



Add-in created in COMSOL Multiphysics 6.4

Plasma Chemistry

Introduction

Plasma chemistries can easily have 10s of species and 100s of reactions. When reaching this level of complexity it is laborious to create a plasma chemistry at the user interface level. This add-in automatically creates a complete plasma chemistry from a text file for models using the **Plasma** and **Plasma, Time Periodic** interfaces. The following aspects of a plasma chemistry can be specified in the file:

- Species properties including thermodynamic parameters
- Electron impact reactions from cross sections and rate constants
- Heavy species reactions
- Surface reactions

Plasma Chemistry File Format

The chemistry file is organized using blocks that define four important aspects of a plasma chemistry: species properties, electron impact reactions, heavy species reactions, and surface reactions. Each block starts with a keyword like SPECIES or HEAVYSPECIESREACTIONS and must always end with an END.

In the file the following rules apply:

- Any line that starts with % is treated as a comment
- It is possible to use model variables to define expressions. The following keywords can be used: TE is the electron temperature in eV, NE is the electron density in m^{-3} , TGAS is the gas temperature in K, and EN is the reduced electric field in $\text{V}\cdot\text{m}^2$.
- It is also possible to use any variable in the model using the scope *plasma* before the variable. As an example, if the variable `plas.rho` or `plas2.rho` is to be used, write `plasma.rho`. The correct physics interface scope will replace `plasma`. The instructions below show two equivalent ways to define the same ionization rate constant using TE and `plasma.Te`:

```
e+Ar=>2e+Ar+ ! Ionization 15.7 2.3e-14*TE^0.56*exp(-17.1/TE)
e+Ar=>2e+Ar+ ! Ionization 15.7 2.3e-14*plasma.Te^0.56*exp(-17.1/
plasma.Te)
```

SPECIES PROPERTIES

The species properties can be defined in the species block that starts with the SPECIES keyword. It is possible to define species properties using preset data by using the keyword PRESETSPECIESDATA, or set the properties manually using the keyword USERDEFINED. Both options automatically set the species properties in the section

General Parameters of a given **Species** feature. The block below shows how to use preset data to define species properties.

```
SPECIES
PRESETSPECIESDATA
Ar = Ar
Ars = Ar
Ar_1p = Ar
END
```

The PRESETSPECIESDATA keyword below SPECIES indicates that preset species data is used. On the left of = a tag of an existent species should be used and on the right of = a preset species data can be assigned to the existent data. The line $Ars=Ar$ reads: the species with tag Ars is set with the preset species data of Ar (which is argon). Note that ions have a tag that is different than the species name. A positive ion with name Ar^+ has the tag Ar_1p and the negative ion O^- as the tag O_1m . To see a feature's tag, go to **Model Tree Node Text** and select **Tag**.

The block below shows how to define the species properties manually:

```
SPECIES
USERDEFINED
O2 ! 0.032 3.458 107.4 0.000
O_1m ! 0.016 2.750 80.00 0.000
O2b1s ! 0.032 3.458 107.4 0.000
END
```

The USERDEFINED keyword below SPECIES indicates that species properties are defined manually. on the left of ! a tag of an existent species should be used and on the right of ! four numbers separated by spaces should be set. These numbers are, in order, the **Molar mass**, **Potential characteristic length**, **Potential energy minimum**, and **Dipole moment**.

It is also possible to set species thermodynamic parameters using the keyword THERMODYNAMICPARAMETERS as shown in the block below. The first line in the block is a list of species tags to which the properties are to be applied. The second line is in order: **Lower temperature limit**, **Middle temperature limit**, and **Upper temperature limit**. The third and fourth lines are the **Polynomial coefficients, low** and the **Polynomial coefficients, high**, respectively. The fifth and last line is the **Additional enthalpy contribution**.

```
SPECIES
THERMODYNAMICPARAMETERS
O O_1m O1s O1d
200 1000 3500
3.168E00 -3.2791E-3 6.6436E-6 -6.1206E-9 2.1165E-12 2.9122E4 2.0513E00
2.569E0 -8.5941E-5 4.1984E-8 -1.0017E-11 1.223E-15 2.9217E4 4.784364E0
```

```
0
END
```

ELECTRON IMPACT REACTIONS

Electron impact reactions can be defined using a block started with ELECTRONIMPACTREACTIONS. There are two options: create electron impact reactions from cross sections using the keyword CROSSSECTIONDATA, or set a user defined rate constant using the keyword RATECONSTANT.

The block below shows how to define the electron impact reaction from cross sections.

```
ELECTRONIMPACTREACTIONS
CROSSSECTIONDATA
Ar_xsecs.txt
O2_xsecs.txt
END
```

The CROSSSECTIONDATA keyword indicates that a file or more of electron impact cross sections needs to be provided. The files need to be in the same folder as the plasma chemistry file. When CROSSSECTIONDATA is used the electron impact reactions are automatically created using the **Cross Section Import** feature.

The block below shows how to define the electron impact reactions using rate constants.

```
ELECTRONIMPACTREACTIONS
RATECONSTANT
e+O2=>e+O2 ! Elastic 1.71e-5 4.7e-8*TE^0.5
e+O=>e+Os ! Excitation 4.5 2.34e-14*TE^0.56*exp(-17.44/TE)
e+O2=>2e+O2+ ! Ionization 12.06 9e16*T^2*exp(-12.6/TE)
e+O2=>O+O- ! Attachment 8.8e-17*exp(-4.4/TE)
END
```

on the left of ! a formula is defined and on the right of ! the rate constant and other settings are defined. The first field after ! must define the **Collision type** that can be **Elastic**, **Excitation**, **Ionization**, or **Attachment**. If the collision type is

- **Elastic**, the next two fields are for the **Electron mass ratio** and the **Forward rate constant**
- **Excitation** or **Ionization**, the next two fields are for the **Energy loss** and the **Forward rate constant**
- **Attachment**, there is one field for the **Forward rate constant**

HEAVY SPECIES REACTIONS

Heavy species reactions can be defined using a block started with HEAVYSPECIESREACTIONS. The rate constant can be defined by providing an expression using the keyword RATECONSTANT or by coefficients of the Arrhenius

expression using the keyword **ARRHENIUS**. The block below shows how to define heavy species reactions by providing rate constants. The formula is defined on the left of **!** and the rate constant is defined on the right of **!**.

```
HEAVYSPECIESREACTIONS
RATECONSTANT
Ars+Ars=>e+Ar+Ar+ ! 3.734E8
Ars+Ar=>Ar+Ar ! 1807
END
```

The block below shows how to define heavy species reactions by providing the coefficients of the Arrhenius expression. The formula is defined on the left of **!** and the Arrhenius coefficients are defined on the right of **!** in sequence: **Forward frequency factor**, **Forward temperature exponent**, and **Forward activation energy**.

```
HEAVYSPECIESREACTIONS
ARRHENIUS
O2++O2-=>O2+O2 ! 2.e-13 -0.5 0
O2+O3=>O2+O2+O ! 7e-16 0.0 -600
END
```

REACTION GROUP

The reaction group block allows to set a large set of reactions in a single feature. It can add both heavy species reactions and electron impact reactions. A reaction group block can be started using the keyword **REACTIONGROUP**. After the **REACTIONGROUP** keyword, the type of the reaction group block need to be defined using keywords **HEAVYSPECIESREACTIONS** or **ELECTRONIMPACTREACTIONS** for heavy species reactions or electron impact reactions, respectively. For electron impact reactions, there are two ways to supply the reaction rates data. Therefore, following the keyword of **ELECTRONIMPACTREACTIONS**, keywords of either **CROSSECTIONDATA** or **ARRHENIUSPARAMETERS** need to be attached, for defining the reaction rates using cross sections data or Arrhenius parameters respectively.

The following examples show three different ways to define reactions using the reaction group block.

```
REACTIONGROUP
HEAVYSPECIESREACTIONS
H2+H2+>=>H3++H ! 2.1e-9[cm^3/s]*N_A_const 0 0
H2+H2<=>2H+H2 ! 3.7e-16 0 -48300 8.33e-33 1 0
END
```

```
REACTIONGROUP
ELECTRONIMPACTREACTIONS
CROSSECTIONDATA
Ar_xsecs.txt
```

```
02_xsecs.txt
END
```

```
REACTIONGROUP
ELECTRONIMPACTREACTIONS
ARRHENIUSPARAMETERS
e+02=>e+02 ! Elastic 1.71e-5 4.7e-8*TE^0.5 0 0
e+0=>e+0s ! Excitation 4.5 2.34e-14*TE^0.56*exp(-17.44/TE) 0 0
e+02=>2e+02+ ! Ionization 12.06 9e16*T^2*exp(-12.6/TE) 0 0
e+02=>0+0- ! Attachment 8.8e-17*exp(-4.4/TE) 0 0
END
```

For the HEAVYSPECIESREACTIONS block, the reactions are set explicitly below the keyword. The formula is defined on the left of “!” and the Arrhenius coefficients are defined on the right of “!” in sequence: **Forward frequency factor**, **Forward temperature exponent**, **Forward activation energy**, **Reverse frequency factor**, **Reverse temperature exponent**, and **Reverse activation energy**. If the formula is not reversible (defined with =>), only the forward coefficients (3 parameters) are needed. If the formula is reversible (defined with <=>), both forward and reversible coefficients (6 parameters) need to be provided. If a coefficient is not needed to define the reactions it should be set as “0”.

For the ELECTRONIMPACTREACTIONS with CROSSSECTIONDATA block, one or more files of electron impact cross sections data need to be provided. The files need to be in the same folder as the main plasma chemistry file. All the data within these files will be read simultaneously and be used to populate the same table in a Reaction Group feature.

For the ELECTRONIMPACTREACTIONS with ARRHENIUSPARAMETERS block, the reactions are set explicitly below the keyword. Each line represents one electron impact reaction and the format is similar to the one described above in the **ELECTRON IMPACT REACTIONS** section except that now two extra Arrhenius coefficients need also be provided at the end of each line.

It should be noted that the REACTIONGROUP block is intended to put simple reaction sets conveniently all in one place, that is, in the main plasma chemistry file. Multiple different types (or same type) of REACTIONGROUP blocks can be put into the same main file, and all the contents will be read. However, at maximum only two Reaction Group features will be automatically generated, one for heavy species reactions and one for electron impact reactions. Both the **Reaction Group** features will contain all the reactions defined within the related REACTIONGROUP blocks.

If one wants to put different reaction sets into different **Reaction Group** features, for example, separate argon chemistry and oxygen chemistry into different Reaction Group

features and label them directly and properly, this can be achieved by using another type of block with keyword REACTIONGROUPIMPORT.

REACTION GROUP IMPORT

The reaction group import block allows to separate large sets of reactions into different **Reaction Group** features. A reaction group import block can be defined using the keyword REACTIONGROUPIMPORT such as

```
REACTIONGROUPIMPORT
Ar_C12_plasma_chemistry_import_Ar.txt      ! Ar
Ar_C12_plasma_chemistry_import_Cl.txt     ! Cl
Ar_C12_plasma_chemistry_import_mixed.txt
END
```

Each line should contain a filename that points to a text subfile. Each subfile should contain one or more REACTIONGROUP blocks. The subfiles need to be in the same folder as the main plasma chemistry file. The data in all the blocks with the same reaction group type (Heavy species reactions or Electron impact reactions) in the same subfile will be put into the same **Reaction Group** feature, therefore each subfile will automatically generates one or two Reaction Group features depending on the availability of HEAVYSPECIESREACTIONS and ELECTRONIMPACTREACTIONS blocks in that subfile. It is also possible to conveniently customize the Reaction Group features' names with user defined labels after the delimiter "!" such as "Ar" or "Cl", then the generated Reaction Group features will be automatically labeled such as "Ar - Electron Impact Reactions" or "Cl - Heavy Species Reactions". If no label has been provided, the generated Reaction Group features will have the default labels such as "Reaction Group 5 - Heavy Species Reactions".

SURFACE REACTIONS

Surface reactions can be defined using a block starting with SURFACEREACTIONS as shown in the block below. The formula is defined on the left of ! and on the right of ! the **Forward sticking coefficient**, **Secondary emission coefficient**, and the **Mean energy of secondary electron** are defined.

```
SURFACEREACTIONS
Ar+=>Ar ! 1 0.07 4.5
Ars=>Ar !1 0.0 3.0
END
```

Add-in Library path: Plasma_Module/plasma_chemistry

COMPONENT AND INTERFACE SELECTION

In the **Component and Interface selection** choose the **Component** and **Interface** to which the plasma chemistry is going to be imported.

PLASMA CHEMISTRY IMPORT

In the **Plasma Chemistry Import section** browse to the text file where the plasma chemistry is defined and import the plasma chemistry.