

## MESMER quick start guide using the GUI.

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### Creating the input file.

This tutorial demonstrates how to set up a simple MESMER input file with aid of the recently developed graphical user interface (GUI). This tutorial will look at a simplified version of the  $\text{H} + \text{SO}_2$  reaction a more comprehensive example of which can be found in the `mesmer\MesmerQA\HSO2\` folder. Two reaction steps will be considered:

**The association  $\text{H} + \text{SO}_2 \rightarrow \text{HSO}_2$**  : This step will be treated as barrierless using an ILT approach.

**The isomerisation  $\text{HSO}_2 \rightarrow \text{HOSO}$** : This step occurs via the transition state TS1.

To begin open a web browser (ideally Firefox) and direct it to the URL:

<http://www.mesmergui.cn/>

To begin with double click in the “MESMER title” box located in the top left corner and enter the following text, “simple  $\text{H} + \text{SO}_2$ ”. Once this is done click on the molecule list box and then click the “Add Molecule” button located in the top right hand corner.

For this system there are 6 species which need to be defined,  $\text{H}$ ,  $\text{SO}_2$ ,  $\text{HSO}_2$ ,  $\text{HOSO}$ , the transition state TS1 and the bath gas  $\text{N}_2$ . Name the first species “H” by typing in the ID box. For each species a number of properties need to be defined depending upon the role this species plays in the system. This role is specified by the “type” drop down menu:

- The **excessReagent** and **deficientReactant** types specify bimolecular reactants in an association process, commonly referred to as a bimolecular source term.
- The **modelled** type refers to any species in the system which can undergo collisional energy transfer and reaction processes. Generally all wells on a potential energy surface should be classed as modelled and the **deficientReactant** species can also optionally be classed as **modelled**.
- The **sink** type refers to a species which once formed is considered to reaction no further. Reaction to a **sink** molecule will thus be irreversible and the **sink** type should be used with care and only when the reverse reaction is known to be negligible.

- The **transitionState** type is used for all barriers, (saddled points) in the system.
- Finally the **bathGas** type, is used to define the colliding bath gas for the system.

Choose the “deficientReactant” type for H, the other properties will be added later. Next click the “add molecule” button, type “SO2” in the “ID” box for this new species, and select “excessReactant” from the drop down menu. You can cycle between the molecules you have defined by clicking on the appropriate box, in the molecule list. Next create the following molecules and types: HSO2 = modelled; HOSO = modelled; TS1=transitionState. The N<sub>2</sub> molecule is present in the MESMER library, so for this species simply click the add from library button, select N2 and change the type of the N2 species to “bathGas”. Your screen should then look like the screenshot below.

The screenshot shows the MESMER GUI interface. On the left is a sidebar with navigation links: MESMER Title, Molecule List (highlighted in blue), Reaction List, Conditions, Model Parameters, and Control. The main window is titled 'Molecule List' and contains a list of defined molecules: H deficientReactant, SO2 excessReactant, HSO2 modelled, HOSO modelled, TS1 transitionState, and N2 bathGas. Each molecule name is in a box with a small 'x' icon to its right. At the top right of the main window are buttons for 'Add Molecule' and 'Add From Library'. Below the molecule list, the properties for the selected 'N2 bathGas' molecule are displayed in a form. The properties are: ID (N2), Epsilon(K) (48), Type (bathGas with a dropdown arrow), Sigma(Angstroms) (3.9), and MW(amu) (28).

**Figure 1: Molecule list from the GUI.**

For each species the molecular properties now need to be entered and the exact combination of properties required depends upon the type specified. The data for this system is given in table 1 and a brief description of each property is given below.

- VibFreqs: The harmonic frequencies for each vibrational modes. These can be obtained from electronic structure theory calculations or from computational databases such as <http://cccbdb.nist.gov/>.
- RotConsts: Rotational constants, which can be obtained from the same sources as the vibrational frequencies. The desired units can be selected from the drop down menu.
- Scaling Factor: Scaling factor for the level of theory used to calculate the vibrational frequencies (if known). Default is 1 (unscaled).
- Symmetry: Overall rotational symmetry number for the molecule.
- MW: Molecular weight in amu.
- Spin Multiplicity: 1 for a singlet, 2 for a doublet (radical), 3 for a triplet.

- ZPE: Energy of the species relative to the other stationary points of the system. The energy of a bimolecular source term equals the sum of the energies of the bimolecular species. These are generally gained from electronic structure theory calculations. The desired units can be selected from the drop down menu.
- Epsilon (K) and sigma (angstrom): These are the parameters for a Lennard Jones interaction potential for the species with itself. These are generally estimated from tables (one such can be found in the Multiwell manual: <http://aossresearch.engin.umich.edu/multiwell/content/download/Manual-2013.pdf>) of known values or from group additivity relationships. Codes also exist for the calculation of these from first principles (<http://www.sandia.gov/~ajasper/>).
- DeltaEDown(cm-1): Energy transfer is modelled using an exponential down model and DeltaEDown is the average energy transferred in a downward direction upon collision with a bath gas molecule. This parameter is usually varied in order to fit experimental data but there have been recent advances in *a priori* determinations of this and as such there is a growing database of acceptable values.
- deltaEDownTExponent and reference temperature: This parameter allows DeltaEDown to vary with temperature and therefore energy according to the following relationship:

	H	SO2	HSO2	TS1	HOSO
ZPE / kJ mol <sup>-1</sup>	165	0	102	214	0
RotConsts / cm <sup>-1</sup>	-	2.016 0.345 0.295	1.703 0.3 0.263	1.506 0.295 0.256	1.14 0.309 0.243
VibFreqs / cm-1	-	518 1151 1362	411 777 1027 1094 1578 2284	407 639 854 1216 2191	183 336 722 991 1283 3493
Scaling factor	-	1	1	1	1
MW / amu	1	64	65	-	65
Symmetry number	1	2	1	1	1
Spin Multiplicity	2	1	2	2	2
deltaEDown	-	-	230	-	230
deltaEDownTExponent	-	-	-	-	-
Epsilon	-	-	380	-	380
Sigma	-	-	4.3	-	4.3

**Table 1: Input parameters for the H + SO<sub>2</sub> system**

Now that all the molecular information has been entered, the reactions involved in this system may be defined. Click on the reaction list box on the left hand side and then click the Add Reaction button. For the first reaction keep the id as "R0" and select "A + B -> C" from the Type dropdown menu. In this case the reactants will be H and SO2 and the product will be HSO2. Selects the appropriate types for these species and then select the species names from the dropdown menu. The excess reactant concentration must also be defined, and for this example enter a value of "1E16".

This association reactions is barrierless, so there is no transition state associated with it and an ILT method must be used. In the ILT method the high pressure limiting rate coefficients for the reaction are assumed to be described the equation:

The ILT method requires the parameters A, n and Ea as input. These values are commonly fit to available experimental data or guessed based upon chemical intuition or comparison with other species. Variational transition state theory methods can be used to calculate the high pressure limiting rate coefficients for barrierless processes and there are freely available codes which can do this (<http://comp.chem.umn.edu/polyrate/>). For this example enter values of A, n and Ea of “1E-10” “0.0” and “0.0” respectively.

Next the isomerisation step needs to be defined, for this reaction there is a well defined bottleneck to the reaction, the transition state TS1. Click the add new reaction and choose reaction type “A->B”. Both reactant and product should have the “modelled” type, and then select HSO2 and HOSO as the reactant and product respectively. Select RRKM as the MCRMethod and then select TS1 for the transition state.

The screenshot shows the MESMER web interface. On the left is a sidebar with tabs: MESMER, index, MESMER Title, Molecule List, Reaction List (selected), Conditions, Model Parameters, and Control. The main area is titled 'Reaction List' and contains a table for defining reactions. Two reactions are listed: 'R0 A + B -> C MesmerILT' and 'R1 A -> B SimpleRRKM'. The configuration for R0 is shown in detail below:

id	R0		MCRMethod	ILT	RRKM
reaction type	A + B -> C		PreExponential	1E-10	orderMoleculeList
reactant 1	H	deficientReactant	ActivationEnergy	0.0	units
reactant 2	SO2	excessReactant	NInfinity	0.0	
product 1	HSO2	modelled	Excess Concentration	1E16	

**Figure 2: Reaction list from the GUI.**

Next it is necessary to define the conditions over which the master equation simulation will be run. Select the conditions tab on the left hand side and select the bath gas N2 from the drop down list. In this case leave the initial conditions box empty and MESMER will assign the starting population of H as 1 by default. Change the pressure units to “Torr” from the drop down menu. The “Add Pressure and Temperature” can now be used to add any number of conditions. In this case press the button three times. For each condition pair assign the temperature as 298, and then assign the pressure as 250 and 500 and 750. For these calculations “double” precision is fine, but higher numerical precision may be required in some cases particularly in systems with deep wells, or when studying very low temperatures (<200 K).

Now the master equation model parameters need to be defined. Select the “Model Parameters” tab on the left hand side, and then you will find two boxes which require input, GrainSize, and EnergyAboveTheTopHill. For this example a grain size of 75 cm<sup>-1</sup> and an EnergyAboveTheTopHill (the energy above TS1 at which the system will be truncated) of 25 k<sub>B</sub>T will be sufficient. When approaching a new system, these parameters should be checked for convergence. Decreasing the

grain size and increasing EnergyAboveTheTopHill will increase the accuracy of the calculations, but will also increase the execution time.

The final input required is found in the "Control" tab. This tab consists of a number of boxes, which when selected produce different outputs from the MESMER calculation. Keep the calculation method as simpleCalc, and enter the number 3 into the eigenvalues box which tells MESMER to print the 3 eigenvalues of the smallest magnitude, from the calculation. From the tick boxes select the printSpeciesProfile box and leave all others unticked. This will produce a time resolved concentration profile of each species involved in your system. Descriptions of all other keywords can be found in the main MESMER manual.

### Viewing the MESMER output in Firefox

The input file for the  $\text{H} + \text{SO}_2$  reaction should now be complete. Create a new folder Mesmer\myexamples\H\_SO2\, click save, and save the .xml file produced in this folder. This is your MESMER input file. If Firefox is configured correctly (as described in the MESMER manual), then your saved input file can be opened with this in order to view additional graphical information. Instructions for configuring Firefox can be found in the main MESMER manual, and opening your current input file should give the following diagram. Usually the Firefox representation will only display correctly if the input file is two folders above the root Mesmer folder, however with some additional steps the Firefox representation can be viewed directly from the GUI.

Having downloaded and installed Mesmer and configured Firefox as described in the Mesmer manual, go to the top level Mesmer folder and select all the files with extension .xsl, and copy them. In the command box in the Start menu, type %TEMP%, click the folder symbol that is produced to open the temporary folder in Windows Explorer. Move to the folder 2 levels above this (it is probably AppData) and paste the xsl files into it.

To see the Firefox representation (including the diagram) while editing, click save (in the top right) and select to Open the file with Firefox (rather than saving it). You may have to initially go to "Other" but Firefox will remember your choice if you tick the checkbox. You can go back to the Mesmer GUI window and continue editing.

## - Molecules

Name	Energy kJ/mol	Rotational constants cm <sup>-1</sup>	Vibrational frequencies cm <sup>-1</sup>
H	165		
SO2	0	2.016 0.345 0.295	518 1151 1362
HSO2	102	1.703 0.3 0.263	411 777 1027 1094 1578 2284
HOSO	0	1.14 0.309 0.243	183 336 722 991 1283 3493
TS1	214	1.506 0.295 0.256	407 639 854 1216 2191
N2			

## - Reactions

R0 H + SO2  $\Rightarrow$  HSO2  $A = 1E-10 E = 0.0\text{kJ/mol}$   
 R1 HSO2  $\Rightarrow$  HOSO (Transition State TS1)

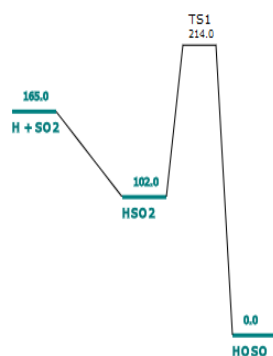


Figure 3: H + SO<sub>2</sub> input file viewed using Firefox.

### Running and viewing the output file

The SO<sub>2</sub> + H input file is now ready to run, instructions on how to run MESMER on different operating systems can be found in the manual. For this example, right click on the newly created input and select the “open with” option. The input file can then be opened using the MESMER executable (eg. C:\Mesmer-3.0\Mesmer.exe ). The calculation will then run and three output files will be created, mesmer.log, mesmer.test and mesmer\_out.xml . Open the mesmer\_out.xml file using Firefox. The rate coefficients can be found under the phenomenological rate coefficients heading, clicking this text will produce a dropdown list and a table of comma delimited text which can be pasted directly into a spreadsheet. This rate coefficient list will include rate coefficients for all elementary and well skipping processes for the system. The output file also has species profile information, both plotted graphically and tabulated.

### Commonly encountered problems

#### **Eigenvalue overlap.**

One of the most commonly encountered problems is that of insufficient separation between eigenvalues which leads to warning messages of the form “WARNING: Chemically significant eigenvalues (CSE) not well separated from internal energy relaxation eigenvals (IEREs).”. The solution

of the master equation gives time resolved species populations in the form of species profiles. These are robust regardless of the separation between the eigenvalues of the system and these will be independent of the method used to solve the master equation, be it using matrix methods as in MESMER, or stochastic methods. Once the species profiles are obtained MESMER uses an additional Bartis Widom analysis in order to resolve phenomenological rate coefficients from the eigenvalues of the system. This analysis relies on a separation of timescales between the energy transfer processes and the reactive processes and when these timescales merge, the Bartis Widom rate coefficients may not represent the time resolved species behaviour over the entire timescale of the simulation. When the warning message appears the Bartis Widom rate coefficients should be compared with the species profiles for consistency. The keyword `me:printPhenomenologicalEvolution` will produce time resolved species concentrations from the Bartis Widom rates which can be compared directly with the species profiles. In cases where the two diverge, this is often indicative of a fundamental complexity to the system, at this particular temperature and pressure, which means that resolving the entire behaviour of the system into rate coefficients, may not be possible.

### ***The “Sink” approximation.***

Treating a species as a Sink can be a useful way of simplifying a system, however this should be used with caution. A model should only be classed as “sink” rather than “modelled” if the reaction is truly irreversible. If there is any significant flux in the reverse direction then treating the product as a sink will over predict the rate coefficients for forming this species.

### ***Quantum mechanical rotors versus classical rotors.***

In MESMER rotational densities of states can be calculated using either the “ClassicalRotors” or “QMRotors” keyword. Care should be taken over the choice of which method to use. For molecules consisting of a very small number of atoms, a fully quantum mechanical treatment will give more accurate results, however as the number of atoms increases the rotational density of state will rapidly approach the classical limit and both calculations using Classical and QM methods should converge. Using the QM method with a large number of atoms, the execution time of the MESMER calculation will be significantly increased due to time taken to diagonalise the rotational Hamiltonian of this species.