

## Project 2: Chemical Kinetics (PR2\_kinetics)

### 1. Stiff ODE's

This exercise illustrates stiff ordinary differential equations and the numerical difficulties they cause.

1. Run the Matlab script `overall1`. This uses `ode45` to integrate the ODE for the reaction progress variable  $c(t)$

$$\frac{dc}{dt} = S(c), \quad (1)$$

$$S(c) = \omega_c A c^n (1 - c), \quad (2)$$

for  $\omega_c = 1, n = 6, c(0) = 0.3$ , where  $A$  is such that

$$\max_c \{S(c)\} = \omega_c. \quad (3)$$

Plot the function  $S(c)$  versus  $c$  (for  $0 \leq c \leq 1$ ). Note the number of steps and function evaluations used by `ode45`.

2. Instead of Eq. (1), consider the pair of ODEs for  $c(t)$  and  $r(t)$

$$\frac{dc}{dt} = \omega_c r \bar{A} c^p (1 - c)^{\frac{1}{2}}, \quad (4)$$

$$\frac{dr}{dt} = \omega_r (R(c) - r), \quad (5)$$

$$R(c) \equiv B c^q (1 - c)^{\frac{1}{2}}, \quad (6)$$

where  $B$  is such that  $\max\{R(c)\} = 1$ ; and  $\bar{A}$  is such that, for  $r = R(c)$ ,  $\max\{dc/dt\} = \omega_c$ . We take  $p = 4$  and  $q = 2$ .

The variable  $r(t)$  represents a normalized radical mass fraction:  $r(t)$  relaxes towards the steady-state or partial equilibrium value  $R(c)$  at the rate  $\omega_r$ . Note that  $dc/dt$  is proportional to  $r$ .

Consider the limit  $\omega_r \rightarrow \infty$ . Eq. (5) yields  $r = R(c)$ , and then Eq. (4) becomes

$$\begin{aligned} \frac{dc}{dt} &= \omega_c \bar{A} R(c) c^p (1 - c)^{\frac{1}{2}} \\ &= \omega_c A c^{p+q} (1 - c), \end{aligned} \quad (7)$$

where  $A = \bar{A}B$ . This is identical to Eq. (1) for  $p + q = n$ . (i.e.,  $4 + 2 = 6$ ).

3. On the same figure plot:

- a)  $S(c)$  given by Eq. (1)

- b)  $R(c)$  given by Eq. (6)
  - c)  $dc/dt$  given by Eq. (4) with  $\omega_c = 1, r = R(c)$ .
4. Run the Matlab script `stiff` which uses `ode45` to integrate Eqs. (4) and (5) for  $\omega_r = 10$ . Note the number of steps and function evaluations used by `ode45`. What initial condition is used for  $r(0)$ ?
  5. Change  $\omega_r$  (`omr`) to  $\omega_r = 10^3$  and re-run `stiff`. Comment on your observation.
  6. Change the call to `ode45` to a call to `ode23s` (with the same arguments) and re-run `stiff`. Comment.
  7. Change  $\omega_r$  to  $\omega_r = 10^6$  and investigate the performance of different ODE solvers.

## 2. H<sub>2</sub>-Autoignition

In this exercise you use the Closed 0-D Reactor Models, particularly the Closed Homogeneous Reactor Model, in Chemkin IV to study the autoignition of a hydrogen-air mixture.

1. Read Section 2.2.2 in `CHEMKIN_Tutorials.pdf`. Set up the hydrogen-air autoignition project using the file `RD_H2_a.inp` and the parameters in `auto_H2.inp`
2. Run the autoignition application and make a plot of the reactive species mass fractions as functions of time.
3. Read `CHEMKIN_Input.pdf`, especially Section 7.1.2 to understand the parameters for the closed 0-D Homogeneous Reactor Mode. What parameters affect the numerical accuracy of the results? Are the solutions numerically accurate? Change and/or add parameters as necessary.
4. Examine the behavior of the radicals during the induction phase. Discuss their relative magnitudes and the timescale characteristic of their growth. Which reactions are primarily responsible for the production of  $HO_2$  and  $H$ ?
5. To study the fuel-consumption phase, plot the species mass fractions (or specific mole numbers) against that of water. What timescale is associated with the fuel consumption? Examine the production of  $H_2O$  by the different reactions.
6. Examine the sensitivity of  $H_2O$  to the rates of the different reactions.
7. Extend the time of the calculation to study the radical-recombination phase. Identify the dominant radical. Which reactions contribute to the recombination of  $H$ ? What timescale is associated with this recombination process?

## 3. CH<sub>4</sub>-PSR

In this exercise you use the Open 0-D Reactor Models, particularly the Perfectly Stirred Reactor Model, in Chemkin IV to study the combustion a lean methane-air mixture in a PSR.

1. Read Section 2.2.1 in CHEMKIN\_Tutorials.pdf. Set up the methane-air PSR project using the file `RD_CH4.inp` and the parameters in `psr_CH4.inp`.
2. Run the PSR application and plot temperature against residence time.
3. Change the sequence of residence times to get fairly close to blow-out (but without including an extinguished case). Plot the temperature (i.e., gas temperature) and the species mole fractions (i.e., outlet values) against residence time.
4. Let  $c$  denote a reaction progress variable defined in terms of  $Y_{CO_2}$ . From the data on  $Y_{CO_2}$  vs.  $\tau_r$  (residence time), estimate a global reaction rate  $S(c)$ . Comment on the difference when  $c$  is based on  $Y_{H_2O}$  instead.
5. Re-run the PSR application to produce a rate-of-production analysis for the case  $\tau_r = 2 \times 10^{-4}$  sec. Construct a partial reaction flow diagram to show the dominant path in the conversion of the carbon in  $CH_4$  to  $CO_2$ . Starting with  $CH_4$  identify the dominant destruction reaction, and the carbon-containing product of this reaction. Repeat this process for successive carbon-containing products until you reach  $CO_2$ . On your diagram you should show: the carbon-containing products; the dominant destruction reactions; the rates of these reactions.
6. Re-run the PSR application for the same case as in (5), but using the mechanism file `GRI211.inp`. Compare the temperature and selected species mole fractions given by the two mechanisms. Comment on the rates of the dominant reactions identified in (5) given by the two mechanisms.

#### 4. PSR using arclength continuation

In this exercise you explore both the stable and unstable branches of the solution to the steady-state PSR equations (with and without heat loss).

The program `psr.exe` (obtained from `psr.f`) uses arc-length continuation in the  $\omega$ - $T$  plane to obtain the solution. In addition to `chem.bin`, it takes `psr.inp` as an input file and it generates the output file `psr.out`. This consists of two columns containing corresponding values of  $\omega$  ( $s^{-1}$ ) and  $T$  ( $K$ ).

1. Examine the file `psr.inp` and refer to `psr.f` to understand the definitions of the variables.
2. Run `psr.exe` using `chem.bin` generated from the standard hydrogen mechanism `RD_H2_a.inp` and using the input file `psr.inp` provided. From the results, make a plot of  $T$  against  $\omega$  (on a log scale).
3. Run CHEMKIN IV for the same conditions and for one or two values of  $\omega$  to check the consistency of the results.

4. Experiment with different values of the heat loss parameter, e.g.,  $QLOS = \pm 10^{-3}$ . Explain the observed behavior.

**Report**

Your report should consist of: the principal plots obtained; answers to the questions; and a brief statement of your explanations and conclusions. The narrative should not be much longer than one page.