Iran First International Combustion School (ICS2019)
Tehran, 24-26 August 2019

Combustion modeling: Training Sessions

1. Pre-processing of kinetic mechanisms, thermodynamic equilibrium and adiabatic flame temperature

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Outline

1. **Introduction to OpenSMOKE++ Suite**

2. **Preprocessing/Analysis of kinetic mechanisms**
   1. Task 1: pre-processing and analysis of thermodynamics
   2. Task 2: pre-processing and analysis of transport properties
   3. Task 3: pre-processing and analysis of kinetics

3. **Thermodynamic equilibrium & adiabatic flame temperature**
   1. Task 4: adiabatic flame temperature and NOX for H_2/air systems
   2. Task 5: adiabatic flame temperature as a function of equivalence ratio
   3. Task 6: adiabatic flame temperature of n-heptane and EGR effects

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The OpenSMOKE++ Suite

- The **OpenSMOKE++ Suite** (developed by the CRECK Modeling Group at Politecnico di Milano) is a collection of standard solvers for simulating reacting systems with detailed kinetic mechanisms, with hundreds of species and thousands of reactions.

- The solvers currently available move from ideal reactors (batch reactors, continuously stirred tank reactors, plug flow reactors, …) to laminar premixed and diffusive laminar flames. Heterogeneous catalytic reactions are also accounted for.

- The OpenSMOKE++ Suite can be freely downloaded from the following website address, after registration from an Academic email address: https://www.opensmokepp.polimi.it/

- Details are available in the following paper:

Cuoci, A., Frassoldati, A., Faravelli, T., Ranzi E., *OpenSMOKE++: An object-oriented framework for the numerical modeling of reactive systems with detailed kinetic mechanisms*, Computer Physics Communications, 192, p. 237-264 (2015), DOI: 10.1016/j.cpc.2015.02.014

The OpenSMOKE++ Suite (II)

1. Kinetic preprocessor

   Fully compatible with CHEMKIN® standard

   Training session 1

2. Ideal reactors

   Batch, plug flow, CSTR, shock-tube, rapid compression machine

   Training session 2

3. Laminar flames

   1D premixed flat flames, counterflow diffusion flames, burner stabilized stagnation flames

   Training session 3

4. Laminar flamelets

   Steady-state flamelet generator, look-up table generator

5. Heterogeneous catalytic reactors

   Batch, plug-flow, honeycomb, CSTR

6. Reduction of kinetic mechanisms

   `DoctorSMOKE++` (flux-based (DRG with error propagation) and sensitivity analyses)

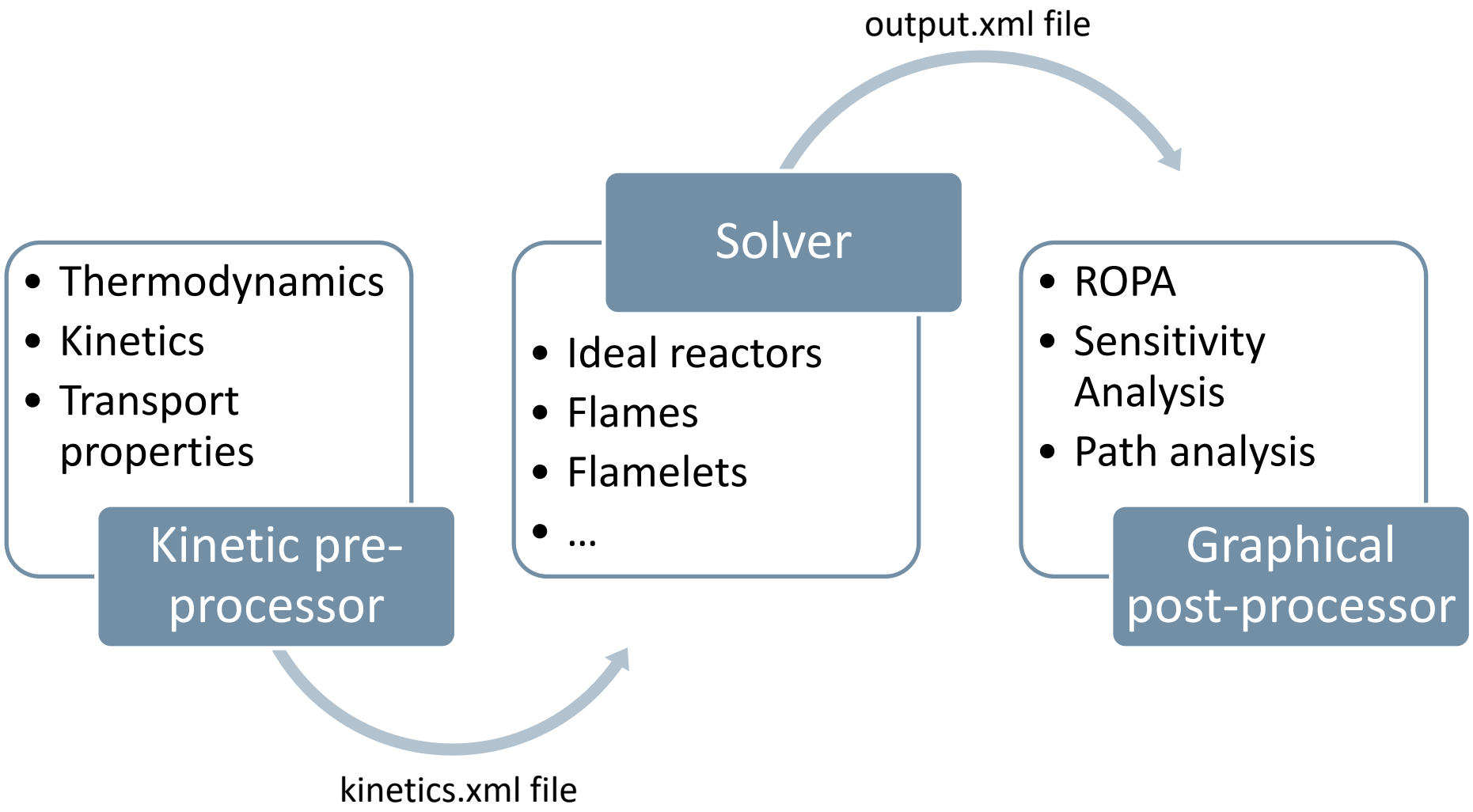
Relevant features of OpenSMOKE++

- Fully compatible with CHEMKIN® format
- Heterogeneous catalytic reactions (CHEMKIN® format)
- Detailed transport properties
- Species bundling (efficient calculations of diffusion coefficients)
- Semi-analytical Jacobian evaluation
- Dense and sparse (direct and iterative) linear solvers
- Coupling to a wide range of external ODE, DAE, and NLS solvers
- On-the-fly sensitivity and rate of production analysis

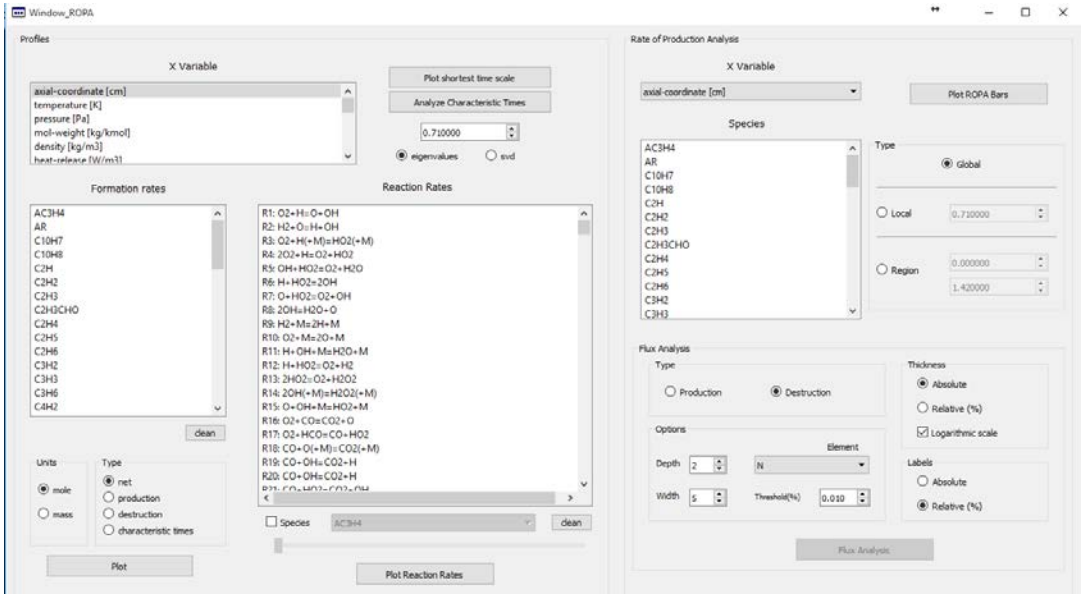
Work in progress

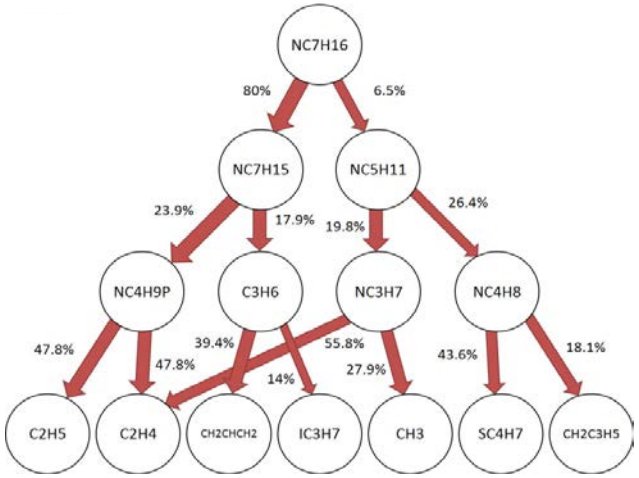
- Stefan-Maxwell approach for estimation of transport properties
- On-the-fly mechanism reduction (through DRG)
- On-the-fly stiffness removal
- Parallelization of ODE and DAE solvers (based on OpenMP®)

Solvers in OpenSMOKE++ Suite



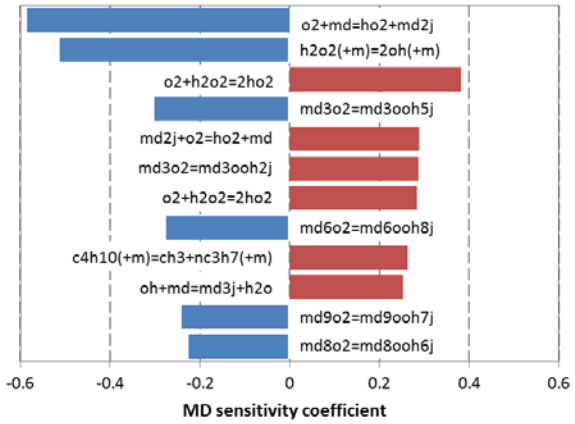
The Graphical Post-Processor (GPP)





adiabatic batch reactor (1 atm, 1200 K, Φ=1) burning a mixture of nC7 and air (276 species, 8439 reactions)

adiabatic batch reactor (2 atm, 750 K, Φ=1) burning a mixture of MD and air (460 species, 16,000 reactions)



Automatic generation of bar charts and time/space profiles:

- Sensitivity analysis
- ROPA (Rate of Production Analysis)

Automatic generation of flux diagrams:

- Reaction Path Analysis

Coupling with OpenFOAM®

OpenFOAM®

Unstructured, multidimensional meshes
Spatial discretization of transport equations
Density/Pressure coupling algorithms
Input/Output management
MPI Parallelization
Turbulence models (RANS, LES)

OpenSMOKE++

Thermodynamics and detailed kinetics
Multicomponent transport properties
ODE solvers for stiff chemistry
Tools for kinetic analysis (ROPA)

laminarSMOKE

- Simulation of reacting flows in laminar conditions (coflow flames, burner stabilized stagnation flames, …)

flameletSMOKE

- Simulation of turbulent flames based on the steady-state laminar flamelet

edcSMOKE

- Simulation of turbulent flames based on the Eddy Dissipation Concept (EDC) model

catalyticFOAM

- Simulation of catalytic heterogeneous (gas/solid) reactors (in cooperation with M. Maestri, Energy Dep. Polimi)

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Download and installation of OpenSMOKE++ Suite

The **OpenSMOKE++ Suite** can be freely downloaded (Windows, Linux and MacOS) from the following website address, after registration from an Academic email address:

https://www.opensmokepp.polimi.it/

The installation instructions are reported in the User's Guide provided with the installation files. They can be alternatively found at the following web address:

https://www.opensmokepp.polimi.it/menu-documentation/menu-documentation-ospp-suite/menu-documentation-ospp-suite-installation

Quick-start

After the installation of **OpenSMOKE++ Suite**, we strongly recommend to get familiar with the basic features of the solver by looking at the Quick-Start chapter of the User's Guide, also available online at the following web address:

https://www.opensmokepp.polimi.it/menu-documentation/menu-documentation-ospp-suite/menu-documentation-ospp-suite-quick-start

Organization of ICS2019 Training Session Material

`TrainingSessions`

- `TS1`
- `TS2`
- `Docs`
- `KineticMechanisms`

`TS1, TS2, …`
Folders containing the input files needed to carry out the tasks corresponding to the training sessions 1, 2, etc

`Docs`
OpenSMOKE++ User's Guide and additional documentation files

`KineticMechanisms`
Collection of several detailed kinetic mechanisms in `CHEMKIN` format (thermodynamics, transport and kinetic files) adopted for running the simulations

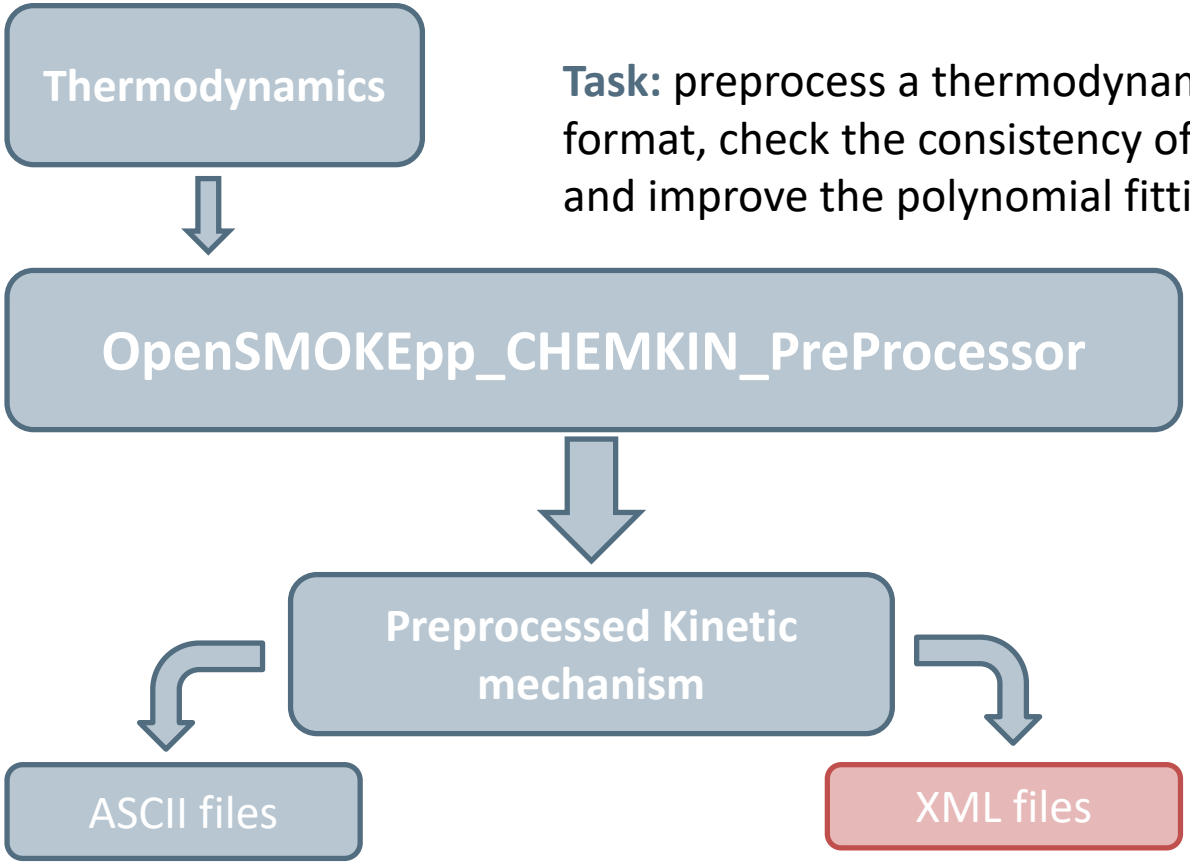
OpenSMOKE++ User's Guide & Tutorials

- The OpenSMOKE++ User's Guide is available in the Docs folder
- All the available options for each solver are reported there, together details about the installation process
- Additional examples and tutorials are available at the following web address: https://github.com/acuoci/OpenSMOKEppTutorials

Task 1: pre-processing thermodynamic data

Objective: get familiar with the pre-processing operations and analysis of pre-processed results

Task: preprocess a thermodynamic database in CHEMKIN® format, check the consistency of thermodynamic functions, and improve the polynomial fitting



For this preliminary task we will use the `POLIMI_TOT_NOX_1412.CKT` thermodynamic database.

Task 1.1: pre-processing thermodynamic data

1. Preparation of input data

Go to the `Task1.1` folder, containing the `input.dic`. This file contains instructions for pre-processing the thermodynamic data

```
Dictionary CHEMKIN_PreProcessor
{
  @Thermodynamics ../../KineticMechanisms/POLIMI_1412/Thermodynamics/POLIMI_TOT_NOX_1412.CKT;
  @Output         kinetics-POLIMI_TOT_NOX_1412;
}
```

`@Thermodynamics`
path to the file containing the thermodynamic data to be pre-processed (local or absolute paths are allowed)

`@Output`
path to the folder where the user want to put the results of post processing operations (local or absolute paths are allowed)

Task 1.1: pre-processing thermodynamic data

2. Run the kinetic preprocessor

From the same `Task1.1` folder, run the `OpenSMOKEpp_CHEMKIN_PreProcessor` utility.

a) Windows

Run the `Run.bat` file by double-clicking on it or, from the Command Prompt, type:

```
"%OPENSMOKEPP_EXE_FOLDER%\OpenSMOKEpp_CHEMKIN_PreProcessor.exe" --input
input.dic
```

b) Linux and Mac OSX

Run the `Run.sh` file of, from the command line, type:

```
OpenSMOKE_CHEMKIN_PreProcessor.sh --input input.dic
```

Task 1.1: pre-processing thermodynamic data

3. Analyze the pre-processing results

If everything was done properly, the `kinetics-POLIMI_TOT_NOX_1412` output folder will be created, containing the following files:

log
possible errors and/or warnings are reported here. Remember to have a look at it every time you pre-process a thermodynamic database (or more in general a kinetic mechanism)

Thermodynamics_Coefficients.out
for each species the 14 NASA coefficients are reported in a more readable format

Thermodynamics_Tables.out
for each species, the most important thermodynamic data are reported as a function of temperature, according to the 14 NASA coefficients provided in the thermodynamic database

kinetics.xml
this is the only file needed by OpenSMOKE++ Suite solvers

Task 1.2: pre-processing thermodynamic data

4. Refine the analysis of thermodynamic data

You can refine the analysis by asking additional tests to check the consistency of data supplied through the thermodynamic database. Move to the `Task1.2` folder:

```
Dictionary CHEMKIN_PreProcessor
{
  @Thermodynamics ../../KineticMechanisms/POLIMI_1412/Thermodynamics/POLIMI_TOT_NOX_1412.CKT;
  @Output         kinetics-POLIMI_TOT_NOX_1412;
  @CheckThermodynamics    true;
}
```

Task 1.2: pre-processing thermodynamic data

`thermo.CHEMKIN.CKT`

The original thermodynamic file provided by the user is corrected by applying small correction to the coefficients in order to ensure perfect continuity of thermodynamic functions and their first-order derivatives

`thermo.CHEMKIN.fixedT.CKT`

The original thermodynamic coefficients are rewritten after fitting the thermodynamic properties in order to ensure the same break temperature (1000 K) for all the species

`Thermodynamics_Status.out`

possible existence of unphysical maxima/minima in specific heat, possible discontinuities in thermodynamic properties are detected and reported here

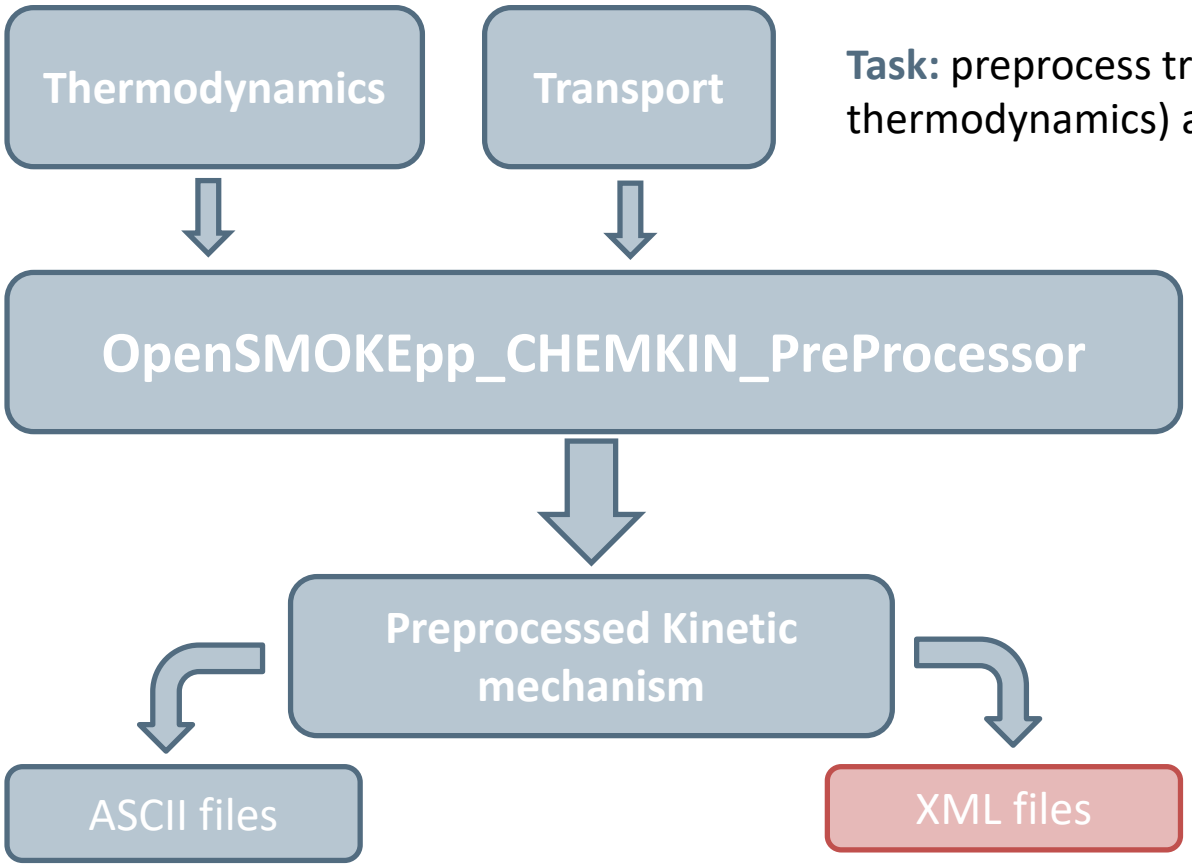
`Thermodynamics_Reformulated.out`

if possible, a new set of 14 NASA coefficients is proposed for each species in order to ensure higher thermodynamic consistency (continuity of functions and derivatives)

Task 2: pre-processing transport data

Objective: get familiar with the pre-processing operations and analysis of pre-processed results

Task: preprocess transport data (together with thermodynamics) and analyze the polynomial fitting



We will use the POLIMI_TOT_NOX_1412.TRC database, containing transport data for more than 400 species. Remember that in order to preprocess transport properties, you need always the thermodynamic properties for all the species

Task 2.1: pre-processing transport data

1. Preparation of input data

Go to the `Task2.1` folder, containing the `input.dic`. This file contains instructions for pre-processing the transport and thermodynamic data

```
Dictionary CHEMKIN_PreProcessor
{
  @Thermodynamics ../../KineticMechanisms/POLIMI_1412/Thermodynamics/POLIMI_TOT_NOX_1412.CKT;
  @Transport      ../../KineticMechanisms/POLIMI_1412/Transport/POLIMI_TOT_NOX_1412.TRC;
  @Output         kinetics-POLIMI_TOT_NOX_1412;
}
```

`@Transport`

path to the file containing the transport data to be pre-processed (local or absolute paths are allowed)

2. Run the kinetic preprocessor

Task 2.2: pre-processing transport data

1. Preparation of input data

We want now to have more details about the transport properties we are pre-processing. Go to the `Task2.2` folder. We add a new keyword.

```
Dictionary CHEMKIN_PreProcessor
{
  @Thermodynamics ../../KineticMechanisms/POLIMI_1412/Thermodynamics/POLIMI_TOT_NOX_1412.CKT;
  @Transport      ../../KineticMechanisms/POLIMI_1412/Transport/POLIMI_TOT_NOX_1412.TRC;
  @TransportFittingCoefficients    true;
  @Output                          kinetics-POLIMI_TOT_NOX_1412;
}
```

`@TransportFittingCoefficients`

Use this option only if you want to write no a file the result of polynomial fitting. Please consider that this option is not compulsory and results in large output files.

Task 2.2: pre-processing transport data

2. Run the kinetic preprocessor

3. Analyze the pre-processing results

If everything was done properly, the `kinetics-POLIMI_TOT_NOX_1412` output folder will be created, containing the following files (in addition to the usual files associated to thermodynamics):

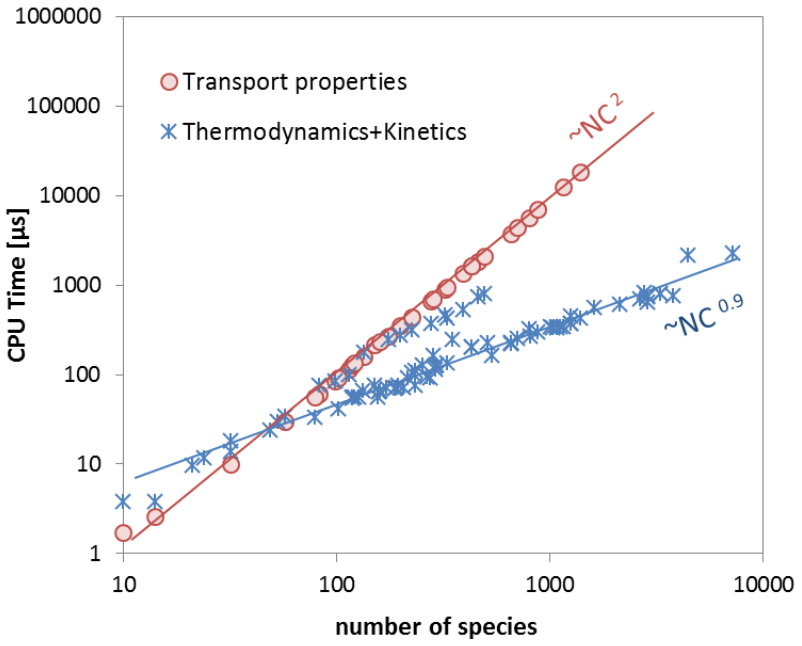
`TransportProperties_Coefficients.out`

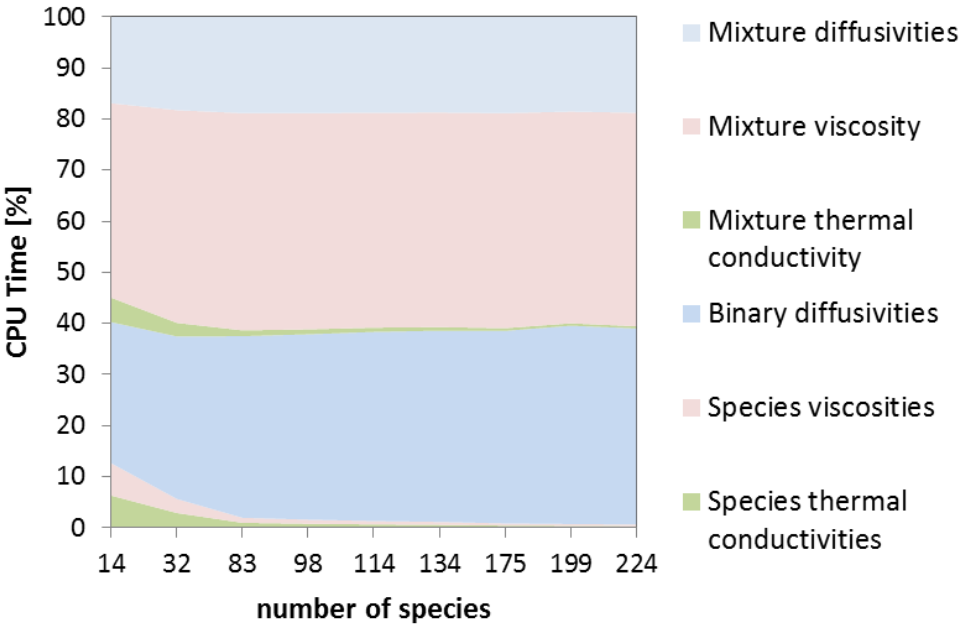
For each species and transport property, the coefficients of 4th order polynomial fitting described in previous slides are reported here (very large file!)

`kinetics.xml`

this is the only file needed by OpenSMOKE++ Suite solvers. It contains the pre-processed thermodynamic and transport data in XML format

Computational cost of transport properties





- The cost of evaluation of transport properties (in particular diffusion) increases **quadratically** with the number of species
- For large mechanisms (>100 species) the computational cost of transport properties is not negligible
- In fully-coupled methods proper techniques must be applied to **reduce the computational cost of transport properties** (they can be the **bottleneck** in evaluation of Jacobian matrix)

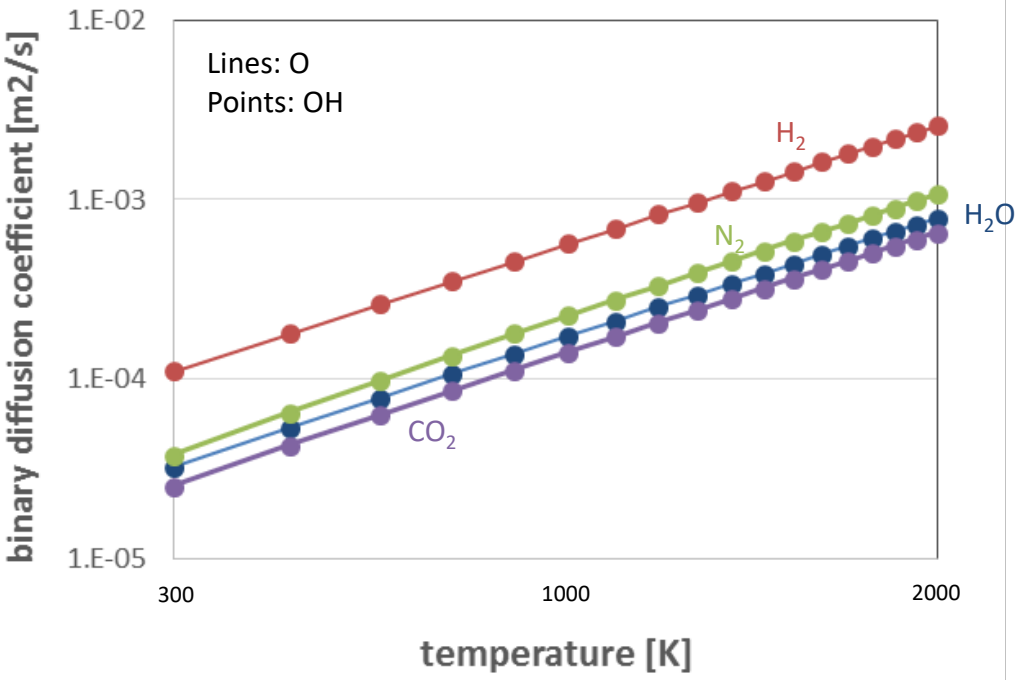
Species bundling (I)

This topic (species bundling will be covered in Lesson 4)

Many species possess similar diffusivities because of similar molecular properties (molecular weight, structure, collision cross section, etc.)

Such species are expected to behave similarly in terms of diffusive transport

The diffusivities of O and OH with other species are almost identical



Species with similar diffusivities can be bundled in a same group with a representative species

Lu, Law, *Diffusion coefficient reduction through species bundling*, Combustion and Flame, 148, p. 117-126 (2007)

Species bundling (II)

1. How to measure the similarity between species i and j?

Similarity of a pair of species

$$\epsilon_{i,j} = \max_{\substack{k=1,\dots,NC \\ T_{min}<T<T_{max}}} \left| \ln\left(\frac{\Gamma_{i,k}}{\Gamma_{j,k}}\right) \right|$$

Relative error induced by representing the species i by the species j
(i.e. a measure of how much species i and j are similar in terms of diffusion coefficients)

Given a user-specified threshold value ϵ, species I and j are considered similar if and only if $\epsilon_{i,j} < \epsilon$

Usually the binary diffusion coefficients are fitted with an N-th order polynomial

$$p\Gamma_{i,j} \approx e^{\sum_{n=0}^{N} a_{n,i,j} (\ln T)^n}$$

$$\epsilon_{i,j} = \max_{\substack{k=1,\dots,K \\ T_{min}<T<T_{max}}} \left| \sum_{n=0}^{N} \left(a_{n,i,k} - a_{n,j,k}\right) (\ln T)^n \right|$$

The pressure can be removed from the definition, since it is the same for all the species

Species bundling (III)

2. How to find the minimum number of groups?

NC x NC adjacency matrix

$$A_{i,j} = \begin{cases} 1 & if\ \epsilon_{i,j} < \epsilon \\ 0 & otherwise \end{cases}$$

Integer programming

Minimize: $\sum_{j=1}^{NC} x_i$

Each $x_i = 1$ indicates a group represented by the i-th species

The objective is to minimize the number of groups

Constraints:

$$\begin{cases} \sum_{j=1}^{NC} A_{i,j} x_j \geq 1 & i = 1, 2, \dots, K \\ x_i \in \{0, 1\} & i = 1, 2, \dots, K \end{cases}$$

Each species j must be represented at least by one group (i.e. by at least by one i species)

If a j species is represented by more than one i species, the i species ensuring the minimum error is chosen as the representative species

Task 2.3: pre-processing transport data

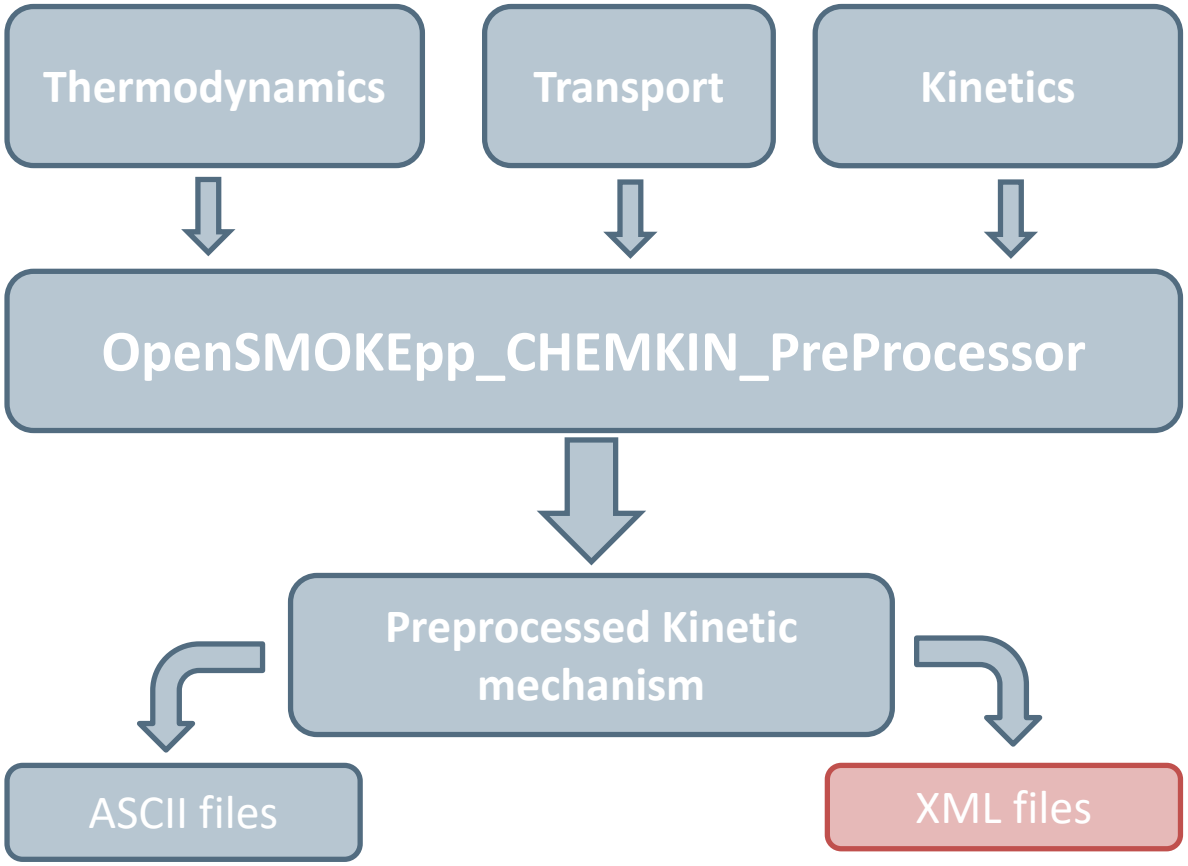
We want now to pre-process the transport properties by applying species bundling for future use in CPU expensive calculations. Go to the `Task2.3` folder. We add a new keyword.

```
Dictionary CHEMKIN_PreProcessor
{
  @Thermodynamics ../../KineticMechanisms/POLIMI_1412/Thermodynamics/POLIMI_TOT_NOX_1412.CKT;
  @Transport      ../../KineticMechanisms/POLIMI_1412/Transport/POLIMI_TOT_NOX_1412.TRC;
  @SpeciesBundling        true;
  @Output                 kinetics-POLIMI_TOT_NOX_1412;
}
```

`@SpeciesBundling`

The species bundling technique is applied in the pre-processing phase. Relevant data are written directly in the kinetics.xml file. The user will be free to use the species bundling in his simulations at different level of accuracy.

Task 3: pre-processing kinetic mechanisms



Objective: get familiar with the pre-processing operations and analysis of pre-processed results

Task: preprocess a complete kinetic mechanism (together with thermodynamics and transport properties)

We will use the POLIMI_H2CO_1412.CKI kinetic mechanism, describing the combustion chemistry of hydrogen and carbon monoxide (14 species and 33 reactions)

Remember that, in order to preprocess a kinetic mechanism, the thermodynamic properties are needed.

Task 3.1: pre-processing kinetic mechanisms

1. Preparation of input data

Go to the `Task3.1` folder, containing the `input.dic`. This file contains instructions for pre-processing the complete kinetic mechanism

```
Dictionary CHEMKIN_PreProcessor
{
  @Thermodynamics ../../KineticMechanisms/POLIMI_1412/Thermodynamics/POLIMI_TOT_NOX_1412.CKT;
  @Transport      ../../KineticMechanisms/POLIMI_1412/Transport/POLIMI_TOT_NOX_1412.TRC;
  @Kinetics       ../../KineticMechanisms/POLIMI_1412/Kinetics/POLIMI_H2CO_1412.CKI;
  @Output         kinetics-POLIMI_H2CO_1412;
}
```

`@Kinetics`

path to the file containing the transport data to be pre-processed (local or absolute paths are allowed)

Task 3.1: pre-processing kinetic mechanisms

2. Run the kinetic preprocessor

3. Analyze the pre-processing results

If everything was done properly, the `kinetics-POLIMI_H2CO_1412` output folder will be created, containing the following files (in addition to the usual files associated to thermodynamics):

`Kinetics_Summary.out`
This file simply contains the kinetic mechanism written in a more readable format

`kinetics.xml`
`reaction_names.xml`
these are the only file needed by OpenSMOKE++ Suite solvers. They contain the pre-processed thermodynamic (and transport) data together with the whole reaction mechanism in XML format

Task 3.2: pre-processing kinetic mechanisms

1. Refine the analysis

We can refine the analysis by performing additional tests to check the consistency of reactions or asking for additional data in output files

```
Dictionary CHEMKIN_PreProcessor
{
  @Thermodynamics ../../KineticMechanisms/POLIMI_1412/Thermodynamics/POLIMI_TOT_NOX_1412.CKT;
  @Transport      ../../KineticMechanisms/POLIMI_1412/Transport/POLIMI_TOT_NOX_1412.TRC;
  @Kinetics       ../../KineticMechanisms/POLIMI_1412/Kinetics/POLIMI_H2CO_1412.CKI;
  @Output                 kinetics-POLIMI_H2CO_1412;
  @ReactionTables         true;
  @ReverseFitting         true;
}
```

`@ReactionTables`

For each reaction detailed information is reported on a file (kinetic constants, change of moles, etc.)

`@ReverseFitting`

For each reversible reaction the reverse kinetic constants are estimated assuming the Arrhenius' law

Task 3.2: pre-processing kinetic mechanisms

2. Run the kinetic preprocessor

3. Analyze the pre-processing results

If everything was done properly, the `kinetics-POLIMI_H2CO_1412` output folder will be created, containing the following files (in addition to the files previously discussed):

`Reaction_Tables.out.out`
this file simply contains a tabulation of kinetic and equilibrium constants for each reaction, together with the corresponding reaction enthalpies

`Reaction_FittedKinetics.out`
For each reversible reaction, the reverse (or backward) kinetic constant is reported in the Arrhenius form

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Thermodynamic equilibrium

Objective: to determine the chemical state (i.e. temperature, pressure and composition) of a mixture under thermodynamic equilibrium conditions

The equilibrium state depends only on the **thermodynamic properties** of the species accounted for, as well as the **starting composition and conditions** specified. In particular, the starting composition determines the relative amount of chemical elements in the system.

Typically the state parameters can be specified in a number of different ways. The most common are reported below:

1. temperature and pressure
2. pressure and entropy
3. enthalpy and pressure
4. volume and entropy
5. …

Thermodynamic equilibrium calculation (I)

The basic theory for the element-potential method of determining equilibrium is based on the minimization of Gibb's free energy. The Gibb's function G of a system is:

$$G = \sum_{k=1}^{NS} \bar{g}_k N_k$$

where $\bar{g}_k$ is the partial molar Gibb's function and N_k is the number of moles of each species in the system. NS is the total number of species.

For ideal-gas mixtures or ideal solutions, the partial molar Gibb's functions are given by:

$$\bar{g}_k = g_k(T, P) + RTlnX_k$$

where $g_k(T, P)$ is the Gibb's function for the pure species k, evaluated at the system temperature and pressure; R is the universal gas constant; and X_k is the mole fraction of the k species.

Thermodynamic equilibrium calculation (II)

The equilibrium solution at a given temperature and pressure is the distribution of N_k that minimizes the system Gibb's function G, subject to atomic population constraints (and non-negative N_k). The atomic population constraints are:

$$\sum_{k=1}^{NS} n_{jk} N_k = p_j \qquad j = 1, \dots, NE$$

where n_{jk} is the number of the j atoms that appear in the k molecule, is the total population in moles of the j atom in the system, and NE is the total number of different elements that are present in the system.

Several numerical techniques can be used to solve the constrained minimization problem. The one adopted in OpenSMOKE++ is described here:

Pope S.B., *Gibbs function continuation for the computation of chemical equilibrium*, Combustion and Flame 139, p. 222-226 (2004)

Adiabatic flame temperature

- The **adiabatic flame temperature** is a measure of the maximum temperature that could be reached by combusting a particular gas mixture under a specific set of conditions.
- In a real system which includes heat losses, chemical kinetic and/or mass transport limitations, the flame temperature is likely to be lower than the adiabatic flame temperature.
- **Thermodynamic equilibrium** calculations can be conveniently adopted to determine the adiabatic flame temperatures for combustible gas mixtures.
- Such a estimation can be carried out by specifying an initial (reagent) gas mixture and constraining equilibrium for constant enthalpy (adiabatic) and constant pressure.
- The calculation can also be performed using constant internal energy and constant volume.

Task 4.1: Adiabatic flame temperature of H_2 (I)

Objective: to calculate the adiabatic flame temperature and the corresponding composition for an initial mixture of H2 and air (stoichiometric conditions) at ambient temperature (300 K)

As a first step we will carry put our calculation using the minimum number of species to have a sufficiently accurate result:

H2	O2	H2O	H2O2
OH	H	O	HO2
N2			

It is important to include all likely radical species as well as stable species in the product list so as to obtain an accurate flame temperature prediction.

it is better to include many unimportant species than to leave out species that may turn out to be important.

Task 4.1: Adiabatic flame temperature of H_2 (II)

1. Selection of thermodynamic data

The first step is the preprocessing of thermodynamic data. Remember that in thermodynamic equilibrium calculations only thermodynamic data are needed.
As usual we will use the POLIMI_TOT_NOX_1412 database, which includes more than 400 species.

However, we want to perform the calculation considering only the 9 species reported in the previous slides. The list of relevant species can be provided through a kinetic mechanism: obviously, the reactions included in it, will be completely ignored during the thermodynamic equilibrium calculations. The only relevant information is the list of species.

Thermodynamics:
`KineticMechanisms/POLIMI_1412/Thermodynamics/POLIMI_TOT_NOX_1412.CKT`

List of species:
`KineticMechanisms/POLIMI_1412/Kinetics/POLIMI_H2_1412.CKI`

Task 4.1: Adiabatic flame temperature of H_2 (III)

2. Pre-processing of thermodynamic data

Go to the `Task4.1` folder, containing the `input.preprocessing.dic` file. This file contains instructions for pre-processing the thermodynamic data.

```
Dictionary CHEMKIN_PreProcessor
{
  @Thermodynamics ../../KineticMechanisms/POLIMI_1412/Thermodynamics/POLIMI_TOT_NOX_1412.CKT;
  @Kinetics       ../../KineticMechanisms/POLIMI_1412/Kinetics/POLIMI_H2_1412.CKI;
  @Output         kinetics-POLIMI_H2_1412;
}
```

Remember that the only relevant information contained in the kinetic file is the list of species. The reactions contained in it are not used for equilibrium calculations.

The preprocessing is carried out by the `OpenSMOKEpp_CHEMKIN_PreProcessor` utility.

Task 4.1: Adiabatic flame temperature of H_2 (IV)

2. Preparing the input for thermodynamic equilibrium

The `Task4.1` folder contains also the `input.equilibrium.dic` file, containing instructions for performing the desired thermodynamic equilibrium calculation/analysis.

```
Dictionary Equilibrium
{
        @KineticsFolder   kinetics-POLIMI_H2_1412;
        @Type             Fixed_H_P;
        @InitialStatus    initial-status;
}

Dictionary initial-status
{
        @Temperature      300. K;
        @Pressure         1 atm;
        @Moles            H2 2 O2 1 N2 3.76;
}
```

Main Dictionary, specifying the type of equilibrium calculation and the location of pre-processed data

Dictionary specifying the initial conditions of the mixture

Task 4.1: Adiabatic flame temperature of H_2 (V)

3. Run the thermodynamic equilibrium calculation

Always from the same `Task4.1` folder, we can now run the `OpenSMOKEpp_ThermodynamicEquilibrium` utility.

a) Windows

Run the `Run.equilibrium.bat` file by double-clicking on it or, from the Command Prompt, type:

```
"%OPENSMOKEPP_EXE_FOLDER%\OpenSMOKEpp_ThermodynamicEquilibrium.exe" --
input input.equilibrium.dic
```

b) Linux and Mac OSX

Run the `Run.sh` file of, from the command line, type:

```
OpenSMOKEpp_ThermodynamicEquilibrium.sh --input input.equilibrium.dic
```

Task 4.1: Adiabatic flame temperature of H_2 (VI)

4. Look at the results

Results are written in the `Output` folder.

```
-------------------------------------------------------------------------------
Status                          Initial             Equilibrium
-------------------------------------------------------------------------------
T[K]                            300.000             2388.426
P[atm]                          1.00000             1.00000
rho[kg/m3]                      0.84947             0.12384
MW[kg/kmol]                     20.91163            24.27152
H[J/kg]                         2.868106e+03        2.868106e+03
U[J/kg]                         -1.164118e+05       -8.153123e+05
Conv.(%) H2                     0.000e+00           9.572e+01
Conv.(%) O2                     0.000e+00           9.680e+01
Conv.(%) N2                     0.000e+00           3.040e-12
Element H                       2.829602e-02        2.829602e-02
Element O                       1.414801e-02        1.414801e-02
Element N                       5.319652e-02        5.319652e-02
-------------------------------------------------------------------------------
...
```

Task 4.1: Adiabatic flame temperature of H_2 (VII)

4. Look at the results

Results are written in the `Output` folder.

```
-------------------------------------------------------------------------
Mole fractions                 Initial              Equilibrium
-------------------------------------------------------------------------
H2                             2.958580e-01         1.470587e-02
O2                             1.479290e-01         5.494131e-03
H2O                            0.000000e+00         3.237540e-01
H2O2                           0.000000e+00         1.358275e-07
H                              0.000000e+00         1.815824e-03
O                              0.000000e+00         5.983708e-04
OH                             0.000000e+00         8.050260e-03
HO2                            0.000000e+00         1.259119e-06
HE                             0.000000e+00         0.000000e+00
AR                             0.000000e+00         0.000000e+00
N2                             5.562130e-01         6.455801e-01
-------------------------------------------------------------------------
...
```

Task 4.2: NOX at equilibrium (I)

Objective: to calculate the amount of NOX corresponding to thermodynamic equilibrium conditions for an initial mixture of H2 and air (stoichiometric conditions) at ambient temperature (300 K)

The type of problem we want to face is exactly the same we already considered in the previous step. The only difference is that we need now to include additional species relevant for NOX to the list of 9 species previously adopted:

NO	NO2	N2O	HNO	HNNO	HONO
NNH	NH2	H2NO	HNO2	HONO2	N2H2
N2H3	NH3	N2H4N	NO3	NH	

Thermodynamics:
`KineticMechanisms/POLIMI_1412/Thermodynamics/POLIMI_TOT_NOX_1412.CKT`

List of species:
`KineticMechanisms/POLIMI_1412/Kinetics/POLIMI_H2_NOX_1412.CKI`

Task 4.2: NOX at equilibrium (II)

Results

Status	Initial	Equilibrium
T[K]	300.000	**2381.402**
P[atm]	1.00000	1.00000
rho[kg/m3]	0.84947	0.12419
MW[kg/kmol]	20.91163	24.26794
H[J/kg]	2.868106e+03	2.868107e+03
U[J/kg]	-1.164118e+05	-8.130266e+05
Conv.(%) H2	0.000e+00	9.553e+01
Conv.(%) O2	0.000e+00	9.728e+01
Conv.(%) N2	0.000e+00	2.030e-01
Element H	2.829602e-02	2.829602e-02
Element O	1.414801e-02	1.414801e-02
Element N	5.319652e-02	5.319652e-02

...

The adiabatic flame temperature is only $\sim 7\ K$ lower than previous calculations. As expected, NOX play a marginal role on combustion

Task 4.2: NOX at equilibrium (III)

Results

Mole fractions	Initial	Equilibrium
...		
NO	**0.000000e+00**	**2.620187e-03**
NO2	**0.000000e+00**	**3.621134e-07**
N2O	**0.000000e+00**	**1.184133e-07**
HNO	0.000000e+00	1.402304e-07
HNNO	0.000000e+00	1.102159e-13
HONO	0.000000e+00	1.278343e-08
NNH	0.000000e+00	4.283166e-09
NH2	0.000000e+00	7.098777e-09
H2NO	0.000000e+00	1.053438e-10
HNO2	0.000000e+00	5.654883e-10
HONO2	0.000000e+00	2.695567e-13
N2H2	0.000000e+00	2.327617e-13
N2H3	0.000000e+00	6.448474e-16
NH3	0.000000e+00	1.889622e-08
N2H4	0.000000e+00	1.791543e-18
N	0.000000e+00	7.355917e-08
NO3	0.000000e+00	1.279334e-13
NH	0.000000e+00	1.669518e-08
...		

Task 5.1: Adiabatic flame temperature vs ϕ (I)

Objective: we want to calculate the adiabatic flame temperature and the amount of NO (at equilibrium) as a function of equivalence ratio for a mixture of H2 and air at ambient temperature

We adopt the same list of species used in the previous step:

H2	O2	H2O	H2O2		
OH	H	O	HO2		
NO	NO2	N2O	HNO	HNNO	HONO
NNH	NH2	H2NO	HNO2	HONO2	N2H2
N2H3	NH3	N2H4N	NO3	NH	
N2					

Thermodynamics:
`KineticMechanisms/POLIMI_1412/Thermodynamics/POLIMI_TOT_NOX_1412.CKT`

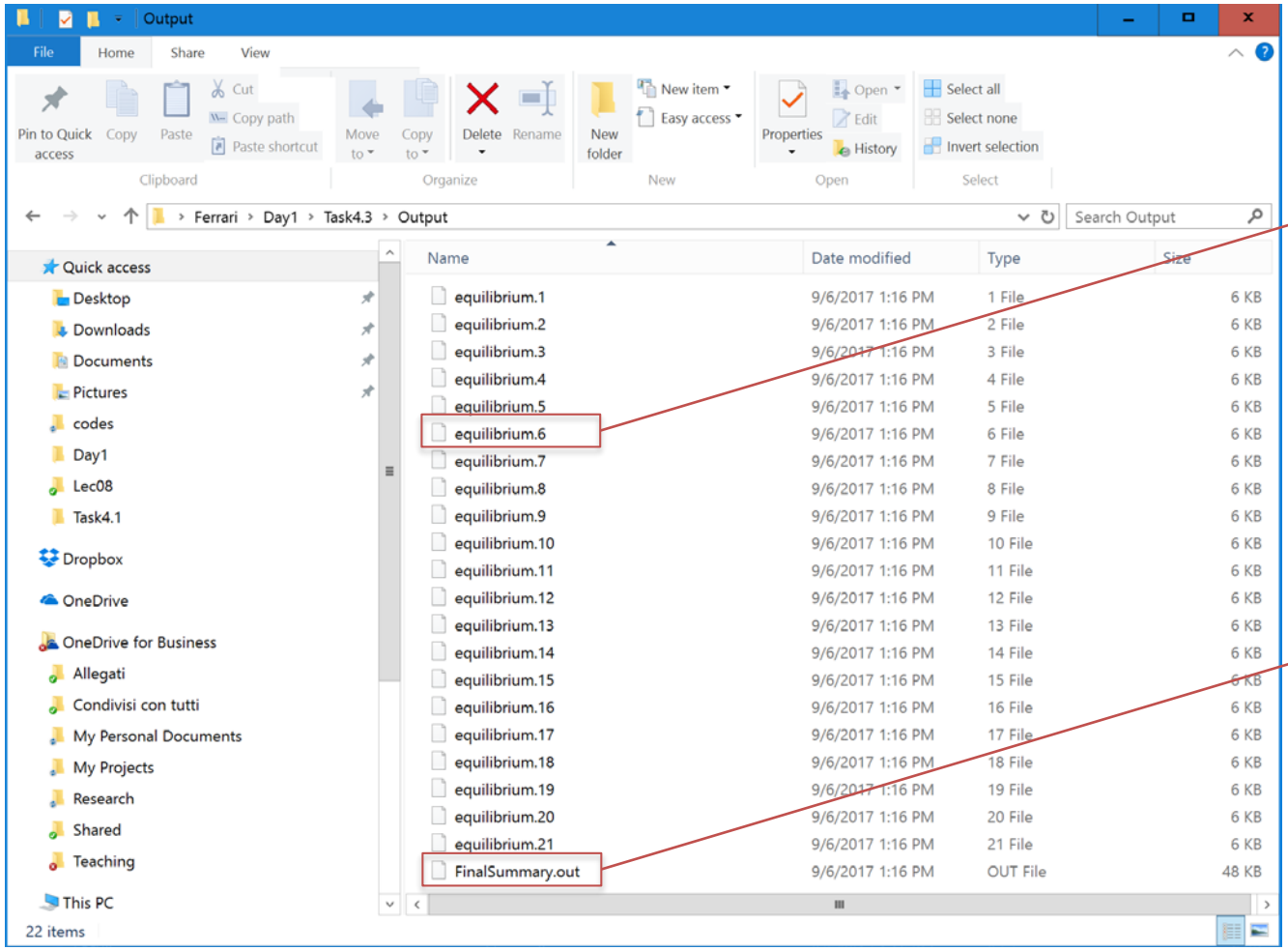
List of species:
`KineticMechanisms/POLIMI_1412/Kinetics/POLIMI_H2_NOX_1412.CKI`

Task 5.1: Adiabatic flame temperature vs ϕ (II)

Instead of performing the analysis by hand, i.e. for single equivalence ratios, we can ask OpenSMOKE++ to carry out this operation automatically, by specifying the list of equivalence ratios we are interested in:

```
Dictionary Equilibrium
{
        @KineticsFolder             kinetics-POLIMI_H2_NOX_1412;
        @Type                       Fixed_H_P;
        @InitialStatus              initial-status;
}

Dictionary initial-status
{
        @Temperature                300. K;
        @Pressure                   1 atm;
        @EquivalenceRatio           0.5  0.55 0.60 0.65 0.70 0.75 0.80
                                    0.85 0.90 0.95 1.00 1.05 1.10 1.15
                                    1.20 1.25 1.30 1.35 1.40 1.45 1.50;

        @FuelMoleFractions          H2 1;
        @OxidizerMoleFractions      N2 0.79 O2 0.21;
}
```

Task 5.1: Adiabatic flame temperature vs ϕ (III)

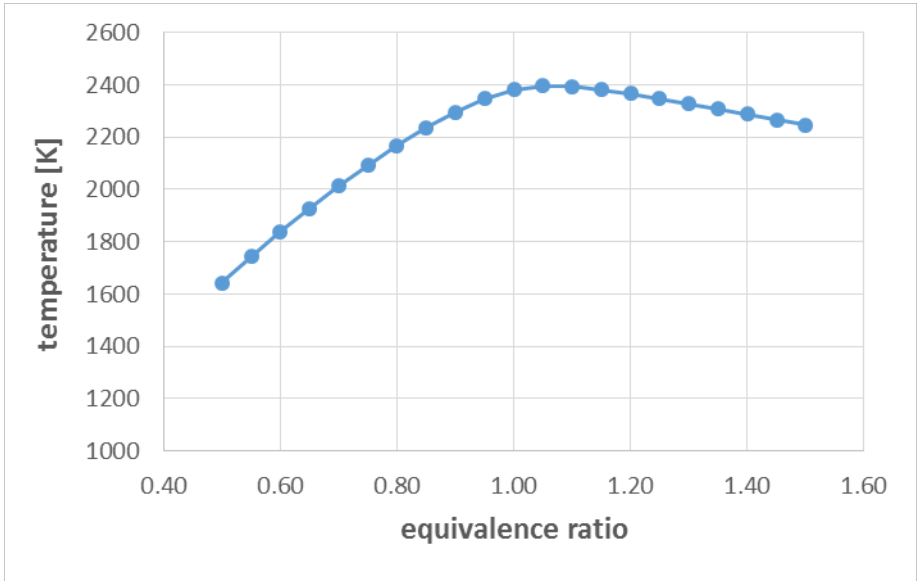


For each equivalence ratio, details are reported in a single file (numbered from 1 to N)

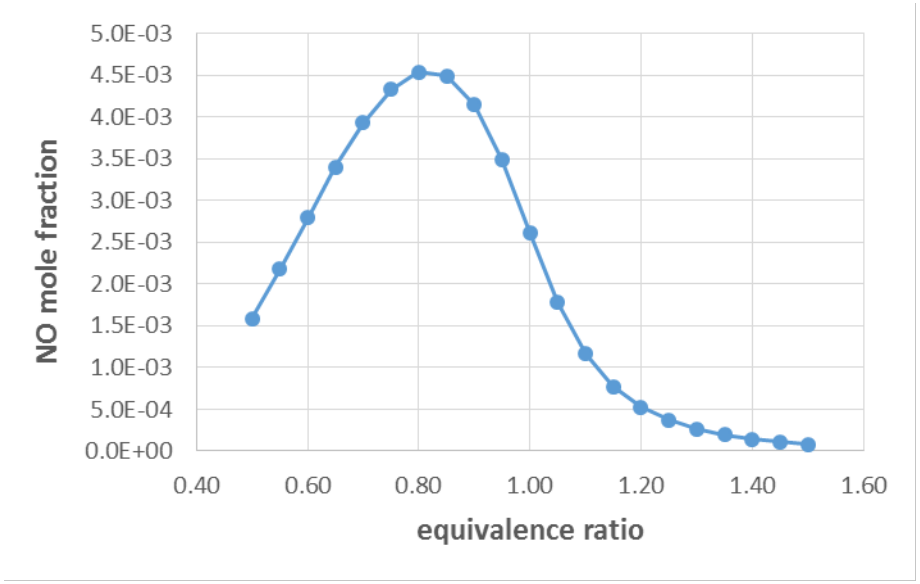
The results are also collected in a single file, which is very convenient for analysis or post-processing of data

Task 5.1: Adiabatic flame temperature vs ϕ (IV)

Adiabatic flame temperature



NO mole fraction



Task 5.2: Adiabatic flame temperature vs ϕ (I)

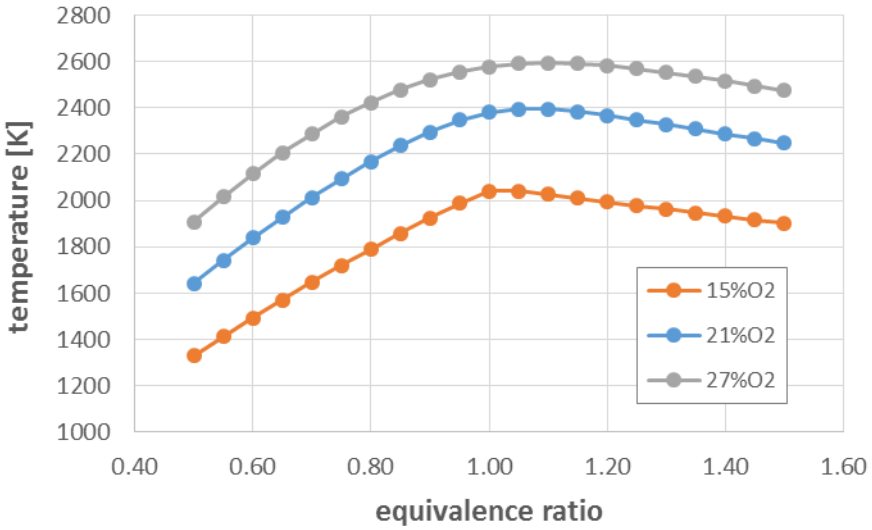
Now we want to study how the thermodynamic conditions (temperature and NO mole fractions) are affected by the amount of O_2 in air. In particular, we want to study two different air mixtures:

- O_2 15% + N_2 85%
- O_2 27% + N_2 73%

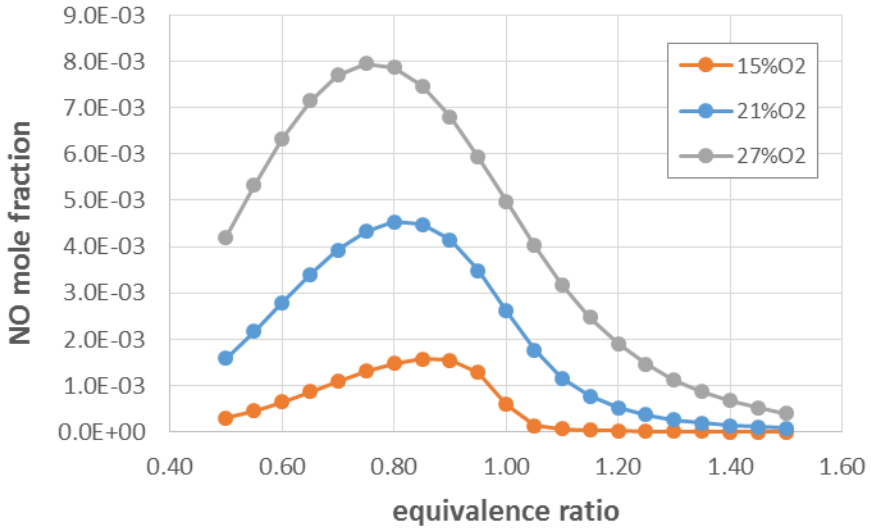
```
Dictionary initial-status
{
        @Temperature                300. K;
        @Pressure                   1 atm;
        @EquivalenceRatio           0.5  0.55 0.60 0.65 0.70 0.75 0.80
                                    0.85 0.90 0.95 1.00 1.05 1.10 1.15
                                    1.20 1.25 1.30 1.35 1.40 1.45 1.50;

        @FuelMoleFractions          H2 1;
        @OxidizerMoleFractions      N2 0.85 O2 0.15;
}
```

Task 5.2: Adiabatic flame temperature vs ϕ (II)

Adiabatic flame temperature



NO mole fraction



Task 6.1: Adiabatic flame temperature (I)

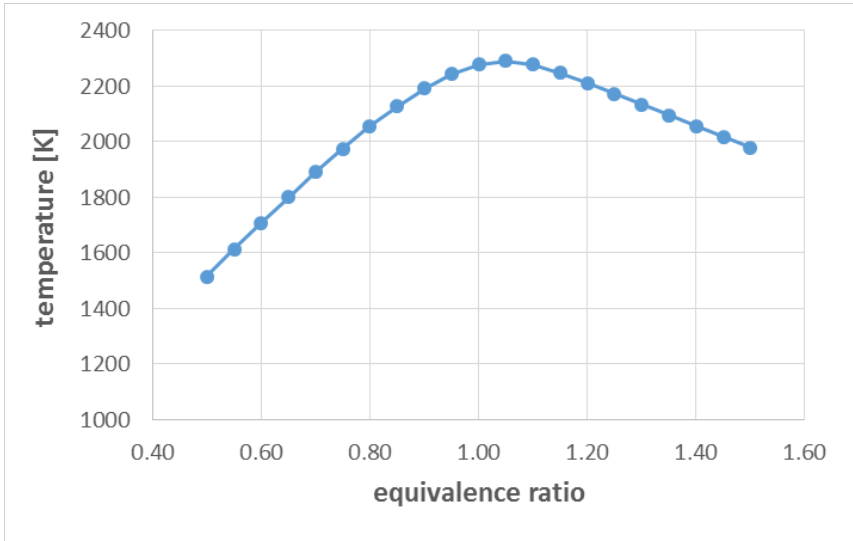
Objective: we want to calculate the adiabatic flame temperature as a function of equivalence ratio for n-heptane in air at initial ambient temperature

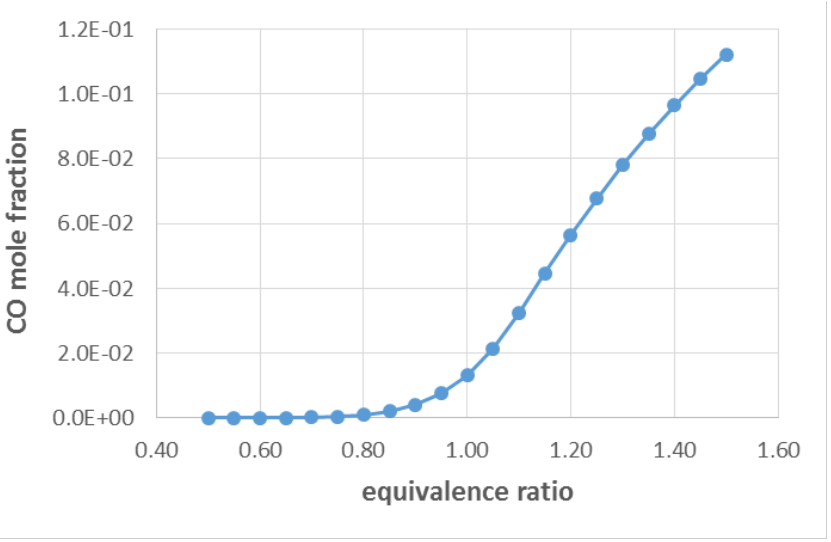
In order to have accurate calculations, we have to include now all the relevant species for n-heptane. The simplest choice consist in taking advantage of one of the available kinetic mechanisms from CRECK Modeling:

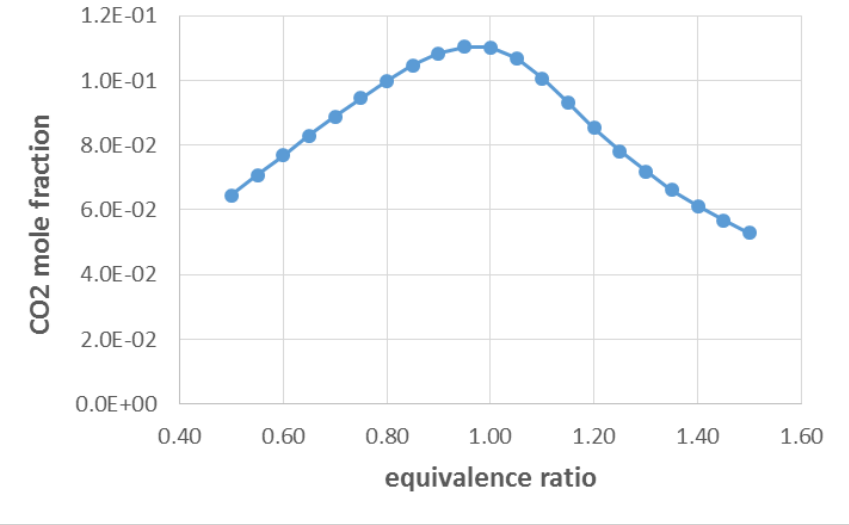
Thermodynamics:
`KineticMechanisms/POLIMI_1412/Thermodynamics/POLIMI_TOT_NOX_1412.CKT`

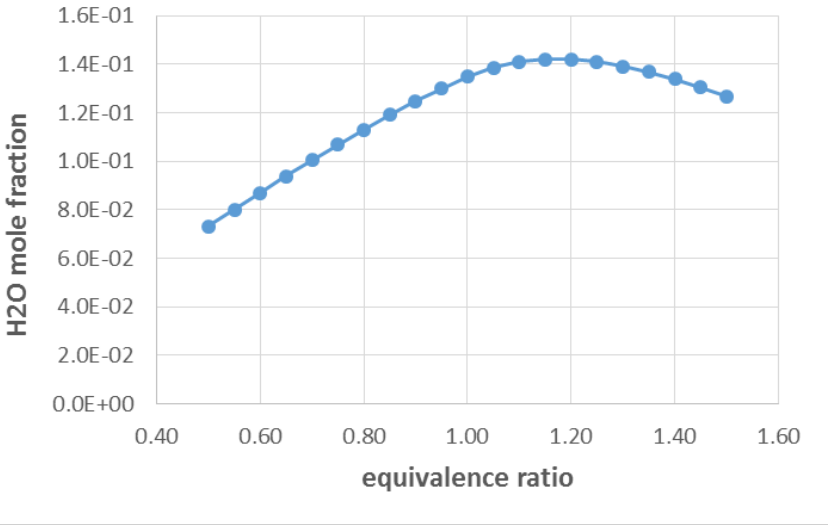
List of species:
`KineticMechanisms/POLIMI_1412/Kinetics/POLIMI_PRF_PAH_RFUELS_HT_1412.CKI`

Task 6.1: Adiabatic flame temperature (II)









Task 6.2: Adiabatic flame temperature (I)

Objective: now we want to refine our analysis by simulating the presence of a possible EGR (Exaust Gas Recirculation) in the initial mixture. In particular we want to consider (in addition to the case without EGR simulated in Task 6.1) two conditions:

- EGR = 10%
- EGR = 20%

First of all we have to evaluate the composition of exhaust gases. For simplicity, we just assume a global reaction with CO_2 and H_2O as final products:

$$C_7H_{16} + 11O_2\ (+41.38N_2) \rightarrow 7CO_2 + 8H_2O\ (+41.38N_2)$$

Thus, the molar composition of exhaust gases become:

$$\begin{cases} X_{CO2} = 0.1241 \\ X_{H2O} = 0.1418 \\ X_{N2} = 0.7339 \end{cases}$$

Task 6.2: Adiabatic flame temperature (II)

Once we fixed the EGR, on the basis of exhaust gases composition, we can calculate the composition of air mixture (including exhaust gases) to be mixed to the fuel. For simplicity, here we consider the EGR on a molar basis. Since the molecular weight of the exhaust gas mixture (28.58 kg/kmol) is very similar to the molecular weight of regular air (28.85 kg/kmol), we can see that the difference in considering the EGR on a mass basis is around 1%.

Thus, the composition of air mixture accounting for exhaust gases, is:

EGR = 10%

$$\begin{cases} X_{CO2} = 0.01241 \\ X_{H2O} = 0.01419 \\ X_{O2} = 0.189 \\ X_{N2} = 0.7844 \end{cases}$$

EGR = 20%

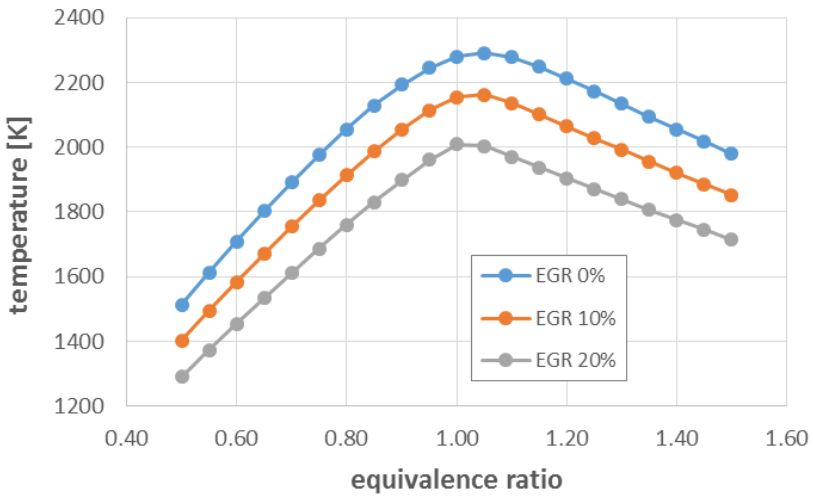
$$\begin{cases} X_{CO2} = 0.02483 \\ X_{H2O} = 0.02838 \\ X_{O2} = 0.168 \\ X_{N2} = 0.7788 \end{cases}$$

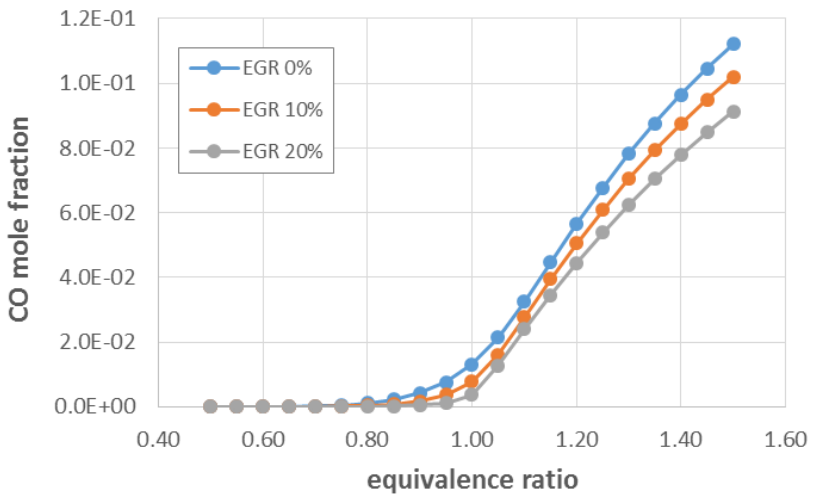
Task 6.2: Adiabatic flame temperature (III)

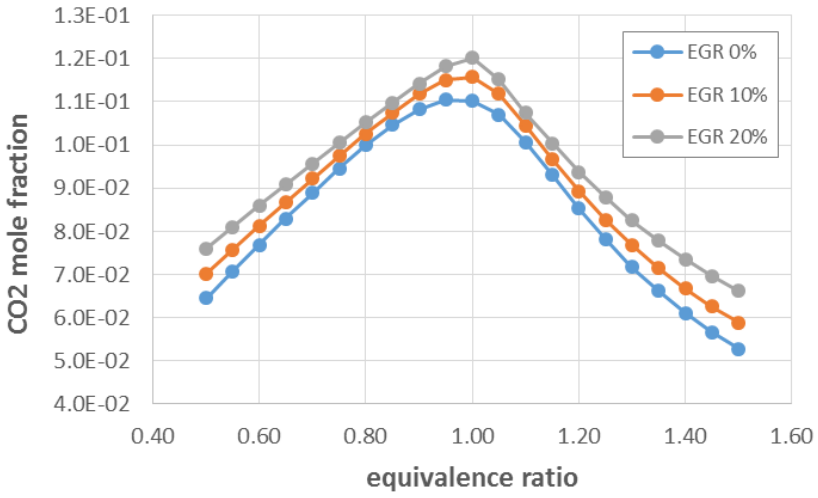
We are now ready to simulate the cases corresponding to the 2 different EGRs. We just need to change (with respect to Task 6.1, corresponding to no EGR) the composition of oxidizer mixture, according to the results reported in the previous slide.

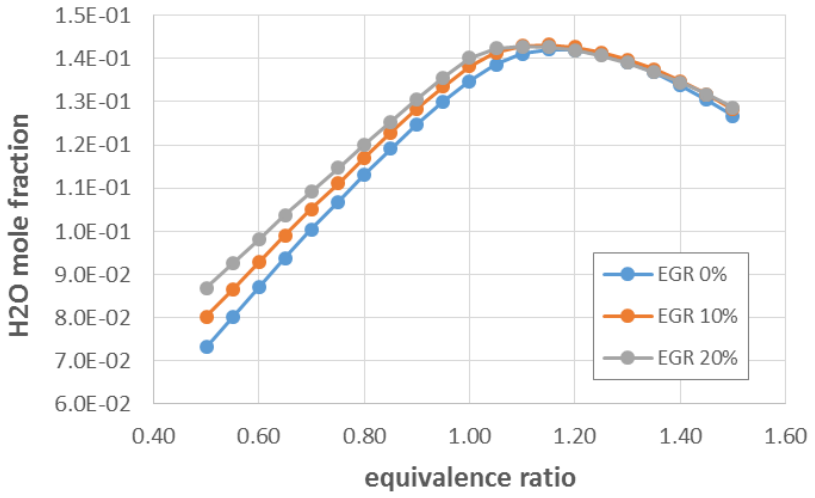
```
Dictionary initial-status
{
        @Temperature                300. K;
        @Pressure                   1 atm;
        @EquivalenceRatio           0.5  0.55 0.60 0.65 0.70 0.75 0.80
                                    0.85 0.90 0.95 1.00 1.05 1.10 1.15
                                    1.20 1.25 1.30 1.35 1.40 1.45 1.50;

        @FuelMoleFractions                  NC7H16 1.00;

        // EGR: 10%
        @OxidizerMoleFractions      N2  0.78439527  O2  0.189
                                    CO2 0.012415541 H2O 0.014189189;
}
```

Task 6.2: Adiabatic flame temperature (IV)









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Web: https://www3.nd.edu/~powers/ame.60636/chemkin2000.pdf

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Web: https://www3.nd.edu/~powers/ame.60636/transport.pdf

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Cuoci, A., Frassoldati, A., Faravelli, T., Ranzi, E. *Numerical modeling of laminar flames with detailed kinetics based on the operator-splitting method* (2013) Energy and Fuels, 27 (12), pp. 7730-7753, DOI: 10.1021/ef4016334

Cuoci, A., Frassoldati, A., Faravelli, T., Ranzi, E. *A computational tool for the detailed kinetic modeling of laminar flames: Application to C2H4/CH4 coflow flames* (2013) Combustion and Flame, 160 (5), pp. 870-886, DOI: 10.1016/j.combustflame.2013.01.011

M.Maestri, A.Cuoci, *Coupling CFD with detailed microkinetic modeling in heterogeneous catalysis,* Chemical Engineering Science 96(7), pp. 106-117 (2013) DOI: 10.1016/j.ces.2013.03.048