Open∇FOAM Tutorial

reactingFoam

Simple Gas Phase Reaction

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1 Introduction

This tutorial is intended as a first introduction problem to the OpenFOAM solver reactingFoam. The aim of the tutorial is to understand how to setup a simple gas phase reaction scheme. The solver uses the CHEMKIN format to formulate kinetics and supply thermodynamic data for the induvidual componenets. Thus a large part of this tutorial will be spent understanding how CHEMKIN is used. The choosen sample problem consists of two simple, made up, gas phase reactions where the rate of reaction is given on an Arrhenius form. As a reactor the 2D pitzDaily case with a backward facing step will be used. The reactions occuring in the reactor are:

$$\begin{array}{llcl} \text{reaction 1} & \text{A} & \xrightarrow{k_1} & \text{B} \\ \text{reaction 2} & 2\,\text{A} & \xrightarrow{k_2} & \text{C} \end{array}$$

Reaction 1 and 2 are assumed to be of first and second order respectively.

$$\begin{array}{llcl} \text{reaction 1} & r_1 & = & k_1 C_A \\ \text{reaction 2} & r_2 & = & k_2 C_A C_A \end{array}$$

Reaction rates are given by:

$$k_i = A_i \exp\left[\frac{E_i}{R}\left(\frac{1}{300} - \frac{1}{T}\right)\right] \tag{1}$$

Activation energies, material properties and heat of reactions are given in Table (1).

	value	*unit*
A_1	0.01	1/s
A_2	9E-05	m^3/mole/s
E_1	33000	J/mole
E_2	75300	J/mole
ΔH_{R_1}	-20E+03	J/mole of A reacted in reac. 1
ΔH_{R_2}	-30E+03	J/mole of A reacted in reac. 2
C_{p_A}	3000	J/kg/K
C_{p_B}	3000	J/kg/K
C_{p_C}	3000	J/kg/K
M_A	44	g/mole
M_B	44	g/mole
M_C	88	g/mole

Table 1: Species material and reaction data

2 Using CHEMKIN

A description of the reactions and thermodynamic data of the involved species are supplied to reactingFoam using the CHEMKIN format. The case should

contain a folder called **chemkin** where two files *chem.inp* and *therm.dat* should be placed. In *chem.inp* the reaction kinetiks and stoichiometry is described. The standard Arrheniu's expression used for reaction rates in chemkin is given as:

$$k_i = A_i T^{\beta_i} \exp\left(-\frac{E_i}{RT}\right) \tag{2}$$

The default units in CHEMKIN are $\left(cm^3/mole\right)^{(r-1)} s^{-1}$ for the pre-exponetial factor [1] A_i and $(cal/mole)$ for the activation energy E_i. There is an option to specify which units should be used. To change the unit for the activation energy the keyword *JOULES/MOLE* is supplied. Please observe that the pre-exponetial factors in Table (1) are given for Eq. (1) and has to be recalculated to fit the form accepted by CHEMKIN. This is done by pulling out the factor $exp\,(E_i/R\,300)$. A working chem.inp file is given below:

```
ELEMENTS
 H  C   N
END
SPECIE
 N2  H2 AL BL CL
END
REACTIONS JOULES/MOLE
 AL                 =>   BL                6.80E+06   0.0  33500.0! 1
 2AL                =>   CL                1.16E+15   0.0  75300.0! 1
END
```

The file uses keywords to indentify involved species and elements. To make sure that species names, i.e. C is not confused with elementary carbon, all species except N_2 have been renamed to AL, BL and CL. After the keyword REACTIONS the identifier JOULES/MOLE is given to change the unit of the activation energy. The three numbers given before the exclamation mark are A_i,β_i and E_i respectively. In this case the main species are made up, however the molar weights correspond to propane and heptene, the corresponding thermodynamic data however does not. This is due to the fact that CHEMKIN needs to now the elementary composition of the involved species. In order to be able to use constant heats of reaction som care must be taken when constructing the *Thermo.dat* file.

In the file *Thermo.dat* all information about species heatcapacity, enthalpy and entropy is given. These quantities are supplied using polynomials as follows:

$$\frac{C^\circ_{p_k}}{R} = a_{1k} + a_{2k}T_k + a_{3k}T_k^2 + a_{4k}T_k^3 + a_{5k}T_k^4 \tag{3}$$

$$\frac{H^\circ_k}{RT_k} = a_{1k} + \frac{a_{2k}}{2}T_k + \frac{a_{3k}}{3}T_k^2 + \frac{a_{4k}}{4}T_k^3 + \frac{a_{5k}}{5}T_k^4 + \frac{a_{6k}}{T_k} \tag{4}$$

$$\frac{S^\circ_k}{R} = a_{1k}\ln T_k + a_{2k}T_k + \frac{a_{3k}}{2}T_k^2 + \frac{a_{4k}}{3}T_k^3 + \frac{a_{5k}}{4}T_k^4 + a_{7k} \tag{5}$$

where $\circ$ means standard state based on pressure (in our case 1 atm). If C°_p is regarded as constant then:

[1] Where r is the reaction order

$$
\begin{aligned}
a_{1k} &= C^{\circ}_{p_k}/R \\
a_{1A} &= 3000 \cdot 44 \cdot 10^{-03}/8.314 \\
a_{1B} &= 3000 \cdot 44 \cdot 10^{-03}/8.314 \\
a_{1C} &= 3000 \cdot 88 \cdot 10^{-03}/8.314
\end{aligned}
$$

Where $C^{\circ}_{p_k}$ is molar heat cpacity. The enthalpy is then given as

$$\frac{H^{\circ}_k}{RT_k} = a_{1k} + \frac{a_{6k}}{T_k}$$

and the heat of reaction as

$$
\begin{aligned}
\Delta H^{\circ}_r \quad &= \sum H_{\text{prod}} - \sum H_{\text{reac}} = \\
&\sum_i \nu_i \left(a_{1i}RT + a_{6i}R\right) - \sum_j \nu_j \left(a_{1j}RT + a_{6j}R\right)
\end{aligned} \tag{6}
$$

It follows that in order to get a constant heat of reaction, the sum of C_p values between products and reactants has to be equal. In the case above the molar weights and stochoimetric coeffcients are such that this is realized. As an example consider reaction 2 where

$$\Delta H_r = \left(a_{1C}RT + a_{6C}R\right) - 2\left(a_{1A}RT + a_{6A}R\right)$$

and since

$$a_{1C} = 2\ a_{1A}$$

the heat of reaction is

$$\Delta H_r = a_{6C}R - 2\ a_{6A}R$$

Setting the enthalpy for species A to zero and the enthalpies of B and C to the negative of the respective heats of reaction and dividing by R gives constant heats of reaction.

$$
\begin{aligned}
a_{6A} &= 0 \\
a_{6B} &= -20000/8.134 \\
a_{6C} &= -60000/8.134
\end{aligned}
$$

Above, the enthalpy for C has been multiplied by two since it was given as per reacted mole of A.

The format of the *therm.dat* file follows an old Fortran style parsing pattern. This means that the way numbers and words are entered is important for the parsing of the file to be successful. The simplest way to go around this is to use an old file as a template. Below, a working *therm.dat* file is supplied. For reference about the format used see the CHEMKIN manual[2].

[2] http://www.cvd.louisville.edu/Course/Chemical%20Vapour%20Deposition/Manuals/chemkin/chemkin1chemkin.pdf

```
THERMO ALL
   200.000  1000.000  5000.000
AL                SAND87O   1H   8C   3     G   200.000  5000.000  1000.000    1
 0.01587000E+03 0.00000000E-01 0.00000000E-04 0.00000000E-08 0.00000000E-12    2
 0.00000000E+00 0.00000000E+02 0.01587000E+03 0.00000000E-01 0.00000000E-04    3
 0.00000000E-07 0.00000000E-10 0.00000000E+00 0.03950372E+02                   4
BL                SAND88O   1H   8C   3     G   200.000  5000.000  1000.000    1
 0.01587000E+03 0.00000000E-01-0.00000000E-04 0.00000000E-08 0.00000000E-12    2
-0.24055810E+04-0.00000000E+02 0.01587000E+03 0.00000000E-01 0.00000000E-04    3
 0.00000000E-07 0.00000000E-10-0.24054363E+04 0.03950372E+02                   4
CL                SAND89O   2H  16C   6     G   200.000  5000.000  1000.000    1
 0.03175000E+03 0.00000000E-01-0.00000000E-04 0.00000000E-08 0.00000000E-12    2
-0.72167428E+04 0.00000000E+02 0.03175000E+03 0.00000000E-01 0.00000000E-04    3
 0.00000000E-07 0.00000000E-10-0.72167428E+04 0.03950372E+02                   4
N2                121286N   2               G  0200.00   5000.00  1000.00      1
 0.02926640E+02 0.01487977E-01-0.05684761E-05 0.01009704E-08-0.06753351E-13    2
-0.09227977E+04 0.05980528E+02 0.03298677E+02 0.01408240E-01-0.03963222E-04    3
 0.05641515E-07-0.02444855E-10-0.01020900E+05 0.03950372E+02                   4
END
```

The keyword THERMO ALL is used when all thermodynamic data is taken from Interpreter input. Line number 2 includes the temeperature ranges for two sets of coefficients describing the polynomials. The species name starts line number 3 where also the elemenatry composition must be declared as well as phase and temperature range. Lines number 4-6 represent the coefficinets used in equations (3)-(5) for two set of temperature ranges. In the example above nitrogen is taken from a standard database.

3 Case setup

As mentioned previously the mesh used is taken from the *pitzDaily* tutorial just using a larger scale i.e. $x10$. Start by downloading the case to your **/run/** directory and un-tar it by *tar -xzf reactingFoamTutorial.tgz*.

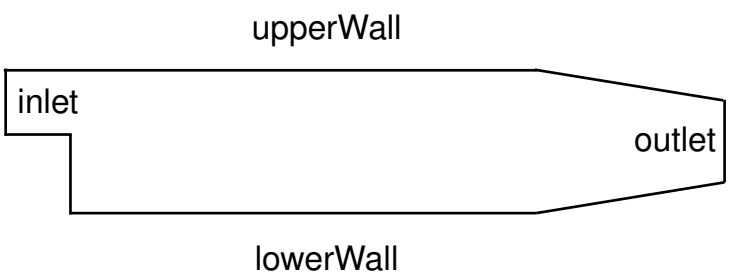

Figure 1: *pitzDaily* domain used in the *reactingFoamTutorial*

3.1 Initial and Boundary conditions

For all the fields except those describing the species, initial and boundary conditions are the same as in the pitzDaily case. In the **0** folder the files *AL*, *BL*, *CL* and *N2* should be present and also a *Ydefault* (and of course the original *pitzDaily* files). The initial and boundary conditions for the new fields are given in table (2)

field	*internalField*	*inlet*	*outlet*	*upperWall*	*lowerWall*
AL	0.0	0.9	zeroGradient	zeroGradient	zeroGradient
BL	0.0	0.0	-	-	-
CL	0.0	0.0	-	-	-
N2	1.0	0.1	-	-	-
Ydefault	0.0	0.0	-	-	-
T	623	623	-	623	623

Table 2: Initial and boundary conditions for species and temperature

All species fractions are given on mass-basis. The *Ydefault* file is used in case a large number of species share a common set of boundary conditions i.e. a default set which is handy incase there are many species involved.

3.2 Enviromental and Chemistry properties

There is also a second set of files used to control the chemistry in the solver. These are:

- *chemistryProperties*
- *combustionProperties*
- *thermophysicalProperties*

In *chemistryProperties* chemistry and *turbulentReaction* should be turned **on** as chemistry solver use *ODE*. Leave the setting in the *combustionProperties* as it is. In *thermophysicalProperties* make sure that the paths to your chemkin files i.e. *chem.inp* and *therm.dat* are correct.

3.2.1 Effective Diffusivity

The effective diffusivity is taken as the effective viscosity which implies a turbulent Schmidt number of one. The laminar viscosity in turn is caluclated using Sutherland's law where the constants are hard coded in to the actual chemkin-reader using $A_s = 1.67212e^{-6}$ and $T_s = 170.672$.

$$\mu = A_s \frac{T^{1/2}}{(1 + T_s/T)}$$

3.3 System setup and running the case

In *controlDict* use the following settings:

```
// * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * //

application     reactingFoam;

startFrom           startTime;

startTime           0;

stopAt              endTime;

endTime             1;

deltaT              1e-02;

writeControl        adjustableRunTime;

writeInterval       1e-01;

purgeWrite          0;

writeFormat         binary;

writePrecision      6;

writeCompression    uncompressed;

timeFormat          general;

timePrecision       6;

adjustTimeStep      yes;

maxCo               0.1;

runTimeModifiable   yes;


// ************************************************************************* //
```

Run the case by:

blockMesh . **reactingFoamTutorial**

reactingFoam . **reactingFoamTutorial**

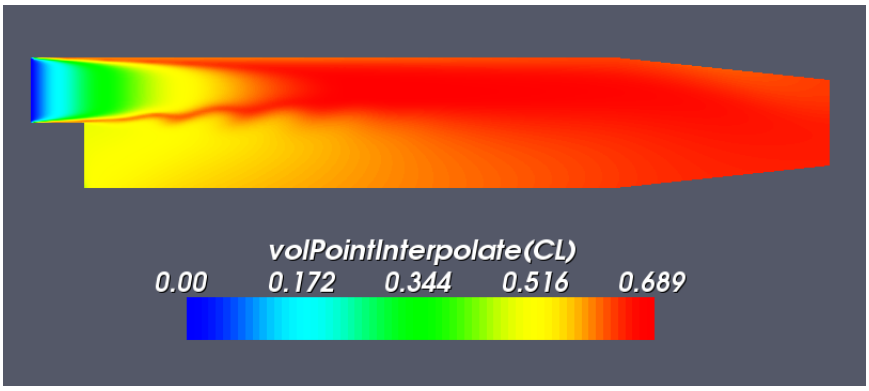

Figure 2: Mass fraction of species C after 0.8 (s)