KINTECUS

KINTECUS

"From thence all things flow; and there is besides necessity, and that which is for the advantage of the whole universe, of which thou art a part. But that is good for every part of nature which the nature of the whole brings, and what serves to maintain this nature. Now the universe is preserved, as by the changes of the elements so by the changes of things compounded of the elements." - Marcus Aurelius / "The Meditations"

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1. Introduction

Kintecus® is a compiler to model the reactions of chemical, biological, nuclear, and atmospheric processes using three input spreadsheet files: a reaction spreadsheet, a species description spreadsheet, and a parameter description spreadsheet. For thermodynamics, an optional thermodynamics description spreadsheet can be supplied. In addition, one can fit/optimize almost any numerical value (rate constants, initial concentrations, Troe factors, third body enhancements, the energy of activation, starting temperature, etc.) against an experimental or "fabricated" dataset. Kintecus® has been designed with ease of use in mind. There is absolutely no programming, compiling, or linking required.

A quick overview of some main features:

- The ability to convert Chemkin-II/Chemkin-III/Senkin models to Kintecus format. Kintecus can run almost any converted Chemkin model. Once converted, you may apply **any Kintecus feature** to the system. Do not be surprised to see the converted system run much faster! In addition, Kintecus can use multiple Chemkin thermodynamic databases simultaneously and provides a way to use "reserve" species to a respective thermodynamic database. One can also convert the databases to a "freeform" format, which can be loaded into Excel or Lotus 1-2-3. The "freeform" database is much easier to maintain and update. In addition, the converted model is not limited to several elements; in fact, your model can contain the entire Periodic Table.

- Kintecus comes with multiple thermodynamic databases containing thermodynamic data (**G, E, H, S, Cp, K, Kp**) on **several thousand** species over a wide temperature range (300K-6000K)!

- Reactions, adiabatic or non-adiabatic (isothermal), can be performed under **isochoric** (constant volume) or **isobaric** (constant pressure) with a simple flick of a switch **along** with optional volume, temperature, concentration wave **perturbations** or set **profiles**.

- An in-depth and easy-to-use **Uncertainty Analysis** (**Monte Carlo** sampling runs) to calculate "**real-life**" averaged behaviors with confidence bands/standard deviations of your chemical system given Gaussian/Poisson/Uniform deviations.

- **Fit/Optimize** or regress rate constants, initial concentrations, Lindemann/Troe/SRI/LT parameters, enhanced third body factors, initial temperature, residence time, energy of activation and many other parameters against your dataset(s) or multiple datasets with different initial conditions (**global data analysis**) with/without **local shared variable regressions.** Note that Kintecus will fit the parameters at EXACTLY the time your data was measured. Unlike other programs, Kintecus DOES NOT interpolate a function against your data and then regress the values against this interpolation. There is no need to "clean" your data, suggest interpolation methods, or specify timing meshes against your experimental data since Kintecus calculates values at precisely the times you specify in your experimental datafile. Kintecus V3.8 and above can also perform accurate **bootstrapping** of errors.

- **Global Data Regression/Fitting/Optimization Analysis**: Kintecus V5.0 and up now supports a compelling global data regression/fitting/analysis. You can regress or fit or optimize multiple datasets that have numerous initial conditions such as temperatures, pressures, concentrations, or any combination and with data sets that have different time scales, different time steps, different species, temperature profiles, heat output, different amounts of data points, etc. Many sample Kintecus-Excel worksheets demonstrate some basics of this new global regression.

- **Fitting/Regressing with Arbitrary Constraints/Conditions/Heat Output**: Apply any type **of constraints of complexity in equation form between any** variable or constants for use in regression/fitting.

- One can now also regress/fit the initial conditions for a species (or temperature) in any of the "initial_conditions.txt" file (some programs call this **local variable fitting/regression**). Suffixing any numeric value can do this in an initial condition file with a question mark, "?". Kintecus V5.00 and up now supports the ability to regress/fit against heat generated during a reaction.

- **User-Defined Chemical Rate Equations:** The **special USER chemical kinetic function** is new in Kintecus V6.51. Using ANY mathematical form, you can use it to define your own chemical kinetic rate equations of any complexity.

- Users can utilize the OUTC[] operator for a species for reaction rates that involve **families of species** such as "ROH=[C2H5OH]+[C3H7OH]+[C4H9OH]+..."

- Kintecus can model thousands and thousands of reactions in a relatively short time. Kintecus has been used with models as large as **120,000+ chemical reactions modeled back in 1996**. You will not find anything faster than Kintecus.

- Kintecus can output complete **global normalized sensitivity coefficients** selectable at any specified time or times. Normalized sensitivity coefficients are used for accurate mechanism reduction, determining which reactions are the primary sources and sinks (network analysis). This feature can also show which reactions require valid rate constants and which ones can have essentially guessed rate constants.

- Kintecus can use **profiles or perturbations of any wave pattern** for any species, temperature, volume, or hv. Using profiles/perturbations can also be used for studying very realistic systems, such as quenching effects, dissolution of various gases into a system over time, induction of current into a system, heat flow into a system, a piston compressing the reaction chamber, and so on.

- Built-in support for unique reactions such as: reactions **involving third-bodies (M)**, fall-off reactions (Troe, Lindemann, JPL, SRI, etc.), **enhanced third bodies**, exclusive multiple enhanced third bodies, vibrational transfer reactions (Landau-Teller), and many other types of reactions.

- Kintecus allow for entering in **fractional coefficients** for species! Now you can finally model that last step in the Oregonator or crunch 100 elementary reaction steps in one reaction step!

- Efficiently perform four types of **scanning** (parametric study): combinatorial, parallel, parallel-repeat, and sequential.

- **Heterogeneous chemistry** can be modeled. For example, a species in the aqueous phase will not contribute to the overall pressure in the system or be involved in third-body reactions or fall-off reactions. Gaseous species can "enter" other phases throughout a simulation and vice-versa.

- The ability to do reactions in a **continuous stirred tank reactor** or homogenized **plug-flow reactors** (CSTR, PFR) with multiple inlets and outlets and **independent FLOW temperatures** in either adiabatic, non-adiabatic, or program temperature runs.

- Kintecus supports **unique IUPAC chemical kinetics** forms from the **Master Chemical Mechanism (MCM)** (see http://mcm.leeds.ac.uk/MCM/parameters/complex.htt , http://www.iupac-kinetic.ch.cam.ac.uk/ and/or http://iupac.pole-ether.fr/ or Google/Bing "Master Chemical Mechanism"). Most of these forms pertain to unique pressure fall-off reactions that cannot be fully cast into the traditional Troe, Lindemann forms.

- **Kintecus can utilize Multiple-well, Multiple-channel Reactions Utilizing Chebyshev Polynomials and PLOG reactions**. Kintecus V5.5 and up now support the Chebyshev expansions proposed by Venkatesh for representing pressure fall off and temperature-dependent rates of multiple well reactions. Please see those references for the list of equations utilized in Kintecus to calculate those rates.

- **Global Equilibrium calculations**. Why design a kinetic scheme when all you have to do is give Kintecus a listing of all the relevant species in your system. **No need for ANY REACTIONS!** You do not even have to specify which species are reactions or products! You can even perform stability plots of systems over ranges of temperatures, pressures, volumes, and concentrations of other species.

- **Mechanism Validation.** Validate a chemical mechanism by identifying the various illegal loops and locating conditions where microscopic reversibility is violated. This feature can be highly useful for accurate chemical mechanism determination, rate constant fitting, regression, and creating accurate deep learning models.

- **Automatic Graphical Chemical Kinetic Diagrams.** Kintecus can automatically create graphical flow plots of one's chemical mechanism in a myriad of ways. This can easily be combined with the **Mechanism Validation** to visualize illegal chemical kinetic loops.

- Quickly and easily, hold one or more concentrations of any species at a constant level just by typing the value in the field of the species.

- A powerful parser with an **automatic mass & charge balance checker** for those reactions that the graduate student "supposedly" entered in correctly, but the model yields incorrect results or is divergent. Do you know a kinetics program that can completely parse and check for mass/charge balance on a reaction like this:

  Rate Constants , (m and Ea), REACTION:
  1.234e-20, 1.2, 3000,CH3(((NO2)3(CO)93)3 (CH2)9)+23.30H2O+ + Co2 = A--- + B++++ +C+C+C+C+C+D+E+59F+G+9.e-3H+I+3.1415J

  Or how about this:

  Rate Constants , REACTION:
  5.043e+20 , 3.43234 (CH4(N(PO342)43(CH3)3)34)(Os(S7)8)34++++ + 199.432 X++++ 5CH5+ ==>5.434 Some_Really_Funky_Long_Enzyme_Name+ 8 HCl + HCO3-

Kintecus can accurately check the above reaction for mass and charge balance because you can create an optional name file containing common names for species and then their mass representation. This brilliant mass balancing can be used for biological and nuclear reactions! Kintecus also provides duplicate reaction and species checking

- Perform complex hierarchical **cluster analysis** on temporal concentration profiles of the network with/without experimentally obtained temporal concentration profiles. Hierarchical cluster analysis in Kintecus can group related and unrelated parts of temporal concentration profiles in a meaningful, quantitative way. This grouping allows a user to see initially indiscernible or hidden patterns.

- It can compute all internal **Jacobians analytically**. This is useful for simulating extensive kinetic mechanisms (more than 50,000+). Finite difference methods can cause underflow or overflow errors in approximately large Jacobians during the simulation.

- Perform **eigenvalue-eigenvector analysis of the Jacobians** of the system as the model runs. This is useful for metabolic control analysis (stability analysis).

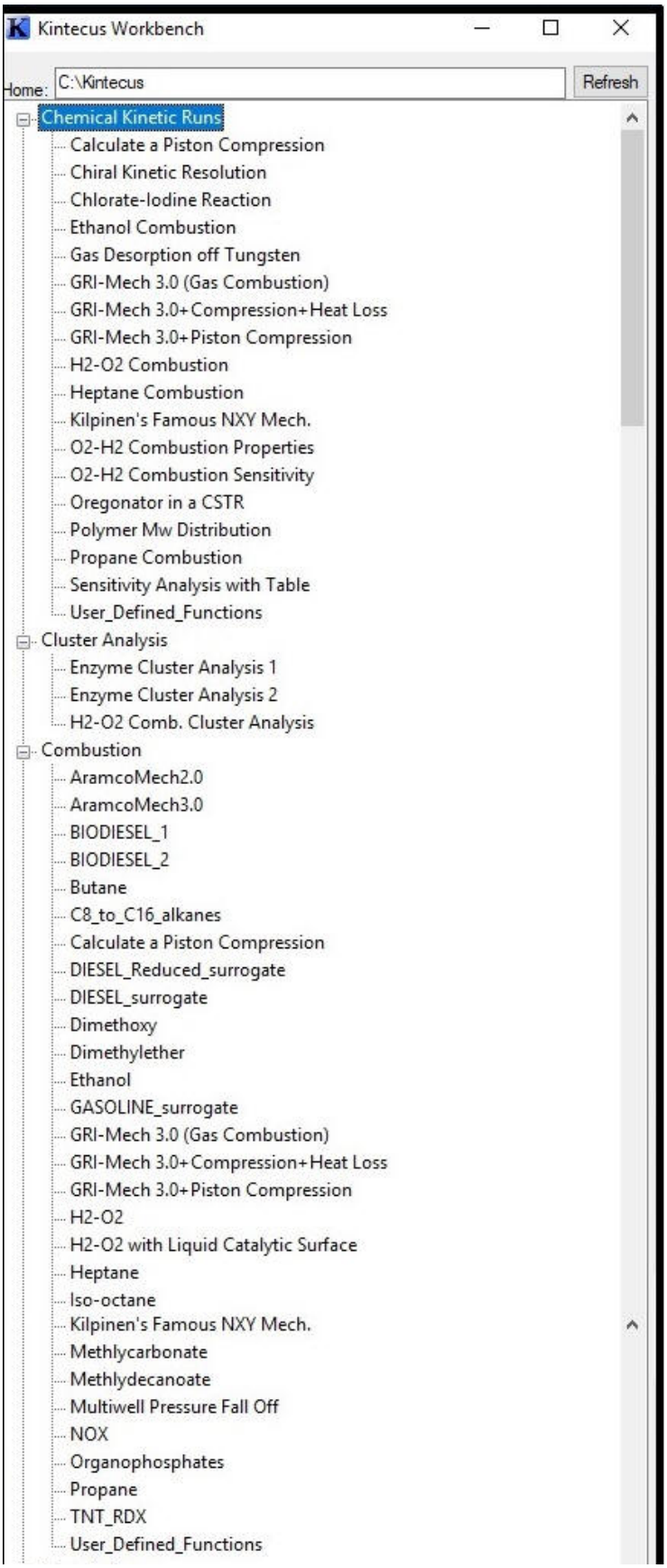
- Dynamic mode for feedback runs and external user control of Kintecus.

- **Automatic generation of the species spreadsheet file** using the reaction spreadsheet file. Why waste time finding, entering, and initializing all the different species in your kinetic scheme?

2. The Program

The Kintecus Workbench

The “Kintecus_Workbench” is relatively new and is an easy GUI launching of models/codes/scripts and allows one to add your own models/scripts/documentation/etc. Just double-click on the program to view most of the Kintecus-Excel and Kintecus-Batch examples and documentation, tools, link, and other items. You can add your own models/documentation/homework/weblinks/etc if you Click the "Other==>Add Your Own Stuff to the Kintecus Workbench". As of 2018, you are shown below most of the items in the Kintecus_Workbench that allow quick and easy access. New items are added to the Kintecus_Workbench with every release.


Kintecus Workbench
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C:\Kintecus
Refresh
Chemical Kinetic Runs
Calculate a Piston Compression
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Ethanol Combustion
Gas Desorption off Tungsten
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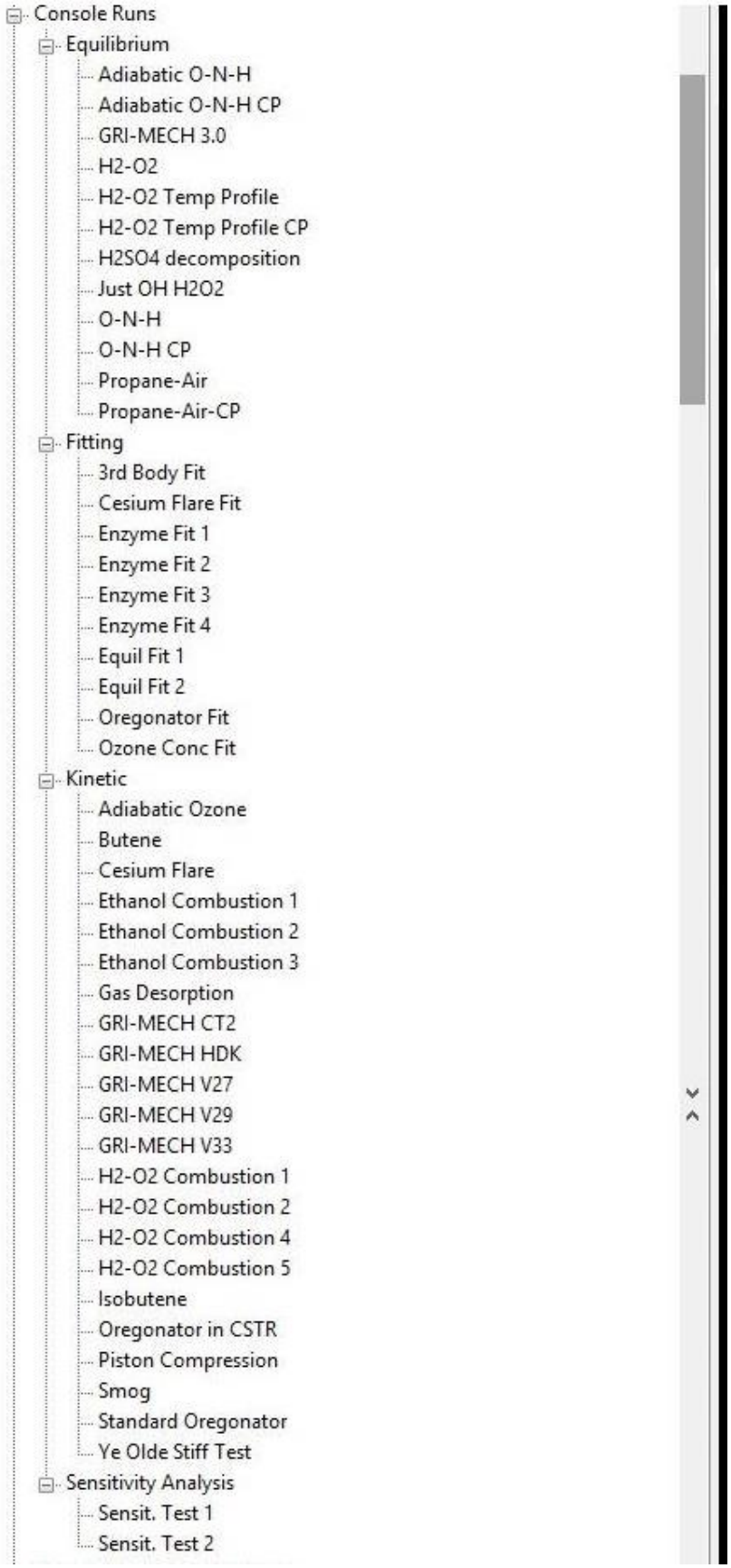
DIESEL_Reduced_surrogate
DIESEL_surrogate
Dimethoxy
Dimethylether
Ethanol
GASOLINE_surrogate
GRI-Mech 3.0 (Gas Combustion)
GRI-Mech 3.0+Compression+Heat Loss
GRI-Mech 3.0+Piston Compression
H2-O2
H2-O2 with Liquid Catalytic Surface
Heptane
Iso-octane
Kilpinen's Famous NXY Mech.
Methlycarbonate
Methlydecanoate
Multiwell Pressure Fall Off
NOX
Organophosphates
Propane
TNT_RDX
User_Defined_Functions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Equilibrium
Adiabatic O-N-H
Adiabatic O-N-H CP
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H2-O2
H2-O2 Temp Profile
H2-O2 Temp Profile CP
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O-N-H CP
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Propane-Air-CP
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Cesium Flare Fit
Enzyme Fit 1
Enzyme Fit 2
Enzyme Fit 3
Enzyme Fit 4
Equil Fit 1
Equil Fit 2
Oregonator Fit
Ozone Conc Fit
Kinetic
Adiabatic Ozone
Butene
Cesium Flare
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Ethanol Combustion 2
Ethanol Combustion 3
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GRI-MECH HDK
GRI-MECH V27
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Isobutene
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Smog
Standard Oregonator
Ye Olde Stiff Test
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Convert Chemkin to Kintecus
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Equilibrium H2SO4 Phase
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Fitting-Regression
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Chlorate-Iodine Reaction
Oregonator in a CSTR
Polymer Mw Distribution
z The Atropos Mechanism Elucidation System
Atropos Console
Atropos Manual
Atropos on the Web
Atropos Reduced Ethanol. Combustion
Atropos Reduced Formaldelhyde Oxidation
Blank Atropos Workbook
Full Formaldelhyde Oxidation Model
Kintecus Reduced Ethanol Combustion
Sort By: Name (Default)
www.kintecus.com

Running Kintecus in Command Mode

Click on the Windows Start button (the icon that looks like a window on the most bottom-left hand side of your screen) and type “command” (in Windows 7, then click on the sphere located in the bottom left-hand corner and type “cmd”) and press the <ENTER> key. You will be in a command prompt. Change to the directory where you uncompressed the Kintecus files (ie. “**cd c:\kintecus**”). You can see what is in the directory by typing, “dir /p”. You can run Kintecus as:
“**Kintecus (any switches you may want to use)**,” or if you wish to capture the on-screen information type: “**Kintecus (any switches you may want to use) > view.txt**.” Sample batch scripts are in the “\Kintecus\Sample_Runs\” (inside C:\kintecus type “**cd sample_runs**”; then type “**ethanol1**” to run one example) This will output any errors, warnings, and information to the file view.txt, which can be viewed with any text editor or word processor. The output file, CONC.TXT, will contain the species’ concentrations and temperature (if the model is in thermodynamics mode). If you are regressing/fitting data to your model, the final optimized parameters are stored in OPTOUT.TXT.
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 Kintecus runs: Kintecus_workbook.xls, Enzyme_Regression_Fitting.xls, Ethanol_Combustion.xls, GRI_MECH_30.xls, Oregonator_in_CSTR.xls, Combustion_Workbook_OH.xls and Wolfrum_with_Temp_Program.xls and many, MANY others.
Although Excel **is NOT required**, it is highly recommended you use Kintecus with the Kintecus-Excel worksheets as it makes it much easier to maintain/create models in one Excel Workbook.

Entering Simple Models

For your reactions, you must first create a model spreadsheet file. **If you have Microsoft's Excel, you can open the Kintecus_workbook.xls or any sample xls workbooks and edit the model, species, or parm data worksheets. Afterward, you can run/plot your model by clicking on one of the buttons located on the CONTROL worksheet.** Suppose you are not going to use a spreadsheet. In that case, it's recommended to use a text editor (such as MS-DOS's "EDIT" or Notepad or Linux's “vi” or “emacs” or install the freely available and user-friendly “Genie” or “nano” text editors and use commas to separate the fields. In the first column, enter the reaction constants, and in the second column, enter the reaction. If you start a line with "#', or double quotes, ' ", 'the line will be taken as a comment. End the reaction sheet with END + RETURN on one line. Use "==>' to represent yields and "=" to represent a reaction that can go forward and backward (with the reverse step having a reverse rate constant, k_b , of one (1.0) if the thermodynamic mode is NOT specified). An example :

#		
# My first reaction		
#		
1.75E-05	CH3C00H + H2O = H3O+ + CH3COO-	Optional comments
END		

Figure 1

When entering reactions, do not use the following characters: “ | ” (vertical bar), the comma, TAB in the spreadsheet cell unless you are using a text editor. Inside a text editor one can use the comma or colon to separate the various fields. Just be sure to pick one separator, do not randomly switch from the comma to the colon on the same line. You can name the reaction file anything you want, and Kintecus will read it, but for now, save the spreadsheet file as a Text (or plain text) file. If you are using Excel, select, under the File menu select “Save As”, enter model.dat as the filename, and select the type as “Text (Tab delimited)”. Kintecus looks for this model.dat as the default reaction filename (you can override this option). As a side note, anything after the END is ignored, so you can have equations entered below the "END" as you modify your model or place a # to comment one whole reaction line out of the model.

Make sure the reaction text file (MODEL.DAT) and a parameter description file (PARM.DAT) are now in the same directory as Kintecus and run it with the following line: “KINTECUS -c” . This will automatically create the species spreadsheet file, ADDSPEC.TXT, with all values and switches set to 0.0 and "No" respectively.

EQUILIBRIUM MODE NOTE: If you are running Kintecus in equilibrium mode, then the model spreadsheet file is NOT UTILIZED.

Go back to your favorite spreadsheet program and load this file. In Excel, under the File menu, select “Open,” and in the file request prompt, select “All files” for “Files of type”. You should see the ADDSPEC.TXT file. If not, make sure you are in the correct directory. Now, double-click on the ADDSPEC.TXT file. The Text Import Wizard will automatically open; just click the Finish button. If you created the model.dat file with Excel, the ADDSPEC.TXT file should easily load into Excel. If it does not load easily, make sure Excel’s Text Import Wizard is installed and Delimited is selected under “Original data type.” Under Step 2 for the Text Import Wizard, make sure that “Tab” is selected under “Delimiters”. Click Finish. Whatever character was used to separate the fields in the model.dat file, Kintecus will use that same character for all its output files. If you are using another spreadsheet program (like Lotus) and save the model.dat spreadsheet as a text file for Kintecus to load, the ADDSPEC.TXT file will also have commas in it. For Excel, you should see something like this:

# Species	Residence	Initial	Display Outpu	External	SSA ?	Constant File?	
#	Time in CSTR(s)	Conc.	(Y/N) ?	Conc.	(Y/N)	(Filename/#/No)	
CH3COOH	0	0	No	0	No	No	Optional comment
H2O	0	0	No	0	No	No	water
H3O+	0	0	No	0	No	No	hydronium
CH3COO-	0	0	No	0	No	No	Acetate
END							

Figure 2

Enter 1.0 and 55.56 in the initial concentration fields (Initial Conc.) for CH3COOH and H2O, respectively. Also, enter "Y" in all the display output fields. This allows you to view the concentration of the species at selected time intervals as the simulation runs. You can name the species description file anything you want, and Kintecus will read it, but for now, save the spreadsheet file as an ASCII (or plain text) file under the name "SPECIES.DAT". Also, be sure to save it in the same directory as Kintecus. That's it! Now run Kintecus. An output file (usually named “CONC.TXT”) containing the concentration profile of all the species that are being displayed is saved in this file. You can now view the concentration profile of all the displayed species by loading this file in your favorite spreadsheet program and plotting it!

If you wish to alter the simulation time, you can load in the PARM.DAT file. Once this file is loaded, you can see the line "Simulation Length," there are five fields: DAYS, HOURS, MINUTES, SECONDS, and PICOSECONDS under that.

# Parameter	Description	SpreadSheet		
# See the	documentation file	for an	explanation	of each field
#				
# Minimum	Maximum	Ea Units	Concentration	
# Integration Time(s)	Integration Time(s)		Units	X0
1.00E-06	1.00E-01	CAL	MOLES/L	0
# Temperature	Pressure-Constant ?	Volume Profile ?		
# (K)	(Yes/No)	(Filename/"NO")	X0	X0
1000	No	No	0	0
# Simulation	Length:			
# DAYS	Hours	Minutes	Seconds	PicoSeconds
0	0	0	1.00E+00	0
#				
#hv(filename)	Sampling Interval	Percent(%)	Accuracy	X9
None1	1	0	1.00E-08	0
#				
# X10	X0	X0	X0	X0
0	0	0	0	0
#				
END				

Figure 3

If you want the simulation to run for one hour, just enter "1" below the Hours field and ensure there are zeroes in the other fields. For now, do not worry about the other fields.

Intermediate Models

The Parameter Spreadsheet File

This section will describe some intermediate modeling techniques Kintecus can do, but first a more detail explanation of the parameter file (PARM.DAT) will be needed. The parameter file is shown below:

# Parameter	Description	SpreadSheet		
#				
#				
# Starting	Maximum	Ea Units	Concentration	
# Integration Time(s)	Integration Time(s)		Units	X0
1.00E-06	1.00E-01	CAL	MOLES/L	0
# Temperature (K)	Pressure-Constant ?	Volume Profile ?	External Heat Source/Sink	
# or Filename	(Yes/No)	(Filename/"NO")	(Values/Filename)	
1000	No	No	0	0
# Simulation	Length:			
# DAYS	Hours	Minutes	Seconds	PicoSeconds
0	0	0	1.00E+00	0
#				
#hv(filename)	Sampling Interval	Percent(%)	Accuracy	X0
None1	1	0	1.00E-08	0
#				
# CSTR/PFR inlet temperature flow	X0	X0	X0	X0
0	0	0	0	0
#				
END				

Figure 4. Sample parameter description worksheet or file.

As one can see, there are several fields. The field name is located directly above the spreadsheet cell. The 'X0' field names are for future use. For example, the Temperature field has 1000 degrees set in it. Most parameter description spreadsheet settings usually do not have to be changed, but it is good to know what each field is precisely.

****EXCEL FEATURE**: If you are utilizing the Excel graphical interface and have a Kintecus-Excel workbook loaded, the PARM.DAT file as described is automatically written out to the PARM.DAT file from the PARM Excel worksheet located in the Kintecus-Excel Workbook. This saving process happens immediately after one clicks the "RUN" button on the CONTROL worksheet. **YOU DO NOT HAVE TO MANUALLY SAVE A PARM.DAT FILE.**

It is obvious what should be entered in the Temperature field; just be sure the units for that field are in Kelvins. If your model is not using the Arrhenius expression, special or unique reactions, or thermodynamics, then this field is not used. You can also enter a filename here containing a temperature program. If you wish to use a programmed temperature, please skip to the section of applying perturbations under the Constant File Field in the Species Description Spreadsheet. Kintecus treats temperature programs exactly like perturbations to species concentrations.

The **"Pressure Constant ?"** field excepts two values: "Yes" or any entry other than "Yes" (which translates to Kintecus, ignore this field). If you specify "Yes," the system's volume will change to keep all gaseous products at the same pressure the simulation started. Kintecus calculates the starting pressure by summing all gaseous species' concentrations and then multiplying that by the gas constant, R, and temperature.

The **volume profile** fields allow one to enter a perturbation file (see the species spreadsheet file section for a full explanation of the types of perturbations allowed) containing the volume profile of the system through a simulation run. This will enable one to model piston compressions. Kintecus treats the numbers in the perturbation file as divisors into the gaseous species concentrations. For example, a value of one does nothing to the system, while a value of 0.5 tells Kintecus to cut the volume in the system by half, so the concentrations of all gaseous species are doubled. A value of two, 2 directs Kintecus to double the volume, so the concentrations of all gaseous species are halved. A gaseous species has no phase information attached to the end of the species name or will have a **{g}** appended to the end of the species name. Look below in the Species Description Spreadsheet for a description of species phase information.

A new field in Kintecus V3.5 is the **External Heat Source/Sink field**. This field allows one to model External Heat Jackets or External Temperature Baths, or dynamic Heat sources and sinks. You can enter one of **four types** of external heat source/temperature related items:

1) A numerical value representing an external Heat Source/Sink. This value will be added to the dH/dt equation and with units in (energy units)/sec/R or (moles-kelvin/sec**). In other words, your heat loss/gain value is either in cal/sec or ergs/sec or kcal/sec is divided by an appropriate gas constant R to get the units to (mol-kelvin/sec).**
2) A filename containing a profile (formatted like a "Constant File?" file) that represents a changing External Heat Source/Sink # Profile (Filename) with units in **(energy units)/sec/R** or **(moles-kelvin/sec**). In other words, your heat loss/gain value's units in cal/sec or ergs/sec or kcal/sec is divided by an appropriate gas constant R to get the units to (**mol-kelvin/sec**).
3) TWO values: One for Conductance of the container/reactor, followed by a COLON, ":", followed by the Extern. Temperature(K). Make sure the final units are in (**mol-kelvin/sec**).
4) One value and a profile: the first number represents the conductance of the container/reactor followed by a COLON, ":", followed by a filename containing a profile (formatted like a "Constant File?" file, see below for a description of what is a "Constant File") that represents a changing External Temperature. Make sure the final units are in (**mol-kelvin/sec**).
The "**GRI-MECH+Compression+Heat Loss.xls**" Kintecus-Excel file demonstrates one aspect of this **External Heat Source/Sink field** feature.

Kintecus has a special flag if you are running a simulation under constant pressure and wish to have your energy input scale with the increasing or decreasing size of the volume. In other words, if the volume increases by 2x, then the energy input decreases by 2x. This new feature can be turned on by utilizing the **"-cphs"** (constant pressure heat source) switch to the Kintecus command line.

The **DAYS, Hours, Minutes, Seconds, and PicoSecond** fields control the simulation length. These five fields easily allow one to set the total time of the simulation during a run from yearly events to femtosecond laser experiments.

The **Ea Units** field allows you to specify the units associated with the energy of activation used in the exponent of the expanded Arrhenius equation (the $\exp(-E_a/\underline{\mathbf{R}}T)$). If you are not using the expanded Arrhenius equation, you do not have to worry about this field.

Possible values (values are case insensitive) and their respective concentration units in this field are:

Energy Type	Other Synonyms allowed
Joule	J
Calorie	CAL
Kelvin	Kelv
KiloCalorie	KCAL
KiloJoule	KJ
KiloKelvin	KKelv

Table 1

The **Units field** allows you to use different concentration units during a run. Possible values (values are case insensitive) and their respective concentration units in this field are:

Concentration Type	Other Synonyms allowed	Other Synonyms allowed	Other Synonyms allowed	Other Synonyms allowed
Moles/Liter	Moles/L	Mol/L	Mol/liter	
Molecules/cm^3	Molecules/cc	Molec/cc	Molec/cm^3	1/cc or 1/cm^3
ppm	Parts per million			
Moles/cm^3	Moles/cc			

Table 2

It is recommended to use moles/cm^3 if you wish to use the thermodynamic databases associated with Chemkin® models.

The hv(filename) and Sampling Interval(s) are used together and are mainly for the simple use of hv in your equations (i.e. M + hv ==> M+ + e-). The hv(filename) can be one of three things: if None1 is entered, then hv=0 always; if None2, then hv=1 always; if anything else, then the field will hold the name of a file containing data that represents a profile for hv. The Sampling Interval holds the spacing in time (in seconds) between each data point. The number of data points in the filename and the sampling interval determines the total length of the hv profile. If the run time goes beyond the total computed time of the hv profile, then the data will repeat itself from the beginning of the profile (time 0). See the example profiles given under the "Constant File Field" below.

*NOTE: The hv(filename) and Sampling Interval(s) fields might be dropped in future Kintecus versions. Please use a species name of hv1 or hv2, etc, with "Constant File ?" Field (see below) for a *hv* profile.

The **Percent (%) field** is used to limit the size of the output concentration file (whose default name is CONC.TXT) without causing distortion. Kintecus will only output the concentration of all the species only when one or more Displayed species (see below in the Species Description Sheet) has changed more than Percent*Previously_Outputted_Value. Through the author's personal experience, using 1% as default does not distort the outputted concentration profile too much and keeps an okay file size. There is a slight distortion at 20% but can drastically reduce the concentration file's size. This field is handy for cutting the size of models that run for simulated years. A value of 7% is suitable for knowing how specific high peaks in concentrations you might be interested. A value of 0% will **output all values**. Since most computers are now quite fast in plotting abilities, **it is recommended to use 0%.**

The **Starting Integration Time, Maximum Integration Time, and Accuracy** fields determine how fast Kintecus can integrate your model and the error in the final concentrations. These fields are critical.

Accuracy determines how far out in the decimal place to keep the concentration accurately computed. Therefore, a value of 1.0E-9 will hold the first nine digits of the integrated concentration calculated accurately. The smaller you make the accuracy field, the slower Kintecus runs your model. If you have a huge model, you may want

to increase this to 1.0E-5 or larger. Of course, if you have stiff reactions and Kintecus can't seem to integrate your model, you should decrease this field to 1.0e-10 or so. See the Overflows, Underflows, Division by Zero, Singularities, Domain Errors section for a further description. Also, integrators 3, 4, and 5 (-INT:3 or -INT:4 or the –INT:5 switch) have extra options specified on the command line. Please see the Kintecus switches section below on these extra options.

The **Starting Integration Time** (in seconds) determines the first time step to integrate your model. After the first integration, this will change and grow larger if your accuracy is large or the stiffness of your model is low (meaning a decrease in execution time of the program). Alternatively, this starting time step could grow smaller if your accuracy is minimal or the stiffness of your model is high (meaning an increase in execution time of the program). It would be best if you did not have to change this in some cases. A special note for combustion modelers: since most combustion reactions happen in the first few tenths of a microsecond, you might wish to decrease this to 1.0e-7 or 1.0e-8 if you are having trouble near the very beginning of the simulation run.

The Maximum Integration Time has a few uses in Kintecus. This field is only used to determine the minimum timing threshold, which has to be exceeded before outputting the concentration of displayed species. In this case, a value of 1 to 10 seconds is acceptable for simulations lasting 10 minutes to a few days. Still, if you are doing a simulation that only lasts a few nanoseconds, then a value of a few femtoseconds (1 x 10(-15)) should suffice. Reducing the maximum integration time will output more concentration values. If you have a final model and wish to have a nice plot full of points that look good for a publication, you can try reducing this field by 10/100/1000. Don't forget to use the '**-obeymaxint**' switch to force Kintecus not to use time steps that exceed the "Maximum Integration Time" value. However, the actual wall time to your run will increase.

EQUILIBRIUM MODE NOTE: If you are running Kintecus in equilibrium mode, then the only fields utilized in the parameter description spreadsheet are the time fields, temperature, "Pressure Constant" and the "Volume Profile" field. The Units field is used, but you must **keep this field to Moles/Liter**. The Maximum Integration Field is used and it is recommended to keep this field set to 60 seconds.

A new feature in Kintecus V3.8 is the "**CSTR/PFR inlet temperature flow" field**, which specifies the global temperature for all the inlets of a CSTR/PFR run. This field will allow additional cooling or heating effects depending on the flow (residence time in the "Species Description Spreadsheet" below), "External Concentration" (also located in the "Species Description Spreadsheet" below), batch reactor/CSTR/PFR temperature, and the pressure are constant or not.

Fields with a heading of "**X0**" are reserved for future use, and their respective entries should be kept at zero, "0".

Kintecus will look for the Parameter Description SpreadSheet under PARM.DAT as the default filename. This default filename of "PARM.DAT" can be overridden. See KINTECUS Switches Section setting below.

The Species Description Spreadsheet

Here is a detailed description of how exactly each field in the species description spreadsheet is used by Kintecus.

****EXCEL FEATURE**: If you are using the Excel graphical interface and have a Kintecus-Excel workbook loaded, then the SPECIES.DAT file as described below is automatically written out to the SPECIES.DAT file from the SPECIES Excel worksheet located in the Kintecus-Excel Workbook. **YOU DO NOT HAVE TO CREATE A SPECIES.DAT FILE**. This saving process happens immediately after one clicks the "RUN" button on the CONTROL worksheet.

The fields in the Species Description Spreadsheet are:

#	Species Description Spreadsheet						
# Species #	Residence Time in CSTR(s)	Initial Conc.	Display Output (Y/N) ?	External Conc.	Species Special Directives (/N)	Constant File? (Filename/#/No)	Comments
E	0	4.00E-09	YES	0	No	No	Blah
S	0	6.00E-02	YES	0	No	No	yipee
ES	0	0	YES	0	No	No	references

Figure 5

The **Species, Initial Concentration, and Display Output** fields are evident in their representation. The Species field holds the name of a species that will show up in a chemical reaction and can be up to 240 characters long. The charge of the species is only computed for species name if a "+" or "-" is appended at the end of the name, but before the phase descriptor, {}.

By default, the phase of any species is in the gas phase if the species name has no phase information at the end. Overriding the default gas phase can be accomplished by appending the species name with the phase name surrounded by braces, for example, {aq} to represent aqueous phase (i.e. CH_3COO^-{aq}), or {l} (i.e. Br_2{l}), to represent the liquid phase. Again, no phase information present at the end of a species name can also represent a species in the gas phase, such as Ar or N_2. It should be **imperative** to note that if all your species are in one phase (such as gas or aqueous), then **you do not have to append each species name with a phase descriptor**. It is just a waste of time to append every species name with {g} or {aq} if they are all in the same phase. Kintecus only really "understands" gas phase, {g}, and any other phase that is not in the gas phase. Kintecus uses the gas phase information mainly for third-body reactions involving [M], pressure fall-off reactions, and enhanced third-body reactions used in [M]. Future versions will incorporate other phases. The phase descriptor must **always** appear at the **end** of the species name. The species Cl^{++}{g} is the chlorine molecule with a +2 charge in the gas phase, **but** Cl{g}++ is some species name of Cl{g} with a +2 charge.

The **Initial Concentration** field holds the starting concentration of each species in the reaction.

The **Display Output** field can hold either a Yes or No ("Y" and "N" also work). If yes, the respective species' concentration will be stored in the default output file, "CONC.TXT", if no, the species' concentration will not be stored.

The **"Constant File ?"** Field can hold one of three things: "No" ("N" works too), a number such as 4.234E-4 (in which case that species will always have that concentration of 4.23E-4), or the name of a file that contains values in a particular format. The format is the first line containing the time spacing (in seconds) between each data point. The lines that follow contain the data. Please make sure the very last data point has a carriage return

or enter! Kintecus will place the respective data point at the respective time of the simulation from the constant file into the species' concentration. If the time in the simulation goes beyond the time of the last data point in the constant file, Kintecus will start over in the constant file using the first data point and continue onward. Suppose the first line (the time spacing) has a minus sign in front of it. In that case, Kintecus will go through the entire data series once and then automatically place the very last value in the data file for the rest of the simulation time. Confused? Okay, here are some examples:

Examples:

In the Profile_A.TXT file contains these values:
43200
2
1

For a species with the filename Profile_A.TXT in its "CONSTANT FILE ?" field, Kintecus will load this concentration pulse step profile. Assuming Molar units, Kintecus will force the species to have a concentration of 2 Molar until at 43201 seconds, and the species concentration will drop to 1 Molar. At 86401 seconds, the species will go back up to 2 Molar, which will repeat. Now, if the 43200 were -43200, then at time 86401, the concentration of the species will go to 1 Molar and stay there for the entire simulation. If "-ADD" was appended to the file name (in this example, "Profile_A.TXT-ADD"), the species will **NOT be a constant**, but a variable with perturbations added to it during the simulation:

In the Profile_A.TXT file contains these values:
-500
0
0
1

When the simulation is running, the instant the time goes over 1000 seconds, 1 Molar will be added to the species containing the "Profile_A.TXT-ADD" in the "Constant File ?" field; afterward, Kintecus will not perform any more perturbations to the respective species no matter how long the simulation continued. Another example: Suppose one wished to add 2 Molar after 1000 seconds, then add 4 Molar after 1030 seconds, then **REMOVE** -3 Molar after 1034 seconds the Profile_A.txt file would look like this:

-1
(999 zeroes)
2
(29 zeroes)
4
0
0
0
-3

A new type or perturbation has been added to Kintecus 3.X, the "-SET" suffix. The "-SET" suffix is similar to the "-ADD" suffix described above. Both suffixes treat the species as a variable. Still, instead of adding (or subtracting) a value at some time(s), the concentration (or volume or temperature) is immediately SET to the value specified in the file. This may sound similar to the standard "Constant File" described above, but the species is still a variable. It is not constrained to the current SET value. Since the species is still a variable and not a constant, the species (or temperature or volume) will almost immediately change its value right after this perturbation. Please keep in mind that to use the "-SET" or the "-ADD" setting, you must only suffix the end of the filename in the "Constant file ?" field in the Species Description Spreadsheet. DO NOT APPEND THE ACTUAL DISK PERTURBATION FILENAME with "-SET" or "-ADD" or else Kintecus will NOT FIND the perturbation file.

EQUILIBRIUM MODE NOTE: When Kintecus is in equilibrium mode, the concentrations and temperature are reset to their respective initial values between each perturbation point. This is to allow **easy calculations of stability and phase plots of systems**. This default process can be overridden by providing the -EQUIL switch with the extra option of **FI (forget initialization)**, i.e. >Kintecus -EQUIL:[filename] or d/D : FI or just >KINTECUS -EQUIL:D:FI

Many Kintecus kinetic and equilibrium examples use various types of perturbations described above. The "Gas Desorption off Tungsten" Excel file (it is also the wolfrum.bat file) uses a temperature program file. The Kintecus-Excel models, "GRI MECH 3.0+Compression+Heat" utilize both temperature and volume profiles. Most of the equilibrium examples in the /EQUIL/ subdirectory use a Constant File for species concentrations (to construct phase diagrams) or hold the system's temperature at a defined value. The Excel file, "H2_O2_Equil_Phases.xls" (also the EQUILA.bat file), uses three perturbation files. One for the temperature program (1,500 K to 6,000 K) and two concentration profiles for H2 and O2 that both use the "-SET" suffix. The model in the Excel file, "H2_O2_Equil_Phases.xls" (again, it is also the EQUILA.bat file) must use the "-SET" suffix because the initial concentrations of H2 and O2 must keep their relative mole fraction constant while maintaining a constant pressure. The two perturbation files for H2 and O2 used in "H2_O2_Equil_Phases.xls" were computed by using an external spreadsheet file "HOW_TO_CALCULATE_CONCENTRATION_PROFILE_FOR_COSTANT_TEMP_P.xls," then by copying the species' respective column concentrations into two files: "O2_START.TXT" and "H2_START.TXT".
As one can see, these perturbation methods are **potent techniques** to study various perturbation methods to kinetic systems with the slightest of ease! Of course, you can have very long perturbation files (up to 25,000 points)! **The above descriptions on perturbation files can also be used for programmed temperature, and volume profile runs. See the example Kintecus-Excel model named "GRMECH_with_compression_heat_loss.xls" file to see how this is done.**

"Constant Files" for Accurate Photolysis

As for the effect of radical generation utilizing UV light, most people precalculate the absorption cross-section (acs) of a molecule interacting with the UV light and use that profile as a "Constant profile" under another species name, such as **O3acs.** Now your reaction would look like this:
(the Arrhenius numbers are arbitrary):

From

1.2345E9, 0, 10, O3 + hv ==> O2 + O.

to

1.2345E9, 0, 10, O3 + O3acs ==> O2 + O.

For a more realistic photolysis rate, if you are performing an atmospheric integrated box model, you would probably want to have a function of the **Solar Zenith Angle** (**SZA**) mapped into a "species" with a "Constant Profile." The species could be named **SZA**, which multiplies your UV-absorption cross-section (O3acs) over time to get the final rate. For example, the following reaction of Ozone with hv (the Arrhenius numbers are arbitrary):

1.2345E9, 0, 10, O3 + hv ==> O2 + O.

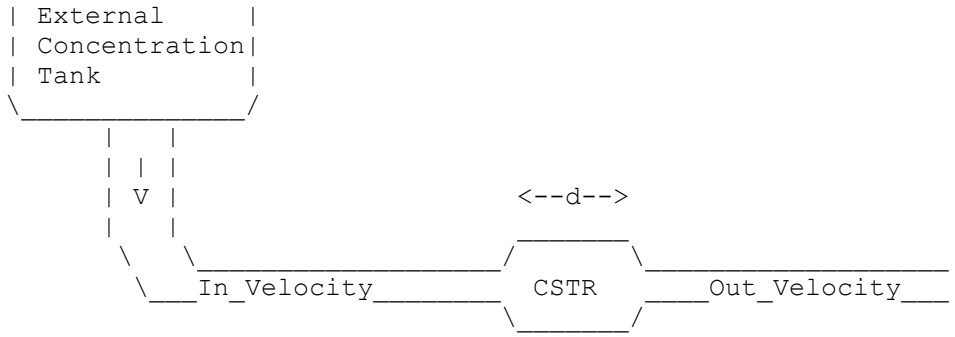
would become

1.2345E9, 0, 10, O3 + O3acs + SZA ==> O2 + O.

Dr. Theodore Dibble (at www.esf.edu) has some excellent spreadsheets to calculate some SZA's at various latitude-longitude values over multiple times that you can copy into a constant-profile. You can have these spreadsheets part of your Kintecus-Excel workbook and use the "O_(sheetname)" option to have the Kintecus-Excel modules automatically write out the "Constant Files." The animation "Create Temp. program" (under the START>Programs>Kintecus>Web Resources Tab or in the Kintecus Workbench/Web Resources/Fast Animations/) demonstrates this technique, and although the animation shows a temperature program, the steps to make a "Constant File" are precisely the same.

****EXCEL FEATURE**: If you are using the Kintecus Excel graphical interface and you are utilizing species, temperature, or volume perturbations, then instead of saving the perturbation into a file, you can prefix the name an Excel worksheet with the letter "**O**," and an underscore, "_," so "FILENAME" becomes "**O**_FILENAME". Excel will write the worksheet as a file named "FILENAME" for Kintecus to load. Excel will output ANY worksheet prefixed with "O_FILENAME" as a Tab-delimited text file. You can even have a graph of the perturbation displayed on the Excel worksheet. For an example of this, see the new GRI-MECH_30.xls workbook. The workbook also has the entire GRI-MECH thermodynamic database stored as a worksheet, allowing easy sharing.

The **Residence Time in CSTR and the External Concentration fields** are used together for the modeling of Continuous Stirred Tank Reactors (CSTR) or any other process that contains well mixed, isothermal reactions with external flux in and flux out:



Naturally, the External Concentration field does not contain the actual concentration of the external tank but the concentration the species will become once it is diluted in the CSTR before any reactions occur. A rough approximation of the residence time in a CSTR can be calculated as follows:2 x d (the distance across the CSTR parallel to the in/out flow) / (In_Velocity+Out_Velocity). You can have different residence times for different species.

Suppose your inlets have a different temperature than the reactor/PFR/CSTR, and you are in thermodynamics mode. You can specify a global inlet temperature for all flows in the **CSTR/PFR inlet temperature flow field** found in the

parameters spreadsheet (see above).

The old **SSA field** stands for Steady-State Approximation and is not used in this version. It would be best if you never used SSA's. It has been shown repeatedly [2,3] that doing SSA's without knowing the actual output can result in disastrous results. This field will change in future versions of Kintecus, so please keep all values at "N" or "No." Kintecus versions above 3.95 now use this field as a **"Special Species Directives"** (see below in the optimization/fitting section). They are currently utilized to output functions of concentrations/temperature during a run. This can be used to fit/regress with experimental data. Other future uses are planned.

At the end of the "Species Description Spreadsheet," make sure there is an **END** + carriage return.

Kintecus will look for SPECIES.DAT at the default filename. This default name of "SPECIES.DAT" can be overridden see KINTECUS Switches Section setting below.

The Species Name Spreadsheet

This spreadsheet is optional. The main reason for this spreadsheet is to keep Kintecus checking for mass balance without typing long molecular, empirical, or mass formulae in the reaction spreadsheet. The fields in this spreadsheet are:

#"Nickname"	**Molecular/Empirical/Mass formula**
# or Common Name	
#	
E-	C0-
Decane	CH3(CH2)8CH3
END	

Figure 6

Common Name can contain any name up to 240 characters long. The Molecular/Empirical/Mass formula field must contain any valid molecular, empirical, or mass formula such as $CH_3CH_2CH_3$ or $CH_3(CH_2CH_2O_2)_{90000}CH_3$ or $Pu_2U_3Pr_{43}$ or $C_{100000}H_{200002}$. The following characters are ignored if they are contained in the molecular, empirical or mass formula: ".", "=", "_", "*", "^", "&", "/", "\", "-", "+". An important note is that the charge of the species is only computed for the common name if a "+" or "-" is appended at the end. The charges are completely ignored if they appear in the molecular, empirical, or mass formula.
An example:

The reaction:
Enzyme_B + $5H_2O$ ==> Enzyme_hydrate.

The SpecName.dat file:

#	
# My nicknames for my own kinetics simulation	
#	
Enzyme_B	C43H70N10S2
Enzyme_hydrate	C43H70N10S2(H2O)5
END	

Figure 7

Kintecus will look for SPECNAME.DAT as the default filename. One can override this default name. See KINTECUS Switches Section setting below.

****EXCEL FEATURE**: If you are using the Excel graphical interface and have a Kintecus-Excel workbook loaded, then the SPECNAME.DAT file described above is automatically written out to the SPECNAME.DAT file from the SPECNAME Excel worksheet. **YOU DO NOT HAVE TO CREATE A SPECNAME.DAT FILE.** This also applies to the SPECIES.DAT file which is created from the SPECIES worksheet Excel tab, the PARM.DAT file (from the PARM worksheet), the FITDATA.TXT file (from the fitdata tab and regression is being performed), and the THERM.DAT file, which is created from the THERM Excel worksheet. This saving process happens **immediately** after one clicks the "RUN" button on the CONTROL worksheet.

The Model Description Spreadsheet

Here is a detailed description of how exactly each field in the model description spreadsheet is used by Kintecus.

****EXCEL FEATURE**: If you use the Excel graphical interface and have a Kintecus-Excel workbook loaded, then the MODEL.DAT file described below is automatically written out to the MODEL.DAT file from the MODEL worksheet. YOU DO NOT HAVE TO CREATE A MODEL.DAT FILE. This also applies to the SPECIES.DAT file, which is created from the SPECIES worksheet Excel tab, the PARM.DAT file (from the PARM worksheet), the FITDATA.TXT file (from the fitdata tab and regression is being performed), and the THERM.DAT file, which is created from the THERM Excel worksheet. This saving process happens immediately after one clicks the "RUN" button on the CONTROL worksheet.

The fields in the Model Description Spreadsheet and some possible reactions listed are:

# Sample				
# Reactions				
#				Optional
# A	T^m	Ea	REACTION	Comments
1.75E-05	0.3	3000	CH3C00H + H2O = H3O+ + CH3COO-	Sample Reaction 1
5.00E+17	-1	0	O+H+M[H2(2);H2O(6);CH4(2);CO(1.5);CO2(2);C2H6(3);AR(.7)]=OH+M	Sample Reaction 2
5.00E+17	-1	0	O+H+M=OH+M	Sample Reaction 3
5.00E+17	-1	0	O+H+M[-H2(2);-H2+(3.5)]=OH+M	Sample Reaction 4
1.00E+17	-1	0	H+C2H+M[TROE;3.750E+33;-4.8;1900;.6464;132;1315;5566]=C2H2	Sample Reaction 5
4.30E+07	1.5	79600	H2+CO+M[TROE;5.07E+27;-3.42;84350;.932;197;1540;10300;CO(1.5);CO2(2);C2H6(3);AR(.7)]=CH2O	Sample Reaction 6
4.30E+07	1.5	79600	H2+CO+M[TROE;5.07E+27;-3.42;84350;.932;197;1540;10300;-N2(1);-N2+(2)]=CH2O	Sample Reaction 7
7.91E+01	0	56020	N2O+M[LIN;6.37E+14;0.3;56640]=N2+O	Sample Reaction 8
1.80E+01	0	2385	O+CO+M[LIN;6.020E+14;0.3;3000;H2(2);O2(6);AR(.5)]=CO2	Sample Reaction 9
5.00E+01	0.3	4433	N2O+M[SRI;6.37E+14;0.3;56640;6.370E+14;0.3;56640]=N2+O	Sample Reaction 10
5.00E+01	0.3	4433	N2O+M[SRI;6.37E+14;0.3;56640;6.370E+14;0.3;56640;H2(2);O2(6);AR(.5)]=N2+O	Sample Reaction 11
2.00E+00	0	6555	O2+O+S[LT;-63;68.8]=O3	Sample Reaction 12
END				

Figure 8. Some sample reaction types Kintecus can read.

Irreversible Reactions

The reaction field holds either a reversible (represented by a single "=") or an irreversible (represented by "==>") reaction, for irreversible reactions:

k_f, A+B+C ==> D+E+F+G+H+I+J+K+L+N, Optional Comment

OR

A, m, E_a, A+B+C==>D+E+F+G+H+I+J+K+L+N, Optional Comment

Although it is not recommended, it is possible to mix the above two formats throughout a model. The commas used to delimit the A, m, and E_a can also be TABS, colons, "|" or "!". If you are using Excel to enter the reactions, the delimiter will be TABs. Do not use the name "M" for a species as M represents third-body reactions involving [M], unless you explicitly need to use it and are familiar with third-body gas reactions.

You can have only up to three unique reactants and up to 10 unique products per reaction line. The multiplicity of a species is represented by using numerical coefficients such as 5A to represent A+A+A+A+A or $98H_2O$ or possibly $4.2343E\text{-}23H_2O$. Signs can be post-fixed to a species such as $Cl^{-------}$ or H_3O^+. Even ylides and zwitterions such as $C_8H_{15}P^{+-}$ (which will have no overall charge.) can be entered. All reactions are checked for mass and charge balance (which can be turned off). At the end of the model description spreadsheet, make sure there is an END plus a carriage return. It is imperative to note that enhanced body, fall-off reactions, and special reactions represented by +M[….] or +S[…] DO NOT COUNT AS REACTANTS! A reaction such as the one shown below is **perfectly fine**.

A + B + C + M[-O2(1);-N2(1) ;H2(1);-Ar(1); -HO2(1);-CO2(1)] ==>
D + 2E + 3F + 9G + 9.431H + 6I + 17J + K + 92L + 92.3N

Reversible Reactions

For reversible reactions (represented by a single "=") the reverse rate will always be one, "1", **but** if you are using the Thermodynamics mode, then the reverse rate constant, k_b , will be calculated through the equilibrium constant, K_c, and the forward rate constant, k_f: $k_b=k_f/K_c$. For a detailed description on the complete calculation of K_p , K_c and k_b turn to the Incorporation of Thermodynamics section. An example of a reversible reaction is shown above in Figure 8 as Sample Reaction 1.

Enhanced Third Bodies

Enhanced third bodies can be represented using the following form:

Reactants + M[SPECIES (enhancement); SPECIES (enhancement);…] ==> Products

as shown in Sample Reaction 2. The difference between "regular" M (Sample Reaction 3) and M[..] is shown by the following two equations:

$$[M]=\sum_{n=1}^{N}[Species]_n \qquad \text{Eqn 1.}$$

$$[M]=\sum_{n=1}^{N}\alpha_n[Species]_n \qquad \text{Eqn 2.}$$

The α character in the above equation represents the enhancement value of the third body species, and the N represents all species in the gas phase. It should be noted that the summation shown in the above equation is only for gaseous species. As you might recall, gaseous species have **no phase information** attached to the end of the species name or have a **{g}** appended to the end of the species name, i.e. Ar{g}. Again, it should be **essential** to note that if all your species are in one phase (such as gas or aqueous), **you do not have to append each species name with a phase descriptor**. Once M is calculated, k_f, is multiplied by it. It is possible to combine the enhanced third bodies with fall-off reactions as described in the fall-off reactions section below.

Kintecus also supports exclusive third-body enhancements by prefixing the enhanced body with a dash, **"-".** More than one species can become an exclusive third body (rate constants/parameters not shown below):

Reactants+M[-SPECIES(enhancement); -SPECIES(enhancement);…] ==> Products

The difference between exclusive third bodies and non-exclusive third bodies is that exclusive third bodies (the species names designated by the user between the M[and]) are the ***only*** species the are summed in Equations 1 and 2 above. An example is shown in Sample Reaction 4.

Pressure Fall-Off Reactions

Lindemann Reactions

Kintecus provides several methods to represent pressure fall-off reactions. The classical Lindemann low-pressure reaction can be described as follows:

Reactants + M[LIN:A_0;m_0;E_{a0}] ==> Products

OR

Reactants + M[LIN:A_0;m_0;E_{a0}; *(Enhanced bodies if present)*] ==> Products

The A_0, m_o, E_{a0} are values used in the Arrhenius rate expression at the low-pressure limit:

$$k_0 = A_0 T^{m_0} \ell^{\left(-E_0/RT\right)} \qquad \text{Eqn 3.}$$

The A, m, and E_a values present before the reaction (not shown) are used in the Arrhenius rate expression at the high-pressure limit. An overall rate constant, k_f, is then computed:

$$k_f = k_\infty \left(\frac{\frac{k_0[M]}{k_\infty}}{1+\frac{k_0[M]}{k_\infty}} \right) F \qquad \text{Eqn 4.}$$

The F parameter shown above is always one for Lindemann reactions. Sample Reaction 8 in Figure 8 shows a Lindemann reaction with no enhanced third bodies. Sample Reaction 9 shows a Lindemann reaction with enhanced third bodies.

Troe Reactions

The TROE fall-off reaction can be represented as follows:

Reactants + M[TROE:A_0;m_0;E_{a0};P_1;P_2;P_3; (P_4)] ==> Products

OR

Reactants + M[TROE:A_0;m_0;E_{a0};P_1;P_2;P_3;(P_4;) *(Enhanced bodies if present)*] ==> Products

The A_0, m_o, and Ea0 are used in the Arrhenius rate expression at the low-pressure limit. The A, m, and E_a values present before the reaction (not shown) are used in the Arrhenius rate expression at the high-pressure limit. The Troe parameters **P_1, P_2** and **P_3** (**P_4** is optional) allow Kintecus to compute the Troe Factor, F:

$$\log F = \left[1 + \left[\frac{\log\left(\frac{k_0[M]}{k_\infty}\right) + c}{n - 0.14\left(\log\frac{k_0[M]}{k_\infty} + c\right)}\right]^2\right]^{-1} \log F_{cent} \qquad \text{Eqn 5.}$$

$$c = -0.4 - 0.67 \log F_{cent} \qquad \text{Eqn 6.}$$

$$n = 0.75 - 1.27 \log F_{cent} \qquad \text{Eqn 7.}$$

$$F_{cent} = (1 - P_1)\ell^{\left(-T/-P_2\right)} + P_1\ell^{\left(-T/P_3\right)} + \ell^{\left(-P_4/T\right)} \qquad \text{Eqn 8.}$$

Once F is computed, it is inserted into equation 4. In some references **P_1=a, P_2=T***, P_3=T* and P_4=T**.** Examples of the Troe reaction (with and without enhanced third bodies) in Kintecus are shown as Sample Reactions 5,6 and 7 in Figure 8.

SRI Reactions

The SRI fall-off reaction can be represented as follows:

Reactants + M[SRI;A_0;m_0;E_{a0};P_1;P_2;P_3 (;P_4(;P_5))] ==> Products

- OR -

Reactants + M[SRI;A_0;m_0;E_{a0};P_1;P_2;P_3(;P_4(;P_5)) *(Enhanced bodies if present)*] ==> Products

The A_0, m_o, E_{a0} are values used in the Arrhenius rate expression at the low-pressure limit. The A, m, and E_a values present before the reaction (not shown) are used in the Arrhenius rate expression at the high-pressure limit. The SRI parameters **P_1, P_2** and **P_3** (**P_4** is optional, and if **P_4** is supplied **P_5** is optional) allow Kintecus to compute the SRI Factor, F:

$$F = \left[P_1\ell^{\left(-P_2/T\right)} + \ell^{\left(-T/P_3\right)}\right]^X P_4 T^{P_5} \qquad \text{Eqn 9.}$$

$$X = \frac{1}{1 + \left(\log\frac{k_0[M]}{k_\infty}\right)^2} \qquad \text{Eqn 10.}$$

In some references **P_1=a, P_2=b, P_3=c, P_4=d and P_5=e.** Examples of the SRI reaction (with and without enhanced third bodies) in Kintecus are shown as Sample Reactions 10 and 11.

Jet Propulsion Kinetic Forms 1 and 2

Jet Propulsion Laboratory 4-parameter fit to the Troe expression (section 2 of JPL Evaluation #18 (2015) at http://jpldataeval.jpl.nasa.gov/download.html) :

JPL form 1:

A , m , E_a, Reactants + M[JPL1; k_0 ; n ; k_{inf} ; m] ==> Products

- OR -

A , m , E_a, Reactants + M[JPL1; k_0 ; n ; k_{inf} ; m; *(Enhanced bodies if present)*] ==> Products

and JPL form 2 (note that subsequent versions of the JPL Data Evaluation no longer use JPL form 2**):**

A , m , E_a, Reactants + M[JPL2; k_0 ; n ; k_{inf} ; m] ==> Products

- OR -

A , m , E_a, Reactants + M[JPL2; k_0 ; n ; k_{inf} ; m; *(Enhanced bodies if present)*] ==> Products

Note that your concentrations ***must*** be in molecules/cm^3 !! The A, m, and E_a values present before the reaction are utilized in the standard Arrhenius rate expression. You would normally set A=1, m=0, Ea=0, but the user can still change these values to allow flexibility of the rate equation. One change A to allow for different units.

Where

$$k_0(T) = k_0^{300}\left(\frac{T}{300}\right)^{-n} cm^6 molecule^{-2} s^{-1} \qquad \text{Eqn 11.}$$

$$k_\infty(T) = k_\infty^{300}\left(\frac{T}{300}\right)^{-m} cm^3 molecule^{-1} s^{-1} \qquad \text{Eqn 12.}$$

Two forms depend on your reaction: JPL1 and JPL2:

JPL1:

$$k_f([M],T) = \left(\frac{k_0(T)[M]}{1+\frac{k_0(T)[M]}{k_\infty(T)}}\right) 0.6^{\left\{1+\left(\log_{10}\left[\frac{k_0(T)[M]}{k_\infty(T)}\right]\right)^2\right\}^{-1}} \qquad \text{Eqn 13.}$$

And JPL2:

$$k_f^{ca}([M],T) = \left(\frac{k_0(T)}{1 + \frac{k_0(T)}{k_\infty(T) / [M]}} \right) 0.6^{\left\{ 1 + \left(\log_{10}\left[\frac{k_0(T)}{k_\infty(T) / [M]} \right] \right)^2 \right\}^{-1}} \qquad \text{Eqn 14.}$$

Jet Propulsion Kinetic Forms 3 and 4

Jet Propulsion Laboratory 4-parameter fit to the Troe expression (see section 2 of JPL Evaluation http://jpldataeval.jpl.nasa.gov/download.html). Kintecus V5.2 and up include two new "forms" of the previous JPL1 and JPL2 forms: Jet Propulsion Kinetic Form 3 (JPL3) and Jet Propulsion Kinetic Form 4 (JPL4).

Jet Propulsion Kinetic Form 3 (JPL3):

A , m , E_a, Reactants + M[JPL3; k_0 ; n ; k_{inf} ; m; scalar; A; B] = Products

- OR -

A , m , E_a, Reactants + M[JPL3; k_0 ; n ; k_{inf} ; m; scalar; A; B; ***(Enhanced bodies if present)*** **] = Products**

NB: Note the equal sign, "=" utilized in the above reactions versus the "==>" symbol!

and Jet Propulsion Kinetic Form 4 (JPL4):

A , m , E_a, Reactants + M[JPL4; k_0 ; n ; k_{inf} ; m; scalar; A ;B] = Products

- OR -

A , m , E_a, Reactants + M[JPL4; k_0 ; n ; k_{inf} ; m; scalar; A; B; ***(Enhanced bodies if present)*** **] = Products**

NB: Note the equal sign, "=" utilized in the above reactions versus the "==>" symbol!

The forward constants for JPL3 and JPL4 are EXACTLY equivalent to JPL1 and JPL2, respectively, but there is a reverse rate calculation:

$$k_r = \left[\frac{k_f([M],T) * scalar}{K_{eq}} \right]; \quad K_{eq} = Ae^{\left(\frac{B}{T}\right)} \qquad \text{Eqn 15.}$$

Again, it is essential to note that you need to utilize **the equal sign, "=" used in the above reactions versus the "==>" symbol** in the above reactions, or the JPL3 and JPL4 forms revert to JPL1 or JPL2 forms (no reverse rate). The rate constants units are usually molecules/cm^3, but supplying any value for **scalar** other than one or zero can allow conversions to different units.

Jet Propulsion Kinetic Forms 5 and 6

Jet Propulsion Laboratory multi-parameter fit to the Troe expression. Please see section 2 in the JPL Evaluation #19, 2019 (http://jpldataeval.jpl.nasa.gov/download.html). For 2019, JPL has performed a complete revision on some of these fits:

JPL form 5:

A , m , E_a, Reactants + M[JPL5; k_0 ; n ; k_{inf} ; m ; *F* value (usually 0.6); [optional scalar]] ==> Products

- OR -

A , m , E_a, Reactants + M[JPL5; k_0 ; n ; k_{inf} ; m; *F* value (usually 0.6); {[optional scalar] ; *(Enhanced bodies if present)}*] ==> Products

and JPL form 6:

A , m , E_a, Reactants + M[JPL6; k_0 ; n ; k_{inf} ; m; *F* value (usually 0.6); scalar; A; B] ==> Products

- OR -

A , m , E_a, Reactants + M[JPL6; k_0 ; n ; k_{inf} ; m; *F* value (usually 0.6); scalar; A; B ; *(Enhanced bodies if present)*] ==> Products

Note that your concentrations ***must*** be in molecules/cm^3 (unless you change the optional scalar to a value other than 1) !! The A, m, and E_a values present before the reaction are utilized in the standard Arrhenius rate expression. You would typically set A=1, m=0, Ea=0, but the user can still change these values to allow flexibility of the rate equation. Both JPL5 and JPL6 forms allow F to take a different value other than 0.6 for some IUPAC forms.

Where

$$k_0(T) = k_0^{298}\left(\frac{T}{298}\right)^{-n} cm^6 molecule^{-2} s^{-1} \qquad \text{Eqn 16.}$$

$$k_\infty(T) = k_\infty^{298}\left(\frac{T}{298}\right)^{-m} cm^3 molecule^{-1} s^{-1} \qquad \text{Eqn 17.}$$

Note the new temperature change in the denominator from 300 K to 298 K.

There are two forms depending on your reaction: JPL5 and JPL6:

JPL5:

$$k_f([M],T) = \left(\frac{k_0(T)[M]}{1+\frac{k_0(T)[M]}{k_\infty(T)}} \right) F^{\left\{1+\left(\log_{10}\left[\frac{k_0(T)[M]}{k_\infty(T)}\right]\right)^2\right\}^{-1}} \quad \text{Eqn 18.}$$

Note that for JPL6, you MUST specify the scalar parameter (it's almost always one, "1"). The scalar parameter is optional for JP5 unless you are setting third-body enhancements, then you MUST include the scalar field for JPL5 (again, almost always one, "1" unless your concentration units differ from molecules/cc).

And JPL6 additional governing equations:

$$k_f^{CA}(T,[M]) = k_{int}(T)[1-(k_f(T,[M]))/(k_\infty(T))] \quad \text{Eqn 19.}$$

$$k_{int}(T) = Ae^{\frac{-B}{T}} \quad \text{Eqn 20.}$$

$$k_f^{total}(T,[M]) = k_f(T,[M]) + k_f^{CA}(T,[M]) \quad \text{Eqn 21.}$$

Where k_f^{total} is the final rate calculated. Again, keep in mind that the A, m, and E_a values present before the reaction are utilized in the standard Arrhenius rate expression. You would typically set A=1, m=0, and Ea=0, but the user can still change these values to allow flexibility of the rate equation. Setting A to zero, "0", will result in a Kintecus user error. If you do not wish to have the reaction present, you can either delete the reaction or place a "#" in front of the reaction line to comment out the entire reaction.

PLOG form

The PLOG form is a generalized polynomial fitting for the temperature and pressure-dependent polynomial[33]. PLOG forms can be entered in Kintecus as:

A , m , E_a, Reactants + M[PLOG; pressure1 ; A1; m1; Ea1 (; pressure2; A2; m2; Ea2 (;pressure3; A3, m3 , Ea3(; etc)))] = Products

A, m and Ea are ignored right now, though A should be set to "1" so Kintecus doesn't flag it as a user error.
Here is an actual example:

4.94E+14, -6.69E-01, -4.46E+02, CH3+OH+M[**PLOG**; .01; 4.936E+14;-.669;-445.8; .1; 1.207E+15;-.778;-175.6; 1; 5.282E+17;-1.518; 1772; 10; 4.788E+23;-3.155; 7003; 100; 8.433E+19;-1.962; 8244]=CH2(S)+H2O

If you have chemkin models with PLOG and wish to translate them to Kintecus format, please have the latest Chemkin to Kintecus translator "ck2kin.exe". The older version of ck2kin will not work.
For examples of PLOG reactions, see the "**AramcoMech2.0__HAS_PLOG.xls**"

Special Reactions

Special reactions usually do not follow the standard Arrhenius form or simply belong in their own category. Additional parameters are supplied to special reactions through +S[….] appearing on the reactant's side.

Landau-Teller Reactions

Landau-Teller reactions are essentially vibrational energy transfer reactions, and they are represented in Kintecus as:

A , m , E_a, Reactants + S[LT; P_1;P_2] ==> Products

The parameters A, m, E_a, P_1 and P_2 are used to compute the forward rate constant:

$$k_f = AT^M \ell^{\left(\frac{-E_a}{RT}+\frac{P_1}{\sqrt[3]{T}}+\frac{P_2}{\sqrt[3]{T^2}}\right)} \qquad \text{Eqn 22.}$$

In some references m= β, E_a=E, P_1=B and P_2=C. An example of a Landau-Teller reaction is shown in Figure 8 as Sample Reaction 12.

The following two sets of fits are primarily intended for those anomalous reactions (mainly plasma and nuclear) that do not obey most expanded forms of Arrhenius or RRKM rate equations.

Transport Catalytic Reactions

Transport catalytic reactions are concerned with gas to liquid interactions. Kintecus provides two types of optional fits to this reaction: :

A , m , E_a, Reactants + S[TRANS1; b_1;b_2 (; b_n;c_1; c_2; c_n)] ==> Products

- OR -

A , m , E_a, Reactants + S[TRANS2; b_1;b_2 (; b_n ;c_1; c_2; c_n)] ==> Products

For TRANS1, the parameters A, m, b_1, b_2 to b_n and the optional c_1, c_2 to c_n are utilized to compute the forward rate constant in the following manner:

$$k = \frac{1}{\left(\frac{1}{AT^M \ell^{\left(-E_0/RT\right)}}+\frac{1}{b_1}+\frac{1}{b_2}+\left(\sum_3^{upto10}\frac{1}{b_n}+\left(\frac{1}{c_1}+\frac{1}{c_2}+\sum_3^{upto10}\frac{1}{c_n}\right)\right)\right)} \qquad \text{Eqn 23.}$$

For TRANS**2**, the parameters A, m, b_1, b_2 to b_n and the optional c_1, c_2 to c_n are utilized to compute the forward rate constant in the following manner:

$$k = \frac{1}{\left(\frac{1}{AT^{M}\ell^{\left(-E_0/RT\right)}} + \frac{1}{b_1} + \frac{1}{b_2} + \left(\sum_{3}^{upto10}\frac{1}{b_n} + \left(\ln c_1 + \ln c_2 + \sum_{3}^{upto10}\ln c_n\right)\right)\right)} \qquad \text{Eqn 24.}$$

In some references b_1=kGa (kGa=Mass transfer coefficient of the gas film) and b_2=De/R (De is the diffusion constant and R is the particle diameter) or b_2=La where La is the mass transfer coefficient of the liquid film and b3 onward and all c's are all ignored. These higher orders can give one extra fitting option if needed in the model. You usually don't have to set these. If you do not specify anything higher than b2, Kintecus assumes not to include those additional terms.

Please see the "H2-O2-combustion-gas-liquid-catalytic-surface-test.xls" sample Kintecus-Excel worksheet for an example of this type of reaction.

The following sets of fits are primarily intended for those anomalous reactions (mainly plasma and nuclear) that do not obey most expanded forms of Arrhenius or RRKM rate equations:

Polynomial Fit to the Logarithm of the Temperature

For the reaction nomenclature:

A , m , E_a, Reactants + S[FIT1; b_1;b_2;…;b_{19};b_{20}] ==> Products

The parameters A, m, E_a, b_1 up to an optional b_{20} coefficients are used to compute the forward rate constant according to this formula fit:

$$k_f = AT^m e^{\left(\frac{E_a}{T} + \sum_{n=1}^{upto20} b_n\left(\ln T\right)^n\right)} \qquad \text{Eqn 25.}$$

The above FIT1 equation can be utilized with electron-hydrogen and electron-helium reactions as given in Janev et al. [30] by setting *m* and E_a to zero.

Power Series Fit within an Exponent

For the reaction nomenclature:

A , m , E_a, Reactants + S[FIT2; b_1;b_2;…;b_{19};b_{20}] ==> Products

The parameters A, m, E_a, b_1 up to an optional b_{20} coefficients are used to compute the forward rate constant according to this formula fit:

$$k_f = AT^m e^{\left(\frac{E_a}{T} + \sum_{n=1}^{upto\,20} \frac{b_n}{T^n}\right)}$$ Eqn 26.

Chebyshev Fit

A , m , E_a, Reactants + S[FIT3;a;b; c_1;c_2;…;c_{31};c_{32}] ==> Products

$$k_f = AT^m e^{\left(\frac{E_a}{T}\right)} Chebyshev\_polynomial[a,b](c_1;c_2;\ldots;c_{31};c_{32})$$ Eqn 27.

Where [a,b] represents the temperature interval on which the original function func was evaluated with the Chebyshev Fit. The coefficients c_1, c_2, up to an option c_{32} are the Chebyshev coefficients. One can obtain these Chebyshev coefficients to fit ***almost any 1D function*** dependent on **temperature** by utilizing the **`chebft`**() FORTRAN subroutine as given in reference [1] on page 186. The user simply provides a function func() that contains the user's special rate functions and an interval [a,b] to determine the function. To use a pure Chebyshev fit set A=1, m=0, and E=0. Please note that E in the above equation has no negative sign in front of it.

You can use the FORTRAN program on the following page (after you insert two Numerical Recipes functions: chebev() and chebft(), see Reference [1]) to enter any smooth function in the SINEY() FUNCTION and the corresponding Chebyshev coefficients, c_1 up to c_{32} will be outputted in the "chubcoefs.txt" file once you run the program. The numbers in the "chubcoefs.txt" file can be directly entered right after the **FIT3** keyword. The program also outputs the original function along with the coordinates [a,b] into the file "siney.txt" and the Chebyshev Fit output into the "chub.txt" file. You should overlay the files in a plot to ensure the Chebyshev Fit is good. The sample program on the following page does a Chebyshev fit to a wave composed of three sine waves (see the SINEY FUNCTION):

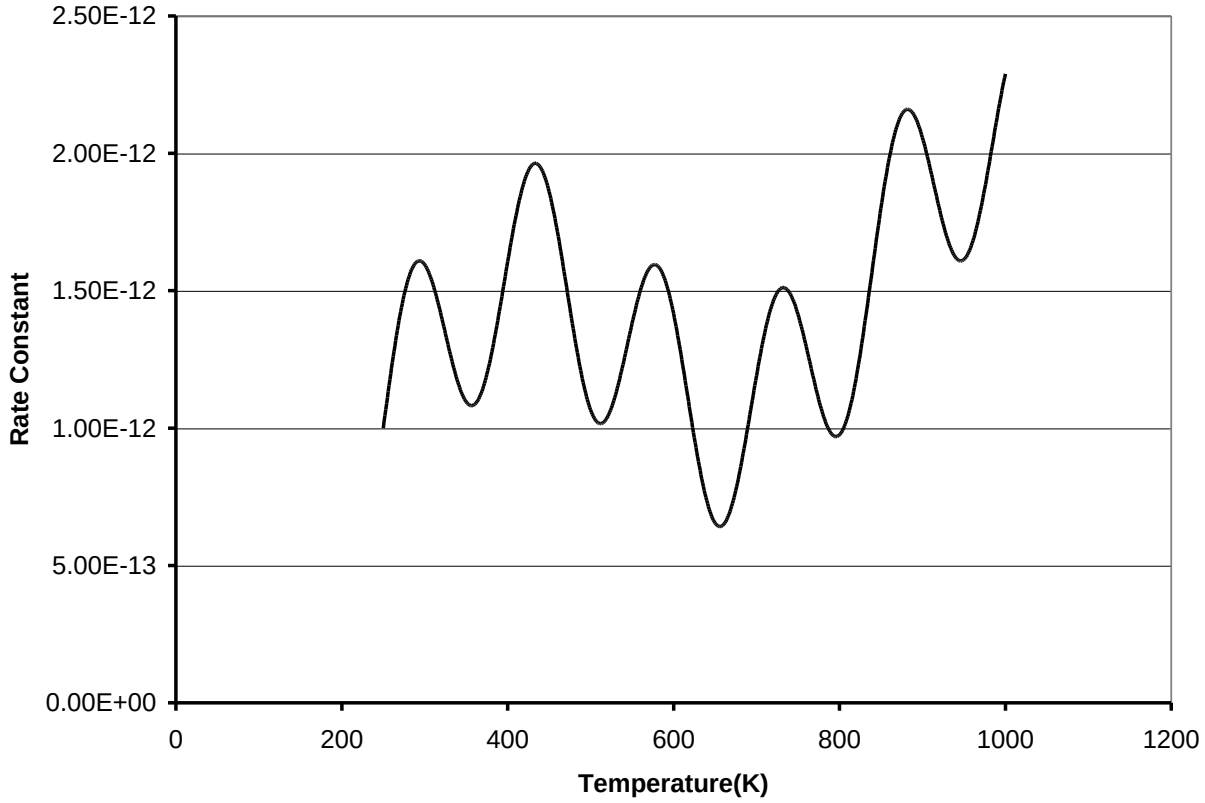


Figure 9. **Sample Chebyshev Fit on a multi-sinewave. (see FORTRAN program below)**

The file "chubcoefs.txt" has these Chebyshev coefficients from the fit:

```
250.; 1000.;0.300062E-11;0.305456E-12;0.239869E-12;0.187750E-12;-.123411E-12;-.250270E-
13;0.681191E-13;0.147765E-12;-.821882E-15;0.144717E-12;-.473757E-13;-.522478E-13;-.258921E-13;-
.181437E-12;0.627484E-13;0.183825E-12;-.408715E-13;-.880782E-13;0.153966E-13;0.271536E-13;-
.399127E-14;-.603488E-14;0.773946E-15;0.101339E-14;-.131604E-15;
```

Deleting the ending semicolon in the above line and inserting in a chemical reaction using Kintecus format we arrive at:

```
1 , 0, 0,  A + B + C + S[FIT3; 250.; 1000.;0.300062E-11;0.305456E-12;0.239869E-12;0.187750E-12;-
.123411E-12;-.250270E-13;0.681191E-13;0.147765E-12;-.821882E-15;0.144717E-12;-.473757E-13;-
.522478E-13;-.258921E-13;-.181437E-12;0.627484E-13;0.183825E-12;-.408715E-13;-.880782E-
13;0.153966E-13;0.271536E-13;-.399127E-14;-.603488E-14;0.773946E-15;0.101339E-14;-.131604E-15]
==> D + E + F
```

The chemical reaction line above will have a rate constant equal to the function SINEY located in the FORTRAN program on the next page and the temperature interval of 250 to 1000 K.

```
        PROGRAM CHEBTEST
        IMPLICIT NONE
        INTEGER NMAX
        PARAMETER (NMAX=35)
        REAL a,b,c(NMAX),x,siney, chebev
        INTEGER n,L
        external SINEY
        a=250.0
        b=1000.0
        n=25   ! 25 points is good, sometimes you might need 30 !
        call chebft(a,b,c,n,SINEY)  ! Fit function SINEY to Chebyshev
C
       open (unit=9,name='siney.txt')
       DO L=250,1000
        x=REAL(L)
        write(9,*) 'Temperature, rate constant=',x,siney(x)
       end do
       close(unit=9,status='keep')
C--
       open (unit=9,name='chub.txt')
         DO L=250,1000
          x=REAL(L)
          write(9,*)'Temperature, rate constant=',x,chebev(a,b,c,n,x)
       end do
       close(unit=9,status='keep')
C----
        open(unit=9,name='chubcoefs.txt')
1       FORMAT(F6.0, ';', F6.0, ';', (G12.6, ';', $), :)
       write(9,1) a,b,(c(L),L=1,n)
        close(unit=9,status='keep')
          stop
       end
C
C Evaluate Chebyshev ...
C
        FUNCTION chebev(a,b,c,m,x) ! Insert Numerical recipes function here...

C
C  Fit Chebyshev function against data....
C
        SUBROUTINE chebft(a,b,c,n,func) ! One more Numerical recipes here...

C
C  Fit Chebyshev against this function below....
C
        REAL FUNCTION SINEY(temp)
        IMPLICIT NONE
        REAL temp,x,f,pi
        pi=3.14159265
        f=1.0e-12+sin((temp-250)/750.)*8.0e-13+
       &sin(8.0*((temp-250)/750.))*4.0e-13+
       &sin(32.0*((temp-250)/750.))*4.0e-13
        SINEY=f
        RETURN
        END
```

Multiple-well, Multiple-channel Reactions Utilizing Chebyshev Polynomials

Kintecus V5.5 and up now support the Chebyshev expansions proposed by Venkatesh [32] for representing pressure fall off and temperature-dependent rates of multiple well reactions. Please see those references for the list of equations utilized in Kintecus to calculate those rates.

To request these Chebyshev polynomials, one uses the “CHEB” keyword in the following format

A , m , E_a, Reactants + M[CHEB; Matching_Keyword; scaling_factor] ==> Products

The presence of the CHEB keyword will cause Kintecus to look for a text file named "**chebdata.txt**." The text file chebdata.txt will contain all your reactions that might use a multiple-well, multiple-channel Chebyshev polynomials reaction. The file should include the following items to represent one multiple-well, multiple-channel Chebyshev polynomials reaction:

"Matching_Keyword" (this can be any alphanumeric that you can use to name this reaction)
Low_Temperature , **High Temperature**
Low_Pressure, **High Pressure**
Number of Rows (the y data), **Number of columns** (x data)
Following by y rows of x columns of Chebyshev polynomials coefficients.

For example: The for this reaction:
1.00E+00, 0, 0, HO2+HO2+M[**CHEB**; markblitz5x7; 1.0] ==> H2O2

One would have a text file named "chebdata.txt" that would have this data:

markblitz5x7						
300	800					
1.00E+16	1.00E+21					
5	7					
-13.0606	2.21021	-0.70072	0.093464	0.07499	-0.10344	0.065816
0.867347	-0.54299	-0.0501	0.0042	0.03079	-0.0228	0.014221
-0.209159	0.067302	0.029007	0.005337	-0.00225	0.001418	-0.00185
0.0532106	-0.00714	-0.00148	-0.00592	0.00436	-0.00456	0.002612
-0.0138968	0.002606	-0.00411	0.005703	-0.0058	0.004976	-0.00274

The Kintecus-Excel worksheet named "**Kintecus_multiwell_cheb_tests.xls**" provides an example.
The scaling_factor allows users to convert the units from the rate to different units. It is usually set to one.

Master Chemical Mechanisms (MCM) Forms

Kintecus V5.5 and up now supports some particular IUPAC chemical kinetics forms from the Master Chemical Mechanism (MCM) (see http://mcm.leeds.ac.uk/MCM/parameters/complex.htt , http://www.iupac-kinetic.ch.cam.ac.uk/ or http://iupac.pole-ether.fr/supp_info/Guide_2001.pdf or Google/Bing Master Chemical Mechanism). Most of these forms pertain to special pressure fall-off reactions that cannot be fully cast into the traditional Troe, Lindemann forms. Shown below are some of those forms. The sample Kintecus-Excel worksheet **"Kintecus_MCM_examples.xls"** workbook contains examples of each MCM reaction explained below. Note that some of these forms have sub-forms that perform differently depending on the number of parameters given. Also, note that all rate forms shown below include **k(T)=A*T^m*exp(-Ea/RT)** as part of their rate equation form, but they are not explicitly shown as part of it.

Also, under the Windows Kintecus TOOLS start-menu is a utility (for linux users, it is under the MCM sub-directory), created by Dr. Fred Winiberg of JPL, that will convert most FACSIMILE codes containing MCM kinetic forms to a Kintecus MODEL spreadsheet.

➢ *MCM1*

The MCM1 forms utilize the Troe formalism and have several sub-forms depending on the number of parameters given:

A , m , E_a, Reactants +
M[MCM1; k_0; n; k_{inf}; m; F_{cent} ; (B) (; and any optional enhanced third-bodies)]
==> Products

The data is evaluated over a different temperature range and the broadening factor F is calculated differently: $\log F = \log F_{cent} / (1 + [\log(k_0 [M]/k_{inf}) / n]^2)$ where $n = [0.75 - 1.27 \log F_{cent}]$

Providing five parameters for MCM1 (k_0; n; k_{inf}; m and F_{cent}) for MCM1 will yield the **KMT01** format (see the **KMT01** format at http://mcm.leeds.ac.uk/MCM/parameters/complex.htt). k_{inf} and k_0 are calculated as in the JPL evaluations described above for the JPL reactions, and F_{cent} is a floating-point number (which would be set to 0.85 for KMT01).

Providing six parameters (k0; n; k_{inf}; m; F_{cent} and B) will yield the **KMT04** format (again, see the **KMT04** form at http://mcm.leeds.ac.uk/MCM/parameters/complex.htt) where k_{inf} and k_0 are calculated using a modified version of the JPL evaluation equations: $k_0 = k_0^{300} * (T/300)^{-n} *$ EXP(-B/TEMP), where B is a whole integer variable.

➢ *MCM2*

The MCM2 form utilizes the Lindemann like formalism :

A , m , E_a, Reactants +
M[MCM2; A_0; m_0; E_{a0}; F_{cent} (; and any optional enhanced third-bodies)] ==> Products

Providing four parameters for MCM2 (**A_0; m_0; E_{a0}; F_{cent}**) for MCM2 will yield the **KBPAN** format (see the **KBPAN** format at http://mcm.leeds.ac.uk/MCM/parameters/complex.htt). k_{inf} and k_0 are calculated as in the Lindemann function (see above under the Linemann reaction), and F_{cent} is a floating-point number

➢ *MCM3*

The MCM3 forms utilizes the Troe formalism and has several sub-forms depending on values of the last two parameters given:

A , m , E_a, Reactants +
+ M[MCM3; k_0; n; k_{inf}; m; coef1; exp1; coef2; exp2; (; and any optional enhanced third-bodies)]
==> Products

If either the **coef1** or **exp2** parameters are zero and coef2 and exp2 are non-zero, then MCM3 will evaluate to the **KMT07** format (see the **KMT07** form at http://mcm.leeds.ac.uk/MCM/parameters/complex.htt). If coef1 and exp1 are non-zero, MCM3 will evaluate to **KMT17**. k_{inf} and k_0 are calculated in JPL format (see above under the JPL1/2 reactions), and F_{cent} is an exponential, F_{cent} = coef1*EXP(-TEMP/coef2), or a bi-exponential: F_{cent} = coef1*EXP(-exp1/TEMP)+coef2*EXP(-TEMP/exp2) (the KMT17 format).

➢ *MCM4*

The MCM4 forms

A , m , E_a, Reactants + M[MCM4; A; B; (; and any optional enhanced third-bodies)] ==> Products

For the rate of $k(T)=A*T^m*\exp(-Ea/RT)*(T/300)^{-A}*\exp(-B/T)*[M]$

➢ *MCM4 (no [M])*

This "+S[MCM4" form is exactly like "+M[MCM4" but without the "[M]" term:

A , m , E_a, Reactants + M[MCM4; A; B; (; and any optional enhanced third-bodies)] ==> Products

For the rate of $k(T)=A*T^m*\exp(-Ea/RT)*(T/300)^{-A}*\exp(-B/T)$

➢ *MTD1*

The MTD1 form is::

A , m , E_a, Reactants + M[MTD1; A2; B2; (third-bodies)*(enhancements)] ==> Products

For the rate of $k(T)=A*T^m*\exp(-Ea/RT)*$ (1.0+ (A2*(third-bodies)*(enhancement)*exp(B2/T))). For example:
A, m, Ea, A+B+M[MTD1; A2; B2; H2O(1.234)] ==> products will yield a rate of
of $k(T)=A*T^m*\exp(-Ea/RT)*$ (1.0+ (A2*[H2O]*1.234*exp(B2/T))).

➢ *MTD2*

The MTD2 is similar to MTD1 but multiplies the rate expression by [M]

A , m , E_a, Reactants + M[MTD1; A2; B2; (third-bodies)*(enhancements)] ==> Products

For the rate of $k(T)=A*T^m*\exp(-Ea/RT)*$ (1.0+ (A2*(third-bodies)*(enhancement)*exp(B2/T))). For example:
A, m, Ea, A+B+M[MTD1; A2; B2; H2O(1.234)] ==> products will yield a rate of
of $k(T)=$ **[M]** $* A*T^m*\exp(-Ea/RT)*$ (1.0+ (A2*[H2O]*1.234*exp(B2/T))).

➢ *TDBR1 to TDBR2*

The Temperature Dependent Branching Ratio (TDBR) reactions forms also don't fit into one specific category, but they are listed in the MCM database (at http://mcm.leeds.ac.uk/MCM/parameters/complex.htt) and are shown below.

TDBR1:

A , m , E_a, Reactants + S[TDBR1; A ; B] ==> Products

Representing this form A*Exp(Ea/TEMP) *(1-1/(1+A*EXP(-B/TEMP))), so to represent :
3.8D-13*EXP(780/TEMP)*(1-1/(1+498*EXP(-1160/TEMP))) : CH3O2 + HO2 = CH3OOH, one would have "3.8e-13,0,780, CH3O2+HO2+**S[TDBR1**; 498; -1160]==>CH3OOH" in Kintecus notation.

TDBR2:

A , m , E_a, Reactants + S[TDBR2; A ; B] ==> Products

Representing this form A*EXP(Ea/TEMP)*(1/(1+A*EXP(-B/TEMP))), so to represent:
3.8D-13*EXP(780/TEMP)*(1/(1+498*EXP(-1160/TEMP))) : CH3O2 + HO2 = CH3OOH, one would have "3.8e-13,0,780, CH3O2+HO2+**S[TDBR2**; 498; -1160]==>CH3OOH" in Kintecus notation.

➢ *TDBR3 to TDBR4*

The Temperature Dependent Branching Ratio (TDBR) reactions forms also don't fit into one specific category, but they are listed in the MCM database (at http://mcm.leeds.ac.uk/MCM/parameters/complex.htt) and are shown below. Note the presence of "+M[" and not "+S[" as these reactions involve [M] unlike TDBR1 and TDBR2 shown above. Also, note that all rate forms below include k(T)=A*T^m*exp(-Ea/RT) as part of their equation rate form.

TDBR3:

A , m , E_a, Reactants
+ M[TDBR3; A1; B1; A2; B2(; and any optional enhanced third-bodies)] ==> Products

TDBR3's form represents
A1 * EXP(-B1/TEMP) * (A2 * EXP(-B2/TEMP)*[M]

TDBR4:

A , m , E_a, Reactants
+ M[TDBR4; A1; B1; A2; B2 (; and any optional enhanced third-bodies)] ==> Products

TDBR4's form represents
A1 * EXP(-B1/TEMP) * (1 - A2 * EXP(-B2/TEMP)) * [M]

➢ *SP1 to SP4*

The SPx gas reaction forms don't fit into one specific category, but they are listed in the MCM database (at http://mcm.leeds.ac.uk/MCM/parameters/complex.htt). They are shown below as sample Kintecus syntaxes followed by an example:

SP1:

A , m , E_a, Reactants + M[SP1; coef1; denom] ==> Products

SP1 is equivalent to the KMT05 MCM reaction. Example:
:
1.44D-13*(1+(M/4.2D+19)) = M[SP1; 1.44e-13;4.2e+19]

SP2:

A , m , E_a, Reactants + M[SP2; k1; Ea_k1; k3; Ea_k3; k4; Ea_k4]==> Products

SP2 is equivalent to the KMT11 MCM reaction. Example:
For
KMT11 = k1(T) + k3[M]/(1 + k3[M]/k4) where k1 = 2.4 x 10^{-14} exp(460/T) cm^3 / (molecule * s) ;
k3 = 6.5 x 10^{-34} exp(1335/T) cm^6 $molecule^{-2}$ s^{-1} and k4 = 2.7 x 10^{-17} exp(2199/T) cm3 molecule-1 s-1 then in Kintecus syntax M[**SP2**;2.4e-14;460; 6.5e-34;1335; 2.7e-17;2199]

SP3:

A , m , E_a, Reactants + M[SP3 ; A ; Ea ; A2; Ea_A2]==> Products

SP3 is equivalent to **KMT18** in the MCM database. Example:
KMT18 = 9.5 x 10^{-39} exp(5270/T)/{1 + 7.5 x 10^{-29} exp(5610/T)} cm^3 $molecule^{-1}$ s^{-1} in Kintecus SP3 syntax the reaction would be M[SP3 ; 9.6e-39 ; 5270 ; 7.5e-29; 5610]

SP4:

A , m , E_a, Reactants + M[SP4; A1; B1; n; A2; B2;]==> ==> Products

SP4 is equivalent to **KMTxx** in the MCM database. Example:
2 * (K298CH3O2 * A1 * EXP(-B1/TEMP))^n, where K298CH3O2 = A2 * EXP(-B2/TEMP) the equivalent Kintecus SP4 syntax would be 2CH3C(O)O2+M[SPEC1; A1; B1; n; A2; B2;]==>2CH3C(O)OH

Kintecus will look for MODEL.DAT as the default filename. One can override the default filename of "MODEL.DAT." Please see the KINTECUS Switches Section setting below on the flag to do this.

EQUILIBRIUM MODE NOTE: If you are running Kintecus in equilibrium mode, the Model Description Spreadsheet (model spreadsheet file) is NOT USED. Only the species description and the parameter spreadsheets are used for equilibrium runs.

Cell Compartments and Diffusion

You can use fractional rate-stoichiometric coefficients for cell compartments of different volumes. For example, to describe the peroxynitrate (PNA) diffusion/convection from the cell-nucleus to the cell-membrane where the cell membrane is, say, 1/7 the volume of the nucleus and one also knows the diffusion-rate-constants between the nucleus and membrane (let's just say, D=.1, D'=.01) for PNA, the two reactions can be written as (keep in mind 0.14286 is about 1/7):

0.1 , PNA{nucleus} ➔ 7 PNA{membrane}
0.01, PNA{membrane} ➔ 0.14286 PNA{nucleus}

The above two reactions can also be written with the coefficients in front, but the rate constant is then very hard to define from diffusion constants.

??? , 0.14286 PNA{nucleus} ➔ PNA{membrane}
??? , 7 PNA{membrane} ➔ PNA{nucleus}

It is easier to specify the change in volume through the products. An important side note, please stay away from describing phases with one character, such as PNA{a} or PNA{g}, as future versions of Kintecus will interpret the phases as actual physical states and alter any related differential or algebraic equations. The current version of Kintecus only recognizes the gas phase, {g}, which can significantly alter gas-phase rates through [M], third-body enhancements, TROE, SRI factors, and other related gas-phase kinetics.

User Defined Chemical Rate Equations

The special USER function is new in Kintecus V6.51. You can use it to define your own chemical kinetic rate equations like this:

"A+B+**S[USER;**(variable list separated by commas, “,”, or vertical bars, “|”) : (chemical kinetic function)]" (<=== Note the semi-colon, ";", after USER and a colon, ":" after the variable list!)

Example:

"H+O2+S[USER;M,T,cH2,cN2,cH2O:(M-cH2-cN2-cH2O+cH2*2.86+cN2*1.26+cH2O*18.6)*3.61e17 *T^(-1*0.72)*exp(-0.0/(8.314*T))]=HO2"

OR

"H+O2+S[USER;M|T|cH2|cN2|cH2O:(M-cH2-cN2-cH2O+cH2*2.86+cN2*1.26+cH2O*18.6)*3.61e17*T^(-1*0.72)*exp(-0.0/(8.314*T))]=HO2"

(1) You must define all variables utilized in the function as a comma-delimited or vertical bar, “|” delimited list. You can use **T** for the current temperature, **P** for Pressure, **M** for Loseschmidt's value, **R** for gas constant, and **c**XXXXXX for the concentration of species XXXXXX, ie. concentration of CH4 would be **c**CH4.

(2) the length of variable names are limited to **23 characters** (for now)

(3) **Be careful!** Variables are case INSENSITIVE! **So cCo, cco and cCO are all the SAME! (for now)**

(4) Errors are not too clear. If you are missing a parenthesis or didn't define a variable used in a function you get an error about that function and that something is wrong.

The user function supports natural logarithm (log), logarithm base 10 (log10), most trig functions (sin, cos, tan, atn, acos), hyperbolics (cosh, sinh, tanh, etc) and their inverses (atan, asin, acos), square root (sqrt), absolute value (abs), exponent (exp), floor and other functions. **For negative exponents (for example, 1^-.6) you have to multiply it by minus one (-1), so 1^-0.6 becomes 1^(-1*0.6).**

One of the main problems you might have is the pairing of parenthesis. A trick is to type the formula as an Excel equation (type in a cell "=", then type the formula), and Excel will highlight the matching parenthesis.

(5) Please see the Kintecus-Excel spreadsheet "Combustion_workbook_OH_user_defined_functions.xls" as an example of various user defined chemical kinetic rate equations.

****EXCEL TRICK**: This part explains how to run Kintecus using the MODEL/SPECIES/PARM/FITDATA/etc worksheets in Excel without having Excel constantly open up, waste cpu cycles, and annoy you.

Click the Windows Start Button in the button, left-hand corner of the screen, and type "command" and press enter. A console window should pop up on the screen. Alternatively, hold the Windows key (usually, the key is at the bottom left of the keyboard, in between the CTRL and ALT keys) and tap the "x" key. A menu will pop up, select "Command" or "run" (and type **"cmd" or "command"**) or select "Windows Powershell", a new console should pop up.

1) Once you are in the console window (or Powershell window), type "**cd C:\Kintecus**" or where ever you have Kintecus installed.

2) In the Excel Window, click on "CONTROL" tab, click "RUN", once Kintecus starts, stop it with "**ctrl-c**" (hold ctrl key and tap the "c" key) or ctrl-break (hold ctrl key and tap the Pause/Break key). The reason for this step is that once you press the RUN button, the Kintecus-Excel VBA macros will output all your worksheets as input files for Kintecus.

3) In the same "CONTROL" worksheet, click on the contents of the "Kintecus Switches" cell (A12) and select COPY (right-click, select Copy)

4) Click in the console/command/powershell line window, in Powershell/command type "**./kintecus**". In command console, just type "**kintecus**" (**don't press enter yet!**)

5) Hold down the CTRL key and type "V" (for paste) and press ENTER. This should paste your Kintecus switches from cell A12 on the CONTROL worksheet into the command line.

6) Kintecus is now running outside of Excel using all your inputs from the Excel Worksheet. Once Kintecus is finished, click the "Plot Results" button on the CONTROL worksheet. Also, note that you can copy the entire Kintecus folder into a new directory (C:\Kintecus2\), change the "Kintecus Path" located on the CONTROL worksheet, then change one or two parameters in the Kintecus-Excel worksheet and perform the same steps above. You will be running two different Kintecus simulations/optimizations simultaneously. Repeat as much as necessary assuming you have enough cores on your cpu.

The Periodic Table SpreadSheet

This is another optional spreadsheet invoked through the "-P" or "-p" Kintecus command-line option. Once either "-P" or "-p" is specified on the command line, Kintecus will look for a spreadsheet file named PERIOD.DAT. The Periodic Table Spreadsheet (PTS) allows you to redefine or add new elements/isotopes to the periodic table. Kintecus has the molecular weight of the elements internally stored. The PTS PERIODDF.DAT contains a copy of those elements stored internally in Kintecus. If you wish to modify or add new elements/isotopes, copy the PERIODDF.DAT file to PERIOD.DAT and modify that file. Kintecus will report an error if elements appear more than once in the PTS if the "-P" switch is used, **but** if the "-p" switch is used, only the first instance of an element will be used. The duplicate element appearing further down the list will simply be ignored. You can insert comments in this file or comment out lines by placing a "#" or a quote ' " ' as the first character on a line.

Advanced Modeling

Incorporation of Thermodynamics

Kintecus provides a powerful means to control various thermodynamic aspects in a model. Isothermal, non-isothermal, constant pressure, constant volume, programmed temperature runs/perturbations, programmed volume runs/perturbations, multiple thermodynamic databases can be used, and much more.

The Thermodynamic Description SpreadSheet

Specifying the **"–THERM"** switch on the Kintecus command line directs Kintecus to thermodynamics mode. Thermodynamics mode forces Kintecus to compute enthalpies, heat capacities, and reverse rate constants (for any reversible reactions present) for all the reactions. The temperature evolution of the system can be described by an ordinary differential equation (ODE) as

$$\frac{dT}{dt} = -\left(\frac{1}{C_p(T)}\right)\sum_{i=1}^{N_S}\left(\frac{dc}{dt}\right)_i H_i(T) \qquad \text{Eqn 28.}$$

Where T is the temperature of the system, N_s is the total number of species present in the system, $C_p(T)$, $H_i(T)$ and dc/dt are equations representing, respectively, the heat capacity of the entire system, enthalpy for a species and the rate of change of a species' concentration:

$$C_p(T) = \sum_{i=1}^{N_S} c_i C_{p,i} \qquad \text{Eqn 29.}$$

for which $C_{p,i}$ is a split function

$$\left.\begin{aligned} C_{p,i} &= R\left(la_{1,i} + la_{2,i}T + la_{3,i}T^2 + la_{4,i}T^3 + la_{5,i}T^4\right) \quad ,if\ T_L \le T < T_C \\ C_{p,i} &= R\left(ha_{1,i} + ha_{2,i}T + ha_{3,i}T^2 + ha_{4,i}T^3 + ha_{5,i}T^4\right) \quad ,if\ T_C \le T < T_H \end{aligned}\right\} \qquad \text{Eqn 30.}$$

and $H_i(T)$ is also a split function

$$\left.\begin{aligned} H_i(T) &= RT\left(la_{1,i} + \frac{la_{2,i}}{2}T + \frac{la_{3,i}}{3}T^2 + \frac{la_{4,i}}{4}T^3 + \frac{la_{5,i}}{5}T^4 + \frac{la_{6,i}}{T}\right) \quad ,if\ T_L \le T < T_C \\ H_i(T) &= RT\left(ha_{1,i} + \frac{ha_{2,i}}{2}T + \frac{ha_{3,i}}{3}T^2 + \frac{ha_{4,i}}{4}T^3 + \frac{ha_{5,i}}{5}T^4 + \frac{ha_{6,i}}{T}\right) \quad ,if\ T_C \le T \le T_H \end{aligned}\right\} \qquad \text{Eqn 31.}$$

Equations 30-31 use the coefficients of $la_{1\text{-}6}$ for the low temperature range, T_L to T_C, and the coefficients $ha_{1\text{-}6}$ for the higher temperature range, T_C to T_H, are taken from the thermodynamic databases described in the references. As mentioned above, dc/dt is required in equation 28, and it also represents the time evolution of the concentrations of the species present in the system:

$$\left(\frac{dc}{dt}\right)_i = \sum_j^{products} k_j(T,P) n_{i,j} \prod_k^{reactants} A_k^{n_k} - \sum_j^{reactants} k_j(T,P) n_{i,j} \prod_k^{reactants} A_k^{n_k} \qquad \text{Eqn 32.}$$

where i is each species present in the system with j reactions, A_k is the k^{th} species' concentration present in reaction j raised to its stoichiometric coefficient n_k. $k_j(T,P)$ represents the forward rate constant evaluated using the expanded Arrhenius equation at the current temperature and pressure. Some forward rate constants might also involve third-body and pressure fall-off reactions involving [M], Lindemann or Troe type reactions. The reverse rate constants are calculated through the equilibrium constant at the current temperature,

$$k_r = \frac{k_j(P,T)}{\left(\frac{1}{RT}\right)^{\Delta n} \ell^{\left(-\frac{\Delta H(T)_r - T\Delta S(T)_r}{RT}\right)}} \qquad \text{Eqn 33.}$$

where $\Delta H(T)_r$ and $\Delta S(T)_r$ are changes in the enthalpies and entropies of that particular reaction r

$$\Delta H(T)_r = \sum_{i=1}^{products} n_{r,i} H_i(T) - \sum_{i=1}^{reactants} n_{r,i} H_i(T) \qquad \text{Eqn 34.}$$

$$\Delta S(T)_r = \sum_{i=1}^{products} n_{r,i} S_i(T) - \sum_{i=1}^{reactants} n_{r,i} S_i(T) \qquad \text{Eqn 35.}$$

where the $H_i(T)$ is from equation 3 and the $S_i(T)$ is obtained from the split function

$$\left.\begin{aligned} S_i(T) &= R\left(la_{1,i}\ln(T) + la_{2,i}T + \frac{la_{3,i}}{2}T^2 + \frac{la_{4,i}}{3}T^3 + \frac{la_{5,i}}{4}T^4 + la_{7,i}\right) \quad ,if\ T_L \le T < T_C \\ S_i(T) &= R\left(ha_{1,i}\ln(T) + ha_{2,i}T + \frac{ha_{3,i}}{2}T^2 + \frac{ha_{4,si}}{3}T^3 + \frac{ha_{5,i}}{4}T^4 + ha_{7,i}\right) \quad ,if\ T_C \le T < T_H \end{aligned}\right\} \qquad \text{Eqn 36.}$$

Again, the thermodynamic coefficients shown above are obtained from the thermodynamic database(s) provided in the Thermodynamic Description SpreadSheet. **Also, depending on the system condition (constant pressure, constant volume, adiabatic, non-adiabatic, external heat source or varying external species concentration(s) with residence time), the equations above are altered during a simulation to force those conditions.**

Once Kintecus is in the thermodynamic mode, it will look for the Thermodynamic Description SpreadSheet. The default name of this sheet is **THERM.DAT**. You can override this name. The thermodynamic description spreadsheet contains a listing of all related thermodynamic databases that can be used with your model. The thermodynamic databases contain information describing the heat capacities and entropies for a wide range of temperatures. For a complete description on how the range of heat capacities and entropies are calculated for each species, refer to the Chemkin-II reference [11]. There are many public thermodynamic databases out there in the Internet. Some starting search links are given: www.sandia.gov , www.llg.gov or http://wwwcms.llnl.gov/combustion/combustion2.html .

Suppose you cannot find a thermodynamic database containing information for your species'. You can try to obtain a heat capacity listing from NIST-JANAF tables at http://www.nist.gov/srd/thermo.htm , Burcat & Mcbride Data [22] or roughly estimate them using group additivity [21]. You can also calculate the thermodynamic values using the technique described in Chemkin-II reference[11]. There are programs already available to produce thermodynamic coefficients that fit a user-provided range of heat capacities. One such program is THERM [20]. If you still cannot find either a thermodynamic database containing information on your species' or NIST heat capacities to compute the thermodynamic coefficients, you will have to perform experiments to obtain the heat capacities or compute the heat capacities. Methods to calculate heat capacities are provided in manuals for Gaussian, GAMESS, DISCOVER, COLUMBUS, CHARM, Jaguar, Mopac and many other quantum programs. Be warned! It is highly recommended to use high-level *ab initio* (such as MP2/MP4/CCSD(T)/CASPT2/MRSCF

theory) using large basis sets for accurate heat capacities or combination methods such as the G2/G3 theory or at the very least DFT theory (such as B3LYP using large basis sets). Blindly using semi-empirical techniques (such as AM1, PM3, MINDO, and many others) can provide disastrous results.

A sample "Thermodynamic Description Spreadsheet" is shown below:

# Database			Database	Species
# FileName	INPUT	MAP	Special Switches	Reservation List
1995_NASA_data	F18:IG26:F1:F10:F10:F10:NL	SP:PH:LT:HT:MW:HA1:HA2:HA3:	U1234:UPPL:CHF:FLUFF:PHS:SET(CT=1000):SYN	
1994_thermo.dat	F18:IG26:F1:F10:F10:F10:NL	SP:PH:LT:HT:CT:HA1:HA2:HA3:H	U1234:UPPL:CHF:PHS:UPC	O2:O3:C2H4
freeoh1.dat	FREE	SP:LT:CT:HT:LA1:LA2:LA3:LA4:L	UPPL	CH4
#1995_Burcat_data	F18:IG26:F1:F10:F10:F10:NL	SP:PH:LT:HT:MW:HA1:HA2:HA3:	U1234:UPPL:CHF:FLUFF:PHS:SET(CT=1000):SYN	
END				

Figure 10

There are five columns for the thermodynamic description spreadsheet. The first column, Database Filename, contains the filename for the thermodynamic database. As one might recall, the thermodynamic database contains the thermodynamic coefficients for the species in your model. Kintecus provides a means to provide multiple thermodynamic databases by allowing one to enter additional Database Filenames in column one. It should be noted that Kintecus uses the thermodynamic coefficients for a species from the first match in a thermodynamic database. This can be overridden by using the Species Reservation List explained below.

The INPUT and MAP columns are shown in the "Thermodynamic Description Spreadsheet". These two fields direct Kintecus on how exactly to read in the thermodynamic database**. YOU SHOULD NOT HAVE TO DERIVE INPUT AND MAP FIELDS!** It **is highly recommended** that you copy the sample thermodynamic description spreadsheet, THERMCK.DAT, as THERM.DAT and follow the quick instructions in CK2KIN.EXE (CHEMKIN-II/III ➔ KINTECUS MODEL CONVERTER).

Of the many thermodynamic example simulations that come with Kintecus, copying and pasting the entire INPUT, MAP and Database Special Switches from a preexisting thermodynamic description spreadsheet should allow you to read most thermodynamic databases. Sometimes, the removal or addition of a Database Special Switch might also be needed to read in that stubborn database.

There are only four keywords in the INPUT field:**F**(characters to read), **IG**(characters to skip) , **NL** (new line or carriage return), and the exclusive **FREE**. A colon must delimit all keywords**, ":".**

A sample INPUT field is shown below:

F18:IG26:F1:F10:F10:F10:NL:F15:F15:F15:F15:F15:NL:F15:F15:F15:F15:F15:NL:F15:F15:F15:F15

The F(nn) keywords shown above direct Kintecus, an essential field of length (nn) characters (where nn is an integer number up to 99). The IG(nn) keyword directs Kintecus to "ignore" or skip (nn) characters. The NL keyword directs Kintecus to go to the following line. The F(nn) keyword and the fields in the MAP column must have a perfect one-to-one mapping. The FREE keyword directs Kintecus that this thermodynamic database is in a FreeForm. FreeForm allows each field to be separated by a delimiter (spaces are ignored). The delimiter is a TAB by default, but this can be overridden by entering the ASCII value of the delimiter after the FREE keyword, i.e., FREE(44) directs Kintecus to use commas to delimit each field in the thermodynamic database. The oh2f.bat model and its related files illustrate this feature's use.

The MAP fields convert the value each F() field into a MAP keyword. A listing of all MAP keywords and their respective thermodynamic value are shown below:

Map Keyword(s)	Thermodynamic Value
SP	Species Name
LT	Low Temperature for Low Range
CT(optional)	Common Temperature Separating Low/High
HT	High Temperature for High Range
LA1, LA2,LA3,LA4,LA5,LA6,LA7	Thermodynamic Coefficients for the Low Range
HA1,HA2,HA3,HA4,HA5,HA6,HA7	Thermodynamic Coefficients for the High Range
PH (optional)	Phase of Species
CH(optional)	Numeric charge of species (usually not needed). Charge can be retrieved from end of species name
MW (optional)	Molecular Weight of Species. This will override Kintecus' internally calculated Mw for that species.
CMW (optional)	Convert Chemkin empirical molecular weight (usually in columns 25-44 on first row) to Mw. Note, some thermo. databases have more than 4 elements defined for a species, you can specify a larger field to encompass it. Specifying the CMW Map Keyword will override Kintecus' internally calculated Mw for that species.

Table 3. Possible Map keywords available to read physical properties from a thermodynamic database.
A sample MAP field is shown below:

SP:PH:LT:HT:MW:HA1:HA2:HA3:HA4:HA5:HA6:HA7:LA1:LA2:LA3:LA4:LA5:LA6:LA7

Using the sample INPUT field given above here are exactly how the values from F() to MAP keywords are converted:SP=F18, PH=F1, LT=F10, HT=F10, MW=F10, HA1=F15, HA2=F15, HA3=F15, HA4=F15, HA5=F15, HA6=F15, HA7=F15, LA1=F15, LA2=F15, LA3=F15, LA4=F15, LA5=F15, LA6=F15, LA7=F15. Obtaining the following RUN-TIME error indicates that your INPUT field is not correctly defined.

Run-time error F6103 : READ(internal)
-invalid REAL

Your INPUT field is probably "capturing" non-numeric characters, and you should go over the "F" and "IG" field lengths to be sure they are of the right length.

The Database Special Switches Field has an assortment of Text Filtering and Value Setting for those databases which do not precisely conform to Chemkin/NASA format. A listing of all the Database Special Switches keywords and a short explanation of what they do are shown below:

Database Special Switch Keyword	Action
UPC	Convert all database species' names to and user's species names to UPPERCASE
FLUFF	Any extra characters after the first space in a database species name is erased.ie. SP="C3CH8 #Hanson et a," is converted to SP=C3CH8
SET(Any Map Keyword = default value)	You can set ANY MAP keyword to any default value. Mainly useful for setting the Common Temperature to some value. Ie. SET(CT=1000) .
SYN	Some databases have two species names in one field. Ie, C4H8,butene. SYN allows Kintecus to match either C4H8 or butene to a species in your model. Without this keyword, Kintecus will literally interpret C4H8,butene as the full species name!

U1234	Directs Kintecus that this thermodynamic database is using the Chemkin/NASA standard format of using the numerals 1,2,3,4 in column 80 to continue species thermodynamic values onto multiple lines.
UPPL	Convert any uppercase “L” present in a database species name to a lowercase “l”. ie. If SP=”CL” then SP=”Cl”
CHF	Ignore charge field CH
PHS	Interpret possible phase information at the end of the database species name. Ie. Ga(IV) is converted to Ga{IV}.

Table 4. Special switches available for the parsing of thermodynamic databases.

The Species Reservation List field explicitly allows one to direct Kintecus to use the thermodynamic values for a species from a specific database. It allows one to switch values from one thermodynamic database to another without deleting and re-inserting rows of data, leading to a big mess. This will test various thermodynamic values created by different authors or groups. As with all values in the thermodynamic description spreadsheet, the Species Reservation List field list is delimited by a colon, “:”.

Some users have reported that Kintecus could not find a species name or loaded the incorrect phase of a species from a specific thermodynamic database. In actuality, the root cause was when the "Phase of Species" Map keyword, "PH," or the "PHS" Database Special Switch, was not applied. The table below lists the possible interpretations Kintecus can apply to your species names and the species names in the thermodynamic database. Always keep in mind that the "PHS" Database Special Switch will always override any phase information given by the "PH" Map keyword and given that appropriate phase information is provided at the end of a Kintecus Species Name (ie. H2SO4{L}).

CASE	Thermodynamic Database Name Field (SP)	Thermodynamic Database Phase Field (PH)	Kintecus Species Name	Phase Keyword (PH) Specified ?	Database Switch (PHS) applied ?	Will Kintecus Match the thermodynamic database species with the Kintecus Species Name?
1	H2SO4	g	H2SO4	Yes or No	Yes	**YES**
2	H2SO4(g)[1]	g	H2SO4	Yes	Yes	**YES**
3	H2SO4(g)	g	H2SO4	Yes	No	**NO**
4	H2SO4(g)	g	H2SO4(g)	Yes or No	No	**YES**
6	H2SO4(L)	C[2]	H2SO4(L)	Yes	Yes	**NO**
7	H2SO4(L)	C	H2SO4(L)	Yes	**NO**	**YES**
8	H2SO4(L)	C	H2SO4**{**L**}**[3]	Yes or No	NO	**NO**
9	H2SO4(L)	C	H2SO4**{**L**}**	Yes or No	Yes	**YES**
10	H2SO4	L	H2SO4**{**L**}**	No	Yes or No	**NO**
11	H2SO4	L	H2SO4**{**L**}**	Yes	Yes or No	**YES**

Table 5. Kintecus' interpretation of various forms of phase information. 1. practically all NASA thermodynamic databases NEVER suffix a gaseous species name with (g); it is used only here as a demonstration. 2. All NASA thermodynamic databases have a C in this field when the species is a non-gas and non-liquid phase. 3. *NOTE the braces, {, }, are used to surround the phase descriptor!

Creating Freeform Thermodynamic Databases

A NASA/Chemkin thermodynamic database can be converted to Freeform simply by providing the "–OF" switch on the Kintecus command line. This switch will direct Kintecus to output a spreadsheet file in freeform containing all the thermodynamic values in columns delimited by whatever delimiter is used in the MODEL.DAT file. It is important to note that ONLY the species used in your model.dat will be stored in the freeform spreadsheet.

The name of the freeform spreadsheet will always be "FREETHRM.TXT." A sample is shown below in which the model modoh.dat using the NASA thermodynamic databases was run with the "–OF" switch. The converted database (freeoh1.dat) containing the species used in the modoh.dat file is shown next.

# Species	LOW	Common	Hi	Thermodynamic coeffic. (LOW then HIGH)														
#	TEMP.	TEMP.	TEMP.	LA1	LA2	LA3	LA4	LA5	LA6	LA7	HA1	HA2	HA3	HA4	HA5	HA6	HA7	MW
H2	200	1000	6000	2.344331	7.98E-03	-1.95E-05	2.02E-08	-7.38E-12	-917.935	0.683	2.9329	8.27E-04	-1.46E-07	1.54E-11	-6.89E-16	-813.07	-1.0243	2.01588
O2	200	1000	6000	3.782456	-3.00E-03	9.85E-06	-9.68E-09	3.24E-12	-1063.94	3.6577	3.661	6.56E-04	-1.41E-07	2.06E-11	-1.30E-15	-1216	3.41536	31.9988
OH	200	1000	6000	3.992015	-2.40E-03	4.62E-06	-3.88E-09	1.36E-12	3615.081	-0.104	2.8386	1.11E-03	-2.94E-07	4.21E-11	-2.42E-15	3943.96	5.84453	17.00734
H2O	200	1000	6000	4.198641	-2.04E-03	6.52E-06	-5.49E-09	1.77E-12	-30293.7	-0.849	2.677	2.97E-03	-7.74E-07	9.44E-11	-4.27E-15	-29886	6.88256	18.01528
H	200	1000	6000	2.5	0	0	0	0	25473.66	-0.447	2.5	-5.65E-09	3.63E-12	-9.20E-16	7.95E-20	25473.7	-0.4467	1.00794
O	200	1000	6000	3.168267	-3.28E-03	6.64E-06	-6.13E-09	2.11E-12	29122.26	2.0519	2.5436	-2.73E-05	-4.19E-09	4.95E-12	-4.80E-16	29226	4.92229	15.9994
HO2	200	1000	6000	4.301798	-4.75E-03	2.12E-05	-2.43E-08	9.29E-12	294.808	3.7167	4.1723	1.88E-03	-3.46E-07	1.95E-11	1.76E-16	61.8103	2.95768	33.00674
H2O2	200	1000	6000	4.276113	-5.43E-04	1.67E-05	-2.16E-08	8.62E-12	-17754.3	3.4351	4.5733	4.05E-03	-1.29E-06	1.97E-10	-1.13E-14	-18055	0.70428	34.01468
N2	200	1000	6000	3.531005	-1.24E-04	-5.03E-07	2.44E-09	-1.41E-12	-1046.98	2.9675	2.9526	1.40E-03	-4.93E-07	7.86E-11	-4.61E-15	-923.95	5.87189	28.01348
NO	200	1000	6000	4.218599	-4.64E-03	1.10E-05	-9.34E-09	2.81E-12	9845.1	2.2806	3.2607	1.19E-03	-4.29E-07	6.94E-11	-4.03E-15	9921.43	6.36901	30.00614
N	200	1000	6000	2.5	0	0	0	0	56104.64	4.1939	2.4159	1.75E-04	-1.19E-07	3.02E-11	-2.04E-15	56133.8	4.64961	14.00674
END																		

Figure 11. A sample freeform thermodynamic database was created from a Chemkin file. Note the very easy to modify fields.

Kintecus Command Line Switches

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

> Kintecus (switches, if any)

Here is the current listing of all the switches available for Kintecus:

```
C:\Kintecus>kintecus -help

 The following command line options are:

 -ah See advanced Kintecus settings.
 -QUIET Don't display output or warnings.
 -PARM:filename (Parameter Description Input File)
 -SPNAME:filename (Species Common_Name/Mass Input File)
 -SPEC:filename (Species Description Input File)
 -MOD:filename (Model Description Input File)
 -OUT:filename (Concentration Output File)
 -THERM[:filename[:FORCE]] (Enter thermodynamics mode
  and use filename as the thermodynamic database
  spreadsheet)
 -c Create SPECIES.DAT file from model, then stop.
 -show Display to screen the concentration of species,
       time and dt's.
 -ig:mass Ignore Mass Balance.
 -ig:charge Ignore Charge Balance.
 -ig:warn Ignore all warnings.
 -x Output mole fractions instead of concentrations


 -SENSIT:  Output Sensitivity Analysis Output File
  -SENSIT:1(:n1 (:n2) ) Use sensitivity analysis #1 with
  the following optional numeric entries:
  n1 :perform analysis at various parts in the simulation
  (default is 60 parts=60 NSC matrices)
  -OR- n1=TIMES,t1,t2,tn... where t1,t2 and tn are
  times(in sec.) to perform the sensitivity analysis.
  n2 = percent difference in k's used (5% default)
  just typing -SENSIT:1 is equal to -SENSIT:1:3:5
 -KINSTAT Output statistics on the kinetic system
          into the file KINSTAT.TXT .
 -SEEMW Output all species and their corresponding
  molecular weight into the file MW.TXT.
 -P Load a user provided periodic table from the text
    file PERIOD.DAT
 -o:Y/N:Y/N:Y/N:Y/N Output files based on various
    physical properties/rates on the system as it runs.
 -h/? You get this list.
```

-FIT:a:b:**c**:d:e:f[:g:h:i] Fit/Optimize your model against
    experimental/fabricated data.
  a=Fitting Algorithm=1, 2, 3, 4, 5
  b=Comparison Operator=1, 2, 3, 4
  c=User Dataset Filename=Any allowed text filename
    if **c="FITDATAN"**, then use **MANY DATASETS**(see doc.)
    if **c="FITDATAN,initial_conditions.txt"**, then
      use **MANY DATASETS** each with unique **initial
      conditions**, like concentrations, temp.(see doc.)
     if **c="FITLINK,...,..."** reads a link file
  that **MUST be named "fit_links.txt"** (see doc).
  d=Tolerance=1 to 10(-14)
  e=Maximum Iterations Allowed=1-32767
  f=Starting Vectors=1x10(-99) to 1x10(10)
  g=Starting Temperature=1x10(-100) to 1x10(10)
  h=Number of Cycles to Stay At Current Temperature
  Before Reducing Temperature=1-32767
  i=Percent Temperature Reduction=0 - 0.99999
-FIT sets default values to, a=1, b=1,
c=FITDATA.TXT, d=1x10(-6),e=9000, f=1x10(-35)
-FITWEIGHT:[data column #]:[guess weight]
-FITSTAT:[COVAR|BOOT]:[TYPE]:[AMOUNT]:[% REPEAT]
 Output standard errors on the final fits (see doc).

-EQUIL:a:b:{c}:j:k Run Kintecus in EQUILIBRIUM
 mode using
 a=filename for the thermodynamic database
   spreadsheet or just leave blank or enter 'D' to
   use the default file name "EQTHERM.DAT".
 b=FI: Forget Initialization (see manual under the
   "Constant File ?" field). Typing a 'D' sets the
    default of Initialization.
 c=Sets various important tolerances for the non-linear solver.
   Can be a word containing built in settings or the
   user can specify each tolerance. See manual.
   Some settings: very-loose, loose, tight, very-tight
   The default setting is tight.
   'c' can also be user settings e,f,g,h where
(values in parenthesis are default values for the tight setting)
    e=function tolerance (3.0E-9), f=minimum value tolerance
    (2.0E-9), g=X-value tolerance (3.0E-12), h=maximum search
    step allowed (200.0).
 j=Maximum number of iterations to try before the
   non-linear solver quits. Default is 30,000.
 k=Maximum number of non-linear solver tries. (Default=75)
 -scan:{1,2,3,4} Scan user selected parameters.

-CONF{:a:b:c:d:e:f:g} Run Kintecus and calculate
   uncertainty parameters or confidence bands.
   [defaults are listed in brackets or entering the
    letter "D" or "d" for an option indicates to
    use default value.]
 a=total number of samples (simulations) to run. [100]
 b=Types (0-31), 1=k or A/m/Ea, 2=Concs., res. times,

```
   Bound./Extern. Conc., 4=Temperature, Extern. Temp
   temper.,extern. heat source, 8=all M[] and S[]
   parameters (TROE, SRI, third-body, etc.), 16=All
   thermodynamic parameters from database.
   Sum numbers to vary parameters , ie=31=ALL [31].
 c=factor to multiply the final calculated standard
   deviations [1.0].
 d=% confidence limit to calculate final statistics:
   (0%, 68%, 95%, 99%, 99.9%). 0% states to NOT to
    calculate confidence limits but standard
    deviations only [0%].
 e=Fraction standard deviation difference to use for
   all uncertainty runs [0.02-0.05]. Parameters in
   your model can override this with the (#/#)? flag.
   e can also be a list:(parameter type),STD.DEV.
 f=Random number distribution type to use for e
 (1=Gauss., 2=Unif.,3=Poiss.,4), f can also be a list:
  (parameter type),(1 or 2). Parameters with (#/#)?
  flag will override this flag. [1 for ALL params.]
 g=KEEP/DELETE, KEEP=keep all uncertainty runs. [KEEP]
 It is highly recommended you read the documentation
 on the -CONF flag.
```

-cluster Perform hierarchical cluster analysis

```
-cluster{:a:b:c:d:e:f:g:h:i:j:k}
*remember, a "d" or "D" in any option uses the default
 value (values in brackets, "[", "]" ).
 a=Cluster Type, 1=hierarchical [1]
  if a=101 then skip right to cluster analysis.
 b=Dissimilarity Method (0-8) [0=Euclidean distance]
   another popular method is 6=Correlation (r^2)
 c=Clustering Method (0-4) [0=Minimum distance]
   You can also try Ward's method 4 if b=0
 d=Transformation (0-2) [0=no transformation]
 e=Scale Data (0-2) [0=do not scale]
 f=# of Cluster (only used for K-means clustering has
   no affect on hierarchical clustering. [2]
 *** OPTIONS FOR TREE PRINTING FOLLOW ***
 g=Page Width in characters [101]
 h=Printing of Tree Method (1-3) [1]
 i=Number of Lines Printed before each Node (1-10) [1]
 j=Subtree Printing Specification (0-n) [0]
 k=# of horizontal slices of the tree to
   print,(1-10) [1]
 It is highly recommended you read the documentation
 on the -cluster flag.
```

-MECHV Perform Mechanism Validation Analysis

```
-MECHV{:a:b:c:d:e}
 a=stop or continue after analysis [stop]
 b=which parts to do [15=all=1+2+4+8]
 c=algorithm for rho-reduction [1]
 d=Linear Programming parts [3=both=1+2]
 e=value for LP programming part [-480]
```

```
-chemnet Visualize the Chemical Network
 -chemnet{:a:b}

  a=name of chemnet description input file
     [chemnet.txt]
  b=name of specnet description input file
      [specnet.txt]
  See manual for full details of chemnet.
```

Advanced Kintecus Switches:

```
C:\Kintecus>kintecus -ah

 -anjac Use analytically calculated jacobians.
 -d### Where ### is the ASCII code of the data
        delimiter used in the input files.
 -INT:n1[:list] Where n1 is the type of integrator used
     n1 = 1 Modified Bader-Deuflhard (default)
     n1 = 2 Cash-Karp-Runge-Kutta integrator
     n1 = 3 Gear's BDF Integrator [list=extra options, see doc]
     n1 = 4 DVODE integrator [list=extra options, see doc]
     n1 = 5 DASPK integrator [list=extra options, see doc]
 -OF Output a freeform thermodynamic database spreadsheet
 -y Set the lower threshold for the concentration (-y1e-45).
 -i Run in interactive mode
 -f:F:F Alter format settings for the numbers in CONC.TXT
   where F's represent FORTRAN format descriptors.
 -SIGD:n Set number of significant digits in the fitdata.txt file
  Time(s) column to n decimal places. (default is 6)
  -ojac[:#] Output jacobians/eigenvectors/values into jacobian000.txt files
  -dynamic[:time] dynamic mode to control Kintecus in feedback
  -obeymaxint Force Kintecus to obey the "Maximum Integration Time" field

 For Thermodynamics mode:

 -cphs Alter heat source to scale with volume changes
        during constant pressure runs.

 FOR BOOTSTRAPPING:

 -rand  Randomize internal random seeds to computer
        timer
 -randi:# set integer random number seed to
          integer number #
 -randr:# set real*8 random number seed to
          real*8 number #.

 -validate:(filename) compare a run against an
             external dataset (PyTorch/Tensorflow)
```

For the integrators 3, 4, and 5 (-INT:3 or –INT:4 or –INT:5), [list] represents a pair of numbers,x,y, delimited by a colon. The first number represents the type of integrator parameter to change, and the second number is the value to set to the described parameter. The table below shows the number corresponding to the type of integrator parameter and the default value. Please remember that integrators 1 and 2 should be sufficient for 99% of the chemical kinetics

problems you might encounter**. Integrator #5 can also speed up simulation runs by 2-5 times (200-500%) for some models and may provide better stability for combustion runs.** Also, the Gear[27] integrator has a scaling problem with constant-pressure adiabatic runs causing some values to be off 10-70%. Using the Gear integrator (-INT:3) with such constant-pressure simulations is NOT recommended.

Integrator #4 is also sensitive to the lower threshold for the concentration (-y switch).

Integrator Parameter No.(X)	Parameter type (Y)	Default Value
2	Minimum value of step size can reach	0.0
4	Maximum number of steps allowed	50,000,000
6	The Maximum order of the method.	Gear-BDF method=5 Adams-Moulton=12
9	Scale of the problem. An approximate average norm value of the Jacobian.	1.0
10	Error norm:0=minimum, 1= absolute error, 2=maximum, 3= scaled Euclidean norm	0
11	The norm computation for parameter 10.	1.0
12	Select the type of sub-integrator	2=Gear method or 1=Adams-Moulton method

Table 6. The list of integration parameters available to GEAR integrator #3 (-INT:3) .

For example, to change the order of the Gear method from 5 to 12 and the scale of the problem from 1.0 to 500 simply type the switch -INT:3:6:12:9:500.0.

Integrator Parameter No.(X)	Parameter type (Y)	Default Value
1	Type of sub-integrator method	22 (can be 21-25, 23 sometimes works)
9	Percent increase in step-size after a successful integrator step	0.15 (15 % increase)
10	Maximum number of iterations allowed inside the integrator	200000

Table 7. The list of integration parameters available to DVODE integrator #4 (-INT:4) .

Example, to change maximum number of iterations allowed inside the integrator from 200000 to 400000, and the percent increase in step-size after a successful integrator from 15% to 40%, simply type/add the switch -INT:4:10:400000:9:0.40 .

Integrator Parameter No.(X)	Parameter type (Y)	Default Value
10	Enforce non-negativity of variables during integration, 2 allows each species constraint	0 or 2
20	Maximum number of iterations allowed inside the integrator	10,000
50	Percent increase in step-size after a successful integrator step	0.15 (15 % increase)
59	Set the absolute tolerance for the integrator	Set to the Accuracy value (located in the parameter worksheet)
60	Set the relative tolerance for ALL species	Maximum(Accuracy*[SPECIES] , 1e-35) If Units=molecules/cc then Maximum(Accuracy*[SPECIES] , 1.0). The 1e-35 and 1.0 values can be changed via the "-y" flag

Table 8. The list of integration parameters available to DASPK integrator #5 (-INT:5) .

For example, to change the maximum number of iterations allowed inside the integrator from 10,000 to 250,000 and the percent increase in step-size after a successful integrator from 15% to 40%, type/add the switch -INT:5:20:250000:50:0.40 . Another example: To force the relative and absolute tolerance of the integrator to 1e-9, you would utilize this integration flag "-INT:5:59:1.0e-9:60:1.0e-9".

3. Advanced Analysis

This section will describe the various numerical techniques provided with Kintecus to significantly enhance one's modeling capabilities. In addition, Kintecus can output different physical properties on the system to help one's analysis.

Numerical Techniques

Sensitivity Analysis

Kintecus can generate normalized sensitivity coefficients at any time or time during a simulation run. What are normalized sensitivity coefficients (NSC), and why should I care? Well, first of all, normalized sensitivity coefficients are the partial derivatives of each species with respect to each reaction constant normalized by multiplying by Rate_Constant/Concentration_of_Species:

$$NSC = \left(\frac{\frac{\partial [Species]}{[Species]}}{\frac{\partial k}{k}} \right)_k = \left(\frac{\partial \ln [Species]}{\partial \ln k} \right)_k \qquad \text{Eqn 37.}$$

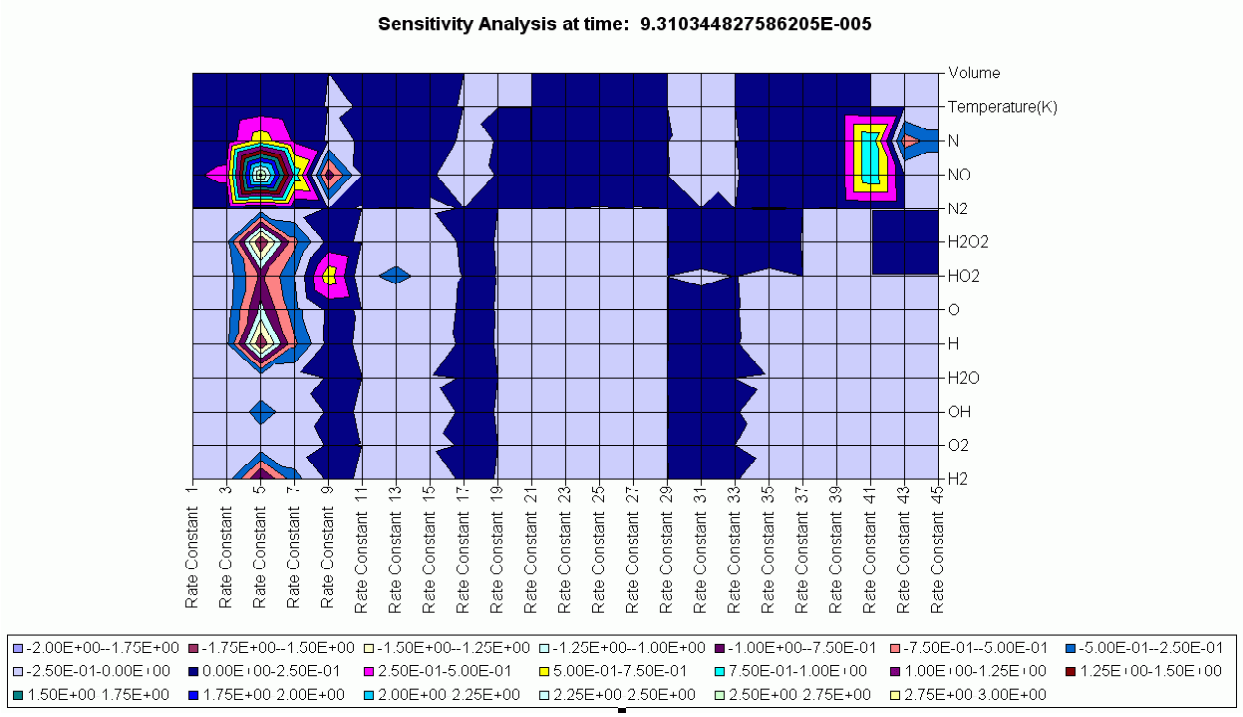
It is a matrix with signed numbers, which indicate the reactions that have the most significant influence on certain species. By examining the matrix and sorting the largest NSCs by reactions for each species, one can see that the large positive NSCs are the major sources, and the large negative NSCs are the major sinks[10]. A reaction with a very small NSC for a species indicates that reaction has almost no influence on the species, no matter the rate constant or the reaction's concentration of reactant species. The method to make Kintecus output the NSC matrix, S, is by using the **-SENSIT:1** switch on the command line. Currently, there is one NSC matrix producing method, and to use it, just enter **-SENSIT:1** on the command line. This will output three NSC matrices at three times:the beginning of the simulation, the middle, and the end. If you wish to produce more S matrices, simply append the number you want at the end of the SENSIT switch. For example, if one wanted 25 S matrices calculated over an evenly spaced time period during a simulation, just place -SENSIT:1:25 on the command line. Kintecus will output 25 files with the names SENSIT01.TXT to SENSIT25.TXT. Please note that Kintecus outputs the transpose of the NSC matrix ($\mathbf{S^T}$).

If you wish for unevenly spaced timed periods to output S matrices, you must use this form of the SENSIT switch: **-SENSIT:1:TIMES,n1,n2,n3.....nn** with **TIMES** in UPPERCASE and commas to delimit the **exact** times you wish to output time periods.

One might think, "Hey, if I just sum up the squares of the NSC's for each reaction, I'll know what reaction to drop because the reactions with very small NSCs should not affect any of the species." This might be true for most kinetic mechanisms, but this is not the case in some cases. NSC only tests for direct routes of influence of species X, it does not directly show strongly interacting reactions. A straightforward method to see which reactions can be "thrown out the window" is a method of principal component analysis used by Turanyi, Vajda and Valko[9] applied to the normalized sensitivity analysis matrix, **S**. The steps described by this paper can easily be done in

MATLAB or Lotus 1-2-3. It involves finding NSC matrices $\mathbf{S_1, S_2, S_3 ... S_n}$, at various times in the simulation, for example, at ten evenly spaced periods (use -SENSIT:1:10 switch). By using a spreadsheet program or MATLAB, you must concatenate all the **S**'s at each calculated time into one big matrix, **BS**. Again, do not forget to transpose each **S** before concatenating all of them into **BS**. Now multiply **BS** by it's transpose, $\mathbf{BS^T * BS = D}$. Determine the eigenvalues, e, and eigenvectors, v, of **D**. Now, calculate the lower threshold for the eigenvalues by multiplying the number of NSC matrices calculated by the number of species (which are NOT constants in your simulation) by 1 x 10^(-4), call this **L**. Note all the eigenvalues that are equal or under **L**, call these **LL**. Now the last step, for all the elements of each eigenvector of each respective **LL** that are greater than 0.2 mark those. Those elements of the eigenvectors corresponding to reactions that have no overall effect on the kinetics scheme and can be safely "thrown out the window". The author has tried this with the formaldehyde oxidation mechanism and obtained similar results that the paper[9] has computed. The Kintecus software addition named **Atropos** (**http://www.kintecus.com/atropos.htm**) can do all of the above automatically and other advanced chemical mechanism analysis not described here. One might first wish to examine **Atropos** for this and other features related to chemical mechanism elucidation. **Atropos** will also automatically show the reduced model spreadsheet with the unimportant reactions highlighted and commented out. **Atropos** also outputs many other important descriptors about one's chemical kinetic model.

The new Kintecus-Excel V3.8 workbooks contain more recent plot macros that can now plot all of the normalized sensitivity analysis (NSA) matrices for easy viewing. Please be sure to use all uppercase letters for the -SENSIT switch or else no NSA plots will be generated in the Kintecus-Excel workbooks. An example of the NSA plot is shown below from the "Combustion_H2_O2_sensit.xls" Excel workbook.



A new feature in Kintecus V3.96 and up is the ability to specify a table of times for which the NSA matrices will be created in a file instead of trying to "shove" them all on a command line. For example, if an Excel worksheet (or a text file) was named "O_sens.txt" (or a text file named sens.txt) was created and had the following contents:

```
#
# The prefix "O_" in front of the worksheet name O_sens.txt forces this worksheet to be
# written out as a text file named sens.txt. This is read in by the Kintecus switch
# "-SENSIT:1:@sens.txt" located on the CONTROL worksheet.
# Since this is an excel worksheet, we can use formulas and anything else on this worksheet
# as eventually everything will be converted to text once you click RUN
#
TIMES
2.9999999E-06
1.3000000E-05
2.3000000E-05
3.3000000E-05
4.3000000E-05
5.3000000E-05
6.3000000E-05
7.3000000E-05
8.3000000E-05
9.3000000E-05
```

And adding this switch on the Kintecus command line: "-SENSIT:1:@sens.txt" (note the textfile/worksheet with a prefixed "@"), will cause Kintecus to read the times that will create NSA matrices dictated by the values specified after the **TIMES** keyword. This allows very detailed NSA matrices creation around important/interesting concentration/temperature/enthalpy spikes in one's model.

Tricks and Tips for NSC Matrix File Creation

1) The creation of 100 NSC matrix files (via the inclusion of the "-SENSIT:1:100" switch on the Kintecus command line), Case #1, **will NOT take 20 times longer** than in the creation of 5 NSC Matrix files (via the "-SENSIT:1:5" switch, Case #2). In both cases, Kintecus has to "march" 3*(number of reactions)*(# of species+temperature+enthalpy) **partial derivatives** in temporal space to compute the last NSC matrix (SENSIT100.TXT for Case #1 and SENSIT005.TXT for Case #2). It is possible that in Case #2 will finish ahead of Case #1 as Kintecus will try to take very large time steps (total simulation time)/5, to get the "marchers" to the end as quickly as possible. Case #1 is forced to take steps no larger than (total simulation time)/100 and will be somewhat slower.

2) It is "safer" to simply create 5 NSC Matrix (Case #2) files than 100 NSC Matrix files (Case #1). **This is wrong.** As mentioned above in point 1, Case #2 can take larger times steps than Case #1. Large time steps can occasionally cause Kintecus to end up with highly wild solutions causing Kintecus to "backtrack" or even crash. In Case #1 above, the time steps are smaller and safer as Kintecus can easily "see" the "terrain" ahead.

Given points 1) and 2) above, the old default action of creating only three NSC Matrix files was changed to **30** NSC matrix files when the "-SENSIT:1" switch was given. You may want to try "-SENSIT:1:90" or "-SENSIT:1:150". The only disadvantage is the creation of many large disk files, but given the size of very cheap hard disks today, this is no longer an issue.

Jacobians

The default integration method used in Kintecus [1] requires the calculation of Jacobians. By default, the Jacobians are calculated by a finite difference method. The earlier versions of Kintecus calculated the Jacobian **analytically**, that is, exactly. It was found that the analytical method was 2-5% slower than the finite difference method for kinetic mechanisms of less than 20,000 reactions, so the finite difference method was selected to be used as the default method for calculating Jacobians. Suppose you happen to experience underflow or overflow errors during the integration process (especially for large stiff systems composed of more than 25,000 reactions), switching to **analytically calculated Jacobians** might alleviate this problem. To switch to the analytically calculated Jacobians, use the -anjac switch on the command line (i.e. > kintecus -anjac). It is important to note that analytically computed Jacobians **are NOT supported** for systems containing Arrhenius expressions, thermodynamics, special/fall-off/[M] reactions or constant pressure settings.

Outputting Jacobians

Since the Jacobians are square matrices of the partial derivatives of d(Overall Species Formation-Destruction Equation) / d(Species/Temperature):

Pope and Maas's ILDM requires a broad range of numerical techniques to get to the final ILDM. In addition, Jacobians must be solved at appropriate time intervals:

$$J = \begin{pmatrix} \frac{\partial c_1}{\partial A_{k_1}} & \frac{\partial c_1}{\partial A_{k_2}} & \cdots & \frac{\partial c_1}{\partial A_{k_{n-1}}} & \frac{\partial c_1}{\partial A_{k_n}} & \frac{\partial c_1}{\partial T} \\ \frac{\partial c_2}{\partial A_{k_1}} & \frac{\partial c_2}{\partial A_{k_2}} & \cdots & \frac{\partial c_2}{\partial A_{k_{n-1}}} & \frac{\partial c_2}{\partial A_{k_n}} & \frac{\partial c_2}{\partial T} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \frac{\partial c_{n-1}}{\partial A_{k_1}} & \frac{\partial c_{n-1}}{\partial A_{k_2}} & \cdots & \frac{\partial c_{n-1}}{\partial A_{k_{n-1}}} & \frac{\partial c_{n-1}}{\partial A_{k_n}} & \frac{\partial c_{n-1}}{\partial T} \\ \frac{\partial c_n}{\partial A_{k_1}} & \frac{\partial c_n}{\partial A_{k_2}} & \cdots & \frac{\partial c_n}{\partial A_{k_{n-1}}} & \frac{\partial c_n}{\partial A_{k_n}} & \frac{\partial c_n}{\partial T} \\ \frac{\partial T}{\partial A_{k_1}} & \frac{\partial T}{\partial A_{k_2}} & \cdots & \frac{\partial T}{\partial A_{k_{n-1}}} & \frac{\partial T}{\partial A_{k_n}} & \frac{\partial T}{\partial T} \end{pmatrix}$$

where A_k is the species, *c* is dc/dt, and *T* is dT/dt if you run Kintecus in thermodynamics mode. If one is running Kintecus *outside* of thermodynamics mode, then the Jacobian looks like this:

$$J = \begin{pmatrix} \frac{\partial c_1}{\partial A_{k_1}} & \frac{\partial c_1}{\partial A_{k_2}} & \frac{\partial c_1}{\partial A_{k_{n-1}}} & \frac{\partial c_1}{\partial A_{k_n}} \\ \frac{\partial c_{n-1}}{\partial A_{k_1}} & \frac{\partial c_{n-1}}{\partial A_{k_2}} & \frac{\partial c_{n-1}}{\partial A_{k_{n-1}}} & \frac{\partial c_{n-1}}{\partial A_{k_n}} \\ \frac{\partial c_n}{\partial A_{k_1}} & \frac{\partial c_n}{\partial A_{k_2}} & \frac{\partial c_n}{\partial A_{k_{n-1}}} & \frac{\partial c_n}{\partial A_{k_n}} \end{pmatrix}$$

Where A_k is the species, *c* is dc/dt. It might be of use to some (such as those interested in finding Intrinsic Low Dimensional Manifolds or ILDMs or for metabolic control analysis) to have Kintecus output these Jacobians (and optional eigenvalues or eigenvectors of the Jacobian) during a run. This is accomplished through the **'-ojac'** switch. It will output the Jacobians at the same interval as the conc.txt file is outputted during a run, and the files will be prefixed with "JACOBIAN" and suffixed with ".TXT" give filenames like JACOBIAN**nnn**.TXT, where **nnn** is a three-digit number. This switch has the following options "-ojac:##" where the number will output various parts in the Jacobian matrices:

2=output title containing time in simulation seconds when Jacobian has been calculated
4=column headings (species names)
8=left title headings (species names)
16=**output eigenvalues** of the Jacobian matrix (into a separate file named jeigenvalues**nnn**.txt)
32=**output eigenvectors** of the Jacobian matrix (into a separate file named jeigenvectors**nnn**.txt)

Add up the numbers above into the "**-ojac"** switch for what you want. i.e., if you wish to output all options above, use "**-ojac:62"** (2+4+8+16+32=62). If one only wishes to have the numbers present in a Jacobian file (no time heading, no title, no left title headings, just all numbers), use a value of 1 on the command line with the -ojac switch (i.e. **-ojac:1**) .

The number of decimals (digits) outputted in the Jacobians and optional eigenvalues/eigenvectors is controlled by the first option in **'-f'** switch (see the explanation of the **'-f'** switch in the **Miscellaneous** section). To add or remove the amount of decimal places in the numbers of the outputted Jacobians and/or the optional eigenvalues/eigenvectors files simply give the '-f' switch on the Kintecus command line.

Also, a new switch named **'-obeymaxint'** will force Kintecus to obey the "Maximum Integration Time(s)" field in the parameter spreadsheet. This allows you to force Kintecus to take many steps and output a lot of Jacobian files at very fine time intervals. Usually, "Maximum Integration Time(s)" is only enforced when you have a temperature program or species concentration perturbation program (using the "Constant file ?" field in the Species Description Spreadsheet) or a volume profile program, but give the **'-obeymaxint'** switch on the Kintecus command line and the time steps will **never** exceed the value in the "Maximum Integration Time(s)" field. One may wish to use this '-obeymaxint' feature to output more plotting points for publications or presentations.

Additional Output

If you supply the –KINSTAT keyword on the Kintecus command line, Kintecus will output a spreadsheet containing some statistics on your kinetic system. An example is shown below in Figure 12.

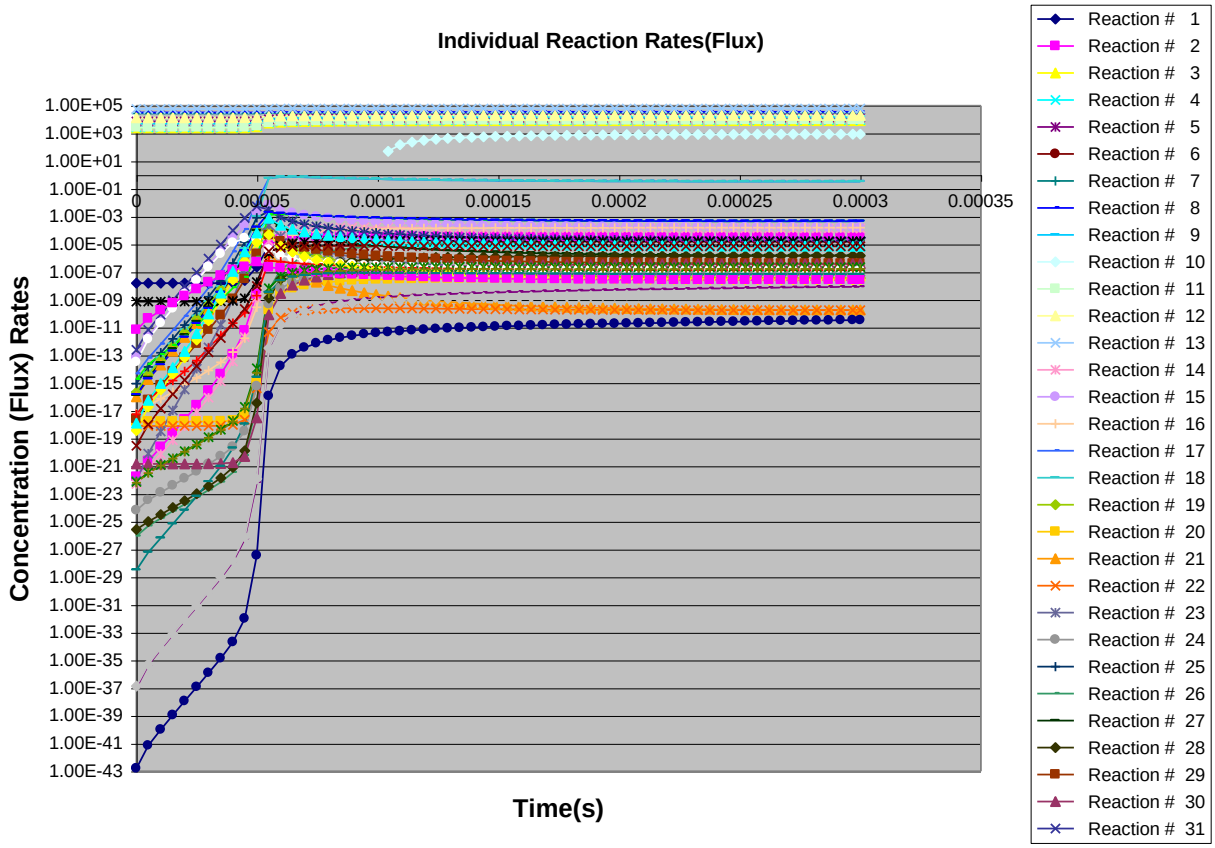
A new feature in Kintecus V2.3 is the ability to output various kinetic and thermodynamic results. Using the "-o" switch, these various system properties can be outputted in four separate files. The "-o" switch has four fields, and **all four** must be included on the command line to output these properties: -o:**1:2:3:4** . The Table below shows the name of file created when a user specifies a "Y" as a field. For example, -o:Y:N:N:Y will create two files: RATESOUT.TXT and the other SYSTEMOUT.TXT.

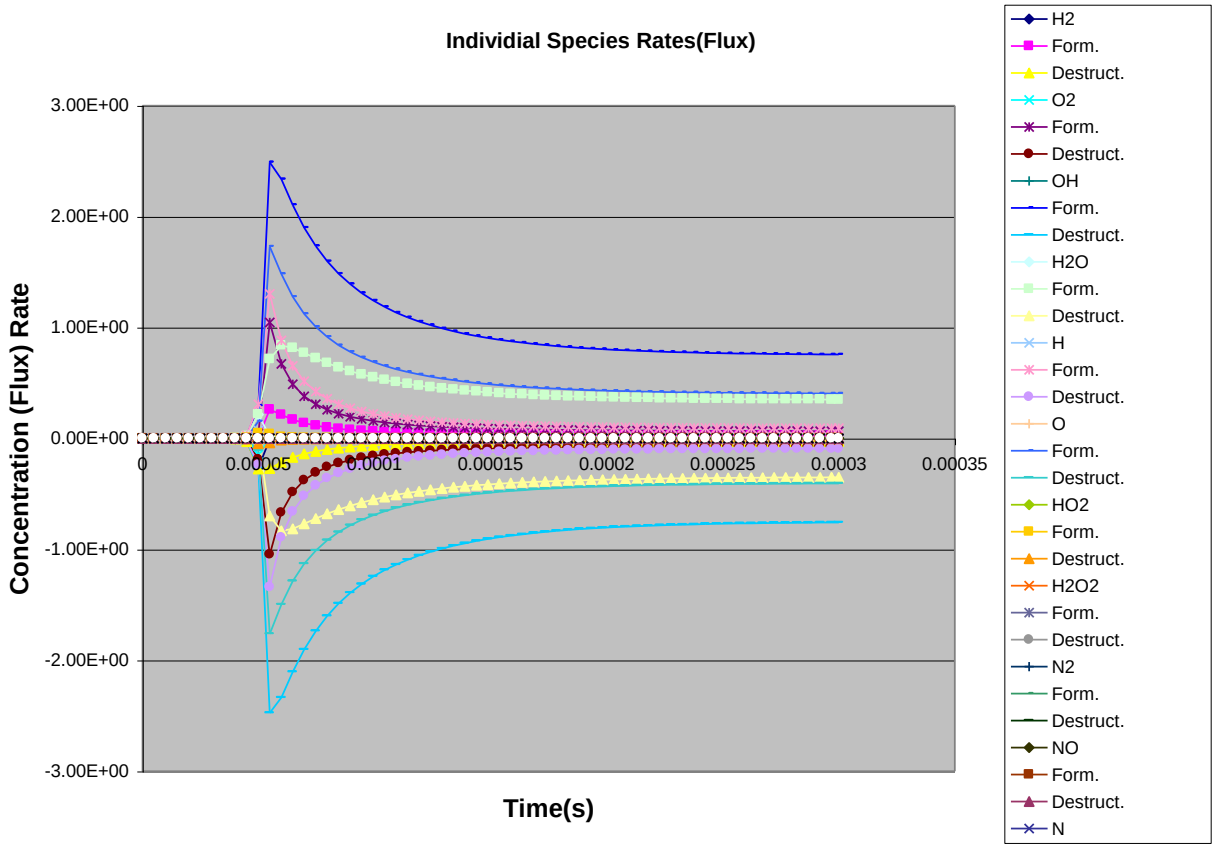
Field	Possible Values	File Created	What the File Contains
1	"Y" or "N"	RATESOUT.TXT	Each Reaction Rate: d[reaction]/dt ***for each reaction*** ! (can be a lot of data)
2	"Y" or "N"	SPECRATE.TXT	Overall Species, Formation and Destruction Rates: d[species]/dt
3	"Y" or "N"	THERMOUT.TXT	Overall System Enthalpy, Entropy, Heat Capacity, Gas Molar Volume, Gas Density
4	"Y" or "N"	SYSTEMOUT.TXT	Enthalpies, Entropies, Gibbs Energy, K_p, K_c, k_f, k_b for ***each reaction!*** (can be a lot of data)

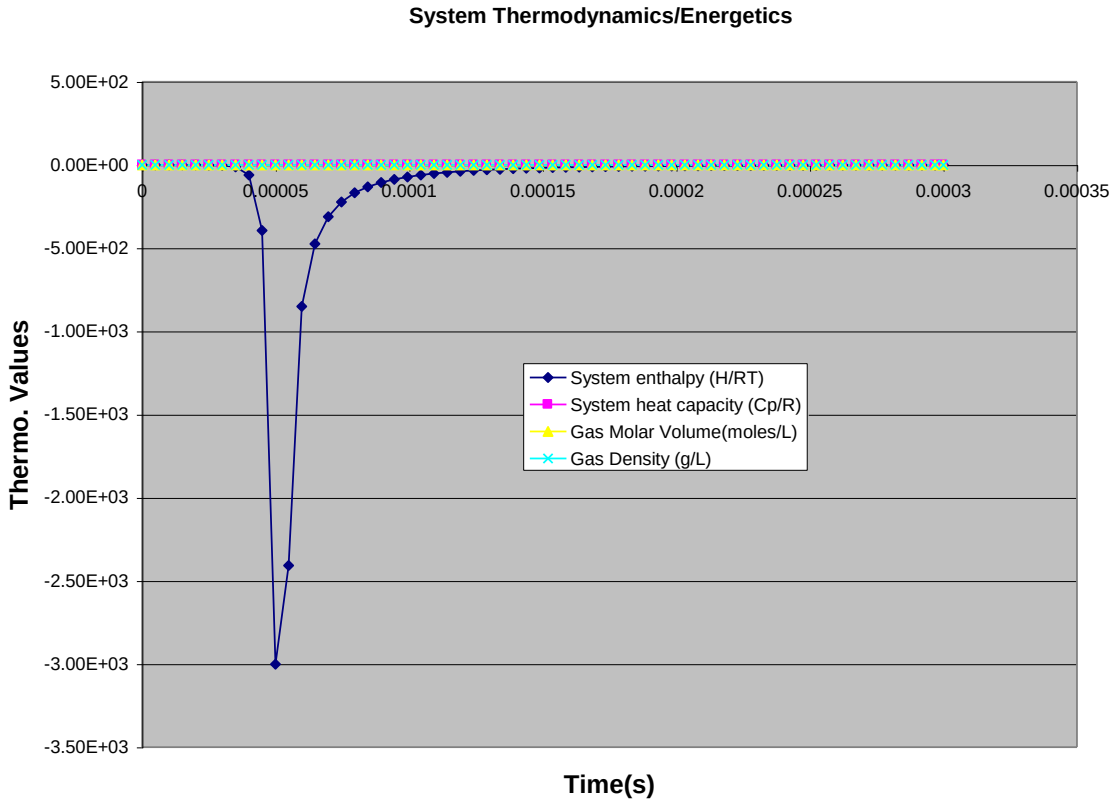
The frequency of the data stored in each of the above four files is directly related to the frequency at which the species/temperature data is stored in the concentration file: CONC.TXT . To refresh your memory, to increase the number of points in any of the above files, you can decrease the Maximum Integration Time in the Parameter Description Spreadsheet and force Kintecus to obey the Maximum Integration Time by using the '-obeymaxint' switch on the Kintecus command line. This can be a lot of data if you have many reactions and are trying to output a RATESOUT.TXT or a SYSTEMOUT.TXT file. Conversely, to decrease the number of points in any of the above files, you can increase the Maximum Integration Time in the Parameter Description Spreadsheet.

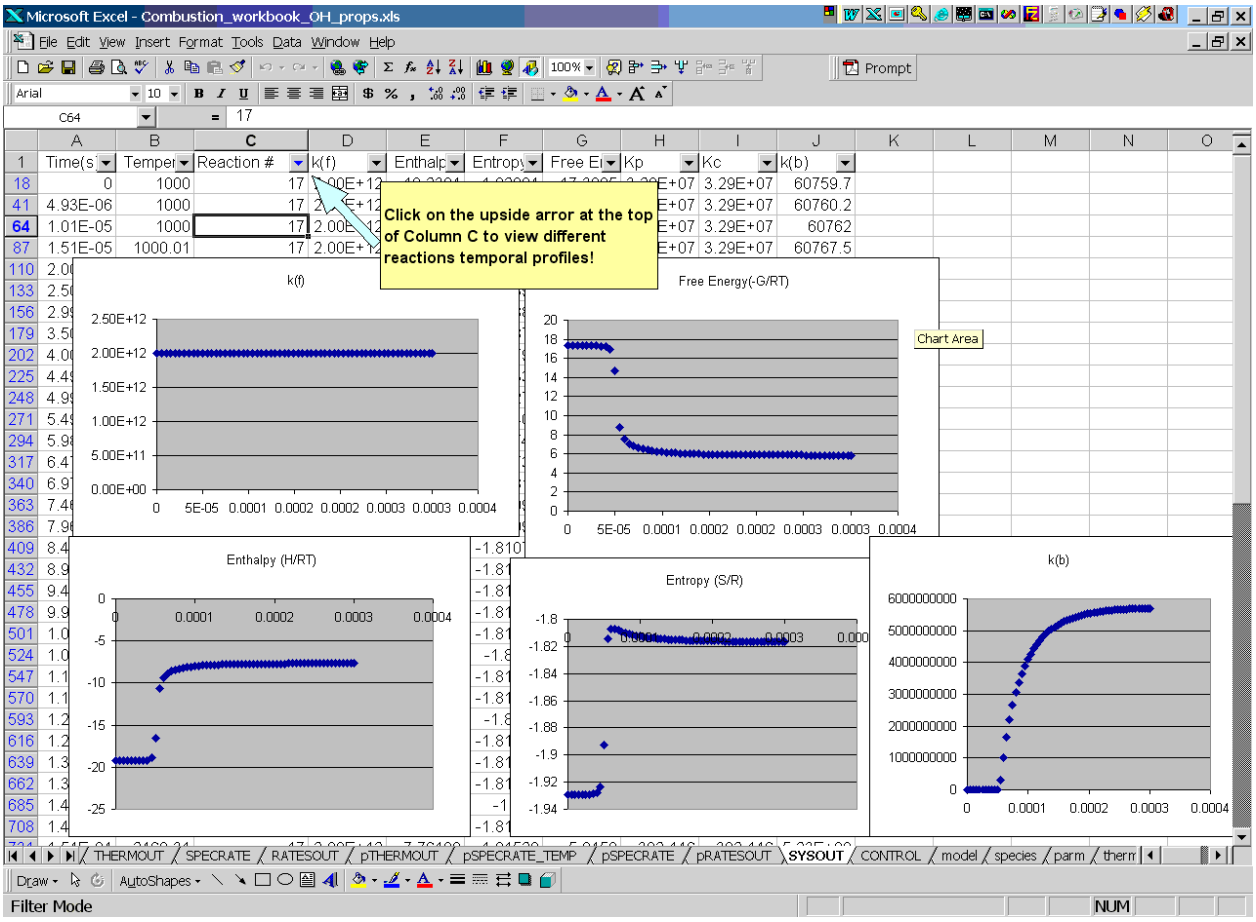
There are sample RATESOUT.TXT, SPECRATE.TXT, THERMOUT.TXT and SYSTEMOUT.TXT files created by specifying the additional Kintecus command line option
"–o:Y:Y:Y:Y" for the adiabatic, constant pressure O_2 combustion model OH2.BAT .

A new feature in the Kintecus V3.7 Excel worksheets and above is that the Excel macros will recognize the "–o" switch and automatically **look for and plot ALL FOUR output files**! The below four samples are from adding the "-o:y:y:y:y" switch to the "Combustion_OH.xls" Kintecus-Excel file command line cell and click the "RUN" button.


Individual Reaction Rates(Flux)
Concentration (Flux) Rates
1.00E+05
1.00E+03
1.00E+01
1.00E-01
1.00E-03
1.00E-05
1.00E-07
1.00E-09
1.00E-11
1.00E-13
1.00E-15
1.00E-17
1.00E-19
1.00E-21
1.00E-23
1.00E-25
1.00E-27
1.00E-29
1.00E-31
1.00E-33
1.00E-35
1.00E-37
1.00E-39
1.00E-41
1.00E-43
0
0.00005
0.0001
0.00015
0.0002
0.00025
0.0003
0.00035
Time(s)
Reaction # 1
Reaction # 2
Reaction # 3
Reaction # 4
Reaction # 5
Reaction # 6
Reaction # 7
Reaction # 8
Reaction # 9
Reaction # 10
Reaction # 11
Reaction # 12
Reaction # 13
Reaction # 14
Reaction # 15
Reaction # 16
Reaction # 17
Reaction # 18
Reaction # 19
Reaction # 20
Reaction # 21
Reaction # 22
Reaction # 23
Reaction # 24
Reaction # 25
Reaction # 26
Reaction # 27
Reaction # 28
Reaction # 29
Reaction # 30
Reaction # 31


Individial Species Rates(Flux)
Concentration (Flux) Rate
3.00E+00
2.00E+00
1.00E+00
0.00E+00
-1.00E+00
-2.00E+00
-3.00E+00
0
0.00005
0.0001
0.00015
0.0002
0.00025
0.0003
0.00035
Time(s)
H2
Form.
Destruct.
O2
Form.
Destruct.
OH
Form.
Destruct.
H2O
Form.
Destruct.
H
Form.
Destruct.
O
Form.
Destruct.
HO2
Form.
Destruct.
H2O2
Form.
Destruct.
N2
Form.
Destruct.
NO
Form.
Destruct.
N


System Thermodynamics/Energetics
5.00E+02
0.00E+00
-5.00E+02
-1.00E+03
-1.50E+03
-2.00E+03
-2.50E+03
-3.00E+03
-3.50E+03
0
0.00005
0.0001
0.00015
0.0002
0.00025
0.0003
0.00035
Thermo. Values
Time(s)
System enthalpy (H/RT)
System heat capacity (Cp/R)
Gas Molar Volume(moles/L)
Gas Density (g/L)


Microsoft Excel - Combustion_workbook_OH_props.xls
Click on the upside arror at the top of Column C to view different reactions temporal profiles!
k(f)
Free Energy(-G/RT)
Chart Area
Enthalpy (H/RT)
Entropy (S/R)
k(b)
THERMOUT
SPECRATE
RATESOUT
pTHERMOUT
pSPECRATE_TEMP
pSPECRATE
pRATESOUT
SYSOUT
CONTROL
model
species
parm
Filter Mode
NUM

If you supply the –SEEMW keyword on the Kintecus command line, Kintecus will output a spreadsheet named MW.TXT containing the molecular weight of each species in your Species Description Spreadsheet.

Species	Sources	Sinks	Total Terms	% Total Terms
NO2	18	15	33	11.4
NO	4	18	22	7.6
O	1	7	8	2.8
O2	8	14	22	7.6
O3	1	6	7	2.4
NO3	7	3	10	3.5
N2O5	1	2	3	1
H2O	4	0	4	1.4
HNO3	2	0	2	0.7
HNO2	3	1	4	1.4
OH	9	9	18	6.2
CO	2	1	3	1
CO2	2	0	2	0.7
HO2	9	3	12	4.2
H2O2	1	0	1	0.3
C3H6	0	8	8	2.8
CH3CH2	1	1	2	0.7
CHO	8	2	10	3.5
CH3	3	1	4	1.4
CH3CO	5	1	6	2.1
C2H4O2	2	3	5	1.7
HCHO	10	4	14	4.8
CH3CHO	9	4	13	4.5
CH2O2	1	3	4	1.4
CH3O2	1	2	3	1
CH3O	4	4	8	2.8
CH3NO3	1	0	1	0.3
CH3CH2O2	1	2	3	1
CH3CH2O	3	4	7	2.4
CH3CH2NO3	1	0	1	0.3
CH3C(O2)HCH2(	1	2	3	1
CH3CH2CHO	1	0	1	0.3
CH3C(O)HCH2O	1	1	2	0.7
HOCH2O2	1	2	3	1
HOCH2O	1	1	2	0.7
CH3C(OH)HCH2	1	2	3	1
(CH3)2CO	1	0	1	0.3
CH3C(OH)HCH2	1	1	2	0.7
CH3C(OH)HO2	1	2	3	1
CH3C(OH)HO	1	2	3	1
CH3COOH	3	0	3	1
CH2CHCH2	1	0	1	0.3
CH3(CO)O2	1	2	3	1
CH3(CO)O	3	4	7	2.4
CH3(CO)O2NO2	1	2	3	1
CH3O2NO2	1	2	3	1
CH3CH2O2NO2	1	2	3	1
H	1	0	1	0.3
CH3OH	1	0	1	0.3
CH3CH2OH	1	0	1	0.3
Average:	Sources	Sinks	Terms	
	2.9	2.9	5.8	

Figure 12

Dynamic Mode

Kintecus V3.5 has a new mode that allows one to pause Kintecus, examine the current concentrations, temperature, rates, and system properties, alter those, and continue. This will enable one to control Kintecus dynamically in a feedback manner. Feedback control can be a very complicated and broad area beyond the scope of this document. Please consult an appropriate textbook on this subject. The dynamic mode in Kintecus is invoked by including the
"**-dynamic[:wait time]**" switch on the command line. Currently, there is only one method for interprocedural communication with Kintecus, and it involves text files. A flow diagram in Figure 12 is shown in the order in which one can write an external program (in Excel VBA code, MATLAB, Python, etc.) to control Kintecus:

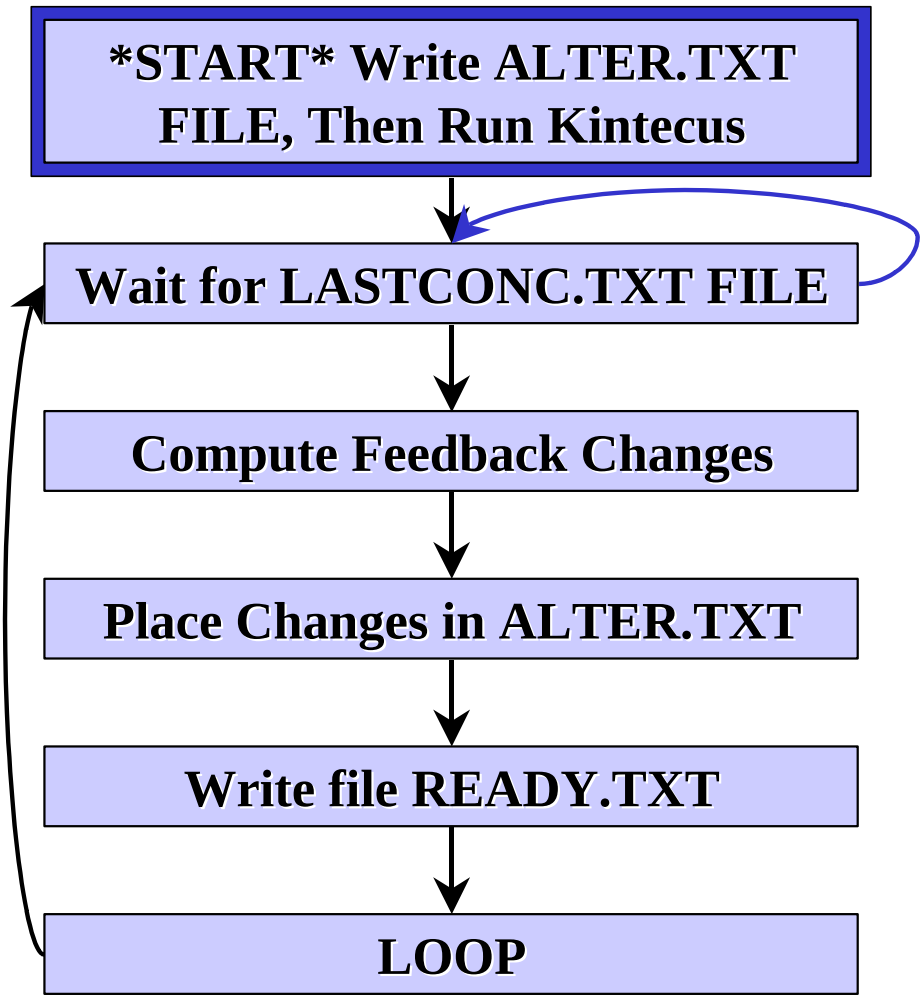


Figure 13. Asynchronous interprocedure communication flow control using three text files that Kintecus requires for dynamic mode. Socket asynchronous interprocedure communication not available in this version.

Three text files must be processed for a full feedback control of Kintecus. The first and only step executed once is shown in Figure 13, "***START*, Write ALTER.TXT file, Then Run Kintecus**" is only executed once. This starting file is only used to state to Kintecus what delta-time (in seconds) to output all the Kintecus concentrations, temperature, and properties, then pause. The ALTER.TXT file (required in steps 1 and 4 in Figure 12) is a user-provided text file containing four columns of data (see Table 9 below for all possible values and Figure 14 down as an example ALTER.TXT file) with an optional comment column 5. The first column contains a keyword representing one of three types of changes: "**set**," "**delta,**" and "**factor**." The "**set**" keyword makes equal the

"Property" (Column B in ALTER.TXT) of Species (Column C in ALTER.TXT) to the value represented in Column D. The "**delta**" keyword adds or subtracts to the "Property" (Column B in ALTER.TXT) of Species (Column C in ALTER.TXT) by the value represented in Column D. The "**factor**" keyword multiplies to the "Property" (Column B in ALTER.TXT) of the Species (Column C in ALTER.TXT) by the value represented in Column D. To set the Time required for the next Kintecus pause, you must place the Property of "Time" in the "Property to Change" column. The Species Name" column is ignored when "Time" is present in "Property to Change" column (See Figure 14 below).

#	DYNAMIC Command Description Spreadsheet			
# Change type # (set/delta/factor)	**Property to Change (conc/res/extern/exttemp/TIME)**	**Species Name or exttemp**	**Value**	**Optional Comments**
delta	Time	like whatever	1.00E-05	
factor	conc	H2	1.2	
factor	conc	Temperature(K)	0.98	
factor	conc	O2	1.06	
delta	conc	H2	5.00E-07	
# do not remove this END (you can move it down)				
END				

Figure 14. A sample ALTER.TXT file. This one is from the "Combustion_OH_DYNAMIC.xls" Excel workbook under the "dynamic" worksheet tab. The Macro in "Combustion_OH_DYNAMIC.xls" writes the "dynamic" worksheet as a text file named, ALTER.TXT for Kintecus to read.

Column Number and Type	Keywords or Setting
1. Change Type	SET, DELTA or FACTOR
2. Property to Change	**Time** = next relative time (in sec) for next Kintecus pause. **CONC** = concentrations or temperature of Species Name (use Temperature(K) for internal temperature) **RES** = residence Time (s) for Species Name **EXTERN** = External Concentration for Species Name **EXTTEMP** = set the external temperature of the system
3. Species Name	Name of the species to alter its property, to alter external temperature, you must also provide the EXTTEMP keyword here too.
4. Value	A valid number
5. Comment	An optional user comment

Table 9 . Possible values and settings for the columns in ALTER.TXT file.

The LASTCONC.TXT is a text file written by Kintecus containing two columns. Your external program should loop and monitor for the existence of this file (Step 2, "**WAIT FOR LASTCONC.TXT** File" in Figure 12) before calculating new values to be placed in ALTER.TXT (Step 3, "**Compute Feedback Changes**" and Step 4, "**Place changes in ALTER.TXT**" in Figure 12). The first column in the LASTCONC.TXT text file will contain the Species Name or Temperature, followed by its value. A comma delimits the two columns, ",". The order of the species names and concentrations will not change during runs, BUT if a species is made into a constant or Constant File, the order will change.

The READY.TXT file is an empty user-written file (Step 5, "**Write file READY.TXT**" in Figure 12.) signifying to Kintecus that the user (or an external program) has read the LASTCONC.TXT file and written an ALTER.TXT file. Once Kintecus "sees" READY.TXT, it will read in and apply all the changes in the ALTER.TXT file, delete LASTCONC.TXT and the READY.TXT file and then continue. Your external program then should loop to Step 2 in Figure 12.

There is a small "waiting" period in which Kintecus checks to see if the READY.TXT is written. Kintecus is "pushed" into the background and consumes zero CPU cycles during this waiting period. The default waiting period is 200 milliseconds. One can change this waiting period by specifying (in milliseconds where 1,000 ms = 1 second) after the -dynamic switch. To specify a 2-second waiting delay, use the switch '-dynamic:2000'. A new

feature in Kintecus V3.7 and up is that specifying a negative time will signal to Kintecus NOT TO WAIT for an update of the Dynamic Spreadsheet, but continue running with the current feedback settings.

Sample Excel Feedback Workbook

A straightforward example is provided by using VBA scripts to control Kintecus in dynamic mode as Excel Workbook, "**Combustion_H2_Dynamic.xls**". Most of the VBA code in the Excel spreadsheet demonstrating the Kintecus dynamic mode is simple overhead, and the actual feedback loop is around lines 1413-1420 in the Excel Macro: Module1. Again, any programming language that can output files can be used to control Kintecus, though, be warned, be sure to flush all read-write buffers before your code reads or writes the dynamic files: LASTCONC.TXT, ALTER.TXT, READY.TXT. The "dynamic" worksheet is written as an ALTER.TXT file with automatic updates of two graphs provided in the "dynamic_plot" worksheet. Keep in mind, that you can add more plots in the "dynamic_plot_ worksheet to see Excel dynamically update graphs as Kintecus runs. Don't forget to minimize Kintecus to see the plots updated in real-time.

Miscellaneous

A smaller version of Kintecus is provided, and it is named **Kintecus_small**. The smaller version requires **much less memory** than the regular version. If one wishes to include Kintecus in a mass/fluid flow 1D/2D/3D-grid calculations, the smaller version is provided. However, the Kintecus_small version can only handle about 800 reactions because of the memory constraints.

An interactive mode has been implemented for users who wish to create a separate "control" program or graphical interface that runs Kintecus remotely. The interactive mode is turned on by including the **"-i**" or **"-I**" switch on the command line. Once this switch is specified, Kintecus will output various small files during its execution. The table below shows all the files outputted during the Kintecus run in an interactive mode:

File	When It Appears	What It Contains
KRUN.TMP	Kintecus starts up and is running. Kintecus delete this file once the program is finished running through Successful or Fatal completion.	Usually nothing
KDONE.OUT	Once Kintecus is finished.	Successful or Fatal Error
KERR.OUT	Kintecus has experienced a FATAL error and has halted	Fatal Error #. View the output to see a more detailed description.
KWARN.OUT	Kintecus has come across one or more warnings.	Warning Error #'s, could be more than one. View the output to see a more detailed description.

Table 10

It is very important to note that if Kintecus experiences an error, it cannot trap, such as an Overflow error or Domain error, the files KDONE.OUT or KERR.OUT may never appear. The user is directed to look at the Visual Basic scripts in the Kintecus_workbooks.xls files for examples of monitoring these error exceptions. A new additional file is written in Kintecus V2.8. The file's name is always view.txt, and it will contain everything displayed on the screen plus some additional output redirected into this file. It would be best to make sure no other application has the filename "view.txt," opened in the same directory as Kintecus is running while using the interactive switch.

The '-x' Switch

One can now output concentrations in mole fractions by including the "**-x**" switch on the command line.

The '-obeymaxint' Switch

There is a new switch in Kintecus V3.2 named '-obeymaxint.' This new switch will force Kintecus to obey the "Maximum Integration Time(s)" field in the parameter spreadsheet. This allows you to force Kintecus to take many steps and output a lot of Concentration or Jacobian or Eigenvector/Eigenvalue files at very fine time intervals (which can lead to large files and longer execution times). In earlier versions of Kintecus, the "Maximum Integration Time(s)" is only enforced when you have a temperature program or species concentration perturbation program (using the "Constant File ?" field in the Species Description Spreadsheet) or a volume profile program.

The '-f:F:F' Switch

A switch has been provided to add or remove the number of decimal places for the "Time(s)" column and concentrations/temperature columns in the CONC.TXT output file. The first field in the '-f' switch is also used to add or remove decimal places when outputting Jacobians or eigenvalues/eigenvectors of those Jacobians. The switch and its arguments are "**-f:F:F"**. This switch's "F" fields stand for a FORTRAN Format Descriptor. The **default** FORTRAN Format Descriptor used is "**E14.6:E14.6**" . An example, if you need four more decimals placed for the Time(s) column, you would place the switch **"-f:E18.10:E14.6"**. If you needed five more decimal places for the Time(s) and four more for the concentrations, you would add the switch: "**-f:E19.11:E18.10"** . Other FORTRAN Format Descriptors such as F, I or G can be used, i.e. "**-f:G14.6:G14.6"** . This will display numbers that fit with the field size of 14 with no exponent; numbers that cannot fit in the 14 field size will be displayed with exponents. Consult a FORTRAN manual for a complete listing of Format fields.

The '-validate' Switch

There is a new "validate" feature in Kintecus V2021. This feature will compare a single Kintecus run against an external synthetic/experimental dataset. This feature (invoked by adding the "-validate:<datafile name>:<data comparator>" flag on the command line) will force Kintecus to match precisely all timings and conditions against this externally calculated or measured dataset and produce a comparable output with statistics on that fit. There are five comparators, 1 to 5, as described in the options for "**Fit Switch**" in **Chapter 5, "Fitting/Optimization**." Validation output statistics will always be written to a file named "VALIDOUT.TXT." This validation feature can be primarily utilized for machine learning programs to compare their output against Kintecus' output or for previous Kintecus run verifications.

A typical way to verify an old data file, "old_output.txt" versus the output from a Kintecus, is to use "-validate:old_output.txt:1" using data comparator "1". Sometimes using data comparator "3" may be helpful too. A text file named "VALIDOUT.TXT" will be written at the end of the run. This file will have five lines. The first will have the total sum of the differences for each column of fitted data created with the user's comparator on the "-validate" command line. The second line will contain the sum of the RMS of all the columns of the computed data versus the user-provided data. The third line will contain the RMS of each column of data versus the computed values. The fourth line will have the output for each column calculated by the comparator operator the user provided on the "-validate" command line versus the compute output. The final line will contain "PASS" or "FAIL*" for each column. The "FAIL*" is outputted if the compared data versus the user's stored data is less than 0.01. Again, the compared data is generated using the comparators 1 to 5 as described in the options for "Fit Switch" in Chapter 5 "Fitting/Optimization."

The batch file named "tests_validate.bat" demonstrates extensive use of the "-validate" flag in comparing tested Kintecus results versus new results from newer Kintecus versions to ensure no bugs.

The batch file named "Tensor_trained_test.bat" is utilized in a larger Tensorflow framework in generating ML/DL chemistry models.

4. Examples!

This section contains numerous example models that have been tested against refereed published models obtained through extensive custom modeling, programming, and experimentation. The example models range from the very simple stiff.bat, to the more complex ethanol1.bat. The .bat files contain a one-line Kintecus command with the required switches.

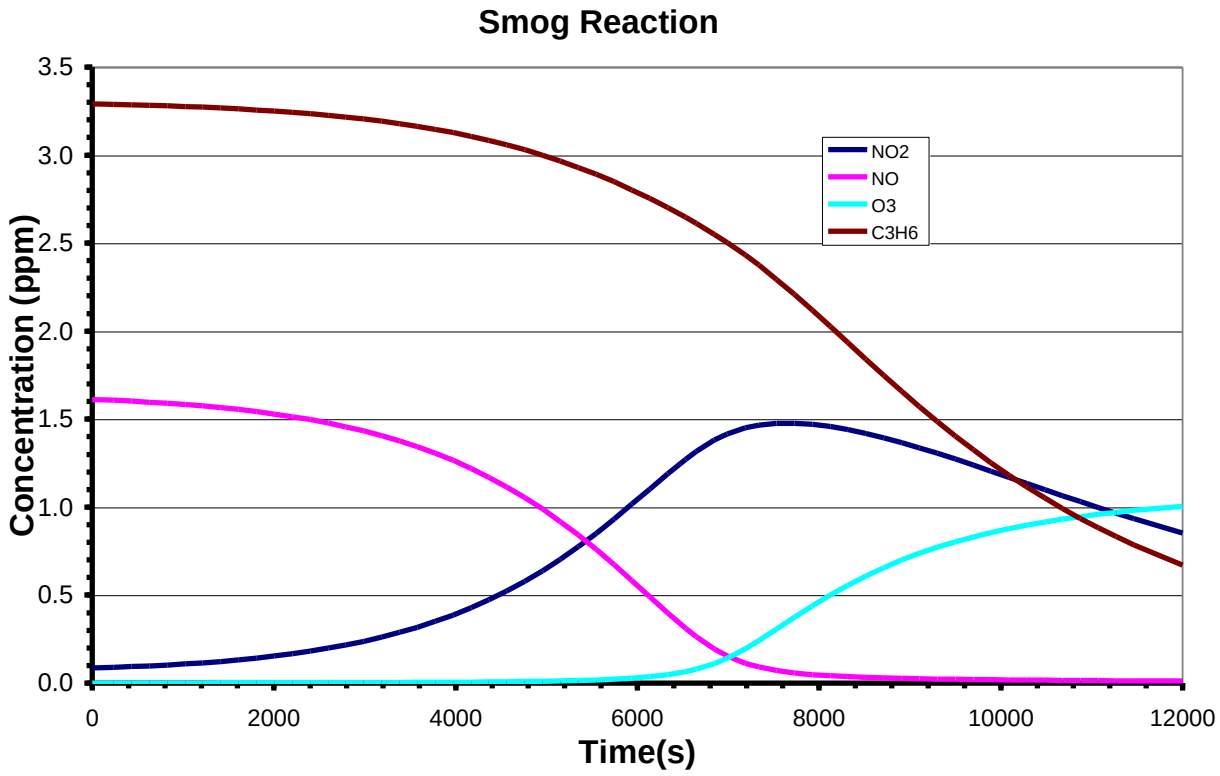
Simple Sample Model Runs

The following sample models below involve non-Arrhenius expressions, no fall-off reactions, no enhanced bodies, no special reactions, no thermodynamics, no perturbations, and no volume changes. Also, some of the following examples have been transferred to Excel workbooks containing specialized Visual Basic code to run the models with a click of the RUN button.

The Smog Reaction Model

The output concentration file, CONCSMOG.TXT, matches Figure 1 in the paper[3].

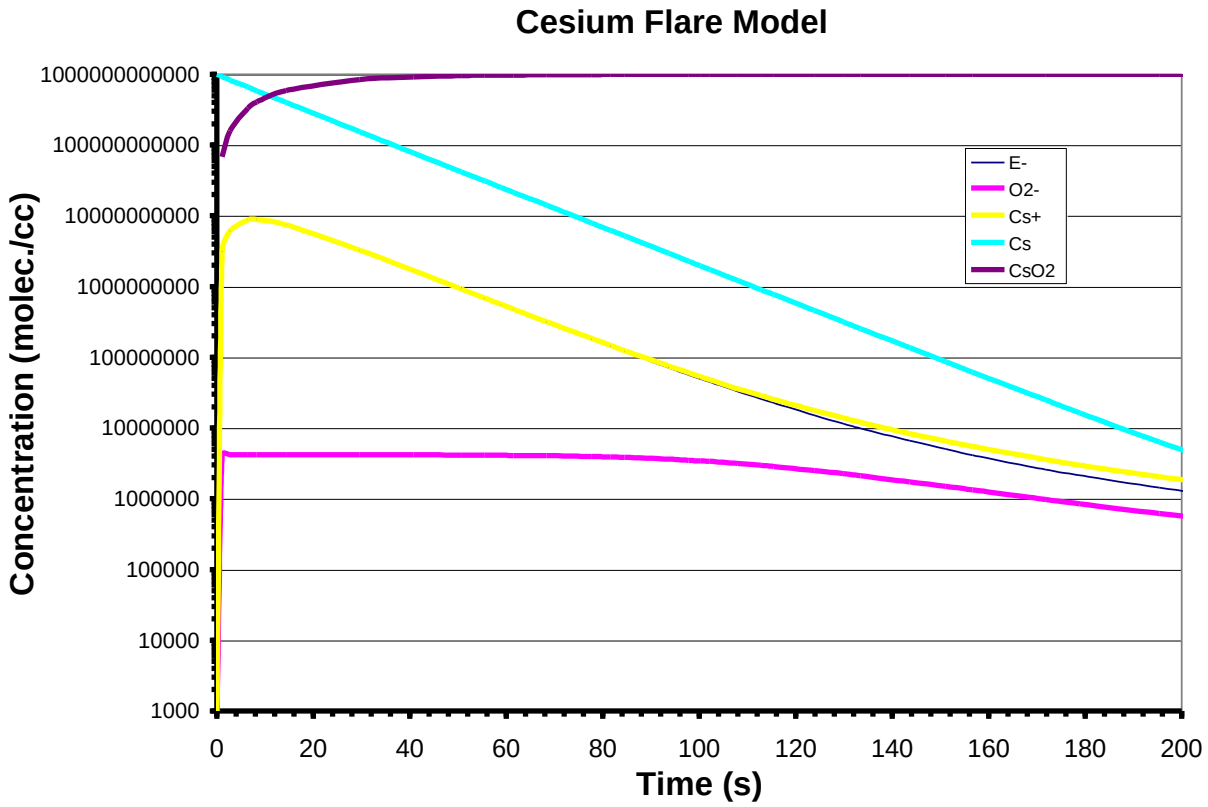
MODSMOG.TX2 - The kinetics reactions
SPECSMOG.TX2 - The species involved
PARMSMOG.TX2 - The parameters used
CONCSMOG.TXT - A simulation run.
SMOG.BAT - A straightforward one-line batch file that will run the above model producing the concentration profile equal to CONCSMOG.TXT.



The Cesium Flare Model

The output concentration file, CONCCES.TXT, matches Table II in the paper[4].

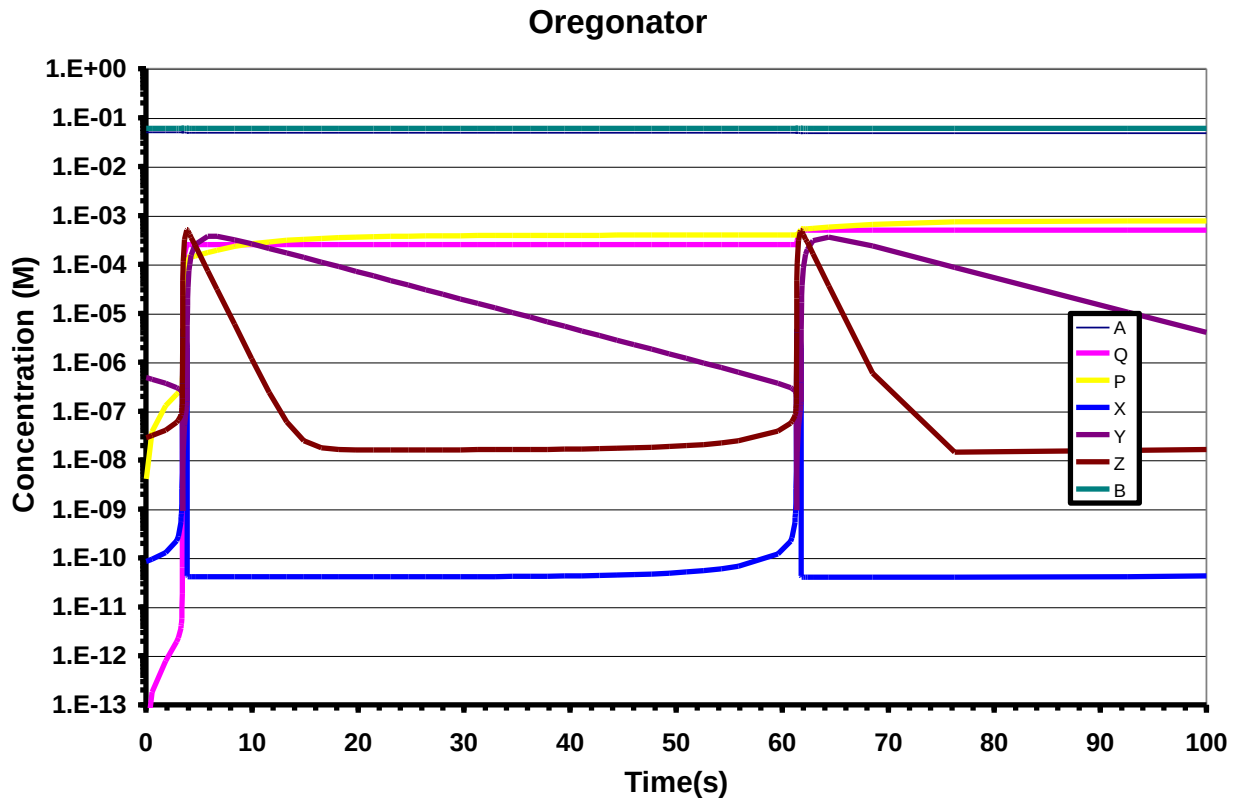
NAMECES.TX2 - A species name file containing common names and their MW.
MODCES.TX2 - The kinetics reactions
SPECCES.TX2 - The species involved
PARMCES.TX2 - The parameters used
CONCCES.TXT - A simulation run.
CES.BAT - A straightforward one-line batch file that will run the above model producing the concentration profile equal to CONCCES.TXT.



The Oscillating Oregonator

The output concentration file, CONCOREG.TXT, matches Figure 1 in the paper[5].

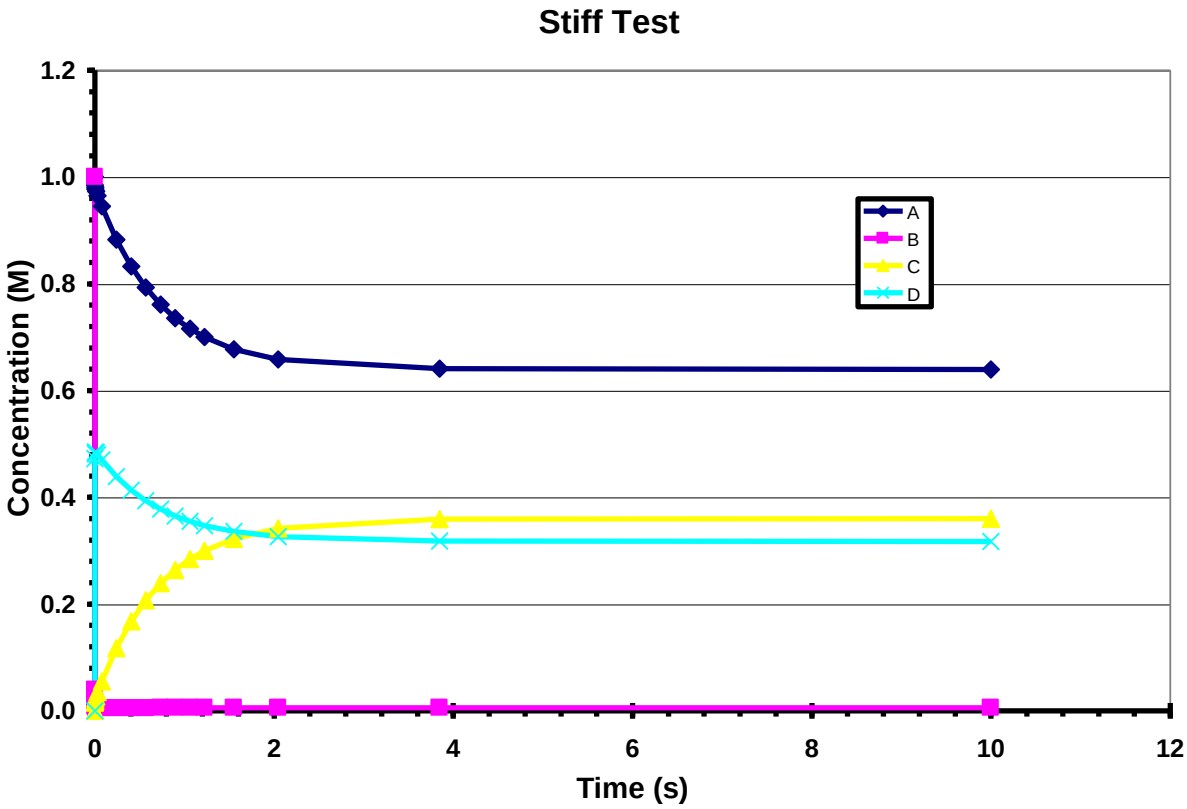
MODOREG.TX2 - The kinetics reactions
SPECOREG.TX2 - The species involved
PARMOREG.TX2 - The parameters used
CONCOREG.TXT - A simulation run.
OREG.BAT - A straightforward one-line batch file that will run the above model producing the concentration profile equal to CONCOREG.TXT.



The Stiff Test

The output concentration file, CONCSTIF.TXT, matches the results on page 89[6].

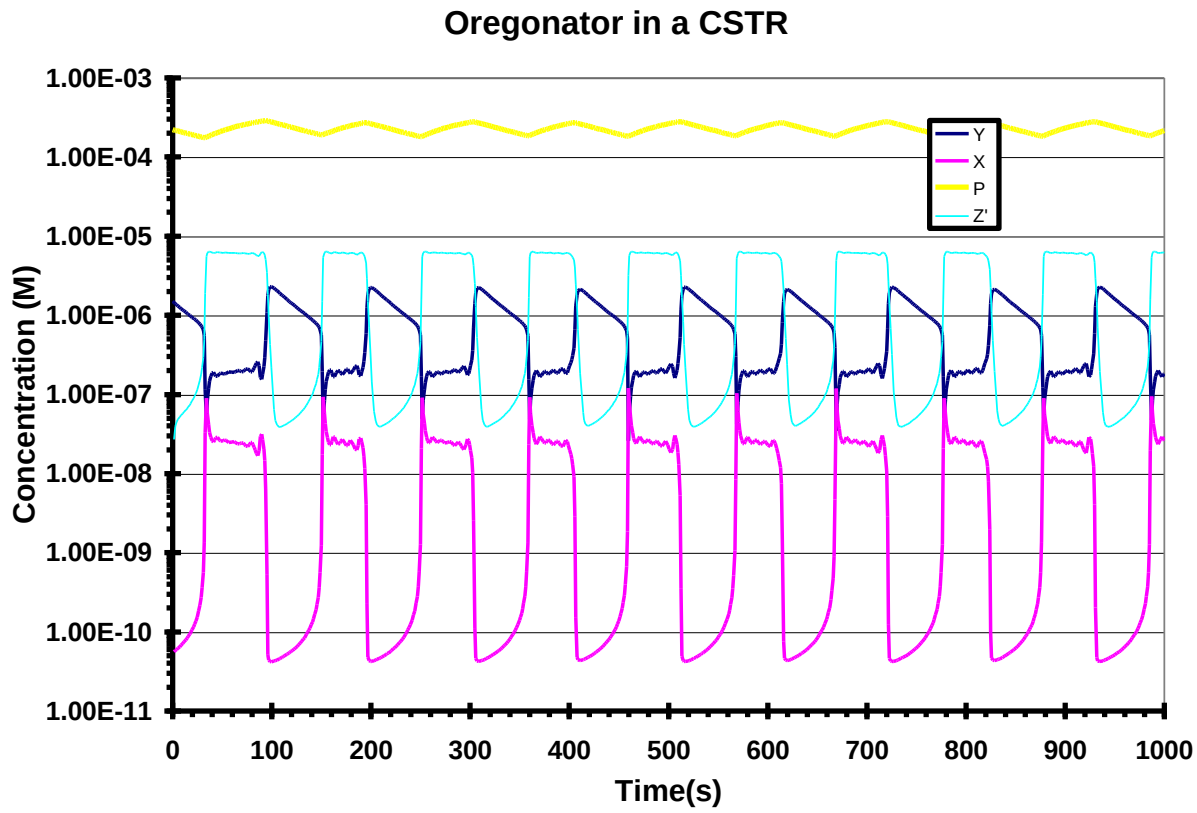
MODSTIF.TX2 - The kinetics reactions
SPECSTIF.TX2 - The species involved
PARMSTIF.TX2 - The parameters used
CONCSTIF.TXT - A simulation run.
STIFF.BAT - A straightforward one-line batch file that will run the above model producing the concentration profile equal to CONCSTIF.TXT.



The Oregonator in a CSTR

The output concentration file, CONCFORG.TXT, matches figures 5 and 6[7]. This model can also be executed by loading the Excel workbook: Oregonator_in_CSTR.xls and then clicking the **RUN** button located on the CONTROL worksheet.

MODFORG.TX2 - The kinetics reactions
SPECFORG.TX2 - The species involved
PARMFORG.TX2 - The parameters used
CONCFORG.TXT - A simulation run.
OREGFLOW.BAT - This is a straightforward one-line batch file that will run the above model producing the concentration profile equal to CONCFORG.TXT.



Advanced Sample Model Runs

The following sample models below now involve any combination of Arrhenius expressions, fall-off reactions, enhanced bodies, special reactions, thermodynamics, perturbations, and volume changes.

Combustion of H_2 and O_2 at constant pressure

The output concentration file, CONCOH2.TXT, matches the results (after converting the concentrations to mole fractions) on page 110 of the Chemkin-II/III manual example [11]. This model can also be executed by loading the Excel workbook: Combustion_Workbook_OH.xls and then clicking the **RUN** button located on the CONTROL worksheet.

MODOH.DAT - The kinetics reactions (Converted from the Chemkin-II/III manual example)
SPECOH.DAT - The species involved
PARMOH2.DAT - The parameters used
THERMOH.DAT – The thermodynamic description spreadsheet
CONCOH2.TXT - A simulation run.

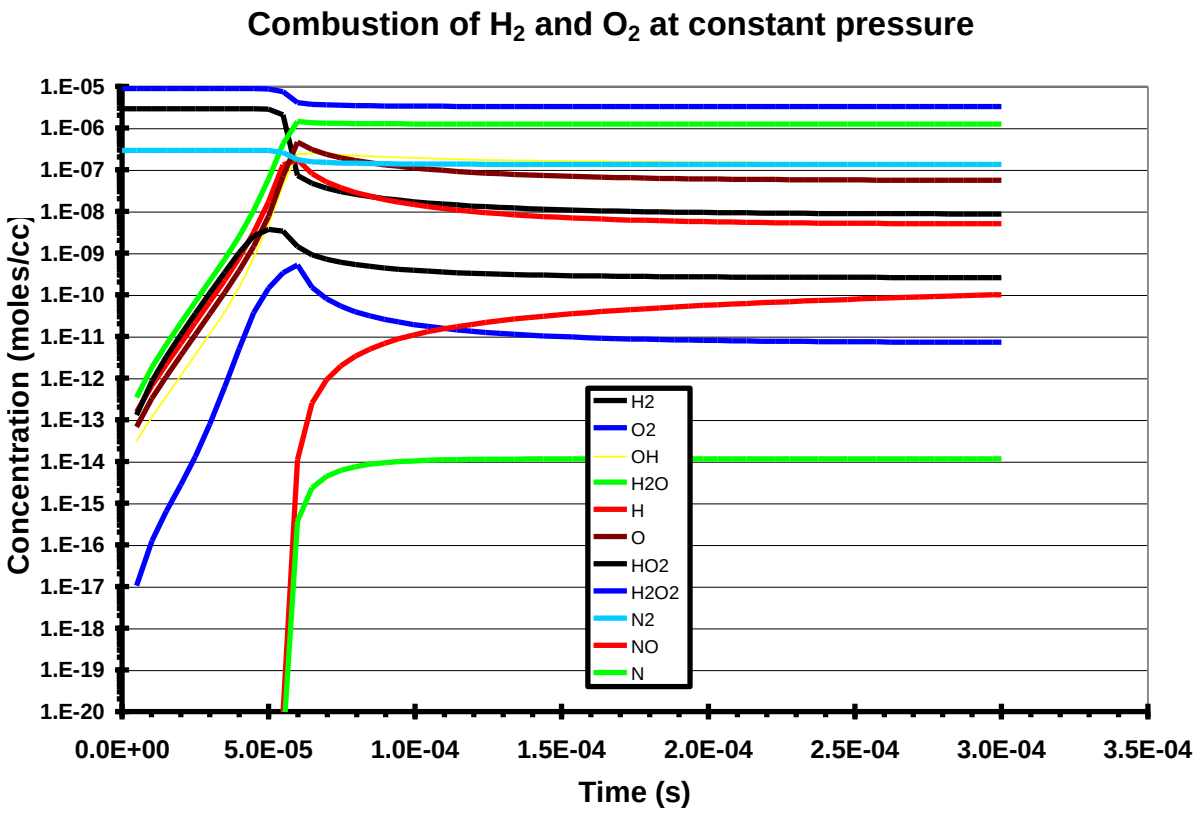
OH2.BAT - A straightforward one-line batch file that will run the above model producing the concentration profile equal to CONCOH2.TXT.

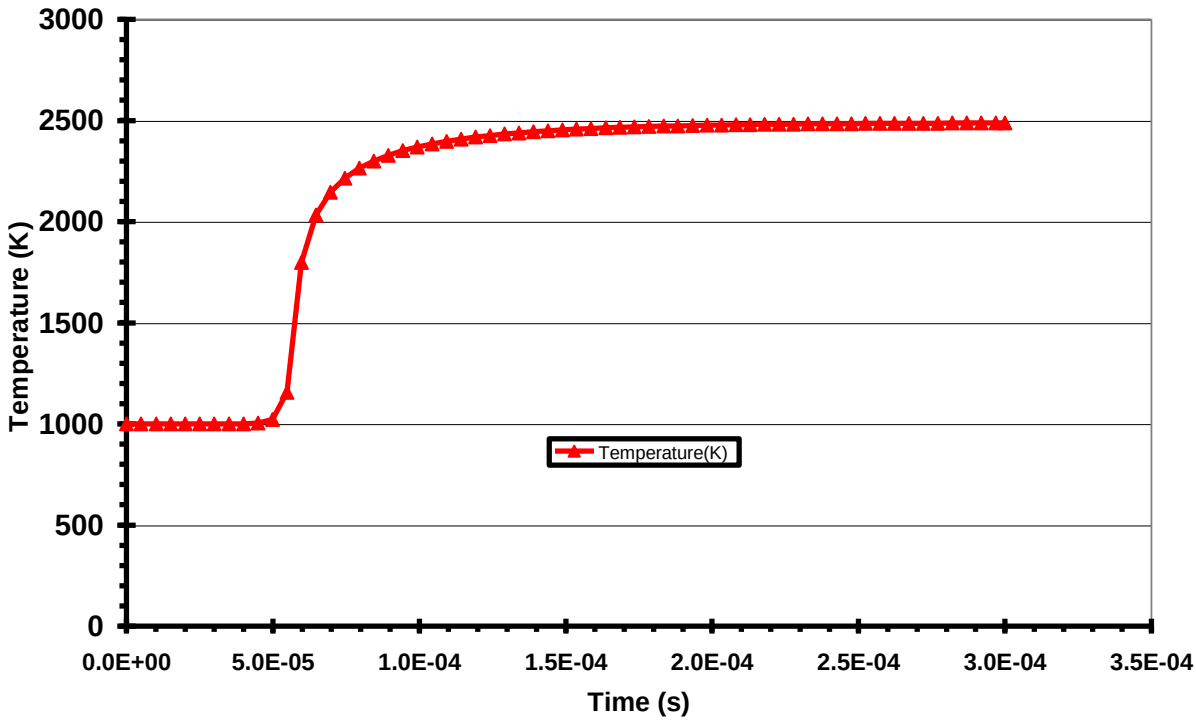
Note: OH.BAT runs the same exact model BUT at constant volume (variable pressure, the default in most models). Compare the two!

In addition, oh2f.bat uses the Chemkin thermodynamic database converted into **FREEFORM**! Examine the THERMFOH.DAT thermodynamic description spreadsheet.

Combustion of H_2 and O_2 at constant pressure
Comparison of results at 3x 10^{-4} seconds

	H_2	O_2	OH	H_2O	H	O
KINTECUS	1.80E-03	6.72E-01	3.02E-02	2.56E-01	1.04E-03	1.15E-02
CHEMKIN-II	1.79E-03	6.72E-01	3.07E-02	2.56E-01	1.03E-03	1.14E-02
Percent Difference	0.6%	0.0%	-1.5%	0.1%	0.9%	0.9%
	HO_2	H_2O_2	N_2	NO	N	Temp.(K)
KINTECUS	5.36E-05	1.50E-06	2.74E-02	2.10E-05	2.41E-09	2.49E+03
CHEMKIN-II	6.00E-05	1.52E-06	2.73E-02	2.17E-05	2.41E-09	2.49E+03
Percent Difference	-10.7%	-1.4%	0.2%	-3.2%	0.1%	0.0%


Combustion of H2 and O2 at constant pressure
Concentration (moles/cc)
1.E-05
1.E-06
1.E-07
1.E-08
1.E-09
1.E-10
1.E-11
1.E-12
1.E-13
1.E-14
1.E-15
1.E-16
1.E-17
1.E-18
1.E-19
1.E-20
0.0E+00
5.0E-05
1.0E-04
1.5E-04
2.0E-04
2.5E-04
3.0E-04
3.5E-04
Time (s)
H2
O2
OH
H2O
H
O
HO2
H2O2
N2
NO
N


Combustion of H2 and O2 at constant pressure
Temperature (K)
3000
2500
2000
1500
1000
500
0
0.0E+00
5.0E-05
1.0E-04
1.5E-04
2.0E-04
2.5E-04
3.0E-04
3.5E-04
Time (s)
Temperature(K)

GRI-Mech-3.0 Sample Runs

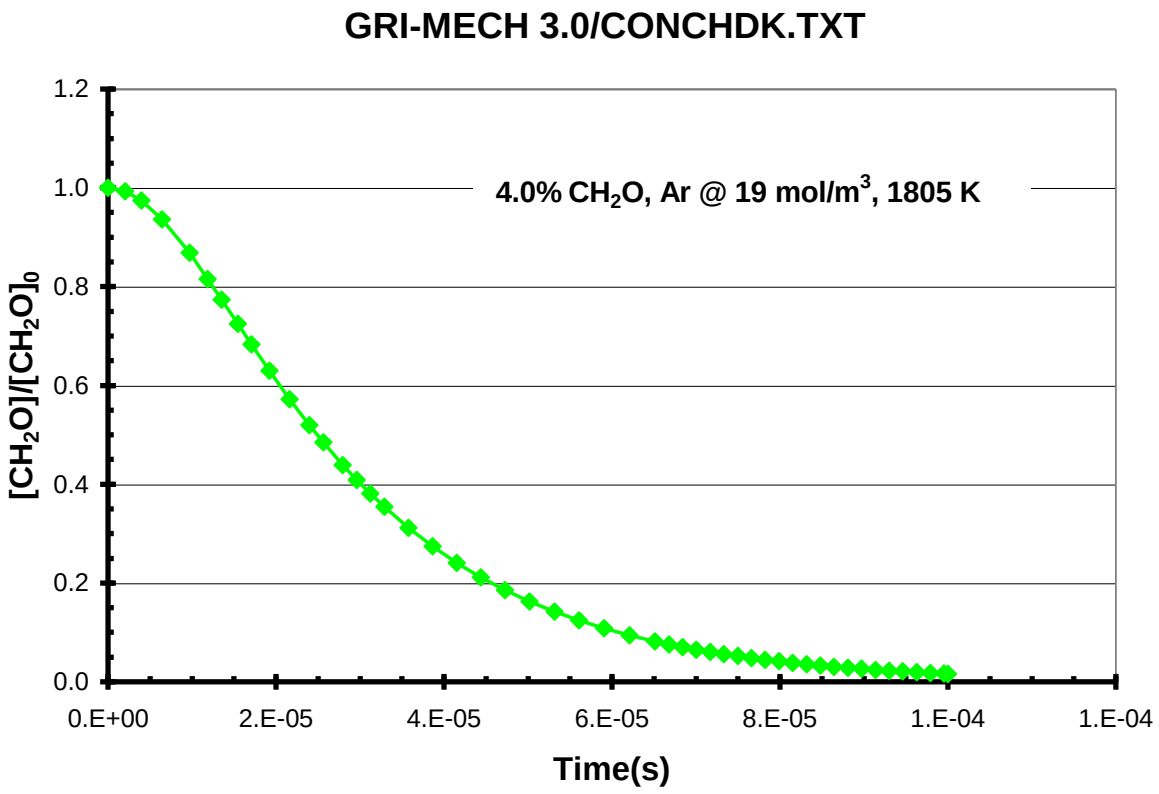
The GRI (Gas Research Institute)-Mech 3.0 mechanism is used by many research groups worldwide for various combustion models. The chemical model MODGRI.DAT is a direct conversion from the Chemkin-II model. No alterations were made to the MODGRI.DAT once the CK2KIN program converted it. You can get more information on this fabulous model at http://www.me.berkeley.edu/gri_mech [19]. There have been many published papers on experiments that have verified their chemical combustion mechanism using GRI-Mech. Examining the home page of GRI-Mech will show many, many references in journals (refereed and non-refereed), conferences, and posters. You may wish to explore the following sample runs using GRI-Mech very closely. These models can also be executed by loading the Excel workbook: GRI_MECH_30.xls and then clicking the **RUN** button located on the CONTROL worksheet.

GRI-MECH RUN 4.0% CH_2O

The output concentration file, CONCHDK.TXT, matches the results by Hidka, et al [12] under the same conditions (4.0% CH_2O in Ar at 19.0 mole/m^3 and T = 1805 K). These models can also be executed by loading the Excel or OpenOffice workbook: GRI_MECH_30.xls and clicking the RUN button on the CONTROL worksheet.

MODGRI.DAT - The kinetics reactions (Converted from the Chemkin-II/III GRI model using the CK2KIN.EXE program)
SPECHDK.DAT - The species involved
PARMHDK.DAT - The parameters used
THERMGRI.DAT – The thermodynamic description spreadsheet
CONCHDK.TXT - A simulation run.

grihdk.BAT – This is a straightforward one-line batch file that will run the above model producing the concentration profile equal to CONCHDK.TXT.

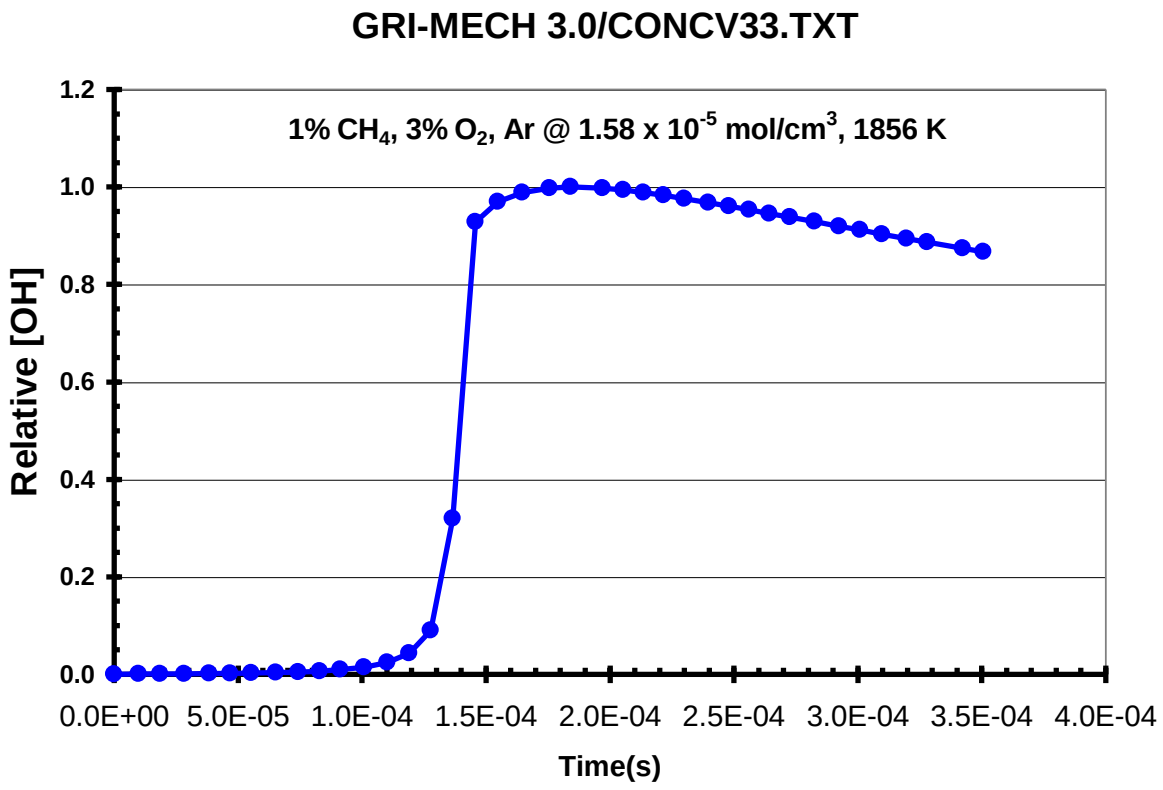


GRI-MECH RUN 1% CH_4 3% O_2

The output concentration file, CONCV33.TXT, matches the results by Yu et al. [13] under the same conditions (1% CH_4, 3% O_2 in Ar at 1.58 x 10^{-5} mole/cm^3 and T = 1856 K). These models can also be executed by loading the Excel or OpenOffice workbook: GRI_MECH_30.xls and clicking the RUN button on the CONTROL worksheet.

MODGRI.DAT - The kinetics reactions (Converted from the Chemkin-II/III GRI model using the CK2KIN.EXE program)
SPECV33.DAT - The species involved
PARMV33.DAT - The parameters used
THERMGRI.DAT – The thermodynamic description spreadsheet
CONCV33.TXT - A simulation run.

griv33.BAT - This is a straightforward one-line batch file that will run the above model producing the concentration profile equal to CONCV33.TXT.

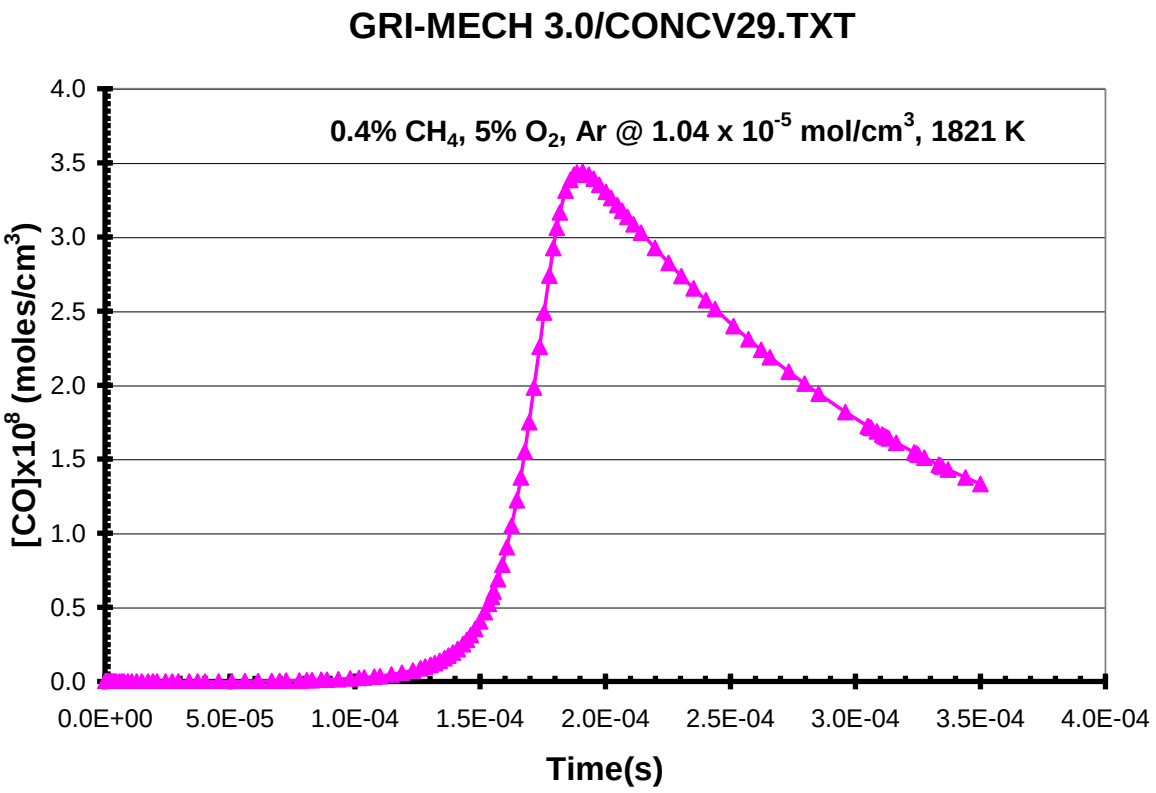


GRI-MECH RUN 0.4% CH_4 5% O_2

The output concentration file, CONCV29.TXT, matches the results by Yu, et al [13] under the same conditions (0.4% CH4, 5% O2 in Ar at 1.04 x 10^{-5} mole/cm3 and T = 1821 K). These models can also be executed by loading the Excel or OpenOffice workbook: GRI_MECH_30.xls and clicking the RUN button on the CONTROL worksheet.

MODGRI.DAT - The kinetics reactions (Converted from the Chemkin-II/III GRI model using the CK2KIN.EXE program)
SPECV29.DAT - The species involved
PARMV29.DAT - The parameters used
THERMGRI.DAT – The thermodynamic description spreadsheet
CONCV29.TXT - A simulation run.

griv29.BAT - This is a straightforward one-line batch file that will run the above model producing the concentration profile equal to CONCV29.TXT.

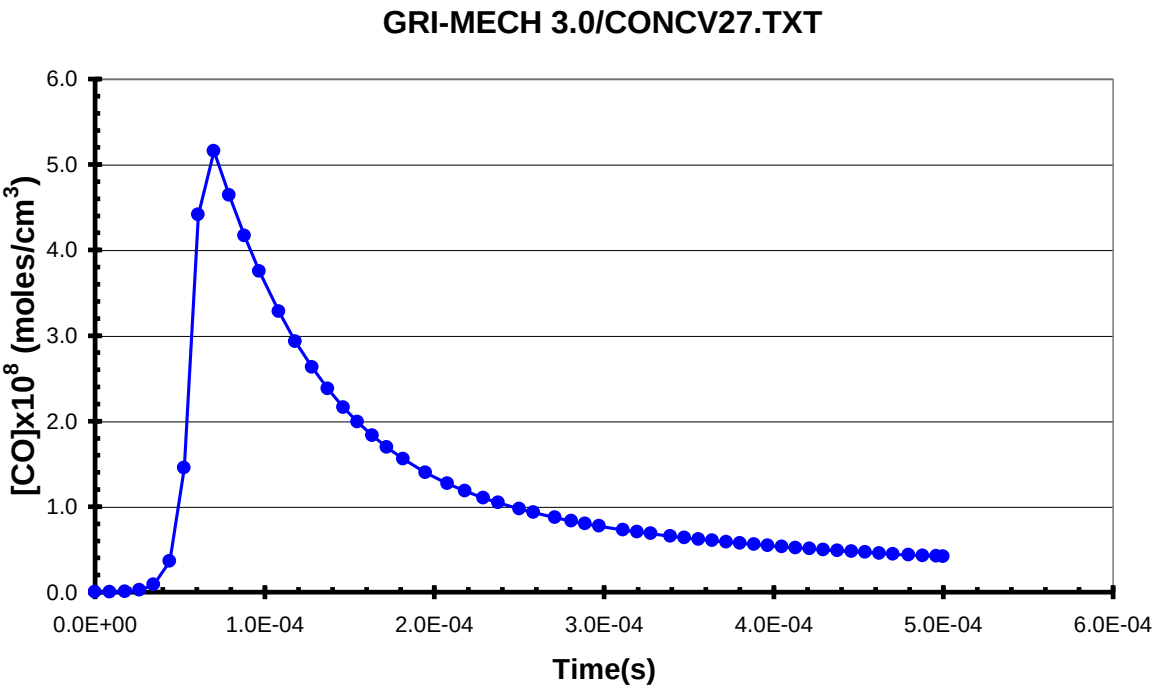


GRI-MECH RUN 0.4% CH_4 5% O_2

The output concentration file, CONCV27.TXT, matches the results by Yu, et al [13] under the same conditions (0.4% CH4, 5% O2 in Ar at 1.58 x 10^{-5} mole/cm3 and T = 1941 K). These models can also be executed by loading the Excel or OpenOffice workbook: GRI_MECH_30.xls and clicking the RUN button on the CONTROL worksheet.

MODGRI.DAT - The kinetics reactions (Converted from the Chemkin-II/III GRI model using the CK2KIN.EXE program)
SPECV27.DAT - The species involved
PARMV27.DAT - The parameters used
THERMGRI.DAT – The thermodynamic description spreadsheet
CONCV27.TXT - A simulation run.

griv27.BAT - This is a straightforward one-line batch file that will run the above model producing the concentration profile equal to CONCV27.TXT.

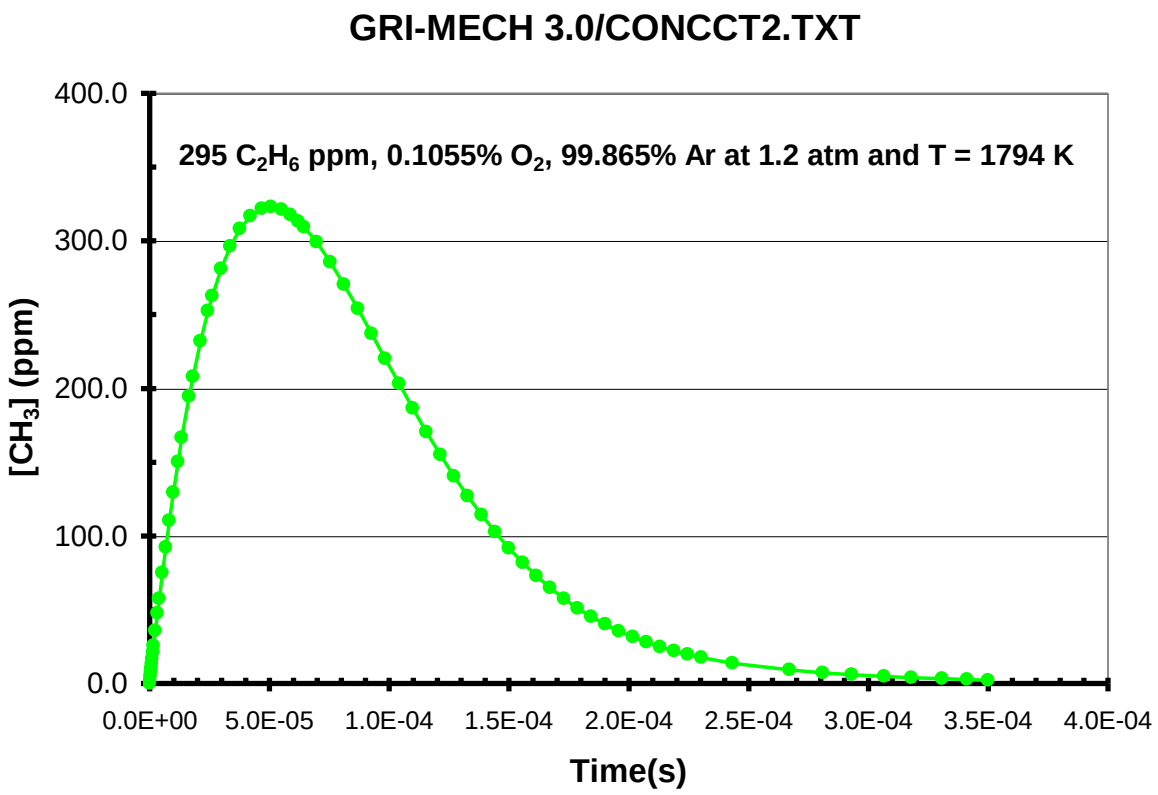


GRI-MECH RUN 295 C_2H_6 ppm, 0.1055% O_2, 99.865% Ar

The output concentration file, CONCCT2.TXT, matches the results by Chang et al. [25] under the same conditions (295 C_2H_6 ppm, 0.1055% O_2, 99.865% Ar at 1.2 atm, and T = 1794 K). These models can also be executed by loading the Excel or OpenOffice workbook: GRI_MECH_30.xls and clicking the RUN button on the CONTROL worksheet.

MODGRI.DAT - The kinetics reactions (Converted from the Chemkin-II/III GRI model using the CK2KIN.EXE program)
SPECCT2.DAT - The species involved
PARMCT2.DAT - The parameters used
THERMGRI.DAT – The thermodynamic description spreadsheet
CONCCT2.TXT - A simulation run.

grict2.BAT - This is an elementary one-line batch file that will run the above model producing the concentration profile equal to CONCCT2.TXT.

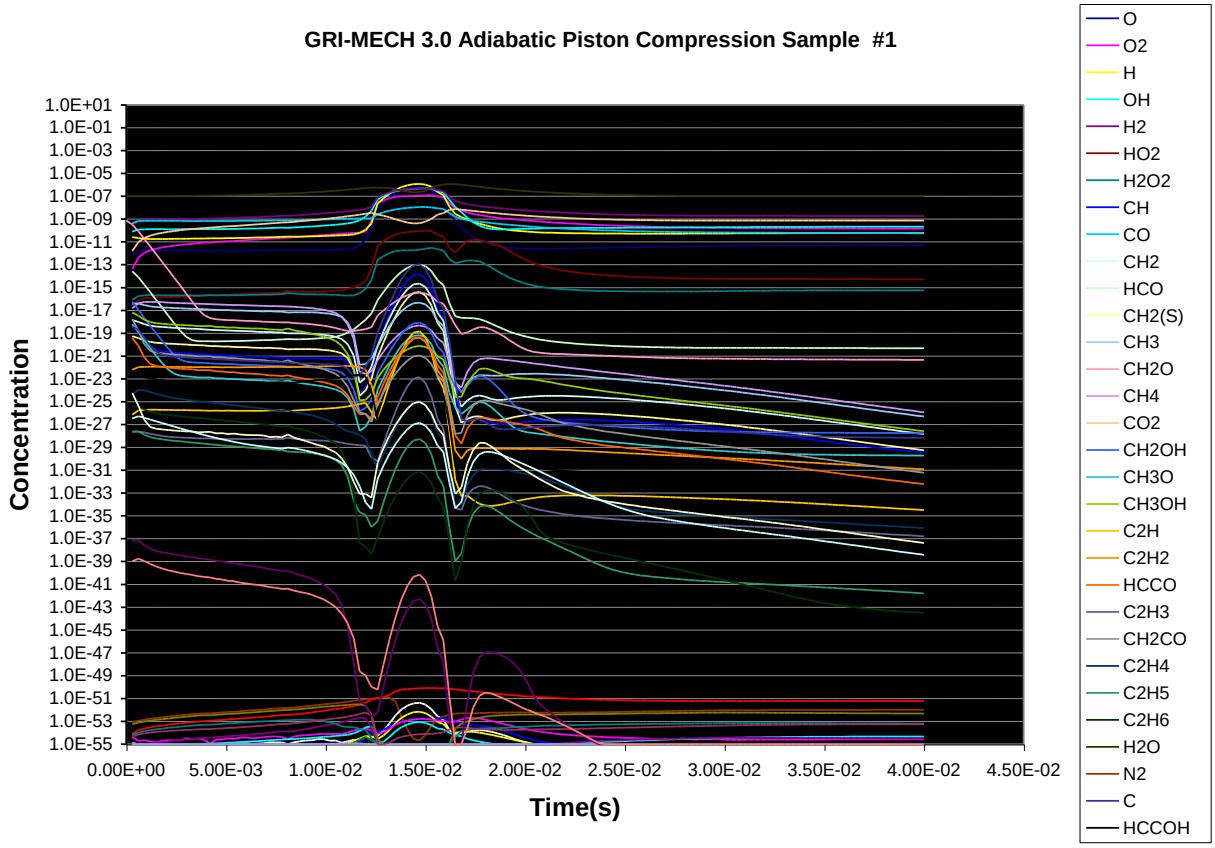


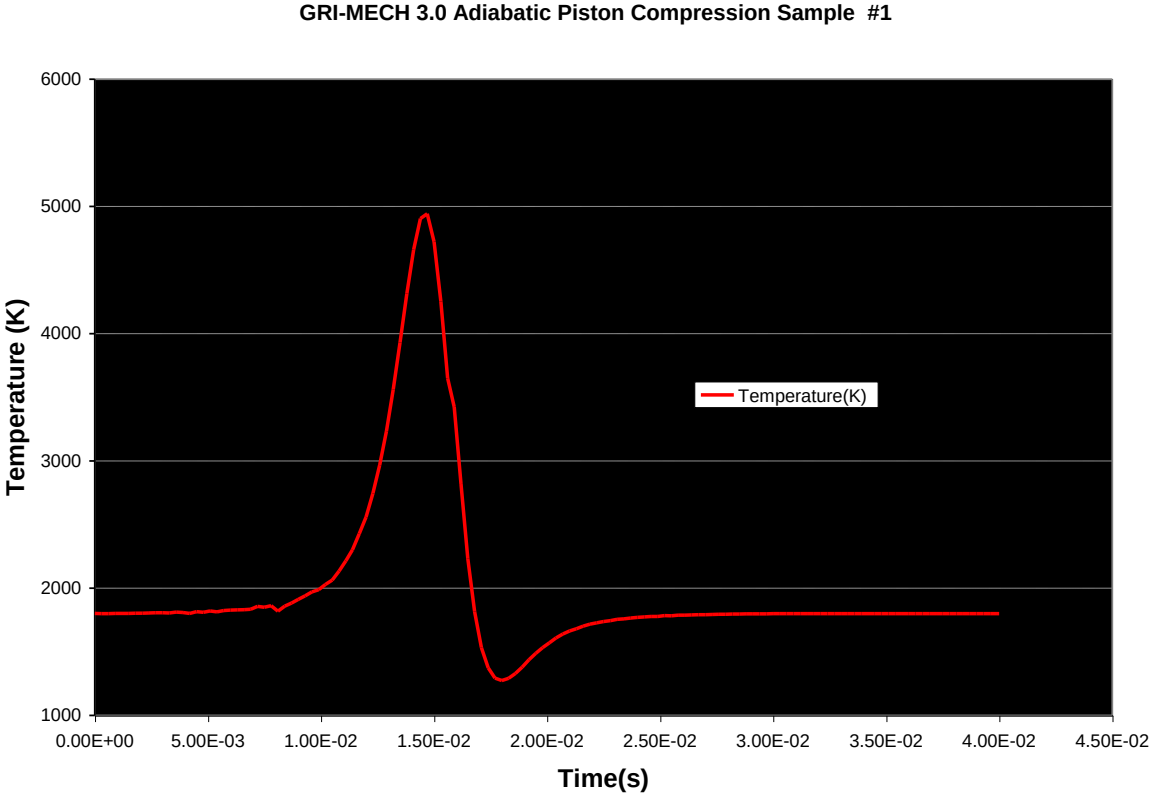
GRI-MECH PISTON COMPRESSION RUN

This sample run shows how to use a volume profile to simulate piston compress on a chamber.

MODGRI.DAT - The kinetics reactions (Converted from the Chemkin-II/III GRI model using the CK2KIN.EXE program)
SPECPIST.DAT - The species involved
PARMPIST.DAT - The parameters used
THERMGRI.DAT – The thermodynamic description spreadsheet
CONCPIST.TXT - A simulation run.

Grimech_with_compression.xls – A Kintecus-Excel file will run the above model producing the below concentration and temperature profiles.




GRI-MECH 3.0 Adiabatic Piston Compression Sample #1
Temperature (K)
6000
5000
4000
3000
2000
1000
0.00E+00
5.00E-03
1.00E-02
1.50E-02
2.00E-02
2.50E-02
3.00E-02
3.50E-02
4.00E-02
4.50E-02
Time(s)
Temperature(K)

Ethanol Combustion Runs

The following three sample runs involve the combustion of ethanol at different starting conditions. The chemical model is a direct conversion of the Chemkin-II model. No alterations were made to the MODETH.DAT once the CK2KIN program converted it. These models can also be executed by loading the Excel or OpenOffice workbook: Ethanol_Combustion.xls and clicking the **RUN** button on the CONTROL worksheet.

Ethanol Combustion Run 1

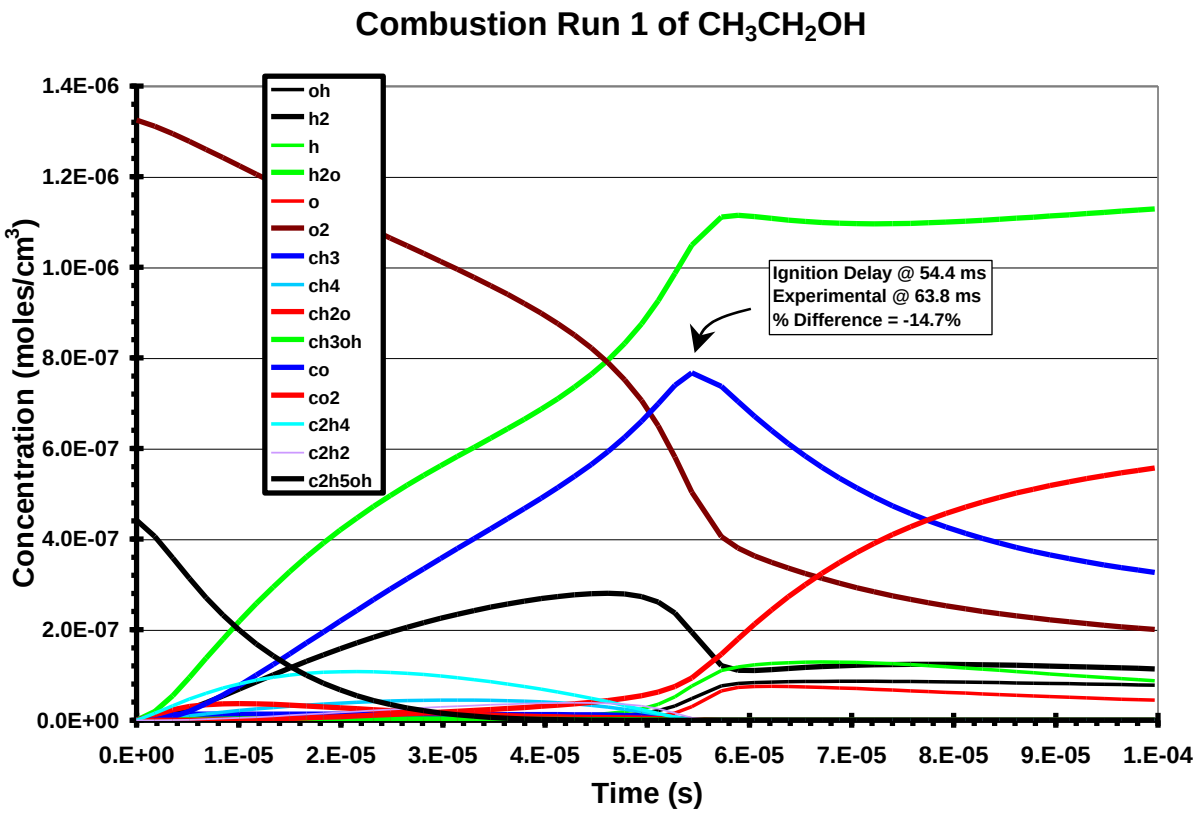
The ignition delay obtained from the output concentration file, CONCETH1.TXT, matches the experimental results given by Dunphy and Simmie [15]. Dunphy and Simmie correlated their experimental ignition times with the expression:

$$\text{ignition\_delay(sec)} = 1.0 \times 10(-14)\ \exp(15500\ K/T)\ [C_2H_5OH]^{-0.315}[O_2]^{-0.78}[Ar]^{0.259}$$

The temperature is in Kelvin, and all the initial concentrations are in moles/cm^3.

MODETH.DAT - The kinetics reactions (Converted from the Chemkin-II/III ethanol combustion model of Marinov [14] using the CK2KIN.EXE program)
SPECETH1.DAT - The species involved / PARMETH1.DAT - The parameters used
THERMETH.DAT – The thermodynamic description spreadsheet
CONCETH1.TXT - A simulation run.

ETHANOL1.BAT - This is a straightforward one-line batch file that will run the above model producing the concentration profile equal to CONCETH1.TXT. These models can also be executed by loading the Excel or OpenOffice workbook: **Ethanol_Combustion.xls** and then clicking the **RUN** button on the CONTROL worksheet.



Ethanol Combustion Run 2

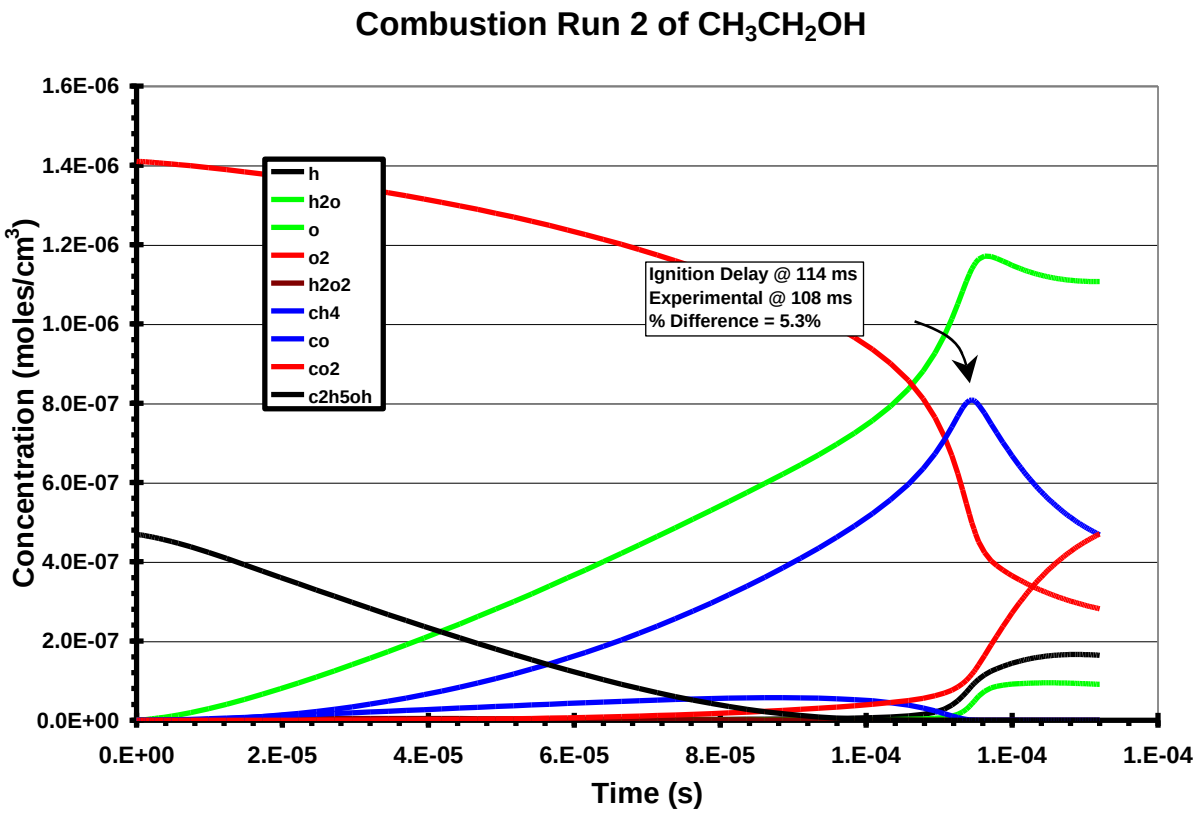
The ignition delay obtained from the output concentration file, CONCETH2.TXT, matches the experimental results given by Dunphy and Simmie [15]. Dunphy and Simmie correlated their experimental ignition times with the expression:

$$\text{ignition\_delay(sec)} = 1.0 \times 10(-14)\ \exp(15500\ K/T)\ [C_2H_5OH]^{-0.315}[O_2]^{-0.78}[Ar]^{0.259}$$

The temperature is in Kelvin, and all the initial concentrations are in moles/cm^3.

MODETH.DAT - The kinetics reactions (Converted from the Chemkin-II/III ethanol combustion model of Marinov [14] using the CK2KIN.EXE program)
SPECETH2.DAT - The species involved / PARMETH2.DAT - The parameters used
THERMETH.DAT – The thermodynamic description spreadsheet
CONCETH1.TXT - A simulation run.

ETHANOL2.BAT - This is a straightforward one-line batch file that will run the above model producing the concentration profile equal to CONCETH2.TXT. These models can also be executed by loading the Excel or OpenOffice workbook: Ethanol_Combustion.xls and then clicking the **RUN** button on the CONTROL worksheet.



Ethanol Combustion Run 3

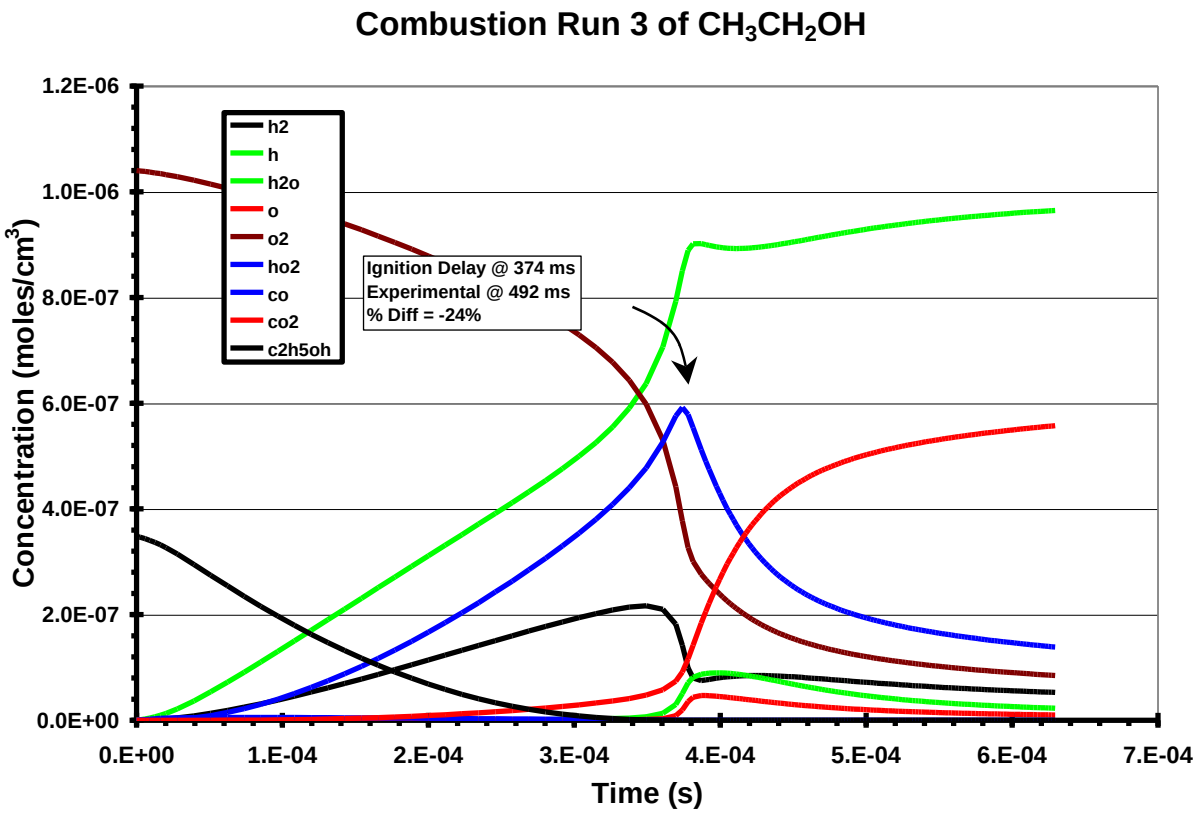
The ignition delay obtained from the output concentration file, CONCETH1.TXT, matches the experimental results given by Dunphy and Simmie [15]. Dunphy and Simmie correlated their experimental ignition times with the expression:

$$\text{ignition\_delay(sec)} = 1.0 \times 10(-14)\ \exp(15500\ K/T)\ [C_2H_5OH]^{-0.315}[O_2]^{-0.78}[Ar]^{0.259}$$

The temperature is in Kelvin, and all the initial concentrations are in moles/cm^3.

MODETH.DAT - The kinetics reactions (Converted from the Chemkin-II/III ethanol combustion model of Marinov [14] using the CK2KIN.EXE program)
SPECETH3.DAT - The species involved / PARMETH3.DAT - The parameters used
THERMETH.DAT – The thermodynamic description spreadsheet
CONCETH3.TXT - A simulation run.

ETHANOL3.BAT - This is an elementary one-line batch file that will run the above model producing the concentration profile equal to CONCETH3.TXT. These models can also be executed by loading the Excel or OpenOffice workbook: Ethanol_Combustion.xls and then clicking the **RUN** button on the CONTROL worksheet.

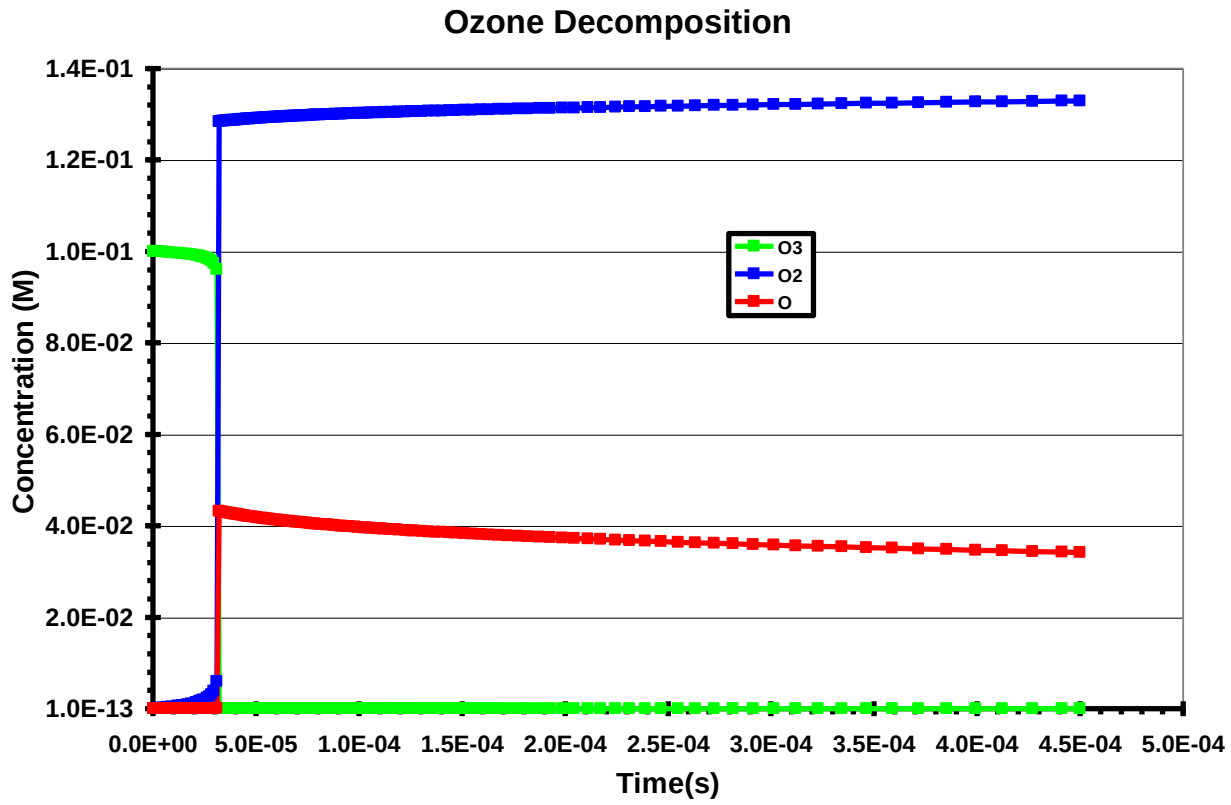


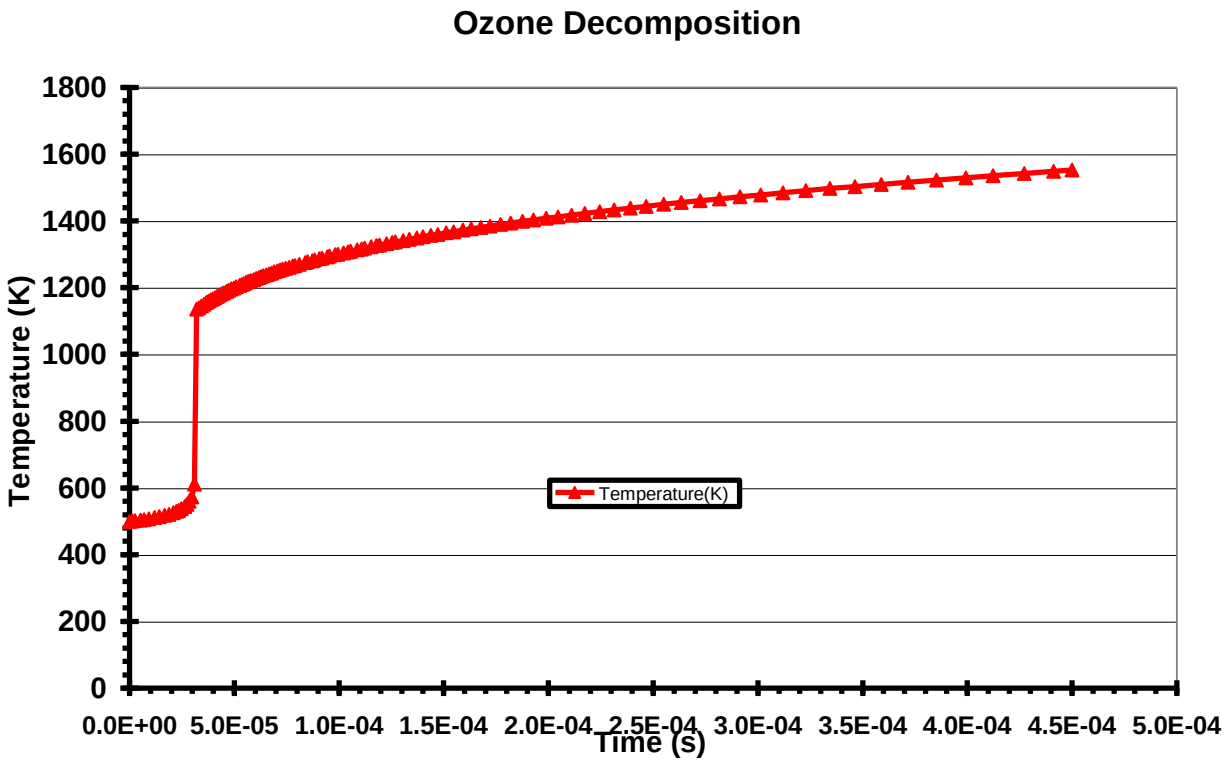
Ozone Decomposition

The concentration output file, CONCOZON.TXT, matches the sample ozone decomposition model in the CKS software[17].

MODOZO.DAT - The kinetics reactions
SPECOZO.DAT - The species involved
PARMOZO.DAT - The parameters used
THRMOZON.DAT – The thermodynamic description spreadsheet
CONCOZO.TXT - A simulation run.

OZONE.BAT - This is a straightforward one-line batch file that will run the above model producing the concentration profile equal to CONCOZON.TXT.



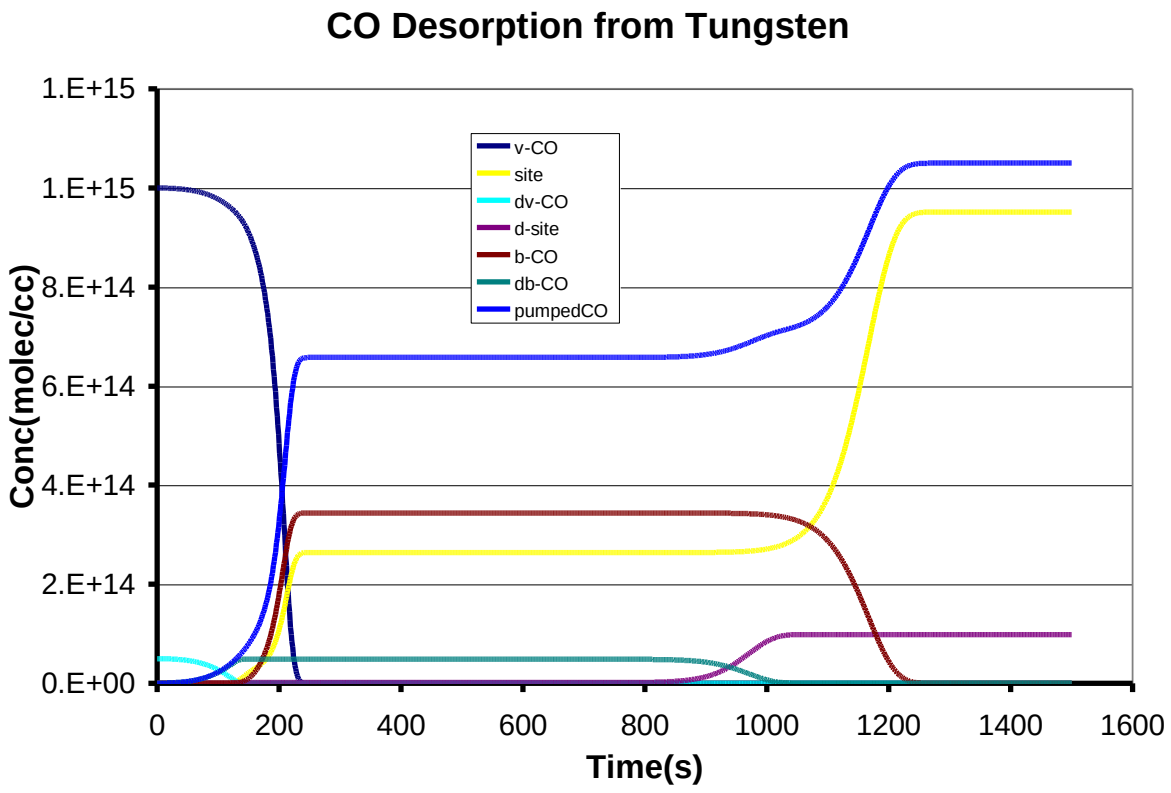

Ozone Decomposition
1800
1600
1400
1200
1000
800
600
400
200
0
Temperature (K)
Temperature(K)
0.0E+00
5.0E-05
1.0E-04
1.5E-04
2.0E-04
2.5E-04
3.0E-04
3.5E-04
4.0E-04
4.5E-04
5.0E-04
Time (s)

CO Desorption from Tungsten

The concentration output file, CONCWOLF.TXT, matches the plots in Houle and Hinsberg [16]. These models can also be executed by loading the Excel Workbook: Wolfrum_with_Temp_Program.xls and clicking the **RUN** button on the CONTROL worksheet.

MODWOLF.TX2 - The kinetics reactions
SPECWOLF.TX2 - The species involved
PARMWOLF.TX2 - The parameters used
CONCWOLF.TXT - A simulation run.
TEMPPROF.TXT – A temperature program

WOLFRUM.BAT - This is a straightforward one-line batch file that will run the above model producing the concentration profile equal to CONCWOLF.TXT.



Isothermal 1-butene = cis-2-butene Isomerization

The results match those calculated by hand using the CRC Handbook of Chemistry & Physics[18]. **This one-line model also shows quotes surrounding species names that begin with a number, i.e., "1-butene". Do not surround the species name in quotes in the species description file!**

MODT1.TX2 - The kinetics reactions
SPECT1.TX2 - The species involved
PARMT1.TX2 - The parameters used
THERMT1.DAT – The thermodynamic description spreadsheet
CONCT1.TXT - A simulation run.

ISOBUT.BAT - A straightforward one-line batch file that will run the above model producing the concentration profile equal to CONCT1.TXT.

Isothermal 2 butene = cis-2-butene + t-butene

The results match those calculated by hand using the CRC Handbook of Chemistry & Physics[18].

MODBUT.DAT - The kinetics reactions
SPECBUT.DAT- The species involved
PARMBUT.DAT - The parameters used
THERMT1.DAT – The thermodynamic description spreadsheet
CONCBUT.TXT - A simulation run.

BUTENE.BAT - A straightforward one-line batch file that will run the above model producing the concentration profile equal to CONCBUT.TXT.

Sensitivity Analysis Sample Runs

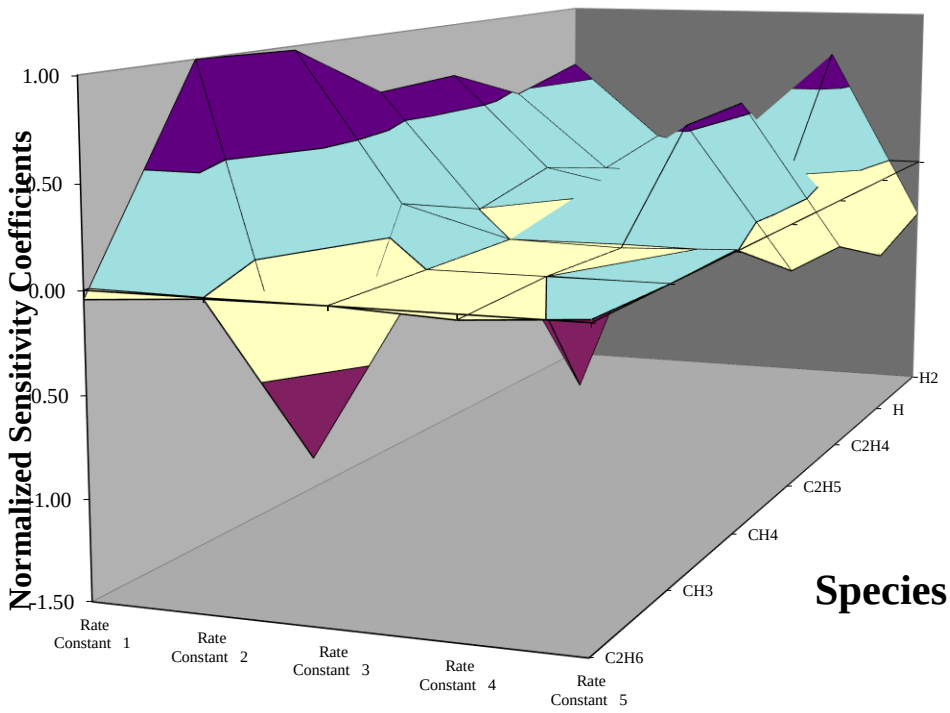
Sensitivity Analysis of Ethane Pyrolysis

Output sensitivity analysis files 1SENSIT1.TXT and 1SENSIT2.TXT match TABLES I & II in the paper[8].

MODSEN1.TX2 - The kinetics reactions
SPECSEN1.TX2 - The species involved
PARMSEN1.TX2- The parameters used

SENSIT1.BAT - A straightforward one-line batch file that will run the above model producing the normalized sensitivity coefficient files equal to 1SENSIT1.TXT and 1SENSIT2.TXT.

Normalized Sensitivity Analysis of Ethane Pyrolysis

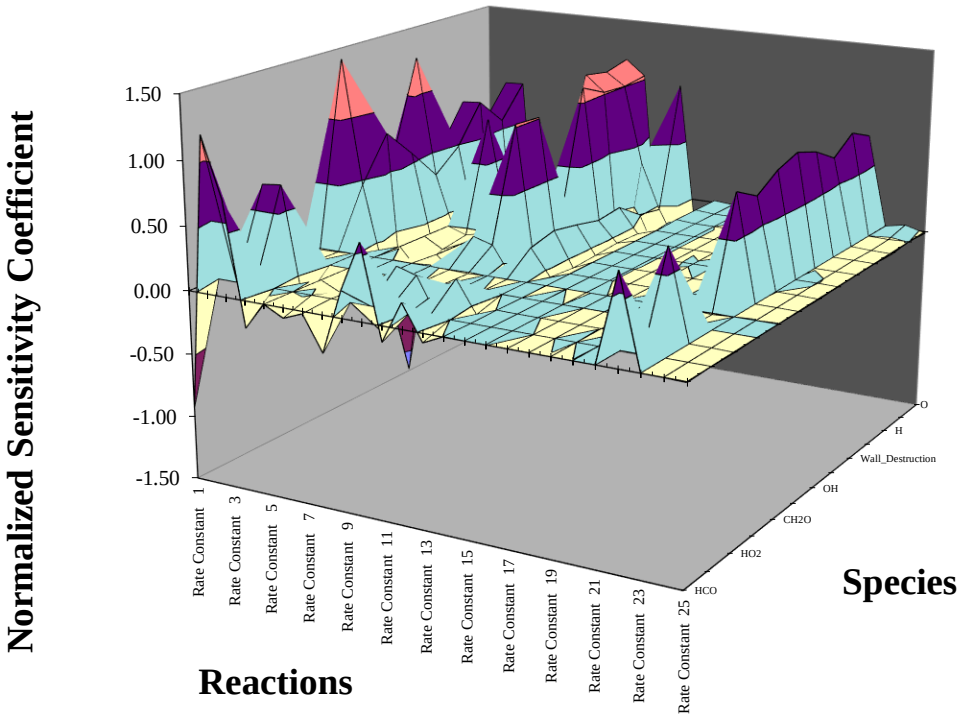


Sensitivity Analysis of the Oxidation of Formaldehyde Mechanism

Output the sensitivity analysis file 2SENSIT1.TXT, which will match TABLE IV in the paper [8].

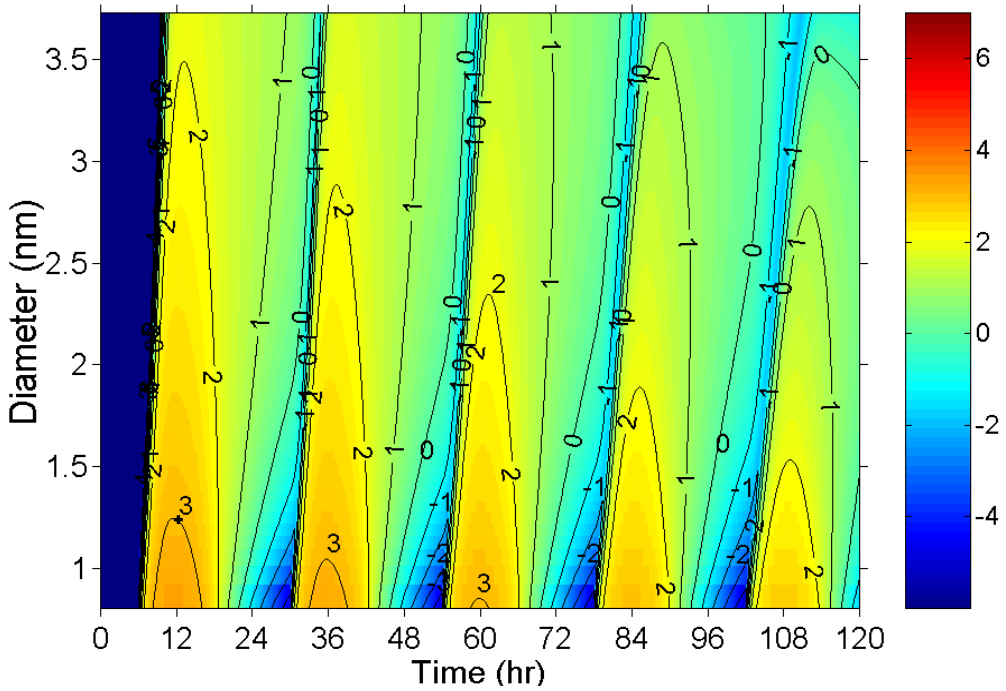
MODSEN2.TX2 - The kinetics reactions
SPECSEN2.TX2 - The species involved
PARMSEN2.TX2- The parameters used

SENSIT2.BAT - A straightforward one-line batch file that will run the above model producing the normalized sensitivity coefficient file equal to 2SENSIT1.TXT



Large Models

Kintecus can handle well over hundreds of thousands of reactions. The color contour plot below shows a kinetics run of over **120,000+** chemical reactions for **several days (that is simulation time, NOT REAL-TIME)!** The model and concentration files were not included because of their vast size. The author can provide these reactions upon request. The thesis chapter 8 explains the contour plot below, and their experimental comparisons are included with Kintecus. The chapter also contains many other large examples Kintecus simulation runs.



5. Fitting/Optimization

This section will explain how one can fit almost any numerical value (rate constants, initial concentrations, Troe factors, third body enhancements, the energy of activation, starting temperature, etc.) against an experimental or "fabricated" dataset. One might wish to use fabricated datasets to optimize numerical values such as initial concentrations of species to values that would minimize the presence of some harmful intermediate species, maximize certain valuable products, reduce/increase temperature, etc. Note that Kintecus will fit the parameters EXACTLY the time values your data were measured. Unlike other programs, Kintecus DOES NOT interpolate a function against your data and then fit the values against this interpolation. There is no need to "clean" your data, suggest interpolation methods, or specify timing meshes against your experimental data since Kintecus calculates values precisely when you specify in your experimental data file. Some example Kintecus-Excel workbooks demonstrating some of these features are:

Enzyme_Regression_Fitting.xls
Enzyme_Regression_Molar_Extinct.xls
Enzyme_Regression_Fitting_WEIGHTS_TEST.xls
Enzyme_Regression_Fitting_reverse_rate_fit.xls
Enzyme_Regression_Fitting_Multi_Absorb.xls
Enzyme_Regression_Fitting_Constraints_fit5.xls
Enzyme_Regression_Fitting_BOOTSTRAPPING.xls
Combustion_workbook_OH_enthalpy_fit.xls

Also, the subdirectory /FITTESTS/ listed inside the /Kintecus directory contains several dozen other sample regression/fitting examples, such as combustion/thermodynamics.

Kintecus V5.0 and up now supports **global data regression/fitting/analysis**. You can regress or fit or optimize multiple datasets with multiple initial conditions such as temperature, pressure, concentration, or any combination with data sets with different time scales, time steps, species, temperature profiles, heat output, etc. Many sample Kintecus-Excel worksheets demonstrate some basics of this new global regression:

Enzyme_Regression_Fitting_Multiple_Datasets_and_initial_conditions.xls
POLYMER_MULTIFIT_MULTICONDITIONS.xls
Combustion_workbook_OH_multifit.xls
Enzyme_Regression_Fitting_Multiple_Datasets.xls

These examples demonstrate biological, combustion, and polymer global experimental regressions.

In addition to the sample batch files shown in the table below, there should be sample Kintecus-Excel sheets showing various fitting examples. On the Windows installation of Kintecus, there is a sub-menu called "Fitting-Regression" in the Kintecus Workbench, demonstrating further points of regression/optimization with Kintecus.

Batch File (located in the FITTESTS/ subdirectory)	Type of Fit/Optimizing Run	Conditions
FITTEST1.BAT	Enzyme Mechanism	Fitting a rate constant against a dataset
FITTEST2.BAT	Enzyme Mechanism	Fitting two rate constants against a dataset
FITTEST3.BAT	Oregonator	Fitting a rate constant against a dataset
FITTEST4.BAT	Enzyme Mechanism	Fitting several rate constants against a dataset
FITTEST5.BAT	Enzyme Mechanism	Fitting Molar Extinction Coefficients and rates
FITTEST8.BAT	Adiabatic Ozone Reactions under Constant Volume	Fitting an unknown concentration against a dataset
FITTEST9.BAT	Cesium Flare Model	Fitting several rate constants against a dataset
FITTESTH.BAT	Adiabatic H2-O2 Combustion Reactions under Constant Pressure	Fitting several third-body rate enhancement factors against a dataset
FITTESTA.BAT	Optimization with a constraint of reverse rates/equilibrium constant	Fitting several rate constants against a dataset
FITTESTB.BAT	Regression with weights/std deviation present in data	Fitting several rate constants against a dataset
FITTESTC.BAT	Optimization with multi-constraints	Fitting several rate constants against a dataset
FITTESTD.BAT	Optimization with special species directives and data arithmetic	Fitting several rate constants against a "contaminated" dataset with overlapping **UV/Vis peaks**
FITTESTE.BAT	Regression with bootstrapping to report the most accurate std/errors	Fitting several rate constants against a dataset
FITTESTG.BAT	***Global data regression***/fitting/analysis with different initial conditions	Fitting energy of activation for several reactions in a combustion system
F1EQUIL.BAT	Fitting of Initial Concentrations for H_2-O_2-N_2 Combustion	Constant Temperature Constant Volume
F2EQUIL.BAT	Fitting of Initial Concentrations for H_2-O_2-N_2 Combustion	Constant Temperature Constant Pressure

Table 11. A small sampling of fitting/optimization runs that Kintecus can perform.

The Fitting Procedure

Fitting Options

The fitting procedure in Kintecus can be specified by including the –FIT switch on the command line. The –FIT switch has many options:

-FIT:a:b:c:d:e:f [:g:h:i]

FIT Switch Option	Description	Possible Values	Default Value
a	Fitting Algorithm	1, 2, 3, 4, 5	1
b	Comparison Operator	1, 2, 3, 4, 5	1
c	User Dataset Filename	Any allowed text filename	FITDATA.TXT
c=fitdatan	Set c to "fitdatan" to turn on global analysis. See examples & description below.	fitdatan	n/a
c=fitdatan,(filename)	Set c to "fitdatan" to turn on **global analysis,** followed by a comma and a filename to a text file of initial conditions and/or local variable fits. See examples below	fitdatan,(filename to a text file containing your initial conditions from your experiments)	n/a
c=FITLINK,fitdatan,(filename)	Constrain rates/concentrations against user-defined equations. It can be combined with fitdatan and initial conditions; however, **FITLINK must be defined FIRST**. See examples below	FITLINK **-OR-** FITLINK,fitdatan **-OR-** FITLINK,fitdatan,(filename to a text file that has initial conditions or local variable fits)	n/a
d	Tolerance	$1 - 10^{-14}$	1×10^{-7} for Fitting Algorithms 1 and 3 1×10^{-5} for Fitting Algorithm 2
e	Maximum Iterations Allowed	$1 - 2 \times 10^{9}$	9000
f	Starting Vectors	$1 \times 10^{-100} - 1 \times 10^{10}$	1×10^{-35}
g	Starting "Temperature"	$1 \times 10^{-100} - 1 \times 10^{10}$	1×10^{6}
h	Number of Cycles to Stay At Current Temperature Before Reducing Temperature	1 - 32767	25
i	Percent Temperature Reduction	0 - 0.99999	0.20 (20%)

Table 12. Options for the –FIT switch. Specifying a "D" on any option field will force Kintecus to use the Default Value. Fit switch options g, h, and i are only for fitting algorithm #3.

The first three options, "a," "b," and "c" (or the fitting algorithm, comparison operator, dataset filename) are the most important. Options d, e, and f can be used with all three optimization algorithms. Options g, h, and i are only for the Simulated Annealing fitting algorithm method 3. Specifying a "D" on any option field will force Kintecus to use the Default Value.

There are five fitting/optimization algorithms: 1=Mead & Nelder [23], 2=Powell [1], 3=Simulated Annealing [24], 4=Levenberg-Marquardt and 5=Complex[26] for option "a". For each optimization algorithm, a user can choose from three comparison operators under option "b": 1=relative least squares or **"$\Sigma(x_{data}-x_{calc})/MAX(x_{data})$"**, 2=standard least squares or **"$\Sigma(x_{data}-x_{calc})^2$"**, and 3=a proprietary function the author

has devised, 4=absolute values of the differences or **"$\Sigma|x_{data}-x_{calc}|$"**, 5=square of the differences (same as 2). The summations are over all data points. If there is more than one column of data, then it is a double summation over all columns, and if there are multiple datasets, then it is a triple summation over all datasets. The comparison operators compare the experimental/fabricated data and the simulated data and respond back to the optimizer with a number showing this difference. Kintecus will display this computed sum next to the "Final SUM[(X(DATA)-X(MODEL))^2]". In addition, Kintecus will report the root-mean-square (RMS), "**$SQRT(\Sigma(x_{data}-x_{calc})^2/n)$**" for each column of data as it is regressing. This RMS value is after the output, "RMS''s for Column (column #,RMS)".

Once the user chooses a fitting/optimization algorithm and comparison operator, he must supply the experimental or fabricated data in a text file named FITDATA.TXT. The default filename, FITDATA.TXT, can be changed to a user-defined filename. The only requirements for the data file are that "Time(s)" must be in the first column, the first row, "END" must be in the first column, the last row, and the measured/fabricated species names/Temperature(K) must be in the first row. The species names/Temperature(K) can be in any order on the first row. You can insert comments in this file or comment out any lines by placing a "#" or a quote ' " ' as the first character on a line. If there is a missing data point(s) for a species, then the cell must have an UPPERCASE "N" as the first letter, so "NaN" or "None" or "Nothing" or just "N" are all allowed to represent no data at that time point. An example data file (created in Excel, then saved as a TAB delimited text file) is shown below (this datafile is used in enzyme fitting test #4, FITTEST4.BAT) :

Time(s)	E	S	ES	EIS
3.55E+00	1.52E-09	5.90E-02	2.48E-09	1.38E-13
2.38E+01	1.62E-09	5.34E-02	2.38E-09	1.33E-13
5.33E+01	1.77E-09	4.56E-02	2.23E-09	1.24E-13
8.28E+01	1.94E-09	3.84E-02	2.06E-09	1.14E-13
1.12E+02	2.13E-09	N	1.87E-09	1.04E-13
1.42E+02	2.33E-09	N	1.67E-09	9.24E-14
1.71E+02	2.55E-09	N	1.45E-09	8.05E-14
2.01E+02	N	N	1.23E-09	6.83E-14
2.30E+02	N	N	1.01E-09	N
2.60E+02	N	N	8.13E-10	N
2.89E+02	N	N	6.33E-10	N
.	.	.	.	.
.	.	.	.	.
.	.	.	.	.
1.65E+03	4.00E-09	N	4.39E-14	N
1.68E+03	4.00E-09	N	4.39E-14	N
1.71E+03	4.00E-09	N	4.39E-14	N
1.74E+03	4.00E-09	N	4.39E-14	7.31E-16
1.76E+03	4.00E-09	N	4.39E-14	7.31E-16
1.80E+03	4.00E-09	N	4.39E-14	7.31E-16
END				

Table 13. Sample user supplied spreadsheet containing experimentally obtained data ready for fitting.

The Fit Switch Option "d" is the optimization tolerance. This tolerance sets the minimum value between successive fits that must be met before the data is considered optimized. Decreasing this value will cause more optimizations (longer execution time but more accurate calculated numbers and fits). Conversely, increasing this value will cause fewer optimizations (shorter execution time but numbers/fits that are less accurate) to be performed. It is essential to note that the tolerance is a minimum threshold needed to stop optimization when successive fits (compares between the data and simulated data) fall at or below this value.

The optimization can occasionally halt even if the data-simulated comparison is **terrible** (huge difference). In other words, just because Kintecus states that optimization is finished, there is a good chance it has not. Kintecus had to stop the optimization because the program was going in circles (trapped in a local minimum) and the user

should try another optimization method, comparison operator, or a different starting guess(es). For more help, see the Optimizing Tips section below.

Optimization algorithm #2 (Powell method) is pretty sensitive to tolerance. It is suggested that you do not set a value above 1 x 10(-5). Setting smaller values (under 1 x 10(-8)) can result in a substantially longer optimization run in some cases. Optimization algorithms #1 and #3 are more insensitive to the tolerance than the Powel method.

The Fit Switch Option "**e"** set the maximum iterations allowed. If the number of optimizations reaches this value, the program will quit. Please note that the average amount of optimization iterations for just two values is between 400-1200 optimizations at a tolerance of 1 x 10(-6).

The Fit Switch Option "f" sets the starting vectors. The optimization of values, N, is an optimization of starting vectors of size, N, in vector space N (or N+1 for the fitting algorithms #1 and #3). Consult references for a full explanation.

The Fit Switch Options "g," "h," and "i" are for the Simulated Annealing Optimization method #3. The g option is the starting "Temperature", and this is NOT the physical, real thermodynamic temperature of the system, but an analogy to a starting data "cooking" temperature. Refer to references for a full explanation. Option h is the actual "annealing" or "cooking" time in cycles. The number of simulations to be performed before a percent reduces the data "temperature" represented by Fit Switch Option "i."

There are many examples (examine the various Kintecus command line options in the BAT files) in the /FITTESTS/ sub-directory demonstrating various parameters and models to which Kintecus can fit data. Some sample Kintecus-Excel workbooks are:

Enzyme_Regression_Fitting.xls
Enzyme_Regression_Molar_Extinct.xls
Enzyme_Regression_Fitting_WEIGHTS_TEST.xls
Enzyme_Regression_Fitting_reverse_rate_fit.xls
Enzyme_Regression_Fitting_Multi_Absorb.xls
Enzyme_Regression_Fitting_Constraints_fit5.xls
Enzyme_Regression_Fitting_BOOTSTRAPPING.xls
Combustion_workbook_OH_enthalpy_fit.xls
Enzyme_Regression_Fitting_Multiple_Datasets_and_initial_conditions.xls
Combustion_workbook_OH_enthalpy_fit.xls ***(Enthalpy/heat fitting example)***
POLYMER_MULTIFIT_MULTICONDITIONS.xls ***(Global analysis sample)***
Combustion_workbook_OH_multifit.xls ***(Global analysis sample)***
Enzyme_Regression_Fitting_Multiple_Datasets.xls ***(Global analysis sample)***
Zhang_aerobic-Fitting_Multiple_Datasets.xls ***(Global analysis sample)***
Zhang_anoxic-Fitting_Multiple_Datasets.xls ***(Global analysis sample)***
Enzyme_Regression_Fitting_reverse_rate_fit_new_way.xls ***(FITLINK example)***
"Enzyme_Regression_Fitting_Multiple_Datasets_and_initial_conditions.xls" ***(Global analysis sample with local shared variable optimization)***

Fitting Optimization algorithm 4 (Levenberg-Marquardt) has been updated as Kintecus V6.70 and up. One feature is the ability to read algorithm parameter values by providing a text file in the same directory as the run. If Kintecus detects a text file with the name "MARQ_PARAMS.txt" present, Kintecus will state it has detected this file in the output and then read in the values in that file. The values will also be repeated into the screen output for user verification. Please double-check! A text file named "MARQ_PARAMS_defaults.txt" (which should be in the /FITTESTS/ subdirectory) has been provided that contains the internal default values Kintecus utilizes for its Levenberg-Marquardt runs. It is recommended to copy this file as MARQ_PARAMS.txt and edit those values. Please use decimal points, "." and scientific notation with "E+/-000" to represent real numbers. Failure to do so can result in **incorrect** values being read. The current contents of "MARQ_PARAMS_defaults.txt" and their explanations:

```
0
0
15
30000
30000
```

```
       30000
       1
       6.05545445E-006
       3.66685286E-011
       3.66685286E-011
       4.93038065E-032
       2.22044604E-014
       -999.0000000000
       -999.0000000000
       !
       ! First value, IBTYPE is:
       ! IF IBTYPE=0 Kintecus will supply all the bounds which are set internally
depending on units.
       !          =1 All variables are nonnegative (=>0).
       !
       ! NB: IN THE THIRD SET OF NUMBERS ABOVE, BE SURE TO ENTER WITH A DECIMAL
       !      POINT!!
       ! And double-check the read-in values! Look in the Kintecus output!
       !
       !    IPARAM(1)=0 ! use default options if =0
       !    IPARAM(2)=15 ! # of good digits in function (default 15)
       !    IPARAM(3)=30000 ! max # of iterations
       !    IPARAM(4)=30000 ! max # of function evaluations
       !    IPARAM(5)=30000 ! max # of jacobians evaulations
       !    IPARAM(6)=1   ! 1=xscale set internally
       !
       ! NB: IN THIS THIRD SET OF NUMBERS, BE SURE TO ENTER WITH A DECIMAL POINT!!
       ! RPARAM(1) = Scaled gradient tolerance.
       !   The i-th component of the scaled gradient at x is calculated
       ! RPARAM(2) = Scaled step tolerance.
       !   The i-th component of the scaled step between two points x and y
       ! RPARAM(3) = Relative function tolerance.
       ! RPARAM(4) = Absolute function tolerance.
       ! RPARAM(5) = False convergence tolerance.
       ! RPARAM(6) = Maximum allowable step size. Default: 1000 max(e1, e2)
       ! RPARAM(7) = Size of initial trust-region radius. Default: based on the
initial scaled Cauchy step.
       !
       ! Double check the Kintecus output to ensure everything was read in correctly!
       !
```

What and How Can I Fit/Optimize ?

Selection of numeric parameters for fitting/optimization can quickly be done simply by appending the number (actually your guess) with a question mark, "?". The sample model spreadsheet below (See **Enzyme_sheet.xls** in the **FITTESTS** sub-directory, this model is run with FITTEST4.BAT) shows three rate constants that have been selected for fitting. These models can also be executed by loading the Excel workbook: Enzyme_Regression_Fitting.xls and then clicking the **RUN** button on the CONTROL worksheet. (note the **extremely poor guesses**! But Kintecus obtains the exact answer that is **orders of magnitude away**!):

# Non-competitive Inhibition # of an enzymatic reaction	
# Example spreahsheet. You can see comments by moving pointer above the red triangles # *Note, if you wish to use this model with KINTECUS, be sure to save # it as a Text Tab Delimited sheet, and don't forget to also save it # as a regular Excel spreadsheet or you lose all your formatting and notes!!	**Equilibrium Constants**
1? E+S==>ES **1?** ES ==> E+S	75
1? E+I==>EI 112687259.7 EI==>E+I	0.07543
9.57E+06 ES+I==>EIS 3782608.696 EIS==>ES+I	2.53
5.53E+07 EI+S==>EIS 3.09E+06 EIS==>EI+S	17.87
7.13E+06 EI+P==>EIS 2.01E+05 EIS==>EI+P	35.5
1.14E+05 ES==>E+P	

END

One can fit initial temperature, initial concentration, external concentration, flux, rate constant, Arrhenius factor, the energy of activation, and any parameters for Troe, Lindemann, SRI, Landau-Teller, and **third body enhancement factors**. There are sample batch files, **FITTESTx.BAT**, located in the **FITTESTS** subdirectory. These sample batch files, when run, will fit various parameters to various data. Some use different –FIT options, such as larger tolerance settings (-FIT switch option 'd' in Table 11 above) which cause the optimization to finish much quicker. You can examine the one-line Kintecus call in those files and modify them.

Once Kintecus is finished optimizing your parameters, it will write a file name **optout.txt** in the current directory. This file will contain the final optimized results, the final data to simulation difference, and the total iterations. These values are also duplicated to the screen. In addition to the output concentration file, CONC.TXT will contain the concentrations/temperature for the final optimized model. You should plot this file, CONC.TXT, against your experimental data and compare them. Note that the heading for CONC.TXT is not present, but it is stored in the file HEADINGS.TXT, which can be inserted at the top of the CONC.TXT file. Since most, if not all, the time series in CONC.TXT should line up with your experimental values, you should be able to easily plot the residuals (your data minus the simulated data) and see if the residuals are small and "noisy" this indicates a good fit.

Fitting Molar Extinction Coefficients

A new feature in Kintecus V3.5 is the ability to extract molar extinction coefficients (also known as molar absorptivity or epsilon ε, from $A = \varepsilon \cdot l \cdot c$) from a series of absorbance values **or** a series of concentration values multiplied by some weight. A sample Excel Spreadsheet named **Enzyme_Regression_Molar_Extinct.xls** demonstrates this feature. The fitdata worksheet now contains absorbance values (instead of the usual concentration values) recorded at some wavelength. To extract molar extinction coefficient(s) (or a weight factor) from your absorbance values, give the -FITWEIGHT switch on the command line with these options:

-FITWEIGHT:X_1:Y_1[:X_2:Y_2:X_3:Y_3:X_n:Y_n]

X represents the column number in your fitdata file/worksheet, and Y represents the starting weight guess. A significant note is that the Y's should be the ***reciprocal*** of your weight (1/weight), so if you had absorbance values for Y, then Y would be equal to (1/ε) assuming a path length, *l*, of one. Multiple columns can be selected to extract/fit multiple weights or molar extinction values. A sample fitweight command can be given as: "**-FITWEIGHT:3:0.1"**. This example will state to the optimizer that column 3 of your fitdata worksheet or file contains data in which a starting guess weight (or factor or absorbance value) of 0.1 will be used. Kintecus will continually integrate your model and change the factor until a data difference between the calculated model and your

data is at a minimum. Again, the **reciprocal** of your absorbance value or factor or weight will be reported (1/weight). Constraints (see below) can also be applied to the -FITWEIGHT switch, i.e**. -FITWEIGHT:1:0.01(1E-9<5)?:5:0.09(1e-4<0.1)?** . This FITWEIGHT switch given shows two columns of absorbance values to extract weights or factors or 1/epsilon. The first column weight has a starting guess of 0.01 and is constrained to stay between (inclusively) 1 x 10^{-9} and 5, while the fifth column has a starting weight of 0.09 and is constrained to stay between 1 x 10^{-4} and 1 x 10^{-1}.

Applying Constraints

A new feature in Kintecus V3.5 is applying constraints to any parameter you wish to fit data. This feature can help when the parameter you are trying to fit/optimize goes into the "wild blue yonder" or heads towards infinity. Usually, when this happens, Kintecus will either error out with an overflow, or your model becomes so stiff by such large values that it may take forever to do a single run. Only when this happens and you have tried these optimizer/comparators: "-FIT:2:1", "-FIT:2:3", "-FIT:1:3" and "-FIT:1:1" should you apply a constraint.

A constraint is designated by enclosing the parameters bounds between parenthesis and delimited by a less-than symbol, "<" and must appear before the question mark, "?". An example is given below of a constraint being applied to a rate constant:

1.2345E+5 (1E+3 < 1E+7) ?	**A+B➔C+D**

Table 14. A sample constraint for a rate constant. The optimizer will stay within the lower bound 1 x 10^3 and upper bound 1 x 10^7.

As usual, the optimizer will alter the rate constant, but the optimizer will always select numbers that full within (inclusive) the constraints of 1 x 10^3 and 1 x 10^7.

Keep in mind that constraints can appear **anywhere.** To apply a constraint, one can select any numeric parameter: rate constants, initial concentrations, Arrhenius parameters, residence times, **third-body enhancements**, TROE factors, molar extinction coefficients, etc. Most of the time, you do not want to apply a constraint as it will not allow the optimizer to gather enough information about the local gradient and it may fail to converge. This failed convergence is noticeable by a "bouncing" of the optimizer about the ceiling (upper-bound constraint) or against the floor (lower bound constraint). If you see such a phenomenon, increase the range of the constraint or remove the constraint on that parameter.

Equilibrium Constant Constrained Rate Constant Fit

Constraining a rate constant against an equilibrium constant is a new feature in Kintecus V3.8. A sample Excel Spreadsheet name Enzyme_Regression_Fitting_REVERSE_Rate.xls demonstrates this feature. If you have determined the equilibrium constant of a reaction,, you can constrain the backward rate constant against the equilibrium constant during a fit. This is accomplished by specifying the forward rate constant of a reaction multiplied by $1/K_{eq}$, i.e.
(assuming in this case K_{eq} is 3.0 and E+S➔ES is the first reaction)

1.0e+8?	E + S ==> ES
k1*0.333333?	ES ==> E + S

If "E+S➔ES" was the 53rd reaction in your model, then you would constrain the reverse rate against the equilibrium constant by specifying "**k53*0.333333?"** as the first field.

This allows one to reduce the total number of rate constants by half, so if you have 20 rate constants to fit, and you determined the equilibrium constants of all 10 reversible reactions, then there are only 10 rate constants to fit.

Please see **"Global Data Fitting/Regressing with Multiple User Defined Constraints**" below for much more complicated constrained fits utilizing user-defined equations. This is a new feature in Kintecus V6.00+.

Fitting/Regressing with weights/standard deviations/error bars

A new feature in Kintecus V3.96 is the ability to fit/regress your model against experimental data that contain errors or "less important" data. This can be accomplished by specifying a weight after your experimental data value. These weights are numbers surrounded by parenthesis after a data value in your fitdata.txt file like this:

Time(s)	A	B
0	1e-5	2e-5(0.1)
1	0.5e-5	2.5e-5(0.1)
3	0.5e-6(50)	3e-4

The above table shows that the data in column B is one-tenth the weight versus the data in column A for Times at 1 and 2 seconds. At 3 seconds, the 0.5e-6 data point of species A is 50 times the weight of 3e-4 for column B. Data without any weights are assumed to be one (1). You can "turn on" the weights option by adding 32 to the optimizer type part of the FIT switch, so -FIT:2:3 would become -FIT:34:3 or -FIT:1:1 would become -FIT:33:1.
A sample Kintecus-Excel spreadsheet (**Enzyme_Regression_Fitting_WEIGHTS_TEST.xls**) demonstrates how one can extract rate constants from such an example.

Fitting/Regressing with Special Outputs Against Experimental Data

Kintecus V3.96 and up allows the creation of special outputs that are functions of species Concentrations or temperature that can be regressed against experiment data. This feature has many essential uses in regression and data analysis. In this example, one is monitoring four wavelengths for absorbance. Still, each wavelength contains the absorbance from another species, so one cannot extract the concentrations from a kinetic run because one does not know how much "contamination" from another species' absorbance that is present, so you could not perform any data analysis with such an experiment. This type if data analysis can now be accomplished by utilizing the new "OUTC[…]" Special Species Directive Operator. These new species operators allow one to output a function of the species concentrations (or temperature) during a simulation run. The OUTC[] operator only allows summation, multiplication, and negation. A semi-colon represents summation, ";" and NOT THE plus sign, "+." This is to eliminate any confusion between a cation and summation. Multiplication is represented by an asterisk, "*." Subtraction can be represented by placing a minus symbol, "-" before a term.

One model example is monitoring four wavelengths for absorbance. Still, each wavelength contains the absorbance from another species, so one cannot extract the concentrations from a kinetic run because one does not know how much "contamination" from another species absorbance is present. You could not perform any data analysis with such an experiment using previous versions of Kintecus. Shown below would be the sample Species Description Worksheet for the model:

#	Species Description Spreadsheet					
# Species #	Residence Time in CSTR(s)	Initial Conc.	Display Output (Y/N) ?	External Conc.	Species Special Directives (/N)	Constant File? (Filename/#/No)
E	0	4.00E-09	YES	0	No	No
S	0	6.00E-02	YES	0	No	No
ES	0	0	YES	0	No	No
I	0	4.00E-05	N	0	No	No
EI	0	0	N	0	No	No
EIS	0	0	YES	0	No	No
P	0	0	N	0	No	No
A(E)	0	0	YES	0	OUTC[E*3200;S*300]	No
A(S)	0	0	YES	0	OUTC[E*300;S*3700]	No
A(ES)	0	0	YES	0	OUTC[ES*4000;EIS*100]	No
A(EIS)	0	0	YES	0	OUTC[ES*100;EIS*5200]	No
END						

For species A(E), Kintecus will output 3200*[E] + 300*[S] during the simulation. For species A(S), Kintecus will output 300*[E] + 3700*S, etc.

In general, species that

(a) have an OUTC[] function and are NOT part of a chemical reaction (ie., such as A(E), A(S), A(ES) and A(EIS) shown in the Species Description Spreadsheet above) will only serve as an output function and NOT participate in any state calculation or rate calculations.

And species that

(b) have an OUTC[] function and ARE part of a chemical reaction will only serve as part of the rate calculation but will NOT participate in any state (system heat capacity, pressure, etc.) calculation.

For (b) to happen, the species that has an OUTC[] operator and is part of a chemical reaction will be designated as (b). Users can utilize type (b) species for reaction rates that involve families of species. Please see the Kintecus-Excel workbook "Kintecus_workbook_MCM_examples.xls" as an example. Note the OUTC[ ] operator present in the "Species Special Directives" columns inside the workbook "Kintecus_workbook_MCM_examples.xls." Species RO2 will always be equal to the sum of the concentrations of CH3O2 and CHO for whatever reaction the species family RO2 appears in. It is possible to define one species' family with other families. One could have R=RO2+RH, where RH is the sum of another set of species. Just be sure the larger families appear further down in column A as Kintecus sums the families top to bottom.

For species, A(E), if one wanted to subtract 300[S] from 3200[ES], the OUTC[] operator can be written as OUTC[E*3200; -S*300], also OUTC[-300*S;3200*E] would also work.

A sample Kintecus-Excel spreadsheet (**Enzyme_Regression_Fitting_Multi_Absorb.xls**) demonstrates how one can extract rate constants from such a multi-absorbance example. Naturally, other examples can be shown with other outputs (heat, temperature, fluorescence, etc)

Fitting/Regressing with Heat Output

Kintecus V5.00 and up now supports the ability to regress/fit against heat generated during a reaction. This is accomplished by specifying "OUTC[SYSTEMH]" in the "Species Special Directives" column listed in the Species worksheet for a species with the name of "enthalpy." An example Kintecus-Excel workbook demonstrating this is "**Combustion_workbook_OH_enthalpy_fit.xls." Note that the experimental output containing the heat output must be named "enthalpy" for Kintecus to latch on and regress against.**

Global Data Fitting/Regressing with Multiple Datasets with/without Initial Conditions

Kintecus V5.00 and up now supports global data regression/fitting/analysis. You can regress or fit or optimize multiple datasets with multiple initial conditions such as temperature, pressure, concentration or any combination with data sets with different time scales, time steps, species, temperature profiles, weights, heat output, etc. Each dataset can be very different from the others. You can also fit local values (concentrations, temperature, etc.) with each dataset. There are many sample Kintecus-Excel worksheets demonstrating some basics of this new global regression:

Enzyme_Regression_Fitting_Multiple_Datasets_and_initial_conditions.xls
POLYMER_MULTIFIT_MULTICONDITIONS.xls
Combustion_workbook_OH_multifit.xls
Enzyme_Regression_Fitting_Multiple_Datasets.xls
Zhang_aerobic-Fitting_Multiple_Datasets.xls
Zhang_anoxic-Fitting_Multiple_Datasets.xls

A user can turn on Global Analysis by setting the third option (option c) of the "-FIT" command to "fitdatan." Once this option is on, you MUST name the datasets like this, "fitdata1.txt", "fitdata2.txt" up to "fitdatan.txt." Kintecus will search the current directory for text files with those names and use those in the regression. If you examine the sample Kintecus-Excel workbooks listed above, one will see worksheets with the name "O_fitdata1.txt", "O_fitdata2.txt," and "O_fitdata3.txt". Once a user clicks RUN in any of the above sample Workbooks, the macros will output all those worksheets prefixed with "O_" as tab-delimited text files.

Global Fitting/Regression with Multiple Initial Conditions

As mentioned above, one can regress or fit or optimize multiple datasets with multiple initial conditions such as temperature, pressure, concentration, or any combination. This is accomplished by providing a tab/comma delimited text file filename to the "fitdatan" option listed above. This results in a "-FIT" switch that will look something like **"-FIT:2:3:fitdatan,initial_conditions.txt"** where "fitdatan" states to turn on global fitting, and the added comma-delimited filename "initial_conditions.txt" states to Kintecus that each "fitdatan.txt" dataset will have a unique initial condition that was utilized to create it. One can set one or more initial conditions for each dataset by specifying the species' name on each line followed by an equal sign, "=," then followed by the value. If there is more than one condition, you must delimit those multiple settings by a semicolon, ";." If you wish to set a temperature for a dataset, use "temp" or "temperature" followed by an equal sign then the temperature. Each "fitdatan.txt" file present MUST have a row defining any initial condition different from the species worksheet or parameter worksheet (such as temperature).

The example Kintecus-Excel workbook named "**Enzyme_Regression_Fitting_Multiple_Datasets_and_initial_conditions.xls"** demonstrates this. The workbook

has two experimental datasets named "fitdata1.txt" and "fitdata2.txt". The first experimental dataset, "fitdata1.txt," was created with the species [E] and [S] concentrations set to 4e-9 M and 6e-2 M, respectively. The second experimental dataset, "fitdata2.txt," was created with the species [E] and [S] set to 8e-9 M and 1.2e-1 M respectively.

The example Kintecus-Excel workbook name "**Combustion_workbook_OH_multifit.xls"** demonstrates a global regression with different starting temperature values for each experimental combustion dataset.

One can now also regress/fit the initial conditions for a species (or temperature) in any of the initial_conditions.txt files. Other numerical codes sometimes call these variables ***local variables,*** while any fitted variables in the "SPECIES.DAT" or "PARAM.DAT" or "MODEL.DAT" are called ***global variables*** to fit.

These types of local fitting can be done by suffixing any numeric value in an initial condition file with a question mark, "?". For example, if the second data set had an unknown concentration of oxygen (using a guess of 2E19 molec/L) and a user wishes to regress this against the data, then these two lines in the initial_conditions.txt will change

FROM:

temp=615 ; isoprene=1.43e14 ; O2=1.89e19
temp=610 ; isoprene=1.73e14 ; O2=2e19

TO:

temp=615 ; isoprene=1.43e14 ; O2=1.89e19
temp=610 ; isoprene=1.73e14 ; **O2=2e19?**

(note the question mark appended to 2e19)

The example Kintecus-Excel workbook name "**Combustion_workbook_OH_multifit.xls"** demonstrates a global regression with different starting temperature values for each experimental combustion dataset.

Global Fitting/Regression with Constant Held Initial Conditions

Kintecus V2021 now supports the option of holding concentrations/temperatures/pressure constant between datasets for global regression runs. In earlier versions of Kintecus, one could set initial conditions for each experimental dataset. These initial conditions could change during a global regression run. One now can hold this initial condition constant for each experimental dataset. For example, suppose one was performing regression with many datasets with different initial conditions for each experiment (such as pH). In that case, one can now set pH values (or temperature or any other value) to different starting constant values for each run in the initial condition file, and that value will not change. It is possible to have different constant initial values for each regressed experimental dataset as specified in the "initial_conditions.txt" file. This feature can be accomplished by setting the first constant value in the "Constant File?" column for that species in the "SPECIES" worksheet. This will flag Kintecus to keep values in the "initial_conditions.txt" for that species to remain a constant for that data set. Again, you can change the constant initial values for each dataset by specifying new constant values in the "initial_conditions.txt" file.

Global Data Fitting/Regressing with Multiple User EQUATION Defined Constraints

To use fitting with fit links, you have to supply the keyword "FITLINK" as the first field in option c of the "-FIT:" switch, so this "-FIT:2:2" becomes "-FIT:2:2:FITLINK" and this "-FIT:2:2:FITDATAN,initial_conditions,txt" becomes "-FIT:2:2:FITLINK,FITDATAN,initial_conditions.txt". FITLINK must always be first, and for plotting, one needs to use the latest Kintecus-Excel worksheets with the latest VBA code to correctly plot and output results.

The "FITLINK" flag will state to Kintecus to look for a text file named "fit_links.txt." This file will contain the list of equations (the links) computed between each iteration. **You can use fairly complicated formats if you want, such as k1=(log10(k2*k3/k4+k5)/(k6+k9))*0.5 or fairly complicated linked parameters such as E6=((E1+E2+E3+E4+E5)/5/k2+LOG10(acos((k3+k4)*k5))**, where LOG10() is the logarithm base10 and acos is the ArcCosine function. You can specify k, A or m or Ea for reaction n in an equation,
Please use this format: k**n**, A**n**, m**n** or E**n** where **n** is the reaction containing the rate constant, Arrhenius constant, m or E value. Use T for the current temperature. One does have to preclude each equation with the list of independent variables that appear delimited by commas, **","** or vertical bars, **"|"** (for those countries that use commas as decimal points). For example:

A23, m23, E23, T ; k24=A23*1e-9*T^m23*exp(-E23/8.314*T)

Or another example:

E19, E20, E21; E24=(E19+E20+E21)/3

OR (**for those countries that use commas as decimal points and cannot use commas as delimiters, so vertical bars, "|" must be utilized instead**)

E19 | E20 | E21; E24=(E19+E20+E21)/3

The last function will force the energy of activation to be constrained by the average of three energy of activations from reactions 19, 20, and 21. Most functions found on standard hand-held calculators are implemented such as COS, SIN, TAN, etc. [34].

"**Enzyme_Regression_Fitting_reverse_rate_fit_new_way.xls"** is an example.

Statistical Output from Fit

Kintecus V3.7 now outputs a slew of statistical information on how well the fit of the calculated outputs compares with the experimental data. To fully explain all the output descriptors is beyond the scope of this document, but some of the more critical and common descriptors will be explained below.

Appendix A shows a sample OPTOUT.TXT file that is created when FITTEST3.BAT is run or from the Excel file "Enzyme_Regression_fitting.xls" with the switch addition of **"–FITSTAT"** on the Kintecus command line. One can now calculate standard deviations for the parameters one is trying to obtain a fit. This is accomplished by adding the **"-FITSTAT"** switch on the command line. Since an asymptotic approximation is implemented to obtain the standard deviations for a set of non-linear differential equations, sometimes this approximation doesn't work.

> **NOTE:** The asymptotic approximation is a common technique to obtain the standard deviations for fitted parameters from a set of non-linear equations, but sometimes can yield incorrect results. A more appropriate technique would be an expensive Bootstrapping via Monte-Carlo runs (**see below under Bootstrapping**).

By examining the sample output in Appendix A we see parameters 1, 2, and 3 have been fitted to: **4999225.21, 66735.0769, 8495129.31** (the red numbers at the top), and with standard deviations (numbers in blue), we can report the fitted values **as 4,999,225 +/- 617,030, 66735 +/- 475 and 8,495,129 +/- 88,399.**

Continuing through the output in Appendix A, we see the title "START OF PREDICTION ANALYSIS," which signifies the beginning of the residual analysis of your experimental data against the calculated data using the final fitted parameters. Some of the essential values to know are the "R-squared," "Correlation Coefficient," the "Est. Std. Dev. Of Model Error," and the "Shapiro-Wilk W-test." As the calculated final concentrations fall closer and closer to the experimental data, the R-squared will approach 100% (1.0), the Correlation Coefficient will approach 1.0 (with a "Probability" close to zero), and "Est. Std. Dev. Of Model Error" will approach zero. While the R-squared and Correlation Coefficient have no units, the "Est. Std. Dev. Of Model Error" has the same parameters as your concentration units (or temperature unit of Kelvin). If one subtracts the calculated concentrations from the final fitted parameters from the experimental data, one obtains residuals. Along with a residual plot (which should be "noisy" that have a Normal distribution and small magnitude relative to the data), an excellent numerical technique to quantify the normality of those residuals is the "Shapiro-Wilk W-test." Perfect normal distribution of the residuals will have a "Shapiro-Wilk W-test" of 1.0 with its corresponding "P-value Test of Normality" close to zero. The user is strongly recommended to obtain a book or a web source with complete definitions of the above-described statistical parameters and the other parameters present in the output file. Kintecus will output statistical descriptions for each column of experimental data located in the FITDATA.TXT spreadsheet or file. Since the Excel file "Enzyme_Regression_fitting.xls" has four columns of experimental data, you will see four sections that all start with "Start of prediction analysis for data-column: **nnn** (SPECIES NAME)" where **nnn** is the column number with the corresponding species name. The PREDICTION ANALYSIS ends with, "END OF PREDICTION ANALYSIS."

Bootstrapping

A new method in Kintecus V3.8 allows one to obtain very accurate standard errors from the fitting process. This method is known as "Bootstrapping" and has recently been accepted as one of the best methods to obtain standard errors[1]. Kintecus will report the bootstrapped errors in the OPTOUT.TXT file. The Bootstrap method of determining standard errors of fits can be summoned by the use of the **"-FITSTAT:BOOT"** switch. There are additional options for this switch:

-FITSTAT: BOOT:[TYPE]:[AMOUNT]:[% REPEAT]

There is currently only one type of bootstrapping method available and [TYPE] should be left set at 1 (one). The [AMOUNT] specifies how many iterations Kintecus should re-optimize the fits to obtain errors. The default for [AMOUNT] is 100. Values between 100-1000 are typical and can improve the errors, BUT can require much more computer time. Keep in mind, [AMOUNT] represents the amount of new data-set iterations Kintecus creates and starts a NEW optimization/fit run. If one fit/optimization run required 20 minutes then the maximum amount of time for 100 optimization runs would require 20 x 100 = 2,000 minutes = about 33 hours maximum. In reality, it probably would take 10-15 hours as Kintecus starts additional optimization runs with near guesses from the first optimization run. You might also want to decrease the accuracy by ten or so (located on the parameter spreadsheet) if the model becomes too stiff during the bootstrapping. This can happen because tens of thousands to millions of kinetics runs will be executed and the probability of your model becoming stiff is high. An example of change in accuracy before starting a bootstrap would be if your accuracy were set at 1.0E-8, you would then decrease it to 1.0E-9 or 1.0E-10.

For large or very slow kinetic systems, even just 20 bootstrapped optimization runs would require a week, so if you have access to more than one computer, you can distribute the optimization on more computers by running Kintecus on each machine with the same switches and including the "-rand" switch on the command line. The "-rand" switch will set all of Kintecus' internal random number generator seeds to values of the system clock. This will create different distributions of your data sets on each machine required for the bootstrapping process. If you do not enter the "–rand" switch on the command line for each computer n, then you will simply create n bootstrap values of the **same exact value(s)**!

***NOTE: When bootstrapping for standard errors, but on many computers, you must include the "-rand" switch on the Kintecus command line! Not including this additional switch will cause Kintecus to create the same exact bootstrapped errors on each machine!**

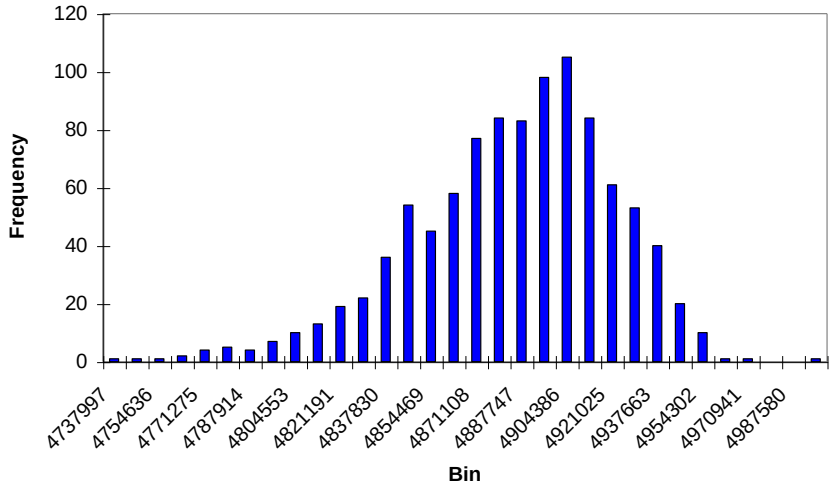
It is unlikely that the computers you run Kintecus on will have the same internal timings, so the random number generators should produce different runs on each computer. Although Kintecus will report bootstrap errors in the OPTOUT.TXT file, those errors are for only the machine Kintecus was running. You will need to concatenate each parameter_nnn.txt (where nnn is an integer) from each machine into one larger parameter_nnn.txt file(s). If you were determining standard errors for three parameters you were fitting (say, three rate constants), there would be three parameter_nnn.txt files: parameter_001.txt, parameter_002.txt, and parameter_003.txt on each computer containing bootstrapped optimized values. You then would concatenate each individual file from each machine into one larger parameter_001.txt file. Now, simply calculate the standard deviation from each of those files. The standard deviation from the large concatenated parameter_001.txt file will represent the bootstrapped standard deviation of parameter 1. Below is a histogram plot of 1,000 bootstrapped runs fitting the rate constants from the enzyme model. A sample Kintecus-Excel model spreadsheet demonstrating bootstrapping on a simple enzyme model includes "Enzyme_Regression_Fitting_BOOTSTRAPPING.xls."

The [% REPEAT] specifies the probability a data-point in your experimental data is replicated into the bootstrapped data (see refs [1]). The default value is 1/e, about 36.8 % and is the recommended value. You shouldn't have to change this value.

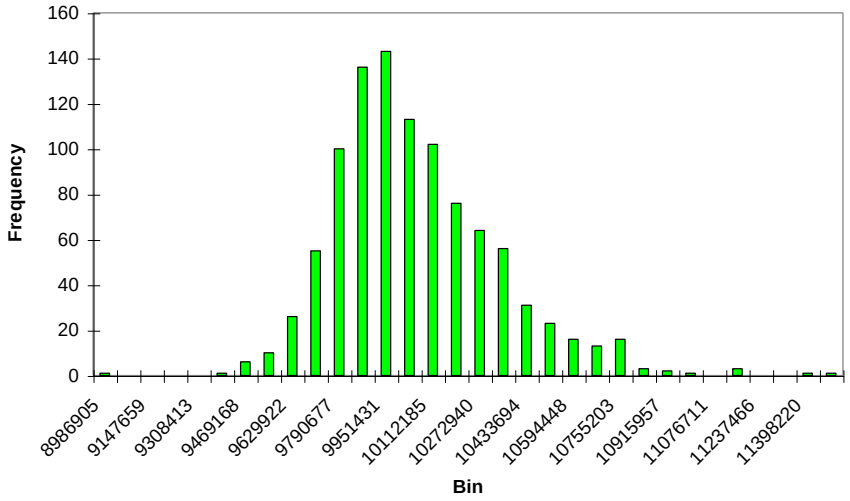
Shown below are the bootstrapped rate constants from 1,000 runs. The rate constants are fits the model in the Kintecus-Excel Spreadsheet: "Enzyme_Regression_Fitting_BOOTSTRAPPING.xls." Kintecus reports their average bootstrap values with bootstrapped standard errors as `4,880,502 +/- 36926, 1,0014,887 +/- 281540, 5,2018,244 +/- 1,907,300.` These histograms were manually plotted in Excel. This can be accomplished by

- Pasting each Parameter_nnn.txt file into a worksheet
- Make sure the "Analysis Toolpak" is present:
- Go to Tools Menu-->Add-Ins, make sure in the Add-Ins window, "Analysis ToolPak" is check marked
- .Make the Histogram: Tools-->"Data Analysis," select Histogram in the "Data Analysis" window, select your "Input Range," click Labels, in the output options select "New Workbook" and click "Chart Output", click OK.

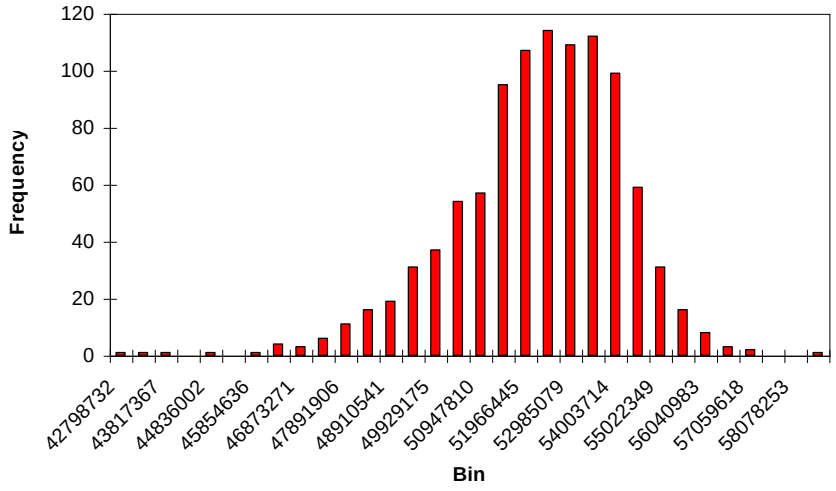
Rate Constant 1 Bootstrapped Values



Rate Constant 2 Bootstrapped Values



Rate Constant 3 Bootstrapped Values



Some Tips To Quickly Start Optimizing

Once you have saved your data in a text file named FITDATA.TXT (this is the default name for your datafile Kintecus looks for, you can name it to another filename by using the –FIT switch), you can quickly get started by using the –FIT:2:3:FITDATA.TXT switch on the Kintecus Command line. **ALSO,** try –FIT:1:3:FITDATA.TXT on the Kintecus Command line and compare the results. In addition, you should also re-run with the –FIT:1:1:FITDATA.TXT and the –FIT:2:1:FITDATA.TXT and compare all four sets. Be prepared; optimizing more than one value can take some time.

Optimizing stiff reactions such as those in a combustion model can be challenging. You will most likely get OVERFLOW ERRORS. These errors are due to the optimizer picking values that make the system stiffer than where it started. A quick solution is to reduce the accuracy in the parameter spreadsheet to 1/100, 1/1000, or even 1/10,000 of the current accuracy value. You should have accuracy in the 1 x 10(-8) to 1 x 10(-12) range. Another problem with optimizing combustion models is that the optimizer might put the system where the temperature is too high (or low) for one or more species' thermodynamic coefficients' range. An additional option has been provided for the –THERM switch: **FORCE**. For example, "-THERM:THERM.DAT:FORCE" or "–THERM:D:FORCE". This new option will "force" the optimizer **AND** the integrator to use temperature values that are within all the species' thermodynamic coefficients' range and should alleviate your OVERFLOW problems. You can also try different integrators like -INT:4 or -INT:2.

You can also apply a constraint for the parameter you are trying to fit (see above on applying constraints).

Be Careful!

The fitted values can be COMPLETELY WRONG even if you managed to get a great fit to your data and it passes every statistical test you can throw at it! This result can be especially true when you fit more than one value. For example, if a user tried to optimize all three expanded Arrhenius options simultaneously at one temperature. Depending on your starting guess, one user might get A=9.20E+16, m=-0.6, and an E_a=1.1841 KJ, but another user might get A=1.10E+15, m=0.588, E_a=2.57 KJ and at 298 K both sets yield the overall rate constant 4.08 x 10(14)! Who's right? That depends on further molecular detail of the system. Can E_a be estimated and frozen in the optimization? Maybe the Arrhenius factor can be calculated or referenced from literature and frozen during the optimization? Perhaps you should just optimize k, and forget about the three expanded Arrhenius parameters? Other examples can be shown! Be careful!

Also, a new feature in Kintecus 3.1 and higher is detecting the number of significant digits in the Time(s) column of one's experimental/fabricated data to fit (the FITDATA.TXT file). Kintecus will only allow time digits of six or less significant digits in the Time(s) column of the experimental/fabricated data. Kintecus will round your Times in the Time(s) column to six significant digits if there are more. If you need more significant digits for your Times in the Time(s) column, you can use the –SIG:n (1<n<16) switch to specify the number of significant digits Kintecus should keep for the times. It is recommended that the number of significant digits should not exceed eight or nine. Selecting eight or more significant digits can slow the fitting procedure tremendously, or data points in the fitdata.txt file might be skipped.

6. Equilibrium Mode

Kintecus allows one to enter an equilibrium mode. This mode can be invoked by including the '-EQUIL' flag on the Kintecus command line. Once Kintecus is in this mode, the system of differential equations used to solve the kinetics problem turns into a problem of minimizing the system's Gibbs Free (or Helmhotz) energy. The model spreadsheet file is no longer required. Only the species spreadsheet and parameter spreadsheet files are needed to run an equilibrium model. One does not need to specify what species are products or reactants, "shove them in," and "churn out the results." Of course, provided the user's species are present in one of the thermodynamic databases described by the Thermodynamic Description SpreadSheet, can Kintecus run an equilibrium run. There are some advantages and disadvantages in constructing an equilibrium model of your system instead of a more accurate kinetic model. A few benefits are listed:

- There is no need to create a kinetic model painstakingly. This can take quite a while to do.
- Equilibrium models always finish. Some kinetic models may require millions of cycles to see the results at a very large ending time (decades, centuries, etc.)

Some disadvantages of an equilibrium model over a kinetic model

- Equilibrium models always finish, so you do not have a time profile evolution of the concentrations, temperature, and other system values. This can lead to a few significant problems:
- You do not know if a poisonous, dangerous, or reactive intermediate grows to too large a concentration or if the intermediate temperature may be too large/small or some other system value at a specific time.
- As the system runs to simulate real-world conditions, you cannot specify a loss/gain of mass, heat, or phase/volume changes.
- Again, with no time profile of concentrations, one cannot maximize the concentration of a valuable product.
- It may take forever to get the system's final state, but you will never know how much time it will take as equilibrium runs assume a time of *zero* always.
- Even in a "perfect" adiabatic, no mass in/out container, the system may change one of its phases so that the initial description of the starting phase(s) is wrong.

Additional "-EQUIL" switches

The EQUIL switch in Kintecus 3.1 has additional, optional sub-options that allow you to speed up slow equilibrium runs or to obtain an answer for rare systems that can cause Kintecus not to converge. There are three new sub-options for the EQUIL switch: c, j, and k:

-EQUIL:a:b:{c}:j:k

Option "a" gives Kintecus the name of The Thermodynamic Description SpreadSheet or enter a "D" to use the default Thermodynamic Description SpreadSheet name of "EQTHERM.DAT." Option "b" is only helpful if you apply perturbations to the system. For a full explanation of species perturbations and their use, click here: Species Description Spreadsheet and look under the "Constant File ?" field description. The new option "c" in Kintecus V3.1 allows one to control the convergence criteria for the non-linear solver. The user can either specify a keyword or individually set the numeric options. The keywords for option "c" are VERY-LOOSE, LOOSE, TIGHT, VERY-TIGHT, where TIGHT is the default setting. Option "c" can also be composed of four numeric parameters {e,f,g,h} separated by commas (values in parenthesis are the default values for the TIGHT setting):

e = function tolerance (3.0E-9)
f = minimum value tolerance (2.0E-9),
g = x-value tolerance (3.0E-12)
h = maximum search step allowed (200.0)

The smaller the e, f, and g parameters are, the slower Kintecus will achieve a final equilibrium solution. Sub-option "h" defines the maximum search step allowed in the non-linear solver. Increasing sub-option "h" usually results in faster solution times for constant temperature runs. Still, it sometimes can "hop" over the correct solution and end in a not-so-correct solution. A good example is the H_2SO_4 equilibrium run with a temperature program (see the console batch file equilb.bat or the Excel worksheet: H2SO4_Equilibrium_Phase.xls). The default setting for the maximum search step allowed is 200. This maximum search step size works fine for most of the program temperature range specified in the H2SO4_Equilibrium_Phase.xls. Still, at the higher temperature values (above 900 K), the non-linear solver "hops" right over the correct solution and converges near a local, somewhat incorrect minimum. This problem is easily solved by specifying a smaller maximum search step size of 50. The final equilibrium solutions for the H2SO4 system above 900 K are now correct, even though Kintecus reports some convergence warnings. Those convergence warnings, in this case, are spurious and can be safely ignored (see below).

The other two new options in Kintecus V3.1: options "j" and "k" allow one to converge those rare equilibrium systems that do not converge with the default settings:

j = Maximum number of iterations to try before the non-linear solver quits. Default is 30,000.
k = Maximum number of non-linear solver tries. (Default=75)

It should be noted that Kintecus V3.1 now double checks the solution the non-linear solver converges to. If Kintecus doesn't "like the solution," Kintecus will "throw" the solution back into the non-linear solver. Kintecus will keep doing this until the "Maximum number of non-linear solver tries" (the default is set to 75) has been reached. If the "Maximum number of non-linear solver tries" is achieved by Kintecus, Kintecus will report a warning about its inability to arrive at a "properly" converged solution. Sometimes this convergence warning is spurious and can be safely ignored, as in the H2SO4 case described above.

A user with problems with the time to finish a final equilibrium run or force Kintecus to converge to a solution can change the default values for options "j" and "k." Typical changes are to decrease the default value "j" to 15,000 and to increase "k" to 100-125, or increase "j" to 45,000 and decrease "k" to 5-10. One can also reduce or increase the maximum search step allowed (option "h" described above) to converge to proper equilibrium solutions or decrease the computational time to arrive at the final equilibrium solution.

Kintecus V3.9 has an additional non-linear solver that a user can utilize if the initial non-linear solver described above does not work even with modifications to the non-linear solver parameters as listed above. The

additional non-linear solver can be invoked by appending the "-EQUIL" switch with the number two, "**2**", i.e. "-**EQUIL2**:(optional non-linear parameters)".

Equilibrium Example Runs

The following table contains a small sampling of Kintecus performing equilibrium runs on various systems in different states. There are also three sample Excel graphical interface spreadsheet files that implement varied equilibrium models: H2SO4_Equilibrium_Phase.xls, H2_O2_Equil_Phases.xls and H2_O2_N2_Equilibrium.xls.

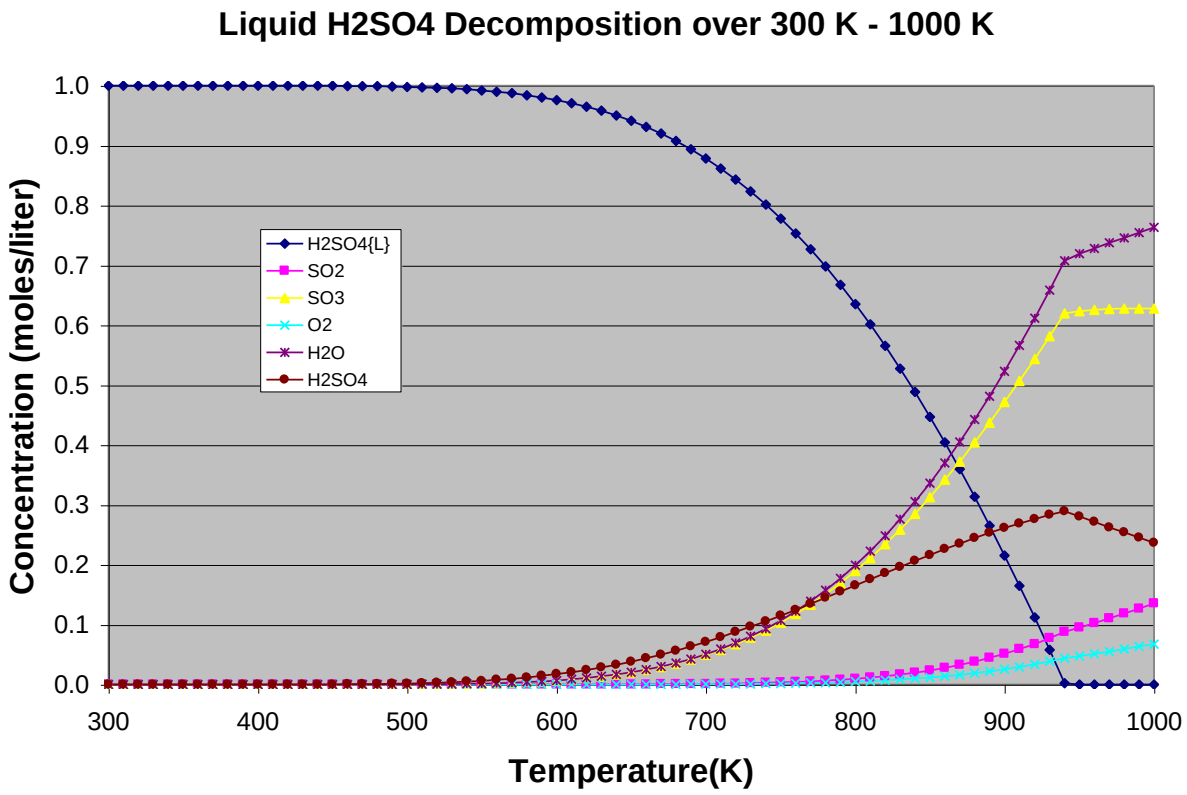
Batch File	Type of Equilibrium Run	Conditions
EQUIL1.BAT	Propane-Air Combustion	Constant Temperature Constant Volume
EQUIL2.BAT	H_2-O_2 Combustion	Constant Temperature Constant Volume
EQUIL3.BAT	Propane-Air Combustion	Constant Temperature Constant Pressure
EQUIL4.BAT	H_2-O_2-N_2 Combustion	Constant Temperature Constant Volume
EQUIL5.BAT	H_2-O_2-N_2 Combustion	Constant Temperature Constant Pressure
EQUIL6.BAT	H_2-O_2-N_2 Combustion	Variable Temperature (Adiabatic Flame) Constant Volume
EQUIL7.BAT	H_2-O_2-N_2 Combustion	Variable Temperature (Adiabatic Flame) Constant Pressure
EQUIL8.BAT	Just OH and H2O2	Variable Temperature (Adiabatic Flame) Constant Volume
EQUIL9.BAT	H_2-O_2 Combustion	Program Temperature (Range 1500K-6000K) Constant Volume
EQUILA.BAT	H_2-O_2 Combustion	Program Temperature (Range 1500K-6000K) Constant Pressure
EQUILB.BAT	LIQUID H2SO4 decomposition into various sulfur and water gases	Program Temperature (Range 300K-1000K) Constant Volume
EQUILGRI.BAT	GRI-MECH 3.0 Model Equilibrium Test Run (takes several minutes on a Pentium III)	Variable Temperature (Adiabatic Flame) Constant Volume
F1EQUIL.BAT	Fitting of Initial Concentrations for H_2-O_2-N_2 Combustion	Constant Temperature Constant Volume

F2EQUIL.BAT	Fitting of Initial Concentrations for H_2-O_2-N_2 Combustion	Constant Temperature Constant Pressure

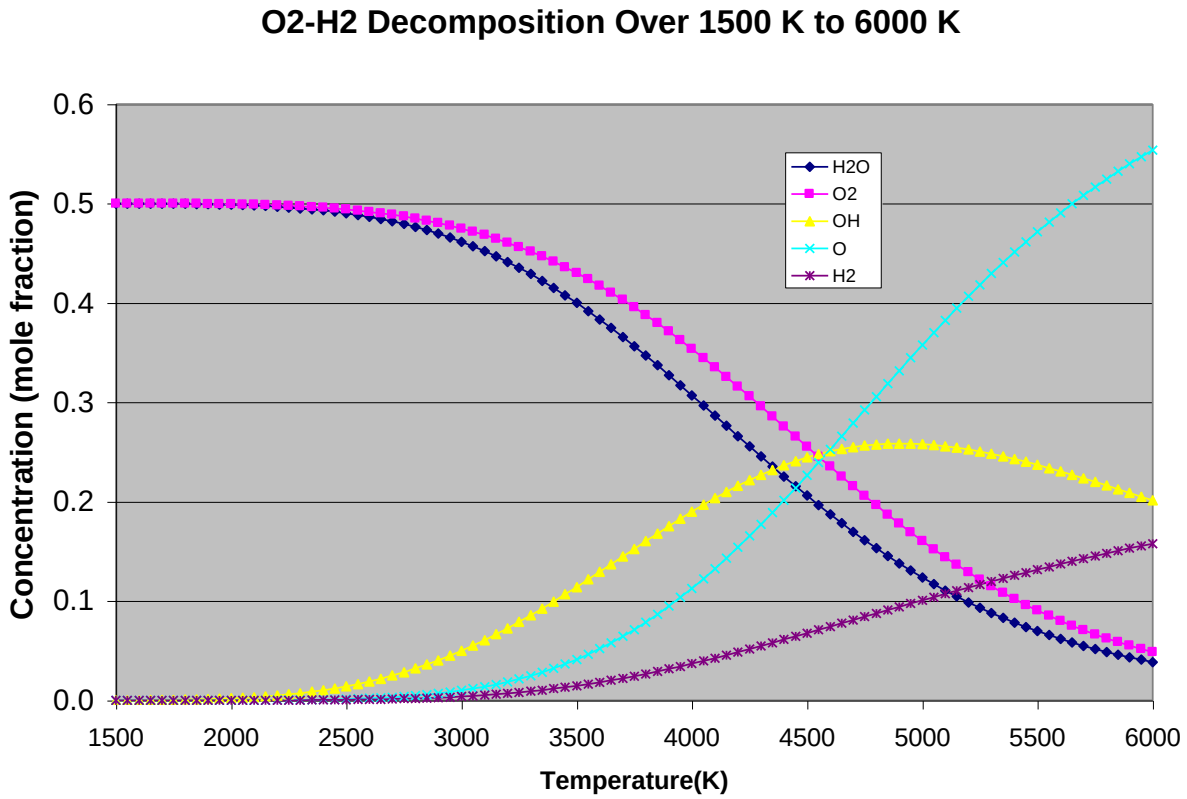
Table 15. Various sample equilibrium runs that are located in the ./Kintecus/EQUIL/ subdirectory.

Sample Equilibrium Run Plots

The equilibrium run plot shown below is from the H2SO4_Equilibrium_Phase.xls Excel file (it is also the equilb.bat file located in the /EQUIL/ subdirectory). It primarily describes the decomposition of liquid sulfuric acid into various gases as the temperature increases from 300 K to 1000 K.



The following equilibrium run plot shown below is from the H2_O2_Equil_Phases.xls Excel file (it can also be created from the equila.bat file located in the /EQUIL/ subdirectory).



True Equilibrium Versus Reaction Equilibrium

A closed, adiabatic chemical kinetic run at infinite time does not necessarily mean the run will finish at a "true" equilibrium solution if the kinetics is not fully described. This appears to be confusing many people who think Kintecus's Equilibrium mode sometimes yields incorrect results because the equilibrium solutions and the kinetics solutions at infinite time are not equal. This is not correct. The equilibrium mode in Kintecus considers ALL chemical paths that can exist for ALL species. ALL CHEMICAL PATHS must exist for a closed, adiabatic chemical kinetic reaction system to yield the same results. Let me repeat that, **CHEMICAL KINETIC PATHS MUST EXIST BETWEEN ALL SPECIES FOR THE SYSTEM TO EQUAL TRUE EQUILIBRIUM RESULTS AT INFINITE TIME.** In reality, some reactions might never happen due to such significant reaction barriers that infinite time extends beyond the end of time of the known universe. Still, in Kintecus' Equilibrium mode, all reactions happen. Which method is correct for a closed, adiabatic system is left to the user to decide.

Still confused? Okay, here is a straightforward example to demonstrate this:

1) There is a one-line sample reaction of
" 2 butene = cis2-buten + t-butene with constant temperature at 298K " can be executed with the Kintecus console run of butene.bat . To obtain the REACTION equilibrium results of this small system, have Kintecus run this to infinite time (about 10 minutes of simulation time, you will have to modify the PARMBUT.DAT file). Record the final values.

2) Now run the system in TRUE equilibrium mode (add the -EQUIL switch on the Kintecus command line of butene.bat, and delete the -THERM switch). One will notice that the EQUILIBRIUM values are DIFFERENT from

the FINAL equilibrium values from step #1 above! Do you know why? The TRUE equilibrium mode in Kintecus automatically included the equilibrium between cis2-butene and t-butene, which is **NOT INCLUDED** in the chemical kinetic model!

3) To have the final equilibrium concentrations in the butene kinetics system equal to the TRUE equilibrium concentrations, add one additional chemical reaction between cis2-buten and t-butene:

100, cis2-buten = t-butene

into the MODBUT.DAT chemical kinetic file. Now that you have provided a path for cis2-butene to isomerize to t-butene, the final equilibrium concentrations of the chemical kinetic run at infinite time (about 10 minutes of simulation time) will **NOW EQUAL** the TRUE equilibrium concentrations.

If one is trying to determine an intrinsic lower-dimensional manifold (ILDM), please remember that Kintecus' Equilibrium mode does not give you the reaction equilibrium (df/dt=0) but the TRUE equilibrium (global minimum dG/dx=0). To calculate df/dt=0, you need to run your kinetic model until the concentrations stop changing or try the –REQ switch on the Kintecus command line to calculate df/dt=0 (it is still in beta).

7. Uncertainty Analysis

Background

The ability to calculate the average concentration (and temperature) time profile with uncertainty (represented by either standard deviation bars or confidence bands) is, most likely, the most important and last procedure one should do to validate a model. Turanyi et al.[28] has shown that NOT performing such a procedure and using only one-run time profiles is quite naïve as it is the chemical kinetics/thermodynamics and **NOT** transport/convection processes that control the concentration and temperature profiles. A good analogy would be a hurricane forecaster that only shows one possible path a hurricane can take with no uncertainty bands or an average path! In addition, the uncertainty analysis in Kintecus also gives one a "smeared-out" sensitivity analysis on ALL the parameters/constants in a model and possible maximum and minimum time profiles concentrations (and temperature) can take on during all the simulations.

Uncertainty analysis/confidence band predictions and the related can now be calculated in Kintecus V3.7. Kintecus V3.7 now incorporates uncertainty analysis with a highly versatile, easy, and quick way of specifying uncertainty in ANY of the constants (rate constants, TROE factors, residence times, temperature, Cp, Cv, H, S, G, A, concentrations, etc., etc.) in several distributions (uniform, gaussian, etc.) with any number of repeated runs (which can range from several hundred to several thousand depending on the size of the model) in a straightforward, straightforward manner with the standard deviations or confidence band plots in Excel (though Excel is NOT required). Also, the maximum and minimum concentrations that a species (or temperature) can take on during all the runs can be displayed and plotted. You may wish to examine two sample Kintecus-Excel spreadsheets: "Enzyme_Uncertainty_Analysis.xls" and "Combustion_workbook_OH_CONF.xls."

Implementation

Uncertainty analysis in Kintecus is turned on by specifying the "-CONF" switch. This switch has numerous options:

-CONF{:a:b:c:d:e:f:g}

All options a, b, c, d, e, f, and g are optional, but all preceding options must be specified when setting options b to g. All options have a default setting which can be specified with the letter "D" or "d" (most Kintecus switches have this feature). Here is a breakdown of all the options (defaults are listed in brackets, [] or by entering the letter "D" for an option indicates to use the default value.):

a) Option "a" states to Kintecus the total number of samples (simulations) to run to gather final averages, standard deviations, confidence predictions, and maximum/minimum values. **[100]**
For the beginning of each simulation, the parameters the user has specified (see other options below and **Selective Parameter Uncertainty Analysis)** are changed by using either a Gaussian or Uniformly generated random number and implementing the parameter as the average (for Gaussian) or central number (for Uniform). The range of the generated random number is given as **one-sigma** for Gaussian generated (which means there is about a 1/100 chance that a three-sigma generated number can "popup") or exactly one-sigma in the plus and one-sigma in the minus

direction centered on the parameter-mean for the uniform distribution. The type of distribution can be selected for whole sets or separate parameters as described below.

b) Option "b" sets of types parameters to randomize. It has a range of 0 to 31. The types include:

Type or Set Number ID	Randomization Includes:
1	Rate constants, k or A, m and Ea
2	Initial concentrations, Residence Times and External Concentrations (if specified)
4	Initial Temperature, External Temperature, External Heat Source
8	Any values enter in M[] or S[] type reactions, such as third-body enhancements, TROE, SRI, Lindeman parameters, etc.
16	All thermodynamic parameters from the thermodynamic database (Cp, H, U, S)
31	ALL sets from 1 to 16.

Table 16. Option "b" settings. To include multiple types in the Monte Carlo/Uncertainty analysis, simply add the Set Number ID's.

In addition, the sets or types described above include default relative standard deviations that are used in the course of the uncertainty analysis:

Type or Set Number ID	Randomization Includes:	DEFAULT Relative Standard Deviation Implement in Uncertainty Analysis
1	Rate constants, k or A, m and Ea	0.05
2	Initial concentrations, Residence Times and External Concentrations (if specified)	0.02
4	Initial Temperature, External Temperature, External Heat Source	0.02
8	Any values enter in M[] or S[] type reactions, such as third-body enhancements, TROE, SRI, Lindeman parameters, etc.	0.02
16	All thermodynamic parameters from the thermodynamic database (Cp, H, U, S)	0.02

Table 17. Option "c" settings.

To define some sets and exclude others, only add the type numbers for the sets you wish to randomize. For example, to only include rate constants and initial concentrations, enter a "3" for option "b" (1+2=3), or just to randomize thermodynamic parameters and initial temperature, enter "12" (8+4) for option "b". **[31]. You can selectively specify items in any worksheet to include in the uncertainty analysis by using the "number(#/#)?" operator. Please see below under "Selective Parameter Uncertainty Analysis."**

c) Option "c" multiplies the standard deviations calculated for all species concentrations at all times (and temperature if –THERM is specified) by this value. The default is one or one sigma. **[1].**
The equation Kintecus uses for standard deviation is:

$$std.dev. = \sqrt{\frac{\sum_{j=1}^{N}(x_i - \bar{x})^2}{n-1}} \quad \bullet \quad (option\,c)$$

where n is the total number of samples or runs (from option "a" above), x_i is the value of a concentration at some time for sample run j, x-bar is the average value for a concentration at some time t for all runs.

d) Specifying one of the below confidence intervals for option "d" specifies Kintecus to calculate confidence bands instead of standard deviations. A confidence interval of 0 specifies Kintecus to calculate standard deviations instead.

There are four confidence intervals a user can specify: 68%, 95%, 99% and 99.9%. The default value is 0 **[0**] which states to Kintecus to **not** calculate confidence bands. The equation Kintecus utilizes to calculate confidence bands is:

$$Conf.Band.=\left(\frac{std.dev.}{\sqrt{n}}\right)\bullet t-value\bullet(option\ c)$$

Std.dev., option "c" and **n** are described above for option "c", the t-value at the percent confidence interval the user has specified is calculated as:

Confidence Interval	t-value
99.9%	3.28
99%	2.57
95%	1.96
68%	1.00
0%	Confidence Bands are NOT CALCULATED (default), but standard deviations are calculated.

Table 18. Option "d" settings.

e) Option "e" overrides the default relative percent standard deviations used in the uncertainty analysis as described in Option "a" and shown in Table 15 above. A user can specify a single number here to override ALL DEFAULT "Relative Standard Deviations Implement in Uncertainty Analysis," as shown in Table 15 above. The user can also specify a list followed by a Relative Standard Deviations all delimited by a comma: (set or type keyword), (relative standard deviation). So to specify the range of random numbers for the initial concentrations as 15% of the initial mean and the starting initial temperature with a random range of 9% on the initial value, we would use the "-CONF" switch as **–CONF:D:D:D:D:CONC,0.15,TEMP,0.09** (note the commas are used to delimit the keyword from its value).

Keyword(s)	Type of Parameters Included
K or A	Rate constants or Arrhenius Parameter
M or MT	Exponent, m, in T^m for expanded Arrhenius expressions
EA or E	Energy of Activation
SPEC	Special Reaction parameters (the values in S[]) and/or Third-body enhancement factors or pressure fall-off reactions as specified in M[].
CONC	Initial Species Concentrations
RESTIME or RESTIM	Residence Time
BOUNDC or BOUND	External Concentration for Species
TEMP or TEMPERATURE	Initial Temperature
EXTERNTEMP or EXTERNTEMPERATURE	External Temperature
HSOURCE or HEATSOURCE	External heat source/sink
CP or H	All thermodynamic parameters from all thermodynamic databases.

Table 19. Option "e" settings.

f) Option "f" is very similar to option "e" with the exception that option "f" handles how the parameters will be randomly distributed: **Gaussian, Uniform, Poisson, or Gamma**. This option overrides the default random number distribution used in the uncertainty analysis as described in Option "a". **Option "f" has four options: "1" for a Gaussian distribution or "2" for a uniform distribution for random numbers, "3" for Poisson distribution of random numbers or "4" for Gamma distributions.** The default is **[1],** Gaussian distribution, for all parameters. Just as in option "e", a list of keywords followed by a distribution type all delimited by a comma: (set or type keyword), (relative standard deviation). Again, the keywords and their respective representation are given in Table 18. So to specify the random distribution type for the initial concentrations as Gaussian and the starting initial temperature using a uniform random distribution about the initial value, we would use the "-CONF" switch as –CONF:D:D:D:D:CONC,0.15,TEMP,0.09**:CONC,1,TEMP,2** (note the commas are used to delimit the keyword from its value).
A note on using Gaussian (normal) distributions is that the value you give represents **one sigma**; there is about 1/100 probability that a value that is **three times greater** than the relative standard deviation you provide will be selected. You should avoid using relative standard deviations of 0.30 (30%) or greater. Using relative standard deviations of 0.30 (30%) or greater can result in negative values for initial rate constants, initial/external concentrations, and residence times. The relative standard deviation you give in uniform distributions will NEVER BE EXCEEDED in the plus or minus direction. All numbers between the parameter +/- the relative standard deviation you give have an equal chance of being selected.

g) Option "g" states to Kintecus whether to remove all the simulation concentration files (that look like CONCnnnnn.txt where n is a numeric digit) after the program is done or keep them. There are only two options for this: KEEP or DELETE. The default is to **[KEEP].**

There are two sample Kintecus-Excel spreadsheets that you may wish to examine: "Enzyme_Uncertainty_Analysis.xls" and "Combustion_workbook_OH_CONF.xls".

Here are some sample "-CONF" switches and a short description on what they do:

Sample "-CONF" switch	What does it do?
-CONF:10000:1	Run 10,000 simulations varying ONLY the rates constants or (if present) the three Arrhenius parameters (A, m and Ea) with a relative standard deviation of 5% using Gaussian distributed random numbers. All the error bars for the average concentration plot are all calculated at one-sigma.
-CONF:D:2	Run 100 simulations varying ONLY the initial concentrations and (if present) residence times and external concentrations using standard deviation of 2% using Gaussian distributed random numbers. All the error bars for the final average concentration plot are all calculated at one-sigma.
-CONF:1000:1:1:99%:k,0.01:k,1	Run 1,000 simulations varying ONLY the rates constants or (if present) the three Arrhenius parameters (A, m and Ea) using a relative standard deviation of 1% using Gaussian distributed random numbers. Calculate confidence bands at 99% confidence level for all the for the final average concentrations.
-CONF:D:4:D:D:temp,.1:temp,2	Run 1,000 simulations varying ONLY the initial temperature or (if present) the external heat source or external bath temperature using a relative standard deviation of 10% using uniform distributed random numbers. All the error bars for the final average concentration plot are all calculated at one-sigma.
-CONF:1000:0	Run 1,000 simulations varying ONLY those constant/parameters that have been "flagged" by the user's "**(#/#)?**" operator. See below under the "Selective Parameter Uncertainty Analysis". All the error bars for the final average concentration plot are all calculated at one-sigma.
-CONF:D:D:D:D: temp,0.05,k,0.02,m,0.08,ea,0.08:temp,1,k,1, m,2,ea,1	Run 100 simulations varying ONLY the rate constants, k, m, Ea and the initial temperature. Rate constants can change 2%, Ea, 8% and temperature 5% all temperature using a relative standard deviation, but the exponent m will vary AT MOST 8% using uniform random numbers. Keep in mind, there is 1 in 100 change that percent changes can triple using a Gaussian (Normal) distribution!. The percent change listed for m (0.08=8%) is the MAXIMUM upper and lower boundary change allowed since a uniform distribution is assumed for this parameter! **Very important to remember that!**

Table 20. Various sample switch values for the "-CONF" switch to perform various uncertainty analyses. The "-CONF" switch can be overrided for single constants/parameters using the "(#/#)?" operator (see below under Selective Parameter Uncertainty Analysis).

Selective Parameter Uncertainty Analysis

There are some parameters/constants whose values are known quite precisely (such as rate constants, initial concentrations, enhanced third-body factors, TROE, SRI factors, etc.), and then there are some parameter values that are not known quite precisely. To specify an average percent standard deviation for such values would be wrong, so Kintecus provides a way to override all the options given in the above section for such parameters. This override is accomplished through the "**(#/#)?**" operator that will follow any number that may appear in any spreadsheet (model, species, parameter). The two numbers located in the parenthesis dictate the relative standard deviation, and the second number dictates the type of distribution to generate the random **number (1=Gaussian, 2=Uniform, 3=Poisson, 4=Gamma)** about the mean. The mean would be the actual preceding parameter/constant.

For example, for the reaction of OH + HO2➔H2O + O2, if we assume the rate constant was 8.0 x 10^{12} +/- 2 x 10^{12} (assuming 2 x 10^{12} represents **one-sigma!)** then the relative standard deviation is 20% or **0.2**. This reaction can be written in the model spreadsheet with an uncertainty override and assuming **a Gaussian distribution (specified by the number "1" after the slash "/"**:

8.0E+12**(0.2/1)?** , OH + HO2➔H2O + O2

Again, the **(#/#)?** uncertainty override can practically appear after any number: initial concentrations, residence times, TROE factor, enhanced third-body factors, temperature, etc.

What About Zero Means?

If you haven't realized it, but if your parameter is zero, it is NOT INCLUDED in the uncertainty analysis. For some parameters, this makes sense, such as initial concentrations, residence times, and external concentrations. Still, for a few (like the exponent **m** for T^{m} in the expanded Arrhenius equation), one would like to include some variation in it during an uncertainty run. One can accomplish this by using the selective parameter uncertainty operator, "**(#/#)?**" and specifying a negative value instead of a relative standard deviation for the first value. The negative value is the ABSOLUTE RANGE for the spread of the random number. For example:

8.0E+12, 0(-0.75/1)?, 4.33, OH + HO2➔H2O + O2

The m=0 shown above will be randomly spread about (using a Gaussian distribution) –0.75 to +0.75 for 1 sigma. Again, there is a 1/100 chance that a number equal to 2.25 or greater (three sigma x range) might be selected since a Gaussian distribution has been chosen. If the –0.75 were a +0.75, then there would be no change during ALL uncertainty runs for m=0 because 0 x 0.75 x (random number) is always equal to zero.

The Output

Kintecus will output several files that contain the average, standard deviation/confidence bands, maximum, minimum concentration (and temperature) time profiles. These files are consistently named **CONCAVG.TXT, CONCSTD.TXT, CONCMAX.TXT,** and **CONCMIN.TXT** and should be located in the same directory as where the Kintecus executable is located. In addition, if the "g" suboption of the –CONF switch is either not given or set to "KEEP," ALL uncertainty runs will also be kept in the same directory as Kintecus.exe have the prefix **CONCnnnnn.TXT**, where n is a digit, 0-9.

The updated Kintecus-Excel spreadsheets will automatically load and plot all four files into the spreadsheet. If you do not see such loaded plots and worksheets, then be sure to use the latest Kintecus-Excel spreadsheets! This is very important!

Some Examples!

The first example of an uncertainty analysis run is the small kinetic system of an enzyme binding, reacting, and then releasing a product (see the **Enzyme_Uncertainty_Analysis.xls** Kintecus-Excel file). The following page shows the output from a single run followed by a plot of the average concentrations with one-sigma errors computed using the uncertainty analysis feature in Kintecus V3.7. Figure 14 below shows a single run using the nominal values. Figure 15 shows an average run from the 100 uncertainty runs. Note the significant concentration variations of over 1,000% (!!!) for [S] and [ES] about the time of 900 seconds. If [S] or [ES] were dangerous, toxic intermediates, figure 15 demonstrates that exact control of some initial conditions is required. All is not lost as the final equilibrium concentrations of all species are all very close.

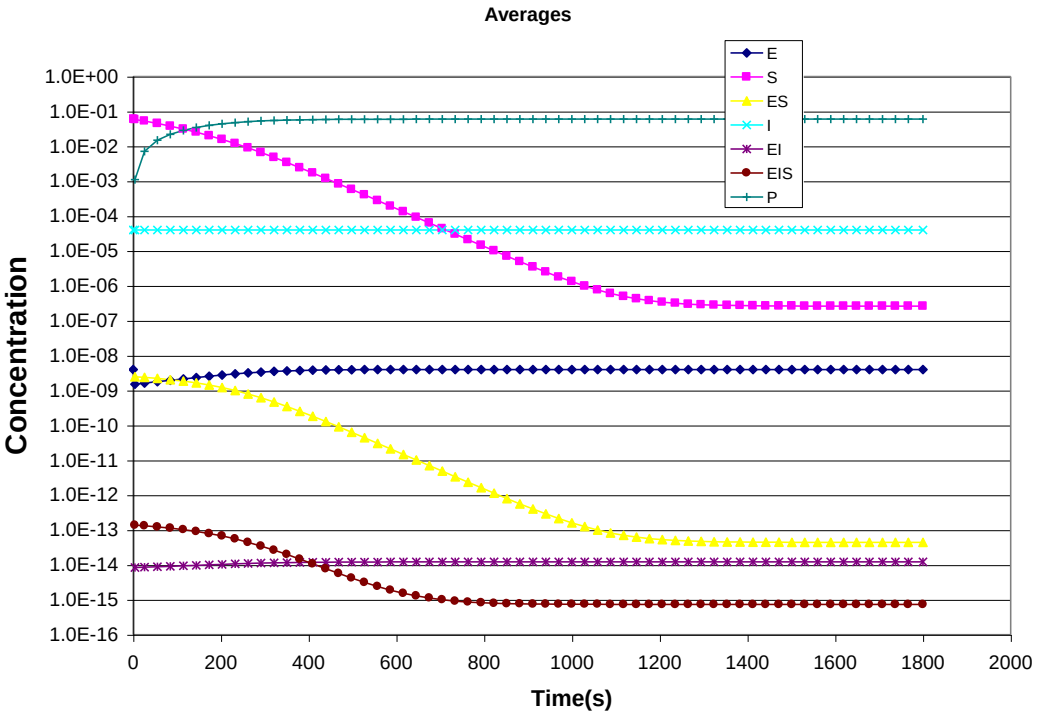


Figure 15. Plot of an enzyme model utlizing one single run. The y-axis is logarithmic.

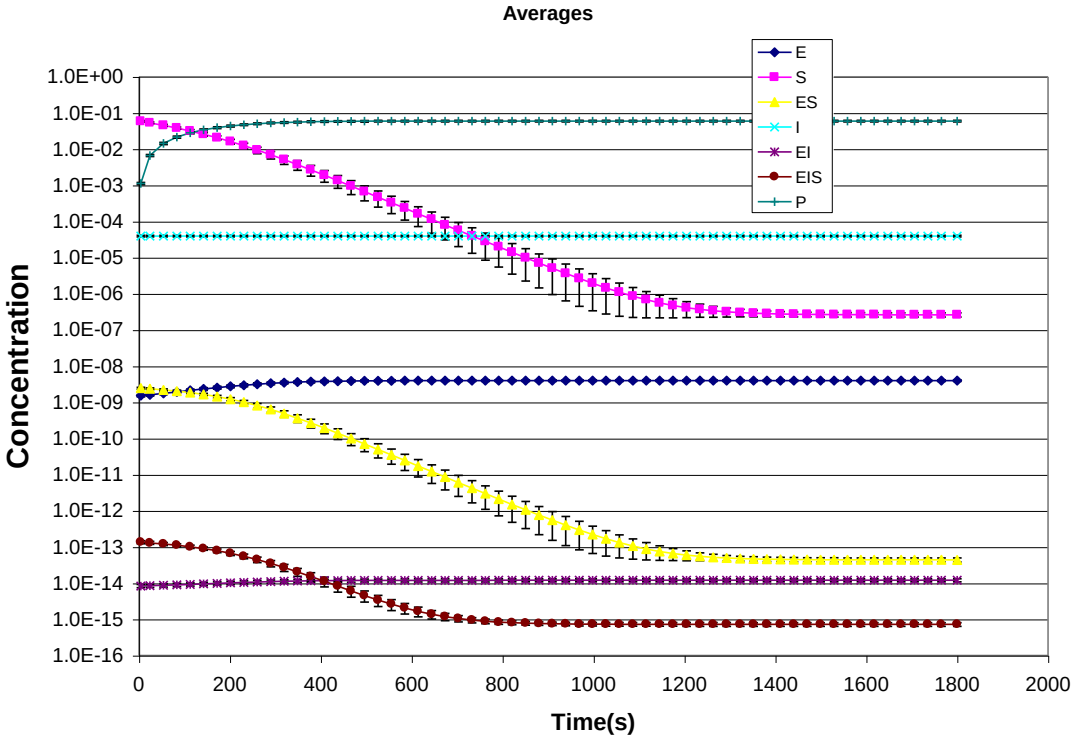


Figure 16. An average plot with one-sigma deviations of an enzyme model utilizing 100 single runs in a Kintecus uncertainty analysis run. The y-axis is logarithmic. Note the significant concentration variations of over 1,000% (!!!) for [S] and [ES] about the time of 900s.

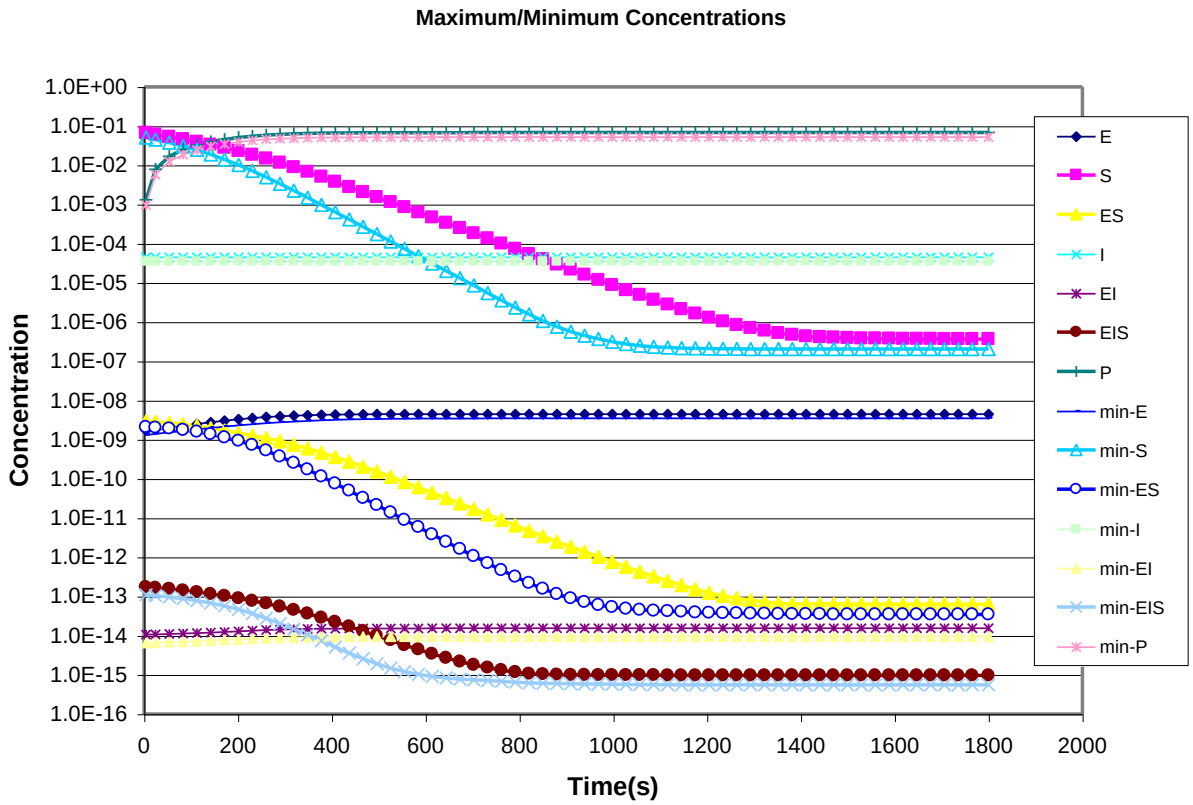


Figure 17. Maximum/minimum of an enzyme model utilizing 100 single runs in a Kintecus uncertainty analysis run. The y-axis is logarithmic. Only the species S and ES show great concentration ranges under the uncertainty analysis, but the final equilibrium concentrations show little changes.

The second example of uncertainty analysis is the H2-O2 combustion model (see the Combustion_workbook_OH_CONF.xls Kintecus-Excel file). Figures 17 and 18 below show a single run, but figures 19 and 20 below show an average model with error bars (one-sigma) generated with the –CONF switch in Kintecus V3.7. As one can see, the average does differ significantly from the single run, with the concentration profile of O_2 containing the greatest scatter. Figure 22 shows a zoomed plot of the HO2 and H2O2 average concentrations with error bars of one-sigma for the uncertainty run of the H2-O2 combustion under adiabatic conditions and constant pressure. These average concentrations are close to the concentrations in figure 21 generated from the single-run using nominal initial conditions. Still, there is a tremendous intermediate variation in the concentration-time profiles. Interestingly, the concentration of H_2O_2 around 1.9x10(-4) seconds shows very little scatter, indicating that at this time point, $[H_2O_2]$ is relatively invariant to the accuracy of rate constants, thermodynamics, third-body reaction enhancements, and even initial concentrations!

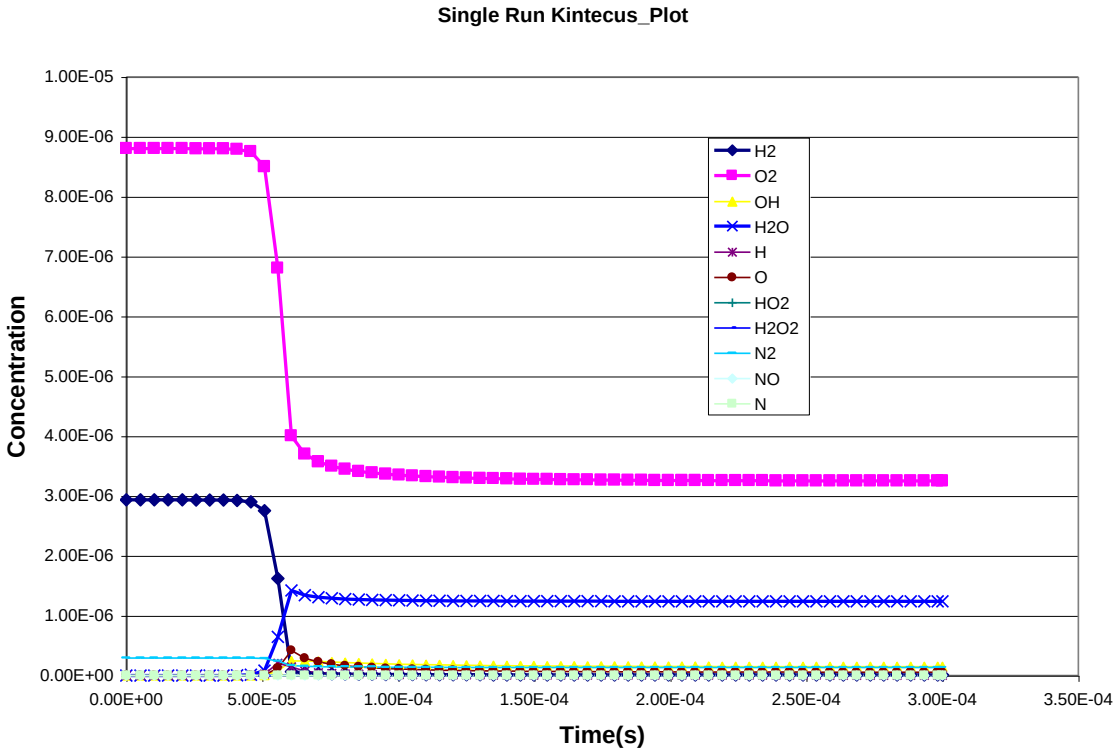


Figure 18. Concentration profiles from a single run of the combustion of H_2 and O_2 at constant pressure.

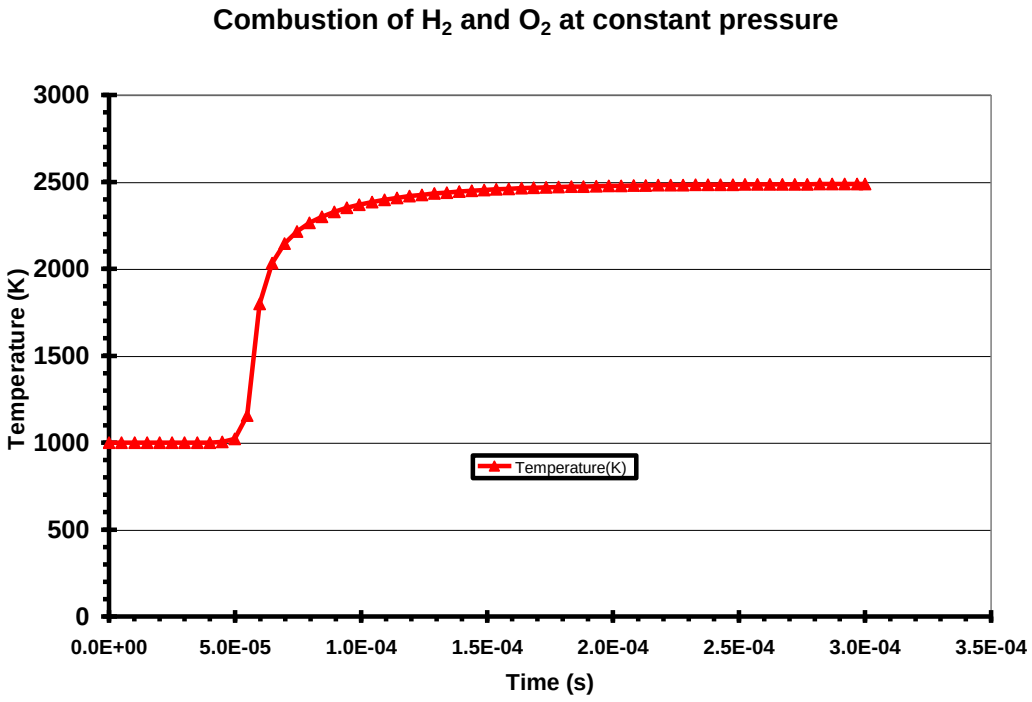


Figure 19. Temperature profile from a single run from a single run of the combustion of H_2 and O_2 at constant pressure.

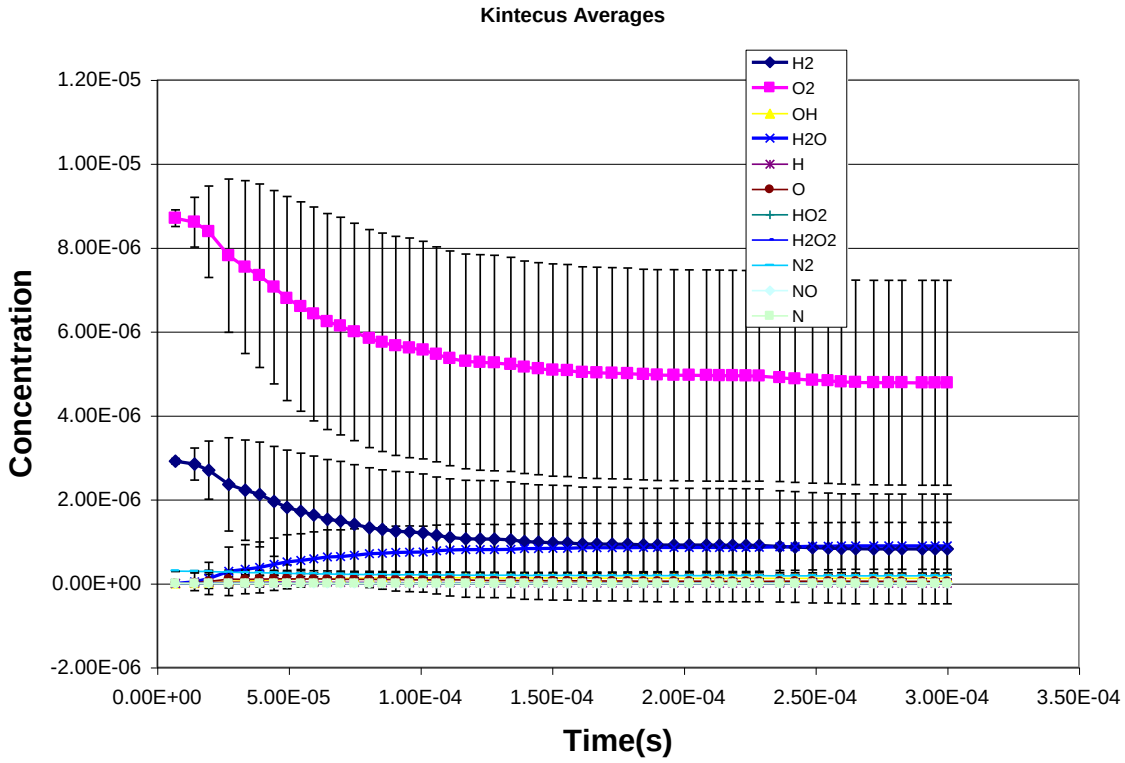


Figure 20. Average concentration profiles from the H_2-O_2 combustion run under constant pressure with error bars from 100 sample runs with "-CONF" switch. These average results are very much different from the single run shown in figure 17 above!

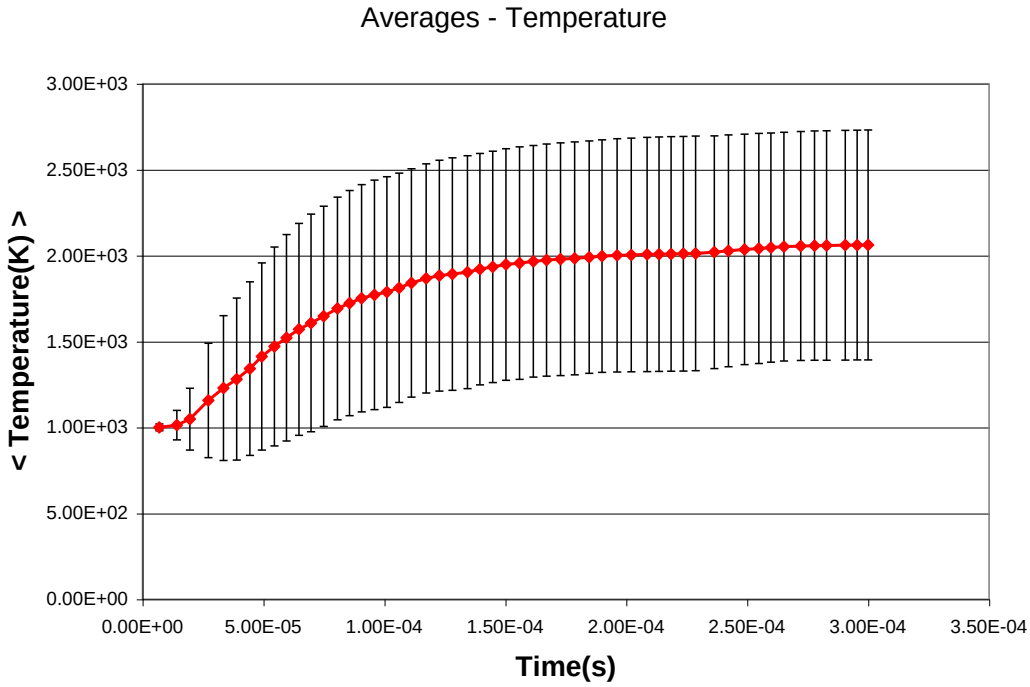


Figure 21. Average temperature profiles from the H_2-O_2 combustion run under constant pressure with error bars from 100 sample runs with "-CONF" switch. Again, these average results are vastly different from the single run shown in figure 18 above!

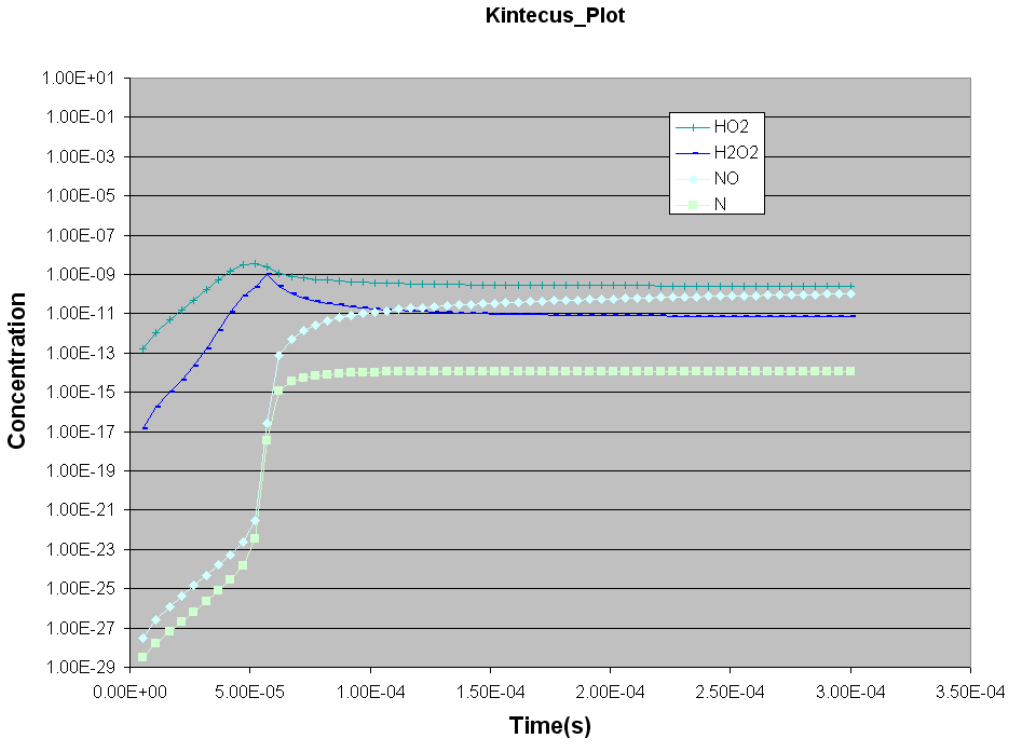


Figure 22. A single run showing the time profile for HO_2, H_2O_2, NO and N.

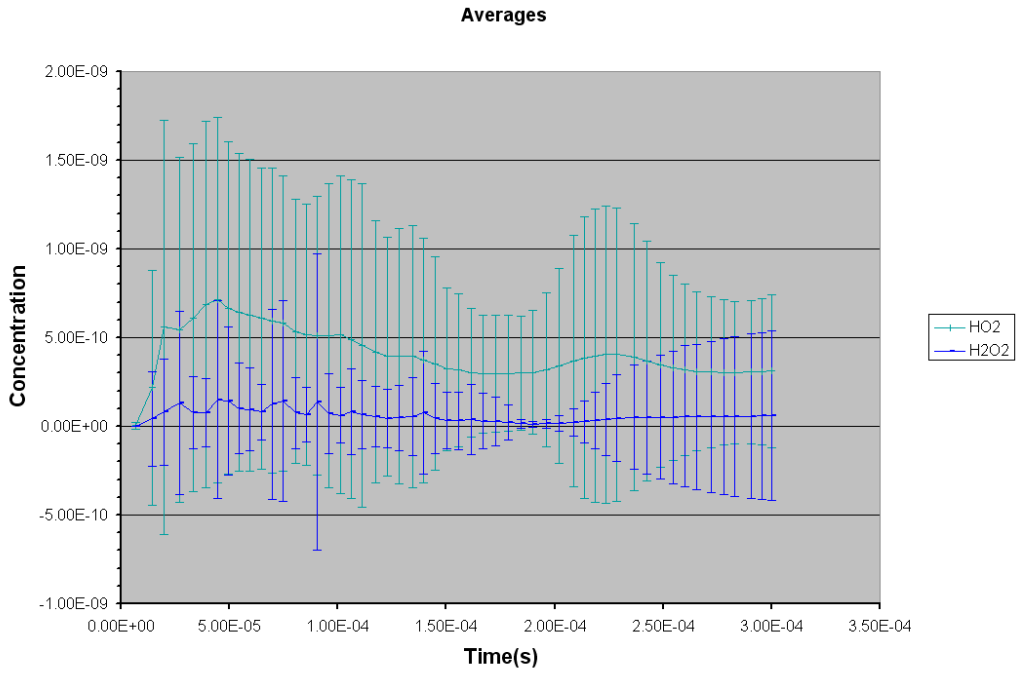


Figure 23. A plot of the HO_2 and H_2O_2 average concentrations with error bars of one-sigma for the uncertainty run of the H_2-O_2 combustion under adiabatic conditions, constant pressure. These average concentrations are close to the concentrations in figure 21 that were generated from single-run using nominal initial conditions. Still, there are large intermediate variations in the concentration time profiles.

8. Scanning

Background

The ability to scan (also known as a sweeping or parametric study) essential parameters (such as rate constants, initial temperature, reactor residence time, third-body enhancements, TROE factors, initial concentrations, etc) over a range of values can yield important insight into one's chemical system. Scanning in Kintecus is turned on by including the "–scan" switch on the command line.

Implementation

Kintecus V3.8 allows one to perform such scans in four different ways efficiently: sequential, parallel with no repeat, parallel with repeating, and combinatorial. Each way of those scanning implementations is discussed below. Scanning in Kintecus is turned on by including the **"–scan"** switch.

Parameters that are to be scanned are set up in the following way:

stepsize(starting value/ending value)?

where **stepsize** is the increment (or decrement) value, **starting value** is the first value your parameter will be set to, and **ending value** is the last value your parameter will be set. Some valid scans are: 0.1(0.1/1)? , -0.1(1/0.1)?, 100(273/1073)?, 1e5(1e5/1e6)? . Please keep in mind the very first value is the **step-size** and NOT THE INITIAL VALUE/STARTING VALUE! Below is a sample scan of a rate constant starting from 1 x 10^5 to 1 x 10^6 in increments of 1 x 10^5 in the model spreadsheet:

1e5(1e5/1e6)? , A + B ➔ C

The outputs from your scans are stored in CONCnnnnn.txt, where nnnnn is a five-digit number starting from conc00001.txt to the total number of scans. The **SCANNED_PARAMETERS.TXT** file contains the parameters/values that were changed at the start of each concnnnnn.txt run. If you use the current V3.8 Kintecus-Excel spreadsheets, then Kintecus will automatically plot all your scans onto the graph. Each species name/temperature will be suffixed with the concnnnnn.txt file it's associated. Sample Kintecus-Excel files named "Enzyme_Scanning.xls" and the "Combustion_H2_O2_scan.xls" have been included to demonstrate scanning abilities!

Kintecus provides several different methods to scan all your parameters if you are scanning more than one parameter (such as initial concentrations vs. temperature vs. third-body rate enhancements, etc.).

Type of Scan Available	Scan Switch Settings
Sequential Scan	-scan:1 (default)
Parallel Scan No Repeat	-scan:2
Parallel Scan With Repeat	-scan:3
Combinatorial Scan	-scan:4

For each of the cases below, let's assume one is doing multiple scans involving

- Temperature from 500 to 1,000 K in steps of 100 K : 100(500/1000)?
- The initial concentration of species X from 0.0 M to 4 M in steps of 0.2 M : 0.2(0/4)?
- A third-body enhancement value from 0 to 10 in steps of 1 : 1(0/10)?

Sequential Scan

The sequential scan (-scan:1) will perform each scan in your list of scans one by one. For the multiple scan example given above, 37 scans will be performed, creating 37 conc**nnnn**.txt files (conc00001.txt to conc00037.txt with associated changing values listed in the SCANNED_PARAMETERS.TXT file). The temperature will be scanned first from 500 K to 1000 K, followed by the initial concentration from 0 M to 2 M, followed by the third-body enhancement from 0 to 10 in steps of 1. The start of each scan will set the other scanned values (that are not changing in the current sequential scan) to their starting values.

Parallel Scan No Repeat

The parallel scan (-scan:2) with no-repeat will scan **ALL** your scanning parameters at the **SAME** time. For the example above, only 20 total scan conc**nnnn**.txt files will be produced (conc00001.txt to conc00020.txt with associated changing values listed in the SCANNED_PARAMETERS.TXT file). The total number of scans is dictated by the slowest changing value, the initial concentration scan of species X. The other scanned values will reach their ending value before the initial concentration scan of species X finishes. Once that happens, all subsequent scans for those “finished” parameters will start with the final scan value.

Parallel Scan With Repeat

The parallel scan (-scan:3) with repeat performs in the same manner as the **Parallel Scan No Repeat** described above. Still, once a scanned value reaches its final value, it starts all over again, thereby repeating until the slowest changing parameter reaches its final scan value.

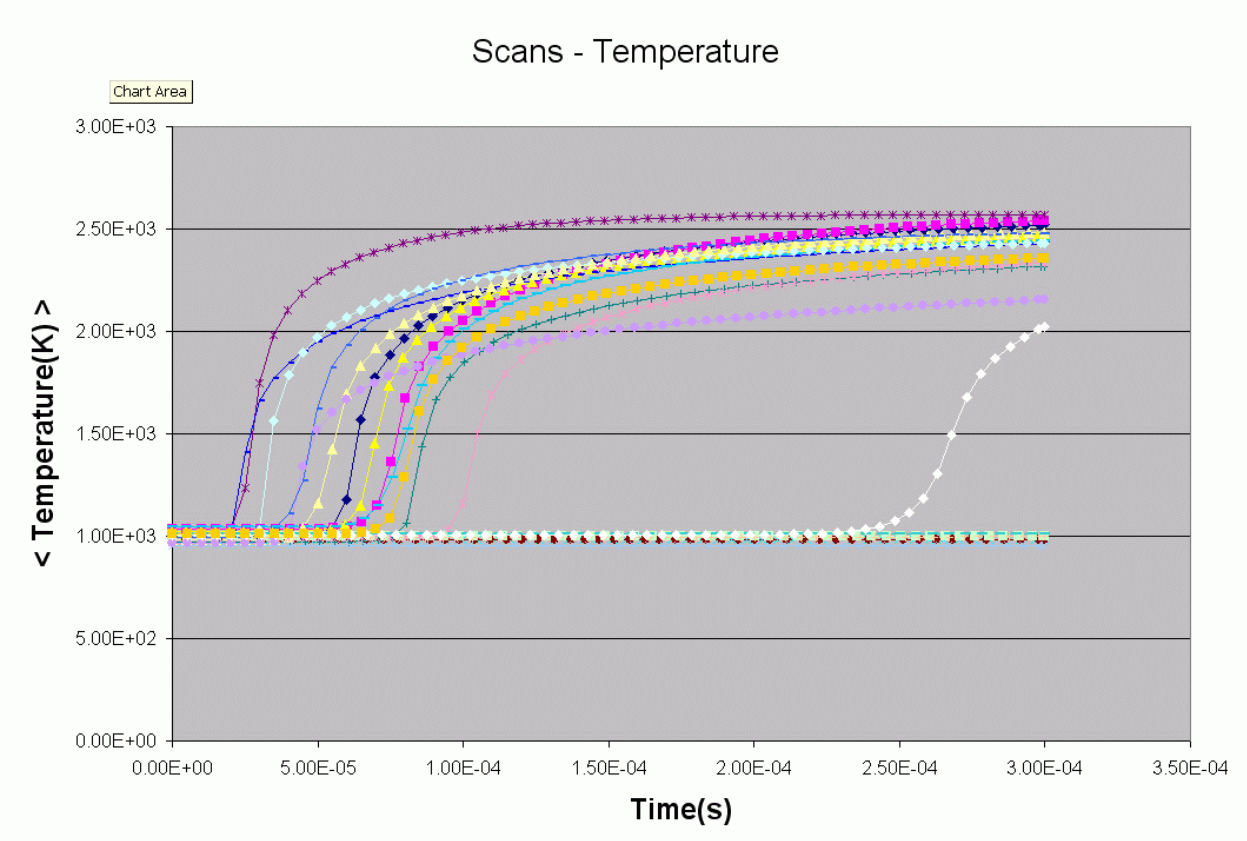
Combinatorial Scan

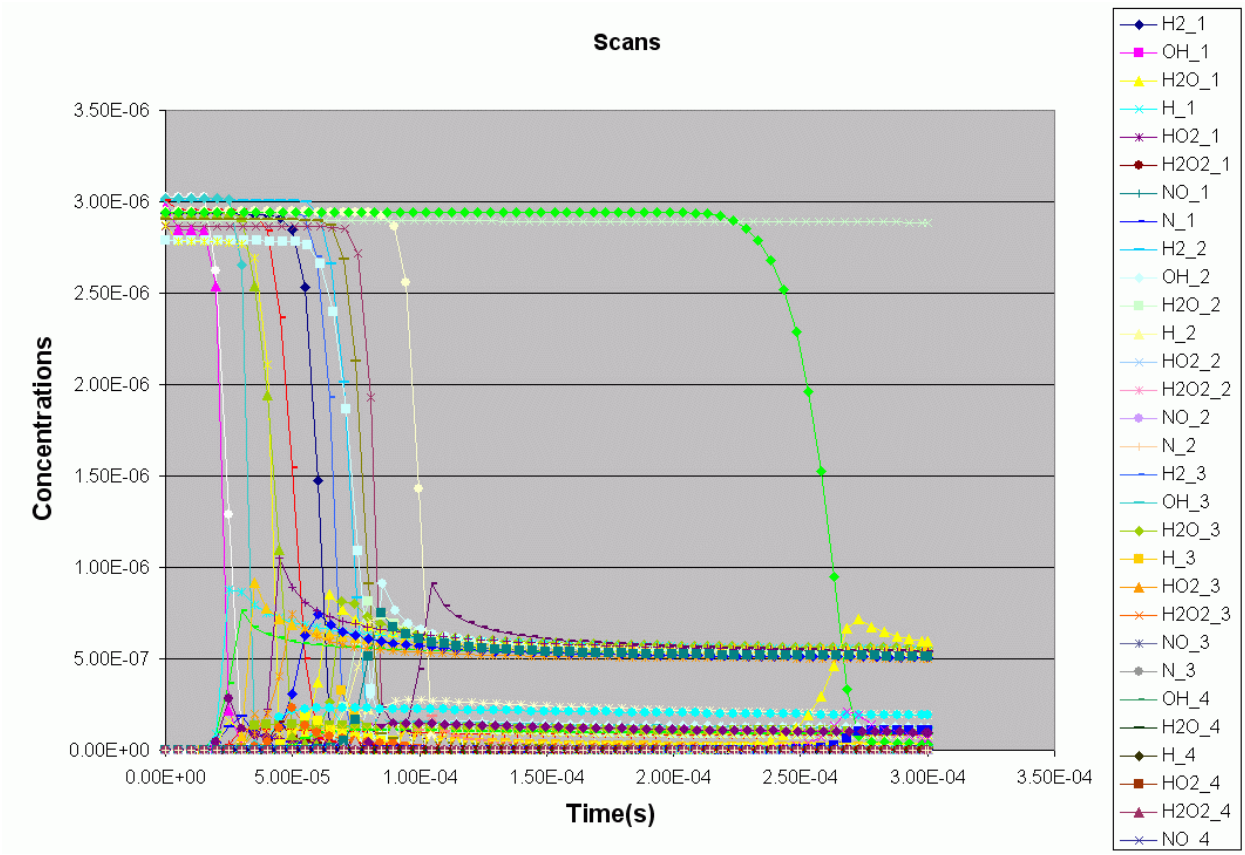
This type of scan will produce all the possible combinations between all the scanning values. Consequently, this type of scan can produce enormous amounts of data. For the scan example above, invoking a combinatorial scan (-scan:4) will produce 1,320 concnnnn.txt files!!! Suppose you are using the Kintecus-Excel spreadsheet and

performing combinatorial scans; then, it is highly recommended that you only display the species you are interested in (go to the species spreadsheet and turn off the Display of the other species by typing a "No" in their respective field).

Sample Plots

Below is a scanning example from the **Combustion_H2_O2.xls** Kintecus-Excel spreadsheet. This straightforward scanning example scans the starting concentration of O2, creating several different runs. Interesting, there is a very long ignition delay for one run. This run has an ignition delay over an order of magnitude (1,000% !!!) longer than the other runs!




Scans
Concentrations
Time(s)
3.50E-06
3.00E-06
2.50E-06
2.00E-06
1.50E-06
1.00E-06
5.00E-07
0.00E+00
0.00E+00
5.00E-05
1.00E-04
1.50E-04
2.00E-04
2.50E-04
3.00E-04
3.50E-04
H2_1
OH_1
H2O_1
H_1
HO2_1
H2O2_1
NO_1
N_1
H2_2
OH_2
H2O_2
H_2
HO2_2
H2O2_2
NO_2
N_2
H2_3
OH_3
H2O_3
H_3
HO2_3
H2O2_3
NO_3
N_3
OH_4
H2O_4
H_4
HO2_4
H2O2_4
NO_4

9. Cluster Analysis

Background

A new feature in Kintecus V3.9 is the ability to perform complex hierarchical cluster analysis[29] on temporal concentration profiles of the network with/without experimentally obtained temporal concentration profiles. Hierarchical cluster analysis in Kintecus can group related and unrelated parts of temporal concentration profiles in a meaningful, quantitative way. This grouping allows a user to see patterns that were initially indiscernible or hidden clearly.

"Why should I care about that?"

Cluster Analysis can significantly help in answering questions:

- Analyze ALL species and determine which species or groups of species (or subgroups, etc.) are positive, zero, or negatively correlated to each other and with other groups/species in either a pictorially or numeric output. This type of analysis allows one to answer questions such as:
- What concentrations of E and S cause EIS to positively (or negatively or zero) correlate with EI ? or ES? Or both? Etc. etc. For combustion, you can now finally answer that question that has been bugging you since you were seven years old: If I combinatorially scan H_2, O_2, and temperature over a wide range, do the O and OH radicals always positively correlate and also do they positively correlate (or negatively or zero) correlate with other species?
- Determine which species in one's experimentally determined concentration profile are positively, zero, or negatively correlated with all the modeled species' temporal profiles. Again, this can be grouped into a pictorial or numeric output.
- Which species' concentration profiles tend to stay in the same range of concentration values?
- There are other questions one can answer utilizing the myriad of cluster techniques Kintecus provides that the author has not thoroughly examined.

Cluster analysis becomes a powerful tool when coupled with combinatorial scanning (see the Scanning Section see how to set up a Combinatorial Scan).

Implementation

Hierarchical Cluster analysis is accomplished in Kintecus by providing the "-cluster" flag on the Kintecus command line:

>kintecus **–cluster**

The "-cluster" flag has many features that the user may want to change:

-cluster{:a:b:c:d:e:f:g:h:i:j:k}

All options a, b, c, d, e, f, g, h, i, j, and k are optional, but all preceding options must be specified when setting options "b" to "k." All options have a default setting which can be specified with the letter "D" or "d" (most Kintecus switches have this feature). Here is a breakdown of all the options (defaults are listed in brackets, [], or by entering the letter "D" for an option indicates to use the default value.).

a) Option "a" determines the type of cluster analysis to perform. Currently, there is only one: Hierarchical Cluster Analysis specified by the number "1" in place of "a." Future versions might incorporate K-means clustering. Adding 100 to this value will state to Kintecus to skip the computation of the concentration/temperature/volume/etc outputs and immediately start the clustering. The output concentration file, CONC.TXT, is assumed to be in the same directory, or the file associated with the "-OUT:filename" switch exists and is readable.

b) Option "b" determines the type of computation implemented in the similarity/dissimilarity matrix computation. Option "b" must be inclusively between zero to eight (0-8). The most common dissimilarity method you will most likely use is the Euclidean distance (set option "b" to zero, "0"), and the other popular method is Correlation (r^2) (six, "6" for option "b"). There are other methods for computing the similarity/dissimilarity matrix:

Option "b" Values	Similarity/Dissimilarity Method	What is it?
[0]	**Sqrt(Sum(distance between $[c_1]_t$ and $[c_2]_t$)^2))**	**Euclidean distance between concentration profiles**
1	Sum(ABS(distance between $[c_1]_t$ and $[c_2]_t$))	Norm of L1 of concentration profiles
2	Max(distance between $[c_1]_t$ and $[c_2]_t$)	Norm of L-at-infinite
3	Mahalanobis distance	Mahalanobis distance
4	Cos(theta between vectors $[c_1]_t$ and $[c_2]_t$)	Dot product between concentration profiles
5	Just theta between vectors $[c_1]_t$ and $[c_2]_t$	Angle
6	**Rho from a plot of $[c_1]_t$ and $[c_2]_t$**	**r, Correlation (-1.0 to +1.0)**
7	ABS of Rho	r, correlation (0.0 to +1.0)
8	Count the number of times values in $[c_1]_t$ match $[c_2]_t$	Matching count

Table 21. Option "b" values. Types of ways to compute the similarity matrix for the hierarchical clustering method. Note that the scaling option, "e" does not affect methods 3-8.

c) Option "c" specifies the type of hierarchical cluster analysis method and can have values from zero to four (0-4). You will most likely set option "c" to zero, "0" in almost all cases. The author hasn't been able to find appropriate uses for the other hierarchical cluster analysis methods.

Option "c" Values	Hierarchical Cluster Analysis Method
[0]	The minimum distance between clusters (by far the most common method)
1	Maximum distance
2	Average distance within clusters
3	Average distance between clusters
4	Ward's method (option "b" should be set to zero=Euclidean distances)

Table 22. Option "c" values. Type of hierarchical cluster analysis methods available.

d) Option "d" specifies whether to perform a transformation on the similarity matrix and can have values from 0-2. Option "d" is primarily utilized for Similarity/Dissimilarity Methods 6 and 7 (correlation).

Option "d" Values	Transformation Method
[0]	No transformation
1	Multiply by –1.0 (not used that often)
2	Convert the values in the similarity/dissimilarity matrix into distances by obtaining the reciprocal of the absolute value: 1/|distance|. This transformation is usually used with Option "b" methods 6 and 7 (correlation matrices).

Table 23. Option "d" values.

e) Option “e” specifies whether to scale the data before calculating the similarity matrix. Typically it is set at zero, “0”, to perform no scaling.

Option “e” values	Type of Scaling
[0]	No scaling; leave concentration data alone.
1	Scale each species' concentration temporal profile by the standard deviation of the same concentration temporal profile.
2	Scale each species' concentration temporal profile by the range of the temporal concentration profile.

Table 24. Option "e" values.

f) Option “f” specifies the number of clusters to form and is NOT USED in the Hierarchical Cluster Analysis Method. It should be left at the numeric value of “2”.

Options g-k are primarily intended in the printing of the cluster tree:

g) Option “g” specifies the page width in characters of the cluster tree output [101].

h) Option “h” specifies the type of cluster printout and ranges from 1 to 3.

i) Option “i” specifies the number of lines printed before each node and can have values from 1 to 10 (one line is the default). You shouldn’t have to change this default value.

j) Option “j” specifies the subtree printing specification and can range from zero [0] up to 100. Zero is the default. You shouldn’t have to change this default value.

k) The final option “k” specifies the number of horizontal slices of a tree to print and can range from 1 to 10. The default value is one, “1”. You shouldn’t have to change this default value.

Entering only the “-cluster” switch on the command line is equivalent to the following cluster switch options:

“-cluster:1:0:0:0:0:2:178:1:1:0:1”

So Now What?

Although the default settings for the "-cluster" switch will always work, it only provides information on which temporal concentration profiles are closest to each other and other groups. You will very likely find the cluster switch with the following settings the **most useful**:

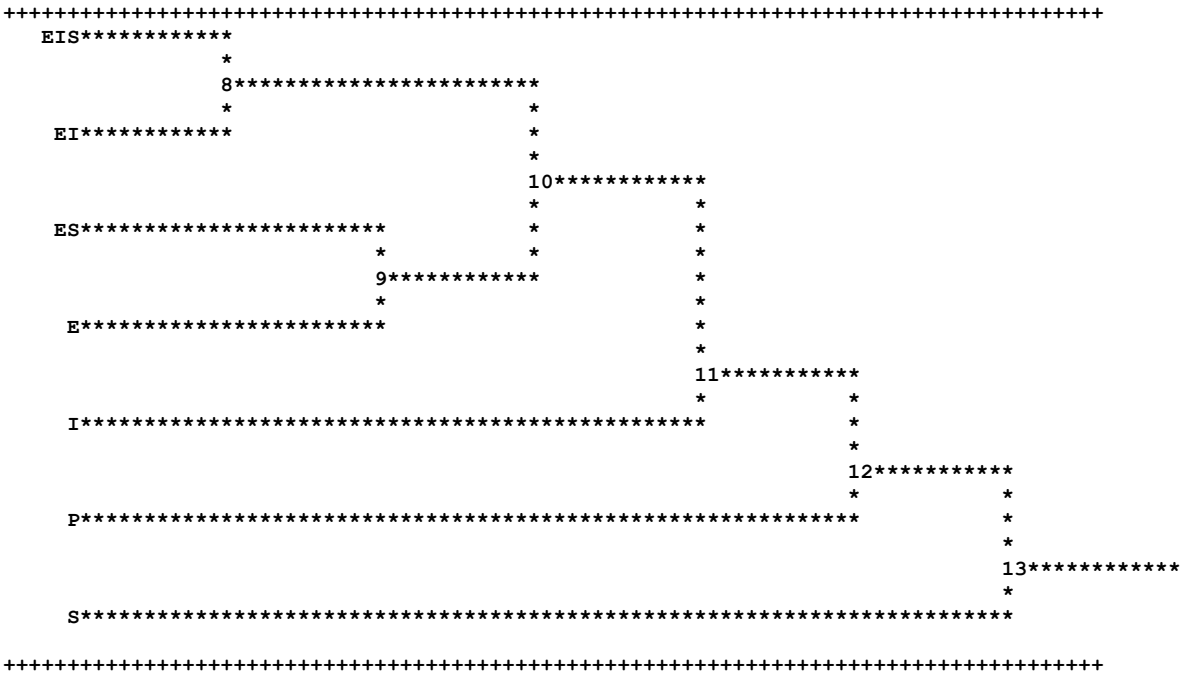
"-cluster:1:6:0:2"

The above cluster option implements the handy clustering technique of correlation, r^2, for the similarity matrix. Please see the sample clustering techniques 2 and 3 below on the next page. This advantageous correlation technique was not set as the default because it occasionally fails. After all, some species' temporal concentration profiles have no change and are near zero. This situation can sometimes cause this clustering technique based on correlation to fail. A simple correction to this is to "NOT DISPLAY" the output of the species which is not changing and is near zero (go to the Species Description Spreadsheet and set the "Display Species?" from Yes to No).

Sample Plots/Output

Cluster Analysis: Sample 1

The following is a simple sample and is mainly for pedagogical purposes. More "real-world" examples follow this. The first example utilizes the default setting implied by the "-cluster" switch (Hierarchical Cluster analysis using Euclidean distances for the similarity matrix and a minimum grouping between clusters). Part of the cluster.txt output file contains the cluster graph after clicking RUN on the **Enzyme_Cluster_Analysis.xls** Kintecus-Excel spreadsheet:



We can see that enzymes EIS and EI and ES and E are both in their clusters, with I, P, and S as the "outsiders." Why this grouping? Remembering that cluster analysis builds on the similarity matrix, and we are using Euclidean distances for the similarity matrix, the species with the closest concentration temporal profiles will be grouped. A log temporal concentration plot (**shown below**) of this run shows that EIS and EI are close together and all by themselves. Species E and ES show a similar pattern hence their little cluster. Species I, P and S are in their branches alone, but species I is closer to the EIS, EI, and ES, E clusters than P or S.

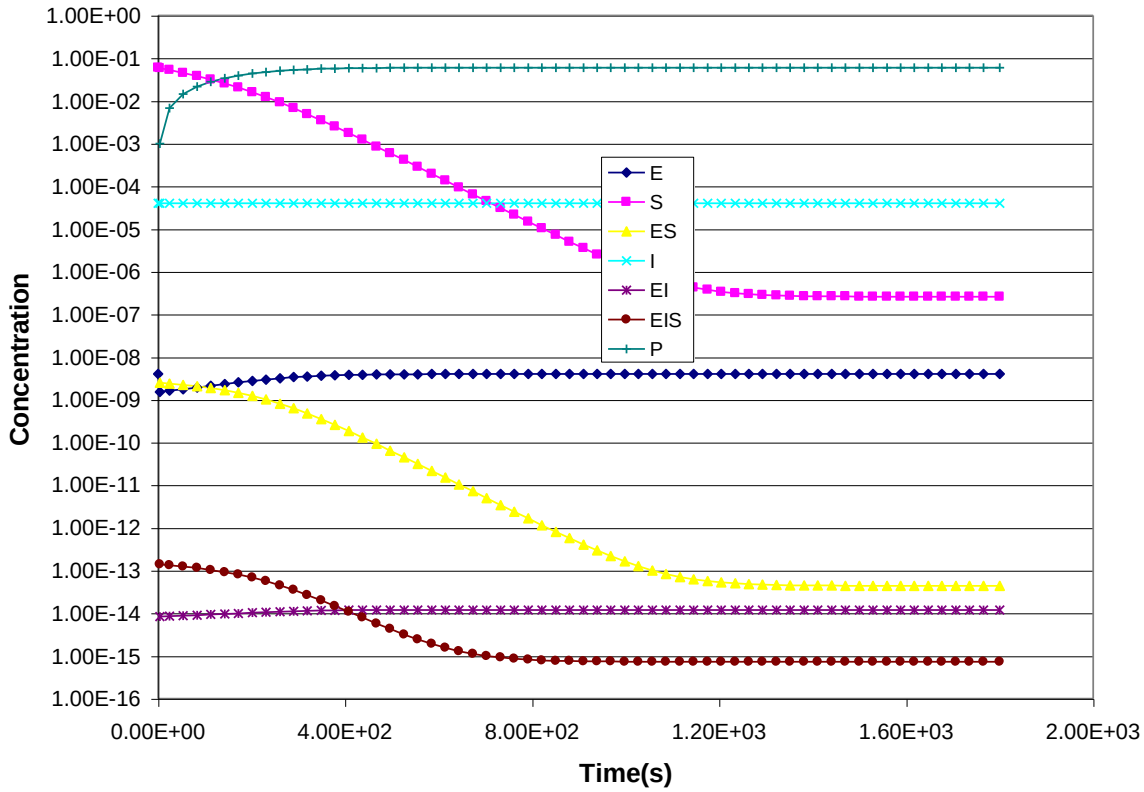
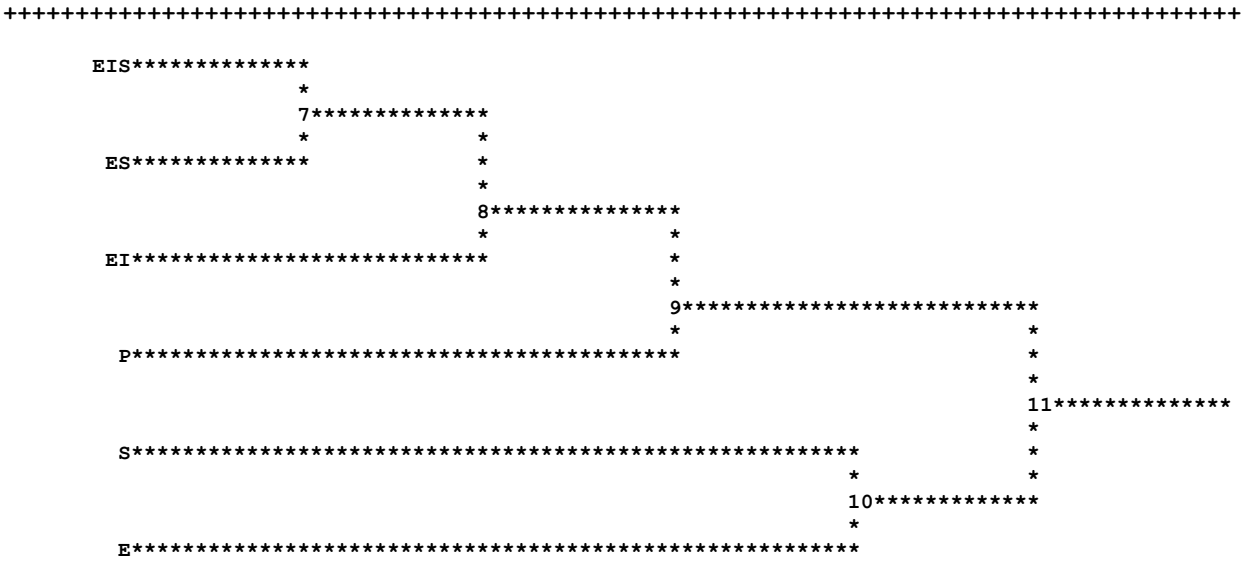


Figure 24. Temporal Concentrations plot of the Sample Enzyme Model. (y-axis is on a logarithmic scale)

Cluster Analysis: Sample 2

Let us see a more helpful clustering technique in that we shall use correlation, r^2, for the similarity matrix, and we will keep the same minimum clustering technique. Note that we have to convert the r^2's to distances. This conversion is accomplished by transforming the r^2's into distances by taking the reciprocal (1/r^2), which can be automatically done by setting Option "d" (Transformation Method)to the value 2. We arrive at the following cluster switch, which will accomplish all this: **"-cluster:1:6:0:2"**. One small problem with this distance measure is that since the concentration of species "I" never changes, the r^2's with plotting species "I" will always be zero. These r^2 values of zero will yield **infinite distances** for the transformation method, and the clustering method will fail. To correct this, the output for species "I" has been turned off by selecting "No" for the "Display Species" field in the "Species Description Spreadsheet." Here is the output after clicking RUN on the **Enzyme_Cluster_Analysis_2.xls** Kintecus-Excel spreadsheet:



with the corresponding similarity matrix (located inside the same cluster.txt file with the untransformed r^2's rounded to three decimal places):

Transposed Similarity/Dissimilarity Matrix

	2	3	4	5	6
1	0.296	0.000	0.000	0.000	0.000
2		0.000	0.000	0.000	0.000
3			0.945	1.000	0.296
4				0.944	0.591
5					0.293

and the numeric id's for the species that appear in the similarity matrix:

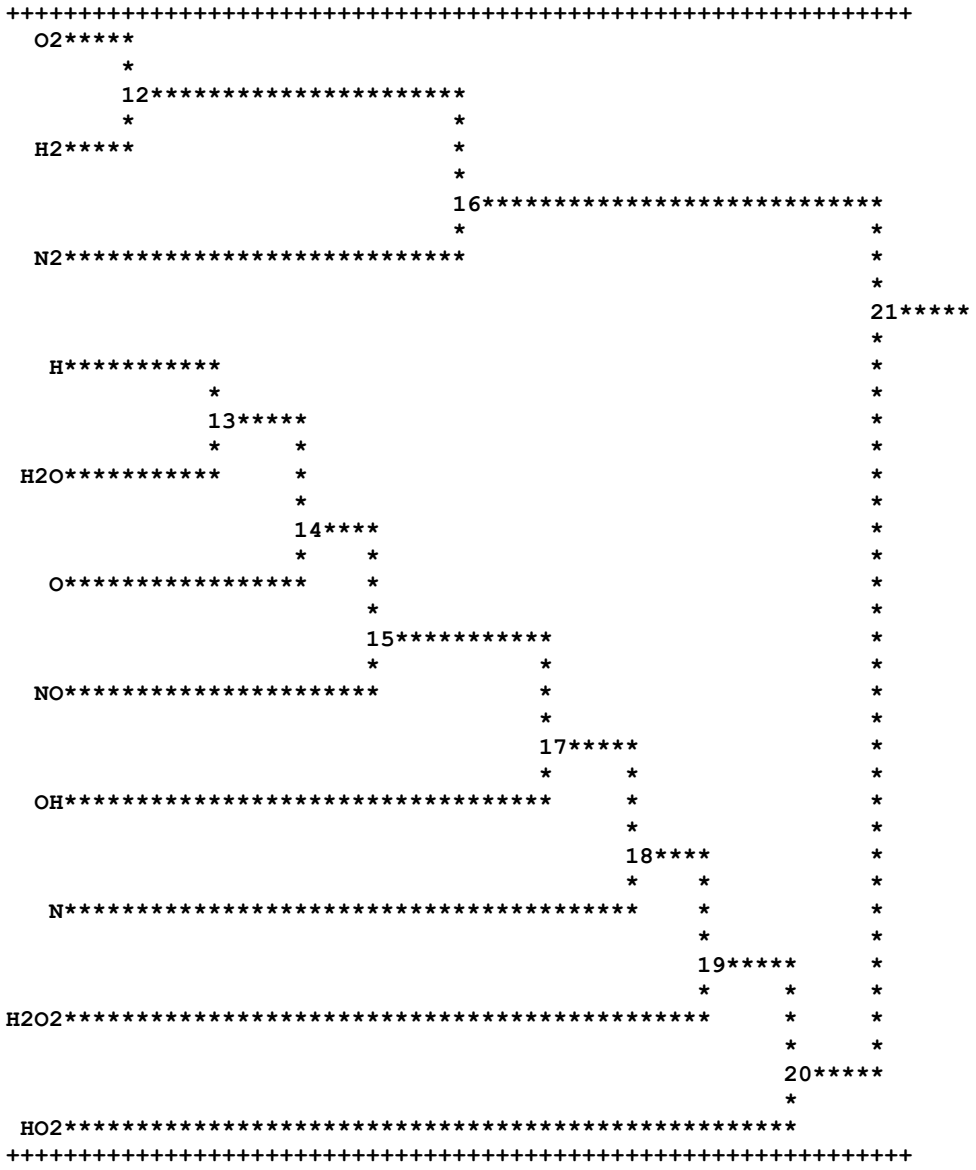
	1	2	3	4	5	6
Time(s)	E	S	ES	EI	EIS	P

Table 25. Numeric id's for the species in the above "Transposed Similarity/Dissimilarity Matrix."

We can immediately see why EIS and ES (5 and 3 respectively in the matrix) are clustered together. They have a perfect correlation of 1.000 (a plot of EIS versus ES will yield a linear equation y=mx+b with perfect correlation: r^2=1.00). We can also see why EI (4 in the similarity matrix) has been clustered with EIS and ES because EI has an excellent correlation (0.94) with EIS. Species P has a semi-good correlation with Species' ES, EI, and EIS (r^2's=0.296, 0.591, and 0.293), so species "P" has been clustered with ES, EI, and EIS. The other cluster only has species S and E as they are only correlated with each other (r^2=0.296).

Cluster Analysis: Sample 3

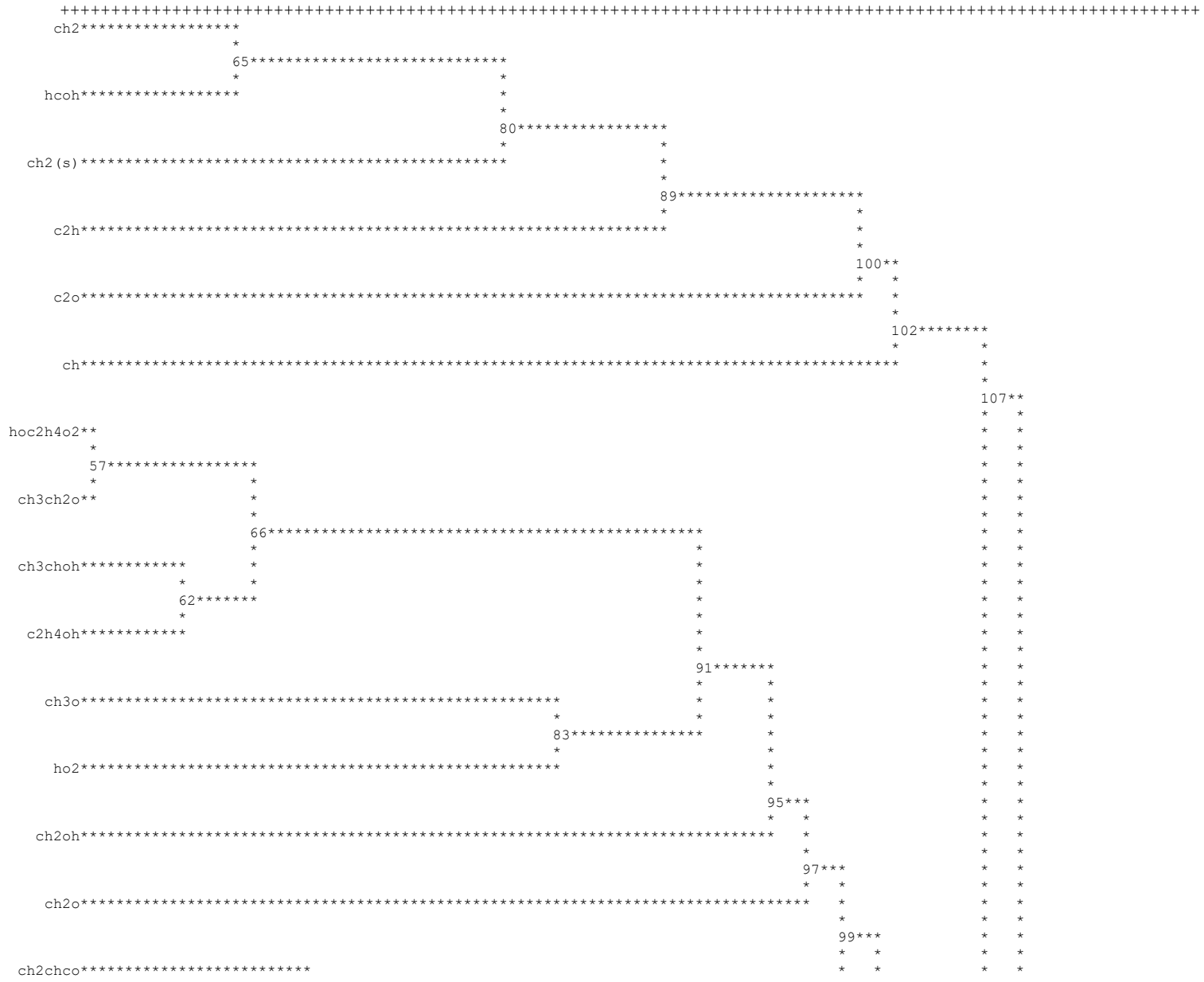
Let's try another Hierarchical Cluster analysis utilizing correlation distances for the similarity matrix and a minimum grouping between clusters on the O_2 and H_2 isobaric (constant pressure) combustion model. Here is the output after clicking RUN on the **Combustion_O2_H2_cluster.xls** Kintecus-Excel spreadsheet:

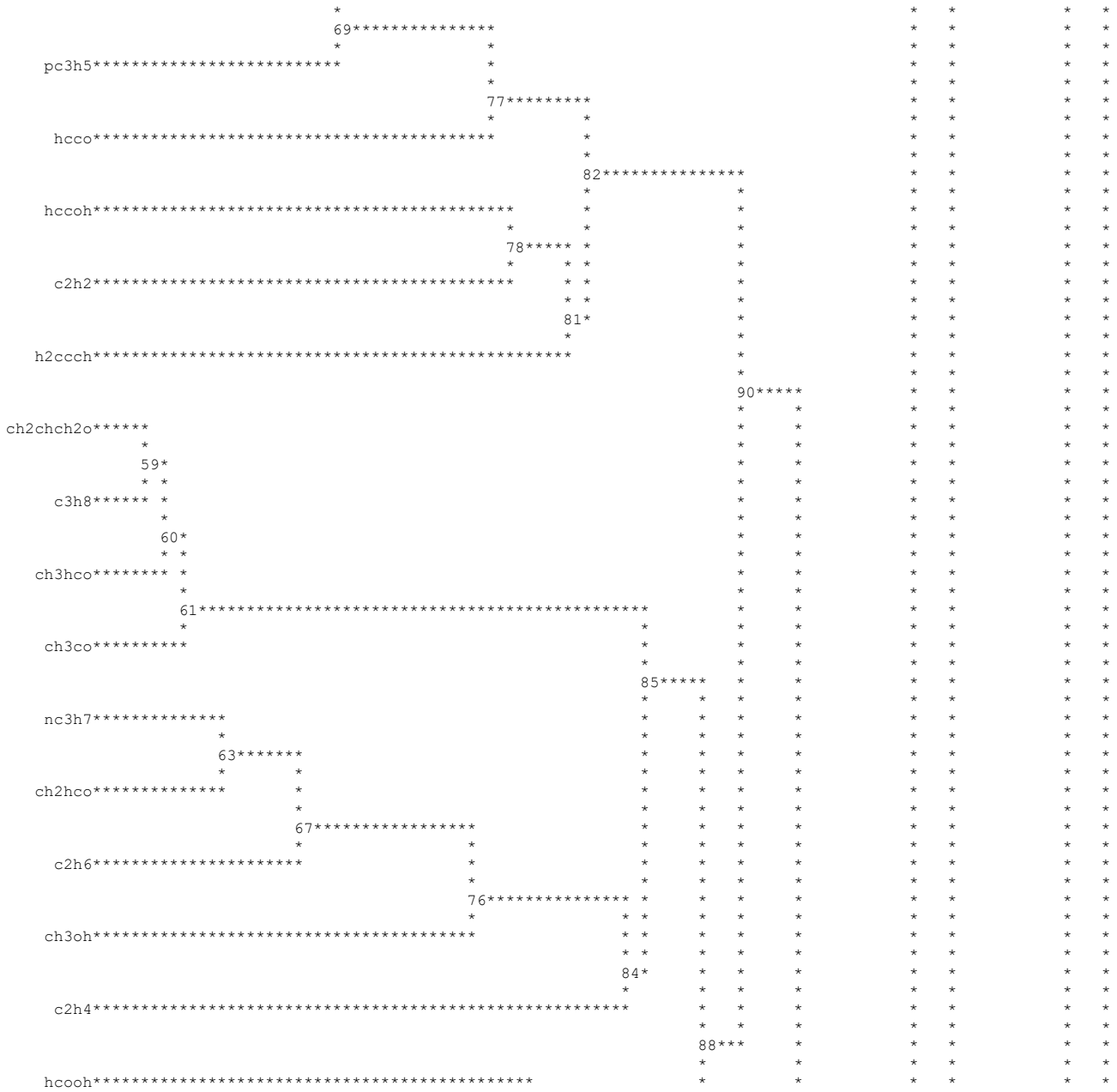


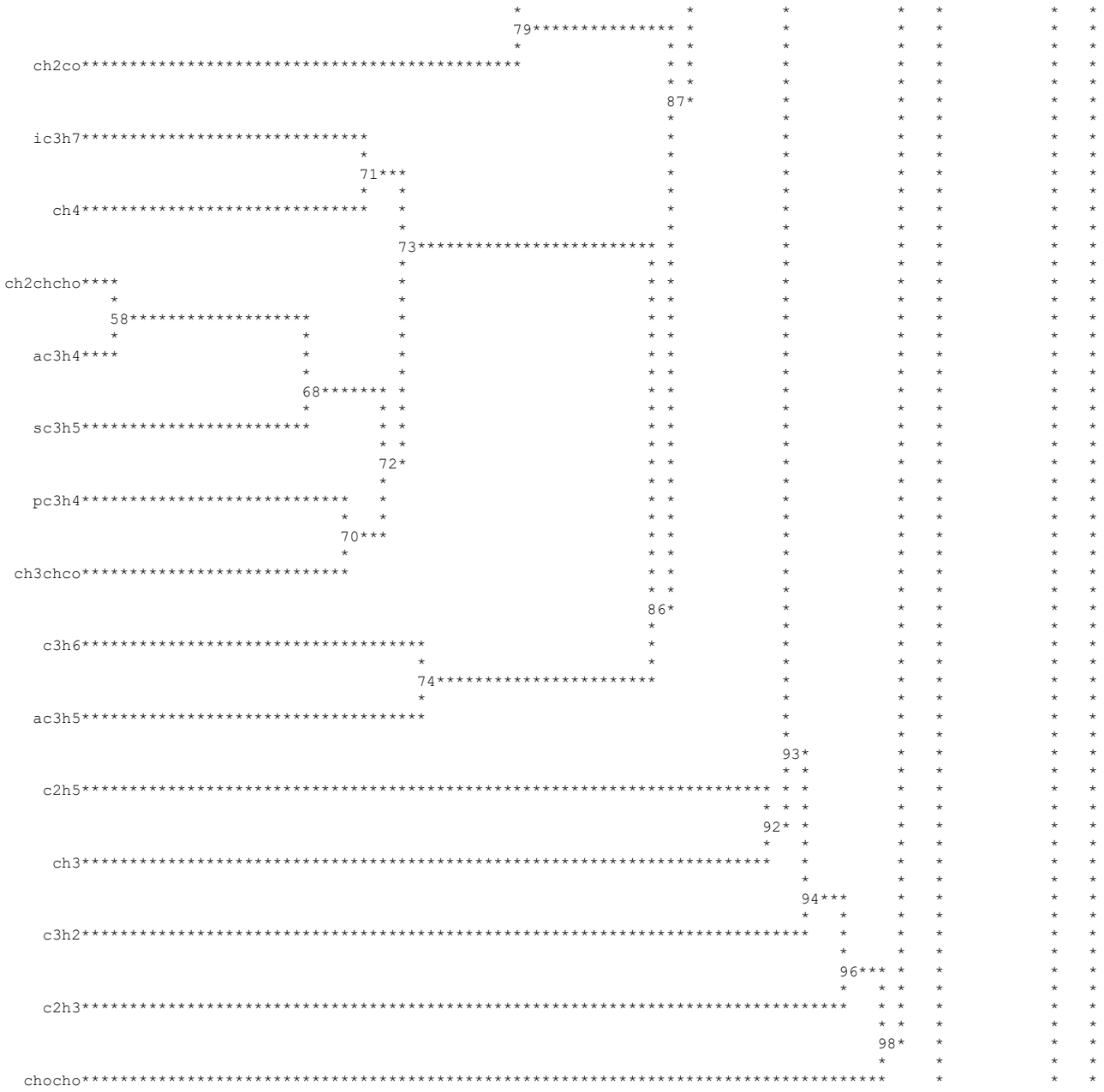
We can see that this cluster makes perfect sense in correlation because all three species, O_2, N_2, and H_2, all decrease in concentration and reach equilibrium nearly at the exact time, so they are in their "own" cluster. At the same time, all the other species slowly grow in concentration, so they are in a separate cluster.

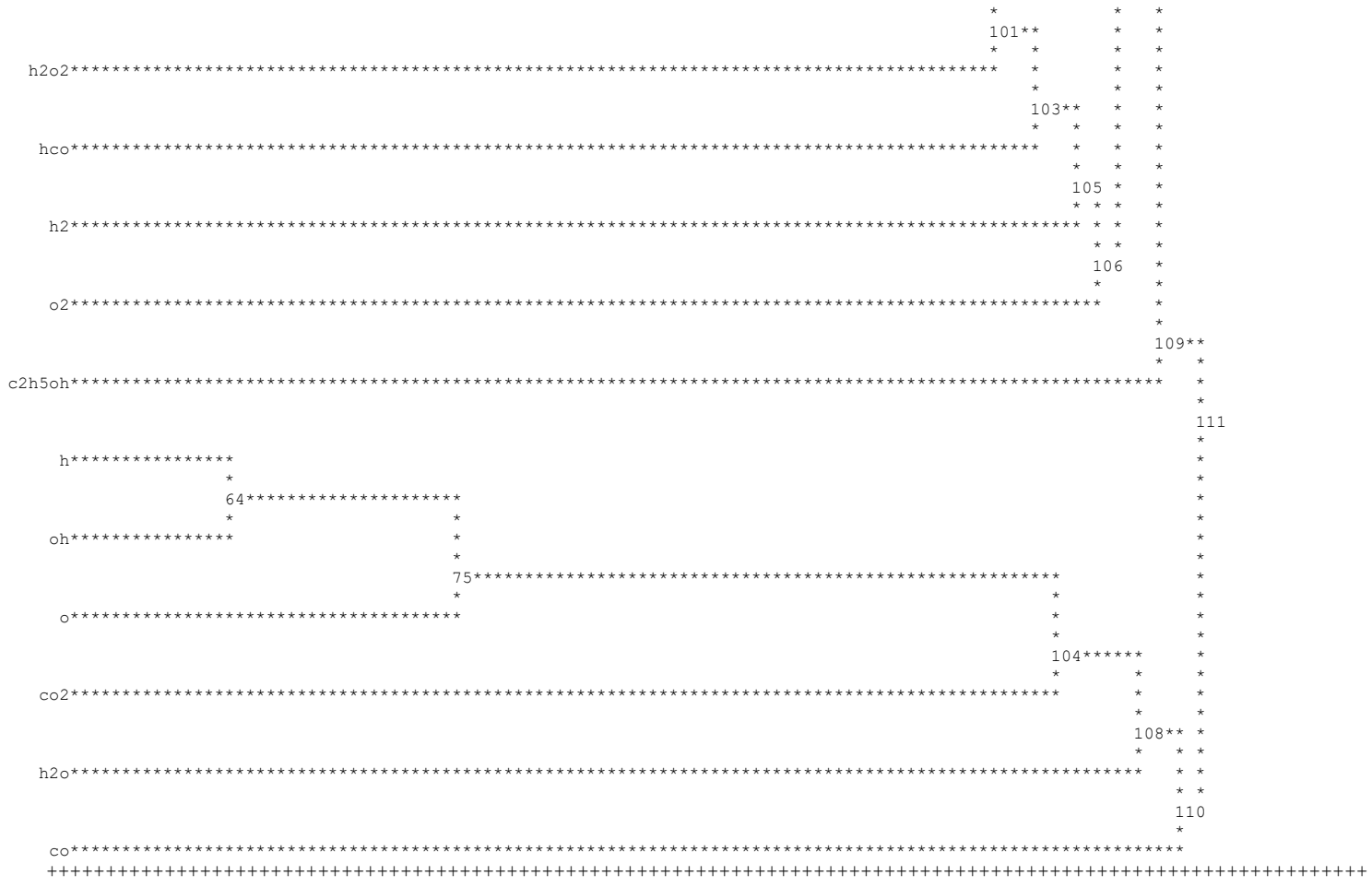
Cluster Analysis: Sample 4

Let's try another Hierarchical Cluster analysis utilizing correlation distances for the similarity matrix and a minimum grouping between clusters on the combustion of ethanol under isochoric (constant volume) conditions. The cluster switch: **"-cluster:1:6:0:2:d:d:127"** was added to the Kintecus command line for the Kintecus-Excel **Ethanol_Combustion.xls** model and executed. The pages that follow are the output from the "cluster.txt" file. It is left as an exercise to the reader to determine why three prominent families of clusters are present.


ch2
65
hcoh
80
ch2(s)
89
c2h
100
c2o
102
ch
107
hoc2h4o2
57
ch3ch2o
66
ch3choh
62
c2h4oh
91
ch3o
83
ho2
95
ch2oh
97
ch2o
99
ch2chco


pc3h5
69
hcco
77
hccoh
82
c2h2
78*****
h2ccch
81*
ch2chch2o******
90*****
c3h8******
59*
ch3hco*******
60*
ch3co**********
61
nc3h7**************
85*****
ch2hco**************
63*******
c2h6**********
67
ch3oh
76
c2h4
84*
hcooh
88***


ch2co
79
ic3h7
71
ch4
73
ch2chcho
58
ac3h4
68
sc3h5
72
pc3h4
70
ch3chco
86
c3h6
74
ac3h5
93
c2h5
92
ch3
94
c3h2
96
c2h3
98
chocho


h2o2
hco
h2
o2
c2h5oh
h
oh
o
co2
h2o
co
101
103
105
106
109
111
64
75
104
108
110

10. Mechanism Validation

A new feature in Kintecus V2021 is to validate a chemical mechanism by identifying the various types of illegal loops and locating conditions where microscopic reversibility is violated. This type of mechanism validation can be beneficial for accurate chemical mechanism determination, rate constant fitting, regression, and accurate deep learning models. Kintecus will apply all the methods listed in Stanbury and Hoffman's 2019 paper "Systematic Application of the Principle of Detailed Balancing to Complex Homogeneous Chemical Reaction Mechanisms"[35].

Mechanism validation is activated by adding the "-MECHV" switch on the Kintecus command line. There are other options to "-MECHV" that can be viewed by typing "kintecus -h." Note that this switch will perform a mechanism validation and then halt the run. Kintecus will not continue to do a complete simulation.

The mechanism validation in Kintecus will detect several illegal conditions and loops:

Case	Type
1.	Microscopic Reversibility/Rate Constant Consistency Test
2.	First rho-reduction: One or more illegal irreversible loops detected
3.	Second rho-reduction: One or more illegal irreversible loops detected
4.	Linear-Programming: One or more illegal irreversible loops detected

If there are no irreversible reactions, only case 1 can occur, and Kintecus will skip testing cases 2-4.

Several Kintecus-Excel example spreadsheets demonstrate various illegal loops in the literature. They can be accessed directly in the Kintecus folder or in the Kintecus Workbench under the "Mechanism Validation" menu. Sample batch scripts are also in the "Kintecus/Mechanism_Validation/" subfolder.

Kintecus-Excel sample mechanism validations available are:

Kintecus_Mechanism_Validation_1.xls
Kintecus_Mechanism_Validation_2.xls
Kintecus_Mechanism_Validation_3.xls
Kintecus_Mechanism_Validation_4.xls
Kintecus_Mechanism_Validation_5_Before.xls
Kintecus_Mechanism_Validation_5_After.xls

If illegal loops are identified, there are a few measures that can be done to correct them:

1. Likely, some illegal loops may not lead to any gross error. This possibility is likely true if the Atropos-Kintecus companion program marks parts of the illegal loop(s) as insignificant and can be safely dropped.
2. If the Atropos-Kintecus companion program does NOT mark such parts of the illegal loop as insignificant, then the user can:
    a. For microscopic reversibility inconsistencies:
        i. You can correct these microscopic reversibility inconsistencies by reevaluating the equilibrium constants that define the illegal loops.
        ii. If you are fitting rate constants and one (or more) rate constants are part of this illegal loop, you can use equations to constrain the rate constant against the equilibrium constants of the other reactions. Please see the section: "Global Data Fitting/Regressing with Multiple User Defined Constraints" in this Kintecus manual
    b. Repair illegal loops by making some steps reversible.
    c. Try making some steps irreversible
    d. Remove some steps
    e. You can email David M. Stanbury (one of the authors of the referenced paper) for suggestions.
3. Also, check back for future versions of Kintecus that might automatically correct (or suggest corrections) to your mechanism.

Example Mechanism Validations of Cases 1-5

Example 1

Shown below is the output after clicking RUN on the "**Kintecus_Mechanism_Validation_1.xls."** Kintecus-Excel spreadsheet model. This example demonstrates the detection of Case 1 where all reactions are reversible, but a subset violates microscopic reversibility, such as Wegschieder's condition[36,37]. Note that the mechanism validation starts at "**Performing mechanism validation ..." in the output:**

```
================================================================================================
 Kintecus V2021  Copyright (c) 1995-2021 James C. Ianni
             All Rights Reserved.

 Kintecus is a registered trademark of James C. Ianni.

------------------------------------------------------------------------------
 Please cite Kintecus in your work:

 Ianni, James C., Kintecus, Windows Version 2021, 2021,www.kintecus.com

 There are some journals that do not allow internet
 references. If you cannot use the above "soft"
 reference, please use the below "hard" reference:

  Ianni, James C. , "A Comparison of the Bader-Deuflhard and the Cash-Karp Runge
 -Kutta Integrators for the GRI-MECH 3.0 Model Base on the
 Chemical Kinetics Code Kintecus", pg.1368-1372,
  Computational Fluid and Solid Mechanics,
  2003, K.J. Bathe editor, Elsevier Science Ltd., Oxford, UK.
------------------------------------------------------------------------------
  Compiled with INTEL FORTRAN

<..SNIP..>

 ***************************************************************
  Performing mechanism validation ....

  Please see references below for further details:
 "Systematic Application of the Principle of Detailed Balancing to
   Complex Homogeneous Chemical Reaction Mechanisms";
  David M. Stanbury and Dean Hoffman;
  J. Phys. Chem A; 2019; 123, p5436-5445

 ***************************************************************************
 Performing Reversible Reactions Loop Analysis on Just Reversible Reactions:


================================================================================
Performing Microscopic Reversibility/Rate Constant Consistency TEST ------vv
 ( Wegscheider's Condition Test )
================================================================
Microscopic Reversibility/Rate Constant Consistency Test FAILURE !
----------------------------------------------------------------
Condition #1 violation: Values of rate constants not consistent
 (Wegscheider's Condition Test)
This illegal loop is composed of these reactions:
```

```
Reaction #, Line number  [+linked reversible reaction] in your MODEL spreadsheet
           1 ,      7 [      8 ]
           2 ,     10 [     11 ]
           4 ,     16 [     17 ]
 FORWARD Rxn ==>  [IO3-+I-+2H+ ==> HIO2+HOI]
   ^^--Reverse Rxn ==> [HIO2+HOI ==> IO3-+I-+2H+]
 FORWARD Rxn ==>  [HIO2+I-+H+  ==>2HOI]
   ^^--Reverse Rxn ==> [2HOI ==> HIO2+I-+H+]
 FORWARD Rxn ==>  [IO3-+HOI+H+ ==>2HIO2]
   ^^--Reverse Rxn ==> [2HIO2 ==> IO3-+HOI+H+]
 ========================================================================


**************************************************************************
*ALERT!* Your model has one or more Rate Constant Inconsistencies!
Listed reactions involved are shown above!
 You can correct these microscopic reversibility inconsistencies by
 reevaluating the equilibrium constants that define this illegal loop.
 If you are fitting rate constants and one (or more) rate constants are
 part of this illegal loop, you can equations to constrain the rate
constant against the equilibriums constants of the other reactions.
Please see the section:
 "Global Data Fitting/Regressing with Multiple User Defined Constraints"
in the Kintecus manual for further details.
**************************************************************************

 There are NO additional irreversible reactions to analyze...leaving...

******** End of Simulation at:

 Date: 10/22/2020
 Time: 10:34:10 PM
==========================================================================================
```

Each illegal loop will be listed, and the listing will show :

1) **Reaction numbers composing of the reactions in each illegal loop. This illegal loop is shown by the reaction number, the actual line number that the reaction is located in your MODEL worksheet, and if it is a reversible reaction, the reverse reaction's line number is enclosed in brackets.**
2) **The actual text of the reactions is listed for (1). They are taken from your MODEL worksheet.**

You can correct the above microscopic reversibility inconsistencies by reevaluating the equilibrium constants that define the illegal loops. If you are fitting rate constants and one (or more) rate constants are part of this illegal loop, you can create equations to constrain the rate constant against the equilibrium constants of the other reactions. Please see the section: "Global Data Fitting/Regressing with Multiple User Defined Constraints" in this manual as an example.

Example 2

Shown below is the output after clicking RUN on the "**Kintecus_Mechanism_Validation_2.xls"** Kintecus-Excel spreadsheet model. Again, note that the mechanism validation starts at "**`Performing mechanism validation ...`**" in the output. This case involves adding all the reactions in Example 1 into this kinetic model. The addition of these irreversible reactions could lead to other illegal loops, but they do not in this example. This condition of no illegal loops is shown by the output, "**`FOR FULL MECHANISM All reactions have valid loops!`**" and in the 2nd rho-reduction analysis output, "**`PART II: FOR FULL MECHANISM All reactions have VALID`**

LOOPS!". Kintecus also checks for illegal loops by two linear programming methods following "David M. Stanbury and Dean Hoffman" papers. The linear programming analyses are delineated by the large text heading "Linear Programming." Two linear programming methods are employed due to the complexity of the analyses and possible missed solutions. The heading of the large **"LP Solution #2"** banner delineates the second linear programming method. In this example, both linear programming methods find no additional illegal loops.
Note this new section, "How to Fix?" (due to the irreversible reactions added to the MODEL worksheet) that now appears in the output near the end:

```
The following mechanism loop issues were identified:
  ====================================================
 > One or more microscopic reversibility inconsistencies were found!
```

All types of illegal loops will be listed. In this case, just the same reactions making up the microscopic reversibility inconsistencies are listed again as in Example 1 above.

```
=============================================================================================

<..SNIP..>

 ***************************************************************
  Performing mechanism validation ....

  Please see references below for further details:
 "Systematic Application of the Principle of Detailed Balancing to
   Complex Homogeneous Chemical Reaction Mechanisms";
  David M. Stanbury and Dean Hoffman;
  J. Phys. Chem A; 2019; 123, p5436-5445

 ***************************************************************************
 Performing Reversible Reactions Loop Analysis on Just Reversible Reactions:


=============================================================================
Performing Microscopic Reversibility/Rate Constant Consistency TEST ------vv
 ( Wegscheider's Condition Test )
=============================================================
Microscopic Reversibility/Rate Constant Consistency Test FAILURE !
-------------------------------------------------------------
Condition #1 violation: Values of rate constants not consistent
 (Wegscheider's Condition Test)
This illegal loop is composed of these reactions:

Reaction #, Line number  [+linked reversible reaction] in your MODEL spreadsheet
           1 ,      7 [      8 ]
           2 ,     10 [     11 ]
           4 ,     16 [     17 ]
 FORWARD Rxn ==>  [IO3-+I-+2H+ ==> HIO2+HOI]
   ^^--Reverse Rxn ==> [HIO2+HOI ==> IO3-+I-+2H+]
 FORWARD Rxn ==>  [HIO2+I-+H+  ==>2HOI]
   ^^--Reverse Rxn ==> [2HOI ==> HIO2+I-+H+]
 FORWARD Rxn ==>  [IO3-+HOI+H+ ==>2HIO2]
   ^^--Reverse Rxn ==> [2HIO2 ==> IO3-+HOI+H+]
 ============================================================

*************************************************************************
*ALERT!* Your model has one or more Rate Constant Inconsistencies!
Listed reactions involved are shown above!
 You can correct these microscopic reversibility inconsistencies by
 reevaluating the equilibrium constants that define this illegal loop.
 If you are fitting rate constants and one (or more) rate constants are
 part of this illegal loop, you can equations to constrain the rate
constant against the equilibriums constants of the other reactions.
Please see the section:
 "Global Data Fitting/Regressing with Multiple User Defined Constraints"
in the Kintecus manual for further details.
*************************************************************************

 Adding in an additional            6  irreversible reactions to analyze...
```

```
 ================================================================
 Now Perform Loop Analysis on entire mechanism:
**********************************************************************
 Performing Reversible Reactions Loop Analysis on FULL MECHANISM:
======================================================================
==================================--====================================
FOR FULL MECHANISM All reactions have valid loops!
Will now proceed to Part 2, Test #2, 2nd rho reduction loop test.
==================================--====================================

=====================================---==================================
PART2: Now check for Illegal loops in second rho reduction ..................

==================================--====================================
PART II: FOR FULL MECHANISM All reactions have VALID LOOPS!
Will now proceed to Linear Programming (LP) to test for further illegal loops.
==================================--====================================
```

```
888      d8b
888      Y8P
888
888      888 88888b.   .d88b.   8888b.  888d888
888      888 888 "88b d8P  Y8b     "88b 888P"
888      888 888  888 88888888 .d888888 888
888      888 888  888 Y8b.     888  888 888
88888888 888 888  888  "Y8888  "Y888888 888


8888888b.                                                                  d8b
888   Y88b                                                                 Y8P
888    888
888   d88P 888d888 .d88b.   .d88b.  888d888 8888b.  88888b.d88b.  88888b.d88b.  888 88888b.   .d88b.
8888888P"  888P"  d88""88b d88P"88b 888P"      "88b 888 "888 "88b 888 "888 "88b 888 888 "88b d88P"88b
888        888    888  888 888  888 888    .d888888 888  888  888 888  888  888 888 888  888 888  888
888        888    Y88..88P Y88b 888 888    888  888 888  888  888 888  888  888 888 888  888 Y88b 888
888        888     "Y88P"   "Y88888 888    "Y888888 888  888  888 888  888  888 888 888  888  "Y88888
                                888                                                                888
                           Y8b d88P                                                           Y8b d88P
                            "Y88P"                                                             "Y88P"
```

****

Now Performing Linear Programming (LP) Test for more illegal loops:

==========

==========

First LP algorithm has detected more than one solution..

Will try and find those extra solutions for this test:

==========

WARNING: Although a solution has been found for the
linear programming part, it may be incomplete

Now check for Linear Programming solution for illegal loops:

LP HAS NOT LOCATED ANY ILLEGAL LOOPS!
for LP solution # 1

```
 ---------------------------------------------------------------------
 LP has found another solution and will now test that LP solution::


 ::::::::::::::::::::::::.##:::::::.########:::::::::::::::::::::::::::::::
 :::::::::::::::::::::::::##:::::::##.... ##:::::::::::::::::::::::::::::::
 :::::::::::::::::::::::::##:::::::##:::: ##:::::::::::::::::::::::::::::::
 ::::::::::::::::::::::::::##:::::::########:::::::::::::::::::::::::::::::
 :::::::::::::::::::::::::##:::::::##.....:::::::::::::::::::::::::::::::::
 ::::::::::::::::::::::::::##:::::::##::::::::::::::::::::::::::::::::::::
 ::::::::::::::::::::::::::########:##::::::::::::::::::::::::::::::::::::
 :::::::::::::::::::::::::.....:..:::::::::::::::::::::::::::::::::::::::::
 :.######::.#######:.##::::::.##::::.##.########.####:.#######:.##::: ##:
 .##... ##.##.... ##:##::::::##:::: ##... ##..:. ##:.##.... ##:###:: ##:
 .##:::..::##:::: ##:##::::::##:::: ##::: ##:::: ##::##::::: ##:####: ##:
 . ######::##:::: ##:##::::::##:::: ##::: ##:::: ##::##::::: ##:## ## ##:
 :..... ##:##:::: ##:##::::::##:::: ##::: ##:::: ##::##::::: ##:##. ####:
 .##::: ##:##:::: ##:##::::::##:::: ##::: ##:::: ##::##::::: ##:##:. ###:
 . ######:. #######::########. #######:::: ##::::.####. #######::##::. ##:
 :......:::.......::........:.......::::::..::::....::.......::..::::..::
 ::::::::::::::::::::::::.##.##:::.#######:::::::::::::::::::::::::::::::
 :::::::::::::::::::::::: ## ##::.##.... ##:::::::::::::::::::::::::::::::
 ::::::::::::::::::::::.#########..:::::: ##:::::::::::::::::::::::::::::::
 ::::::::::::::::::::::.. ## ##.::.#######:::::::::::::::::::::::::::::::
 ::::::::::::::::::::::.#########.##:::::::::::::::::::::::::::::::::::::
 ::::::::::::::::::::::.. ## ##.::##:::::::::::::::::::::::::::::::::::::
 :::::::::::::::::::::::: ## ##:::#########:::::::::::::::::::::::::::::::
 ::::::::::::::::::::::::..:..:::.........:::::::::::::::::::::::::::::::::

 -------------------------------------
 LP HAS NOT LOCATED ANY ILLEGAL LOOPS!
  for LP solution #           2
  ^^^^^^^^^^-----------------  Out of linear program
 ************************************************************************

  888    888
  888    888
  888    888
  8888888888  .d88b.  888  888  888
  888    888 d88""88b 888  888  888
  888    888 888  888 888  888  888
  888    888 Y88..88P Y88b 888 d88P
  888    888  "Y88P"   "Y8888888P"

      88888888888
          888
          888
          888   .d88b.
          888  d88""88b
          888  888  888
          888  Y88..88P
          888   "Y88P"

  8888888888 d8b          .d8888b.
  888        Y8P         d88P  Y88b
  888                        .d88P
  8888888    888 888  888   .d88P"
  888        888  Y8bd8P    888"
  888        888   X88K     888
  888        888 .d8""8b.
  888        888 888  888   888

 ************************************************************************

 ========================================================================

   The following mechanism loop issues were identified:
   ====================================================
  > One or more microscopic reversibility inconsistencies were found!
```

```
  HOW TO CORRECT THESE MECHANISM PROBLEMS?
 ==========================================

 1. It is likely that some illegal loops may not lead to any gross error.
 This is likely true if the Atropos-Kintecus companion program marks parts
 of the illegal loop(s) as insignificant and can be safely dropped.

 2. If the Atropos-Kintecus companion program does NOT mark
 such parts of the illegal loop as insignificant then the user can:
(a) For microscopic reversibility inconsistencies:
  You can correct these microscopic reversibility inconsistencies by
   reevaluating the equilibrium constants that define the illegal loops.
   If you are fitting rate constants and one (or more) rate constants are
   part of this illegal loop, you can equations to constraint the rate
   constant against the equilibrium constants of the other reactions.
   Please see the section:
   "Global Data Fitting/Regressing with Multiple User Defined Constraints"
   in the Kintecus manual
 (b) Repair illegal loops by making some steps reversible
 (c) Try making some steps irreversible
 (d) Removing some steps
 (e) You can email David M. Stanbury (one of the authors of the
       referenced paper) for suggestions.

 Also, check back for future versions of Kintecus that
 might automatically correct (or suggest corrections) to your mechanism.

================================================================================


  Ending mechanism validation ....
================================================================================================
```

Example 3

Shown below is the output after clicking RUN on the "**Kintecus_Mechanism_Validation_3.xls"** Kintecus-Excel spreadsheet model. This example demonstrates the detection of Case 3, where the 2nd rho-reduction analysis part identifies an invalid loop. Note that the Wegschieder's condition test is skipped because no reversible loops are found (as shown by the output, "`INFO: i=m, no reactions with loops.`").
As shown by the output `"PART2: Now check for Illegal loops in second rho reduction,"` there are illegal loops identified. They will be shown in the output as:

```
================================================================================================

 ************************************************************
  Performing mechanism validation...

  Please see references below for further details:
 "Systematic Application of the Principle of Detailed Balancing to
   Complex Homogeneous Chemical Reaction Mechanisms";
  David M. Stanbury and Dean Hoffman;
  J. Phys. Chem A; 2019; 123, p5436-5445

 ************************************************************************
 Performing Reversible Reactions Loop Analysis on Just Reversible Reactions:

INFO: i=m, no reactions with loops.

========================================================================
Microscopic reversibility test SKIPPED because of INVALID LOOPS.
========================================================================
```

```
 Adding in an additional            4  irreversible reactions to analyze...

 ======================================================================
 Now Perform Loop Analysis on entire mechanism:
**************************************************************************
 Performing Reversible Reactions Loop Analysis on FULL MECHANISM:
==========================================================================
==================================--======================================
FOR FULL MECHANISM All reactions have valid loops!
Will now proceed to Part 2, Test #2, 2nd rho reduction loop test.
==================================--======================================

=====================================---==================================
PART2: Now check for Illegal loops in second rho reduction ..................

--------------------------------------------------------------------------

 This illegal loop is composed of these reactions:
-(1)R5+(1)R7+(1)R8

  Again the reactions along with the line numbers:
Reaction #, [ Line Number ] in your MODEL spreadsheet
-    5 [   13 ] [   14 ]
+    7 [   19 ] [   20 ]
+    8 [   22 ]

  And the actual reactions in your MODEL sheet:
  [Cl + H2O ==> ClOH- + H+]
 -=> Reverse [ClOH- + H+ ==> Cl + H2O]
  [Cl + Cl- ==> Cl2-]
 -=> Reverse [Cl2- ==> Cl + Cl-]
  [Cl2- + H2O ==> ClOH- + Cl- + H+]
--------------------------------------------------------------------------
==================================--======================================
Part II: FOR FULL MECHANISM there are reactions that have INVALID LOOPS!
They are listed above....
Will now proceed to Linear Programming (LP) to test for further illegal loops.
==================================--======================================

 User has set MECHV switch to skip Part 2:Linear Programming Test....


**************************************************************************

 888    888
 888    888
 888    888
 8888888888  .d88b.  888  888  888
 888    888 d88""88b 888  888  888
 888    888 888  888 888  888  888
 888    888 Y88..88P Y88b 888 d88P
 888    888  "Y88P"   "Y8888888P"

     88888888888
         888
         888
         888   .d88b.
         888  d88""88b
         888  888  888
         888  Y88..88P
         888   "Y88P"

 8888888888 d8b          .d8888b.
 888        Y8P         d88P  Y88b
 888                          .d88P
 8888888    888 888  888   .d88P"
 888        888  Y8bd8P    888"
 888        888   X88K     888
 888        888 .d8""8b.
 888        888 888  888   888
```

```
**************************************************************************

==========================================================================

  The following mechanism loop issues were identified:
  ====================================================
 > In second rho-reduction: One or more illegal irreversible loops were found!

  HOW TO CORRECT THESE MECHANISM PROBLEMS?
 ==========================================

 1. It is likely that some illegal loops may not lead to any gross error.
 This is likely true if the Atropos-Kintecus companion program marks parts
 of the illegal loop(s) as insignificant and can be safely dropped.

 2. If the Atropos-Kintecus companion program does NOT mark
 such parts of the illegal loop as insignificant then the user can:
(a) For microscopic reversibility inconsistencies:
  You can correct these microscopic reversibility inconsistencies by
   reevaluating the equilibrium constants that define the illegal loops.
   If you are fitting rate constants and one (or more) rate constants are
   part of this illegal loop, you can equations to constraint the rate
   constant against the equilibrium constants of the other reactions.
   Please see the section:
   "Global Data Fitting/Regressing with Multiple User Defined Constraints"
   in the Kintecus manual
 (b) Repair illegal loops by making some steps reversible
 (c) Try making some steps irreversible
 (d) Removing some steps
 (e) You can email David M. Stanbury (one of the authors of the
       referenced paper) for suggestions.

 Also, check back for future versions of Kintecus that
 might automatically correct (or suggest corrections) to your mechanism.

==========================================================================


  Ending mechanism validation ....
```

This example demonstrates the detection of Case 3. Note the heading "`PART2: Now check for Illegal loops in second rho reduction`" starts the listing of one or more illegal loops in the output.

The reactions in this illegal loop are listed in three ways:

1) **The reaction numbers compose the loop as a sum of reactions. Each reaction number is prefixed with "R" and a "+" or "-" sign denoted the summation or removal of said reaction in the loop. In this case, there is one illegal loop made of the sum of these reactions "-(1)R5+(1)R7+(1)R8"**

2) **Reaction numbers composing of the reactions. This is shown by the reaction number, the actual line number that the reaction is located in your MODEL worksheet and if it is a reversible reaction, the reverse reaction's line number is enclosed in brackets. In this case, reactions 5, 7, and 8. Reactions 5 and 7 are reversible reactions on line numbers 13 and 14 for reversible reaction 5 and line numbers 19 and 20 for reversible reaction 7. Irreversible reaction 8 that makes up this illegal loop is located on line number 22 in your MODEL worksheet.**

3) **The actual text of the reactions listed for (2). They are directly taken from your MODEL worksheet.**

Example 4

Shown below is the output after clicking RUN on the "**Kintecus_Mechanism_Validation_4.xls."** Kintecus-Excel spreadsheet model. This example demonstrates the detection of illegal loop Cases 3 and 4. There are several invalid loops identified by the 2nd rho-reduction analysis part and by the **"Linear Programming"** part (both LP solutions find an invalid loop). Note that the Wegschieder's condition test is skipped because no reversible loops are found (as shown by the output, **"INFO: i=m, no reactions with loops.").**

Also, note that the mechanism validation starts at "**Performing mechanism validation ..." in the output:**

```
================================================================================================
************************************************************
  Performing mechanism validation ....

  Please see references below for further details:
 "Systematic Application of the Principle of Detailed Balancing to
   Complex Homogeneous Chemical Reaction Mechanisms";
  David M. Stanbury and Dean Hoffman;
  J. Phys. Chem A; 2019; 123, p5436-5445

 ************************************************************************
 Performing Reversible Reactions Loop Analysis on Just Reversible Reactions:

INFO: i=m, no reactions with loops.

========================================================================
Microscopic reversibility test SKIPPED because of INVALID LOOPS.
========================================================================


 Adding in an additional           22  irreversible reactions to analyze...

 ======================================================================
 Now Perform Loop Analysis on entire mechanism:
************************************************************************
 Performing Reversible Reactions Loop Analysis on FULL MECHANISM:

========================================================================
==================================--====================================
FOR FULL MECHANISM All reactions have valid loops!
Will now proceed to Part 2, Test #2, 2nd rho reduction loop test.
==================================--====================================

=========================================---==================================
PART2: Now check for Illegal loops in second rho reduction ..................

------------------------------------------------------------------------

 This illegal loop is composed of these reactions:
-(1)R1+(1)R5+(1)R6

  Again the reactions along with the line numbers:
Reaction #, [ Line Number ] in your MODEL spreadsheet
-     1 [     3 ] [     4 ]
+     5 [     8 ] [     9 ]
+     6 [    10 ]
  And the actual reactions in your MODEL sheet:
  [S2O3--+IO4-+H+==>S2O3OH-+IO3-]
 -=> Reverse [S2O3OH-+IO3-==>S2O3--+ IO4-+H+]
  [S2O3--+IO3-+2H+==>S2O3OH-+HIO2]
 -=> Reverse [S2O3OH-+HIO2==>S2O3--+IO3-+2H+]
  [IO4-+HIO2==>2IO3-+H+]
------------------------------------------------------------------------
------------------------------------------------------------------------
```

```
 This illegal loop is composed of these reactions:
-(1)R1+(1)R7+(1)R23

  Again the reactions along with the line numbers:
Reaction #, [ Line Number ] in your MODEL spreadsheet
-    1 [    3 ] [    4 ]
+    7 [   11 ]
+   23 [   29 ]
  And the actual reactions in your MODEL sheet:
  [S2O3--+IO4-+H+==>S2O3OH-+IO3-]
 -=> Reverse [S2O3OH-+IO3-==>S2O3--+ IO4-+H+]
  [IO4-+HOI==>IO3-+HIO2]
  [S2O3--+HIO2+H+==>S2O3OH-+HOI]
--------------------------------------------------------------------------
--------------------------------------------------------------------------

 This illegal loop is composed of these reactions:
-(1)R5+(1)R9+(1)R10-(1)R12+(1)R23

  Again the reactions along with the line numbers:
Reaction #, [ Line Number ] in your MODEL spreadsheet
-    5 [    8 ] [    9 ]
+    9 [   13 ] [   14 ]
+   10 [   15 ]
-   12 [   17 ] [   18 ]
+   23 [   29 ]
  And the actual reactions in your MODEL sheet:
  [S2O3--+IO3-+2H+==>S2O3OH-+HIO2]
 -=> Reverse [S2O3OH-+HIO2==>S2O3--+IO3-+2H+]
  [IO3-+I-+2H+==>I2O2+H2O]
 -=> Reverse [I2O2+H2O==>IO3-+I-+2H+]
  [I2+I2O2+2H2O==>2HIO2+2I-+2H+]
  [I2+H2O==>HOI+I-+H+]
 -=> Reverse [HOI+I-+H+==>I2+H2O]
  [S2O3--+HIO2+H+==>S2O3OH-+HOI]
--------------------------------------------------------------------------
--------------------------------------------------------------------------

 This illegal loop is composed of these reactions:
-(1)R12+(1)R19+(1)R26+(1)R27

  Again the reactions along with the line numbers:
Reaction #, [ Line Number ] in your MODEL spreadsheet
-   12 [   17 ] [   18 ]
+   19 [   25 ]
+   26 [   32 ] [   32 ]
+   27 [   33 ]
  And the actual reactions in your MODEL sheet:
  [I2+H2O==>HOI+I-+H+]
 -=> Reverse [HOI+I-+H+==>I2+H2O]
  [S2O3OH-+S2O3I-==>S4O6--+HOI]
  [S4O6--+I2=S4O6I-+I-]
-=> Reverse [S4O6--+I2=S4O6I-+I-]
  [S4O6I-+H2O==>S2O3OH-+S2O3I-+H+]
--------------------------------------------------------------------------
```

```
=====================================--=======================================
Part II: FOR FULL MECHANISM there are reactions that have INVALID LOOPS!
They are listed above....
Will now proceed to Linear Programming (LP) to test for further illegal loops.
=====================================--=======================================

 888      d8b
 888      Y8P
 888
 888      888 88888b.   .d88b.   8888b.  888d888
 888      888 888 "88b d8P  Y8b     "88b 888P"
 888      888 888  888 88888888 .d888888 888
 888      888 888  888 Y8b.     888  888 888
 88888888 888 888  888  "Y8888  "Y888888 888


 8888888b.                                                                  d8b
 888   Y88b                                                                 Y8P
 888    888
 888   d88P 888d888 .d88b.   .d88b.  888d888 8888b.  88888b.d88b.  88888b.d88b.  888 88888b.   .d88b.
 8888888P"  888P"  d88""88b d88P"88b 888P"      "88b 888 "888 "88b 888 "888 "88b 888 888 "88b d88P"88b
 888        888    888  888 888  888 888    .d888888 888  888  888 888  888  888 888 888  888 888  888
 888        888    Y88..88P Y88b 888 888    888  888 888  888  888 888  888  888 888 888  888 Y88b 888
 888        888     "Y88P"   "Y88888 888    "Y888888 888  888  888 888  888  888 888 888  888  "Y88888
                                  888                                                                888
                             Y8b d88P                                                           Y8b d88P
                              "Y88P"                                                             "Y88P"


**********************************************************************
Now Performing Linear Programming (LP) Test for more illegal loops:

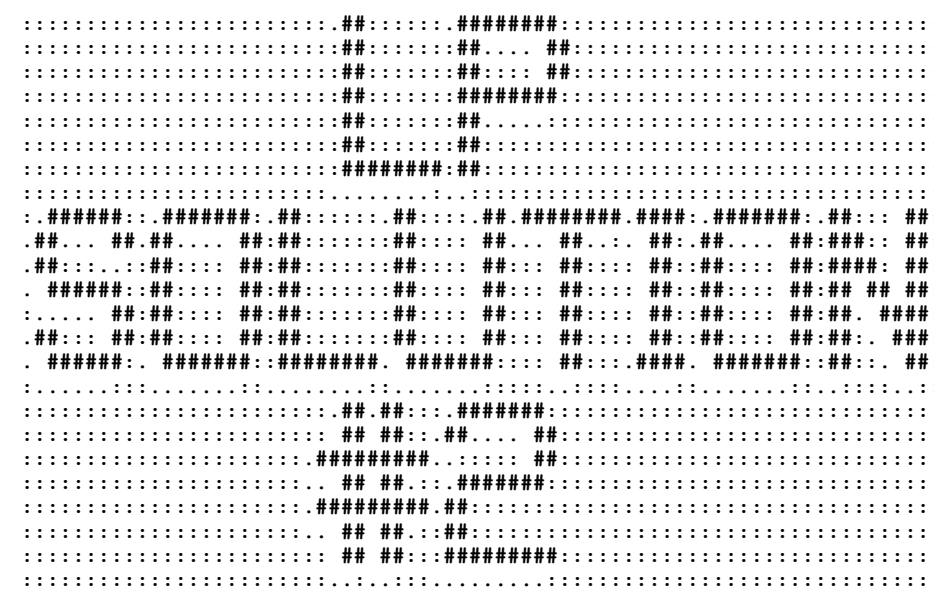
-------------------------------------
LP HAS LOCATED A FEW ILLEGAL LOOPS!

************************************************
Reactions composing this illegal loop::
-(6)R1+(2)R5+(1)R6+(1)R7+(4)R8+(1)R9+(1)R10-
(6)R12+(2)R14+(2)R15+(2)R16+(2)R18+(1)R19+(2)R23+(1)R26+(1)R27
************************************************

  Again the reactions along with the line numbers:
Reaction #, [ Line Number ] ([Reverse Reaction Line]) in your MODEL spreadsheet
-     1 [     3 ] [     4 ]
+     5 [     8 ] [     9 ]
+     6 [    10 ]
+     7 [    11 ]
+     8 [    12 ]
+     9 [    13 ] [    14 ]
+    10 [    15 ]
-    12 [    17 ] [    18 ]
+    14 [    20 ]
+    15 [    21 ]
+    16 [    22 ]
+    18 [    24 ]
+    19 [    25 ]
+    23 [    29 ]
+    26 [    32 ] [    32 ]
+    27 [    33 ]

 < And the actual reactions in your MODEL sheet: >
  - [S2O3--+IO4-+H+==>S2O3OH-+IO3-]
  -=> Reverse [S2O3OH-+IO3-==>S2O3--+ IO4-+H+]
  + [S2O3--+IO3-+2H+==>S2O3OH-+HIO2]
  -=> Reverse [S2O3OH-+HIO2==>S2O3--+IO3-+2H+]
  + [IO4-+HIO2==>2IO3-+H+]
  + [IO4-+HOI==>IO3-+HIO2]
  + [IO4-+I-+H+==>IO3-+HOI]
  + [IO3-+I-+2H+==>I2O2+H2O]
  -=> Reverse [I2O2+H2O==>IO3-+I-+2H+]
  + [I2+I2O2+2H2O==>2HIO2+2I-+2H+]
  - [I2+H2O==>HOI+I-+H+]
```

```
  -=> Reverse [HOI+I-+H+==>I2+H2O]
  + [HIO2+I2+H2O==>IO3-+2I-+3H+]
  + [S2O3--+I2==>S2O3I-+I-]
  + [S2O3I-+H2O==>S2O3--+HOI+H+]
  + [S2O3--+HOI==>S2O3OH-+I-]
  + [S2O3OH-+S2O3I-==>S4O6--+HOI]
  + [S2O3--+HIO2+H+==>S2O3OH-+HOI]
  + [S4O6--+I2=S4O6I-+I-]
  -=> Reverse [S4O6--+I2=S4O6I-+I-]
  + [S4O6I-+H2O==>S2O3OH-+S2O3I-+H+]
-------------------------------------------------------------------------
```



```
-------------------------------------
LP HAS LOCATED A FEW ILLEGAL LOOPS!

************************************************
Reactions composing this illegal loop::
-(1)R1+(1)R5+(1)R8-(1)R12+(1)R14
************************************************

  Again the reactions along with the line numbers:
Reaction #, [ Line Number ] ([Reverse Reaction Line]) in your MODEL spreadsheet
-     1 [     3 ] [     4 ]
+     5 [     8 ] [     9 ]
+     8 [    12 ]
-    12 [    17 ] [    18 ]
+    14 [    20 ]

 < And the actual reactions in your MODEL sheet: >
  - [S2O3--+IO4-+H+==>S2O3OH-+IO3-]
  -=> Reverse [S2O3OH-+IO3-==>S2O3--+ IO4-+H+]
  + [S2O3--+IO3-+2H+==>S2O3OH-+HIO2]
  -=> Reverse [S2O3OH-+HIO2==>S2O3--+IO3-+2H+]
  + [IO4-+I-+H+==>IO3-+HOI]
  - [I2+H2O==>HOI+I-+H+]
  -=> Reverse [HOI+I-+H+==>I2+H2O]
  + [HIO2+I2+H2O==>IO3-+2I-+3H+]
-------------------------------------------------------------------------
 Double Check Final Net reaction=
 ^^^^^^^^^^------------------  Out of linear program
```

```
*****************************************************************************

 888    888
 888    888
 888    888
 8888888888  .d88b.  888  888  888
 888    888 d88""88b 888  888  888
 888    888 888  888 888  888  888
 888    888 Y88..88P Y88b 888 d88P
 888    888  "Y88P"   "Y8888888P"

     88888888888
         888
         888
         888   .d88b.
         888  d88""88b
         888  888  888
         888  Y88..88P
         888   "Y88P"

 8888888888 d8b          .d8888b.
 888        Y8P         d88P  Y88b
 888                        .d88P
 8888888    888 888  888   .d88P"
 888        888  Y8bd8P    888"
 888        888   X88K     888
 888        888 .d8""8b.
 888        888 888  888   888

*****************************************************************************

=============================================================================

  The following mechanism loop issues were identified:
  ====================================================
 > In second rho-reduction: One or more illegal irreversible loops were found!
 > In the Linear-Programming: One or more illegal irreversible loops were found!

  HOW TO CORRECT THESE MECHANISM PROBLEMS?
 ==========================================

 1. It is likely that some illegal loops may not lead to any gross error.
 This is likely true if the Atropos-Kintecus companion program marks parts
 of the illegal loop(s) as insignificant and can be safely dropped.

 2. If the Atropos-Kintecus companion program does NOT mark
 such parts of the illegal loop as insignificant then the user can:
(a) For microscopic reversibility inconsistencies:
  You can correct these microscopic reversibility inconsistencies by
   reevaluating the equilibrium constants that define the illegal loops.
   If you are fitting rate constants and one (or more) rate constants are
   part of this illegal loop, you can equations to constraint the rate
   constant against the equilibrium constants of the other reactions.
   Please see the section:
   "Global Data Fitting/Regressing with Multiple User Defined Constraints"
   in the Kintecus manual
 (b) Repair illegal loops by making some steps reversible
 (c) Try making some steps irreversible
 (d) Removing some steps
 (e) You can email David M. Stanbury (one of the authors of the
       referenced paper) for suggestions.

 Also, check back for future versions of Kintecus that
 might automatically correct (or suggest corrections) to your mechanism.

=============================================================================


  Ending mechanism validation ....
```

This demonstrates the detection of Cases 3 and 4. Note the heading "**PART2: Now check for Illegal loops in second rho reduction**" starts the listing of one or more illegal loops and shows the illegal loops identified in the **"Linear Programming"** parts.
The reactions in these illegal loops are listed three ways:

1) **Displaying the illegal loop composed of the reaction numbers that constitute loop as a sum of reactions. Each reaction number is prefixed with "R" and a "+" or "-" sign denoted the summation or removal of said reaction in the loop.**

2) **Reaction numbers composing of the reactions. This output is shown by the reaction number, the actual line number that the reaction is located in your MODEL worksheet and if it is a reversible reaction, the reverse reaction's line number is enclosed in brackets.**

3) **The actual text of the reactions is listed for (2). They are directly taken from your MODEL worksheet.**

Example 5

Shown below is the output after clicking RUN on the "**Kintecus_Mechanism_Validation_5.xls."** Kintecus-Excel spreadsheet model. This example demonstrates the detection of Cases 3 and 4. The Kintecus-Excel worksheet "**Kintecus_Mechanism_Validation_5_before.xls"** has illegal loops; however, the "**Kintecus_Mechanism_Validation_5_after.xls"** has those illegal loops corrected (shown below). Note that the mechanism validation starts at "**`Performing mechanism validation ..." in the output`**

```
================================================================================================
**************************************************************
  Performing mechanism validation ....

  Please see references below for further details:
 "Systematic Application of the Principle of Detailed Balancing to
   Complex Homogeneous Chemical Reaction Mechanisms"; David M. Stanbury and Dean Hoffman;
  J. Phys. Chem A; 2019; 123, p5436-5445

 ************************************************************************
 Performing Reversible Reactions Loop Analysis on Just Reversible Reactions:

 ========================================================================================
Performing Microscopic Reversibility/Rate Constant Consistency TEST ------vv
 ( Wegscheider's Condition Test )

 Adding in an additional           94  irreversible reactions to analyze...

 ================================================================
 Now Perform Loop Analysis on entire mechanism:
**********************************************************************
 Performing Reversible Reactions Loop Analysis on FULL MECHANISM:

================================================================================
================================--=============================================
FOR FULL MECHANISM All reactions have valid loops!
Will now proceed to Part 2, Test #2, 2nd rho reduction loop test.
==================================--=====================================

=======================================---==================================
PART2: Now check for Illegal loops in second rho reduction ..................
```

```
------------------------------------------------------------------------

 This illegal loop is composed of these reactions:
+(1)R16-(1)R67+(1)R68

  Again the reactions along with the line numbers:
Reaction #, [ Line Number ] in your MODEL spreadsheet
+   16 [   24 ]
-   67 [   82 ] [   85 ]
+   68 [   83 ]
  And the actual reactions in your MODEL sheet:
  [HO + HSO4- ==> SO4- + H2O]
  [HNO3 + HO ==> NO3 + H2O]
 -=> Reverse [NO3 + H2O ==> HNO3 + HO]
  [HNO3 + HO ==> NO3 + H2O]
------------------------------------------------------------------------
------------------------------------------------------------------------

 This illegal loop is composed of these reactions:
+(1)R19-(1)R71+(1)R74+(1)R76-(1)R79

  Again the reactions along with the line numbers:
Reaction #, [ Line Number ] in your MODEL spreadsheet
+   19 [   27 ]
-   71 [   89 ] [   90 ]
+   74 [   95 ] [   96 ]
+   76 [   98 ] [  114 ]
-   79 [  102 ] [  106 ]
  And the actual reactions in your MODEL sheet:
  [SO4- + OH- ==> SO4-- + HO]
  [SO4- + Cl- ==> SO4-- + Cl]
 -=> Reverse [SO4-- + Cl ==> SO4- + Cl-]
  [HO + Cl- ==> ClOH-]
 -=> Reverse [ClOH- ==> HO + Cl-]
  [ClOH- + Cl- ==> Cl2- + OH-]
 -=> Reverse [Cl2- + OH- ==> Cl- + ClOH-]
  [Cl + H2O2 ==> HO2 + Cl- + H+]
 -=> Reverse [Cl + OCl- ==> ClO + Cl-]
------------------------------------------------------------------------
------------------------------------------------------------------------

 This illegal loop is composed of these reactions:
+(1)R20-(1)R71+(1)R74+(1)R75

  Again the reactions along with the line numbers:
Reaction #, [ Line Number ] in your MODEL spreadsheet
+   20 [   28 ]
-   71 [   89 ] [   90 ]
+   74 [   95 ] [   96 ]
+   75 [   97 ] [   99 ]
  And the actual reactions in your MODEL sheet:
  [SO4- + H2O ==> SO4-- + HO + H+]
  [SO4- + Cl- ==> SO4-- + Cl]
 -=> Reverse [SO4-- + Cl ==> SO4- + Cl-]
  [HO + Cl- ==> ClOH-]
 -=> Reverse [ClOH- ==> HO + Cl-]
  [ClOH- + H+ ==> Cl + H2O]
 -=> Reverse [Cl + H2O ==> ClOH- + H+]
------------------------------------------------------------------------
------------------------------------------------------------------------

 This illegal loop is composed of these reactions:
+(1)R76+(1)R77-(1)R79

  Again the reactions along with the line numbers:
Reaction #, [ Line Number ] in your MODEL spreadsheet
+   76 [   98 ] [  114 ]
+   77 [  100 ]
-   79 [  102 ] [  106 ]
  And the actual reactions in your MODEL sheet:
```

```
  [ClOH- + Cl- ==> Cl2- + OH-]
 -=> Reverse [Cl2- + OH- ==> Cl- + ClOH-]
  [Cl + H2O ==> ClOH- + H+]
  [Cl + H2O2 ==> HO2 + Cl- + H+]
 -=> Reverse [Cl + OCl- ==> ClO + Cl-]
-------------------------------------------------------------------------
-------------------------------------------------------------------------

 This illegal loop is composed of these reactions:
-(1)R75+(1)R76-(1)R79+(1)R83-(1)R96

  Again the reactions along with the line numbers:
Reaction #, [ Line Number ] in your MODEL spreadsheet
-   75 [   97 ] [   99 ]
+   76 [   98 ] [  114 ]
-   79 [  102 ] [  106 ]
+   83 [  107 ]
-   96 [  123 ] [  124 ]
  And the actual reactions in your MODEL sheet:
  [ClOH- + H+ ==> Cl + H2O]
 -=> Reverse [Cl + H2O ==> ClOH- + H+]
  [ClOH- + H+ ==> Cl + H2O]
 -=> Reverse [Cl2- + H2O ==> Cl- + HClOH]
  [Cl + H2O2 ==> HO2 + Cl- + H+]
 -=> Reverse [Cl + OCl- ==> ClO + Cl-]
  [Cl2- ==> Cl + Cl-]
  [Cl3- + O2- ==> Cl2- + Cl- + O2]
 -=> Reverse [Cl2 + H2O ==> Cl- + HOCl + H+]
-------------------------------------------------------------------------
-------------------------------------------------------------------------

 This illegal loop is composed of these reactions:
+(1)R75+(1)R79+(1)R89+(1)R91

  Again the reactions along with the line numbers:
Reaction #, [ Line Number ] in your MODEL spreadsheet
+   75 [   97 ] [   99 ]
+   79 [  102 ] [  106 ]
+   89 [  113 ] [  118 ]
+   91 [  116 ]
  And the actual reactions in your MODEL sheet:
  [ClOH- + H+ ==> Cl + H2O]
 -=> Reverse [Cl + H2O ==> ClOH- + H+]
  [Cl + Cl- ==> Cl2-]
 -=> Reverse [Cl2- ==> Cl + Cl-]
  [Cl2- + H2O ==> Cl- + HClOH]
 -=> Reverse [HClOH + Cl- ==> Cl2- + H2O]
  [Cl2- + OCl- ==> ClO + 2Cl-]
-------------------------------------------------------------------------
-------------------------------------------------------------------------

 This illegal loop is composed of these reactions:
+(1)R79+(1)R89+(1)R92

  Again the reactions along with the line numbers:
Reaction #, [ Line Number ] in your MODEL spreadsheet
+   79 [  102 ] [  106 ]
+   89 [  113 ] [  118 ]
+   92 [  117 ]
  And the actual reactions in your MODEL sheet:
  [Cl + Cl- ==> Cl2-]
 -=> Reverse [Cl2- ==> Cl + Cl-]
  [Cl2- + H2O ==> Cl- + HClOH]
 -=> Reverse [HClOH + Cl- ==> Cl2- + H2O]
  [HClOH ==> ClOH- + H+]
-------------------------------------------------------------------------
====================================--=======================================
Part II: FOR FULL MECHANISM there are reactions that have INVALID LOOPS!
They are listed above....
Will now proceed to Linear Programming (LP) to test for further illegal loops.
====================================--=======================================
```

```
888      d8b
888      Y8P
888
888      888 88888b.   .d88b.   8888b.  888d888
888      888 888 "88b d8P  Y8b     "88b 888P"
888      888 888  888 88888888 .d888888 888
888      888 888  888 Y8b.     888  888 888
88888888 888 888  888  "Y8888  "Y888888 888


8888888b.                                                                  d8b
888   Y88b                                                                 Y8P
888    888
888   d88P 888d888 .d88b.   .d88b.  888d888 8888b.  88888b.d88b.  88888b.d88b.  888 88888b.   .d88b.
8888888P"  888P"  d88""88b d88P"88b 888P"      "88b 888 "888 "88b 888 "888 "88b 888 888 "88b d88P"88b
888        888    888  888 888  888 888    .d888888 888  888  888 888  888  888 888 888  888 888  888
888        888    Y88..88P Y88b 888 888    888  888 888  888  888 888  888  888 888 888  888 Y88b 888
888        888     "Y88P"   "Y88888 888    "Y888888 888  888  888 888  888  888 888 888  888  "Y88888
                                  888                                                               888
                             Y8b d88P                                                          Y8b d88P
                              "Y88P"                                                            "Y88P"
```

****

Now Performing Linear Programming (LP) Test for more illegal loops:

==========

Now check for Linear Programming solution for illegal loops:

LP HAS LOCATED A FEW ILLEGAL LOOPS!

****

Reactions composing this illegal loop::

+(1)R16+(1)R19+(1)R20-(1)R67+(1)R68-(2)R71+(2)R74+(1)R75+(3)R76+(1)R77-
()R79+(1)R83+(2)R89+(1)R91+(1)R92-(1)R96

****

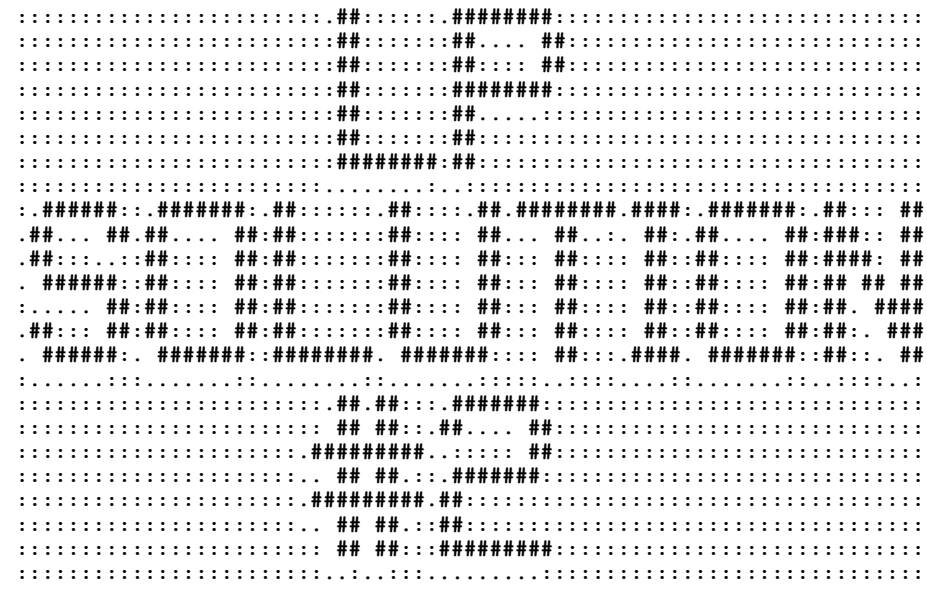
Again the reactions along with the line numbers:

Reaction #, [Line Number] ([Reverse Reaction Line]) in your MODEL spreadsheet

```
+   16 [   24 ]
+   19 [   27 ]
+   20 [   28 ]
-   67 [   82 ] [   85 ]
+   68 [   83 ]
-   71 [   89 ] [   90 ]
+   74 [   95 ] [   96 ]
+   75 [   97 ] [   99 ]
+   76 [   98 ] [  114 ]
+   77 [  100 ]
-   79 [  102 ] [  106 ]
+   83 [  107 ]
+   89 [  113 ] [  118 ]
+   91 [  116 ]
+   92 [  117 ]
-   96 [  123 ] [  124 ]
```

< And the actual reactions in your MODEL sheet: >

+ [HO + HSO4- ==> SO4- + H2O]
+ [SO4- + OH- ==> SO4-- + HO]
+ [SO4- + H2O ==> SO4-- + HO + H+]
- [HNO3 + HO ==> NO3 + H2O]
-=> Reverse [NO3 + H2O ==> HNO3 + HO]
+ [HNO3 + HO ==> NO3 + H2O]



```
-------------------------------------
LP HAS NOT LOCATED ANY ILLEGAL LOOPS!
 for LP solution #           2
*************************************************************************
=========================================================================

  The following mechanism loop issues were identified:
  ================================================
 > In second rho-reduction: One or more illegal irreversible loops were found!
 > In the Linear-Programming: One or more illegal irreversible loops were found!


=========================================================================

  Ending mechanism validation ....
```

The above output demonstrates the detection of cases 3 and 4. Note the heading "`PART2: Now check for Illegal loops in second rho reduction`" starts the listing of one or more illegal loops and the illegal loops identified in the **"Linear Programming"** parts.
The reactions in these illegal loops are listed in three ways:

1) **The reaction numbers that compose the loop as a sum of reactions. Each reaction number is prefixed with "R" and a "+" or "-" sign denoted the summation or removal of said reaction in the loop.**

2) **Reaction numbers composing of the reactions. This illegal loop is shown by the reaction number, the actual line number that the reaction is located in your MODEL worksheet and if it is a reversible reaction, the reverse reaction's line number is enclosed in brackets.**

3) **The actual text of the reactions is listed for (2). They are directly taken from your MODEL worksheet.**

The after model is shown below shows no illegal loops, as one can see by the **"CONGRATULATIONS!! NO ILLEGAL LOOPS WERE IDENTIFIED!"** near the end of the output. This correction of illegal loops was accomplished by making several irreversible reactions into reversible, very slow reactions, identified in the 2nd rho reduction. Changing those irreversible reactions into reversible ones also eliminated the illegal loop identified in case #4 illegal loop (linear programming step). The following irreversible reactions were made reversible (see the MODEL worksheet):

```
HO + HSO4- ==> SO4- + H2O
SO4- + OH- ==> SO4-- + HO
SO4- + H2O ==> SO4-- + HO + H+
HNO3 + SO4- ==> NO3 + HSO4-
Cl + OH- ==> ClOH-
Cl2 + OH- ==> HOCl + Cl-
HClOH ==> ClOH- + H+
HClOH ==> Cl + H2O
```

In addition, both BEFORE and after models have the first three steps were deleted because they utilized photons and do not contribute to any loops. The phenol steps were removed because their products are not defined, and reaction 94 was mass balanced.

```
 ************************************************************
  Performing mechanism validation ....

  Please see references below for further details:
 "Systematic Application of the Principle of Detailed Balancing to
   Complex Homogeneous Chemical Reaction Mechanisms";
  David M. Stanbury and Dean Hoffman;
  J. Phys. Chem A; 2019; 123, p5436-5445

 ************************************************************************
 Performing Reversible Reactions Loop Analysis on Just Reversible Reactions:


================================================================================
Performing Microscopic Reversibility/Rate Constant Consistency TEST ------vv
 ( Wegscheider's Condition Test )


 Adding in an additional           86  irreversible reactions to analyze...

 ====================================================================
 Now Perform Loop Analysis on entire mechanism:
************************************************************************
 Performing Reversible Reactions Loop Analysis on FULL MECHANISM:

================================================================================
=================================--=====================================
FOR FULL MECHANISM All reactions have valid loops!
Will now proceed to Part 2, Test #2, 2nd rho reduction loop test.
=================================--=====================================

=========================================---=================================
PART2: Now check for Illegal loops in second rho reduction ..................

=================================--=====================================
PART II: FOR FULL MECHANISM All reactions have VALID LOOPS!
Will now proceed to Linear Programming (LP) to test for further illegal loops.
=================================--=====================================


 888      d8b
 888      Y8P
 888
 888      888 88888b.   .d88b.   8888b.  888d888
 888      888 888 "88b d8P  Y8b     "88b 888P"
 888      888 888  888 88888888 .d888888 888
 888      888 888  888 Y8b.     888  888 888
 88888888 888 888  888  "Y8888  "Y888888 888


 8888888b.                                                              d8b
 888   Y88b                                                             Y8P
 888    888
 888   d88P 888d888 .d88b.   .d88b.  888d888 8888b.  88888b.d88b.  88888b.d88b.  888 88888b.   .d88b.
 8888888P"  888P"  d88""88b d88P"88b 888P"      "88b 888 "888 "88b 888 "888 "88b 888 888 "88b d88P"88b
 888        888    888  888 888  888 888    .d888888 888  888  888 888  888  888 888 888  888 888  888
 888        888    Y88..88P Y88b 888 888    888  888 888  888  888 888  888  888 888 888  888 Y88b 888
 888        888     "Y88P"   "Y88888 888    "Y888888 888  888  888 888  888  888 888 888  888  "Y88888
                              888                                                                   888
```

Y8b d88P
"Y88P"

```
*****************************************************************
Now Performing Linear Programming (LP) Test for more illegal loops:

Now check for Linear Programming solution for illegal loops:

-------------------------------------
LP HAS NOT LOCATED ANY ILLEGAL LOOPS!
 for LP solution #           1
 ---------------------------------------------------------------------
 LP has found another solution and will now test that LP solution::

 ::::::::::::::::::::::::.##:::::::.########:::::::::::::::::::::::::::::::
 :::::::::::::::::::::::::##:::::::##.... ##:::::::::::::::::::::::::::::::
 ::::::::::::::::::::::::::##:::::::##:::: ##:::::::::::::::::::::::::::::::
 :::::::::::::::::::::::::::##:::::::########:::::::::::::::::::::::::::::::
 :::::::::::::::::::::::::::##:::::::##.....:::::::::::::::::::::::::::::::
 :::::::::::::::::::::::::::##:::::::##:::::::::::::::::::::::::::::::::::::
 ::::::::::::::::::::::::::::########:##:::::::::::::::::::::::::::::::::::::
 :::::::::::::::::::::::::::.....:..:::::::::::::::::::::::::::::::::::::::::
 :.######::.#######:.##:::::::.##::::.##.########.####:.#######:.##::: ##:
 .##... ##.##.... ##:##::::::::##::::: ##... ##..:. ##:.##.... ##:###:: ##:
 .##::::..::##:::: ##:##::::::::##::::: ##::: ##:::: ##::##:::: ##:####: ##:
 . ######::##:::: ##:##::::::::##::::: ##::: ##:::: ##::##:::: ##:## ## ##:
 :..... ##:##:::: ##:##::::::::##::::: ##::: ##:::: ##::##:::: ##:##. ####:
 .##::: ##:##:::: ##:##::::::::##::::: ##::: ##:::: ##::##:::: ##:##:. ###:
 . ######:. #######::########. #######:::: ##:::.####. #######::##::. ##:
 :......:::.......::........::.......:::::..:::....::.......:::..::::..::
 ::::::::::::::::::::::::.##.##:::.#######:::::::::::::::::::::::::::::::
 ::::::::::::::::::::::::: ## ##::.##.... ##:::::::::::::::::::::::::::::::
 ::::::::::::::::::::::::.#########..::::: ##:::::::::::::::::::::::::::::::
 ::::::::::::::::::::::::.. ## ##.::.#######:::::::::::::::::::::::::::::::
 ::::::::::::::::::::::::.#########.##::::::::::::::::::::::::::::::::::::::
 ::::::::::::::::::::::::.. ## ##.::##::::::::::::::::::::::::::::::::::::::
 ::::::::::::::::::::::::: ## ##::::#########:::::::::::::::::::::::::::::::
 :::::::::::::::::::::::::..:..:::.........:::::::::::::::::::::::::::::::::

-------------------------------------
LP HAS NOT LOCATED ANY ILLEGAL LOOPS!
 for LP solution #           2

*************************************************************************
*************************************************************************
                      CONGRATULATIONS!!
                  NO ILLEGAL LOOPS WERE IDENTIFIED!
*************************************************************************
*************************************************************************
```

11. Chemnet

“A picture is worth a thousand words”
(*or thousands of chemical reactions*)

A new feature in Kintecus 2025 is the ability to generate pictural plots of the chemical kinetic mechanism with one switch (“-chemnet”). Many examples are shown below after this section. This plotting is accomplished by utilizing the Graphviz graph language[37]. This plotting ability requires the Graphviz system to be located within the “./Kintecus/.” directory such as “**`C:\Kintecus\Graphviz\*`**” and the related binaries such as “**`C:\Kintecus\Graphviz\bin\dot.exe`**” and “**`C:\Kintecus\Graphviz\neato.exe`**” and many other programs. If Graphviz is not present, please download the Windows (or Linux) version and extract the system into the “./Kintecus/” path such as “**`C:\Kintecus\`**”**`.`**

Kintecus can generate such pictures by including a simple switch: “-chemnet”. The actual picture-generating system utilized is the famous graphviz system [1]. Kintecus will generate specialized graphviz test files (that are named “chemnetout.gv”) that graphviz will parse into a chemical network picture. However, most users will want to alter Kintecus ability to output the picture description file to the graphviz system. This is done by including two *optional* test files: a “chemnet.txt” file and/or a “specnet.txt” file. The first optional file, “chemnet.txt,” describes various global values for the picture layer, including network type, network layout, arrow types, reaction types, preprocessors, box color, box type, and much more. The second optional file, “specnet.txt”, applies various filters to the species drawn in the picture, such as “absorbing” some species into the reaction arrow, hiding certain reactants/products, and highlighting sources and sinks for some species. All these features are described in the following two sections. Note that if a user performs a “Mechanism Validation Analysis” on the chemical network via the “-MECHV” switch (described elsewhere in this Kintecus manual) and a “-chemnet” switch is also provided, then Kintecus will generate a picture and *highlight* the four invalid types of illegal loops (if any are present). This graphical highlighting of illegal reaction loops is described below with examples. The picture or vector drawing outputs should be in the same directory as the Kintecus binary (usually in “C:\Kintecus\” and might be named as “C:\Kintecus\chemnetwork.png” or “C:\Kintecus\chemnetwork.svg”).

The Optional ChemNet File

The ChemNet file, “chemnet.txt”, is optional. This text file contains “key=value” pairs that set various global values for the picture generation. Lines that begin with “#” are treated as comments. The keywords and their default values are shown in the table below. All keywords are optional.

Table 26. Optional Keywords utilized in the optional Chemnet file "chemnet.txt".

KEYWORD	WHAT DOES IT DO?	POSSIBLE VALUES	DEFAULT VALUE
RENDER	Select the type of Renderer	**dot**, **neato**, fdp, **circo**, sfdp, twopi, nop, nop2, osage. See graphviz documentation.	**dot**
TYPE	Chemical network display	Species (there is only one option right now)	**species**
LAYOUT	Distribution of species nodes	Topbottom, leftright, rightleft, bottomtop, circular	**leftright**
OUTSIDE	Set graphic enclosure about species name	Box, circle, oval, diamond, rounded, none	**box**
ARROW	Display reaction numbers above arrow	1=Ordinal reaction number, 2=Actual line numbers, 0=none	**None (0)**
REACTION_TYPE	If reaction numbers are displayed, how to display them above the arrow	0=just the reaction number, 1=prefix with character "k<number>", 2=add "k <number>" (note the space). Use this with the ARROW keyword described above in this table.	**0**
PREPROCESSOR	Select a special network preprocessor (*see below for further information*)	pre+postprocessor(s)=0 (none),1, 2, 3, 4 or 5	**0 (none)**
FILLCOLOR	Fillcolor for graphic enclosure around species names	black|white|gray|blue|red|purple|green|yellow	**white**
LINECOLOR	Color for reaction lines	black|white|gray|blue|red|purple|green|yellow	**black**
SIGN	Select how the species names written on reaction lines are displayed (*see below for more information*)	standard | flip |none | R<character_to_use> | P<character_to_use>	**standard**
ARROW_TYPE	Selects the type of graphic arrow for reactions	vectors (default) , line (none), diamond (diamond ends), circle (circle ends) box, curve, inv, crow, tee (supervector), vee	**vectors**
OUTPUT	Output the chemical network picture into various picture formats	png (default), jpg, gif, svg (vector drawing), json, ps, pdf, imap, cmapx or fig	**png**
LINK	Link forward and reverse reactions into a single double arrow	Yes or No	**No**

The below chemical mechanism of enzyme inhibition will be utilized to describe some basic ChemNet features and all the following sample pictures (please see the “Chemnet_Enzyme_Inhibition_model.xlsm” file):

Table 27. Enzyme Chemical Mechanism utilized in ChemNet output pictures described below.

Non-competitive Inhibition of an enzymatic reaction
E+S==>ES
ES ==> E+S
E+I==>EI
EI==>E+I
ES+I==>EIS
EIS==>ES+I
EI+S==>EIS
EIS==>EI+S
EI+P==>EIS
EIS==>EI+P
ES==>E+P

and we will use this ChemNet description file as a start:

```
#
#  Parameters for Kintecus Visual Graph of Kinetic System
#    (invoked with the "-chemnet:chemnet.txt" or"-chemnet" switch)
#
# All keywords are OPTIONAL and Keywords can be in any order
#
# RENDER
# Select the type of Renderer=dot[default], neato, fdp, circo, sfdp, twopi, nop, nop2, osage
render=dot
#
# TYPE
# type=species
type=species
#
# LAYOUT
# layout=topbottom,  leftright [default], rightleft,  bottomtop,  circular
layout=leftright
#
# Outside enclosure
# Outside=box [default], circle, oval, diamon, rounded, none
outside=rounded
#
# ARROW
#   1=reaction numbers, 2=actual line numbers [default]
ARROW=1
#
# REACTION_TYPE
#  0=just the reaction number [default], 1=prefix with character "k<number>", 2=add "k <number>"
# arrow_type=Reaction # | k | k_SPACE
Reaction_Type=k
#
# Preprocessing and Postprocessing
# pre+postprocessor(s)=0 (none),1, 2, 3, 4 or 5
preprocessor=0
#
# FILLCOLOR
# fillcolor=black, white [default], gray, blue, red, purple, gree, yellow
fillcolor=yellow
#
# LINECOLOR
# linecolor=black[black], white, gray, blue, red, purple, green, yellow
linecolor=black
#
# SIGN
# sign= standard | flip |none | R<character_to_use> | P<character_to_use>
# standard will place a minus sign in front of reactant species names only
# and a plus, "+" in front of the reactions product's species names t
# flip : flips the signage on the reactants and products species names
# R<character> will use the single <character> in front of the reactions reactant species names
#   (the product species names in the arrows with have space or nothing in front of them)
# P<character> will use the single <character> in front of the reactions prodcut species names
#   (the reactant species names in the arrows with have space or nothing in front of them)
sign=flip
#
#
# Arrow_type=vectors (default) , line (none), diamond (diamond ends), circle (circle ends)
#                          box, curve, inv, crow, tee, vee
Arrow_type=vee
#
# Output type
#  Select either  png (default), jpg, gif, svg, json, ps, pdf, imap, cmapx or fig
#
Output=jpg
#
# Combine reversible reactions into a single DOUBLE arror
LINK=YES
#
```

And this is the optional Specnet description file:

# Species # Name	Arrow_Placement (0,1,2,3)	Display Filter (0,1,2,3,4,5,6)	Source Color	Sink Color
I	3	0	black	black
S	3	0	black	black
END				

Note that the species “I” and “S” have the value “3” set in their “Arrow_Placement” column in the SpecNet input file (“specnet.txt” and described in further detail below), indicating to Kintecus to place those two species into the reaction arrow and do not create a species node for them. The created picture is shown below. Although the “Render” keyword has a few options, the most important to know are the “dot”, “neato”, “sfdp”, and “circo” keywords as shown below (no other changes were made to ChemNet nor Specnet files):

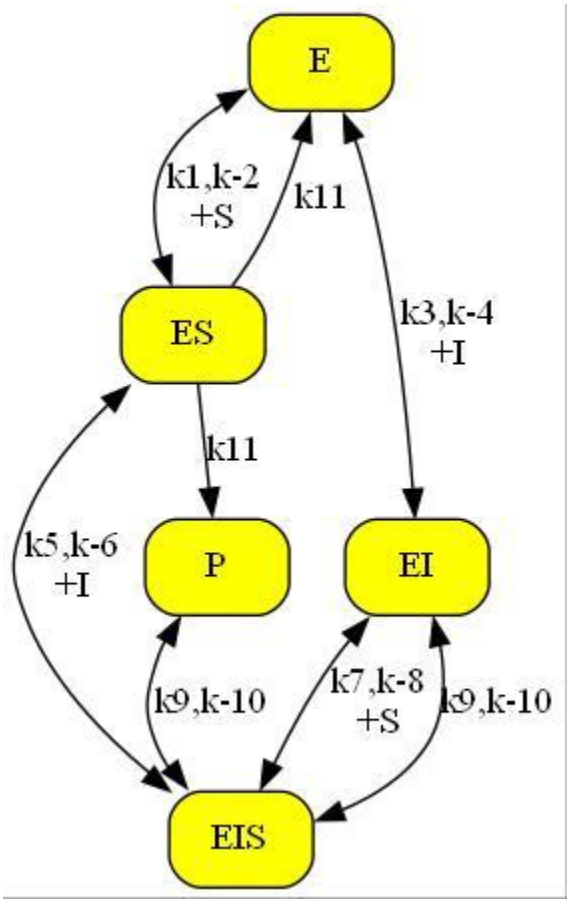


Figure 25. A Chemnet visualization of the reactions listed in Table 2 above, “Enzyme Chemical Mechanism” with Render="dot"

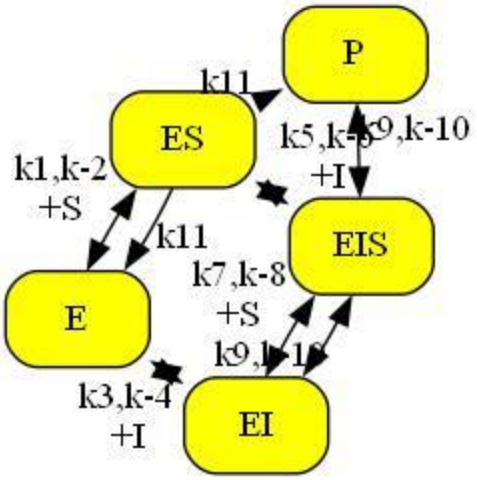


Figure 26. A Chemnet visualization of the reactions listed in Table 2 above, "Enzyme Chemical Mechanism" with Render="neato"

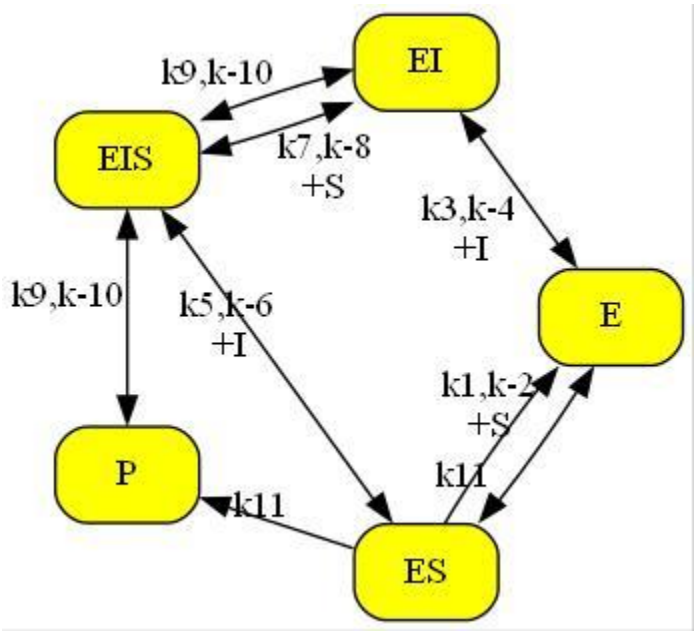


Figure 27. A Chemnet visualization of the reactions listed in Table 2 above, "Enzyme Chemical Mechanism" with Render=circo

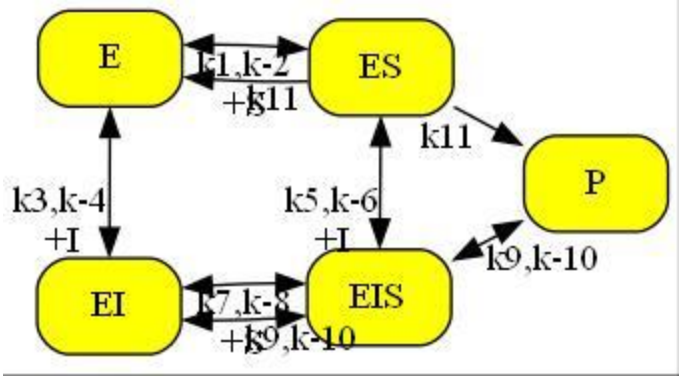


Figure 28. A Chemnet visualization of the reactions listed in Table 2 above, "Enzyme Chemical Mechanism" with Render=sfdp

Although the "layout" keyword supports various display features, the most useful are top-to-bottom (topbottom) and Left-to-right (leftright):

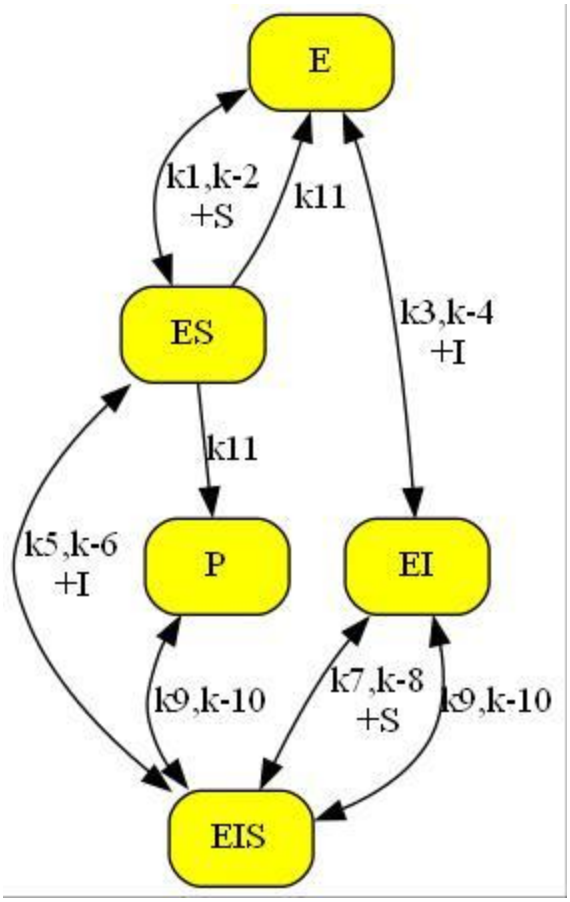


Figure 29. A Chemnet visualization of the reactions listed in Table 2 above, "Enzyme Chemical Mechanism" with Layout=topbottom

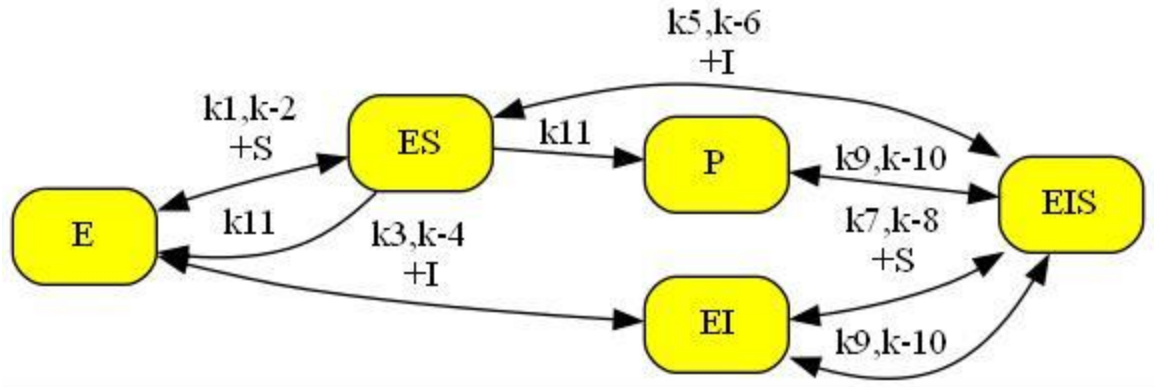


Figure 30. A Chemnet visualization of the reactions listed in Table 2 above, "Enzyme Chemical Mechanism" with Layout=leftright

Changing the "sign=standard" and "link=no" in the ChemNet file and rerunning using the same left-to-right layout as shown above, we now get:

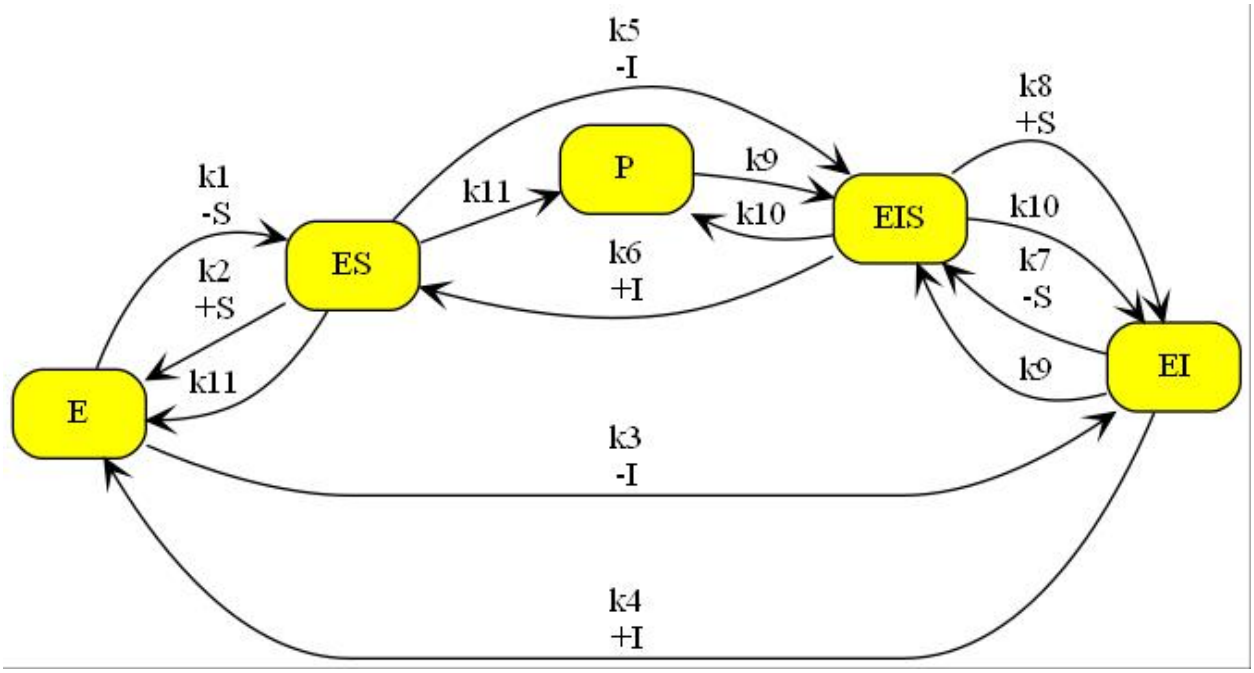


Figure 31. A Chemnet visualization of the reactions listed in Table 2 above, "Enzyme Chemical Mechanism" with Sign=standard, and no linking (LINK=no) of forward/reverse reactions. Note the sign of "S" and "I" in the reaction arrows and the presence of more reaction arrows.

Note the double ended reaction arrows have been replaced with individual single ended reaction arrows. We can also hide species in the plot:

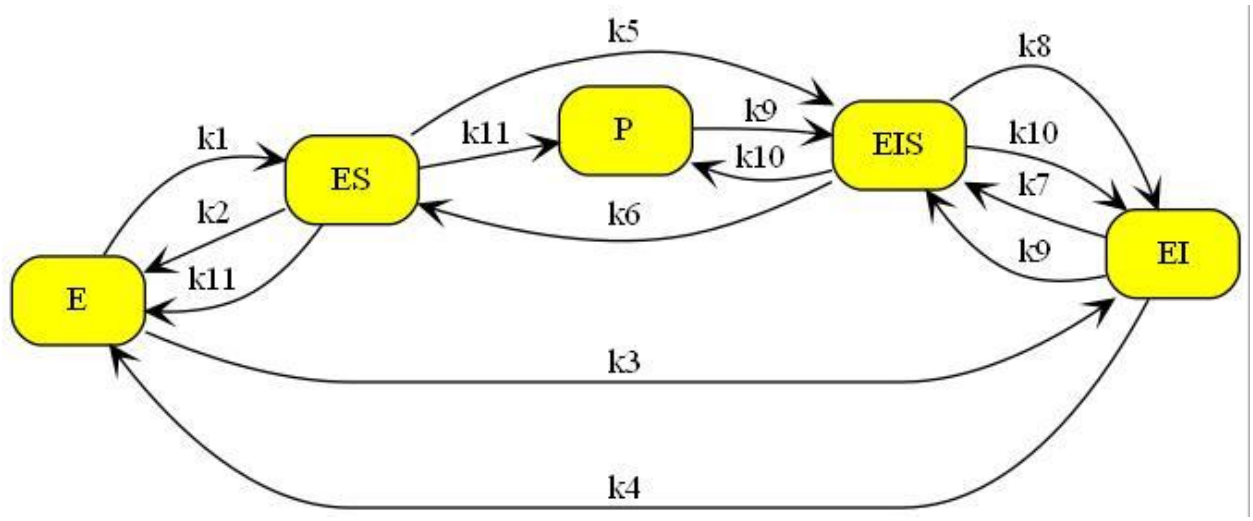


Figure 32. A Chemnet visualization of the reactions listed in Table 2 above, "Enzyme Chemical Mechanism" using the previous plot, the species "I" and "S" are not displayed anywhere by using the Display Filter for species "I" and "S" to a value of "3". This described in more detail in the SpecNet section below.

The figure above shows the complete absence of the species "I" and "S". This is accomplished by setting their display filter to "3" for species "I" and "S" in the Specnet spreadsheet (further described below):

# Species # Name	Arrow_Placement (0,1,2,3)	Display Filter (0,1,2,3,4,5,6)	Source Color	Sink Color
I	0	3	black	black
S	0	3	black	black
END				

As hinted above, the SIGN keyword changes how the "+" or "-" is interpreted when displaying a species above the arrow. In the literature, a prefixed "+" before a species name sometimes translates into "add this reactant." In other literature areas the plus, "+", is interpreted as a product that is formed (such as in some atmospheric journals). Kintecus allows the switching of this interpretation by assigning the +/- sign to "standard" or "flip". One can also use other characters to represent a reactant prefixed with a minus, "-", and the product as a <space> by assigning "SIGN=R-" or a product prefixed with a minus, "-", with "SIGN=P-" or an ampersand, "SIGN=P&".

The ARROW key accepts three values 0-2. Zero, "0" does not place any numbers above the reaction arrows. A value of one, "1", will place the ordinal line numbers (if you deleted all the comments in the MODEL spreadsheet and counted from the top) above the reaction arrows. Setting the ARROW field to two, "2", which will place the actual line numbers in your MODEL worksheet for the reaction's arrows above the reaction arrows. The value two, "2" is the default for the ARROW keyword.

The Reaction_Type keyword accepts three values, 0-2 and will prefix the reaction numbers with nothing, "k<number>" or "k<*space*><number>" respectively.
As mentioned above, the "LINK" keyword will combine the backward and forward arrows for reactions into a single double arrow. This linking of forward and backward reaction arrows into a single double-sided arrow can reduce the clutter in larger chemical network plots.
The output of the ChemNet network is a png file as the default. There are many other output picture formats such as jpg, gif, svg, ps, pdf or fig. Please see the graphviz manual for more explanation of the outputs.
It is **very important** to note that if one uses the Kintecus-Excel workbooks, the workbook will automatically ***delete*** any **previous** "chemnetwork.png" or "chemnetwork.jpg" and "chemnet.txt" or "specnet.txt" files once you click "RUN" on the CONTROL worksheet! Be sure to move/copy those files to a different area or rename them to a different filename!

The preprocessor keyword supports five different values, 0-4. This keyword utilizes several graphviz pre- and postprocessing options to condense networks. Selecting zero performs no network pre- or post-analysis. The preprocessors produce almost no change for simple models like this enzyme inhibition model. For example, preprocessor 3 (setting "preprocessor=3"), "flattens" graphs by looking at one path and deleting redundant paths, so our initial enzyme model becomes:

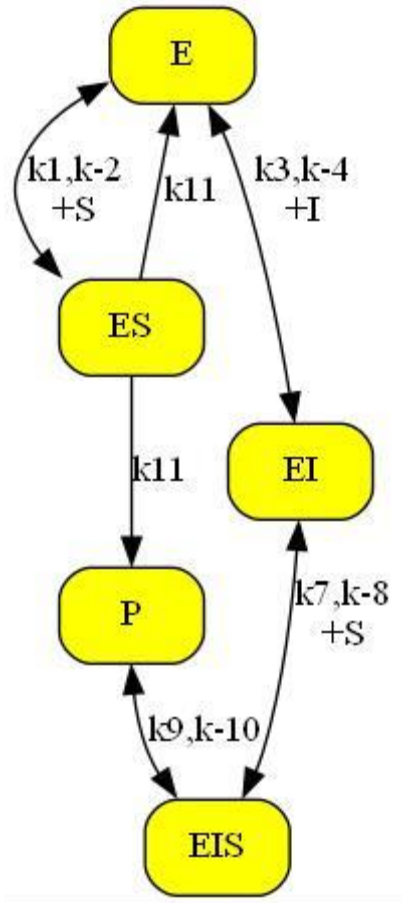


Figure 33. A Chemnet visualization of same Table 28 above, "Enzyme Chemical Mechanism" with "preprocessor=3"

Again, keep in mind that the final picture output should be in the same directory as the Kintecus binary (usually in "C:\Kintecus\" and might be named as "C:\Kintecus\chemnetwork.png" or "C:\Kintecus\chemnetwork.svg"). **IMPORTANT!** Note that if one uses the Kintecus-Excel worksheets, any previous chemnetwork.png or chemnetwork.jpg files will automatically be **DELETED** once one clicks the "RUN" button on the CONTROL worksheet! One should move/copy those files to a different area or rename them to a different filename!

The Specnet Optional File

The Specnet, “specnet.txt”, file is optional. The Specnet file will apply filters and changes to the species drawn in the picture, such as “absorbing” some species into the reaction arrow, hiding certain reactants/products, and highlighting sources and sinks for the user’s selected species. The Specnet file has five fields: “Species name”, “Arrow Placement”, “Display Filter”, “Source Color” and “Sink Color”:

# Species # Name	Arrow_Placement (0,1,2,3)	Display Filter (0,1,2,3,4,5,6)	Source Color (black, blue, red, green, gray, purple)	Sink Color (black, blue, red, green, gray, purple)
# This is a sample specnet.txt input file				
#				
# **Arrow_Placement field values ==** 0 Do not show as part of reaction arrow, 1 show in arrow if reactant,				
# 2 show in arror if product, 3 show in arror if either reactant/product)				
#				
# **Display_Filter** can take several valus == 0=SHOW; 1=If reactant do not show anywhere; 2=If product do not show anywhere;				
# 3=DO NOT SHOW AT ALL				
# 4=ONLY_SHOW_REACTANT,5=ONLY_SHOW_PRODUCT,6=ONLY_REACTANT_PRODUCT				
#				

Adding a species to the “Species Name” column is optional. If a species is listed here, it **MUST** be defined in the “Species Description Spreadsheet” file. Please remember that the species listed in the “Species Description Spreadsheet” must match **exactly** the same species name in the SpecNet file,
as the names are **CaSe SeNsItIvE**.

The Source and Sink color fields should be obvious and they can contain the values, “black, blue, red, green, gray, purple, yellow”. Reaction arrows that point to a species (a source) will be colored as stated in the source color field for that species name. Reaction arrows that point away from a species (a sink) will be colored as stated in the sink color field for that species’ name. If more than one species has a source or sink color, then the species listed first will have that color and override other species down on the list.

The ”Arrow_Placement” forces whether a species is “absorbed” into the reaction arrow. This field contains four possible values: 0, 1, 2, 3:

1) “0” do not place the species into a reaction arrow.
2) “1” place the species into a reaction arrow if it appears as a reactant in any reaction
3) “2” place the species into a reaction arrow if it appears as a product in any reaction
4) “3” place the species into a reaction arrow if it shows up as either a reactant or product in a reaction

When a species is displayed above a reaction arrow, the sign (such as minus, “-“, prefixed in front of a reactant for a reaction) of the species is dictated by the “SIGN” option described in the ChemNet file.
Placing certain “background” or “passenger” chemical species (such as H^+, H_2O, N_2, M, Cl^-, Br^-, etc) can *significantly* reduce the “clutter” in a chemical network graph.
The “Display Filter” field states whether to show a species or whether to not to show *other* species or not.

1) “0” show the species
2) “1” if the species is a reactant, then **do not** show it anywhere in the picture.
3) “2” if the species is a product, then **do not** show it anywhere.
4) “3” if the species is a reactant or product, then do not show it anywhere in the plot
5) “4” show ***ONLY*** this species in reactants(!!)
6) “5” show ***ONLY*** this species in products(!!)
7) “6” show ***ONLY*** this species in products or reactants(!!)

Setting this field to values of four, “4” or above, can drastically change the picture, as it turns off the display of any species that are *not directly related to the said species*. Values of "3" might be used for species that appear throughout a reaction mechanism as it completely hides the species in the graph. These species may not be necessary in the visualization of a chemical scheme such as "M" (Loschmidt's number), "H^+", "H_2O", "CO_2", etc., and can be ignored in larger mechanisms. If one were only interested in viewing all the direct sources or sinks for CO_2 and H_2O in a large chemical mechanism, one would set the "Display_Filter" for the CO_2 and H_2O species to "6." This will

hide ALL species that are not direct sources or sinks for CO_2 and H_2O. Are you confused? Look at the examples below to clarify this further.

A sample Specnet file is shown below. This Specnet file is utilized to plot a chemical network picture of "Photochemical Chlorate–Iodide Clock Reaction", Romulo O. Pires and Roberto B. Faria, Inorg. Chem. 2022. The species I_2 is highlighted with a green source arrow and red sink arrows as shown in the figure below. The passenger ions, Chloride (Cl^-), iodide (I^-) and I_3^- are not shown in the picture. This is because those two passenger ions have a "3" in the "Display_Filter" causing them not to be shown. Hiding such passenger ions can significantly reduce the clutter in large chemical network plots. To further reduce the chemical network clutter, the species, H^+, H_2O and HIO_2 are placed into the reaction arrows by placing a "3" in the "Arrow_Placement" field for the listed species names. Also, the signs of the reactants are negative if they are a product in a reaction and appear in the reaction arrow. This is due to the sign keyword in the Chemnet file is set to the default of "standard". This sign placement is the opposite of the previous enzyme inhibition model samples. The reaction numbers are actually the line numbers the reactions appear on in the MODEL worksheet.

# Species	Arrow_Placement	Display Filter	Source Color	Sink Color
# Name	(0,1,2,3)	(0,1,2,3,4,5,6)	(black, blue, red, green, gray, purple)	(black, blue, red, green, gray, purple)
# This is a sample specnet.txt input file				
#				
# **Arrow_Placement field values ==** 0 Do not show as part of reaction arrow, 1 show in arrow if reactant,				
# 2 show in arror if product, 3 show in arror if either reactant/product)				
#				
# **Display_Filter** can take several valus == 0=SHOW; 1=If reactant do not show anywhere; 2=If product do not show anywhere;				
# 3=DO NOT SHOW AT ALL				
# 4=ONLY_SHOW_REACTANT,5=ONLY_SHOW_PRODUCT,6=ONLY_REACTANT_PRODUCT				
#				
I2	0	0	green	red
Cl-	0	3	black	black
H+	3	0	black	black
H2O	3	0	black	black
I-	0	3	black	black
I3-	0	3	black	black
HIO2	3	0	black	black
END				

Figure 34.Specnet file for the picture generation of " Photochemical Chlorate–Iodide Clock Reaction", Romulo O. Pires and Roberto B. Faria, Inorg. Chem. 2022

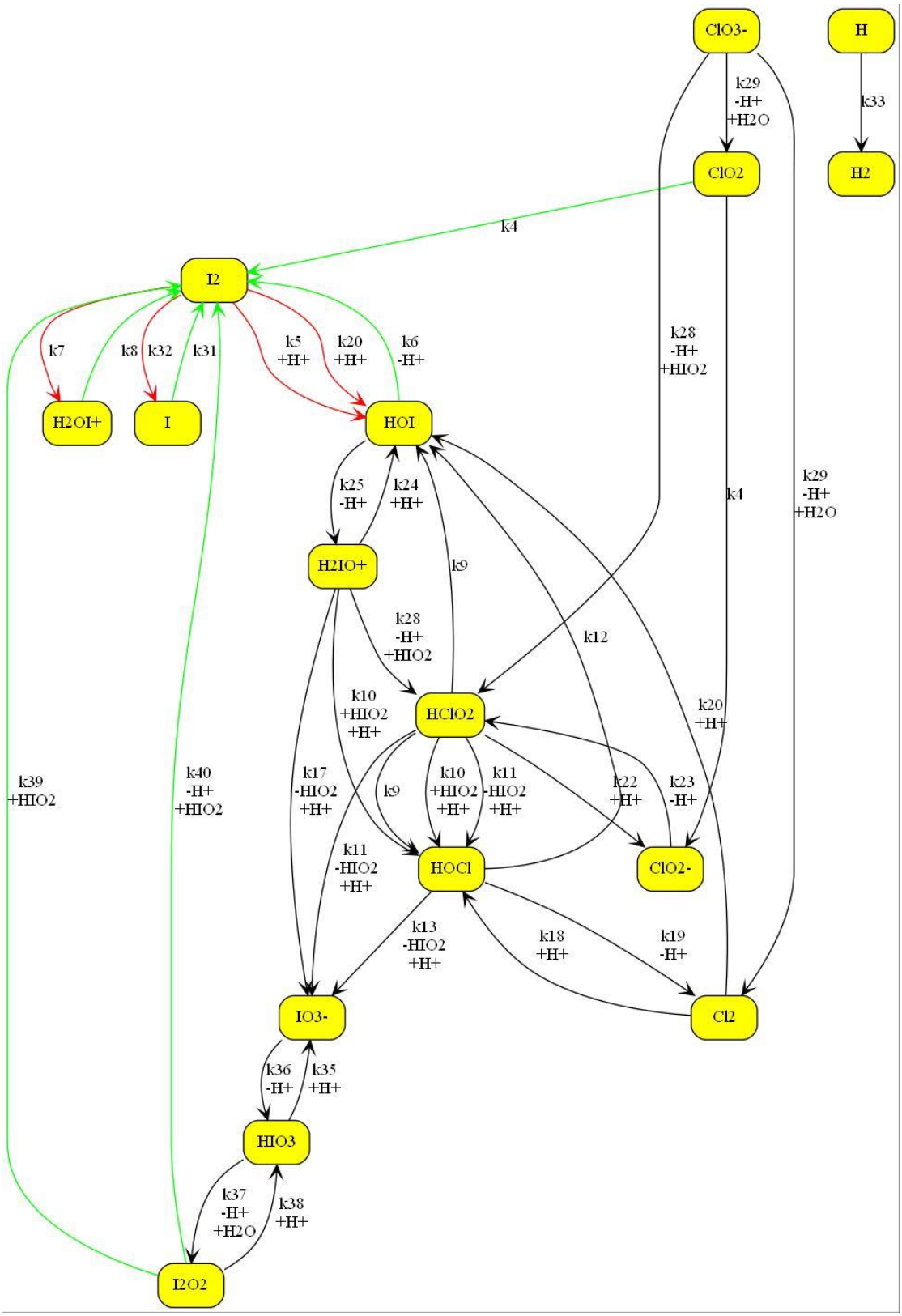


Figure 35. ChemNet picture representation of the " Photochemical Chlorate–Iodide Clock Reaction", Romulo O. Pires and Roberto B. Faria, Inorg. Chem. 2022

```
#
#  Parameters for Kintecus Visual Graph of Kinetic System
#    (invoked with the "-chemnet:chemnet.txt" or"-chemnet:D" switch)
#
# All keywords are OPTIONAL and Keywords can be in any order
#
# RENDER
# Select the type of Renderer=dot, neato, fdp, circo, sfdp, twopi, nop, nop2, osage
render=dot
#
# TYPE
# type=species
type=species
#
# LAYOUT
# layout=topbottom | leftright | rightleft | bottomtop | circular
layout=topbottom
#
# Outside enclosure
# Outside=box|circle|oval|diamond|rounded | none
outside=rounded
#
# ARROW
#   1=reaction numbers, 2=actual line numbers
ARROW=2
#
# REACTION_TYPE
#  0=just the reaction number, 1=prefix with character "k<number>", 2=add "k <number>"
# arrow_type=Reaction #|K|K_SPACE
Reaction_Type=K
#
# Preprocessing and Postprocessing
# pre+postprocessor(s)=0 (none),1, 2, 3, 4 or 5
preprocessor=0
#
# FILLCOLOR
# fillcolor=black|white|gray|blue|red|purple|green|yellow
fillcolor=yellow
#
# LINECOLOR
# linecolor=black|white|gray|blue|red|purple|green|yellow
linecolor=black
#
# SIGN
# sign= standard | flip |none | R<character_to_use> | P<character_to_use>
# standard will place a minus sign in front of reactant species names only
# and a plus, "+" in front of the reactions product's species names t
# flip : flips the signage on the reactants and products species names
# R<character> will use the single <character> in front of the reactions reactant species names
#   (the product species names in the arrows with have space or nothing in front of them)
# P<character> will use the single <character> in front of the reactions prodcut species names
#   (the reactant species names in the arrows with have space or nothing in front of them)
sign=standard
#
#
# Arrow_type=vectors (default) , line (none), diamond (diamond ends), circle (circle ends)
#                          box, curve, inv, crow, tee, vee
Arrow_type=vee
#
# Output type
#  Select either  png (default), jpg, gif, svg, json, ps, pdf, imap, cmapx or fig
#
Output=jpg
#
#
# Combine reversible reactions into a single DOUBLE arror
LINK=NO
#
```

Figure 36. ChemNet file for the " Photochemical Chlorate–Iodide Clock Reaction", Romulo O. Pires and Roberto B. Faria, Inorg. Chem. 2022

Continuing with Pires and Farias model above, suppose we only want to view the reaction paths to $HClO_2$, then one can set the Display_Filter field for $HClO_2$ to a value of six, "6" and replot:

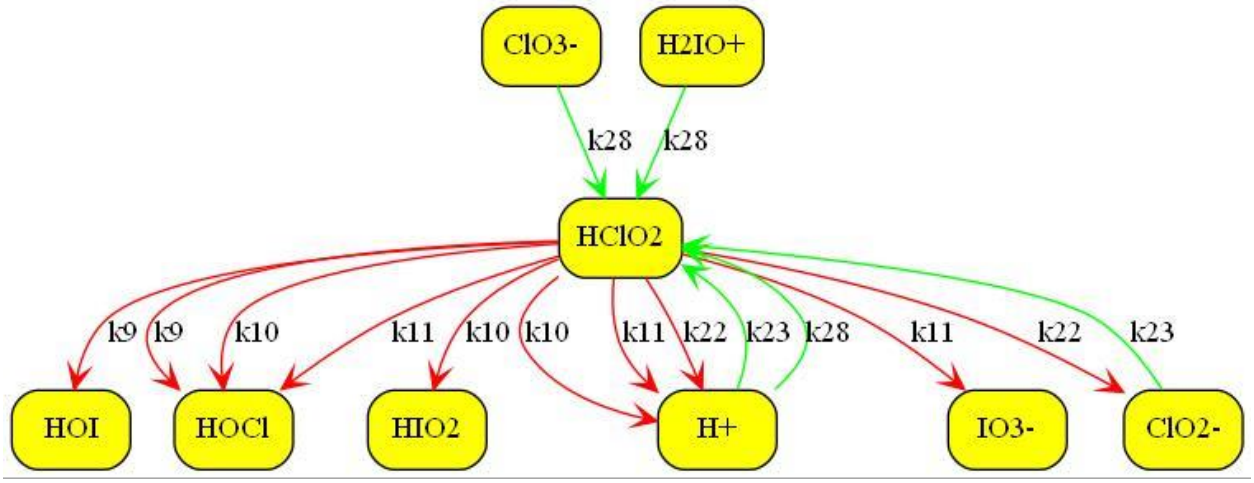


Figure 37. Setting the Display_Filter for HClO2 to six, "6".

Note that we only see all paths that lead to $HClO_2$ and **ignore** all other paths to other species.
We can also set the Display_Filter to six for hydronium, H^+, and we arrive at this final plot:

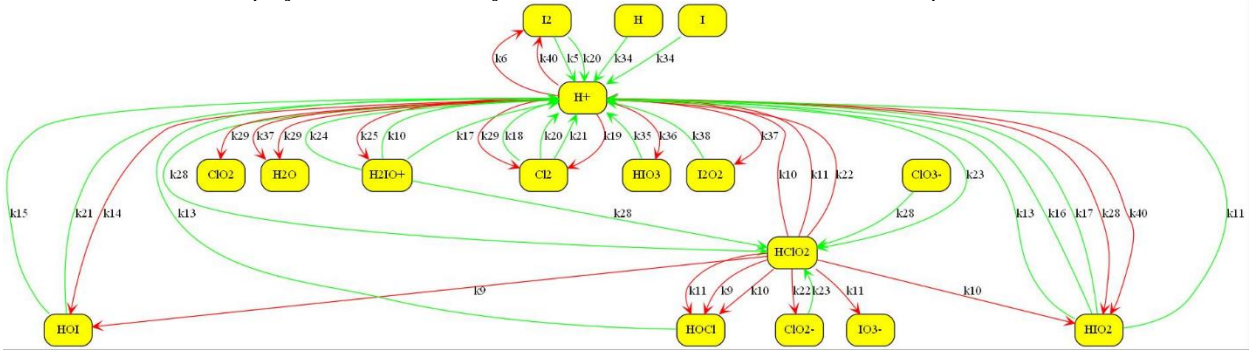


Figure 38. Both $HClO_2$ and H+ have their Display_Filters set to six, "6" in the SpecNet file. Now only the source and sinks are plotted that go to hydronium and $HClO_2$.

# Species # Name	Arrow_Placement (0,1,2,3)	Display Filter (0,1,2,3,4,5,6)	Source Color	Sink Color
HClO2	0	6	green	red
H+	0	6	green	red
END				

Figure 39. SpecNet file for the above plot. Note the values of "6" in the "Display Filter" column. This forces the entire plot to center only around the "$HClO_2$" and "H^+" species sinks and sources.

Note that any source or sink hours from H^+ to $HClO_2$ are green and red because $HClO_2$ has a higher priority in color assignment as that species is listed before H+.

Let's look at the H_2-O_2 combustion model ("ChemNet_Combustion_workbook_OH.xlsm") and view the paths to H_2O. We will use this ChemNet file:

```
#
#  Parameters for Kintecus Visual Graph of Kinetic System
#    (invoked with the "-chemnet:chemnet.txt" or"-chemnet:D" switch)
#
# All keywords are OPTIONAL and Keywords can be in any order
#
# RENDER
# Select the type of Renderer=dot, neato, fdp, circo, sfdp, twopi, nop, nop2, osage
render=dot
#
# TYPE
# type=species
type=species
#
# LAYOUT
# layout=topbottom | leftright | rightleft | bottomtop | circular
layout=leftright
#
# Outside enclosure
# Outside=box|circle|oval|diamond|rounded | none
outside=rounded
#
# ARROW
#   1=reaction numbers, 2=actual line numbers
ARROW=2
#
# REACTION_TYPE
#  0=just the reaction number, 1=prefix with character "k<number>", 2=add "k <number>"
# arrow_type=Reaction #|K|K_SPACE
Reaction_Type=K
#
# Preprocessing and Postprocessing
# pre+postprocessor(s)=0 (none),1, 2, 3, 4 or 5
preprocessor=0
#
# FILLCOLOR
# fillcolor=black|white|gray|blue|red|purple|green|yellow
fillcolor=yellow
#
# LINECOLOR
# linecolor=black|white|gray|blue|red|purple|green|yellow
linecolor=black
#
# SIGN
# sign= standard | flip |none | R<character_to_use> | P<character_to_use>
# standard will place a minus sign in front of reactant species names only
# and a plus, "+" in front of the reactions product's species names t
# flip : flips the signage on the reactants and products species names
# R<character> will use the single <character> in front of the reactions reactant species names
#   (the product species names in the arrows with have space or nothing in front of them)
# P<character> will use the single <character> in front of the reactions prodcut species names
#   (the reactant species names in the arrows with have space or nothing in front of them)
sign=standard
#
#
# Arrow_type=vectors (default) , line (none), diamond (diamond ends), circle (circle ends)
#                          box, curve, inv, crow, tee, vee
Arrow_type=vee
#
# Output type
#  Select either  png (default), jpg, gif, svg, json, ps, pdf, imap, cmapx or fig
#
Output=jpg
#
#
# Combine reversible reactions into a single DOUBLE arror
LINK=YES
#
```

Figure 40.

And this Specnet file:

# Species # Name	Arrow_Placement (0,1,2,3)	Display Filter (0,1,2,3,4,5,6)	Source Color	Sink Color
M	3	0	black	black
O2	3	0	black	black
H2O	0	0	green	red
END				

Which produces this picture:

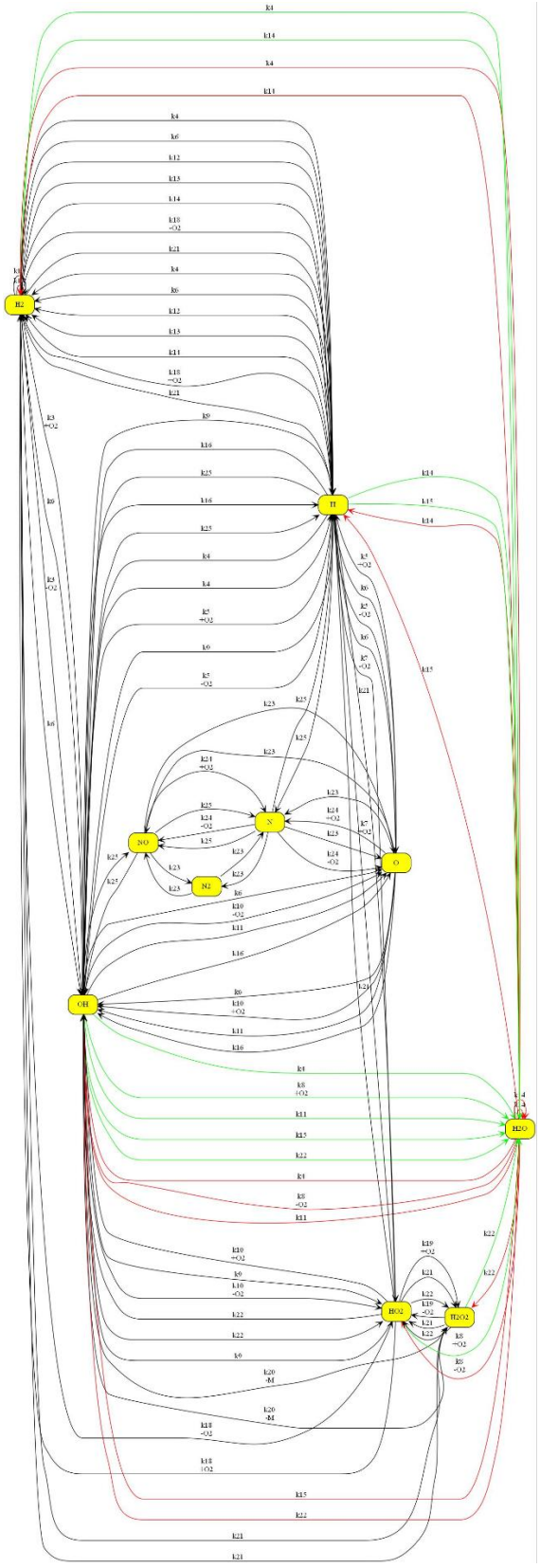


Figure 41.

The plot above is complicated, quite "busy," and "smooshed." If we select the "circo" renderer (setting "render=circo" in the ChemNet file) and combining the forward and reverse reactions (set LINK="yes" in the ChemNet file) and hide O_2 and M (setting the Display_Filter for O_2 and M to "3" in Specnet file) we get this picture of the same chemical mechanism:

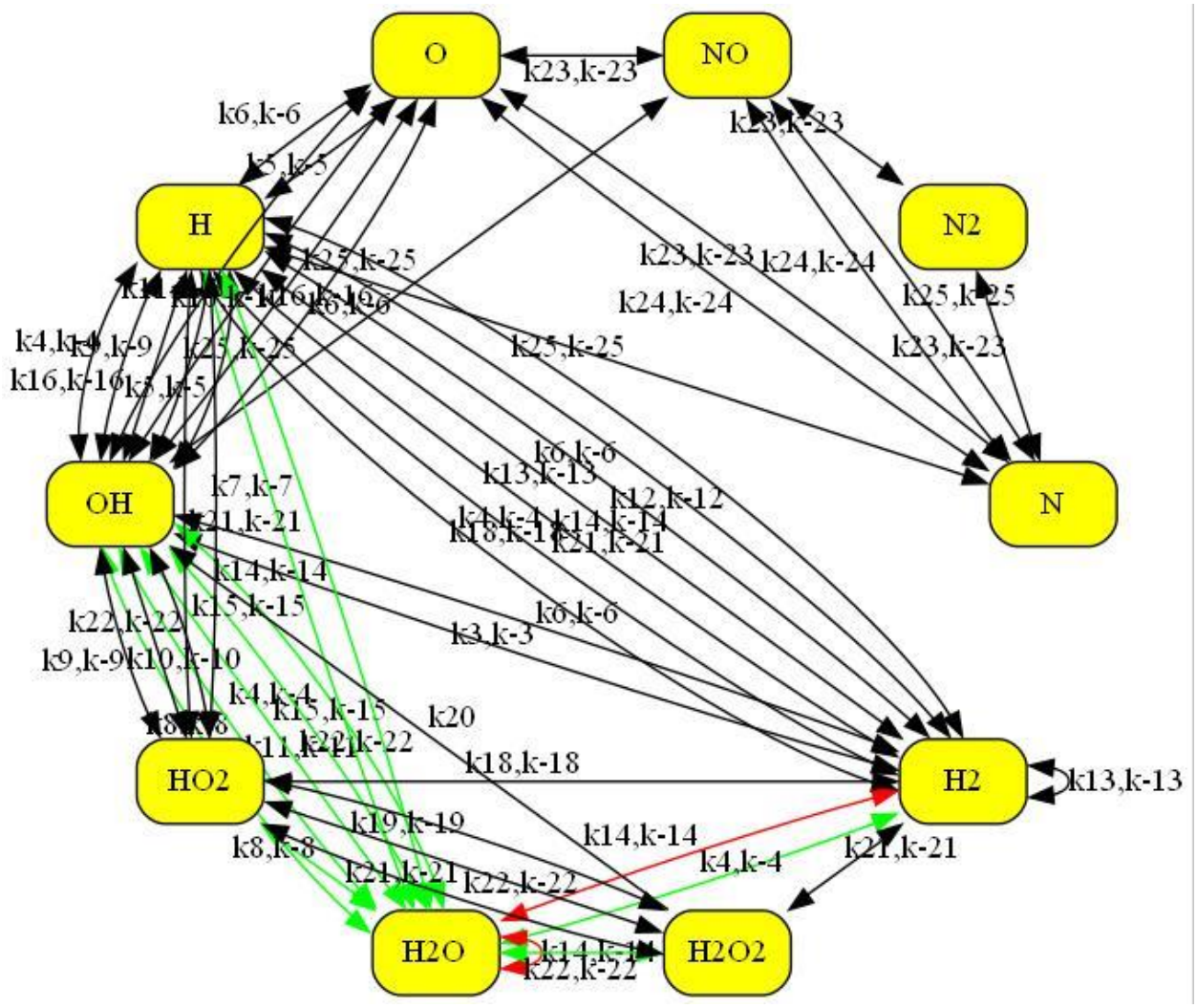


Figure 42. Render="circo" with LINK=YES of the H_2-O_2 combustion model.

The picture is still little complicated. We could remove the reaction labels on the reaction lines to clear it up. We can also just examine paths to H_2O by setting the Display_Filter for H_2O to "6" yielding this Specnet file:

# Species # Name	Arrow_Placement (0,1,2,3)	Display Filter (0,1,2,3,4,5,6)	Source Color	Sink Color
M	3	0	black	black
O2	3	0	black	black
H2O	0	**6**	green	red
END				

This yields a much more compact picture:

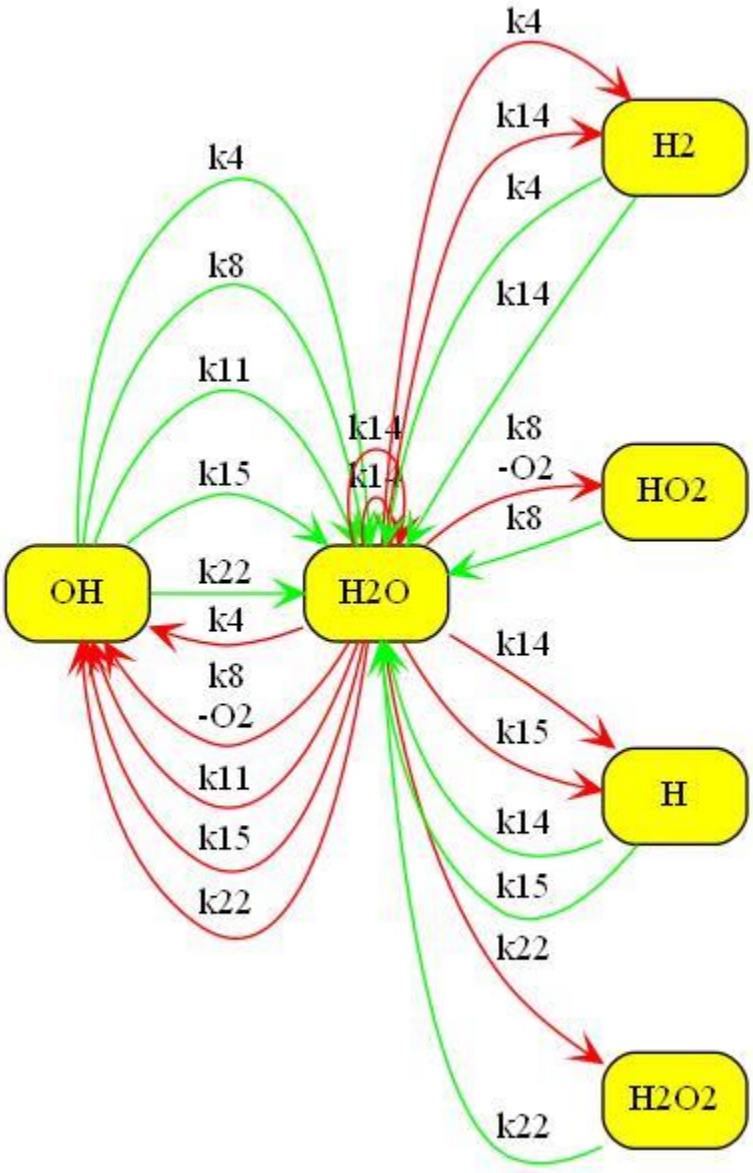


Figure 43. Display_Filter now set to "6" for H_2O.

The above plot is much easier to view.

More Sample Chemnet Plots

The following Chemical Network Description file (ChemNet) settings for the following enzyme inhibition samples are shown in the figure below. Again, all ChemNet keywords are optional and can be in any order. Lines that start with "#" are treated as comment lines and are ignored.

```
#
#  Parameters for Kintecus Visual Graph of Kinetic System
#    (invoked with the "-chemnet:chemnet.txt" or"-chemnet" switch)
#
# All keywords are OPTIONAL and Keywords can be in any order
#
# RENDER
# Select the type of Renderer=dot[default], neato, fdp, circo, sfdp, twopi, nop, nop2, osage
render=dot
#
# TYPE
# type=species
type=species
#
# LAYOUT
# layout=topbottom,  leftright [default], rightleft,  bottomtop,  circular
layout=topbottom
#
# Outside enclosure
# Outside=box [default], circle, oval, diamon, rounded, none
outside=rounded
#
# ARROW
#   1=reaction numbers, 2=actual line numbers [default]
ARROW=1
#
# REACTION_TYPE
#  0=just the reaction number [default], 1=prefix with character "k<number>", 2=add "k <number>"
# arrow_type=Reaction # | k | k_SPACE
Reaction_Type=k
#
# Preprocessing and Postprocessing
# pre+postprocessor(s)=0 (none),1, 2, 3, 4 or 5
preprocessor=0
#
# FILLCOLOR
# fillcolor=black, white [default], gray, blue, red, purple, gree, yellow
fillcolor=yellow
#
# LINECOLOR
# linecolor=black[black], white, gray, blue, red, purple, green, yellow
linecolor=black
#
# SIGN
# sign= standard | flip |none | R<character_to_use> | P<character_to_use>
# standard will place a minus sign in front of reactant species names only
# and a plus, "+" in front of the reactions product's species names t
# flip : flips the signage on the reactants and products species names
# R<character> will use the single <character> in front of the reactions reactant species names
#   (the product species names in the arrows with have space or nothing in front of them)
# P<character> will use the single <character> in front of the reactions prodcut species names
#   (the reactant species names in the arrows with have space or nothing in front of them)
sign=flip
#
#
# Arrow_type=vectors (default) , line (none), diamond (diamond ends), circle (circle ends)
#                          box, curve, inv, crow, tee, vee
Arrow_type=vee
#
# Output type
#  Select either  png (default), jpg, gif, svg, json, ps, pdf, imap, cmapx or fig
#
Output=jpg
#
# Combine reversible reactions into a single DOUBLE arror
LINK=NO
#
```

Figure 44.

Again, the picture below is generated by providing the command line "-chemnet" on the Kintecus command line and using the ChemNet file as shown in the **above** figure. No additional Species Network Description file (SpecNet) has been utilized here.

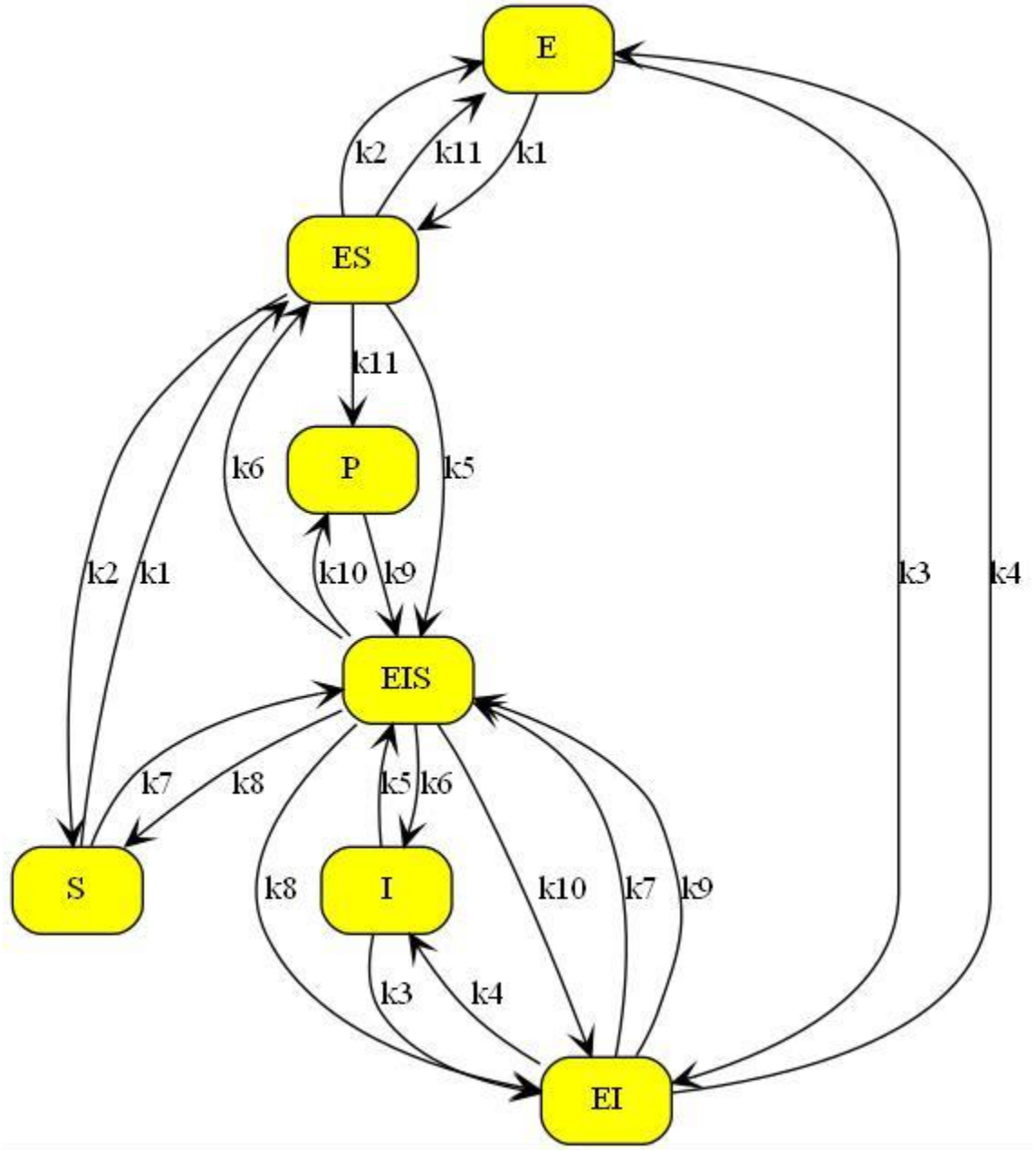


Figure 45.

To produce the picture below, change the ChemNet settings to below, and remove all Specnet settings.
Change the “LINK” keyword in the ChemNet file to “YES”, “**LINK=YES”**
Again, there was no SpecNet file (be sure to delete the “specnet.txt” file if one is present or, it will be read in).

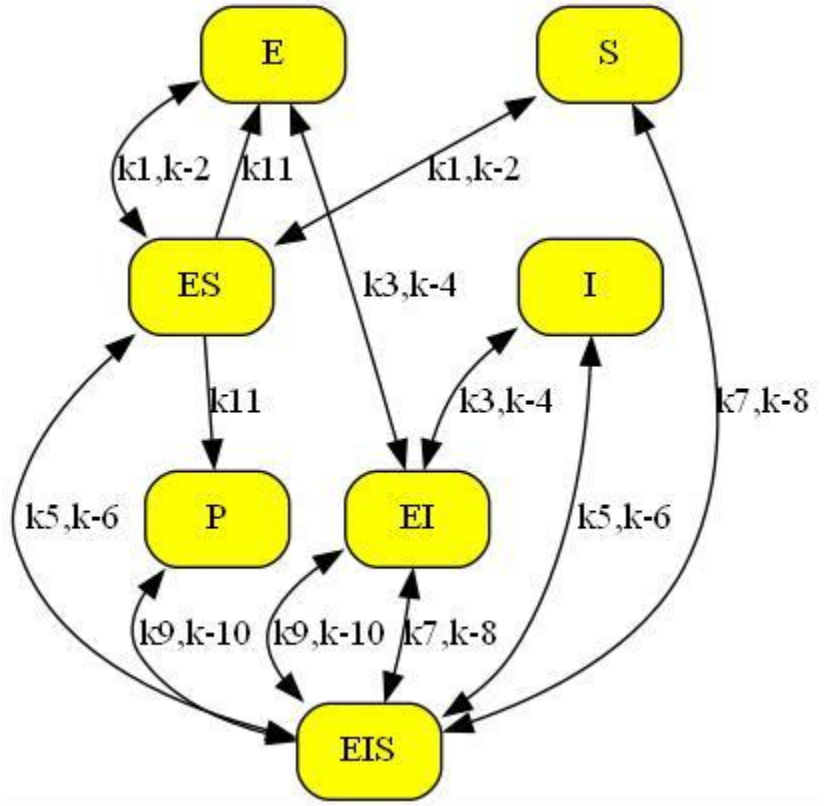


Figure 46.

To produce the picture below, change the Chemnet settings as described below.
Change the ChemNet setting “LINK” to “YES”, “LINK=YES”. This will combine single reaction arrows into a double reaction arrow for reactions with both a forward and reverse rate. This example is also the Kintecus-Excel file, “**Chemnet_Enzyme_Inhibition_Model.xlsm**”
Also, a Species Description Worksheet file has been added with two entries for species, “I” and one for “S” as shown in the below table. Note that placing a “3” in the “Arrow Placement” column forces those two species to only appear as part of a reaction arrow whether they are either a reactant or product.
This is the new Specnet settings:

# Species	Arrow_Placement	Display Filter	Source Color	Sink Color
# Name	(0,1,2,3)	(0,1,2,3,4,5,6)	(black, blue, red, green, gray, purple)	(black, blue, red, green, gray, purple)
# This is a sample specnet.txt input file.				
#				
# **Arrow_Placement field values ==** 0 Do not show as part of reaction arrow, 1 show in arrow if reactant,				
# 2 show in arror if product, 3 show in arror if either reactant/product)				
#				
# **Display_Filter** can take several valus == 0=SHOW; 1=If reactant do not show anywhere; 2=If product do not show anywhere;				
# 3=DO NOT SHOW AT ALL				
# 4=ONLY_SHOW_REACTANT,5=ONLY_SHOW_PRODUCT,6=ONLY_REACTANT_PRODUCT				
#				
#EIS	0	0	green	red
I	3	0	black	black
S	3	0	black	black
END				

And the output picture:

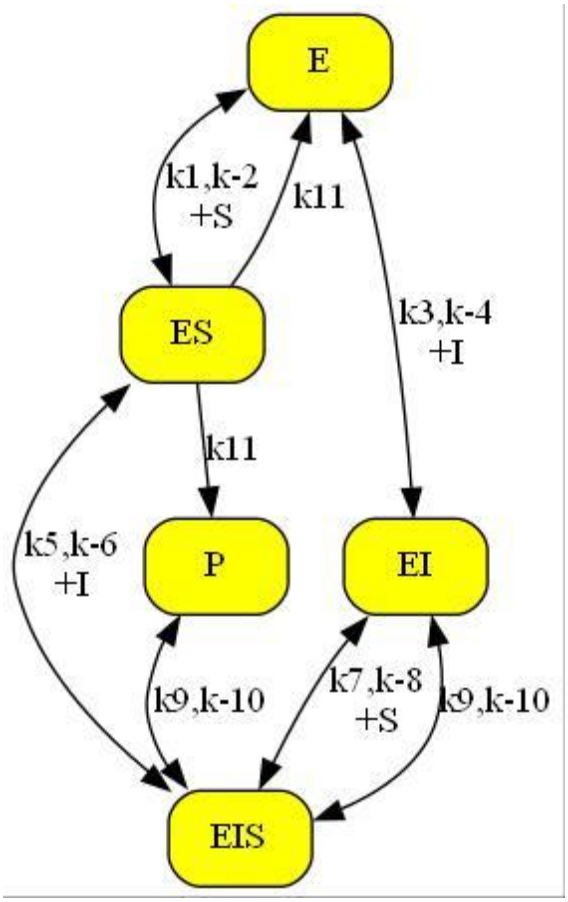


Figure 47.

Some people prefer the back-and-forth arrows but want to have the same species as part of the reaction arrow, highlight, source, and sinks. This arrangement can be accomplished by changing the LINK keyword to “No” in the ChemNet file (not shown) and using this SpecNet file:

# Species # Name	Arrow_Placement (0,1,2,3)	Display Filter (0,1,2,3,4,5,6)	Source Color (black, blue, red, green, gray, purple)	Sink Color (black, blue, red, green, gray, purple)
# This is a sample specnet.txt input file. # # **Arrow_Placement field values ==** 0 Do not show as part of reaction arrow, 1 show in arrow if reactant, # 2 show in arror if product, 3 show in arror if either reactant/product) # # **Display_Filter** can take several valus == 0=SHOW; 1=If reactant do not show anywhere; 2=If product do not show anywhere; # 3=DO NOT SHOW AT ALL # 4=ONLY_SHOW_REACTANT,5=ONLY_SHOW_PRODUCT,6=ONLY_REACTANT_PRODUCT #				
EIS	0	0	green	red
I	3	0	black	black
S	3	0	black	black
END				

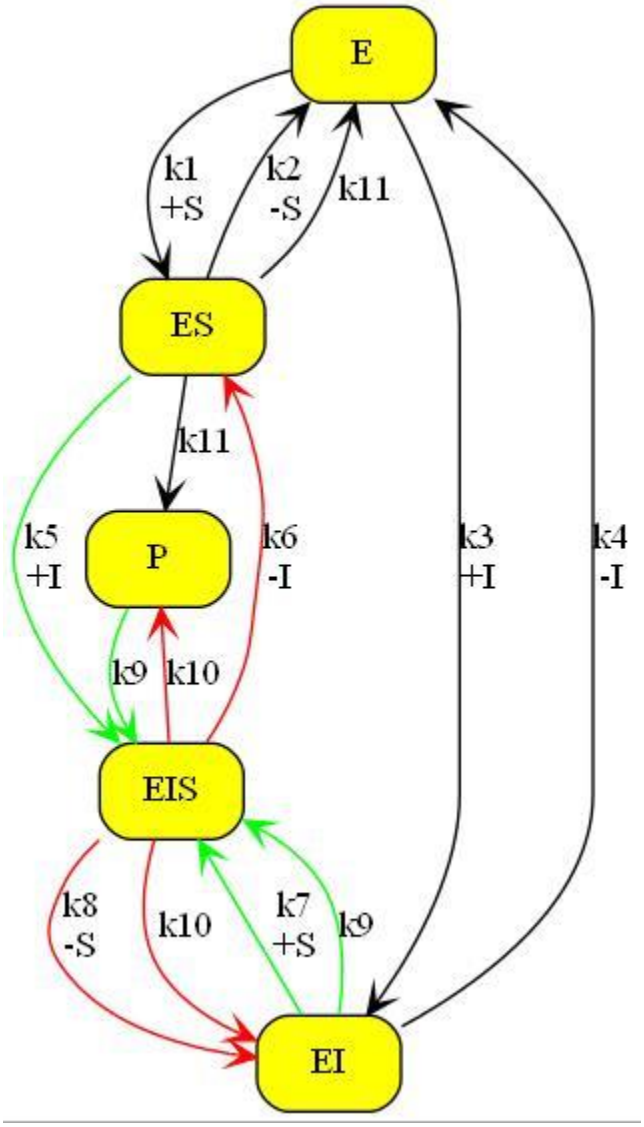


Figure 48. Note that all the sources to EIS are highlighted in green and the sinks are in red.

Note that all the sources to EIS are highlighted in green and the sinks are in red.

Mechanism Validation with Chemnet

Kintecus can perform a full mechanism validation (by providing the "-MECHV" flag on the Kintecus Switches command line as described in the previous "Mechanism Validation" chapter) along with a Chemical Mechanism Plot will result in a chemical network mechanism plot that will highlight the four possible illegal loops (if present) in a mechanism. The illegal loops (if any are identified by "-MECHV") will be drawn with a ***dashed line*** and colored in one of five colors to highlight the illegal loop.

Case	Illegal Loop Type	Illegal Loop Color
1.	Microscopic Reversibility/Rate Constant Consistency Test	Red
2.	First rho-reduction: One or more illegal irreversible loops detected	Blue
3.	Second rho-reduction: One or more illegal irreversible loops detected	Yellow
4.	Linear-Programming: One or more illegal irreversible loops detected	Purple
5.	More than one illegal loop that overlap each other	Green

The table below is generated by running the workbook "Chemnet_Simple_Mechaism_Validations.xlsm" and by deleting/adding reactions for each Case described by David M. Stanbury and Dean Hoffman [35]. The table highlights the case study results (1-7) from the various valid and invalid loops present in a small, three species system as discussed in David M. Stanbury and Dean Hoffman [35]. The reaction numbers above the arrows in Figure 49 pictures shown below are NOT the ordinal reaction numbers but actual line numbers in the MODEL worksheet in the "Chemnet_Simple_Mechaism_Validations.xlsm" workbook. This display of the actual line numbers in the reaction arrows should allow for one to follow which reactions were deleted and added for each case type discussed in reference [35]. The illegal loops are green because there are multiple overlapping illegal loops. The text output from Kintecus will clearly mark and explain those illegal loops. This marking of illegal loops is greatly discussed in Chapter 10, "Mechanism Validation".

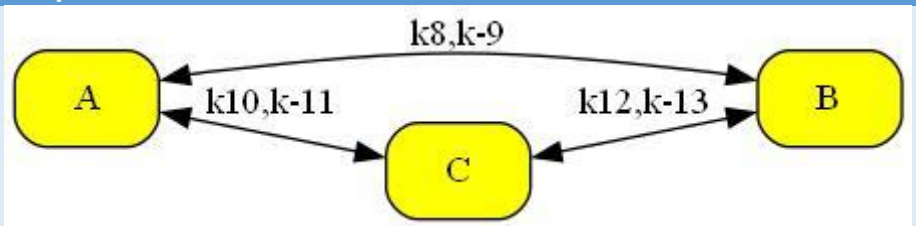
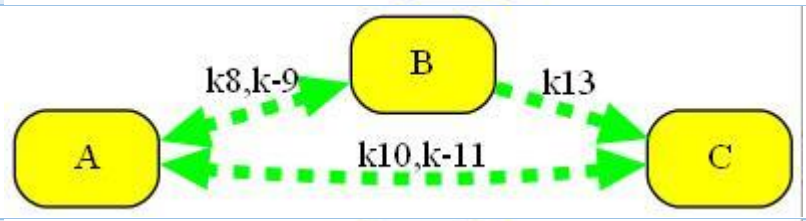
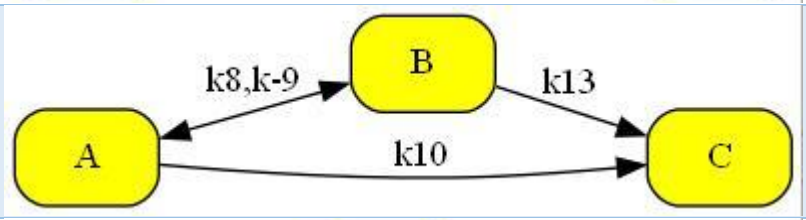
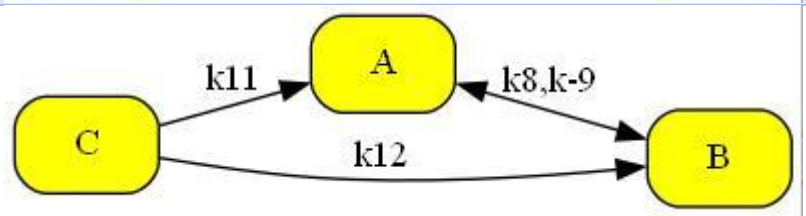
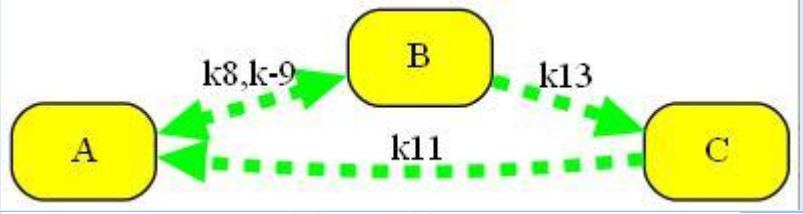
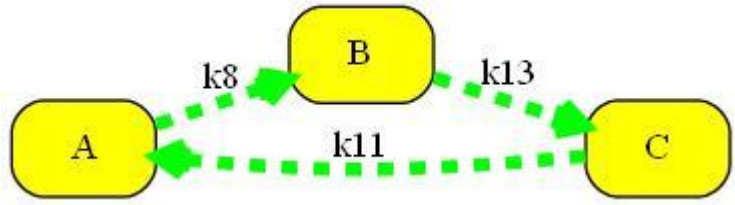
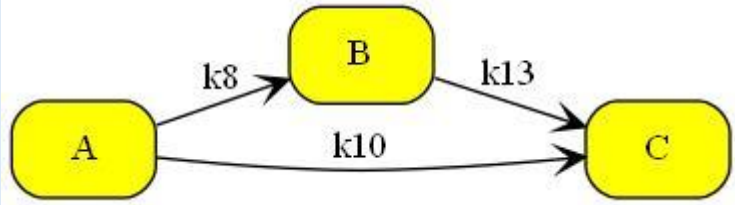
Case	Legality	Output from "-MECHV -chemnet" Kintecus command line switches
Case 1	All legal loops	
Case 2	Multiple Illegal loops	
Case 3	All legal loops	
Case 4	All legal loops	
Case 5	Multiple Illegal loops	
Case 6	Multiple Illegal loops	
Case 7	All legal loops	

Figure 49. Various legal and illegal reaction loops that are highlighted when "-MECHV -chemnet" command switches.

The Kintecus-Excel file, “Chemnet_Visualize_Mechanism_Validation_1.xlsm” also demonstrates an illegal loop (Microscopic Reversibility/Rate Constant Consistency illegal loop) when the model in Figure 1 from Stanbury and Hoffman 2019, J.Phys Chem. [35] is run with the Kintecus Switches set to
“-MECHV -chemnet” which will result in this picture showing the illegal loop as shown in Red:

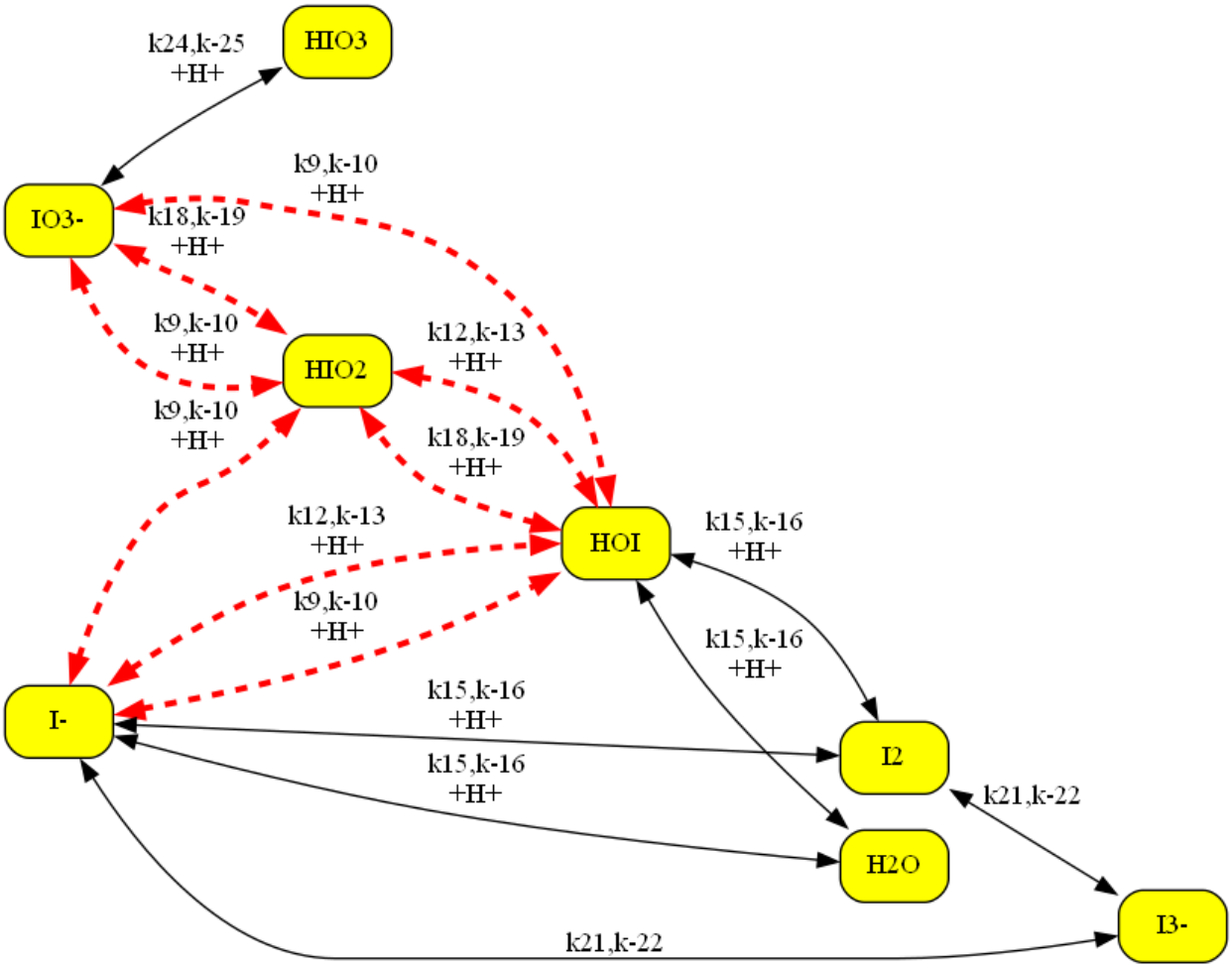


Figure 50. Using "-MECHV" (Mechanism Validation) with "-chemnet" shows illegal loops shown in Figure 1 in Stanbury and Hoffman 2019, J.Phys Chem. One can view the Kintecus text output for full details on this illegal loop as described in the “Mechanism Validation”, Chapter 10.

Also, the Mechanism Validation of test 4 (“Kintecus_mechanism_validation_4.xls”) shows illegal irreversible loops present (purple arrows) and multiple illegal overlapped loops (green arrows) as shown below:

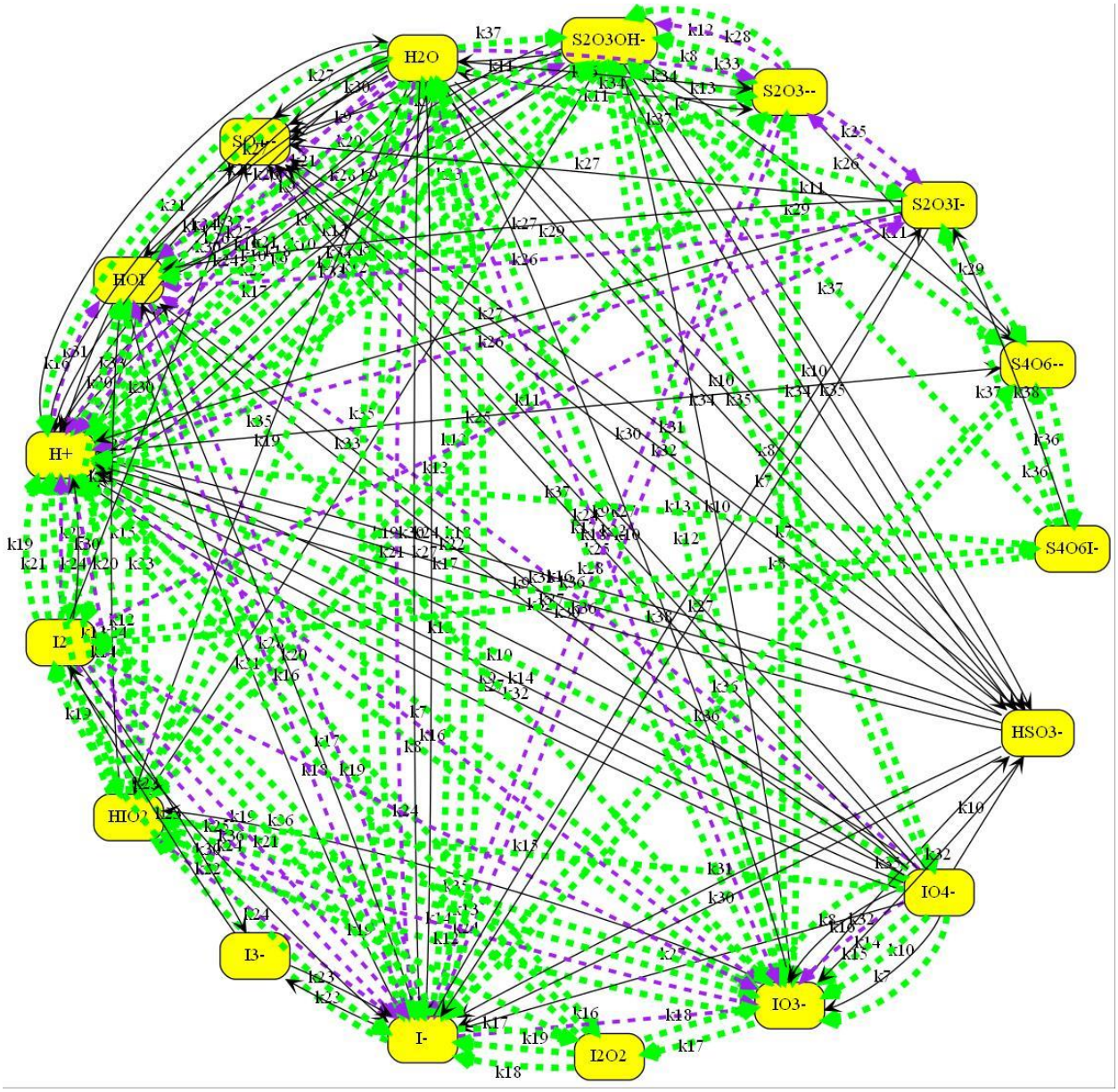
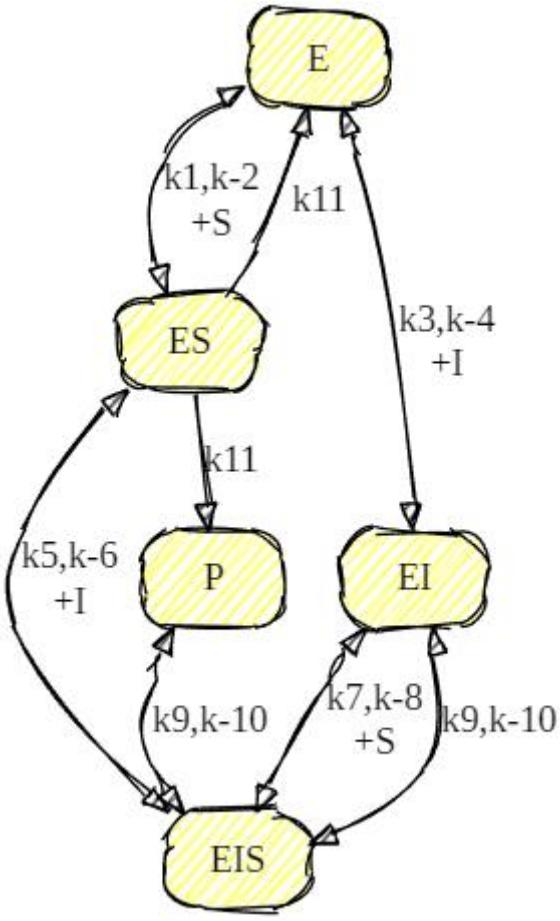


Figure 51. Using "-MECHV" (Mechanism Validation) with "-chemnet" shows illegal loops shown in figure 1, Stanbury and Hoffman 2019, J.Phys Chem. One can view the Kintecus text output for full details on this illegal loop as described in the previous chapter, "Mechanism Validation".

Additional Resources

Kintecus creates the graphiviz text file, “chemnetout.gv” which is then read in by graphviz with various flags to output pictures and other vector drawings. The final picture or vector drawing of one’s chemical mechanism may need some “fine-tuning” or editing for closer examination or better output for publication. A plethora of programs can do this and most are described at www.graphviz.org/resources . Also, some external programs can further analyze one's mechanism, such as "Gephi" at "gephi.org," and for publication output, one can save or output files as "SVG" files for use in "PGF/Tikz" or "dot2tex" or “inkscape.org”. One can even emulate “hand-sketches” of your models by inputing the gv file into “sketchviz” at “sketchviz.org” :



I Don’t Where to Start!

One needs to provide the "-chemnet" flag on the Kintecus command line and run Kintecus. That’s it. A default picture of your chemical mechanism named, “chemnetwork.jpg” will be output where Kintecus is stored (usually “C:\Kintecus\, so your picture will be in “C:\Kintecus\chemnetwork.jpg”). It will be in boring black and white. If you want to add more color and display reaction numbers on the arrows, copy the “O_Chemnet.txt” worksheet from an existing Kintecus-Excel file such as “chemnet_Enzyme_Inhibition_Model.xlsm” or “Chemnet_sample1_Pires and Faria Inorg Chem 2021 photochemical chloration-iodide clock reaction.xlsm” and many others.

WHERE’S MY CHEMNET PICTURE?!

Is Graphviz not producing any picture or taking much too long to produce a picture or is too "messy”?
If you are utilizing a large system with many interconnects between chemical species this may happen.

One can change the type of renderer in the Chemnet File (see "The Optional Chemnet File" section above in this chapter). For example, one could maybe change the render to circo (RENDER=circo) in the Chemnet File.
One could also hide or "absorb" some species in the reaction arrow using the options in the "Display Filter" field of the "The Specnet Optional File". One can do a **massive reduction** in un-important species by using options 4, 5 or 6 for select species of the "Display Filter" field in the Specnet File. Please see "The Specnet Optional File" described above in this chapter for further details.

If one really needs to view the entire mechanism, please look at using specialized codes optimized for this large task. Some of these programs are listed at www.graphviz.org/resources and they can load and interpret the "**chemnetout.gv**" graphviz output text file created by Kintecus. Also, some external programs can further analyze one's mechanism, such as "Gephi" at "gephi.org,".

If your chemical mechanism is small and Kintecus states it is done rendering your picture, then your chemnet picture should be in the same directory as where the Kintecus executable is. This is usually the **“C:\Kintecus\”** directory. If you are using the latest Kintecus-Excel worksheet, then Microsoft’s MSPaint should automatically try and open the picture and “pop up” on your screen. Keep in mind, for this autoload of MSPaint to happen, one must have the **latest** Kintecus-Excel worksheets. Again, your chemnet picture is always saved in the directory path where Kintecus is installed (usually the “C:\Kintecus\” directory). The default chemnet picture name is **“chemnetwork.png**”; however, the name and type of picture (jpg, png, svc, pdf, etc) can change depending on what is set in the chemnet file (see "The Optional Chemnet File" section above in this chapter).

12. Excel Tricks

Kintecus Excel Trick 1:
PUTTING YOUR "STUFF" INTO KINTECUS WORKSHEETS

Although you cannot add extra fields and "stuff" in the MODEL.DAT, SPECIES.DAT, and PARM.DAT text files, YOU CAN add extra columns of data (numbers, formulae, entire Works of Shakespeare) to any of those Excel Spreadsheets. For example, in the Excel Species Description Worksheet, numbers or data or links can be entered in column I (column #9) onto the ending column IV (column #255). These extra columns will NOT BE WRITTEN into the SPECIES.DAT file. Some Kintecus users have already noticed this and use extra columns from converting units to "Goal Seeking" to reading data from a remote Omega TCP/IP device. As a side note, you CAN add drawings, movies, Excel comments, text boxes, graphs, etc. ANYWHERE in any Kintecus Worksheet as floating objects.

Kintecus Excel Trick 2

THE MIGHTY AutoFilter

Since Kintecus has a unique way of defining entire reactions with one row, this allows for some very interesting possibilities with Excel's very powerful AutoFilter. One can perform anything from deleting commented-out lines, to removing all bimolecular reactions that referenced Miller 1992. Here are a few demonstrations with the Ethanol Combustion Kintecus Workbook:

<A> Getting Rid of All Those Comments *****

A.1) Click on the MODEL worksheet in the Ethanol Combustion Workbook.
A.2) Turn on the mighty AutoFilter (select Data => Filter => Autofilter). You should see five (5) select boxes (they look like upside triangles) hovering on row 2 over columns A to E. Reselecting Data => Filter => Autofilter turns OFF the AutoFilter and everything should re-appear!
A.3) For the first filter select box in column A, select the button (upside down looking triangle thingy) and select the "(Custom….)" option.
A.4) A dialog box will appear. Right under where it states "Show rows where:" select the button (upside down looking triangle thingy) and select "Does not begin with" and type a "#" in the box next to your selection. Click OK.

A.5) HEY WHAT HAPPEN TO MY COMMENTS?!?! Relax. They are still there. Autofilter only shows or not shows according to the rules you type in. To permanently delete those comments, you have to copy the entire worksheet into a blank worksheet.
A.6) You are reading this because you don't know how to copy an entire worksheet into a blank worksheet. First, insert a blank worksheet (Insert => Worksheet). Go back to the MODEL worksheet, and click that blank square directly above Row 1 and directly left of column A. The entire Worksheet will be selected. Select Edit=>Copy. Click on the blank worksheet. Click on A1 cell. Select Edit=>Paste. Viola! Don't forget to delete (or rename) the old MODEL worksheet and rename the new worksheet to MODEL!

<B> Sophisticated Filtering of Reaction Mechanisms *****

Okay, suppose we found out that all the bimolecular reactions supplied by the "Miller 1992" reference should be removed from the model. This type of action too can be performed by the Mighty AutoFilter:

B.1) Turn on the AutoFilter (see note A.1 above)
B.2) Select the Filter Select Box for the Reaction column D (click and hold on the upside-down-like triangle floating on Row 2, Column D) and select "(Custom…)"
B.3) A dialog box should appear for "Show rows where:" select "begins with" and type "*?+*?=*" (without the quotes and NO SPACES!). Make sure "AND" is clicked on, and for the second option below, select "does not begin with" and type "*?+*?+*?=*" (again without the quotes and NO SPACES!).
B.4) You should now see all bimolecular reactions, now to filter out just the "Miller 1992", select the Filter button for Comments column (click on the upside-triangle on Row 2, Column E and select "(Custom...)"
B.5) A dialog box should appear for "Show rows where:" select "begins with" and type "Miller".
B.6) You should now see all the bimolecular reactions given by "Miller 1992."
B.7) To delete these reactions, simply highlight all of them, and select Edit=>Delete Row. You should see no reactions (remember, the undeleted reactions are still there, simply not shown because of the AutoFilter)
B.8) Now, to display all the reactions not deleted, simply turn off the AutoFilter (Data=>Filter=>AutoFilter)
B.9) This example can be expanded to include specifying a pattern for bimolecular reactions containing only reactants containing **ch2**, i.e., **"*?+ch2*=*"** instead of "*?+*?=*". Other sophisticated filters can be constructed to filter out TROE, SRI, Lindemann reactions, reactions containing a range of A, Ea, or m's, etc.

ARE YOU STILL USING OLD KINTECUS EXCEL FILES?

The Kintecus-Excel files (suffixed with .xls) contain separate VBA code from the main Kintecus program that permits the execution of Kintecus using the Excel interface. These files **routinely get changed with Kintecus releases**, so if you have created a Kintecus model using an Excel-Kintecus worksheet from Kintecus V3.5 or earlier, **then you must update** your Excel-Kintecus worksheet. You can do this by loading a blank Kintecus worksheet (Kintecus Blank Model in this distribution) and copying all your worksheets from old to new ones. This copy procedure is easy to do as it requires you to right-click on the worksheet tab, select "Move or Copy," then under "To book," select the name of the loaded, NEW Kintecus worksheet, and click OK.

The VBA Macros in the new Kintecus Excel worksheets are more reliable and have extra graphing capabilities. Such graphing capabilities as the plotting the Uncertainty Analysis with confidence limit plotting and will also recognize the "-o:y:y:y:y" and automatically plot all related files.

Run Kintecus Outside of Excel and/or Run Many Copies of Kintecus on one PC ?

This part explains how to run Kintecus using the MODEL/SPECIES/PARM/FITDATA/etc worksheets in Excel without having Excel windows constantly pop up, waste cpu cycles, and constantly annoy you as your Kintecus simulation runs.

Click the Windows Start Button in the left-hand corner of the screen, and type “cmd” or "command," and press enter. A console window should pop up on the screen. Alternatively, hold the Windows key (usually, the key is at the bottom left of the keyboard, in between the CTRL and ALT keys) and tap the "x" key. A menu will pop up, select "Command" or "Run" and then type “cmd” or “command,” and a new console should pop up.

1) Once you are in the console window, type "cd C:\Kintecus" or where ever you have Kintecus installed.

2) In the Excel window, click on the "CONTROL" tab, and click "RUN" once Kintecus starts, stop it with "ctrl-c" (hold the ctrl key and tap the "c" key) or ctrl-break (hold the ctrl key and tap the Pause/Break key). This step is required because once you press the RUN button, the Kintecus-Excel VBA macros will output all your worksheets as input text files for Kintecus.

3) In the same "CONTROL" worksheet, click on the contents of the "Kintecus Switches" cell (A12) and select COPY (right-click, select Copy)

4) Click in the console/command line window, and type "kintecus" **(don’t press enter yet!)**
In the PowerShell command, type "./kintecus."

5) Hold down the CTRL key and type "V" (for paste), and press ENTER. This should paste your Kintecus switches from cell A12 on the CONTROL worksheet into the command line.

6) Kintecus is now running outside of Excel, using all your inputs from the Excel Worksheet. Once Kintecus is finished, click the “Plot Results” button on the CONTROL worksheet. Also, note that you can copy the entire Kintecus folder into a new directory (C:\Kintecus2\), change the “Kintecus Path” located on the CONTROL worksheet, then change one or two parameters in the Kintecus-Excel worksheet and perform the same steps above. You will be running two different Kintecus simulations/optimizations simultaneously. Repeat as necessary, assuming you have enough cores on your cpu.

13. FAQ

How do I ... ?

Plot more than 255 columns of data?

This was an early Excel problem and not a problem with Kintecus. Kintecus has no limit. You can go way beyond 255 columns of data to plot if you have Excel2010 or later. Excel 2010 goes out to 16,000+ columns. However, there is a small trick though to get it to work.

To get Excel2010 (or higher) to plot more than 256 columns of data:

A) Save your Kintecus-Excel workbook as an "Excel Macro-Enabled Workbook." Your file should have an extension of ".xlsm" appended to its end.
B) Close your Workbook.
C) Load the just saved Excel Macro-Enabled Workbook.
D) Replot your data. (click the PLOT button located on the CONTROL worksheet)
E) You should have the ability to plot beyond column IV (which is the 256th column) up to XXD (16,380th column).

On Linux:

If you have access to a Linux system, you can extract specific columns of data via the cut command. For example, to cut column one, columns 260-270, and columns 290 to the end, you can type this (without the quotes)
"cat conc.dat | cut –f1,260-270,290- > new_conc.txt"
The cut command assumes TABs as the data delimiter; if you are using commas, then the command would be
"cat conc.dat | cut –d, –f1,260-270,290- > new_conc.txt"
If colons, then change "-d," to "-d:", etc.

Perturb/Alter the _____ of the system during a simulation run?

Temperature (program temperature runs), species concentrations (simulating the diffusion of oxygen into a solution, pH quenching, induction of current, external concentration alterations), and volume changes (for various piston compressions) can all be simulated using the "Temperature (K) or Filename" in the PARM spreadsheet, the "Constant File?" field in the SPECIES description spreadsheet or the "Volume Profile" field in the PARM spreadsheet respectively. You can see an animation of how this is done if you go under the "Web Resources" tab in the Kintecus Workbench and select "Creating a Temp. Program" under "Fast Animations."

Specify the mass flow rates "in and out" to compute a continuous flow reactor?

In the species flowsheet, there are two columns: "Residence Time in CSTR(s)" and "External Concentration." "The Residence Time in CSTR" is the total time a species stays in the CSTR from once it enters the CSTR (the in part) and the time it exits (out part). I leave it up to the modeler to figure this part out. If the flow is laminar,, then a simple time=distance/velocity can be used, but if there is some turbulence, a more detailed method to calculate the average Residence time will be needed. The "External Concentration" is the concentration of the species once it enters the CSTR and NOT the concentration of the species in the pre-mix tank, i.e., if a 5 MOLAR concentration of species A enters a CSTR tank, that will dilute it by 10:1, then the "External Concentration" will be 0.5 Molar entering the tank. The Oregonator_in_CSTR Excel Spreadsheet demonstrates this, and you might also want to get the paper it references the model and experimental data. As a side note, you might ask yourself, "Shouldn't all the species have the SAME "Residence Time in CSTR(s)" since all the species are being "pushed" out of the CSTR at the same time?" and the answer is "YES." Kintecus allows different Residence Times in the CSTR for "special" instances where zeolites, surfaces, or other species inhibitors might slow one species' average flow against another.

Specify a constant Pressure system ?

This is specified by the "Pressure Constant (YES/NO)" field in the PARM spreadsheet. Specifying "NO" in this field selects a variable pressure (**constant volume**) run.

Register Kintecus ?

Kintecus is not freeware but shareware. Please view the Registration Section in the Kintecus documentation (see the Download Webpage or the zip file) for complete registration forms. Education Institutions or Students can register here: http://www.kintecus.com/academic.htm . Commercial/Industry/Government entities can purchase or buy a license online at www.kintecus.com .

Reference Kintecus ?

Ianni, James C., Kintecus, Windows Version 2021, 2021, www.kintecus.com.

Of course, if you are using a non-Windows Version then specify the platform (Linux, SUN, etc.,)

Some journals do not allow a reference to anything as an Internet address. I suppose they fear the reference is much too "soft" and can easily point to other unrelated sites in the future. If you have a paper accepted in such a journal and cannot use www.kintecus.com for your reference, then please use the following "hard" citation:

Ianni, James C. , "A Comparison of the Bader-Deuflhard and the Cash-Karp Runge-Kutta Integrators for the GRI-MECH 3.0 Model Based on the Chemical Kinetics Code Kintecus", pg.1368-1372, Computational Fluid and Solid Mechanics 2003, K.J. Bathe editor, Elsevier Science Ltd., Oxford, UK., 2003.

Enter in a gas pressure that is much larger than the gas reactant pressure ?

Go into the species description spreadsheet and enter a non-reactive gaseous species such as Ar (Argon) or Nitrogen (N2). The additional gaseous species do not have to be in any chemical reaction. Now, go into the “Initial Concentration” field and enter in a sufficiently high concentration to raise the system's pressure. The ideal gas equation can be used to approximate the initial concentration [Concentration=n/V=P/(R*T)]. Remember that the additional gaseous presence will contribute to the overall heat capacity of the system and any equations containing [M] or pressure fall-off equations.

Run Kintecus Outside of Excel and/or Run Many Copies of Kintecus on one PC ?

This part explains how to run Kintecus using the MODEL/SPECIES/PARM/FITDATA/etc worksheets in Excel without having Excel windows constantly pop up, waste cpu cycles, and continuously annoy you as your Kintecus simulation runs.

Click the Windows Start Button in the left-hand corner of the screen, type “cmd” or "command," and press enter. A console window should pop up on the screen. Alternatively, hold the Windows key (usually, the key is at the bottom left of the keyboard, in between the CTRL and ALT keys) and tap the "x" key. A menu will pop up, select "Command" or "Run" and then type “cmd” or “command,” and a new console should pop up.
1) Once you are in the console window, type "cd C:\Kintecus" or where ever you have Kintecus installed.
2) In the Excel window, click on the "CONTROL" tab, and click "RUN" once Kintecus starts, stop it with "ctrl-c" (hold the ctrl key and tap the "c" key) or ctrl-break (hold the ctrl key and tap the Pause/Break key). This step is required because once you press the RUN button, the Kintecus-Excel VBA macros will output all your worksheets as input text files for Kintecus.
3) In the same "CONTROL" worksheet, click on the contents of the "Kintecus Switches" cell (A12) and select COPY (right-click, select Copy)
4) Click in the console/command line window, and type "kintecus" **(don’t press enter yet!)**
In the PowerShell command, type "./kintecus."
5) Hold down the CTRL key and type "V" (for paste), and press ENTER. This should paste your Kintecus switches from cell A12 on the CONTROL worksheet into the command line.
6) Kintecus is now running outside of Excel, using all your inputs from the Excel Worksheet. Once Kintecus is finished, click the “Plot Results” button on the CONTROL worksheet. Also, note that you can copy the entire Kintecus folder into a new directory (C:\Kintecus2\), change the “Kintecus Path” located on the CONTROL worksheet, then change one or two parameters in the Kintecus-Excel worksheet and perform the same steps above. You will be running two different Kintecus simulations/optimizations simultaneously. Repeat as much as necessary, assuming you have enough cores on your cpu.

Why doesn't...

The Graphical Interface Appear When I Run Kintecus.exe ?

The graphical interface for Kintecus is encoded inside the Excel spreadsheet files that end in ".xls," such as "Enzyme_Regression_Fitting.xls," "GRI_MECH_30.xls," or the blank xls file "Kintecus_workbook.xls." Naturally, you need Excel or a program to run the xls files.

The results from my Excel model DO NOT precisely match the Kintecus model run from the COMMAND line ?

Some users have noticed this, and its mainly due to Excel saving "What you see on the screen." numbers to the temporary Kintecus files and not exactly what the cell value holds. Example: you entered 3.14159265E+10 in an Excel cell. After pressing <ENTER>, Excel shows 3.14E+10 in the cell, but if you click the cell, Excel now shows the total number 3.14159265E+10 in the command line above. You click the "RUN" button, and temporary Kintecus files are saved. The cell holding 3.14159265E+10 is written as 3.14E+10 and NOT the entire number! For some models, this is OK, but keep that in mind. If you need Excel to write the entire value out to the last decimal place, BE SURE first to select the rows, columns, or sheets containing those numbers; then, under the FORMAT menu, select the sub-menu item "Cells." A prompt will pop open. In the Category, select Scientific and increase the decimal places to 6, 8, or 10. Click OK. Done.

I'm still getting NaN's or Overflows or "singularities" in my runs even after following the hints in the "Overflows, Underflows, Division by Zero, Singularities, Domain Errors" part of the Kintecus manual ?

This problem seems to be happening to users who convert their model from one of those "other" expensive simulation packages to Kintecus and are running under thermodynamics mode (the –THERM switch is given on the command line). The solution(s) is/are to re-check your units given in the parameter's worksheet (the worksheet named "PARM") and double-check the "Arrhenius Units" field is set to the same units for the Arrhenius parameters given in your reaction set (the MODEL worksheet). Having a mismatch of these units will most certainly cause NaN's. Please check for the same thing for the concentration Units and the concentrations given on the SPECIES worksheet; make sure they match! If you are pretty sure your units are consistent, change to the fifth integrator (-INT:5) and set the Accuracy to 1e-4 to 1e-9. This can solve the rest of the integration problems. If that doesn't help, you can set the "Starting Minimum Integration" and the "Maximum Integration Time" to 1e-8 to 1e-11 and give the "-obeymaxint" Kintecus flag. This flag will force Kintecus to integrate, taking very small time steps. These small time steps will cause a significant delay in getting to the final integration time.

I am getting an "*ERROR* 99 Unable to get id for this computer..." that immediately shows up when I start Kintecus ???

Please be sure you have access to the "ipconfig" command under Windows or the "ifconfig" command for Linux. If you do not have access or permissions to these commands, ask the administrator to give you access and/or copy the command into the directory where Kintecus is located (i.e. for Windows, it may be ("C:\Kintecus" or "C:\Program Files\Kintecus") .

Do Graphs of regressions of 60 points or less may look off when plotting in Excel ????

Note that the regressed Kintecus values and statistics outputted by Kintecus are not affected. This issue is an Excel-only issue. You can ignore this part if you don't use the Kintecus-Excel workbook fitted plots.
Some users have noticed that if you are regressing/fitting less than 60 points of data with Kintecus, and you plot your data against the Kintecus fit, the x-axis may not overlap correctly. This only happens with less than 60 points of data and with different starting time steps. You can manually produce a correct regressed plot by overlapping your experimental data with the Kintecus fit. Again, the Kintecus regressed values and statistics outputted by Kintecus are not affected. Please see below:

A) Click on the "FDATA" worksheet and delete your columns of experimental data. Your experimental data will have column names that do NOT start with "FIT(" near the top, and they will always be the last columns.

B) We now must delete non-Excel numbers from your "fitdata" worksheet. Click on the "fitdata" worksheet that has your experimental data. You might want to work with a worksheet copy (right-click on the worksheet tab, and select Move or Copy). Keep in mind to (1) delete all excel rows that have a "#" prefixed, (2) Search and replace all "N" or "NaN" with blanks, (3) delete any "END" or "ED" (a search and replace on "N" to blank will change the "END" keyword to "ED") keywords in the first column (4) delete any standard deviations that are suffixed to any values. If you fail to delete the items above, part (C) below will NOT work.

C) Once you are sure all non-Excel-related values are removed from "fitdata". Click on the FITPLOT worksheet tab, click on the graph (the graph should highlight or be surrounded by eight small, black squares in each corner), select "Paste Special" from Edit==>"Paste Special," or click on the "Paste Special" button located on the "Home" tab. A small window will appear in the middle of the screen. Make sure the buttons "New series" and "Columns" are clicked on (they are usually on by default, so you might not have to click on them). Also, make sure "Series Names in First Row" and "Categories (X Values) in First Column" are check marked; click "OK." Your experimental data should now be aligned with the regressed/fitted data.

Again, if you have more than 60 points or don't use graphical plots from Excel, you can ignore this.

What is ...

The History of Kintecus ?

Kintecus was first developed on Commodore Amiga Computers back in 1992. It was written on an Absoft Fortran compiler 900k diskette that also was the boot disk on an Amiga 500 with 1 floppy disk, no hard disk, 1 meg memory. It has evolved somewhat from 1992-1995 mainly to conversion to PC's with Microsoft's buggy Fortran Powerstation. It was released as shareware back in 1995. It is written in FORTRAN77 with FORTRAN95.

The deal with the name "KINTECUS" ?

Kintecus was initially named "KINETICUS" which is Latin for "movement" or "energized movement". Molecules/atoms/particles have to move before they react, hence the name. In 1995, Kineticus was moved from the Amiga to the DOS platform, which only supports filenames of eight characters, so a letter was deleted. The letter, "E" was deleted, and the "I" was replaced with "E," so we get the current name "KINTECUS." The program was also Copyrighted in 1995 under "KINTECUS", so that name has been kept due to legal reasons.

This error when I try to run Kintecus with Excel after inserting the unlock key?

I get the following prompt/message:

```
"ALERT:

Please close any programs that have the CONC.txt file opened...or any
of these related kintecus files:

krun.tmp
kdone.out
kwarn.out
kerr.out
view.txt
addspec.txt"
```

This error seems to happen under Windows 7/Windows 10. You probably have to install Kintecus into "C:\" and NOT "C:\Program Files\" as, for some reason, Windows will not allow Kintecus to write files into "C:\Program Files\." This error can also happen if you do not have write permission in the directory Kintecus is installed in. Kintecus writes various temporary and output files into the directory it is installed in. You MUST have write permissions in the directory Kintecus is stored. Please be sure you don't have any of the files listed above opened in a text editor as that may lock the file and prevent it from being deleted or written to.

14. FASTSTART

This section is for people who do not read or even scan the main documentation. If you still cannot run your model after following the below short procedure, you should read the tutorial in the first section of the documentation.

1) Go into command mode (on the Windows start button, select RUN, type “command” and press the <ENTER> key **or in Windows 7**, click the sphere in the bottom left-hand corner, type “cmd” and press the <ENTER> key) and create a file named MODEL.DAT. If you have Microsoft **Excel,** you can use the *blank* **Kintecus_workbook.xls** or **Enzyme_Regression_Fitting.xls** or **GRI_MECH_30.xls** and click the **MODEL tab** located at the bottom. If you use a text editor, then enter your reactions like so:

```
1.323e-4, A- + Widget-- + C==>G+++ + F---+H20
3.2     , E+F ==> G + DNA_A_Replicated
54.34   , G = A
END  ( <==-- Make sure this END is here)
```

If you have Arrhenius expressions, then do your reactions like this (make sure you specify the correct Energy of Activation units in the parm.dat spreadsheet, look for the Ea Units field and type either Calories, Cal, Joules, J, KJ, KCAL, or Kelvin:

```
1.323e-4, -1.2, 3000, A- +Widget-- + C==>G+++ + F---+H20
3.2     ,  0.3, 2000, E+F == > G + DNA_A_Replicated
54.34   , 2.1,5430, G = A
END  ( <==-- Make sure this END is here)
```

2) Run Kintecus with the following switch: >Kintecus –c
(**EXCEL**: click the **"Make Species Worksheet from Model" button** located on the **CONTROL** worksheet)

3) Now copy the created ADDSPEC.TXT file as a SPECIES.DAT file
(ie. >COPY ADDSPEC.TXT SPECIES.DAT if you are using the **EXCEL** interface, then skip this step)

4) Edit the Initial concentration fields in species.dat for your model and type "Y" in the DISPLAY field for the species' concentrations you want to save. (**EXCEL:** click the **species tab** located near the bottom and then edit the same fields in the species worksheet)

5) Run kintecus: >KINTECUS -ig:mass -show. (**EXCEL:** click the **CONTROL tab** located near the bottom and then click the **RUN button** to start your model!)

6) If you are using the EXCEL modules on the **CONTROL** worksheet, click the **Plot Results** button to plot your results!

7) ***OPTIONAL:*** If you wish to do include thermodynamics (temperature and reverse rate autocalculations), just use the –THERM switch on the command line.

8) ***OPTIONAL:*** If you wish to do sensitivity analysis, just use the –SENSIT:1 on the command line.

9) ***OPTIONAL:*** If you wish to FIT experimental data to a model, have your data in a text file named, FITDATA.TXT with Time(s) as the first column, first row. The species names should follow the same row's Time(s) heading. Place your species/temperature data under the appropriate species column (if a species is missing data for a time point, place an “N” in the cell). Append a question mark, "?", to the end of ***any number*** you wish for Kintecus to regress/fit. Run Kintecus with –FIT:2:3:FITDATA.TXT. You can also try –FIT:1:3:FITDATA.TXT , -FIT:1:1:FITDATA.TXT and –FIT:2:1:FITDATA.TXT .

10) ***OPTIONAL:*** You can calculate uncertainty bands by adding the **“-conf**” switch on the command line. If you are in Excel and using the latest Kintecus-Excel spreadsheets, you will automatically see these plotted!

11) ***OPTIONAL:*** You can perform hierarchical cluster analysis by adding the **"-cluster**" switch on the command line. A file name, "CLUSTER.TXT" will be created containing Hierarchical Cluster.
12) ***OPTIONAL:*** If you wish to do perform MechansimValidation and detection of illegal loops, use the "-MECHV" option on the command line.

15. Errors, Warnings and Convergence Problems

This file explains each Fatal and Warning message you may receive when running a simulation. In addition, it is quite possible to obtain errors which Kintecus cannot catch.

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

Overflows, Underflows, Division by Zero, Singularities, Domain Errors

Kintecus quits and reports some error with one of the above following words.

To eliminate these errors:

1) *Make sure you entered the initial concentrations for relevant reactants. If all the reactants have an initial concentration of zero, this will cause problems.*

2) *If you are sure, you've done that, then it's very likely you have a very stiff system of reactions, so you must first make sure the value in the Minimum Integration Field has a value of 1 x 10(-7) or smaller, then decrease the number in the Accuracy field in the Parameter Spreadsheet file. Decrease it by ten and try again; keep trying until the Accuracy is around 1 x 10(-13). If you still get errors, it's likely that your system of reactions is not mass or charge balance or is a different type of "stiffness" (see below).*

3) *Try to eliminate any mass or charge balance warnings.*

4) *If you did and you still have these errors, make sure your equations make sense, i.e., A==> A is a meaningless reaction.*

5) *If your reaction scheme consists of thousands of reactions, you could be experiencing a large round-off error; try using the analytically calculated Jacobians using the -anjac program switch. The -anjac switch used on the command line will force Kintecus to calculate Jacobians analytically instead of trying to approximate it by finite-difference.*

6) *Try a different integrator through the –INT switch i.e., Kintecus –INT:2. Also, the new integrator 4 (-INT:5) can handle different stiff problems than –INT:1, so please try changing the integrator to #5 (by adding the –INT:5 switch on the Kintecus command line)*

For combustion reactions or systems using thermodynamics you can try these additional recommendations:

7) *One solution(s) is/are to re-check your units given in the parameters worksheet (the worksheet named, "PARM") and double-check the "Ea Units" field is set to the same units for the Ea parameters given in your reaction set (the MODEL worksheet). Having a mismatch of these units will most certainly cause NaNs or a model that runs extremely slow. Please check for the same thing for the Concentration Units and the concentrations given on the SPECIES worksheet; make sure they match! If you are pretty sure your units are consistent, be sure to change to the fifth integrator (-INT:5) and set the Accuracy somewhere from 1e-5 to 1e-9. This integrator can solve the rest of the integration problems. If that doesn't help, you can set the "Starting Minimum Integration" and the "Maximum Integration Time" somewhere from 1e-8 to 1e-11 and give the "-obeymaxint" Kintecus flag. This will force Kintecus to integrate, taking very small time steps. This might cause a significant delay in getting to the final integration time.*

8) *If you are using the "-THERM" switch, i.e., you are doing a combustion reaction, append :FORCE to the end of the –THERM switch like so –THERM:THERMO.DAT:FORCE . This will force the integrator to stay within the temperature limits of the thermodynamic coefficients of all the species.*

9) ***NEW in Kintecus V4.00: The new integrator #5 (-INT:5) can handle different stiff problems than the default integrator #1 (–INT:1), so please try changing the integrator to #5 (by adding the –INT:5 switch on the Kintecus command line). Don't forget to set the accuracy to 1.0E-5 or lower (the accuracy field is located on the parameter spreadsheet). Integrator #5 works best with accuracies in 1e-4 to 1e-7 range and with the FORCE option: "-INT:5 –THERM:D:FORCE"*

10) *If the thermodynamic coefficients in the thermodynamic database have a very narrow temperature range (the low temperature and high temperatures) for a species can cause possible problems. Can the simulation be started with a different temperature, and starting concentration? Can you get new coefficient values with a broader range for that species?*

11) *Some thermodynamic databases are not formatted correctly. Occasionally, the sequence 1,2,3,4 is missing or is off by a space in column 79 of a database. This will cause Kintecus to miss a line of thermodynamic coefficients for one species and pick up the next species' thermodynamic coefficients. The solution is to delete the extra space in column 79 for that species. One might have to double-check the thermodynamic coefficients by outputting the Kintecus read-in thermodynamic coefficients using the "-OF" flag and double-check the thermodynamic coefficients in the FREEFORM.TXT file or examine the Kintecus output as it reads in the values from the database. However, the former method might be easier to read.*

Common Fatal Error Messages

These severe errors, when encountered, will not allow the simulation to run. These errors must be corrected.

Fatal Error #1

```
No data fields in (filename).
Make sure data delimiters (comma, TAB, etc.) are'
in (filename)  and/or the correct data delimiter is'
set. If you haven't set it, then by default a TAB'
is used to separate fields.
Use the -d option to change this (Type Kintecus ?).
```

Explanation:
Kintecus will try to figure out what data delimiter you are using. It will try TABS, commas, semi-colons, colons, and '|'. If you are not using any of those characters to delimit your data please do so. Do not use space to delimit your data!

Fatal Error #2

```
'ERROR!, MORE THAN (number) COLUMNS OF DATA IN '
  (filename)
```

Explanation:
You use a data delimiter, which is part of the field data. You can not use TABS, commas, colons, and '|' as part of a field; these characters are only used for data delimiters. Do not use space to delimit your data! Kintecus ignores all spaces in all data spreadsheets!

Fatal Error #3

```
NO DATA DELIMITERS FOUND IN (filename)
Make sure data delimiters (comma, TAB, etc.) are'
in (filename) and/or the correct data delimiter is'
set. If you haven't set it, then by default a TAB'
is used to separate fields. '
Use the -d option to change this (Type Kintecus ?).'
```

Explanation:
Make sure you use either TABS, commas, colons, or '|' as a data delimiter. You can not use a space as a data delimiter. Kintecus ignores all spaces in all data spreadsheets!

Fatal Error #5

```
The hv energy output file (filename)
does not exist. Please correct.'
```

Fatal Error #6

```
Too many data items in (filename)
```

```
on a line. Make sure the Data Separator in your '
file is a valid ASCII Separator.'
```

Explanation:
Make sure you use either a TABS, commas, semi-colons, colons, or '|' as a data delimiter.
Kintecus ignores all spaces.
There may be extra data delimiters accidentally put at the end of the line.

Fatal Error #10

```
Duplicate species found in (filename)
has duplicate! Please correct.'
```

Explanation:
Remove one of the duplicates you entered.

Fatal Error #11

```
Concentration profile file:(filename)
 can not be loaded. Please correct.'
```

Fatal Error #14

```
Ill-formed reaction line in the model description'
file :(filename)
Remember to use ''==>'' to represent ''produces''
on a reaction line. Check for other possible errors.'
```

Fatal Error #15

```
Missing Reactant/Product on reaction line'
in (filename) Please correct.'
```

Fatal Error #21

```
You have exceeded the maximum number of species'
allowed in this version of Kintecus.'
(Number)
```

Explanation:
If you need this to be larger, email the author. For the disabled shareware version, buy the registered version (see Registration) which allows a very large amount.

Fatal Error #22

```
You have exceeded the maximum number of reactions'
allowed in this version of Kintecus.'
```

Explanation:
If you need this to be larger, email the author. For the disabled shareware version, buy the registered version (see Registration) which allows a very large amount.

Fatal Error #23

```
You have exceeded the maximum number of times a'
species can appear as a reactant/product in each'
reaction in this version of Kintecus.'
```

Explanation:
If you need this to be larger, email the author. For the disabled shareware version, buy the registered version which (see Registration) allows a very large amount.

Fatal Error #24

```
An illformed reaction line has been found '
in (filename) !!'
Remember to place charges on species on the'
right-hand side, i.e. Cl+++ .'
Remember to use ''==>'' to represent ''produces'' '
on a reaction line. Check for other possible errors.'
```

Fatal Error #28, 29

```
Not a valid species name in (filename)
(invalid species name)
```

Explanation
You cannot use TABS, commas, semi-colons, colons and '|' as characters in your species names, nor can you use the characters

Fatal Errors #30, 31, 32

```
Species description file (filename),  or parameter description file
(filename)
Model description file (filename)
CAN NOT BE FOUND !!!!'
Make sure the file exists and/or is in the correct'
directory. (Usually the same directory as KINTECUS.)'
```

Fatal Error #33

```
Thermodynamic description file (filename)
CANNOT BE FOUND !!!!
Make sure the file exists and/or is in the correct
directory. (Usually the same directory as KINTECUS.)
```

Explanation:
The –THERM switch was provided on the command line, so now Kintecus is looking for a Thermodynamic description file THERM.DAT which must now be provided.

Fatal Error#34

```
Thermodynamic database file (filename)
CANNOT BE FOUND !!!!
Make sure the file exists and/or is in the correct
directory. (Usually the same directory as KINTECUS.)
```

Explanation:
The thermodynamic description spreadsheet provided when thermodynamics is invoked (through the –THERM switch) contains thermodynamic database filenames in the first column.
Kintecus cannot find the thermodynamic database (filename) in the current directory.

Fatal Error #35

```
A duplicate reaction has been found!'
'Reaction #'s (Number1) and (Number2)
 ( Source line numbers (Number3) & (Number4)
 in (filename)
 are duplicates! Please correct or delete.'
```

Explanation:
Get rid of one of the same reaction lines. Go to the line (Number3) or (Number4) and correct the reaction line or delete it.

Fatal Error #36

Obsolete. You should not get this error.

Fatal Errors #39, 40

```
You have exceeded the number of reactants
that can appear in one reaction.
Try to split the global reaction
into two global reactions. You can do this
with ANY global reaction.
 -OR-
Contact company for an upgrade.
LINE READS:
```

Explanation:
Currently, you can only have three unique reactants and 20 unique products in one reaction. This restriction DOES NOT include +M[…] or +S[…] appearing as a reactant, so the following reaction is allowed:

A+B+C+M[-O2(1);-N2(1) ;H2(1);-Ar(1); -HO2(1);-CO2(1)]==>D+E+F

Fatal Errors #70, 71, 72, 73, 75, 77, 78

All these errors have to do with the thermodynamic database descriptor fields used in the Thermodynamic Description SpreadSheet .

Fatal Error #74

```
The species (species name)
has NOT been located in any of the thermodynamic
database(s) specified in the thermodyamic description
file:THERM.DAT
```

Explanation:
If you wish to use thermodynamics in your model, you must provide all species' thermodynamic coefficients. If you are sure you did do this, then make sure that you are using the Species Reservation field in the Thermodynamic Database Description Spreadsheet correctly. You will get this error if you reserve a species for a database that does not contain the reserved species.

Fatal Error #76

```
To compute reverse rates using the thermodynamic
database, please use UNITS of mol./liter, mol./cc or
molecules/cm^3.
```

Fatal Errors #79-85,87,89,91

Please refer to The Model Description Spreadsheet for full explanations on handling these types of reactions.

Fatal Error #90

```
There are NO reactions to compute!!!'
```

Explanation:
Did you accidentally put in an END before all the reaction lines?
A '#' or a double quote as the first non-space character on a line will comment the whole line out.

Fatal Error #123 and Fatal Error #124

```
An invalid number was found in the parameter or species or model description
spreadsheet
```

Explanation:
Kintecus expects numbers to have a period, ".", as the decimal in a number, i.e. 3.14159. If you are in a country that uses commas as the decimal point for a number (i.e., 3,14159), you must convert the numbers to periods ".". You can do this easily in the Kintecus-Excel workbook by clicking the checkbox named "I am using the German/Russian version of Excel" located on the **CONTRO**L worksheet.

Fatal Error #177

```
*ERROR: Cannot create unique ID for this computer!!!
 *Enable your network connection or insert
  an ethernet (network) card in your computer.
  Is a hard drive c: present?
```

Explanation:

Kintecus is having trouble identifying your computer.

There are three possible solutions:

(A) Enable a valid Windows hard drive with a “C:” partition (nearly all Windows PC’s have this so this shouldn’t be an issue).

(B) It is possible that your anti-virus software prevents the Kintecus executable or Kintecus_Workbench executable or the “cmd.exe” Windows program from running. Most anti-virus software has a “safe” list or an exception list. Please add those executables to that list. This error can also happen from anti-Ransomware software preventing Kintecus from writing to the “..\Kintecus\” folder. Please remove such protections or enable the above executables to a safe list. See below under “VIRUS SOFTWARE PREVENTING KINTECUS TO RUN?”

(C) Uninstall Kintecus/Reinstall Kintecus: First, make a backup of your Kintecus directory (select the Kintecus folder, hold "control-C", then "control-V" and a copy of your Kintecus directory should appear), then un-install Kintecus (the old Kintecus folder may still be there), delete the Kintecus folder, then re-install Kintecus. If Kintecus is running, copy back any of your files from the old backup back to the newly created Kintecus folder.

VIRUS SOFTWARE PREVENTING KINTECUS TO RUN?
==========
Several anit-virus software programs scan the Kintecus package before distribution.
You can always run an entire gauntlet of 60+ virus scans by using Google's free VirusTotal website too!

Here are some options to get Kintecus or Kintecus to run under some pesky anti-virus code:
---
(1) Your anti-virus software may be preventing the Kintecus executable or Kintecus_Workbench executable or the “cmd.exe” Windows program from running. Most anti-virus software has a “safe” list or an exception list. Please add those executables to that list. This can also happen from anti-Ransomware software preventing Kintecus from writing to the “..\Kintecus\” folder. Please remove such protections or enable the above executables to a safe list.

(2) Even if you have zero anti-virus software installed, **Microsoft has an internal anti-virus procedure in Excel** that can prevent some Kintecus-Excel macros from running. This depends on the version of Office and site policies. You can set all Kintecus-Excel Workbooks to Trusted by setting the directory "C:\Kintecus" as a "Trust Location" in the Excel Trust Center. You can do this by going to File==>Options==>"Trust Center", click the "Trust Center Settings..." button, click "Trust Locations", click "Add new location...", click "Browse", select the "C:\Kintecus\" directory (or whatever PATH you installed Kintecus), click 'OK', then click OK again. You should now be able to fully run all Kintecus-Excel Workbooks with no interference from Excel errors.
You can also see
https://support.microsoft.com/en-us/office/add-remove-or-change-a-trusted-location-7ee1cdc2-483e-4cbb-bcb3-4e7c67147fb4
for more details.

(3) If you still have trouble running Kintecus in Excel, don't run Kintecus in Excel.
Please see the section "Run Kintecus Outside of Excel or Run Many Copies of Kintecus on one PC?"

inside the manual:

How to Run Kintecus Outside of Excel and/or Run Many Copies of Kintecus on one PC?

This part explains how to run Kintecus using the MODEL/SPECIES/PARM/FITDATA/etc worksheets in Excel without having Excel windows constantly pop up, waste cpu cycles, and constantly annoy you as your Kintecus simulation runs.

Click the Windows Start Button in the left-hand corner of the screen, and type “cmd” or "command," and press enter. A console window should pop up on the screen. Alternatively, hold the Windows key (usually, the key is at the bottom left of the keyboard, in between the CTRL and ALT keys) and tap the "x" key. A menu will pop up, select "Command" or "Run" and then type “cmd” or “command,” and a new console should pop up.

1) Once you are in the console window, type "cd C:\Kintecus" or where ever you have Kintecus installed.

2) In the Excel window, click on the "CONTROL" tab, and click "RUN" once Kintecus starts, stop it with "ctrl-c" (hold the ctrl key and tap the "c" key) or ctrl-break (hold the ctrl key and tap the Pause/Break key). This step is required because once you press the RUN button, the Kintecus-Excel VBA macros will output all your worksheets as input text files for Kintecus.

3) In the same "CONTROL" worksheet, click on the contents of the "Kintecus Switches" cell (A12) and select COPY (right-click, select Copy)

4) Click in the console/command line window, and type "kintecus" **(don’t press enter yet!)**
In the PowerShell command, type "./kintecus."

5) Hold down the CTRL key and type "V" (for paste), and press ENTER. This should paste your Kintecus switches from cell A12 on the CONTROL worksheet into the command line.

6) Kintecus is now running outside of Excel, using all your inputs from the Excel Worksheet. Once Kintecus is finished, click the “Plot Results” button on the CONTROL worksheet. Also, note that you can copy the entire Kintecus folder into a new directory (C:\Kintecus2\), change the “Kintecus Path” located on the CONTROL worksheet, then change one or two parameters in the Kintecus-Excel worksheet and perform the same steps above. You will be running two different Kintecus simulations/optimizations simultaneously. Repeat as necessary, assuming you have enough cores on your cpu.

Warning Messages

Warnings will not halt a simulation run, but it may lead Kintecus to crash, or to yield incorrect results. They can also just waste computer time for Kintecus to correct automatically. They should be eliminated.

Warning #1

```
'You can not define ''hv'' and ''M'' as species.'
'These are internal species that have special'
'definitions in Kintecus. Remove ',
(hv or M) from your species file: (Filename)
'You DO NOT have to define these species.'
'(Ignoring line...)'
```

Warning #3

```
'THE SPECIES: (Species Name)
' DOES NOT EXIST (spelling? or watch your letter 'O' '
' from the numeral zero, '0', or the lowercase'
'letter ,''l'',and the numeral one, ''1'')'
'in the species containing file: ',
'Adding in the species and initializing all values as 0.'
```

Explanation:
You have entered in a reaction, which has an undefined species. Kintecus cannot locate the species in the Species Description Spreadsheet. You should halt the simulation, append the created species file (ADDSPEC.TXT) to the end of your The Species Description Spreadsheet , and initialize any fields. Re-run.

Warning #6

```
'???? Possible error ????:'
'A negative concentration was detected!!!'
'Halt program and re-RUN with MIN.-Interg.=Min. Interg./10 and/or'
'Accuracy=Accuracy/10.'
'Also CHECK YOUR EQUATIONS!!! Do they make sense? '
```

Explanation:
See "Overflows, Underflows, Division by Zero, Singularities" under the above section "[Errors That Can Not Be Caught by Kintecus]".

Warning #8

```
'You are not displaying the output of ANY SPECIES!'
'You will not be able to see the concentration of any'
 'species!!!'
```

Explanation:
You have not entered a single "yes" or "y" on the “Display Output ?” field of any of the species in the The Species Description Spreadsheet .

Warning #9

```
'One or more left parenthesis are missing for species:'
(Species Name) in your species file: (Filename)
'any equations containing this species can not be'
'checked for mass balance.'
```

Explanation:
You have entered an invalid species name such as CN2)2. Correct by placing in a left parenthesis, i.e. C(N2)2.

Warning #10

```
'You have reached the maximum amount of parenthesis'
'nesting in the species , (Species Name)
'in your species file: , (Filename)
'Expand the inner most parenthesis.'
'Any equations containing this species can not be'
'checked for mass balance.'
```

Warning #11

```
'One or more right parenthesis are missing for species:'
(Species Name),in your species file: , (filename)
'Any equations containing this species can not be'
'checked for mass balance.'
```

Explanation:
You have entered an invalid species name such as C(N22. Correct by placing in a right parenthesis, i.e. C(N2)2.

Warning #12

```
'The species (SpeciesName)
 can not be mass determined nor does it exist as'
 an entry in your names file:(filename)
 Any equations containing this species can not be'
 checked for mass balance.'
```

Explanation:
You have entered an invalid Species Name such as OPL or DNA. If you wish to use such names and still check for mass balance you must create a The Species Name Spreadsheet file containing the name and it's mass.

Warning #13

```
'One or more left parenthesis are missing for '
 mass formula ,(Mass Formula Shown)
of the name: (Species Common Name)
in your name file: (File Name)
 any equations containing this species can not be'
 checked for mass balance.
```

Explanation:

You have entered an invalid species name such as CN2)2. Correct by placing in a left parenthesis, i.e. C(N2)2.

Warning #15

```
One or more right parenthesis are missing for '
mass formula,(Mass Formula Shown)
of the name:,(Species Common Name)
in your name file: (File Name)
Any equations containing this species can not be'
checked for mass balance.'
```

Explanation:
You have entered an invalid species name such as C(N22. Correct by placing in a right parenthesis, i.e. C(N2)2.

Warning #16

```
The mass formula (Mass Formula Shown) of the name: (Common Name Shown) can
not be mass determined in your names file: (File Name)
Any equations containing this species can not be'
checked for mass balance.
```

Explanation:
Kintecus can not determine the mass of the (Mass Formula Shown). Please make sure it's a valid molecular weight or mass.

Warning #17

```
Charge conservation is *NOT CONSERVED*'
in reaction # (Number)
( Source line number (Number) )
This can possibly lead to divergence in the solution!'
'Please correct.'
```

Warning #18

```
'Mass conservation is *NOT CONSERVED*'
' in reaction # (Number)
'( Source line number (Number) )'
'This can possibly lead to divergence in the solution!!'
'Please correct.'
```

Warning #19

```
Mass conservation for reaction # (line)
( Source line number (Source Line) )
can not be determined because one of the species in'
the reaction has either an illegal molecular weight'
or it's name is not located in the name file or'
'a name file has not been created. A name file'
'contains the common name of the species and it's
'molecular weight such as: Methanol , CH3OH .'
'This can possibly lead to divergence in the solution!!'
'Please correct.'
```

Warning #20

```
Parameter description file (filename),
CAN NOT BE FOUND !!!!'
Make sure the file exists and/or is in the correct'
directory. (Usually the same directory as KINTECUS.)'
Using default values:
```

Explanation:
The Parameter Spreadsheet File contains fields that tell Kintecus how long to run the simulation, the accuracy of the simulation, and many other very important fields (see the Kintecus.doc file for a full description). If Kintecus can't find this file, it will assume values for all the fields. Those values are equivalent to the supplied parameter spreadsheet file:PARMDEF.DAT, which you should copy as PARM.DAT and go over any relevant fields to your simulation.

16. Support Programs

Most of these programs listed below are designed to help you transfer your experimental data into concentration profiles or convert text files from another platform (such as the Mac, UNIX or Amiga) to MS-DOS or the other way around. To run these programs ending in .bas, just type at the Command prompt >qbasic /run program.bas or run the compiled executable that should be already provided.

CK2KIN.EXE (CHEMKIN-II/III → KINTECUS MODEL CONVERTER)

Running this program from the Windows command prompt (click START→RUN, type command, use command cd to change directories) will start this program. CK2KIN will ask you for the Chemkin model file. Ensure the Chemkin model file is a valid Windows/MS-DOS text file. If the Chemkin model (a text file) was downloaded from a UNIX site, the text file will be in UNIX format and will NOT be readable by this program. Use the CRADD program below to add carriage returns to the text file, or before downloading the Chemkin model from the UNIX site, run a unix2dos program on the Chemkin Text file. The Chemkin→Kintecus converted model file will always be named: MODEL.DAT. Also, please be sure to download the thermodynamic database that came with the Chemkin Model. Sometimes the thermodynamic database is inside the Chemkin file, and you will have to cut and paste this into a text file. The last step, copy the **parmck.dat** to **parm.dat** and the **THERMCK.DAT** to **THERM.DAT** or paste the model into any current Kintecus-Excel combustion model worksheet such as "Combustion_isooctane3.xls" or "Combustion_DIESEL_surrogate.xls" or any of the other 20+ sample combustion models which were originally Chemkin models. Ensure that the first column's thermodynamic database filename matches the filename to the extracted Chemkin thermodynamic database. In addition, not all Chemkin thermodynamic databases are alike, and you might have to try different reading methods to read in that database. You can simply uncomment out the other lines in the THERM.DAT file to see if one of those lines will read in the chemkin database.

Example:

ORIGINAL THERM.DAT

#Database			Database	Species
#FileName	INPUT	MAP	Special Switches	Reservation List
NAME_OF_MY_DATABASE	F18:IG26:F1:	SP:PH:LT:HT	U1234:FLUFF:CHF:PHS	
#(insert THERM database name)	F18:IG26:F1:	SP:PH:LT:HT	U1234:CHF:PHS	
#(insert THERM database name)	F18:IG26:F1:	SP:PH:LT:HT	U1234:UPPL:CHF:PHS:UPC	
#(insert THERM database name)	F18:IG26:F1:	SP:PH:LT:HT	U1234:UPPL:CHF:FLUFF:PHS:SET(CT=1000):SYN	
#(insert THERM database name)	FREE	SP:LT:CT:HT	UPPL	
END				

CHANGED TO

#Database			Database	Species
#FileName	INPUT	MAP	Special Switches	Reservation List
## NAME_OF_MY_DATABASE	F18:IG26:F1:	SP:PH:LT:HT	U1234:FLUFF:CHF:PHS	
NAME_OF_MY_DATABASE	F18:IG26:F1:	SP:PH:LT:HT	U1234:CHF:PHS	
#(insert THERM database name)	F18:IG26:F1:	SP:PH:LT:HT	U1234:UPPL:CHF:PHS:UPC	
#(insert THERM database name)	F18:IG26:F1:	SP:PH:LT:HT	U1234:UPPL:CHF:FLUFF:PHS:SET(CT=1000):SYN	
#(insert THERM database name)	FREE	SP:LT:CT:HT	UPPL	
END				

If you still cannot read in your thermodynamic database, then comment out the current line (note the "#" at the beginning of the line) and enter the database name on the following line, and so on:

#Database			Database	Species
#FileName	INPUT	MAP	Special Switches	Reservation List
## NAME_OF_MY_DATABASE	F18:IG26:F1:	SP:PH:LT:HT	U1234:FLUFF:CHF:PHS	
## NAME_OF_MY_DATABASE	F18:IG26:F1:	SP:PH:LT:HT	U1234:CHF:PHS	
NAME_OF_MY_DATABASE	F18:IG26:F1:	SP:PH:LT:HT	U1234:UPPL:CHF:PHS:UPC	
#(insert THERM database name)	F18:IG26:F1:	SP:PH:LT:HT	U1234:UPPL:CHF:FLUFF:PHS:SET(CT=1000):SYN	
#(insert THERM database name)	FREE	SP:LT:CT:HT	UPPL	
END				

Error codes from ck2kin.exe

ERROR HAPPENED OF TYPE: 64

This error pops up in the chemkin to Kintecus converter when the chemkin text file is in Unix format and NOT in Windows/MS-DOS text file format. This error is easily corrected by loading the chemkin Unix text file into Windows WordPad program and resaving it as a "Text document MS-DOS Format." then re-try and convert the mechanism with ck2kin.exe.

Known Bugs

Occasionally ck2kin.exe will encounter enhanced third body values for one reaction scattered on multiple lines. The translated Kintecus reaction line will have a missing semi-colon, ";" between the species enhanced third-body values where the value is line separated. You'll get a Kintecus error for that translated line. **The fix is manually placing in a semi-colon between the species enhanced third body values and removing any remaining backslash, "\".**

Example, original Chemkin reaction source line**:**

'CH2(S) + M = CH2 + M 1.51E13 0.00 0.00 !'
'N2/.4/ O2/.4/ CO/.75/ CO2/1.5/ H2O/6.5/ CH4/.48/ C2H2/3.2/ C2H4/1.6/'
'C2H6/1.44/ AR/.24/'

The converter "forgot" to place a semi-colon between the C2H2 and the C2H6
third-body reaction, so you'll get this Kintecus line:

1.51E13, 0, 0, CH2(S)+M[N2(.4);O2(.4);CO(.75);CO2(1.5);H2O(6.5);CH4(.48);C2H2(3.2);C2H4(1.6)**C2H**
6(1.44);AR(.24)]=CH2+M

The fix is simply place a semi-colon between the C2H4 and C2H6 third-bodies and remove the backslash, "\":

1.51E13, 0, 0, CH2(S) +
M[N2(.4);O2(.4);CO(.75);CO2(1.5);H2O(6.5);CH4(.48);C2H2(3.2);C2H4(1.6);C2H6(1.44);AR(.24)]=CH2+M

INTERPOL.BAS

"Program to convert scattered data file of time,data to"
"a sequential list of data spaced exactly at an "
"entered timing interval."
"(Values in-between are linearly interpolated...)"

CRADD.BAS

This program converts text files from another platform (such as the Mac, Unix or Amiga) to Windows/MS-DOS.

LOOK.BAS

A program to look at the ASCII values in a file.

FILTER.BAS

This will convert MS-DOS text files to Mac/Unix text files.

Master Chemical Mechanism (MCM)

The Kintecus Workbench has a Master Chemical Mechanism (MCM) submenu for MCM support. MCM is the **special IUPAC chemical kinetics** forms from the **Master Chemical Mechanism (MCM)** (see http://mcm.leeds.ac.uk/MCM/parameters/complex.htt , http://www.iupac-kinetic.ch.cam.ac.uk/ and/or http://iupac.pole-ether.fr/ or Google/Bing "Master Chemical Mechanism") In this submenu there are items that will help you convert MCM mechanisms into Kintecus format.

17. Trademarks

18. References

[1] Vetterling, W.,T.; Flannery, B.P.; Teukolsky, S.A; Press, W.H., "Numerical Recipes in FORTRAN", Second Edition, Cambridge University Press, Cambridge, 1992.

[2] Frei, K.; Hs. H. Gunthard, Hel. Chim. Act., 50(132), 1967, pp1294-1304.

[3] Farrow, L.A.; Edelson, D., Int. J. Chem. Kin., 6, 1974, pp787-800.

[4] Kennealy, J.P.; Moore, W.M.; J. Phys. Chem., 81(25), 1977, pp2413-2419.

[5] Field, R.J.; Noyes, R.M., J. Chem. Phys., 60(5), 1974, pp1877-1884.

[6] Edsberg, L., "International Symposium on Stiff Differential Systems", Plenum Press, 1974.

[7] Showalter, K.; Noyes, Richard M.; Eli-Bar, Kedma, J. Chem. Phys., 69(6), 1978, pp2514-2524.

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

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

[10] Gautier, O.; Carr JR., R. W.; Seigneur, C., Int. J. Chem. Kin., 17, 1985, pp1347-1364.

[11] Kee, R.J., Rupley, F.M.; Miller, J.A. “CHEMKIN-II: A Fortran Chemical Kinetics Package for the Analysis of Gas Phase Chemical Kinetics”, Sandia Report #SAND-89-8009, Sandia National Laboratories, 1989

[12] Hidaka, Y., Taniguchi, T., Tanaka, H., Kamesawa, T.,Inami, K., and Kawano, H. (1993) Combust. Flame, 92, 365.
Some of their results can be found on this web page:
http://www.me.berkeley.edu/gri_mech/version30/text30.html .

[13] Yu, C.-L., Wang, C., and Frenklach, M., 'Chemical Kinetics of Methyl Oxidation by Molecular Oxygen,' J. Phys. Chem., 99, 14377 (1995).
Some of their results can be found on this web page:
http://www.me.berkeley.edu/gri_mech/version30/text30.html .

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

[15] Dunphy, M. P.; Simmie, J. M., J. Chem. Soc. Faraday Trans., 87, 1691-1695, 2549-2559 (1991)

[16] Houle and Hinsberg,Surface Science 338 (1995) 329-346

[17] Hinsberg, W., Houle, F, Allen, F. CKS, Chemical Kinetics Simulator 1.1 IBM Almaden Research Center 1996.

[18] Handbook of Chemistry and Physics, CRC Press, 53rd Edition, 1972-1973, D-76.

[19] GRI-Mech 3.0 ,Gregory P. Smith, David M. Golden, Michael Frenklach, Nigel W. Moriarty, Boris Eiteneer, Mikhail Goldenberg, C. Thomas Bowman, Ronald K. Hanson, Soonho Song, William C. Gardiner,Jr., Vitali V. Lissianski, and Zhiwei Qin http://www.me.berkeley.edu/gri_mech/

[20] Ritter, E.R.; Bozzelli, J.W., Int. J. Chem. Kinet. 1991, 23, pg767-778

[21] Benson, S.W. Thermochemical Kinetics, 2nd Edition.; John Wiley & Sons, New York, 1976

[22] Burcat, A.; McBride, B. "1994 Ideal Gas Thermodynamic Data for Combustion and Air-Pollution Use", Technion Report #TAE 697, 1993

[23] Nelder, J.A.; Mead, R., Computer Journal, vol. 7, 1965, pg. 308-313.

[24] Kirkpatrick, S.; Gelatt, C.D.; Veccho, M.P., Science, vol. 220, 1983, pp. 671-680

[25] Chang, A.Y., Davidson, D.F., DiRosa, M., Hanson, R.K., and Bowman, C.T., "Shock Tube Experiments for Development and Validation of Kinetic Models of Hydrocarbon Oxidation," (1994) 25th Symposium (International) on Combustion, Poster 3 - 23
http://www.me.berkeley.edu/gri_mech/version30/targets30/ch3.t2.html

[26] Gill, Philip E., Walter Murray, and Margaret Wright (1981), *Practical Optimization*, Academic Press, New York.

[27] Gear, C.W. (1971), *Numerical Initial Value Problems in Ordinary Differential Equation*s, Prentice-Hall, Englewood Cliffs, New Jersey.

[28] Tamás Turányi, Lajos Zalotai, Sándor Dóbé, Tibor Bérces, Phys.Chem.Chem.Phys, 4, 2002, pp2568-2578.

[29] Anderberg, Michael R. (1973), *Cluster Analysis for Application*s, Academic Press, New York; Hartigan, John A. (1975), *Clustering Algorithm*s, John Wiley & Sons, New York.; as implemented in IMSL libraries.

[30] Janev, R. K., Langer, W. D., K. Evans, J. and D. E. Post, J.: *Elementary Processes in Hydrogen-Helium Plasmas*, Springer-Verlag, New York (1987).

[31] (a) L. R. Petzold, A Description of DASSL: A Differential/Algebraic System Solver, in Scientific Computing, R. S. Stepleman et al. (Eds.), North-Holland, Amsterdam, 1983, pp. 65-68. (b) K. E. Brenan, S. L. Campbell, and L. R. Petzold, Numerical Solution of Initial-Value Problems in Differential-Algebraic Equations, Elsevier, New York, 1989. (c) P. N. Brown and A. C. Hindmarsh, Reduced Storage Matrix Methods in Stiff ODE Systems, J. Applied Mathematics and Computation, 31 (1989), pp. 40-91. (d) P. N. Brown, A. C. Hindmarsh, and L. R. Petzold, Using Krylov Methods in the Solution of Large-Scale Differential-Algebraic Systems, SIAM J. Sci. Comp., 15 (1994), pp. 1467-1488. (e) P. N. Brown, A. C. Hindmarsh, and L. R. Petzold, Consistent Initial Condition Calculation for Differential-Algebraic Systems, LLNL Report UCRL-JC-122175, August 1995; submitted to SIAM J. Sci. Comp.

[32] P. K. Venkatesh, J Phys. Chem. A 104(2):280-287 (2000). P. K. Venkatesh, A.Y. Chang, A.M. Dean, M. H. Cohen and R.W. Carr, J. AIChE 43:1331-1340 (1997).

[33] X. Gou, J.A. Miller, W. Sun and Y. Ju, http://engine.princeton.edu, 2011.

[34] Wilton P. Silva - wiltonps@uol.com.br and Ivomar B. Soares - ivomarbrito@uol.com.br

[35] David M. Stanbury and Dean Hoffman; "Systematic Application of the Principle of Detailed Balancing to Complex Homogeneous Chemical Reaction Mechanisms"; J. Phys. Chem A; 2019; 123, p5436-5445 and references therein.

[36] (a) Wegscheider, R. Über simultane Gleichgewichte und die Beziehungen zwischen Thermodynamik und Reactionskinetik homogener Systeme. Monatsh. Chem. 1901, 22, 849−906 (b) Wegscheider, R. Über simultane Gleichgewichte die Beziehungen zwischen Thermodynamik und Reaktionskinetik homogener Systeme. Z. Phys. Chem. 1902, 39, 257−303.

[37] Graphivz by John Ellson (drivers and plugins, scripting and codegen extensions, build), Emden Gansner (dot, neato, twopi, circo, fdp, osage, smyrna, gvmap, prism, gvpr), Yifan Hu (sfdp, prism, gvmap, cluster, mm2gv), Stephen North (dot, neato) and many others (see www.graphviz.org/credits/)

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Appendices

Appendix A – Sample Statistical Output

The following output is from the OPTOUT.TXT file created when FITTEST3.BAT is run or from the Excel file "Enzyme_Regression_fitting.xls" with the switch addition "–FITSTAT" on the Kintecus command line.

```
Parameter 1 (k or A) in file:F4MODEZY.DAT @ source line:9 optimized to:4999225.21
      Parameter 2 (k or A) in file:F4MODEZY.DAT @ source line:12 optimized to:66735.0769
      Parameter 3 (k or A) in file:F4MODEZY.DAT @ source line:16 optimized to:8495129.31


 Final SUM[ ( X(DATA)-X(MODEL) )^2 ] =   5.550593731763186E-003
 Final RMS's for Data Columns (column # ,RMS):
  1  0.50281E-03  2  0.12290E-02  3  0.38147E-02  4  0.35446E-02
 Final AVG RMSD=  2.272783306375678E-003

 Total optimization iteration count=         281
 ** Total amount of simulations performed=         918


 Parameter,    Variance,   Standard Deviation,   % Stand. Deviat.
  1         0.38073E+12         0.61703E+06          12.3     %
  2         0.22641E+06          475.83              0.713    %
  3         0.78144E+10          88399.              1.04     %

 Covariance Matrix:
   380726511738.027         84395658.4478283        -12399590966.1360
 -0.955964597865071         226412.539349878        -37329936.5835151
 -0.293481851329124        0.832548732773235         7814427078.66344
 -3.009470109205987E-004  1.743535911345125E-004 -1.687514284307081E-004


 ********************************************************************
 >>>>>>>>>>>>>>>>>> START OF PREDICTION ANALYSIS <<<<<<<<<<<<<<<<<<<<
 ********************************************************************

 ================================================================
 **** Start of prediction analysis for data-column:      1  ( E )

 R-squared   Adjusted  Est. Std. Dev.              Coefficient of
 (percent)  R-squared  of Model Error        Mean  Var. (percent)
   100.000    100.000       1.801E-12   3.584E-09         0.05025

                 * * * Analysis of Variance * * *
                             Sum of        Mean             Prob. of
 Source                 DF     Squares      Square  Overall F  Larger F
 Regression              1   2.353E-17   2.353E-17  *********    0.0000
 Residual               32   1.038E-22   3.243E-24
 Corrected Total        33   2.353E-17
```

The calculated stand. devs. and covariance matrix can be outputted by entering the **"-FITSTAT"** switch on the Kintecus command line.

* * * Inference on Coefficients * * *

Coef.	Estimate	Standard Error	t-statistic	Prob. of Larger |t|	Variance Inflation
1	0.0000	1.366E-12	0.5	0.5931	19.55
2	0.9999	3.712E-04	2693.5	0.0000	1.00

* * * Variance-Covariance Matrix for the Coefficient Estimates * * *

	1	2
1	1.86495E-24	-4.93805E-16
2		1.37799E-07

* * * Test for Lack of Fit * * *

Source	DF	Sum of Squares	Mean Square	Overall F	Prob. of Larger F
Lack of fit	18	1.038E-22	5.766E-24	Inf	0.0000
Pure error	14	0.000E+00	0.000E+00		
Residual	32	1.038E-22			

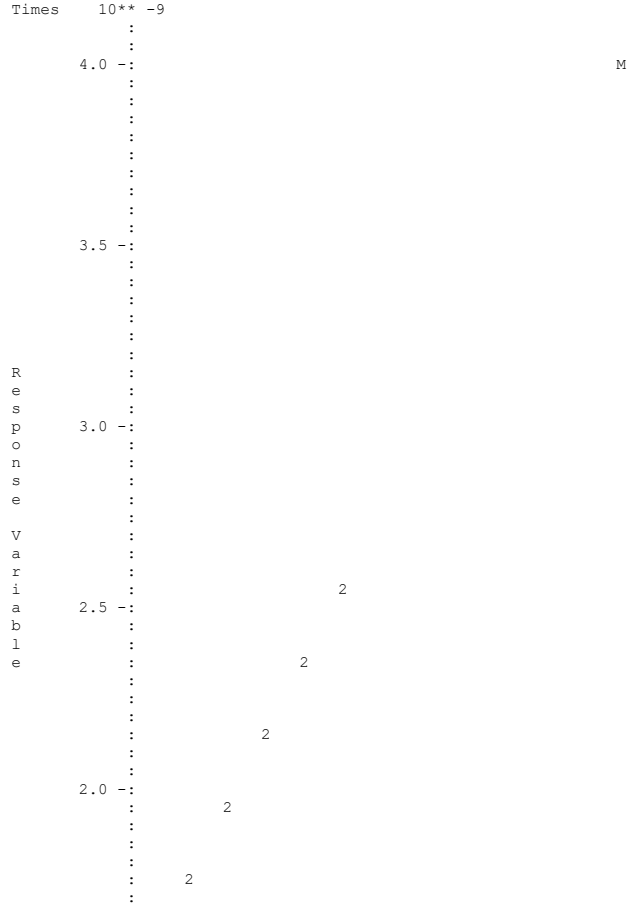
* * * Case Analysis * * *

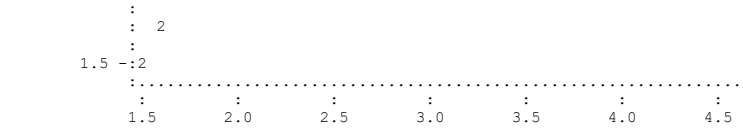
	Obs.	Observed	Predicted	Residual	Leverage	Std. Res.	Jack Res.
		Cook's D	DFFITS	95.0% CI	95.0% CI	99.0% PI	99.0% PI
X	1	0.0000	0.0000	0.0000	0.2102	-0.7954	-0.7908
		0.0842	-0.4080	0.0000	0.0000	0.0000	0.0000
XY	2	0.0000	0.0000	0.0000	0.1939	2.1013	2.2275
		0.5309	1.0924	0.0000	0.0000	0.0000	0.0000
X	3	0.0000	0.0000	0.0000	0.1692	0.0093	0.0092
		0.0000	0.0041	0.0000	0.0000	0.0000	0.0000
X	4	0.0000	0.0000	0.0000	0.1441	-0.7382	-0.7328

..<SNIP>..

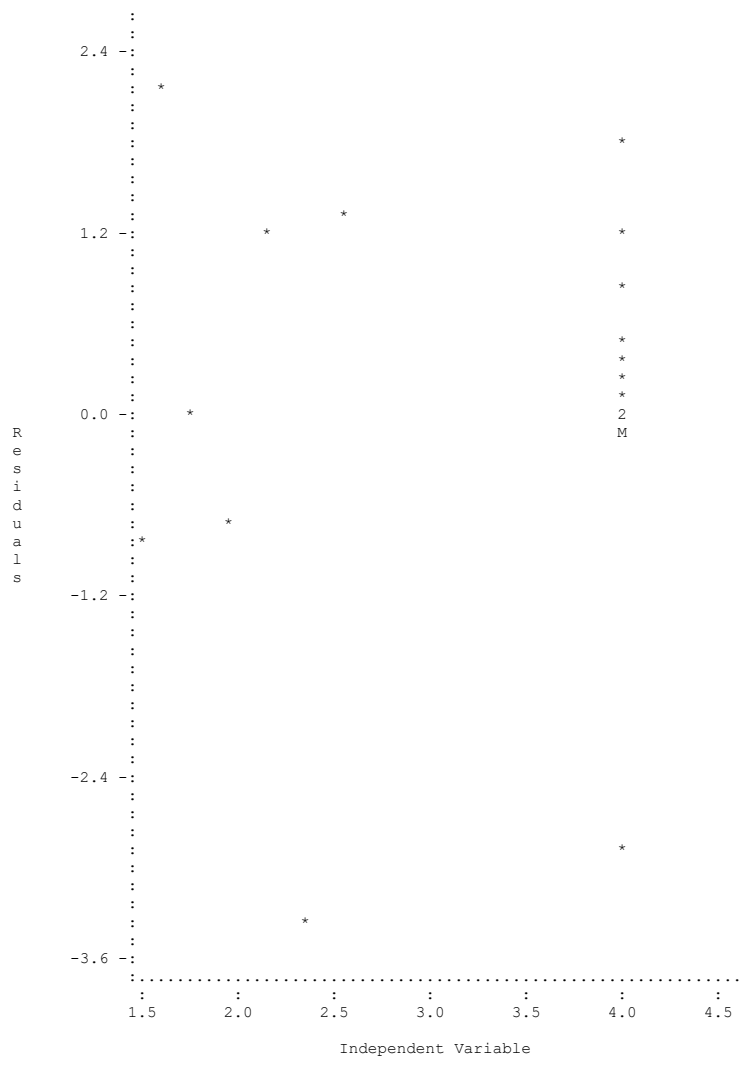
1

Observed-O and Predicted-P vs. Independent Variable





1



..<SNIP>..

```
 ================================================
 *****  CORRELATION COEFFICIENT ANALYSIS  *****
 ================================================
 ( this is also called Pearson's r, or the product-
   moment correlation coefficient )
 This test will indicate how well the predicted
 values correlate with your experimental values.

Correlation Coefficient:      0.999572     Probability:       0.00000
 ( a perfect fit will have a correlation coefficient = 1.0 )
 ( small probability [=0.0] indicates significant correlation )
```

```
Fisher's z-coefficient:       4.22505

 ================================================
       ***** RESIDUALS MOMENT ANALYSIS  *****
  ( Residuals = Experim. Data - Predicted Values )
 ================================================

 ----------------------------------------------
 Residual Gaussian Normality Test #1

 **** Shapiro-Wilk W-test for Gaussian Normality ****
 ( how your residuals are distributed )
W =    0.763 ( Perfect Normality : W=1.0 )
 P-value Test of Normality =   9.5367432E-07

 ----------------------------------------------
 *** Residual Statistics:
 Mean(Average) =   2.9842470E-13
 Average Deviation =   1.0046757E-12
 Standard Deviation =   1.7764005E-12
 Variance =   3.1555990E-24
 Skewness =   -1.072193
 Kurtosis =    5.277860


 **** End of prediction analysis for data-column:      1
 ================================================================


 ================================================================
 **** Start of prediction analysis for data-column:      2  ( S )

 R-squared   Adjusted  Est. Std. Dev.              Coefficient of
 (percent)  R-squared  of Model Error        Mean  Var. (percent)
   100.000    100.000       5.044E-06    0.004338          0.1163

                  * * * Analysis of Variance * * *
                              Sum of        Mean             Prob. of
 Source                 DF     Squares      Square  Overall F  Larger F
 Regression              1    0.009008    0.009008  *********    0.0000
 Residual               46    0.000000    0.000000
 Corrected Total        47    0.009008

               * * * Inference on Coefficients * * *
                        Standard                 Prob. of    Variance
 Coef.    Estimate       Error  t-statistic  Larger |t|   Inflation
     1          0.   7.638E-07         -1.6      0.1226         1.1
     2          1.   5.316E-05      18814.8      0.0000         1.0

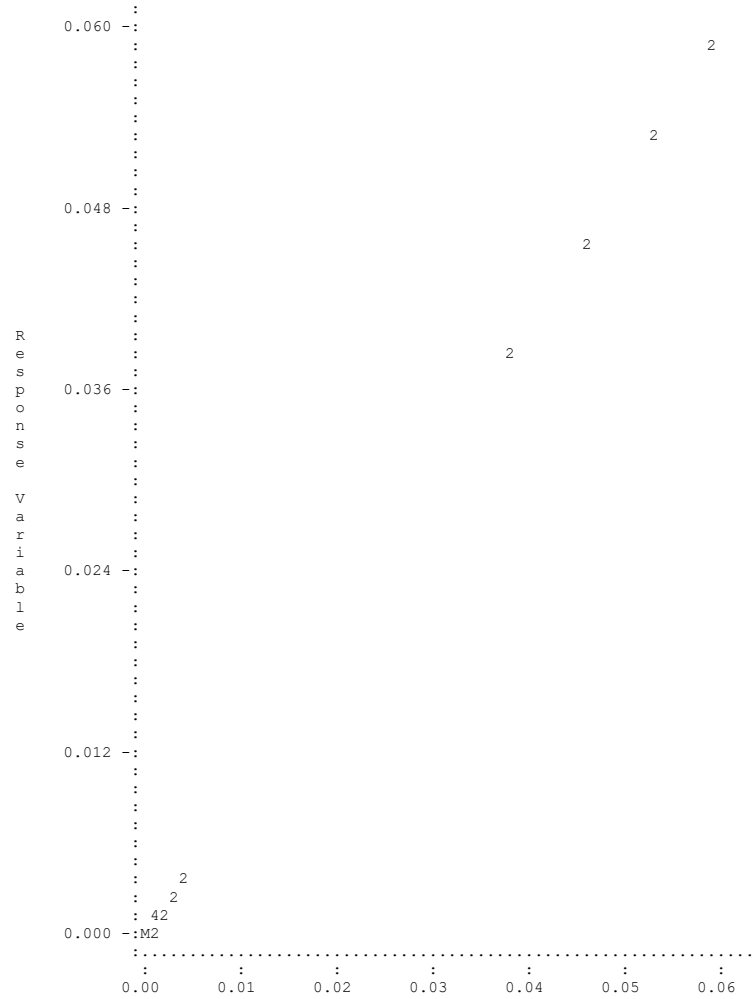
 * * * Variance-Covariance Matrix for the Coefficient Estimates * * *
                                   1             2
                     1   5.83329E-13  -1.22605E-11
                     2                 2.82560E-09

                          * * * Case Analysis * * *
       Obs.   Observed  Predicted   Residual   Leverage  Std. Res.  Jack Res.
              Cook's D     DFFITS   95.0% CI   95.0% CI   99.0% PI   99.0% PI
 X         1     0.0590     0.0590     0.0000     0.3525     0.0844     0.0835
                 0.0019     0.0616     0.0590     0.0590     0.0590     0.0590
 XY        2     0.0534     0.0534     0.0000     0.2879     3.7945     4.5280
                 2.9102     2.8789     0.0534     0.0534     0.0534     0.0534
 XY        3     0.0456     0.0456     0.0000     0.2100    -4.1062    -5.1028
                 2.2411    -2.6309     0.0456     0.0456     0.0456     0.0456
 X         4     0.0384     0.0384     0.0000     0.1496     0.2362     0.2338
                 0.0049     0.0981     0.0384     0.0384     0.0384     0.0384

    ..<SNIP>..

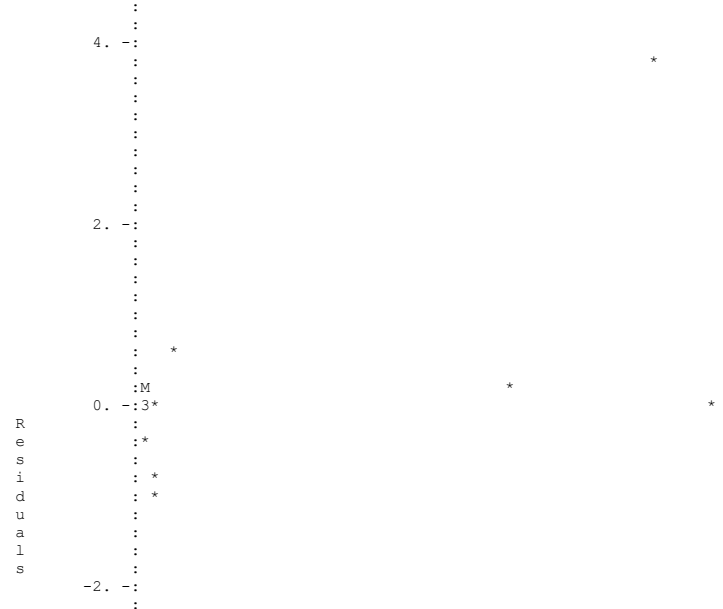
1
                Observed-O and Predicted-P vs. Independent Variable

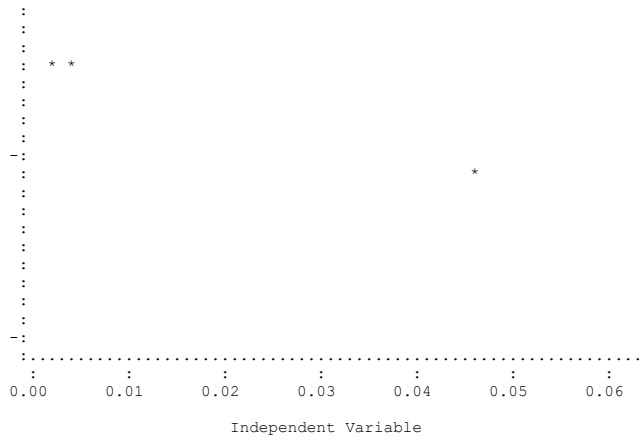
          :
```



1

Standardized Residuals vs Independent Variable





..<SNIP>..

```
 ================================================
 *****  CORRELATION COEFFICIENT ANALYSIS  *****
 ================================================
 ( this is also called Pearson's r, or the product-
   moment correlation coefficient )
 This test will indicate how well the predicted
 values correlate with your experimental values.

Correlation Coefficient:       1.00000     Probability:       0.00000
 ( a perfect fit will have a correlation coefficient = 1.0 )
 ( small probability [=0.0] indicates significant correlation )
Fisher's z-coefficient:       7.85962


 ================================================
       ***** RESIDUALS MOMENT ANALYSIS  *****
  ( Residuals = Experim. Data - Predicted Values )
 ================================================

 ------------------------------------------------
 Residual Gaussian Normality Test #1

 **** Shapiro-Wilk W-test for Gaussian Normality ****
 ( how your residuals are distributed )
W =    0.612 ( Perfect Normality : W=1.0 )
 P-value Test of Normality =   0.0000000E+00

 ----------------------------------------
 *** Residual Statistics:
 Mean(Average) =  -6.5119849E-07
 Average Deviation =   2.4359003E-06
 Standard Deviation =   5.2913529E-06
 Variance =   2.7998416E-11
 Skewness =   0.2438821
 Kurtosis =    7.688009


 **** End of prediction analysis for data-column:      2
 ================================================================


 ================================================================
 **** Start of prediction analysis for data-column:      3  ( ES )

 R-squared   Adjusted  Est. Std. Dev.              Coefficient of
 (percent)  R-squared  of Model Error        Mean  Var. (percent)
```

```
  100.000    100.000       1.663E-12   4.426E-10          0.3756

                 * * * Analysis of Variance * * *
                             Sum of        Mean             Prob. of
Source                 DF     Squares      Square  Overall F  Larger F
Regression              1   2.489E-17   2.489E-17  *********    0.0000
Residual               42   1.161E-22   2.764E-24
Corrected Total        43   2.489E-17

               * * * Inference on Coefficients * * *
                    Standard                 Prob. of    Variance
Coef.    Estimate       Error  t-statistic  Larger |t|   Inflation
    1      0.0000   2.909E-13         -0.7      0.5052       1.347
    2      0.9997   3.332E-04       3000.4      0.0000       1.000

* * * Variance-Covariance Matrix for the Coefficient Estimates * * *
                                  1             2
                    1   8.46079E-26  -4.91731E-17
                    2                 1.11018E-07

                          * * * Case Analysis * * *
```

...**<SNIP>**...

```
**** End of prediction analysis for data-column:      3
======================================================================


======================================================================
**** Start of prediction analysis for data-column:      4  ( EIS )

R-squared   Adjusted  Est. Std. Dev.              Coefficient of
(percent)  R-squared  of Model Error        Mean  Var. (percent)
  100.000    100.000       9.729E-17   2.730E-14          0.3564

                 * * * Analysis of Variance * * *
                             Sum of        Mean             Prob. of
Source                 DF     Squares      Square  Overall F  Larger F
Regression              1   7.177E-26   7.177E-26  *********    0.0000
Residual               30   2.840E-31   9.465E-33
Corrected Total        31   7.177E-26

               * * * Inference on Coefficients * * *
                    Standard                 Prob. of    Variance
Coef.    Estimate       Error  t-statistic  Larger |t|   Inflation
    1          0.   1.985E-17         -0.1      0.8886       1.332
    2          1.   3.633E-04       2753.6      0.0000       1.000

* * * Variance-Covariance Matrix for the Coefficient Estimates * * *
                                  1             2
                    1   3.94100E-34  -3.60163E-21
                    2                 1.31956E-07

...<SNIP>...

**** End of prediction analysis for data-column:      4
======================================================================


**********************************************************************
>>>>>>>>>>>>>>>>>>>> END OF PREDICTION ANALYSIS <<<<<<<<<<<<<<<<<<<<
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