

## Reaction kinetics modelling

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submission deadline: 17 October 2021, 24:00

1. Program 'ckinterp' of the CHEMKIN-II simulation program package creates a binary reaction mechanism file from the CHEMKIN-format text mechanism file. Run ckinterp in a command (cmd) window of a Windows operating system:

> ckinterp

input: chem.inp (text file containing the reaction mechanism)  
output 1: chem.out (interpreted echo of the input file)  
output 2: chem.bin (binary file containing the reaction mechanism)

The mechanism provided describes the detonating gas ( $H_2-O_2$ ) reaction. The hydrogen combustion mechanism of Varga et al. [T. Varga; T. Nagy; C. Olm; I. G. Zsély; R. Pálvölgyi; É. Valkó; G. Vincze; M. Cserhádi; H. J. Curran; T. Turányi, *Proc. Combust. Inst.* **35** (2015) 589-596] is investigated. For the heterogeneous reactions, the approach of Wang and Law [X. Wang; C. K. Law, *J. Chem. Phys.* 138 (2013) 134305] was adopted, who modelled the wall-loss of species H, O, OH,  $HO_2$  and  $H_2O_2$  as first order removal reactions. The other species have low sticking coefficients and therefore the corresponding rate coefficients are nearly zero. The wall-loss rate parameters were calculated for a 7.4 cm diameter, spherical quartz reactor using the kinetic theory of gases. The present mechanism has been investigated in the article of Valkó *et al.* [É. Valkó, T. Varga, A.S. Tomlin, T. Turányi, *Proc. Combust. Inst.* **36**, 681-689 (2017)].

2. Program 'senkin' of the CHEMKIN-II simulation program package carries out spatially homogeneous gas kinetics simulations. Run senkin in a command (cmd) window of a Windows operating system:

> senkin <senkin.inp >senkin.out

input 1: chem.bin (binary file containing the reaction mechanism)  
input 2: senkin.inp (text file with keywords containing the initial conditions)  
  
output 1: senkin.out (echo of input data and the calculated  $t$ - $T$  values)  
output 2: tign.out (text file containing the calculated  $t$ ,  $p$ ,  $T$  and concentration data; units: s, atm, Kelvin, mole fractions)  
output 3: save.bin (binary file containing the simulation results)

Files created for making Origin plots; the first line contains the names of the variables:

output 4: konc\_c\_molem3.txt ( $t$ ,  $p$ ,  $T$  and concentrations in  $\text{mol cm}^{-3}$  units)  
output 5: konc\_c\_x.txt ( $t$ ,  $p$ ,  $T$  and concentrations in mole fraction units)  
output 6: konc\_c\_dbcm3.txt ( $t$ ,  $p$ ,  $T$  and concentrations in  $\text{molecule cm}^{-3}$  units)

Note that "p/Pa" in the output is wrong. It has to be interpreted as "p/atm".

The meaning of keywords in file „senkin.inp”:

CONV simulation of a constant volume adiabatic system  
 TEMP 1250 the initial temperature is 1250 K  
 PRES 1 the initial pressure is 1 atm  
 REAC H2 2 ratio of the initial mole fractions of H<sub>2</sub>, O<sub>2</sub> és N<sub>2</sub>  
 REAC O2 1  
 REAC N2 3.76  
 TIME 1 the final time (end of simulation) is 1 second  
 DELT 1E-9 the initial time step is 10<sup>-9</sup> seconds  
 ATOL 1E-20 absolute tolerance (= largest permitted error) for the calculated mole fractions  
 ATLS 1E-20 absolute tolerance for the calculated local sensitivity coefficients (not used)  
 RTOL 1E-09 relative tolerance (= largest relative error in each step) for the mole fractions  
 RTLS 1E-09 relative tolerance for the calculated local sensitivity coefficients (not used)  
 END

### Problems to be solved

Name	Neptun code	$T$ K	$p$ atm	$\varphi$
Keresztes Barbara	TORM9E	1000	1	0.65
Galvács Ákos	A5BQZJ	1000	1	1.05
Fehér Ferencz	JY6ZKU	1000	1	1.45
Barcza Bónis	F9U8DH	1000	1	1.95

1. Carry out simulations using your personal initial conditions above assuming a constant volume adiabatic system. The initial mixture contains H<sub>2</sub> and O<sub>2</sub> only. The final time is 1 second.  $\varphi$  is the fuel equivalence ratio, defined as  $\varphi = (n_{\text{fuel}}/n_{\text{oxidizer}})_{\text{actual}} / (n_{\text{fuel}}/n_{\text{oxidizer}})_{\text{stoichiometric}}$

Prepare a series of Origin plots that show the 'time vs. temperature' and all 'time vs. species mole fraction' functions. Please select the axes in such a way that all changes be well visible. Interpret the shapes of the functions. Some 'time vs. species mole fraction' functions show multiple extrema. What is the chemical explanation of these extrema?

2. Carry out the calculations in such a way that the oxidizer is not pure O<sub>2</sub>, but

- 21% O<sub>2</sub>, 79% N<sub>2</sub>
- 21% O<sub>2</sub>, 79% Ar
- 21% O<sub>2</sub>, 79% He
- 21% O<sub>2</sub>, 79% H<sub>2</sub>O

Use the previous initial temperature  $T$ , pressure  $p$  and equivalence ratio  $\varphi$ .

Interpret the change of ignition delay time and final temperature, using the following facts:

The constant volume molar heat capacity of the bulk gases (units:  $\text{J K}^{-1} \text{mol}^{-1}$ )

$\text{N}_2$ : 24.37, Ar: 12.48, He: 12.48,  $\text{H}_2\text{O}$ : 32.98

Relative third body efficiency of the bulk gases in reaction step  $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$

$m(\text{N}_2) = 1$ ,  $m(\text{Ar}) = 0.54$ ,  $m(\text{He}) = 0.65$ ,  $m(\text{H}_2\text{O}) = 12.03$

3. What is the lowest initial temperature where ignition is observed within 1 second using the four mixtures above? Accuracy within 10 K is enough.

4. Using the original  $\text{H}_2/\text{O}_2$  mixture and initial temperature, calculate the ignition delay time and final temperature by changing pressure in interval  $10^{-3}$  atm to 100 atm. Plot the results using at least 15 points, taken equidistantly on a logarithmic pressure scale. Explain the results!

Please send text file „konc\_c\_molcm3.txt” and a single Word file that contains all figures, plots and their interpretation to e-mail address [turanyi@chem.elte.hu](mailto:turanyi@chem.elte.hu).