Reaction kinetics modelling

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Please upload the prepared pdf file to the Moodle site of the course!

1. Unzip the rkin_codes.zip package to a folder!
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. Cserháti; 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_molcm3.txt	(*t*, *p*, *T* and concentrations in 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 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_2, O_2 and N_2
REAC O2 1	
REAC N2 3.76	
TIME 1	final time (end of simulation) is 1 second
DELT 1E-9	the initial time step is 10^{-9} 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	p	φ
Balázs Krisztina	JJS8IN	1000	1	0,65
Burlacu Péter Dániel	UV0XM9	1000	1	0,85
Fábián Lizett	JMHILE	1000	1	1,05
Galanics Kitti Csenge	CE6COC	1000	1	1,25
Gargya Noémi Éva	JJDXN7	1000	1	1,45
Nagy Eszter	RU4P0X	1100	1	0,65
Palik Dezső István	BGG35F	1100	1	0,85
Rácsai Balázs	WM82LC	1100	1	1,05
Radócz Roland	G73MSE	1100	1	1,25
Riznychenko Tetiana	YOJWT5	1100	1	1,45
Sajósi Benedek	PRVEB8	1000	1	0,80
Terbák Enikő Krisztina	D4GW6X	1000	1	1,00
Voigt Inga Maria	IML2PL	1000	1	1,20

1. Carry out simulations using your personal initial conditions above, assuming a constant volume adiabatic system. The initial mixture contains only H_2 and O_2. The final time is 1 second. φ is the fuel equivalence ratio, defined as
$\varphi=(n_{\mathrm{fuel}}/n_{\mathrm{oxidizer}})_{\mathrm{actual}}/(n_{\mathrm{fuel}}/n_{\mathrm{oxidizer}})_{\mathrm{stoichiometric}}$

Prepare a series of Origin plots that show the ’time *vs.* temperature’ and all ’time *vs.* species mole fraction’ functions. Please select the axes so that all changes are clearly 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_2, but
a) 21% O_2, 79% N_2
b) 21% O_2, 79% Ar
c) 21% O_2, 79% He
d) 21% O_2, 79% H_2O
Use the previous initial temperature T, pressure p and equivalence ratio φ.

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

The constant volume molar heat capacity of the bulk gases (units: J K^{-1} mol^{-1})
N_2: 24.37 , Ar: 12.48 , He: 12.48, H_2O: 32.98

Relative third body efficiency of the bulk gases in reaction step $H+O_2+M=HO_2+M$
$m(N_2) = 1$, $m(Ar) = 0.54$, $m(He) = 0.65$, $m(H_2O) = 12.03$

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. We consider ignition to occur if the temperature change exceeds 400 K.

4. Using the original H_2/O_2 mixture and initial temperature, calculate the ignition delay time and peak temperature by changing pressure in the 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 upload to the Moodle site a single pdf file that contains all figures, plots and their interpretation.