

COST CM1404 Training School on the analysis, uncertainty quantification, validation, optimization and reduction of detailed combustion mechanisms for practical use of smart energy carriers

# Lecture 1-1

## Reaction kinetics basics



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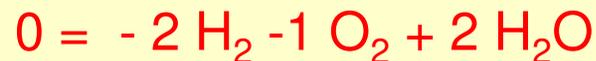
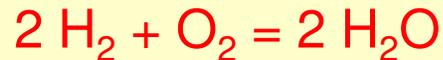
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# Reaction kinetics basics

## Characterization of chemical changes with a stoichiometric (overall) equation:

- properly indicates the ratio of reactants and products
- usually there is no such a real chemical process



$$0 = \sum_j \nu_j A_j$$

$$\nu_1 = -2$$

$$\nu_2 = -1$$

$$\nu_3 = +2$$

$$A_1 = \text{„H}_2\text{“}$$

$$A_2 = \text{„O}_2\text{“}$$

$$A_3 = \text{„H}_2\text{O“}$$

$\nu_j$  stoichiometric coefficient  
(negative for reactants, positive for products)

## Features:

- the order of the species is arbitrary
- the stoichiometric coefficients can be multiplied with the same real number



# Reaction rate

production rate of a species:

$$\frac{dY_j}{dt}$$

reaction rate:

$$r = \frac{1}{\nu_j} \frac{dY_j}{dt}$$

$Y_j$  is the molar concentration of species  $A_j$  e.g. [mole dm<sup>-3</sup>]

in a small domain of concentrations always applicable:  $r = k \prod_j Y_j^{\alpha_j}$ ,

$k$  rate coefficient

$\alpha_j$  reaction order with respect species  $j$

$\alpha = \sum_j \alpha_j$  overall reaction order

# Complex reaction mechanisms

Almost always there are many simultaneous reaction steps:

$$\sum_j \nu_{ij}^L A_j = \sum_j \nu_{ij}^R A_j$$

A reaction step

can be an elementary reaction (physically occurs this way) or

can be a non-elementary reaction lumped from elementary reactions

$\nu_{ij}^L$

matrix of left hand side stoichiometric coefficients

elementary: sum is not more than 2; zero or positive integer

non-elementary: zero or positive integer

$\nu_{ij}^R$

matrix of right hand side stoichiometric coefficients

elementary: sum is not more than 2; zero or positive integer

non-elementary: any real number (can be zero, negative, fraction)

$$\Delta \nu_{ij} = \nu_{ij}^R - \nu_{ij}^L$$

calculation of the (previous) stoichiometric matrix

# Kinetic system of differential equations

law of mass action (Guldberg and Waage, 1865):

$$r_i = k_i \prod_j Y_j^{\nu_{ij}^L}$$

$k_i$  rate coefficient of reaction step  $i$

$r_i$  rate of reaction step  $i$

Definition of the kinetic system of differential equations:

$$\frac{dY_j}{dt} = \sum_i \Delta \nu_{ij} r_i; \quad j = 1, 2, \dots, n$$

The kinetic system of differential equations in matrix-vector form:

$$\frac{d\mathbf{Y}}{dt} = \mathbf{v}\mathbf{r}$$

# Matrices to be mentioned frequently

Initial value problem in reaction kinetics:

$$\frac{d\mathbf{Y}}{dt} = \mathbf{f}(\mathbf{Y}, \mathbf{k}), \quad \mathbf{Y}(t_0) = \mathbf{Y}_0$$

Jacobian: 
$$\mathbf{J} = \left\{ \frac{\partial f_i}{\partial y_j} \right\}$$

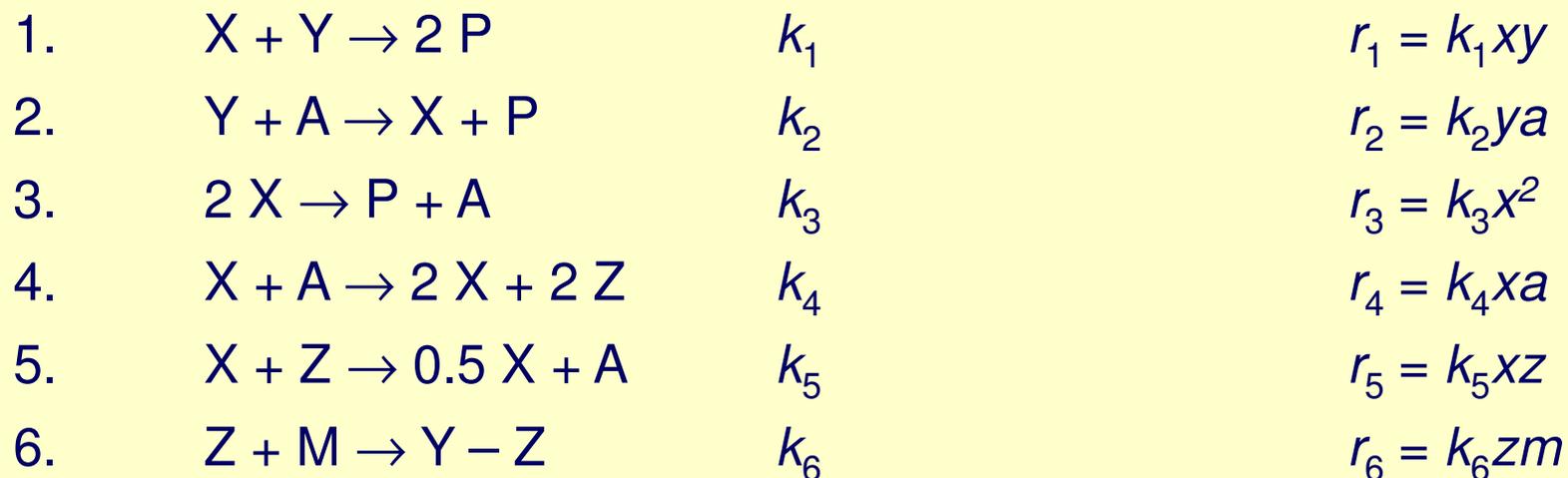
The Jacobian usually changes with changing concentrations

matrix  $\mathbf{F}$ : 
$$\mathbf{F} = \left\{ \frac{\partial f_i}{\partial k_j} \right\}$$

also depends on the concentrations

# Kinetic system of differential equations: an example

The Oregonator model of the Belousov-Zhabotinskii oscillating reaction:



The detailed 80-step reaction mechanism could be reduced to this 6 reaction step.

Note, that negative and fractional stoichiometric coefficients are present on the right hand side!

## Kinetic system of differential equations: an example 2

$X = \text{HBrO}_2$	variable of a diff. equation
$Y = \text{Br}^-$	variable of a diff. equation
$Z = \text{Ce}^{4+}$	variable of a diff. equation
$A = \text{BrO}_3^-$	constant concentration
$P = \text{HOBr}$	product only
$M = \text{malonic acid}$	constant concentration

1.  $X + Y \rightarrow 2 P$
2.  $Y + A \rightarrow X + P$
3.  $2 X \rightarrow P + A$
4.  $X + A \rightarrow 2 X + 2 Z$
5.  $X + Z \rightarrow 0.5 X + A$
6.  $Z + M \rightarrow Y - Z$

$$\frac{dx}{dt} = -1r_1 + 1r_2 - 2r_3 + 1r_4 - 0.5r_5 \quad \Rightarrow \quad \frac{dx}{dt} = -k_1xy + k_2ya - 2k_3x^2 + k_4xa - 0.5k_5xy$$

$$\frac{dy}{dt} = -1r_1 - 1r_2 + 1r_6 \quad \Rightarrow \quad \frac{dy}{dt} = -k_1xy - k_2ya + k_6zm$$

$$\frac{dz}{dt} = +2r_4 - 1r_5 - 2r_6 \quad \Rightarrow \quad \frac{dz}{dt} = 2k_4xa - k_5xz - 2k_6zm$$

$$\frac{dx}{dt} = -k_1xy + k_2ya - 2k_3x^2 + k_4xa - 0.5k_5xz$$

## calculation of the Jacobian

$$\frac{dy}{dt} = -k_1xy - k_2ya + k_6zm$$

$$\frac{dz}{dt} = 2k_4xa - k_5xz - 2k_6zm$$

$$\mathbf{J} = \left\{ \frac{\partial f_i}{\partial y_j} \right\}$$

$$\frac{\partial \frac{dx}{dt}}{\partial x} = -k_1y - 4k_3x + k_4a - 0.5k_5z$$

$$\frac{\partial \frac{dx}{dt}}{\partial y} = -k_1x + k_2a$$

$$\frac{\partial \frac{dx}{dt}}{\partial z} = -0.5k_5x$$

$$\frac{\partial \frac{dy}{dt}}{\partial x} = -k_1y$$

$$\frac{\partial \frac{dy}{dt}}{\partial y} = -k_1x - k_2a$$

$$\frac{\partial \frac{dy}{dt}}{\partial z} = +k_6m$$

$$\frac{\partial \frac{dz}{dt}}{\partial x} = 2k_4a - k_5z$$

$$\frac{\partial \frac{dz}{dt}}{\partial y} = 0$$

$$\frac{\partial \frac{dz}{dt}}{\partial z} = -k_5x - 2k_6m$$

$$\frac{dx}{dt} = -k_1xy + k_2ya - 2k_3x^2 + k_4xa - 0.5k_5xz$$

$$\frac{dy}{dt} = -k_1xy - k_2ya + k_6zm$$

$$\frac{dz}{dt} = 2k_4xa - k_5xz - 2k_6zm$$

## calculation of matrix F

$$\mathbf{F} = \left\{ \frac{\partial f_i}{\partial k_j} \right\}$$

$\frac{\partial \frac{dx}{dt}}{\partial k_1} = -xy$	$\frac{\partial \frac{dx}{dt}}{\partial k_2} = ya$	$\frac{\partial \frac{dx}{dt}}{\partial k_3} = -2x^2$	$\frac{\partial \frac{dx}{dt}}{\partial k_4} = xa$	$\frac{\partial \frac{dx}{dt}}{\partial k_5} = -0.5xz$	$\frac{\partial \frac{dx}{dt}}{\partial k_6} = 0$
$\frac{\partial \frac{dy}{dt}}{\partial k_1} = -xy$	$\frac{\partial \frac{dy}{dt}}{\partial k_2} = -ya$	$\frac{\partial \frac{dy}{dt}}{\partial k_3} = 0$	$\frac{\partial \frac{dy}{dt}}{\partial k_4} = 0$	$\frac{\partial \frac{dy}{dt}}{\partial k_5} = 0$	$\frac{\partial \frac{dy}{dt}}{\partial k_6} = zm$
$\frac{\partial \frac{dz}{dt}}{\partial k_1} = 0$	$\frac{\partial \frac{dz}{dt}}{\partial k_2} = 0$	$\frac{\partial \frac{dz}{dt}}{\partial k_3} = 0$	$\frac{\partial \frac{dz}{dt}}{\partial k_4} = 2xa$	$\frac{\partial \frac{dz}{dt}}{\partial k_5} = -xz$	$\frac{\partial \frac{dz}{dt}}{\partial k_6} = -2zm$

# Properties of kinetic differential equations

- The system of differential equations contains only first order derivatives ( $dc / dt$ ), which are usually nonlinear functions of the concentrations.  
⇒ **first order nonlinear system of differential equations**
- In general, several other concentrations influence the production rate of each species.  
⇒ **coupled differential equations**
- The reaction rates differ several orders of magnitude  
⇒ **stiff differential equations**
- Simulation results of laboratory experiments do not depend on the wall clock time, **BUT** the results of atmospheric chemical models depend on the actual pressure, temperature and solar radiation ⇒ depend on the physical time.  
⇒ **autonomous OR non-autonomous differential equations**
- Some laboratory reactions can be (approximately) spatially homogeneous, but outside the laboratories most chemical reactions are spatially inhomogeneous. In most cases the transport of species and heat have to be taken into account.  
⇒ **partial system of differential equations, with chemical source term**

# Conserved properties

## Isolated system:

The total enthalpy is constant

## Constant volume closed system:

the sum of the concentrations is constant,  
if each the change of the number of moles in each reaction step is zero.

## Closed system, elementary reactions only:

the number of moles of the elements is constant.

The moles of moieties (e.g. benzene ring) can remain constant

Example for conserved properties in a  $C_2H_4, CH_4, C_6H_6$  mixture:

C-atom  $\rightarrow 2 [C_2H_4] + 1 [CH_4] + 6 [C_6H_6] = \text{constant}$

H-atom  $\rightarrow 4 [C_2H_4] + 4 [CH_4] + 6 [C_6H_6] = \text{constant}$

Some linear combinations of the concentrations are constant.

## $N$ conserved property:

$\Rightarrow$  the rank of the stoichiometric matrix is lower by  $N$

$\Rightarrow$  the system can be simulated **exactly** with  $(n-N)$  variables

# Trajectory

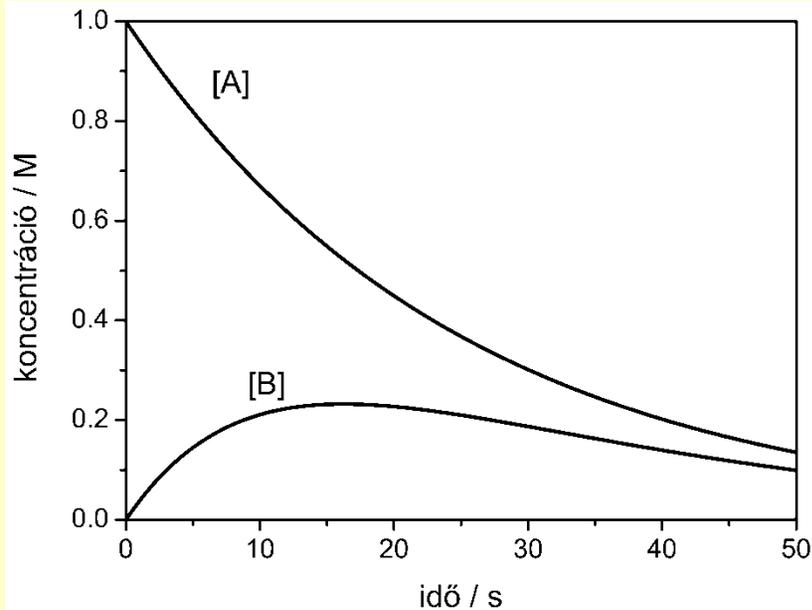
Actual state of the system: a point in the phase space

History of events: trace of this point in the phase space (a solid line)

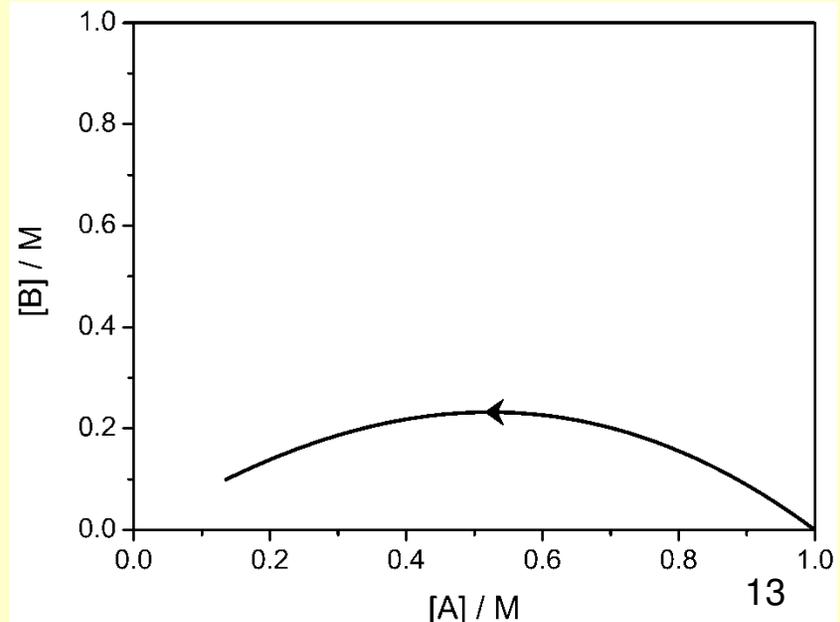
In chemical kinetics this phase space can be the space of concentrations. This figure does not show time, but can be more interesting than the usual concentration vs. time curves.

Example: reaction  $A \rightarrow B \rightarrow$

concentration vs. time



trajectory



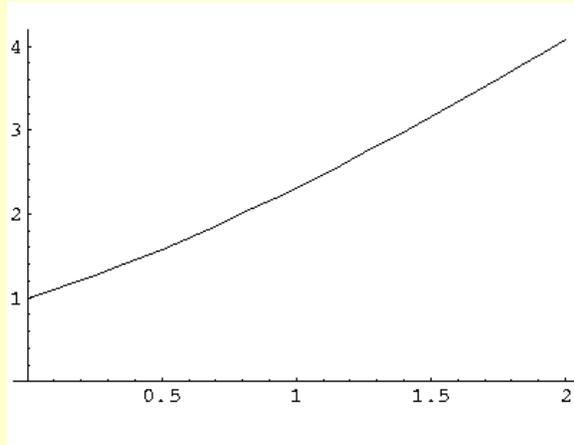
# Trajectories 2

closed systems:

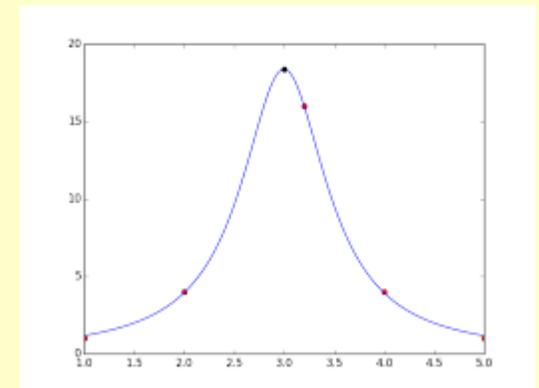
The concentrations are continuously changing from the initial state to an equilibrium point

Possible variations:

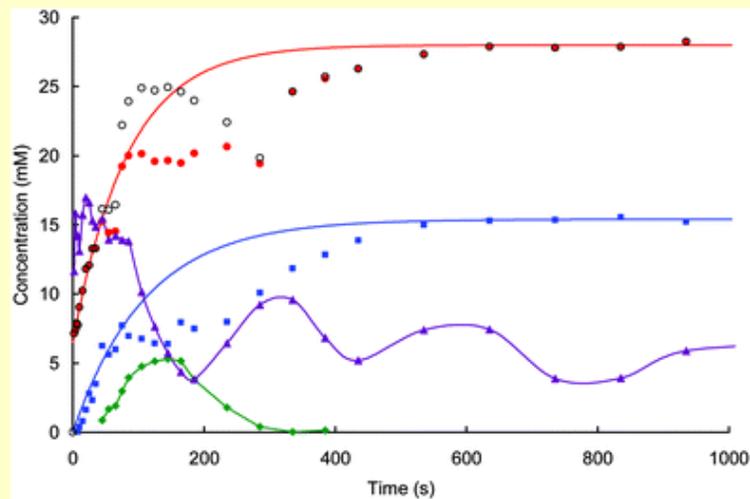
Monotonic



Maximum / minimum



Oligo oscillation

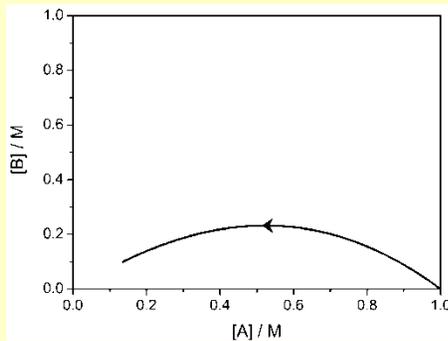


# Trajectories 3

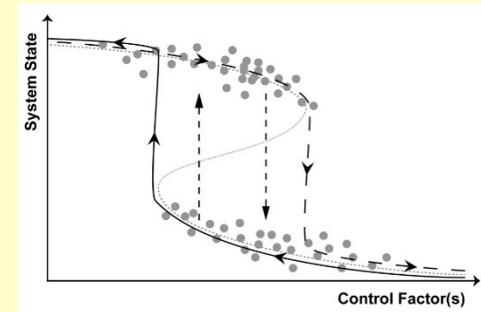
open systems:

The concentrations are continuously changing from the initial state to a ...

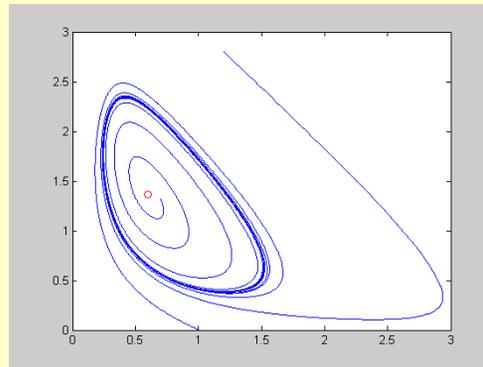
single stationary point



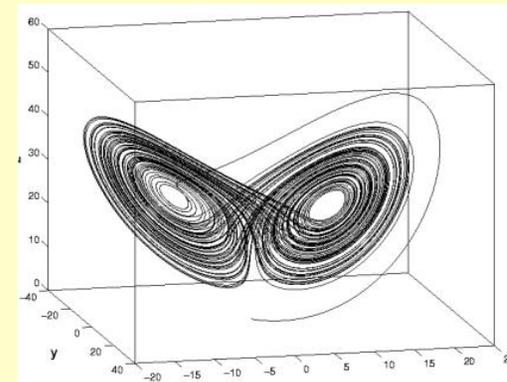
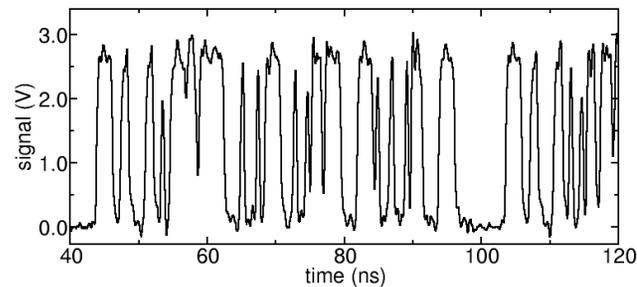
bistable behaviour



closed loop (limit cycle)



strange attractor



# Temperature dependence of rate coefficient $k$

Described by the Arrhenius equation:

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

$$\ln k = \ln A - \frac{E_a}{RT}$$

A      preexponential factor  
E<sub>a</sub>    activation energy

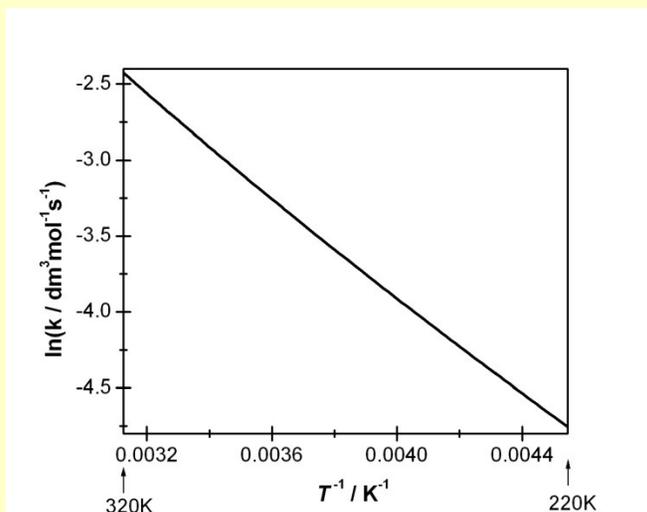
If the rate coefficient  $k$  is measured at several  $T$  temperatures and

**$\ln k$  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:

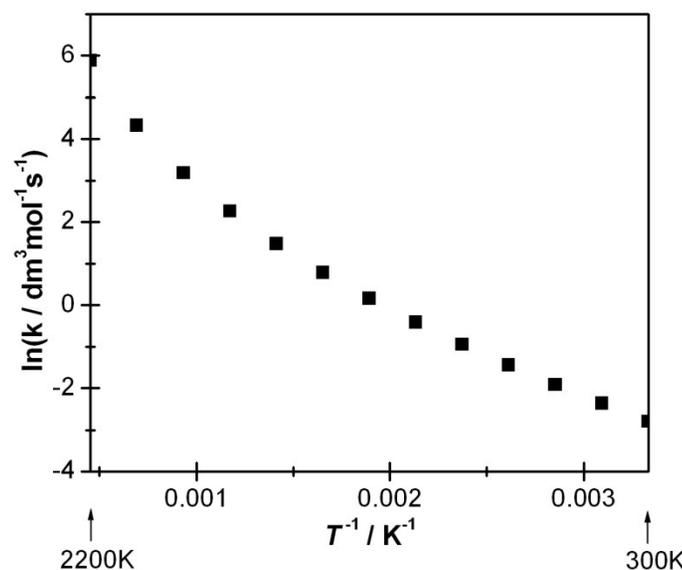
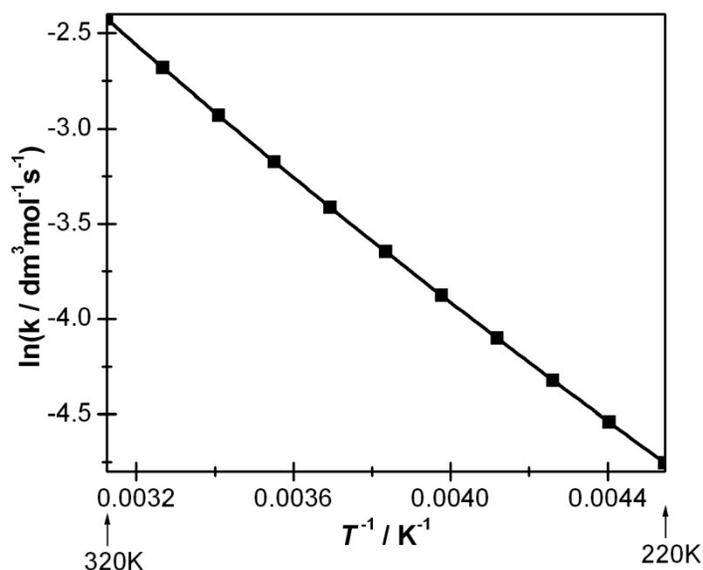


## Example: reaction $\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$

- 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)



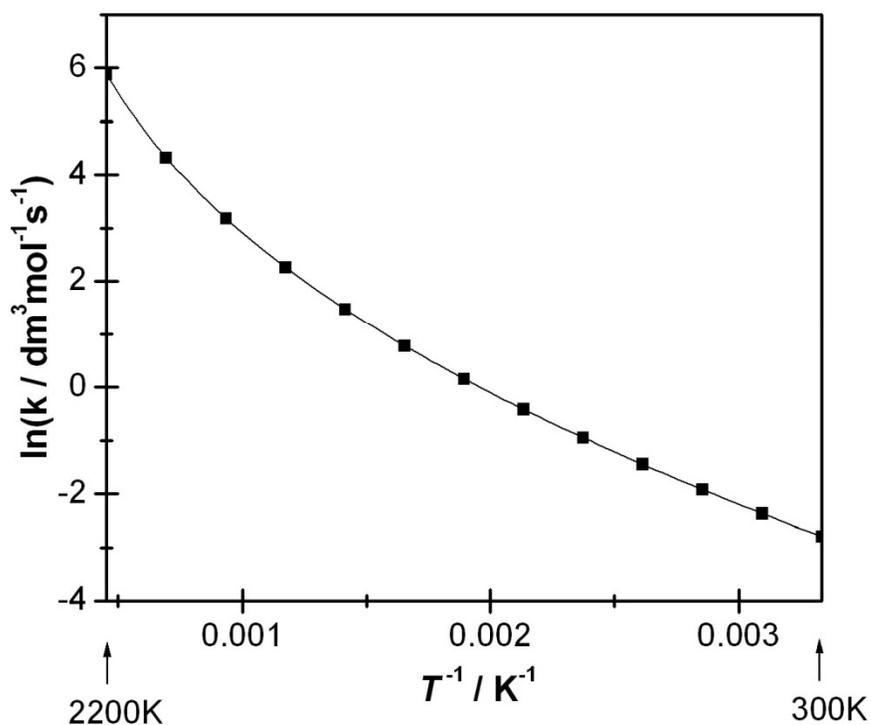
the Arrhenius equation is usually  
very accurate in a small  
(few times 10 K) temperature range.  
(solution phase and atmospheric chemistry)

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

# Temperature dependence of the rate coefficient 2

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

extended Arrhenius equation



Important!

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

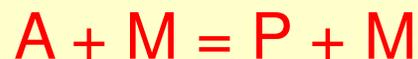
General definition of activation energy:

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

# Pressure dependence of the rate coefficients 1

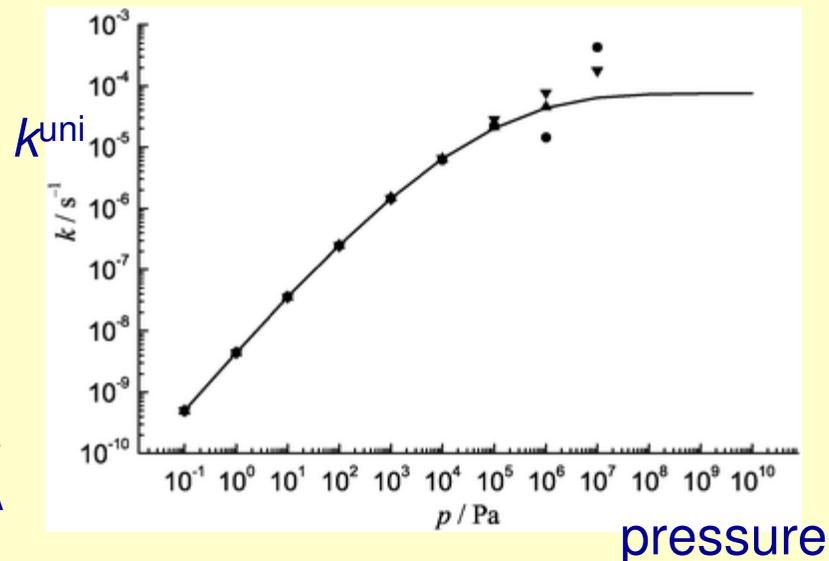
## unimolecular decomposition

decomposition or isomerization of a species



A reactant  
 P product  
 M colliding partner for energy transfer

low pressure                      2<sup>nd</sup> order decay of A  
 high pressure                    1<sup>st</sup> order decay of A



„pseudo first order” rate coefficient:

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

The temperature dependences of  $k_0$  and  $k_{\infty}$  are described independently by extended Arrhenius equations:

$$k_0 = A_0 T^{n_0} \exp\left(\frac{-E_0}{RT}\right) \qquad k_{\infty} = A_{\infty} T^{n_{\infty}} \exp\left(\frac{-E_{\infty}}{RT}\right) \qquad 19$$

## Lindemann – Hinshelwood model

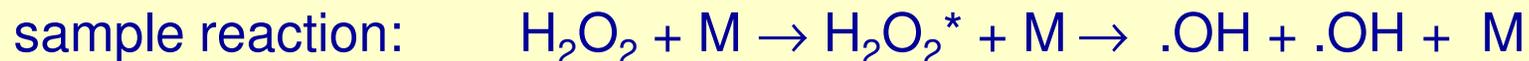


$$\begin{array}{ll}
 \text{high pressure: } [M] \rightarrow \infty & k_{\text{uni}} \approx \frac{k_3 k_1}{k_2} \qquad k_{\infty} = \frac{k_3 k_1}{k_2} \\
 \text{low pressure: } [M] \approx 0 & k_{\text{uni}} \approx k_1 [M] \qquad k_0 = k_1
 \end{array}$$

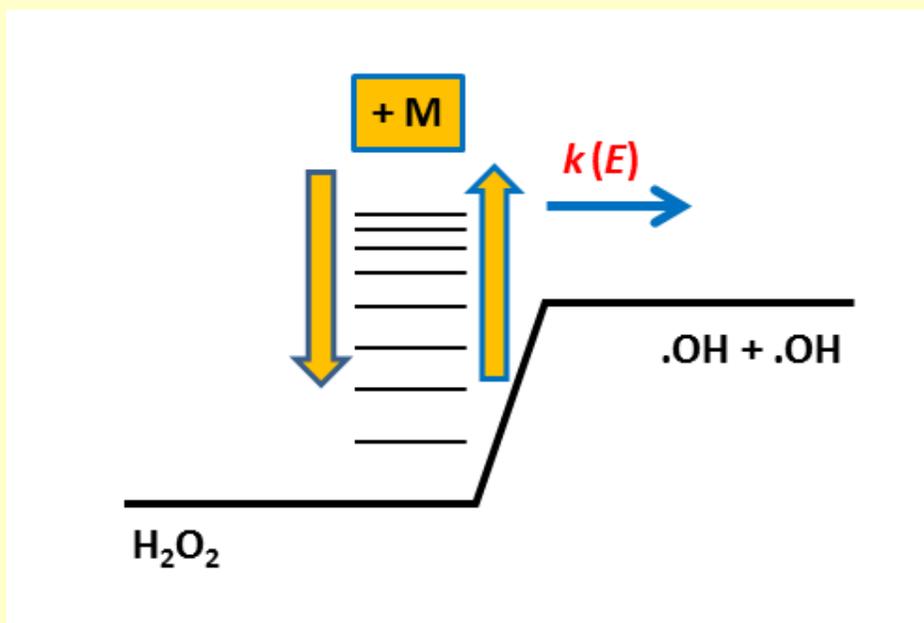
unimolecular decomposition rates:

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

# Refined Lindemann – Hinshelwood model of unimolecular reactions



- instead of assuming a single excited species,  $\text{H}_2\text{O}_2^*$  exists in a range of different rovibrationally excited states.
- the rate of the decomposition step increases with the increasing rovibrational energy of  $\text{H}_2\text{O}_2^*$



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  $\text{H}_2\text{O}_2^*$
- the overall decomposition rate is independent of pressure



2<sup>nd</sup> order at low pressure, 1<sup>st</sup> order at high pressure

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

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

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

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

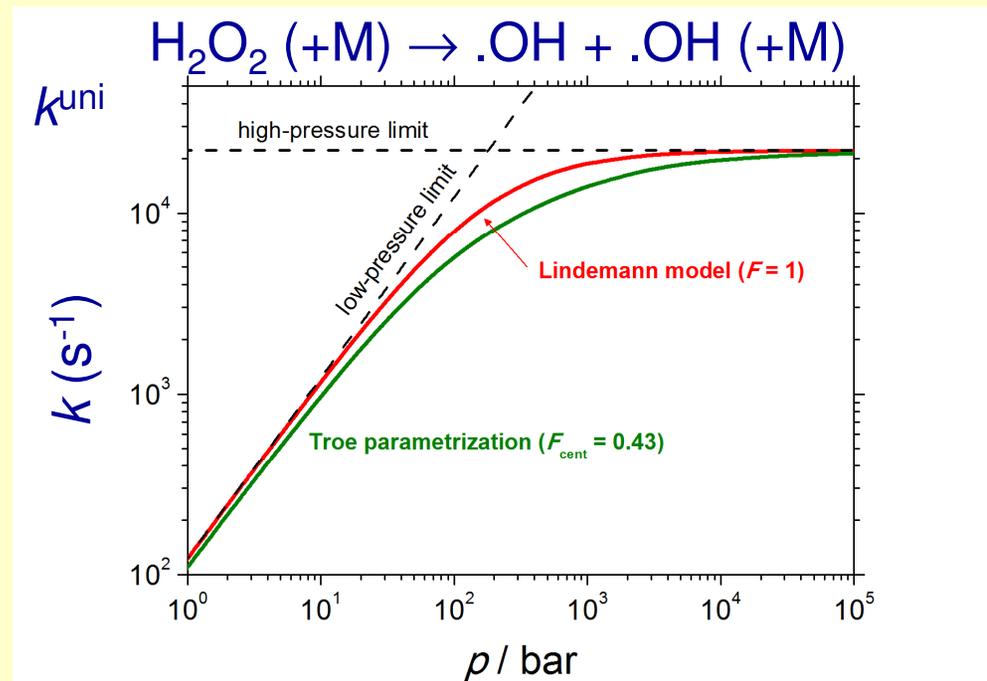
in the Lindemann model  $F = 1$

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

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

$$\begin{aligned} c &= -0.4 - 0.67 \log F_{\text{cent}} \\ n &= -0.75 - 1.271 \log F_{\text{cent}} \\ d &= 0.14 \end{aligned}$$

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

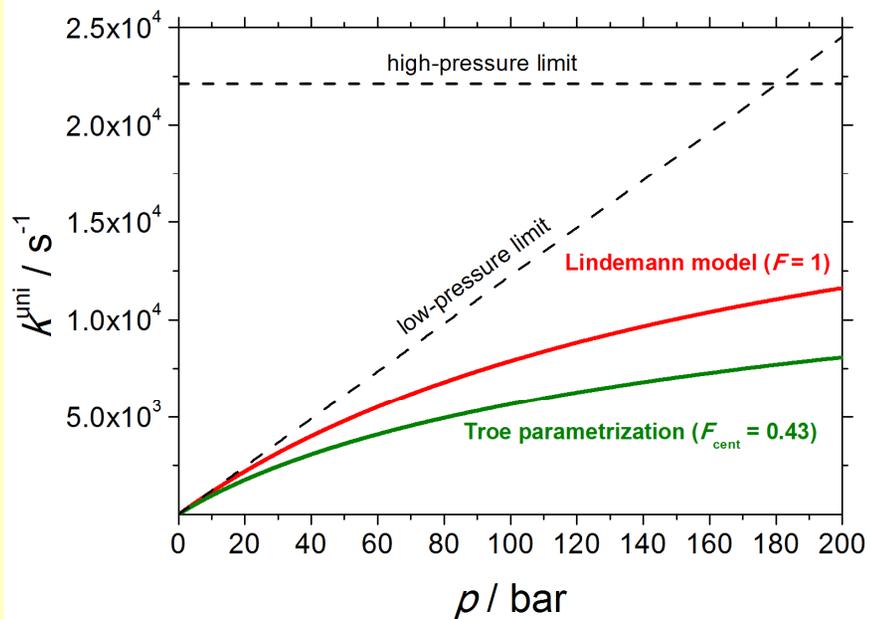
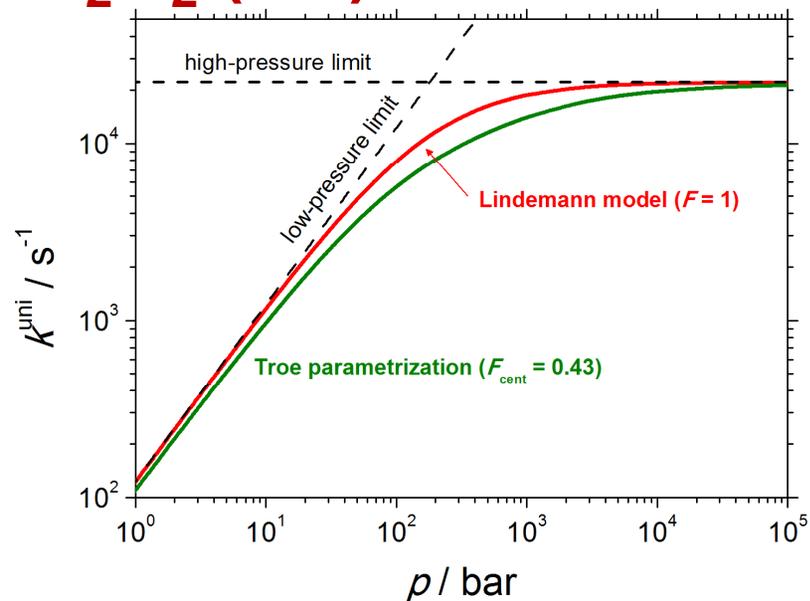


# Reaction $\text{H}_2\text{O}_2 (+\text{M}) \rightarrow \cdot\text{OH} + \cdot\text{OH} (+\text{M})$

$\lg k^{\text{uni}} - \lg p$  plot

$T = 1000 \text{ K}$

$k^{\text{uni}} - p$  plot



# 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

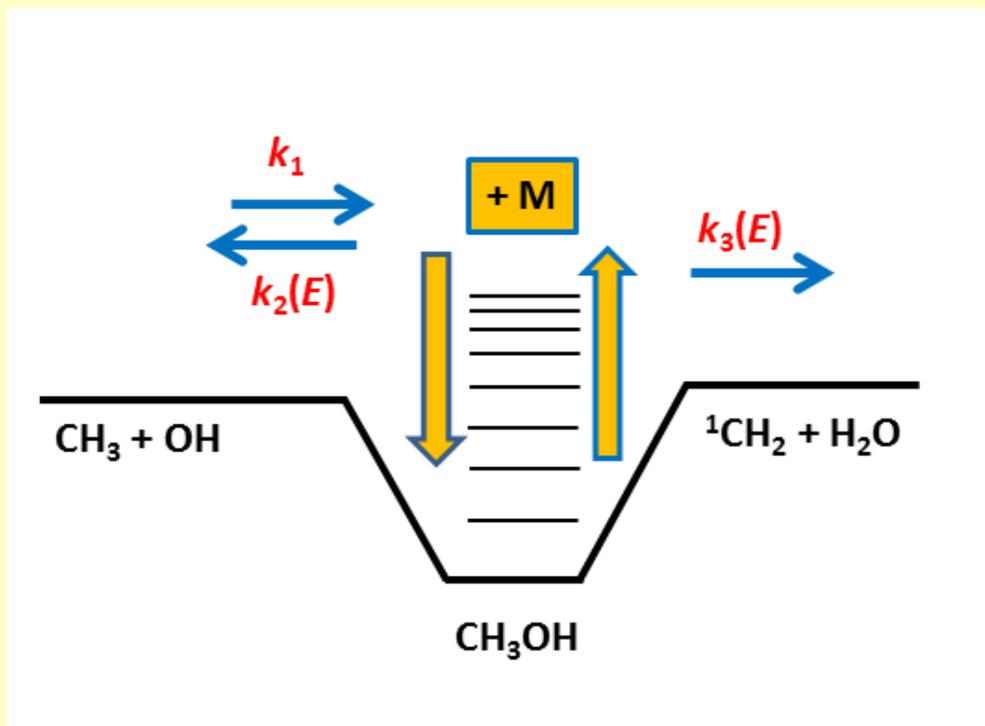
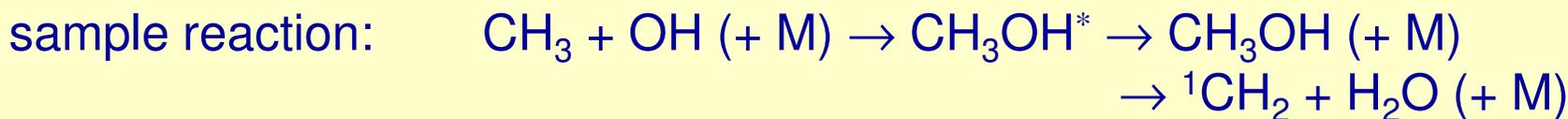
$$[M] = \sum_i m_{y_i} [Y_i]$$

calculation for reaction  $\text{H}_2\text{O}_2 (+M) \rightarrow \cdot\text{OH} + \cdot\text{OH} (+M)$ :

$$[M] = 5[\text{H}_2\text{O}] + 5.13[\text{H}_2\text{O}_2] + 0.8[\text{O}_2] + 2.47[\text{H}_2] + 1.87[\text{CO}] + 1.07[\text{CO}_2] + 0.67[\text{Ar}] + 0.43[\text{He}] + [\text{all others}]$$

# Pressure dependence of the rate coefficients 2

## complex-forming bimolecular reactions



**low pressure:**  
 mainly  $\text{CH}_3\text{OH}^*$  decomposition to  
 ${}^1\text{CH}_2 + \text{H}_2\text{O}$

( ${}^1\text{CH}_2$  = singlet  $\text{CH}_2$  =  
 electronically excited  $\text{CH}_2$ )

**high pressure:**  
 mainly  $\text{CH}_3\text{OH}^*$  stabilization,  
 giving  $\text{CH}_3\text{OH}$

$\text{CH}_3 + \text{OH} \rightarrow \text{CH}_3\text{OH}$       3<sup>rd</sup> order at low pressure, 2<sup>nd</sup> order at high pressure

$\text{CH}_3 + \text{OH} \rightarrow {}^1\text{CH}_2 + \text{H}_2\text{O}$       3<sup>rd</sup> order at low pressure, 2<sup>nd</sup> order at high pressure

# Formation of the stabilization product

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

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

$P_r$  reduced pressure

$F$  controls the shape of the  $k(p)$  curve

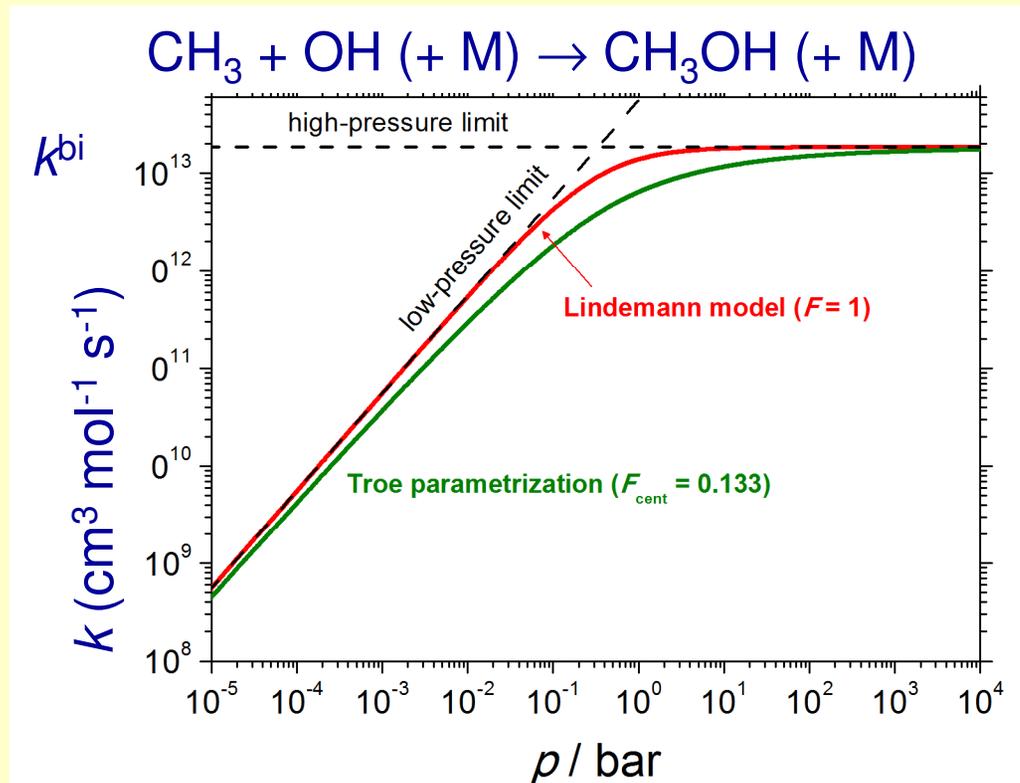
in the Lindemann model  $F = 1$

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

$k^{\text{bi}}$  „pseudo second order” rate coefficient

at low pressure:  $k^{\text{bi}} = k_0 [\text{M}]$

at high pressure:  $k^{\text{bi}} = k_{\infty}$



# 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

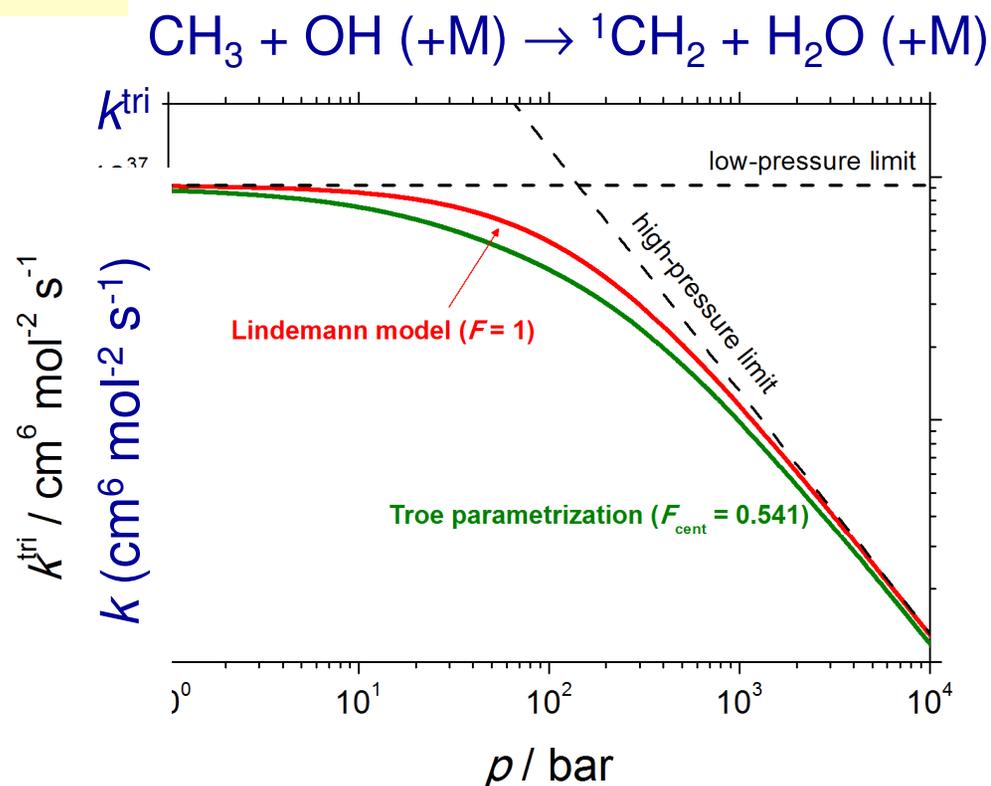
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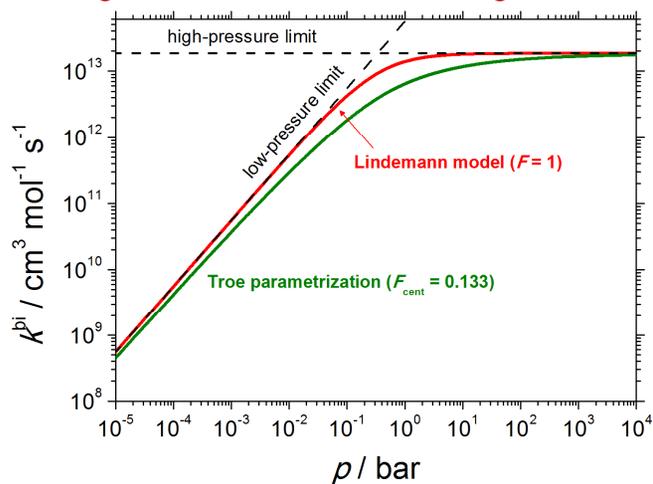
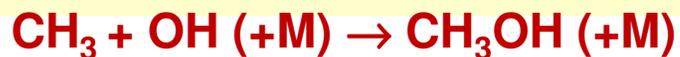
$k^{\text{tri}}$  „pseudo third order” rate coefficient

at low pressure:  $k^{\text{tri}} = k_0$

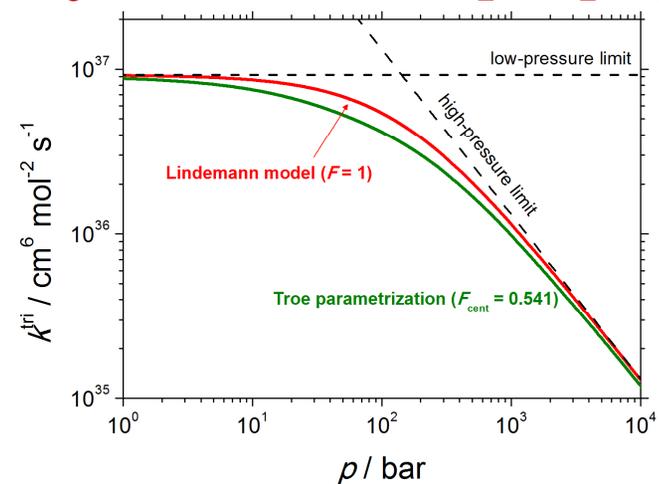
at high pressure:  $k^{\text{tri}} = k_\infty / [\text{M}]$



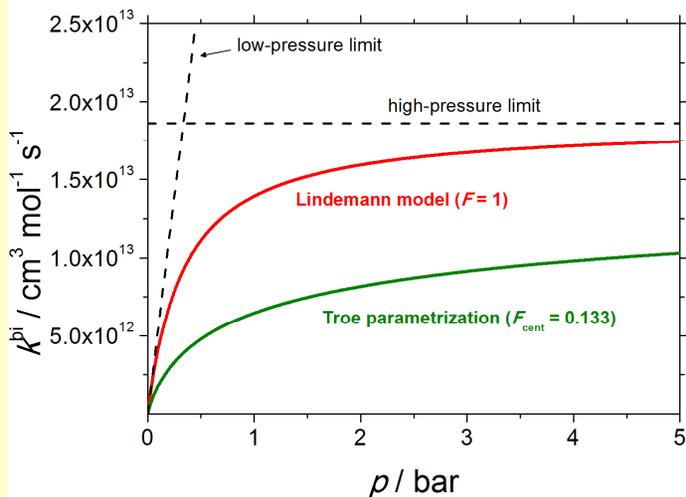
# Reaction $\text{CH}_3 + \text{OH} \rightarrow \text{products}$



$\lg k^{\text{bi}} - \lg p$  plot

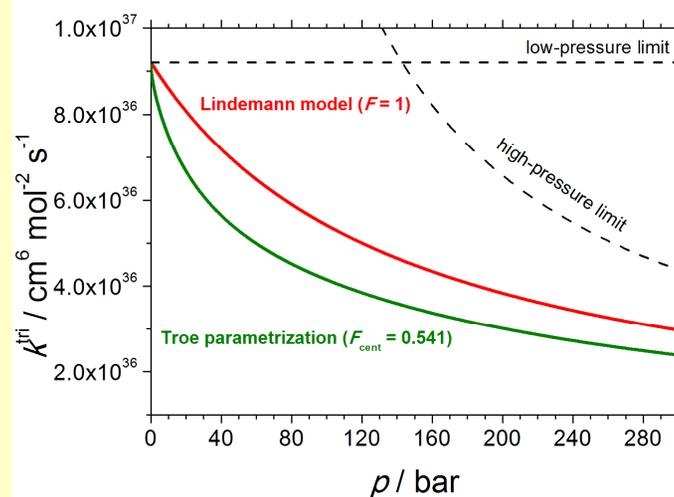


$\lg k^{\text{tri}} - \lg p$  plot



$k^{\text{bi}} - p$  plot

**$T = 1000 \text{ K}$**



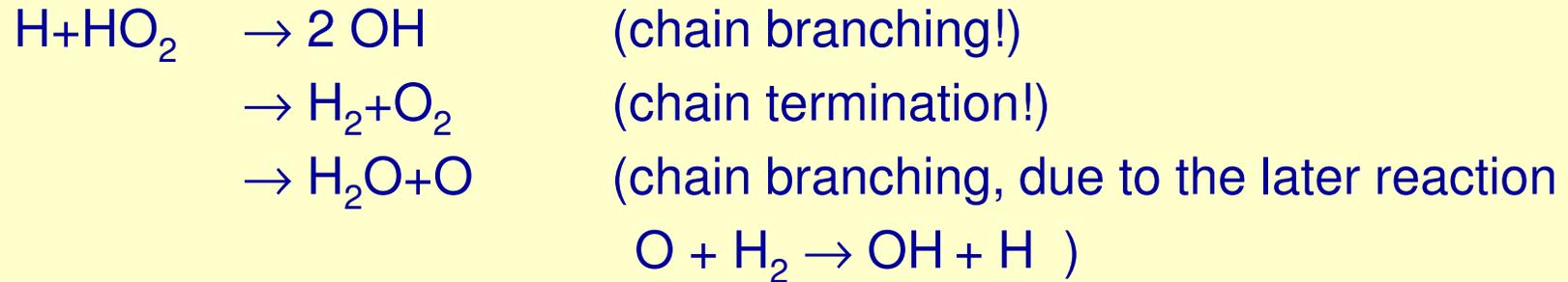
$k^{\text{tri}} - p$  plot

# 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.*  $2 \text{CH}_3 + \text{M} \leftrightarrow \text{C}_2\text{H}_6 + \text{M}$ )  
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:



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

# Reaction kinetics simplifying principles

Reaction kinetics simplifying principles: can be used for the simplification of a reaction mechanism (kinetic system of differential equations) in such a way that the obtained reaction mechanism (or system of differential equations) provides an almost identical (say within 1%) solution.

## Reaction kinetic simplifying principles:

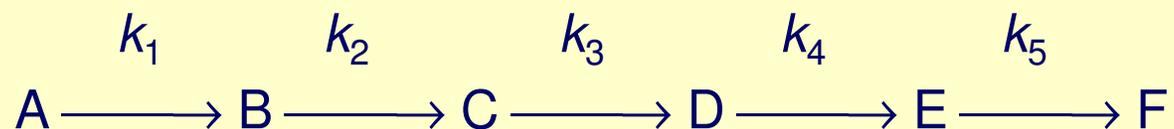
- rate determining step
- quasi steady state approximation (QSSA)
- fast pre-equilibrium approximation
- pool component approximation

# Rate determining step

## The case of consecutive first order reactions

Reaction step having the smallest rate coefficient is the rate determining.

The rate of production of the end product is equal to the rate coefficient of the rate determining step times the concentration of its reactant.



$$k_2 \ll k_1, k_3, k_4, k_5 \Rightarrow \quad d[F]/d t = k_2 [B]$$

**In the case of any reaction mechanism:** small increase of the rate coefficient of the rate determining step results in a large increase of the rate of production of the end product.

**In general, the reaction step having the smallest rate coefficient is not the rate determining step!**

# Quasi steady-state approximation (QSSA)

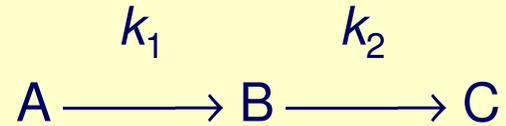
Highly reactive and low-concentration species in a mechanism are selected. These species (usually very reactive radicals) are called the QSSA species. The left-hand-sides of the kinetic differential equations are zeroed, converting these differential equations to algebraic equations. The obtained set of algebraic equations describe the dependence of the concentrations of the QSSA species on the concentrations of the non-QSSA species. Solving together the sets of differential and algebraic equations provides a solution that is in good accordance with the solution of the original kinetic system of differential equations.

In most cases the system of algebraic equations can be solved analytically, the concentrations of the QSSA species can be given explicitly and this solution can be inserted to the remaining system of differential equations for the non-QSSA species.

⇒ smaller system of differential equations

The QSSA species are usually highly reactive and therefore low concentration species (*e.g.* radicals).

# Application of the QSSA



if  $k_1 \ll k_2$       B "QSSA species"      A and C "non-QSSA species"

$$d[B]/dt = k_1 [A] - k_2 [B]$$

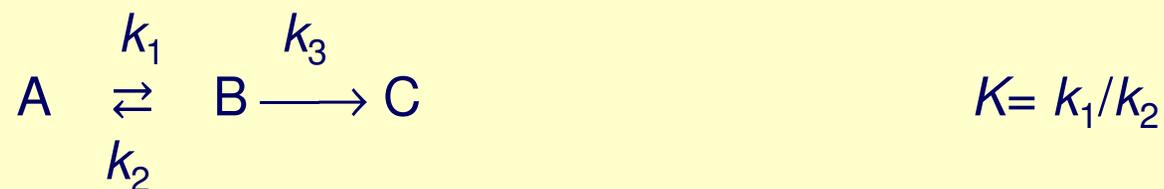
$$0 = k_1 [A] - k_2 [B]$$

$$[B] = k_1/k_2 [A]$$

[B] can be calculated from [A]

## Pre-equilibrium approximation

If the reactants of a fast equilibrium reaction is consumed by much slower reactions, then  
the concentrations of the species participating in the fast equilibrium can be calculated from the equilibrium equations only and the effects of other reactions should not be taken into account.



if  $k_3 \ll k_2$  and  $d[B]/dt \approx 0$  (state of equilibrium)

$$\Rightarrow k_1 [A] = k_2 [B]$$

$$\Rightarrow [B] = k_1/k_2 [A] = K [A]$$

$$\Rightarrow d[C]/dt = k_3 [B] = k_3 K [A]$$

# Pool component approximation

If the concentration of one of the reactants is much higher than those of the others, then this concentration will not change significantly during the reaction.

This way a second order reaction can be converted to an equivalent first order reaction by merging the rate coefficient and the concentration of the pool component.

$$\frac{d[C]}{dt} = k[A][B] = k'[A]$$

where  $k' = k[B]$  is constant.  $\Rightarrow$  „pseudo first order reaction”

Example: „inversion of sucrose”

Hydrolysis of sucrose in an acidic solution. The products formed are optically active and their optical rotation can be determined by using a polarimeter. The decomposition of sucrose can be described by a first order decay reaction.

# 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



# Reaction fluxes

S.R. Turns:  
*An introduction to combustion.*  
*Concepts and applications.*  
 second edition,  
 Boston, McGraw-Hill, 2000.

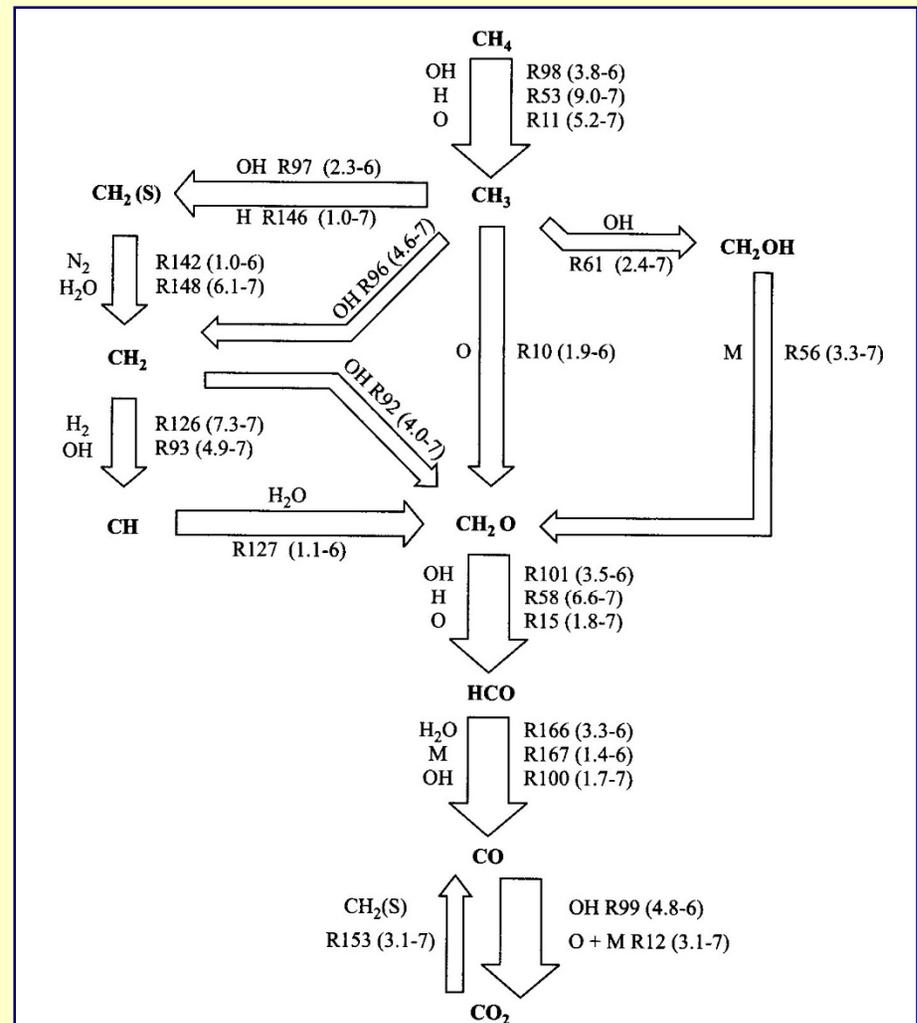
„each arrow indicates a reaction step”

„the width of the arrows is proportional to the consumption rate of the reactant”

Not a good idea, since consecutive arrows having different width may belong to identical fluxes.

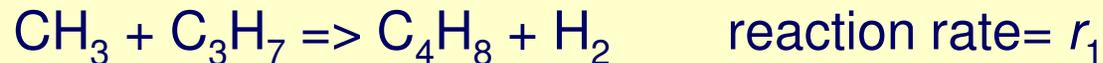
⇒ **Flux of a conserved property has to be plotted!!!**

⇒ Fluxes of elements (Revel *et al.*, 1994)



**Figure 5.4** High-temperature reaction pathway diagram for combustion of methane in a well-stirred reactor at  $T = 2200\text{ K}$  and  $P = 1\text{ atm}$  for a  $0.1\text{-s}$  residence time. Reaction numbers refer to Table 5.3, while reaction rates are shown in parentheses. For example, 2.6-7 implies  $2.6 \cdot 10^{-7}\text{ (gmol/cm}^3\text{-s)}$ .

# Fluxes of elements

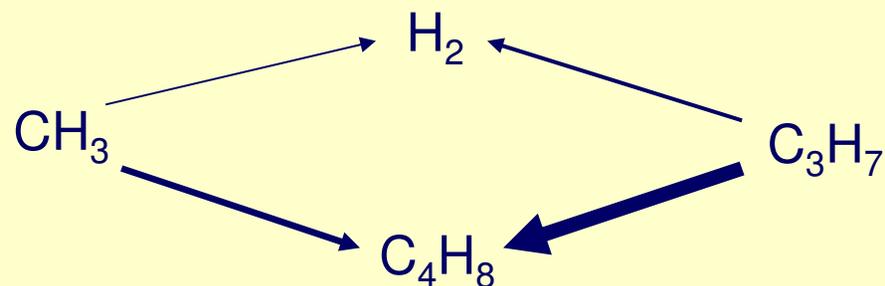


number of H-atoms:            3            7            8    2

number of H-atoms on the left hand side:    10

flux of H-atoms from one species to another:

$\text{CH}_3$	$\rightarrow$	$\text{C}_3\text{H}_7$	0	
$\text{CH}_3$	$\rightarrow$	$\text{C}_4\text{H}_8$	$3/10 \cdot 8 \cdot r_1 =$	$2.4 \cdot r_1$
$\text{CH}_3$	$\rightarrow$	$\text{H}_2$	$3/10 \cdot 2 \cdot r_1 =$	$0.6 \cdot r_1$
$\text{C}_3\text{H}_7$	$\rightarrow$	$\text{CH}_3$	0	
$\text{C}_3\text{H}_7$	$\rightarrow$	$\text{C}_4\text{H}_8$	$7/10 \cdot 8 \cdot r_1 =$	$5.6 \cdot r_1$
$\text{C}_3\text{H}_7$	$\rightarrow$	$\text{H}_2$	$7/10 \cdot 2 \cdot r_1 =$	$1.4 \cdot r_1$



$$A_{ijk} = \frac{n_{A,j} n_{A,k} r_i}{N_{A,i}}$$

J. Revel, J. C. Boettner, M. Cathonnet, J. S. Bachman: Derivation of a global chemical kinetic mechanism for methane ignition and combustion. *J. Chim. Phys.* **91**, 365-382 (1994)

# Calculation of element fluxes using KINALC

- c **ATOMFLOW** Fluxes of elements from species to species are investigated
- c The name(s) of elements are listed after the keyword.
- c Usage: **ATOMFLOW** <element1> <element2> ...

## ATOMFLOW C H

=== ATOMFLOW =====

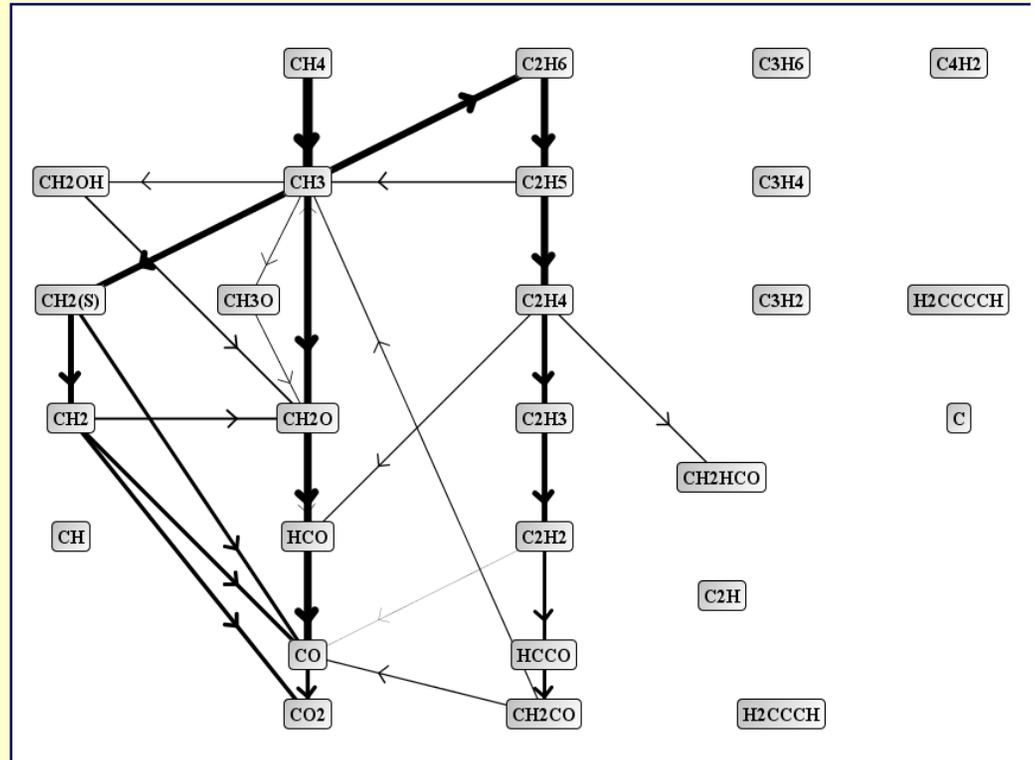
Fluxes of elements from species to species

Net fluxes of element H			absolute	rel.
1	H2	=> H2O	6.843E-02 mole/(cm3 sec)	1.0000
2	H2	=> H	4.584E-02 mole/(cm3 sec)	.6699
3	OH	=> H2O	4.034E-02 mole/(cm3 sec)	.5895
4	H	=> OH	3.360E-02 mole/(cm3 sec)	.4910
5	H	=> HO2	2.370E-02 mole/(cm3 sec)	.3463
6	OH	=> H	2.302E-02 mole/(cm3 sec)	.3364
7	HO2	=> OH	1.797E-02 mole/(cm3 sec)	.2626
8	H2	=> OH	1.162E-02 mole/(cm3 sec)	.1699
9	H	=> H2	6.346E-03 mole/(cm3 sec)	.0927
10	H	=> H2O	4.084E-03 mole/(cm3 sec)	.0597
11	HO2	=> H2	3.334E-03 mole/(cm3 sec)	.0487
12	HO2	=> H2O	2.689E-03 mole/(cm3 sec)	.0393
13	OH	=> H2	1.049E-03 mole/(cm3 sec)	.0153
14	H2O	=> OH	7.891E-04 mole/(cm3 sec)	.0115
15	OH	=> H2O2	7.617E-04 mole/(cm3 sec)	.0111
16	H2O	=> H2	7.010E-04 mole/(cm3 sec)	.0102
17	H2O2	=> H2O	5.367E-04 mole/(cm3 sec)	.0078
18	H2O2	=> OH	2.131E-04 mole/(cm3 sec)	.0031

# KINALC → FluxViewer

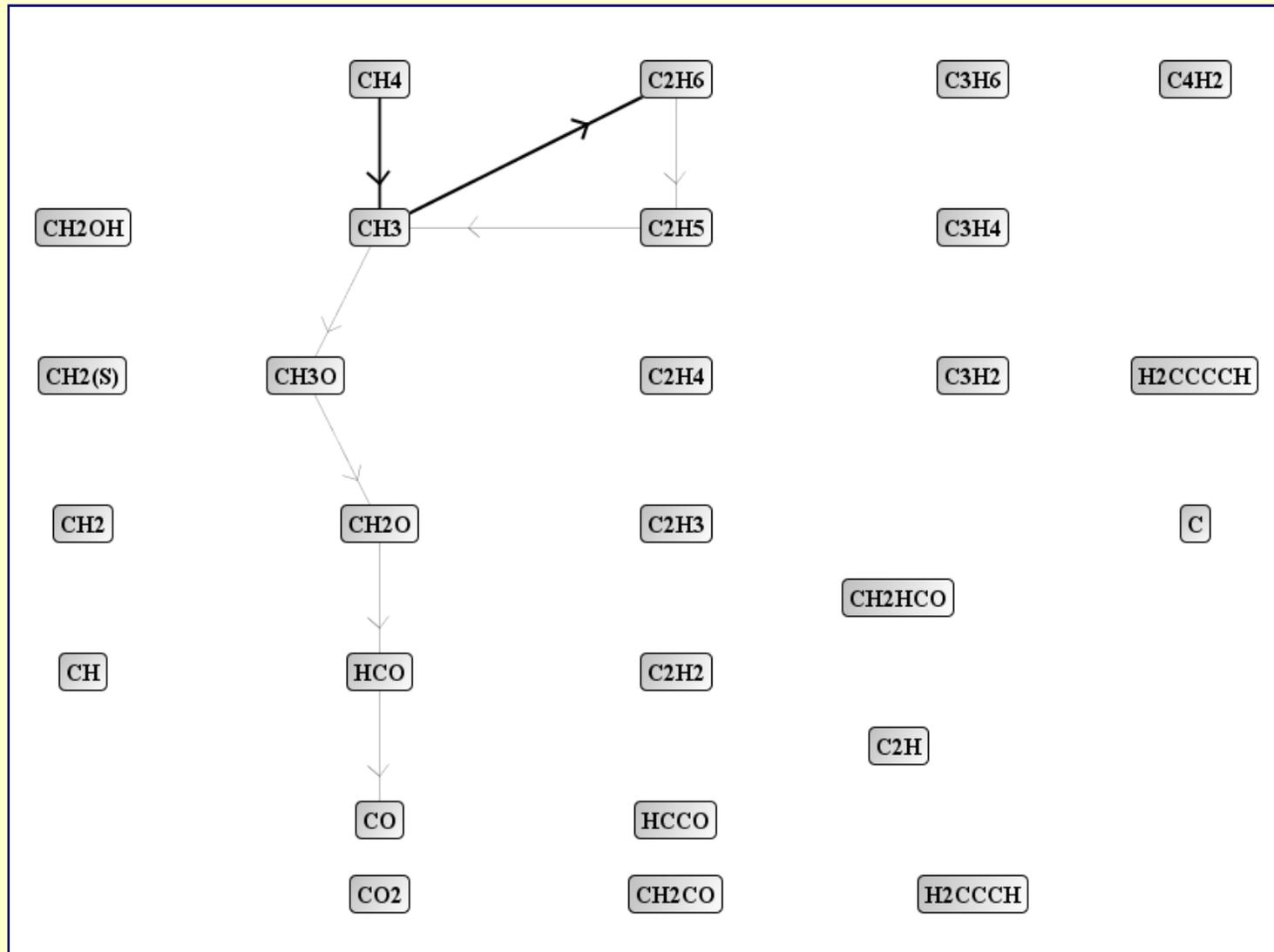
FluxViewer: JAVA code for the visualization of the element fluxes

- the labels of the species can be moved („drag-and-drop”)
- the width of the arrows is proportional to the log of the element fluxes
- the width of the arrows can be hanged
- creation of drawings or movie films



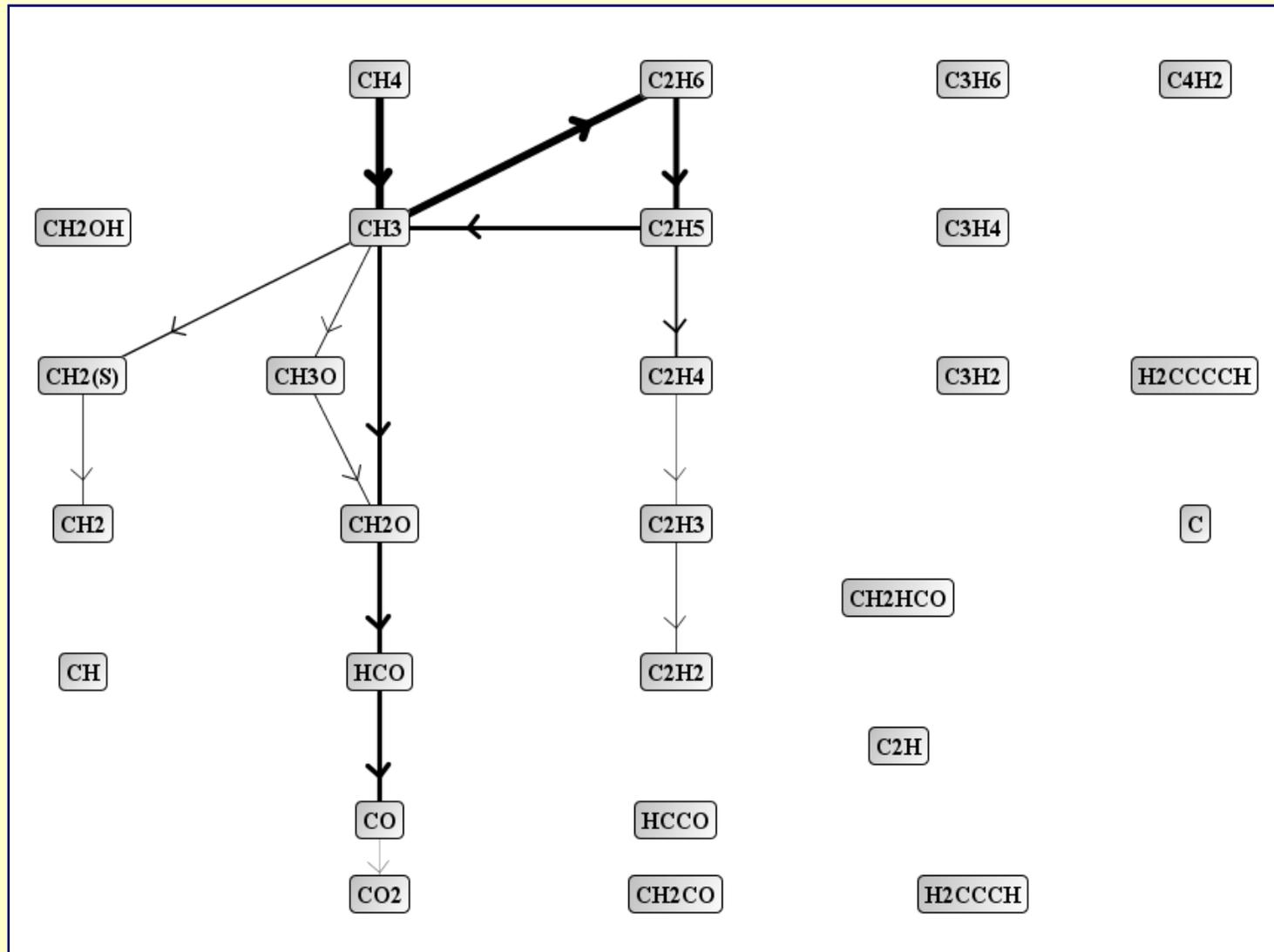
I. Gy. Zsély, I. Virág, T. Turányi:  
Investigation of a methane oxidation mechanism via the visualization of element fluxes  
Paper IX.4 in: Proceedings of the 4th Mediterranean Combustion Symposium,  
Lisbon, Portugal, 5-10 October, 2005, Eds: F. Beretta, N. Selçuk, M.S. Mansour

# C-atom fluxes, $\phi = 1.0$ , methane–air flame



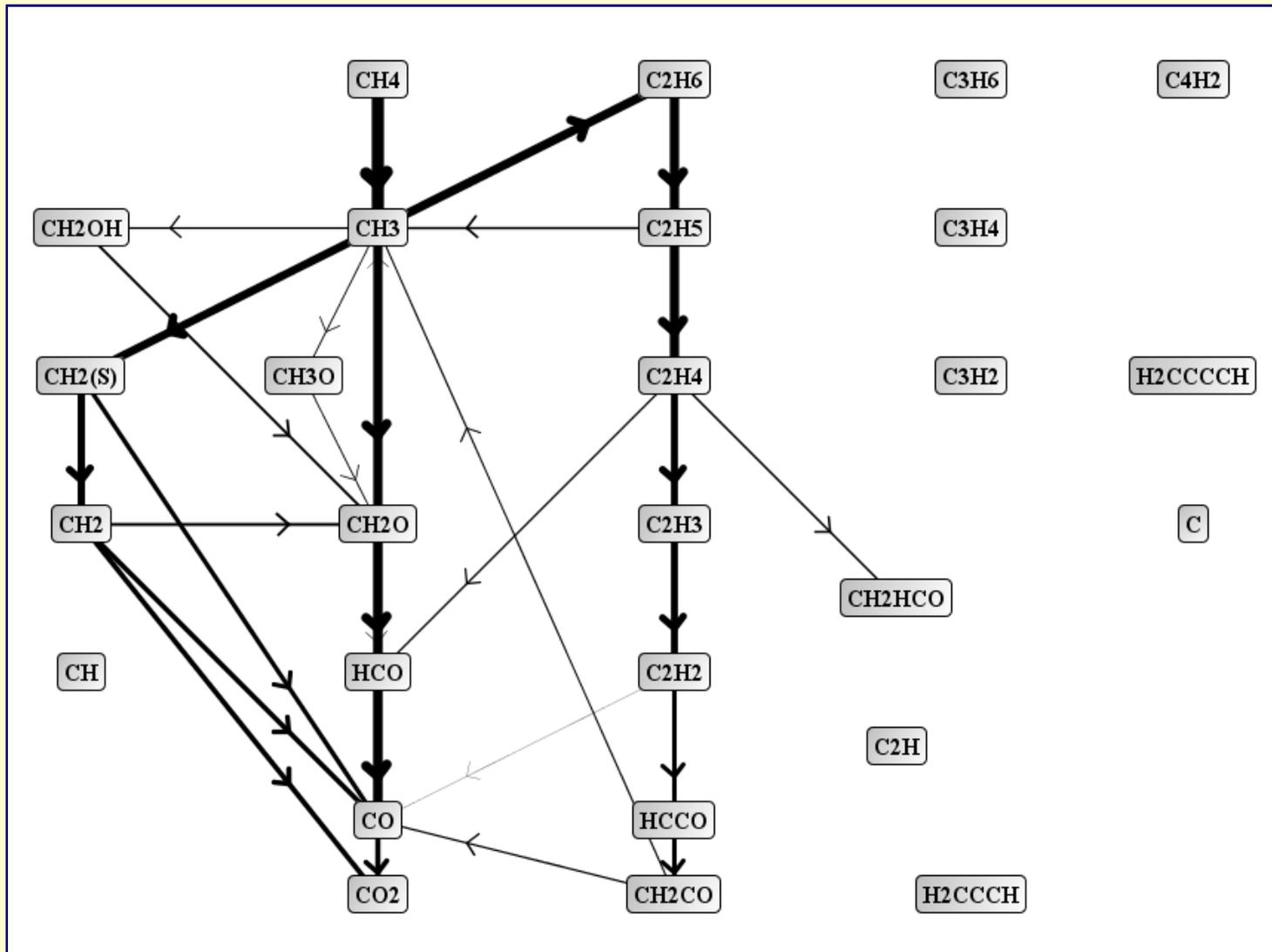
$T = 815 \text{ K}$

# C-atom fluxes, $\phi = 1.0$ , methane–air flame



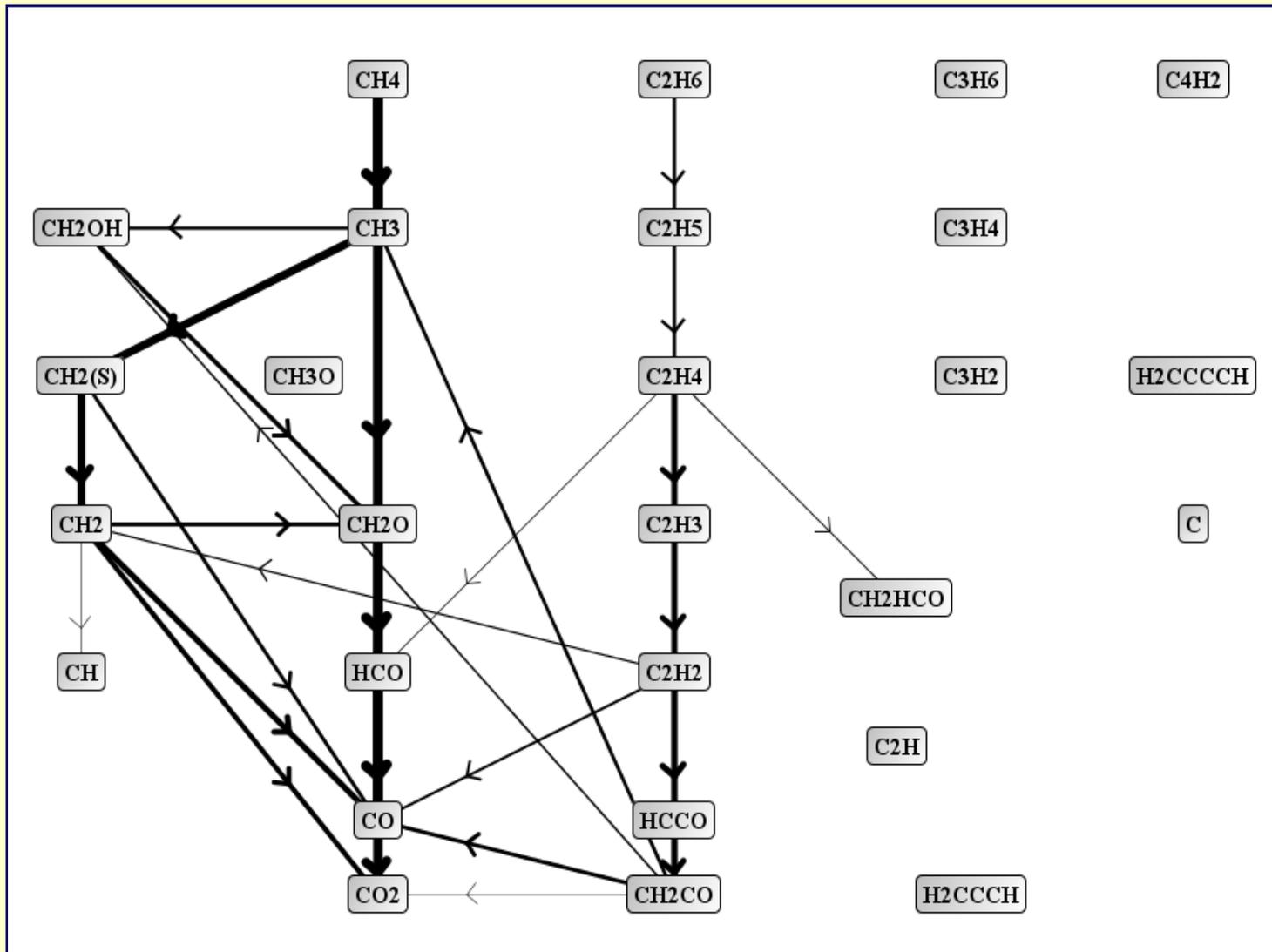
$T=1155 \text{ K}$

# C-atom fluxes, $\phi = 1.0$ , methane-air flame



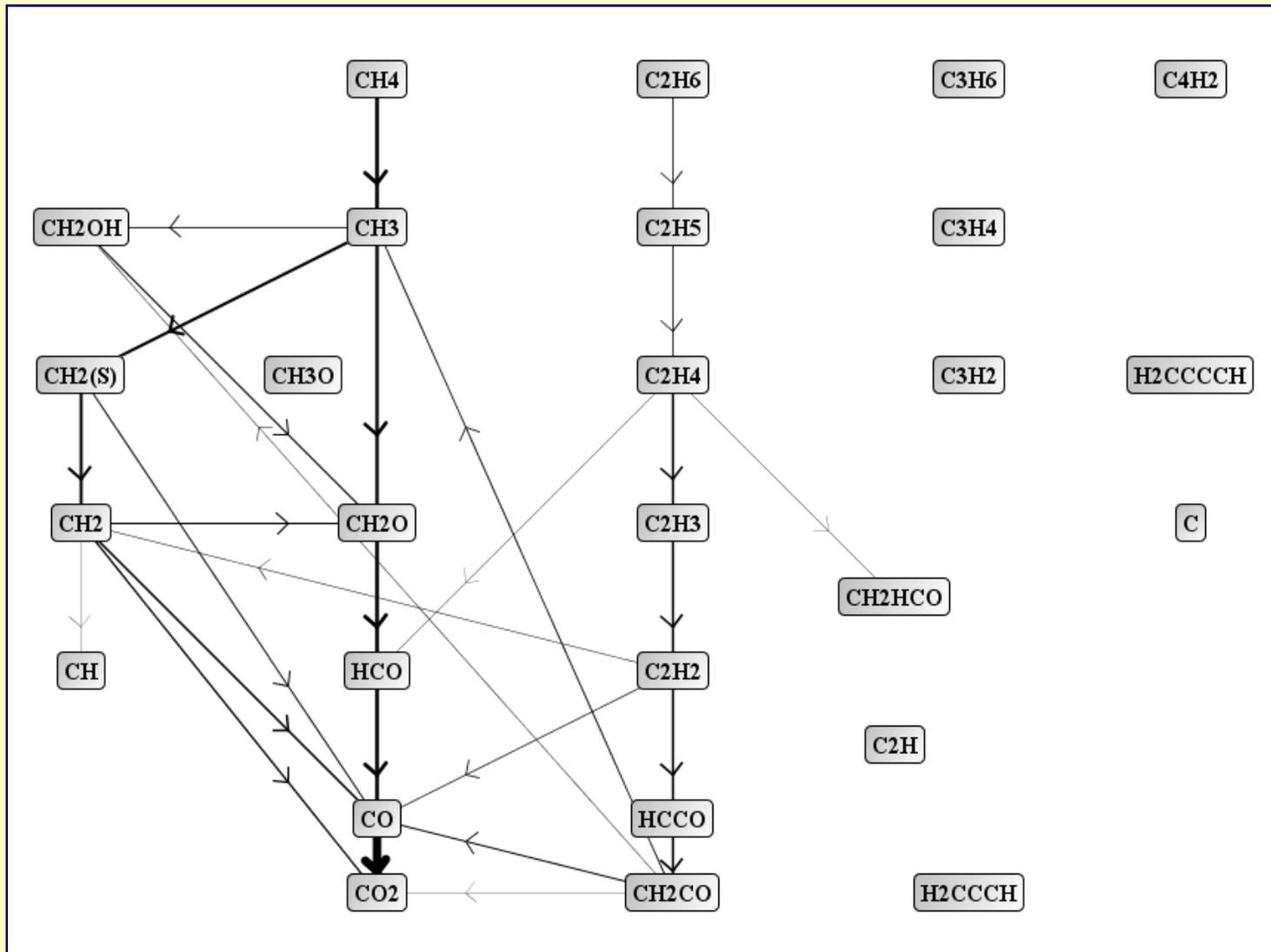
$T=1500$  K

# C-atom fluxes, $\phi = 1.0$ , methane-air flame



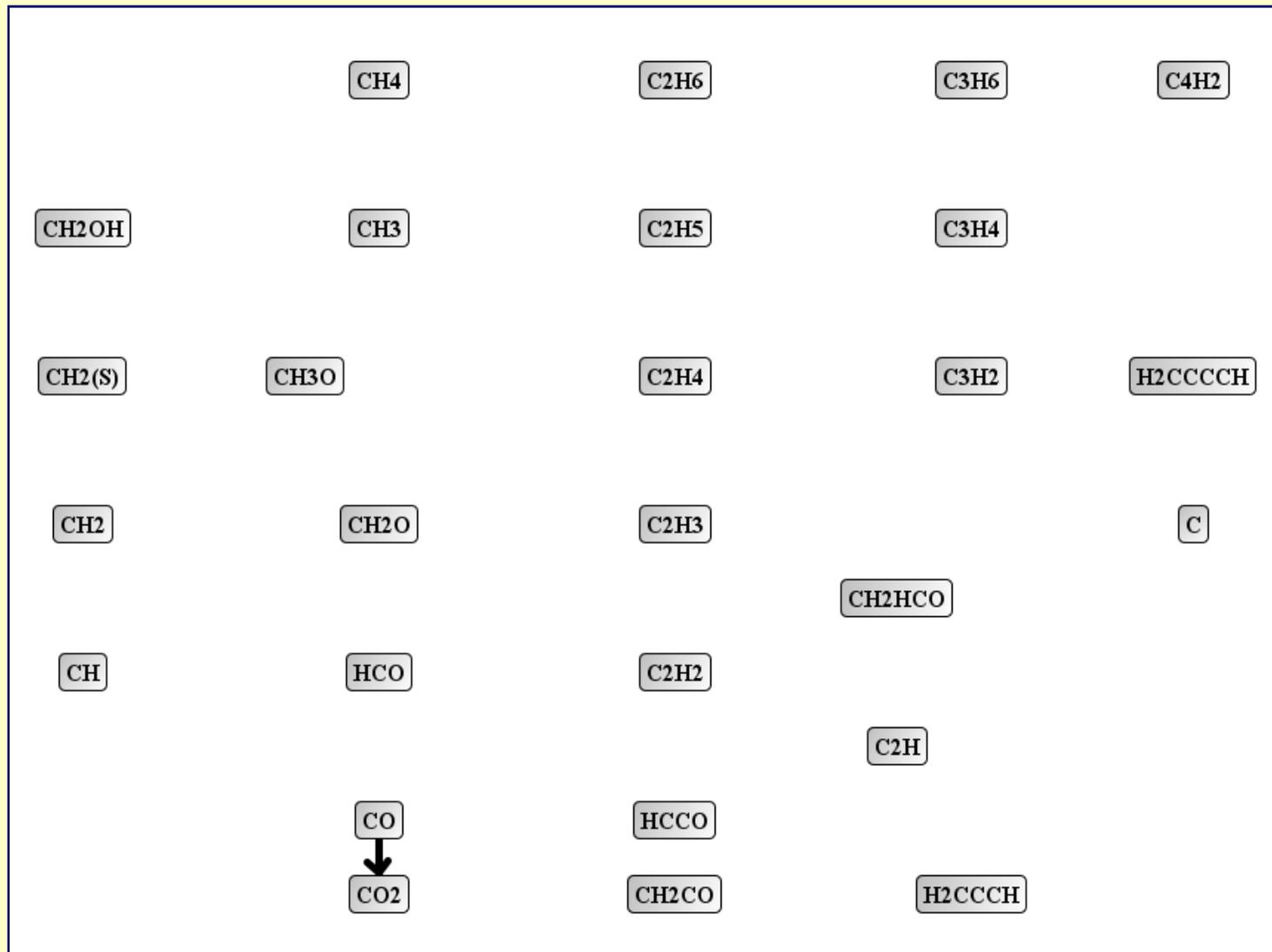
$T = 1805$  K

# C-atom fluxes, $\phi = 1.0$ , methane-air flame



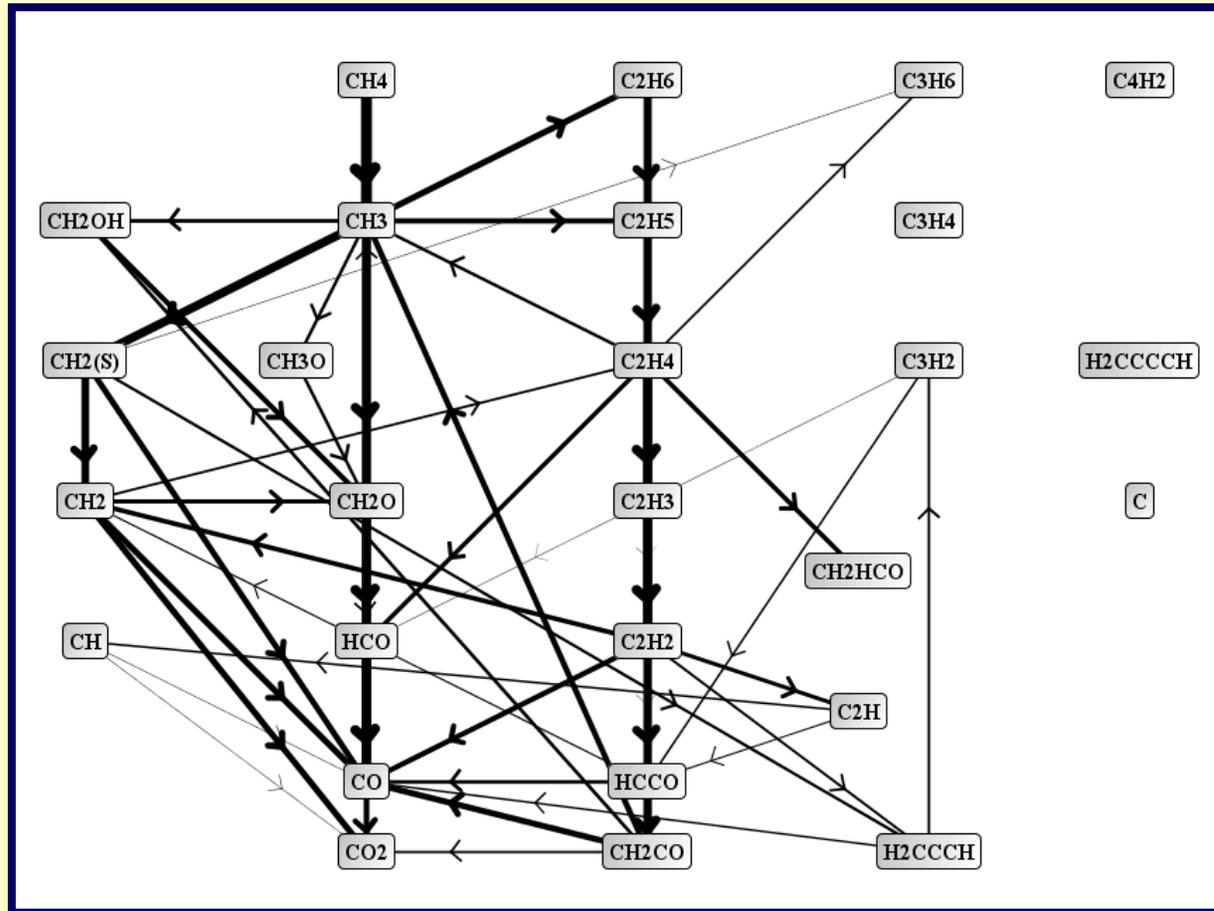
$T = 1865$  K

# C-atom fluxes, $\phi = 1.0$ , methane–air flame



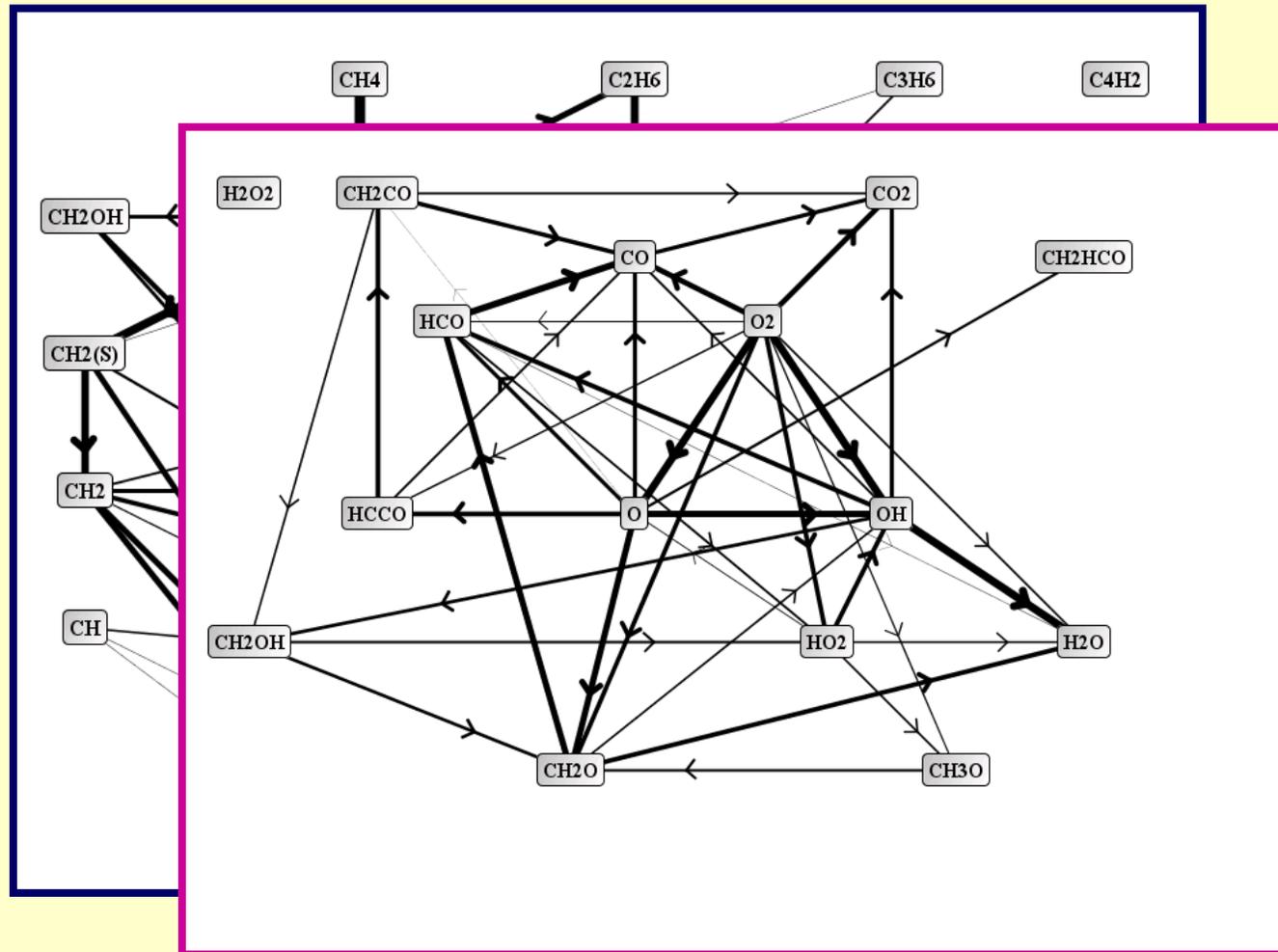
$T=1915$  K

# Comparison of element fluxes in a methane–air explosion ( $\phi = 1.0$ , $T = 1800$ K)



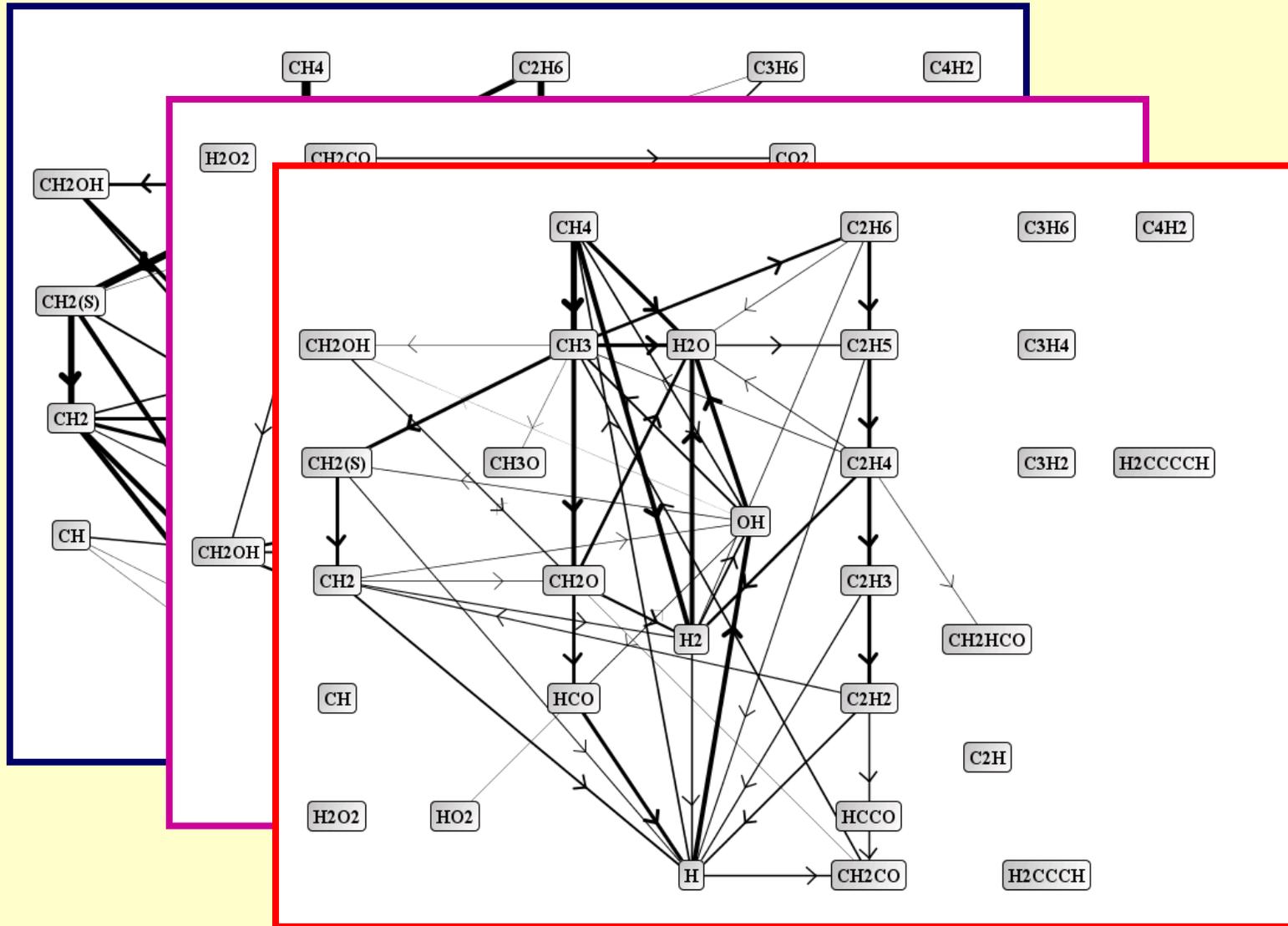
C-fluxes

# Comparison of element fluxes in a methane–air explosion ( $\phi = 1.0$ , $T = 1800$ K)



O-fluxes

# Comparison of element fluxes in a methane–air explosion ( $\phi = 1.0$ , $T = 1800$ K)



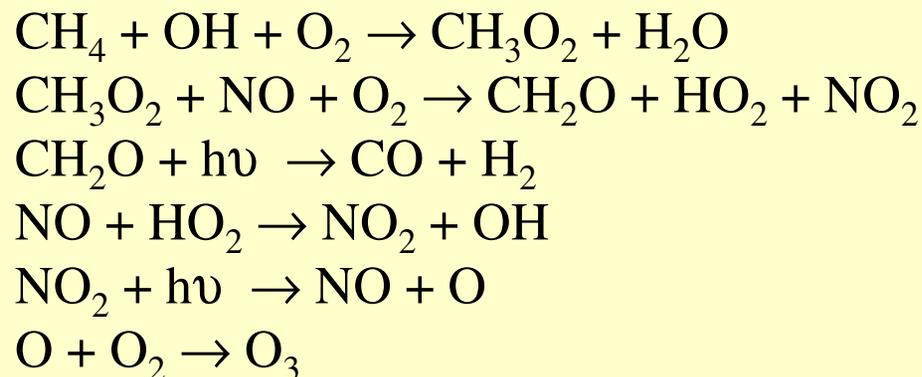
H-fluxes

## Pathways for the consumption/production of a given species

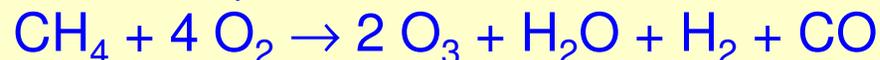
**Problem:** What is the sequence of reactions that leads to the consumption (or production) of a given species? The detailed reaction mechanism is known.

**Example:** What is the sequence of reactions that leads to the consumption of methane in the stratosphere?

**Answer:**



The global reaction for CH<sub>4</sub> consumption:



R. Lehmann: An algorithm for the determination of all significant pathways in chemical reaction systems. *J. Atm. Chem.* **47**, 45-78 (2004)



*Thank you for  
your attention!*