POLITECNICO DI MILANO
Department of Chemistry, Materials,
and Chemical Engineering “G. Natta”

Alberto Cuoci

TECHNICAL UNIVERSITY OF DENMARK
Department of Chemical and
Biochemical Engineering

Peter Glarborg

Exercise 1
Introduction to detailed kinetic mechanisms

Combustion Fundamentals and New Technologies

Conservatorio delle Orfane a Terra Murata
Isola di Procida, Napoli, Italy
May 31 – June 5, 2015

Setting up your problem

1. Prepare your thermodynamic/kinetic/transport files and pre-process them

2. Choose the most appropriate reactor model to describe your system
   For some problems the choice of reactor model is obvious. In other cases, you may have different options and the choice is not so easy. As an example, in some cases a single, a perfectly stirred reactor may be the sufficient, while in other cases your system must be described using a network of reactors.

3. Setup the reactor parameters and inlet/initial conditions
   Each type of reactors has specific parameters (residence time, volume, length, etc.) which have to properly setup by the user.

4. Setup the numerical parameters
   In some cases the correct setup of numerical parameters (tolerances, stopping criteria, mesh strategy, etc) is of fundamental importance to correctly solve the problem

5. Run the simulation

6. Analyze your results
   You may consider different tools (native graphical post-processor, 3rd party tools, analysis of text files, etc.)

Setting up your problem

1. Prepare your thermodynamic/kinetic/transport files and pre-process them

2. Choose the most appropriate reactor model to describe your system
   For some problems the choice of reactor model is obvious. In other cases, you may have different options and the choice is not so easy. As an example, in some cases a single, a perfectly stirred reactor may be the sufficient, while in other cases your system must be described using a network of reactors.

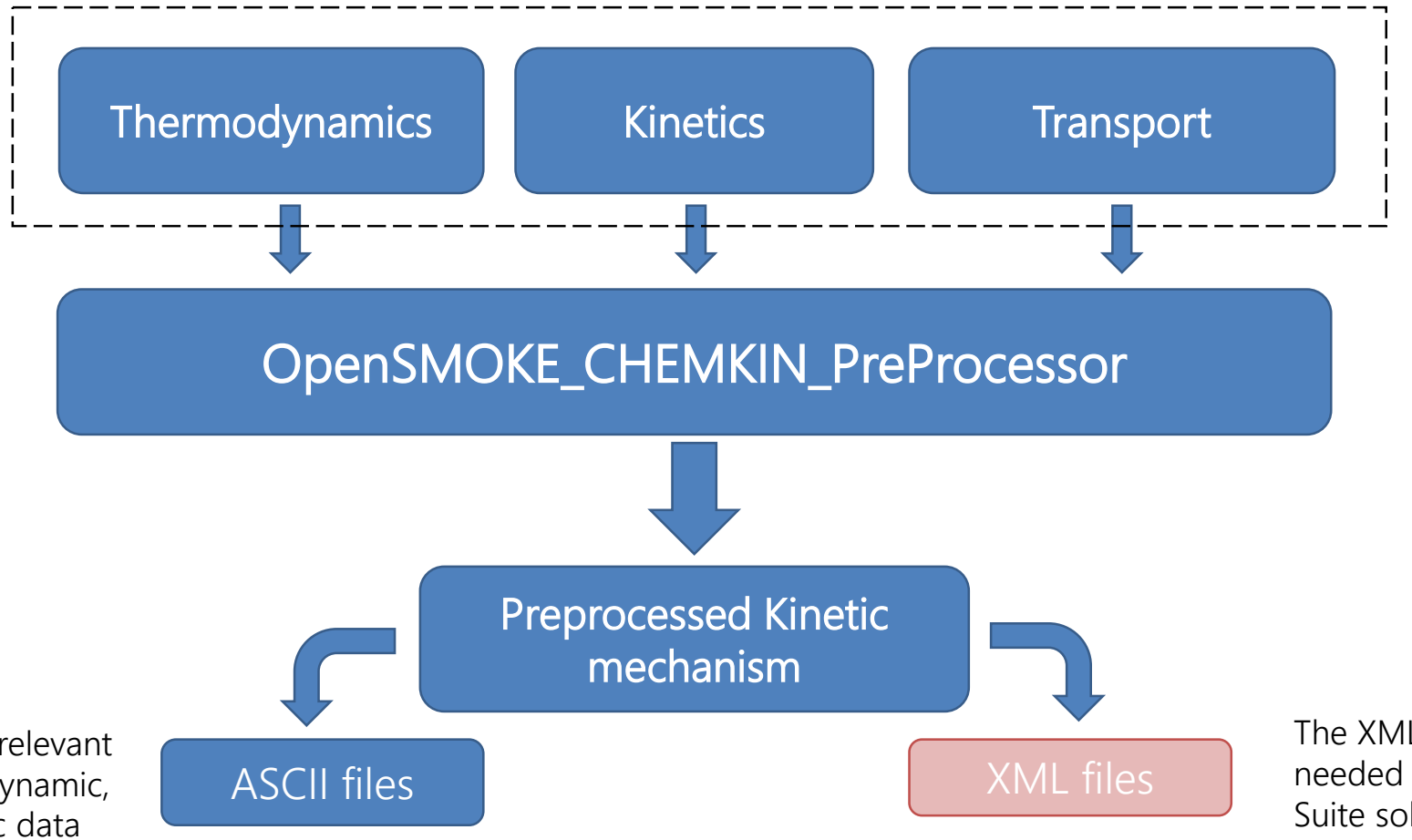
3. Setup the reactor parameters and inlet/initial conditions
   Each type of reactors has specific parameters (residence time, volume, length, etc.) which have to properly setup by the user.

4. Setup the numerical parameters
   In some cases the correct setup of numerical parameters (tolerances, stopping criteria, mesh strategy, etc) is of fundamental importance to correctly solve the problem

5. Run the simulation

6. Analyze your results
   You may consider different tools (native graphical post-processor, 3rd party tools, analysis of text files, etc.)

Kinetic pre-processing in OpenSMOKE++



files in CHEMKIN format

These files contains relevant data about thermodynamic, transport and kinetic data

The XML files are the only files needed by OpenSMOKE++ Suite solvers

Thermodynamics: NASA coefficients

Users must first supply the thermodynamic data for each species in the chemical system. These data are in the form of polynomial fits to temperature, for species enthalpy, entropy, and specific heat capacity.

$$\frac{C_P}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

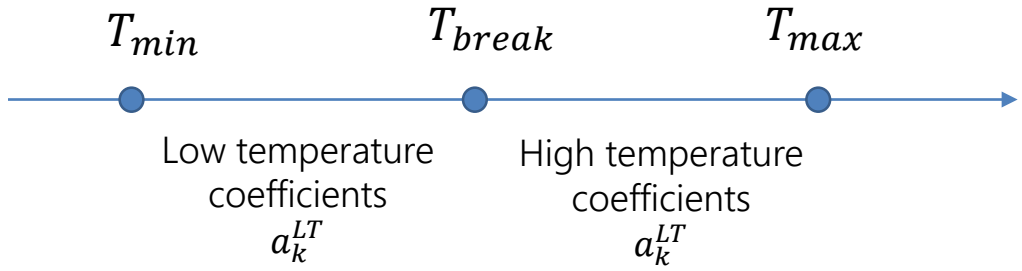
$$\frac{H}{RT} = a_1 + \frac{a_2}{2} T + \frac{a_3}{3} T^2 + \frac{a_4}{4} T^3 + \frac{a_5}{5} T^4 + \frac{a_6}{T}$$

$$\frac{S}{R} = a_1 lnT + a_2 T + \frac{a_3}{2} T^2 + \frac{a_4}{3} T^3 + \frac{a_5}{4} T^4 + a_7$$

7 coefficients are required to completely characterize the thermodynamic properties of each species
Additional thermodynamic quantities (free Gibbs energy, Helmotz energy, internal energy, etc.) can be evaluated from enthalpy, entropy, and specific heat capacity reported on the left

In order to ensure higher accuracy in the evaluation of thermodynamic properties, two sets of NASA coefficients are usually accounted for, by dividing the temperature field in 2 ranges

This means that each species is completely characterized by a total of 14 NASA coefficients



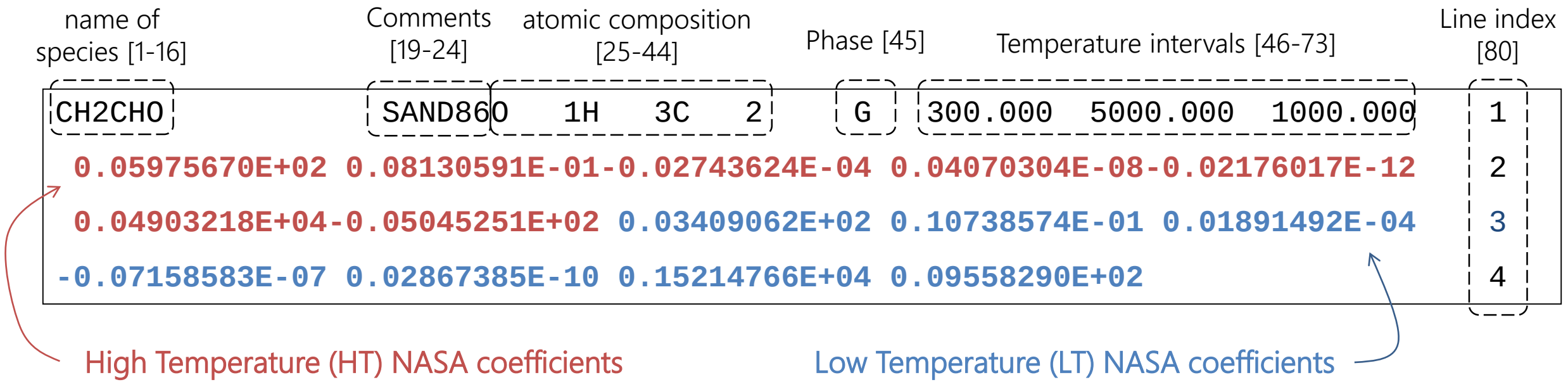
Thermodynamic input file

the first line specifies that the following is a set of thermodynamic data, while the second line provides the three temperatures used in the fitting process (low temperature, break temperature, and high temperature).

```
THERMO ALL
300.000 1000.000 5000.000

CH2CHO             SAND86O   1H   3C   2     G   300.000  5000.000  1000.000     1
 0.05975670E+02 0.08130591E-01-0.02743624E-04 0.04070304E-08-0.02176017E-12    2
 0.04903218E+04-0.05045251E+02 0.03409062E+02 0.10738574E-01 0.01891492E-04    3
-0.07158583E-07 0.02867385E-10 0.15214766E+04 0.09558290E+02                   4
AL                  62987AL  1                G   300.000  5000.000  1000.000     1
 0.02559589E+02-0.10632239E-03 0.07202828E-06-0.02121105E-09 0.02289429E-13    2
 0.03890214E+06 0.05234522E+02 0.02736825E+02-0.05912374E-02-0.04033937E-05    3
 0.02322343E-07-0.01705599E-10 0.03886794E+06 0.04363879E+02                   4
(CH2O)3             70590C   3H   6O   3     G   300.00   4000.00   1500.00     1
 0.01913678E+03 0.08578044E-01-0.08882060E-05-0.03574819E-08 0.06605142E-12    2
-0.06560876E+06-0.08432507E+03-0.04662286E+02 0.06091547E+00-0.04710536E-03    3
 0.01968843E-06-0.03563271E-10-0.05665403E+06 0.04525264E+03                   4
END
```

Thermodynamic data: CHEMKIN format



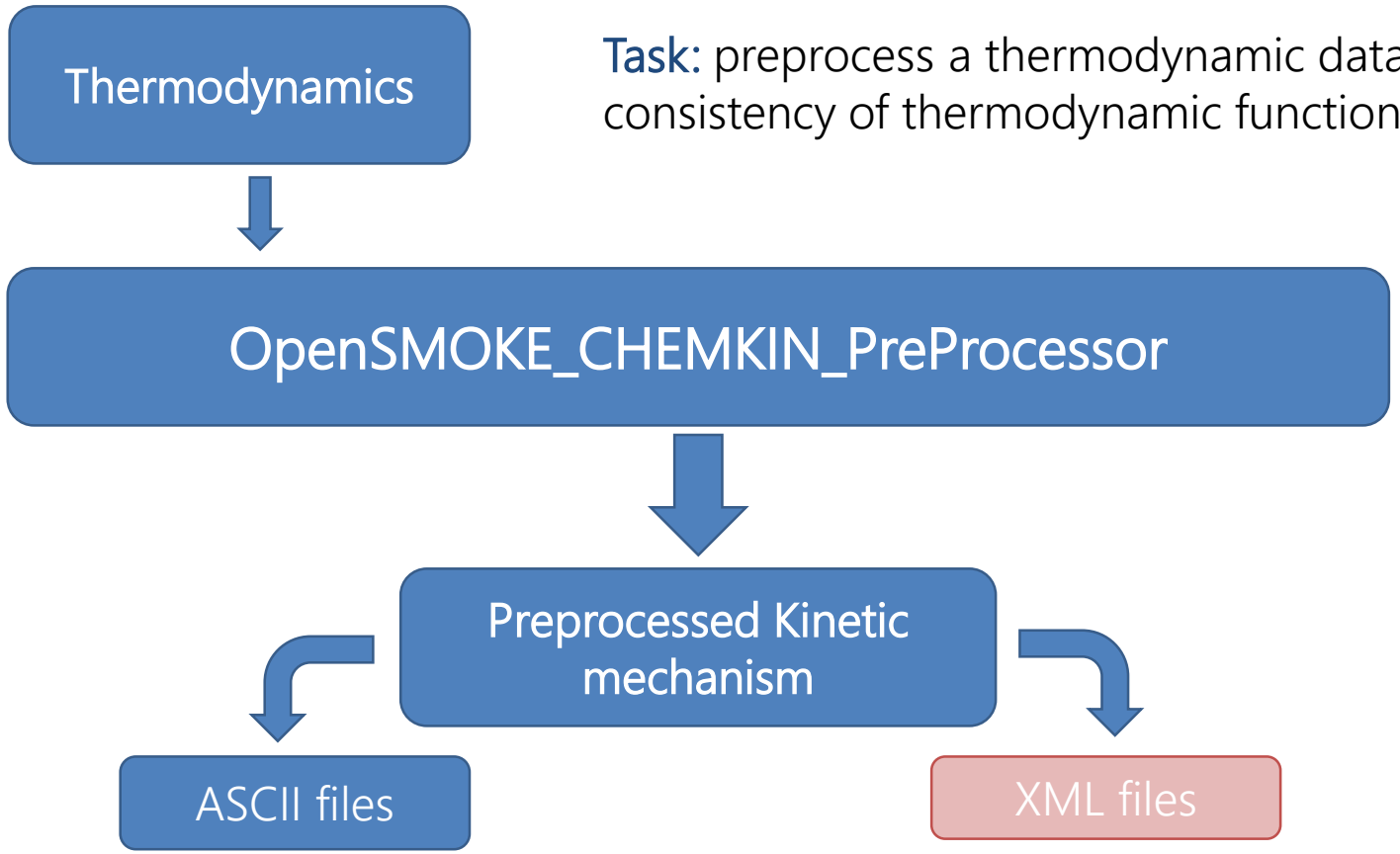
Very strict syntax rules apply:

1. The data for each species requires 4 formatted lines of length 80 characters.
2. The data on the first line must be properly formatted, in fields with predefined length
3. The 7 HT NASA coefficients must be followed by the 7 LT NASA coefficients
4. The NASA coefficients have to be written in blocks of 15 chars

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 result, 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.

This is the database shared by every kinetic scheme from CRECK modeling. It is based on data available in the literature, NIST and Burcat's databases

Task 1: pre-processing thermodynamic data

1. Preparation of input data

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

```
Dictionary CHEMKIN_PreProcessor
{
        @Thermodynamics         ../../Kinetics/POLIMI_TOT_NOX_1412.CKT;
        @Output                 thermodynamics;
}
```

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

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

Task 1: pre-processing thermodynamic data

2. Run the kinetic preprocessor

From the same `Tasks/Task1` folder, run the `OpenSMOKE_CHEMKIN_PreProcessor` utility.

a) Windows

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

```
%OPENSMOKEPP_EXE_FOLDER%\OpenSMOKE_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.exe --input input.dic
```

Task 1: pre-processing thermodynamic data

3. Analyze the pre-processing results

If everything was done properly, the `thermodynamics` 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: 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

```
Dictionary CHEMKIN_PreProcessor
{
        @Thermodynamics         ../../Kinetics/POLIMI_TOT_NOX_1412.CKT;
        @Output                 thermodynamics;
        @CheckThermodynamics    true;
}
```

Additional file will be written:

`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 perfect thermodynamic consistency

Transport properties

Characterizing the molecular transport of species, momentum, and energy in a multicomponent gaseous mixture requires the evaluation of diffusion coefficients, viscosities, thermal conductivities, and thermal diffusion coefficients.

Although evaluation of pure species properties follows standard kinetic theory expressions, one can choose from a range of possibilities for evaluating mixture properties. Moreover, computing the mixture properties can be expensive, and depending on the use of the results, it is often advantageous to make simplifying assumptions to reduce the computational cost (Kee et al., 2003)

For most applications, gas mixture properties can be determined from pure species properties via certain approximate mixture averaging rules. More advanced and accurate approaches are possible, but usually the computational cost increases

Mixture averaging rules

In most cases the transport properties of the species can be evaluated by using the standard kinetic theory expressions (Hirschfelder, 1964). Then we can apply averaging rules to have the transport properties of the mixture

Thermal conductivity

$$\lambda = \frac{1}{2}\left[\sum_{i=1}^{N} x_i \lambda_i + \left(\sum_{i=1}^{N} \frac{x_i}{\lambda_i}\right)^{-1}\right]$$

Mixture averaged diffusion coefficient

$$\Gamma_{i,mix} = \frac{\sum_{j\neq i}^{N} x_j W_j}{W_{mix} \sum_{j\neq i}^{N} \frac{x_j}{\Gamma_{ji}}}$$

Dynamic viscosity

$$\eta = \sum_{i=1}^{N} \frac{x_j \eta_j}{\sum_{j=1}^{N} x_j \phi_{i,j}}$$

$$\phi_{i,j} = \frac{1}{\sqrt{8}} \sqrt{\frac{W_j}{W_i + W_j}} \left[1 + \sqrt{\frac{\eta_i}{\eta_j}} \left(\frac{W_j}{W_i}\right)^{1/4}\right]^2$$

Transport data input file

```
AR          0        136.5     3.33          0.   0.   0.
C           0        71.4      3.298         0.   0.   0.
C2H2OH      2        224.7     4.162         0.   0.   1.
C2N         1        232.400   3.828         0.   0.   1.
```

The first 16 columns in each line of the database are reserved for the species name. Columns 17 through 80 are free-format, and they contain the molecular parameters for each species.

1. An index indicating whether the molecule has a monatomic, linear or nonlinear geometrical configuration. If the index is 0, the molecule is a single atom; 1 means the molecule is linear; 2 the molecule is nonlinear.

2. The Lennard-Jones potential well depth in Kelvins.

3. The Lennard-Jones collision diameter in angstroms.

4. The dipole moment in Debye

5. The polarizability in cubic angstroms.

6. The rotational relaxation collision number at 298 K.

7. A “comment” line is one that has an exclamation mark (!) as the first non-blank character. In addition, on any line, any input that follows an exclamation mark is taken as a comment.

Fitting of transport properties

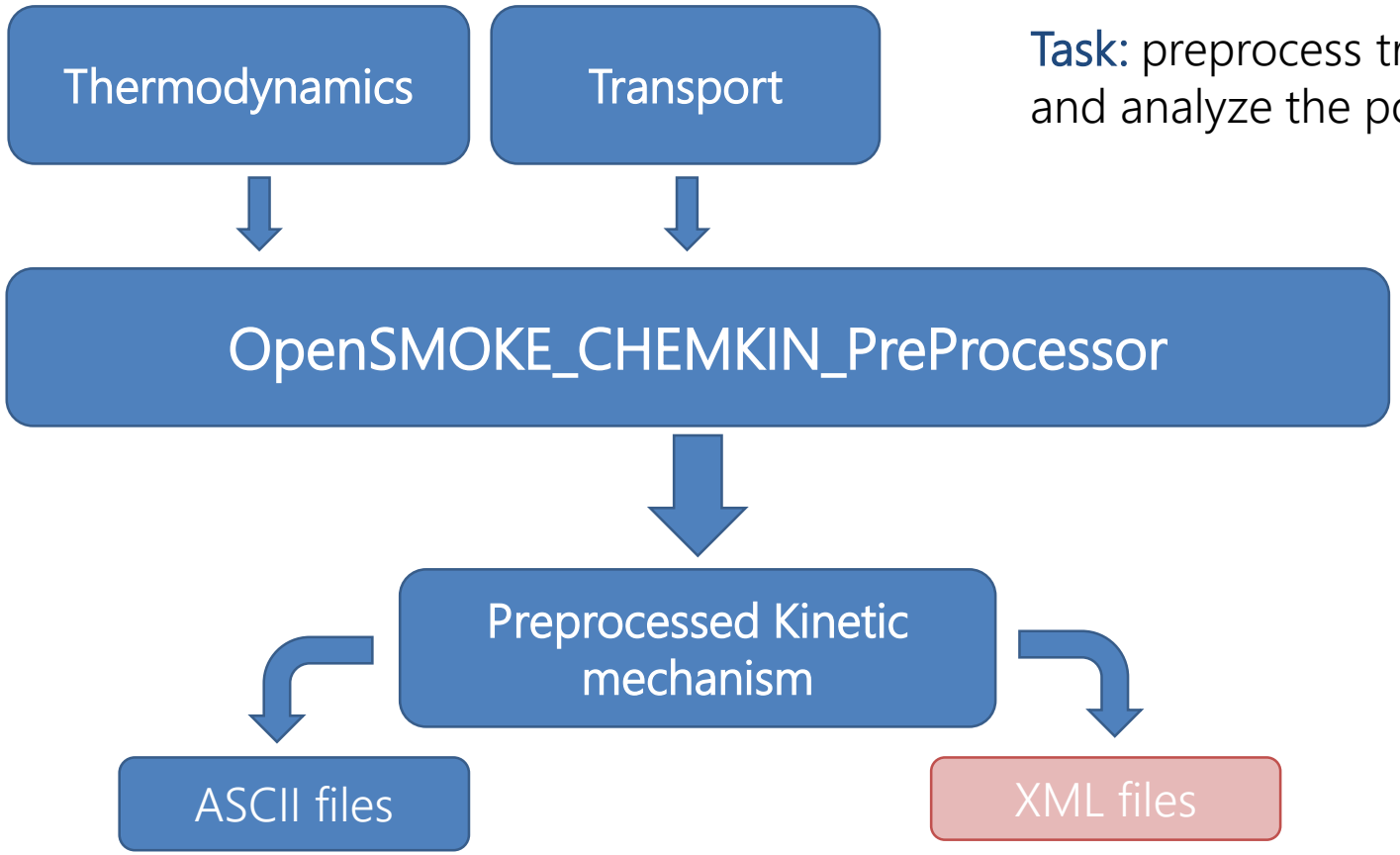
To expedite the evaluation of transport properties in OpenSMOKE++, the temperature dependent parts of the pure species property expressions are fitted. This means that, rather than re-evaluating the complex expressions for the properties, only simple fits need to be evaluated. In particular, following the approach proposed by Kee et al. (1996) ad adopted in CHEMKIN, a polynomial fit of the logarithm of the property versus the logarithm of the temperature is adopted:

Viscosity	$ln(\eta) = \sum_{k=1}^{4} b_k^{\eta} T^{k-1} = b_1^{\eta} + b_2^{\eta} T + b_3^{\eta} T^2 + b_4^{\eta} T^3$	4 fitting coefficients
Thermal conductivity	$ln(\lambda) = \sum_{k=1}^{4} b_k^{\lambda} T^{k-1} = b_1^{\lambda} + b_2^{\lambda} T + b_3^{\lambda} T^2 + b_4^{\lambda} T^3$	4 fitting coefficients
Binary diffusion coefficient with species j	$ln(\Gamma_j) = \sum_{k=1}^{4} b_{j,k}^{\Gamma} T^{k-1} = b_{j,1}^{\Gamma} + b_{j,2}^{\Gamma} T + b_{j,3}^{\Gamma} T^2 + b_{j,4}^{\Gamma} T^3$	4N fitting coefficients

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



For this preliminary task we will use the POLIMI_TOT_NOX_1412.TRC database, containing transport data for more tha 400 species. Rememember that in order to preprocess transport properties, you need always the thermodynamic properties for all the species

Task 2: pre-processing transport data

1. Preparation of input data

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

```
Dictionary CHEMKIN_PreProcessor
{
        @Thermodynamics                 ../../Kinetics/POLIMI_TOT_NOX_1412.CKT;
        @Transport                      ../../Kinetics/POLIMI_TOT_NOX_1412.TRC;
        @TransportFittingCoefficients true;
        @Output                         transport;
}
```

`@Transport`
full path and name of file containing the transport data to be pre-processed (local or absolute paths are allowed)

`@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: pre-processing transport data

2. Run the kinetic preprocessor

3. Analyze the pre-processing results

If everything was done properly, the `transport` 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

Kinetic file: CHEMKIN format (I)

```
ELEMENTS
C     H     O
N     AR    HE
END

SPECIES
HE          AR          N2          O2          H2
H2O         H2O2        CO          CO2         O
H           OH          HO2         HCO
END

REACTIONS
H+O2=OH+O                        0.9600E+15   -0.2  16625.0
O+H2=OH+H                        0.4330E+14    0.0  10000.0
CO+O(+M)=CO2(+M)                 0.9640E+11    0.0   3800.0
LOW/   .2070E+27   -3.340    7610.0/
H2O/12.00/ H2/2.00/ CO/1.50/ CO2/2.00/ AR/0.50/
END
```

Section 1:
List of elements

Section 2:
List of species

Section 3:
List of reactions

Kinetic file: CHEMKIN format (II)

Basic rate expression: $r = r_f - r_b = k_f \prod_j C_j^{v_j^f} - k_b \prod_j C_j^{v_j^b}$

v_j^f forward stoichiometric coefficient of species j
v_j^b backward stoichiometric coefficient of species j
C_j concentration of species j
K_{eq} equilibrium constant

$$k_b = \frac{k_f}{K_{eq}}$$

$$r = k_f \prod_j C_j^{v_j^f} - \frac{k_f}{K_{eq}} \prod_j C_j^{v_j^b}$$

H + O2 = OH + O	**0.9600E+15**	**-0.2**	**16625.0**
reactants products	Frequency factor A [cm^3/mol/s]	Temperature exponent n	Activation energy E [cal/mol]

(Arrhenius' law)

$$k_f = AT^n e^{-\frac{E}{RT}}$$

Kinetic file: CHEMKIN format (III)

Reversible reaction

```
H + O2 = OH + O                  0.9600E+15    -0.2   16625.0
```

Non-reversible reaction

```
H + O2 => OH + O                 0.9600E+15    -0.2   16625.0
```

Third-body reaction

```
HCO +M = CO + H +M               0.1200E+18    -1.0    17000.0
H2O/5.00/  CO2/3.00/  H2/1.90/  CO/1.90/
```

Pressure dependent reaction

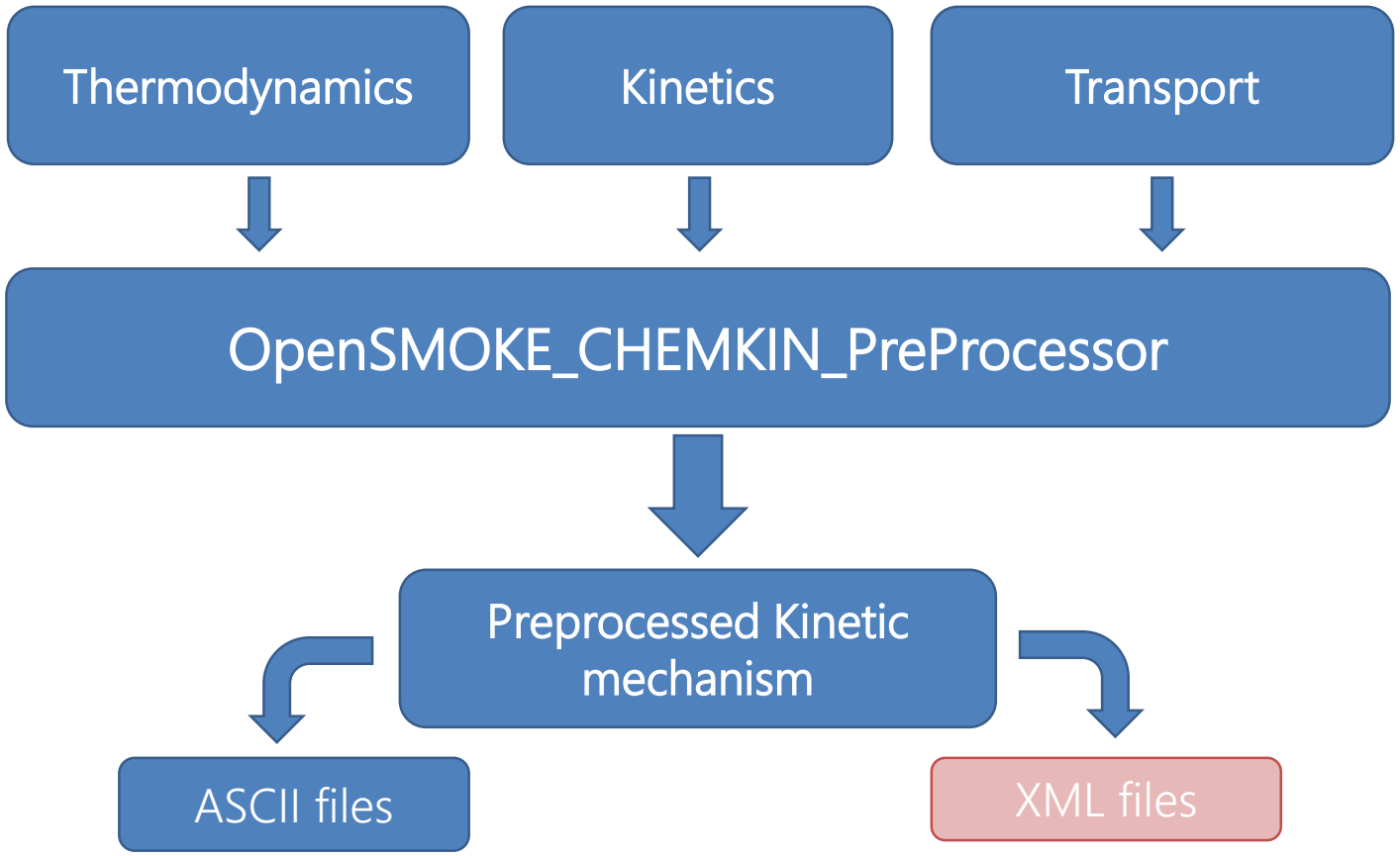
```
OH+OH (+M) = H2O2 (+M)           0.7400E+14    -0.37   0
LOW/  .1300E+19    -.900   -1700.0/
TROE/ 0.7346 94.00  1756. 5182. /
H2/2.00/  H2O/6.00/  CO/1.50/  CO2/2.00/  AR/.70/  HE/0.70/  N2/0.90/
```

Kinetic file: CHEMKIN format (IV)

Additional types of reactions and options available in OpenSMOKE++

- Chebyshev Polynomial Rate Expressions (CHEB)
- Power series within the exponential of a modified Arrhenius expression (FIT1)
- Janev-Langer reaction rates (JAN)
- Landau-Teller reaction rates (LT)
- Pressure Dependence Through Logarithmic Interpolation (PLOG)
- Explicit reverse reaction rates (REV)
- Explicit reaction orders (FORD and RORD)

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)

For this task 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: pre-processing kinetic mechanisms

1. Preparation of input data

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

```
Dictionary CHEMKIN_PreProcessor
{
        @Thermodynamics                 ../../Kinetics/POLIMI_TOT_NOX_1412.CKT;
        @Transport                      ../../Kinetics/POLIMI_TOT_NOX_1412.TRC;
        @Kinetics                       ../../Kinetics/POLIMI_H2CO_1412.CKI;

        @Output                         transport;
}
```

`@Kinetics`
full path and name of file containing the transport data to be pre-processed (local or absolute paths are allowed)

Task 3: pre-processing kinetic mechanisms

2. Run the kinetic preprocessor

3. Analyze the pre-processing results

If everything was done properly, the `kinetics` 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: pre-processing kinetic mechanisms

4. 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         ../../Kinetics/POLIMI_TOT_NOX_1412.CKT;
        @Transport              ../../Kinetics/POLIMI_TOT_NOX_1412.TRC;
        @Kinetics               ../../Kinetics/POLIMI_H2CO_1412.CKI;
        @Output                 transport;

        @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

References

J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids (Revised Edition)*, John Wiley and Sons, New York (1964)

Kee, R., Coltrin, M., Glarborg, P., Chemical Reacting Flows: Theory and Practice. Wiley-Interscience (2003)

Kee, R., Rupley, F., Meeks, E., Miller, J., CHEMKIN-III: A FORTRAN chemical kinetics package for the analysis of gas phase chemical and plasma kinetics, SAND96-8216 Techical Report (1996)

Curtiss, C., Hirschfelder, J., *Transport properties of multicomponent gas mixtures*, Journal of Chemical Physics 17, 550 (1949)