Atropos

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1. Introduction

Atropos - Of the three Greek Fates that spun, measured, and cut the yarn of life, Atropos held the shears that determined the final yarn length.

The Atropos software addition to Kintecus allows one to accurately “cut” reactions out of larger systems without bearing on the results. It also allows one to examine and **rank** the important to the least essential reactions. This process is accomplished through a sophisticated principal component analysis (PCA) [1] enacted on the Normalized Sensitivity Coefficients (NSC) files outputted by Kintecus. If your chemical mechanism is already in Kintecus, then this analysis **is easily** performed **in two steps**. You should NOT use just the NSC’s to justify your mechanism[1]. This can sometimes lead to incorrect results!

Why is this important?

- It is becoming essential for those submitting large reaction mechanisms to journals whose referees claim your large mechanism is superfluous and redundant. One must back up such large chemical mechanisms with solid objective numeric proof.

- Expanding your chemical mechanism model into 1D, 2D, or 3D models can require immense computational power and time. This is primarily due to the prolonged solution finding to the large ODE systems of the large chemical models present in each micro iteration of the larger 2D/3D transport model. Using a smaller, reduced chemical mechanism can dramatically decrease those computational times while not losing the chemical accuracy of the previous larger chemical model.

- Understanding larger and larger chemical kinetic reaction models are becoming much more complicated. Using Atropos will not only eliminate superfluous and redundant chemical steps, but it will rank which chemical steps are most important to the least important.

- Allow for easier and faster intrinsic low dimensional manifold (ILDM) creation and models for machine learning. Reducing a chemical mechanism will alter its manifold allowing for an easier determining of an ILDM.

2. The Program

Chemical Mechanism Reduction and Performing PCA on the NSC matrix files

Running Atropos from Command Line

On the Windows Start button, select RUN, type "command," and press the <ENTER> key. You will be in a command prompt. Change to the directory where you uncompressed/installed the Atropos files
(ie. cd c:\Atropos or cd c:\program files\Atropos). You can see what is in the directory by typing "dir /p". You can run Atropos as:
"**Atropos (any switches you may want to use)**," or if you wish to capture the on-screen information type:
"**Atropos (any switches you may want to use) > view.txt**".
This will output any errors, warnings, and information to the file view.txt, which can be viewed with any text editor or word processor.

If you have Microsoft's Excel, you can load and edit one of the following xls worksheets that contain **Visual Basic code for easy running, editing, and plotting** of Atropos runs named Atropos_workbook.xls. Please note if **you do not** have an **Atropos key**, after clicking the RUN button, you will have **to press the <ENTER> key three times** to continue the run.

Running Atropos within the Excel Interface

Atropos requires at least several Normalized Sensitivity Coefficient matrices to be stored somewhere on your hard disk (such as "C:\kintecus" or "C:\program files\kintecus"). The kinetics program Kintecus will automatically generate these matrix files. Refer to the Kintecus documentation under the Kintecus FASTSTART section to see how easily this is accomplished.

First, load the *blank* Excel **Atropos_workbook.xls.** Be sure to type -PREF: "C:\program files\kintecus\sensit" OR -PREF: "C:\kintecus\sensit" under the Atropos Switches cell (the -PREF switch should point to the directory containing your normalized sensitivity coefficient analysis files created by the Kintecus software and the prefixed filename which is usually "sensit"). In Excel, click on the "model" worksheet tab located at the bottom. Copy your chemical kinetic reaction model into that Excel worksheet named “model”. Click the RUN button. Click “YES” to see Atropos results. A new reduced chemical kinetic model should have automatically been loaded into Excel into a Worksheet named “newmodel.” The new reduced chemical kinetic model will have the unimportant reactions commented out with a prefixed “##,” and the entire reaction line will be highlighted yellow. You might wish to examine the output from Atropos as it contains various important principal components, eigenvalues, eigenvectors, and overall normalized sensitivity coefficients about your system that are extremely useful in chemical mechanism elucidation. For a full explanation of all those very important quantities, refer to the main paper[1] or examine a recent paper[3] that explicitly uses most of these values to verify a medium-sized biochemical model on the free-radical mechanism of peroxynitrite decomposition.

Sample Formaldehyde Oxidation Example

Included with the Atropos package is the sample Excel Spreadsheet, “Atropos_Reduced_Formaldehyde.xls,” containing a final reduced model of the formaldehyde oxidation mechanism[2] that is very similar[1] to the results obtained by Vajda, Valko, and Turanyi[1]. Also, a sample Kintecus Excel sheet containing the more extended formaldehyde mechanism is included (Formaldehyde_oxidation.xls). It is left to the user to copy the newmodel worksheet from “Atropos_Reduced_Formaldehyde.xls” to the model worksheet in “Formaldehyde_oxidation.xls” and see if the concentration results from the reduced mechanism do not change from the more extensive chemical kinetic mechanism concentration results.

Reduction of the Ethanol Combustion Model

Kintecus comes with a medium-sized chemical reaction model that involves the combustion of ethanol. The original model[4] includes some 380 reversible reactions. The sample Atropos Excel spreadsheet, “Atropos_ethanol_reduction.xls,” contains the reduced ethanol combustion model of around 230 reactions! This reduced, smaller ethanol combustion model was pasted into the “model” worksheet in the Kintecus ethanol combustion Excel workbook (see the “Ethanol_combustion_reduction.xls”). Running this reduced model yields the same concentration profile and temperature profile (see Figures 1-4 below). An important note is that a safe value of 0.001 (enter “`-safe:0.001`” on the Atropos switch/command line) was required to get a good enough accurate model. Using the default safe value of 0.5 eliminated too many reactions yielding a not-so-good final (but much, much smaller reaction kernel) ethanol combustion model.

[1] The results are not in perfect agreement due to two reasons: **1)** [M] in Kintecus is treated as a variable (sum of all gaseous products at time t) while [M] was treated as a constant in [1] **2)** The NSC's are derived from the longer more exact indirect method, while [1] implemented a different non-indirect method.

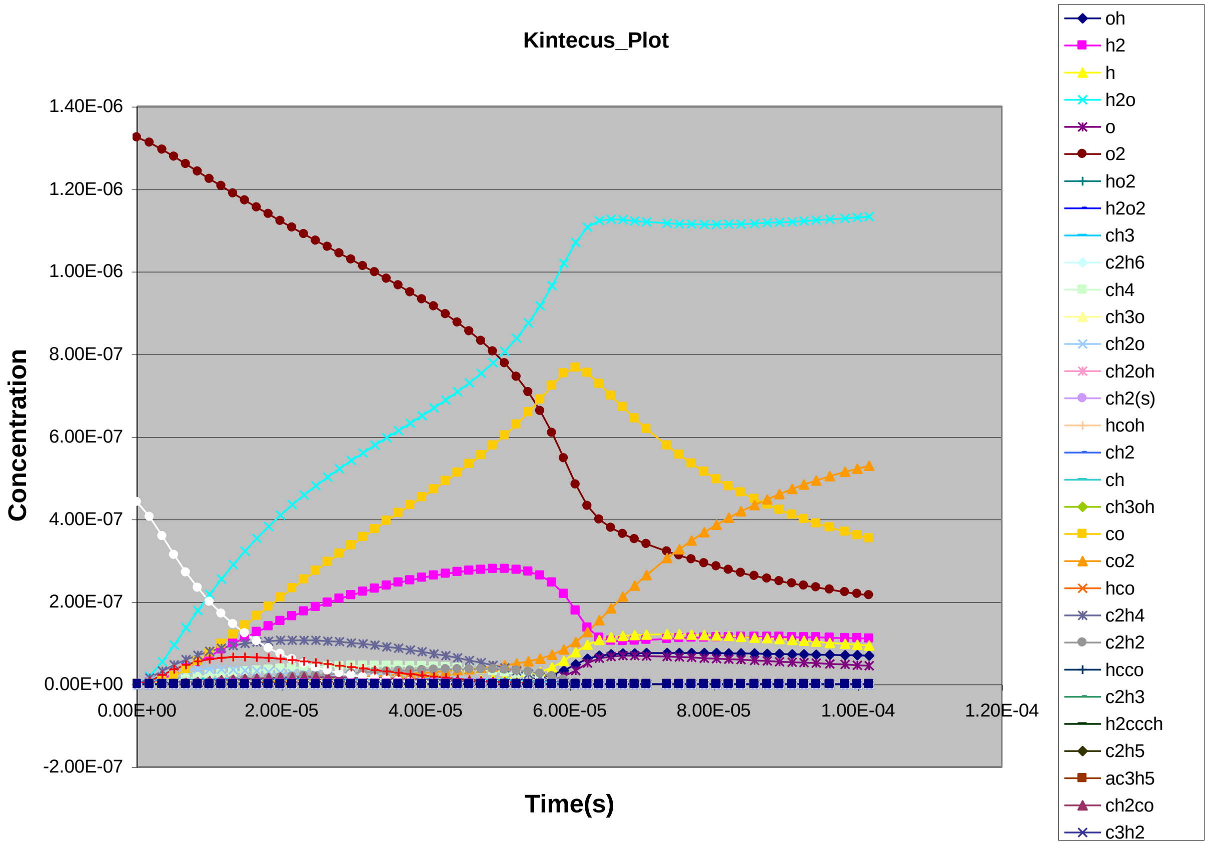

Figure 1. The results from the original ethanol combustion model[4]. The original model contains 400 reactions and requires 43 seconds to run on a 866 Mhz Pentium III.

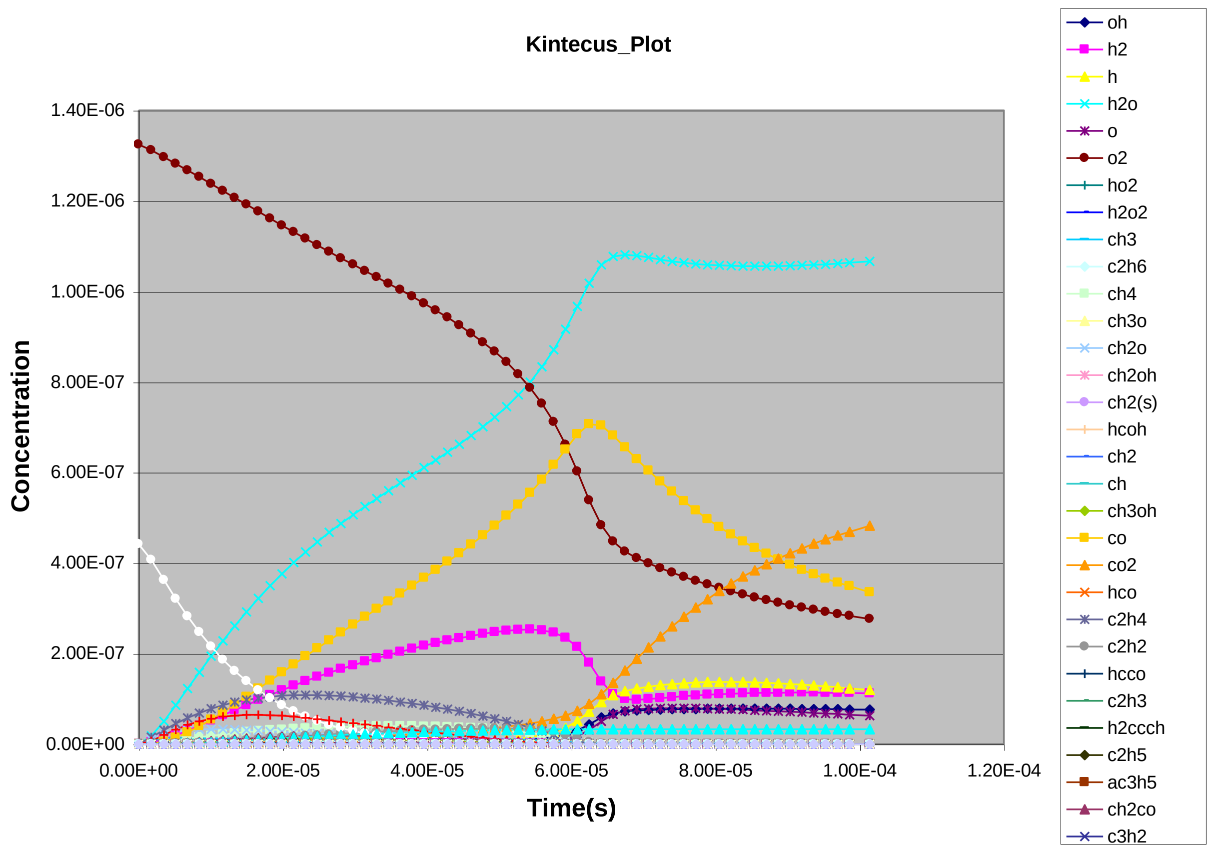

Figure 2. The results from the reduced ethanol combustion model[4]] (using a safe value of 0.001).. This reduced model contains 235 reactions and requires only 8 seconds to run on a 866 Mhz Pentium III.

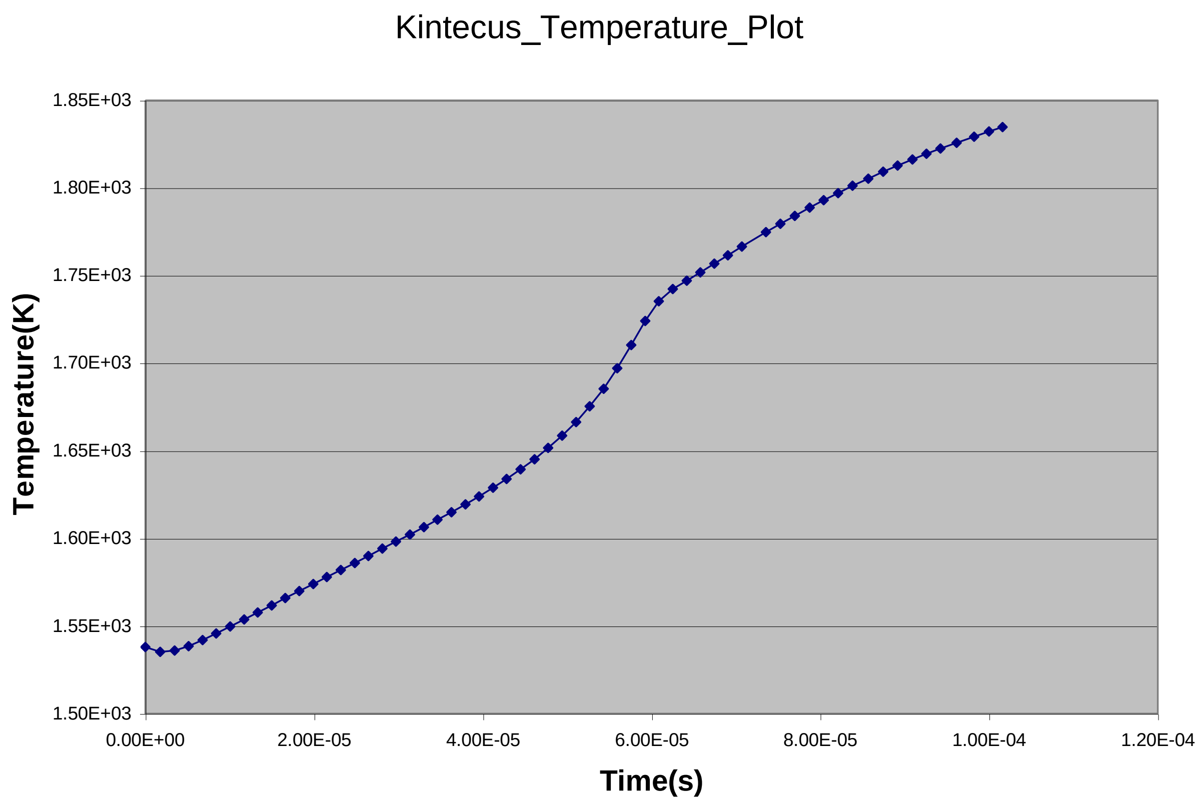

Figure 3. The temperature results from the original ethanol combustion model[4]. The original model contains 400 reactions and requires 43 seconds to run on a 866 Mhz Pentium III.

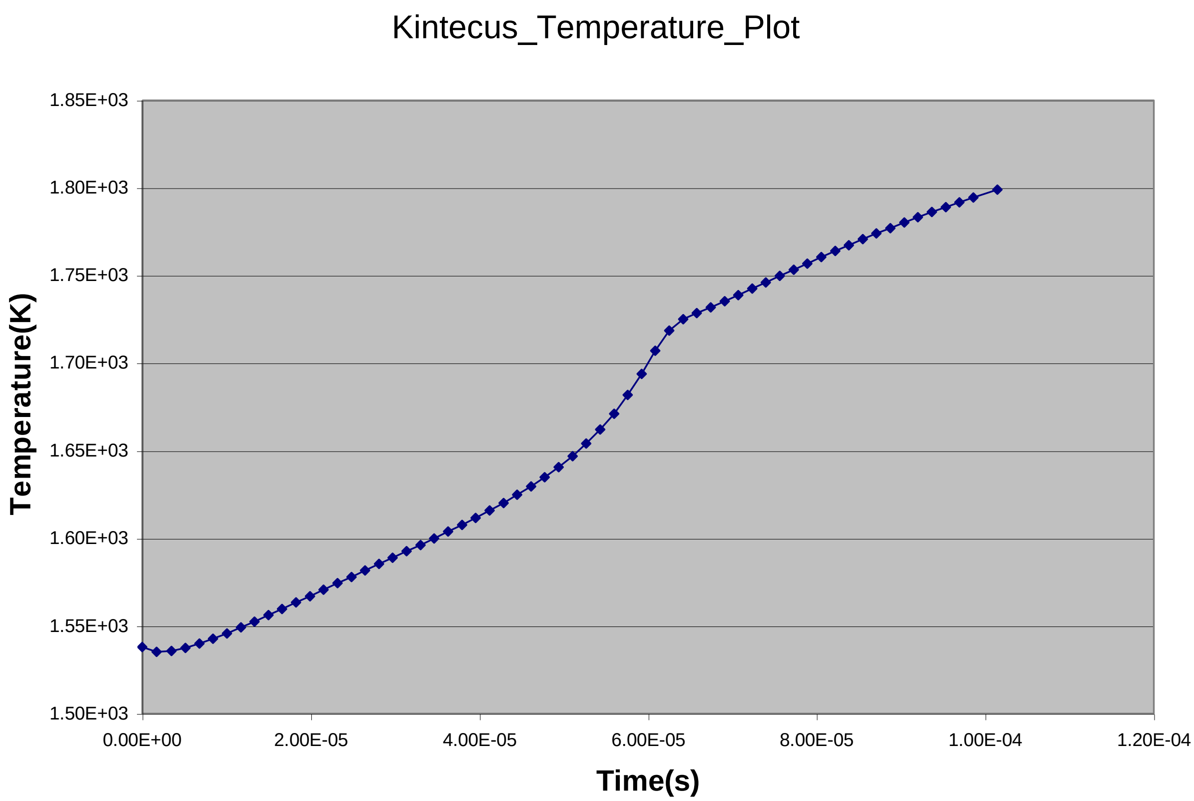

Figure 4. The temperature results from the reduced ethanol combustion model[4] (using a safe value of 0.001). This reduced model contains 235 reactions and requires only 8 seconds to run on a 866 Mhz Pentium III. The final temperature differs only less than 3% from the original, more extensive, slower combustion model.

Intrinsic Low Dimensional Manifold Analysis

For a future version…

Atropos Switches

Atropos provides various switches/options to control the program's behavior, input files, outputs files, and even screen messages. The switches are always supplied in the command line for Atropos right after the program name:

> Atropos (switches, if any)

```
The following command-line options are:

 -PREF Set directory/prefix sensitivity analysis filenames.
       ( Default is 'Sensit')
 -QUIET Don't diplay output or warnings.
 -MOD:filename (Model Description Input File)
 -NEWMOD:filename (New, Reduced MODEL Output File)
 -safe:(number) Use number for determination of transitional
                reactions being removed (Default is 0.5)
 -PCUT:(number) Principal Components that are under this number
       are NOT displayed. Default values is: 1.0000000E-002
 -i  Enter interactive mode for graphical interface.
 -o:(number) Output files based on numerical value:
     1=Eigenvalues.txt file, 2=Eigenvectors.txt file,
     4=Principal Components to standard output console, 8=New
     Reduced Chemical Kinetic model into NEWMODEL.DAT file. Add
     up values to output multiple files, ie number=1+2+4+8=15 =
     Output All files.
 -h/? You get this list.
```

3. Advanced Analysis

This section will describe the various numerical techniques provided with Atropos to enhance one's modeling capabilities significantly.

Numerical Techniques

Mechanism Reduction and the "-safe" Switch

Sometimes "transitory" principal components show up in Atropos' chemical kinetic mechanism reduction. Depending on the starting conditions, these transitory components could be significant, so a safety factor was implemented to prevent Atropos from accidentally removing those possibly critical chemical reactions. By trial and error, a safety factor of 0.5 was the best. A smaller safety factor will allow more reactions to "get by" the chemical reaction reduction algorithm. A safety factor of zero will not drop a single reaction. Larger safety factors will possibly remove reactions that could change the concentration distributions of some species but will allow a more condensed, faster, and much easier-to-understand mechanism. The "-safe" switch should be used in a heuristic manner to get the best, smallest chemical mechanism eventually. One might try the default safe value and retry Atropos with a logarithmic scale of safe values such as:0.1, 0.01, 0.001, and 0.0001 to see which ones yield a smaller, faster, and a more precise chemical mechanism.

The sample Atropos worksheet, "Atropos_ethanol_reduction.xls" demonstrates this heuristic manner with the safe switch ending with a final value of 0.001 to get a final, accurate, smaller, faster ethanol combustion model (see the Kintecus worksheet Ethanol_combustion_reduction.xls).

Overall Sensitivity Coefficients : B_r

The following equation describes the Overall Sensitivity Coefficients B_r :

$$B_r = \sum_{i=1}^{(total\#of\ NSC\ files)} \sum_{j}^{(total\#of\ species)} \left(\frac{\partial \ln[Species]_{i,j}}{\partial \ln k_r} \right)^2$$

One can see that B_r are the diagonal entries of $S^T S$ and are an excellent way to represent the total "flux" or movement of mass that any reaction r can accomplish. The larger the reaction's $B_{r,}$ the more overall system movement of the mass is going through it. These values can be seen in Atropos' output beginning with the line, "`The diagonal entries of TRANSPOSE(S)*S (B_r) are shown below.`".Keep in mind B_r **does not** represent the importance of a reaction r. That can only be determined by analyzing the principal components of the top eigenvalues. After the following line in Atropos' output, one can examine these important values: "`All eigenvalues with Principal Components displayed and`." The reactions containing the most significant principal components for the largest eigenvalues are the most influential reactions throughout the chemical kinetic run. The reactions containing the most important principal components for the smallest eigenvalues are the most negligible effective reactions throughout the chemical kinetic run. For a full explanation of all those significant quantities, refer to the main paper[1] or examine a recent paper[3] that explicitly uses most of these values to verify a medium-sized biochemical model on the free-radical mechanism of peroxynitrite decomposition.

FASTSTART

This section is for those who do not read or scan the primary documentation. If you cannot run your model after following the short procedure below, you should read the primary documentation above.

1) Atropos requires at least several Normalized Sensitivity Coefficient matrices to be stored somewhere on your hard disk (such as “C:\kintecus” OR "C:\program files\kintecus"). The kinetics program Kintecus will automatically generate these matrix files. Refer to the Kintecus documentation under the FASTSTART section to see how easily this is accomplished.

2) Go into command mode (on the Windows start button, select RUN, type “command,” and press the <ENTER> key) and create a file named MODEL.DAT. If you have Excel97/2003 you can use the *blank* **Atropos_workbook.xls** for a starting point.

3) Run Atropos with the following switch:
>Atropos -PREF:"C:\program files\kintecus\sensit" -MOD:"C:\program files\kintecus\oxidation-mechanism.dat". The above switch assumes your chemical kinetic model and its corresponding normalized sensitivity coefficicent files (such as SENSIT01.TXT, SENSIT02.TXT, SENSIT03.TXT, SENSITnn.TXT) are located in “C:\program files\kintecus” It would help if you appropriately changed the directory path when necessary.
If you are using the **EXCEL Atropos Graphical Interface,** then be sure to type the -PREF: “C:\program files\kintecus\sensit” option under the Atropos Switches cell **and** copy your chemical kinetic model into the Excel worksheet named “model.” Click the RUN button.

4) A new reduced chemical kinetic model will be generated named NEWMODEL.DAT. You can now use this new model in future runs.
If you are using the **EXCEL Atropos Graphical Interface**, the new reduced chemical kinetic model should have automatically been loaded into an Excel Worksheet named “newmodel.”

5) ***OPTIONAL:*** You might wish to examine the output from Atropos as it contains various essential Principal Components, eigenvalues, eigenvectors, and overall normalized sensitivity coefficients about your system that will be extremely useful in chemical mechanism elucidation. To fully explain all those significant quantities, refer to the primary documentation.

Errors and Warnings

Most errors and warning messages should be sufficiently detailed to allow a user to figure out what is causing the main problems. This section in the documentation might be further detailed in later versions.

Some errors list the line to screen and the source line. The source line is the actual line number in the original file that is giving Atropos trouble. Suppose you have many warnings/errors that scroll by on the computer screen too fast. In that case, you can pause the listing by pressing the Pause/Break key and resuming by pressing the Enter key, or you can output everything that usually goes to the screen to a file by using redirection such as: “`Atropos -show -PARM:C/FL/P1.TXT > View.txt`”. All screen output can be seen in the file view.txt using a text editor.

Citation

If you utilize Atropos in any paper, publication, book, conference, proposal, etc., then please cite Atropos as:

[1] Ianni, J.C., Atropos, V1.40, 2019, www.kintecus.com [2] Vajda, S.; Valko, P.; Turanyi, T, *Int. J. Chem. Kin*., 17, **1985**, pp55-81.

References

[1] Vajda, S.; Valko, P.; Turanyi, T, *Int. J. Chem. Kin*., 17, **1985**, pp55-81.

[2] Dunker, A.M., *J. Chem. Phys*., 81(5), **1985**, pp2385-2393.

[3] Kirsch, M.; Korth, H.; Wensing, A; Sustmann, R.; de Groot, H, *Arch. Biochem. Biophys*. , 418, **2003**, pp133-150.

[4] Marinov, N.M., “A Detailed Chemical Kinetic Model for High Temperature Ethanol Oxidation”, *Inter. J. of Chem. Kin*. Vol. 31, **1999**, Iss. 3 pg 183-220.

Registration

Atropos Version 1.40 Registration

Industrial Registration

Use this section to register Atropos if you are **an industrial/governmental/commercial entity.**

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Please go to www.kintecus.com for further Atropos registration details.