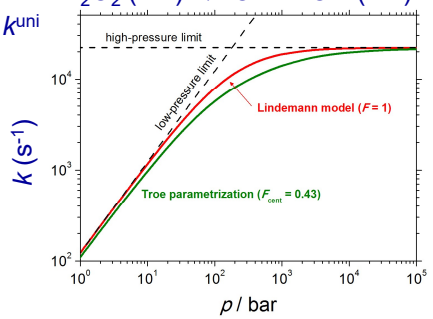
Unimolecular decomposition: calculation of the rate coefficient at an intermediate pressure

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

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

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):

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

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

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

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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

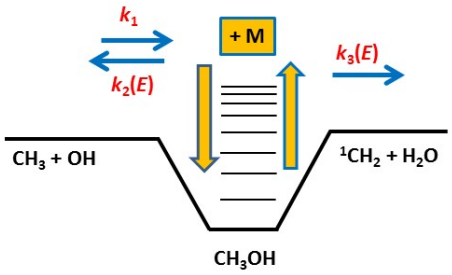
$$[M] = \sum_i m_{y_i} [Y_i]$$

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

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

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

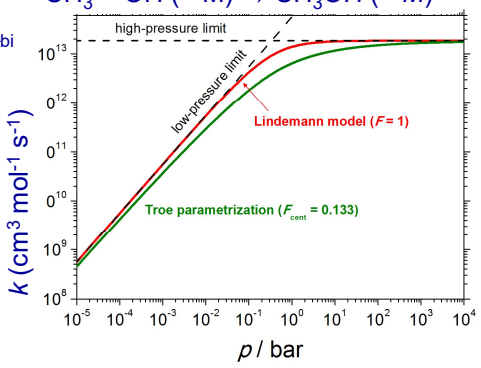
$$k^{bi} = k_\infty \left(\frac{P_r}{1+P_r} \right) F$$

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

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

in the Lindemann model $F = 1$

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



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

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

Formation of the decomposition products

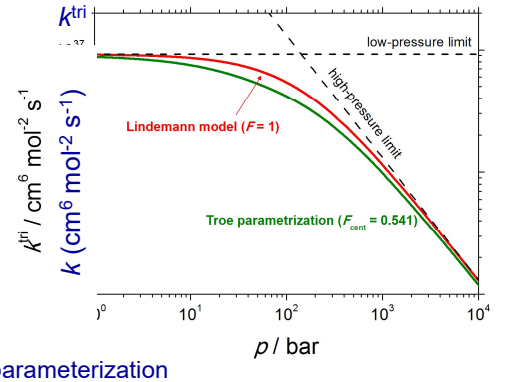
$$k^{\text{tri}} = k_0 \left(\frac{1}{1+P_r} \right) F$$

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

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

in the Lindemann model $F = 1$

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



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

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

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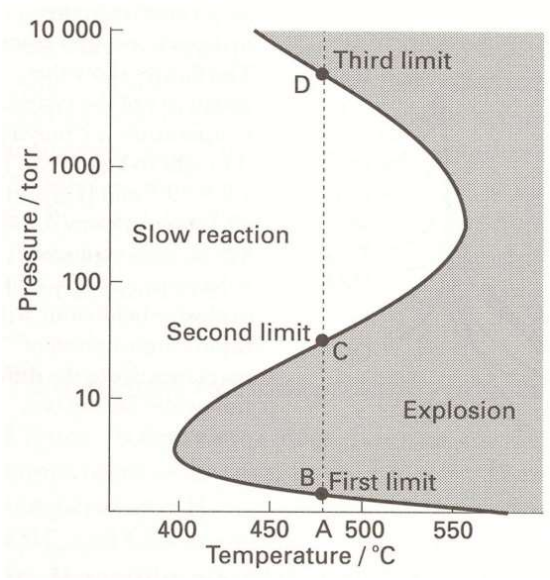
Explosion of a hydrogen-oxygen mixture

$2\ H_2 + O_2 = 2\ H_2O$



1	$H_2 + O_2 \rightarrow .H + .HO_2$	chain initiation
2	$.H + O_2 \rightarrow .OH + :O$	chain branching
3	$.OH + H_2 \rightarrow .H + H_2O$	chain continuation
4	$:O + H_2 \rightarrow .OH + .H$	chain branching
5	$.H + O_2 + M \rightarrow .HO_2 + M$	chain termination*
6	$.H \rightarrow$ wall	chain termination
7	$:O \rightarrow$ wall	chain termination
8	$.OH \rightarrow$ wall	chain termination
9	$.HO_2 + H_2 \rightarrow .H + H_2O_2$	chain initiation*
10	$2\ .HO_2 \rightarrow H_2O_2 + O_2$	chain termination
11	$H_2O_2 + M \rightarrow 2\ .OH + M$	chain initiation
12	$.HO_2 \rightarrow$ wall	chain termination

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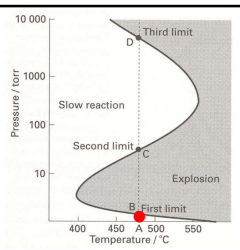

below the 1st explosion limit:

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

→ no explosion

1	$H_2 + O_2 \rightarrow .H + .HO_2$	chain initiation
2	$.H + O_2 \rightarrow .OH + :O$	chain branching
3	$.OH + H_2 \rightarrow .H + H_2O$	chain continuation
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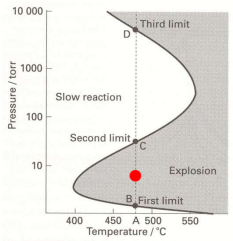
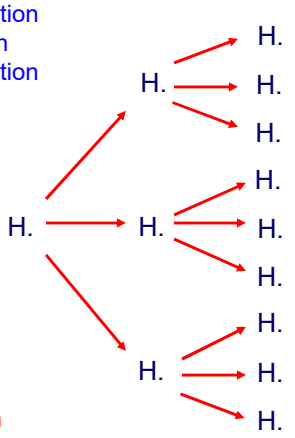


between explosion limits 1 and 2:

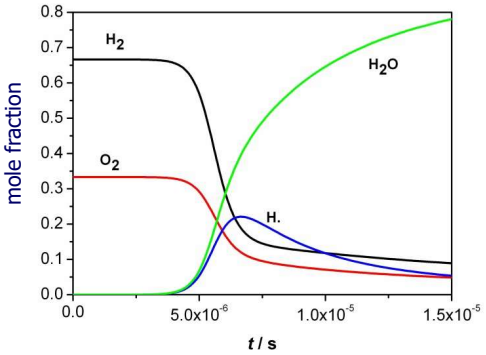
2-3-4 chain branching steps

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

$.H + O_2 + 3\ H_2 \rightarrow$ **3** $.H + 2\ H_2O$ → **explosion**



Hydrogen-oxygen explosion between limits 1 and 2



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

1	$H_2 + O_2 \rightarrow .H + .HO_2$	chain initiation
2	$.H + O_2 \rightarrow .OH + :O$	chain branching
3	$.OH + H_2 \rightarrow .H + H_2O$	chain continuation
4	$:O + H_2 \rightarrow .OH + .H$	chain branching
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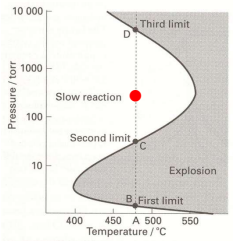

between explosion limits 2 and 3:

5	$.H + O_2 + M \rightarrow .HO_2 + M$	chain termination*
12	$.HO_2 \rightarrow$ wall	chain termination

→ no explosion

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

1	$H_2 + O_2 \rightarrow .H + .HO_2$	chain initiation
2	$.H + O_2 \rightarrow .OH + :O$	chain branching
3	$.OH + H_2 \rightarrow .H + H_2O$	chain continuation
4	$:O + H_2 \rightarrow .OH + .H$	chain branching
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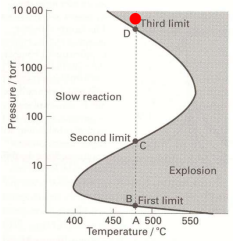


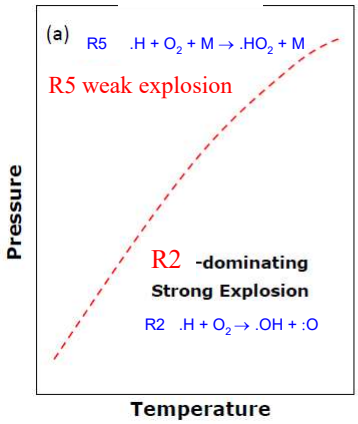
above explosion limit 3

- high pressure ⇒ reaction step 5 produces much $.HO_2$
- reaction steps 9 and 10 convert $.HO_2$ to H_2O_2
- at high pressure the decomposition of H_2O_2 is fast (reaction 11) and it produces highly reactive OH radicals

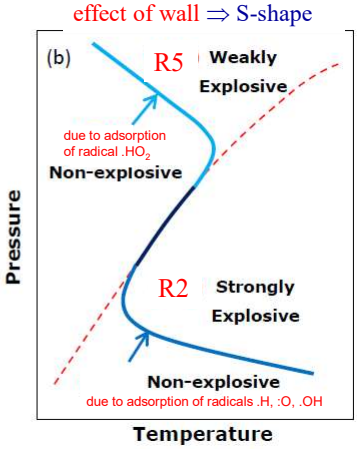
→ explosion

Effect of the heterogeneous reactions 2

without wall



effect of wall ⇒ S-shape



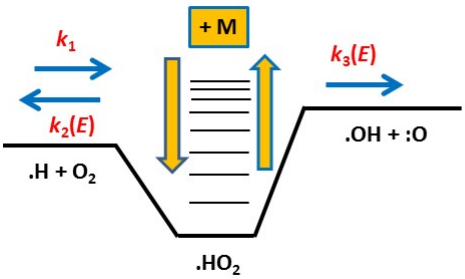
The dashed line corresponds to pressure where [M] = 2 k_2/k_5
(R2 .H + O_2 → .OH + :O R5 .H + O_2 + M → .HO_2 + M)

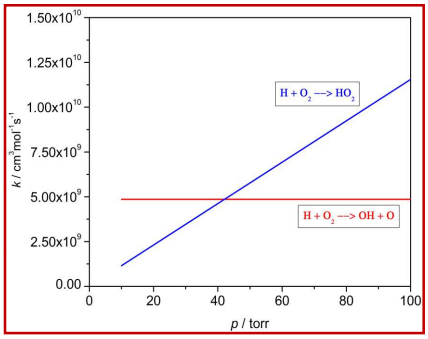
The wall reactions result in the non-explosive regions!
lower non-explosive region (below limit 1): **adsorption of radicals H, :O, .OH**
upper non-explosive region (between limits 2 and 3): **adsorption of radical .HO_2**

between limits 1 and 3

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

at temperature 650 K
below about 40 torr .H + O_2 → .OH + :O → explosion
above about 40 torr .H + O_2 + M → .HO_2 + M → **NO** explosion





.H + O_2 → .HO_2*
low pressure: .HO_2*→ .H + O_2 or .HO_2*→ .OH + :O → explosion
high pressure: .HO_2*→ .HO_2 (stabilization) → **NO explosion**

Computer codes for the study of complex reaction systems

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Reaction kinetics simulation codes

WINPP/XPP Windows simulation code
solving systems of ODEs, DAEs and PDEs.
The user has to provide the rate equations ⇒ applicable for small systems only
http://www.math.pitt.edu/~bard/classes/wppdoc/readme.htm

KPP: Kinetic Preprocessor http://people.cs.vt.edu/~asandu/Software/Kpp/
production of the kinetic ODE from the reaction mechanism
numerical solution of stiff ODEs; sparse matrix routines

V. Damian, A. Sandu, M. Damian, F. Potra, G. R. Carmichael:
The Kinetic PreProcessor KPP - A software environment for solving chemical kinetics.
Comp. Chem. Eng. **26**, 1567-1579 (2002)

SUNDIALS: SUite of Nonlinear and DIfferential/ALgebraic equation Solvers
https://computation.llnl.gov/casc/sundials/main.html

MATLAB interface to the following solvers:

CVODE	solves initial value problems for ordinary differential equation (ODE) systems
CVODES	solves ODE systems and includes sensitivity analysis capabilities
ARKODE	solves initial value ODE problems with additive Runge-Kutta methods
IDA	solves initial value problems for differential-algebraic equation (DAE) systems
IDAS	solves DAE systems and includes sensitivity analysis capabilities
KINSOL	solves nonlinear algebraic systems.

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CHEMKIN

Developed at the SANDIA National Laboratories, Livermore, CA, USA
CHEMKIN-I (1975-1985)
CHEMKIN-II (1985-1995)
Simulation codes: SENKIN, PSR, PREMIX, SHOCK, EQLIB
+ utility programs, data bases
FORTRAN codes, controlled by the input files

> Kee R. J., Rupley F. M., Miller J. A.
> CHEMKIN-II: A FORTRAN *Chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics*
> SANDIA report No. SAND79-8009B

AnSys https://www.ansys.com/ (formerly ReactionDesign)
Commertial codes; source code is not provided

Chemkin 3.x,
Graphical User Interface (GUI) to CHEMKIN-II
Chemkin 4.x
really new solvers, graphical interface, versatile
Chemkin Pro
Chemkin + additional utility codes (*e.g.* pathway plotting)

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CHEMKIN simulation codes

https://www.ansys.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 (now: Ansys)

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

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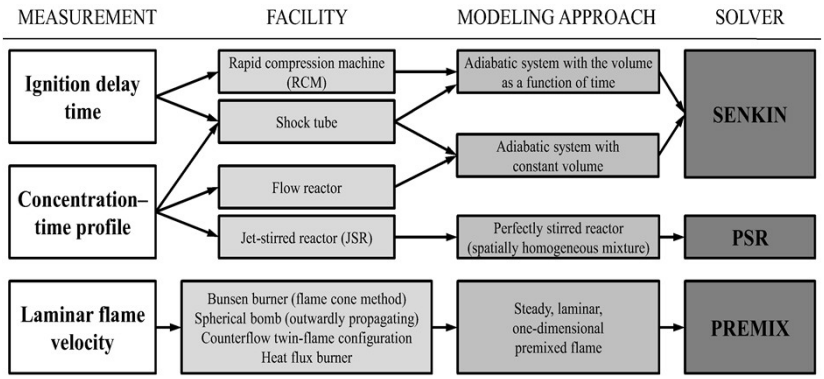
CHEMKIN-II simulation codes



Relation between the
- measured quantity
- experimental setup
- modelling approach
- the corresponding CHEMKIN-II simulation code

C. Olm, I. Gy. Zsély, R. Pálvölgyi, T. Varga, T. Nagy, H. J. Curran, T. Turányi: Comparison of the performance of several recent hydrogen combustion mechanisms. *Combust. Flame*, **161**, 2219-2234 (2014).

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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
 1.31387700E-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[illegible]                                                            3
 6.96858[illegible]
H2O2
 4.57316[illegible]                                                            2
-1.80069[illegible]                                                            3
-4.62580[illegible]
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

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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
 N2/0.67/ O2/0.4/ H2O/0./ AR/0.28/
HO2+H             => OH+OH             7.079E+13   .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+18  -.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

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Alternatives to CHEMKIN

Cantera www.cantera.org
Open source code, available from SourceForge.net
chemical equilibrium, homogeneous and heterogeneous kinetics
reactor networks, 1D flames

Kintecus www.kintecus.com
Excel workbook; free for academic use
Simulation of combustion, atmospheric chemical and biological systems

COSILAB www.softpredict.com
commertial combustion simulation and mechanism analysis code

- visualization of reaction pathways
- reduction of kinetic mechanisms
- simulation of reactor networks
- two-dimensional reactors and flames
- spray and dust flames

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Alternatives to CHEMKIN 2

OpenSmoke (Milano; http://www.opensmoke.polimi.it/)
freely available program
numerical modelling of laminar reacting flows
built on the OpenFOAM framework
homogeneous reactions, heterogeneous reactions on catalytic surfaces

FlameMaster (Aachen; http://www.itv.rwthaachen.de/downloads/flamemaster/)
free for academic use
- homogeneous reactor and perfectly stirred reactor calculations
- freely propagating premixed flames
- steady counter-flow diffusion flames

Chem1D (Eindhoven; https://www.tue.nl/)
flame simulations with both detailed and few-step mechanisms

laminar flames:
adiabatic, burner stabilized, ceramic burner stabilized and counterflow flames
special effects in laminar flames:
simulation of stretch, curvature, gas radiation

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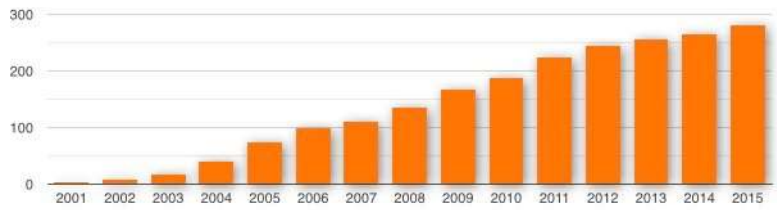
SBML

SBML: Systems Biology Markup Language http://sbml.org/

SBML model definition format was created
to promote the exchange of systems biology models
(similar to the role of CHEMKIN format in gas kinetics)

281 SBML-compatible software packages are available (January 2016)
The list of these simulation codes can be looked at http://sbml.org/



Increase of the number of SBML-based computer codes
(these include both academic and commertial codes)

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Copasi

COPASI (COmplex PAthway SImulator)
http://copasi.org/

Simulation and ***analysis*** of biochemical network ***models***.
Free, support, but source code is not provided.

Homogeneous kinetic systems in interacting compartments
Import and export of models in the SBML format (levels 1 to 3).
Export of models in many format (XPP, C code, Latex).

- ODE-based and stochastic simulatons
- stoichiometric analysis of the reaction networks
- optimization of models; parameter estimation
- local sensitivity analysis.
- time scale separation analysis
- characterization of non-linear dynamics properties (oscillations and chaos)

S. Hoops, S. Sahle, R. Gauges, C. Lee, J. Pahle, N. Simus, M. Singhal, L. Xu, P. Mendes, U. Kummer: COPASI — a COmplex PAthway SImulator. *Bioinformatics* **22**, 3067-3074 (2006)

Global uncertainty analysis codes

GUI-HDMR http://www.gui-hdmr.de
The GUI-HDMR software is based on the RS-HDMR approach, where all component functions are approximated by orthonormal polynomials using random (or quasi-random) samples. Calculation of up to second-order global sensitivity indices based on user supplied sets of input/output data. The component functions are approximated by up to 10th order orthonormal polynomials.

T. Ziehn, A. S. Tomlin: GUI-HDMR - A software tool for global sensitivity analysis of complex models *Environmental Modelling & Software*, **24**, 775-785 (2009)

SimLab https://ec.europa.eu/jrc/en/samo/simlab
Developed at the EC Joint Research Centre (EC-JRC) in Ispra, Italy.
Versions up to 2.2: GUI based nice education tool
(1) generation of random or quasi-random parameter sets
(2) running the models (within SimLab or externally)
(3) processing of the simulation results (FAST, Morris' and Sobol methods)
visualisation of the outcome of uncertainty/sensitivity analyses.

SimLab versions from 3.0:
subroutine can be called from Fortran, Python, C++, or Matlab

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Thank you for your attention!

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